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EFFECTS, PATHWAYS, PROCESSES, AND TRANSFORMATION OF PUGET SOUND CONTAMINANTS OF CONCERN

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PREFACE

This report was prepared for the MESA Puget Sound Project, Office of Marine Pollution Assessment, National Oceanic and Atmospheric Administration in Seattle. The overall goal of the Project is to develop an understanding of the existing levels, fates and effects of contaminants in Puget Sound. The Project supports and coordinates many individual studies conducted by private, academic and government groups. This report was prepared by scientists of E.V.S. Consultants Ltd. for the Project. It summarizes information available on the physical and toxicological properties of contaminants previously found in Puget Sound and suggests which of those chemicals are likely of greatest ecological concern. The Project technical monitor for this study was Edward Long.

EXECUTIVE SUMMARY

During the MESA Puget Sound Project, sediment samples and tissues of sediment-associated invertebrates and bottom fish were analyzed for petroleum hydrocarbons, chlorinated organic compounds and metals. Similar analyses were performed on suspended particulates and water samples at selected sites. From the data of this study and of a Seattle METRO (1980) study of Seattle Harbor sediments, 183 organic compounds and 37 inorganic ions were identified and/or quantitated in sediments, biota, and waters of Puget Sound. The intent of this report is to:

- briefly review existing knowledge on the 183 organic compounds and 37 inorganic ions;
- identify the contaminants of concern on the basis of their toxicity and distribution;
- document the present level of understanding of the biogeochemical fate and effects of the contaminants of concern; and
- recommend a research strategy to define further the biogeochemical processes that influence the fate of selected toxic substances identified in Puget Sound.

To identify the contaminants of concern, selection schemes were developed for ecological hazard assessments of both organic contaminants and inorganic ions. Compounds were placed in six categories of concern rather than two categories, i.e., of concern and of no concern, for the following reasons:

- Some contaminants were quantified in all or some compartments of the environment, and others were only identified during research efforts to determine "what is in the environment." In other words, there was significant variability in data.
- Data on toxicity and environmental fate of many compounds were sparse.

Fifteen contaminants or classes of contaminants were selected to be of concern on the basis of their toxicity and distribution. For these contaminants, attempts were made to retrieve information relevant to their biogeochemical fate in marine waters. Computerized data bases and manual searches of the literature were used for information retrieval. The information was reviewed and summarized for each contaminant of concern. Research needs were subsequently identified.

Of the 15 contaminants or classes of contaminants chosen to be of concern we have, upon request of the project officer, selected those of especially high priority on the basis of their possible ecological impact to Puget Sound.

Contaminants or Classes of Contaminants Selected to be of Greatest Concern in Puget Sound

1. Polychlorinated Dibenzofurans (PCDFs) and their possible precursors, tetra- and pentachlorophenol

Polychlorinated dibenzofurans were chosen on the basis of their toxicity and potential distribution throughout Puget Sound. Although the toxicity of PCDFs to aquatic biota is poorly known, feeding studies indicate that PCDFs are highly toxic to mammals and birds. Three polychlorinated dibenzofurans were detected in sediments of Central Puget Sound; however, the levels were not determined. Chlorinated dibenzofurans have been associated with the manufacture and disposal of both PCBs and pentachlorophenols. The high levels of PCBs in Puget Sound and the extensive usage of pentachlorophenols in the Puget Sound area suggest a potential widespread dispersal of chlorinated dibenzofurans. Sedimentation and bioaccumulation are probably the major fate processes for PCDFs. Additional assessments of PCDFs and their possible precursors, tetra- and pentachlorophenol, in Puget Sound biota and sediments are recommended.

2. Chlorinated Butadienes

Chlorinated butadienes have been found in sediments and biota of Puget Sound. Hexachlorobutadiene (HCBD) was found in livers of sole at concentrations as high as 9.1 ppm. Some sediment samples also contained appreciable levels of hexa-, penta-, tetra-, and trichlorobutadiene. Studies with chlorinated butadienes have been sporadic. Bioaccumulation and sorption to sediments are the probable major fate processes. Sublethal effects were noted upon exposure of crayfish to HCBD levels as low as 3 ppb. Data gaps include evaluation of uptake from sediments and chronic toxicity studies for marine organisms.

3. Polyaromatic Hydrocarbons (PAHs) and their Halogenated Derivatives

PAHs are widely dispersed in sediments and biota of Puget Sound, with especially high levels in sediments of Elliott and Commencement Bays. It was extremely difficult to identify the PAHs of greatest concern in Puget Sound, and several PAHs are reviewed in detail. The PAHs were chosen on the basis of their known toxicities and were also chosen to enable a review on several types of PAH structures.

a. Naphthalene and Substituted Naphthalene

Naphthalene, seven methylated forms of naphthalene, ethyl naphthalenes, and propyl naphthalenes were quantified in sediments and biota of Puget Sound. Up to 4000 ppb of naphthalene and 1600 ppb 2-methyl naphthalene were detected in sediments. The literature indicates that naphthalene is readily biodegraded in the environment; however, constant inputs are apparent. Low levels of naphthalenes appear to especially affect newly hatched bottom species such as Dungeness crab and spot shrimp. Metabolites of naphthalenes have been suggested as possible carcinogens. Research needs include the identification and assessment of the possible effects of such metabolites.

b. Benzo(a)anthracene and Dibenzo(a)anthracene

Sediments of Central Puget Sound were found to contain benzo(a)anthracene levels from 1 to 13,000 ppb. Biota from Puget Sound contained high levels of benzo(a)anthracene. Metabolites of benzo(a)anthracene may be of environmental concern. The compound was found to be persistent in the environment, with carcinogenic and/or neoplastic potential. Sedimentation was the most probable environmental fate process. Research needs include the assessment of metabolites and determination of possible chronic effects on benthic organisms.

c. Fluoranthenes

Fluoranthenes are widely dispersed throughout Puget Sound and benzofluoranthene is the most dominant PAH in Hylebos Waterway. One sediment sample contained 14,000 ppb benzofluoranthene. Fluoranthene is considered a potent co-carcinogen. Concentrations in biota are generally low, indicating that biodegradation is a significant fate process. Sorption is also a significant fate process. Metabolites of fluoranthenes may be of concern. Research needs include the identification and assessment of metabolites.

d. Benzo(a)pyrene

Benzo(a)pyrene is a recognized carcinogen which has been detected in sediments (up to 6700 ppb) and biota (up to 730 ppb) from Puget Sound, particularly in the vicinity of industrial areas. Sorption to sediments is a major fate process for benzo(a)pyrene. Metabolites of benzo(a)pyrene may be *in vivo* carcinomas in biota. The effects of high levels of benzo(a)pyrene in sediments of bottom-dwelling biota are not known, and, therefore, are identified as one of the research needs.

e. Chlorinated and Bromo-Naphthalenes (PCNs)

No concentrations of PCNs in Puget Sound were reported; however, the presence of PCN with one to seven substituted chlorine derivatives was indicated. Low levels of PCNs have been shown to cause sublethal effects in marine organisms.

Sediments are probably the major sinks of PCNs. Metabolites of PCNs may be of concern because of their additional lipophilic properties due to the presence of halogens. Additional assessments of PCN distributions in Puget Sound and effects of metabolites are identified as research needs.

f. Other Halogenated Polyaromatic Hydrocarbons

In addition to chlorinated naphthalenes, 25 other halogenated polyaromatic hydrocarbons were reported in sediment samples from Central Puget Sound. The compounds were selected on the basis of their potential toxicity and distribution. The literature contained minimal information on these compounds. Nonetheless, the compounds are probably more persistent and toxic than the parent PAH compounds. The halogenated PAHs in sediments and biota of Puget Sound need to be quantified. Also, the predominant halogenated PAHs should have their toxicities, metabolites, and environmental fates evaluated. Sources need to be identified.

4. Arsenic

The Puget Sound Basin has a major anthropogenic source of arsenic. Sediments in the vicinity of the source contained up to 10,000 ppm arsenic. Concentrations as high as 640 ppm arsenic have been found in sediments during the MESA program. Puget Sound is also exposed to high quantities of arsenic via atmospheric precipitation. Arsenic is somewhat unusual as an inorganic element; it has been shown to bioaccumulate and while it is a definite human carcinogen, this effect has not been demonstrated on any animal models. The minimal toxicological data available prohibit an assessment of the possible biological effects arsenic would have on marine biota in Puget Sound. Other data gaps include speciation of arsenic in Puget Sound, effects of sediment-associated arsenic on bottom-dwelling biota, and the significance of volatilization of organo-arsenic species in Puget Sound.

5. Cadmium

Cadmium levels in sediments of Central Puget Sound are highly elevated when compared to regulatory criteria for classifying sediments. Concentrations as high as 18.3 ppm were observed in the sediments. The cadmium levels appear to be high enough to affect behavioral patterns of bottom-dwelling species. Data gaps include assessment of sources and fluxes of cadmium in Puget Sound, evaluation of sublethal effects of cadmium-contaminated sediments on behavior of bottom-dwelling biota, and evaluation of the speciation of cadmium in the ambient and interstitial waters.

Contaminants or Classes of Contaminants Also Chosen to be of Concern in Puget Sound

6. DDT and its Metabolites

Despite a ban on DDT in the United States since 1972, concentrations of DDT and its metabolites in Puget Sound biota and sediments remain high. Studies in other areas of the world show a predominance of the metabolite DDE in marine sediments; however, DDT rather than DDE is dominant in Puget Sound sediments. This observation implies that either recent inputs to Puget Sound have occurred or that there is a lack of metabolic activity of DDT within the sediments. Research needs include the evaluation of metabolic activity in Puget Sound sediments.

7. Polychlorinated Biphenyls (PCBs)

PCBs are the most predominant contaminants in Puget Sound sediments and biota. Up to 440 ppb hexachlorobiphenyl were detected in sediments and up to 15,000 ppb were detected in livers of fish. Despite the ban on the use of PCBs, the levels in edible species of biota from certain areas of the Sound show that PCBs are of potential concern to consumers of the biota. During the evaluation of the present level of understanding on the biogeochemical fate of PCBs, it was found: that more information is required on the physical chemical properties of PCB in seawater; that the issue of PCB release from contaminated sediments remains unresolved; that metabolites of PCBs may be of ecological significance because of their toxicity; and that there is still a need for standardization and quality assurance for analytical programs. The study also indicated that "biodegradable" di- and trichlorobiphenyls were at concentrations in Puget Sound sediments which indicated possible reduced metabolic rates in sediments.

8. Hexachlorobenzene (HCB) and Other Chlorinated Benzenes

This study indicated that HCB was found in Puget Sound at levels indicative of industrial areas with appreciable pollution by organic chemicals. Up to 1300 ppb HCB were detected in sediments and up to 3700 ppb were detected in livers in fish. HCB has been shown to cause histological changes in aquatic biota at low concentrations (i.e., 25 ppb). Benzene rings with four to six chlorines are expected to be quite persistent in the environment. Data gaps include the need to determine the effects of high levels of HCB in sediments on biota, sources of high HCB levels, and the role of the surface microlayer in concentrating organic contaminants such as HCB in Puget Sound.

9. Chlorinated Ethylenes

The concentrations of chlorinated ethylenes in Hylebos Waterway of Puget Sound exceed values reported in other marine environments. Volatility is a major fate process and concentrations of 3 ppb trichloroethylene as observed in waters from the Hylebos Waterway imply appreciable discharges of chlorinated ethylenes. The sources and effects of chlorinated ethylenes in Puget Sound are among the research needs identified.

10. Phthalate Acid Esters (PAEs)

PAEs are widely distributed throughout Puget Sound. Concentrations up to 1600 ppb of one PAE were reported in sediments. Much of the literature indicates that phthalate esters are probably not of environmental significance. One overriding concern is the possible chronic effects of low concentrations of PAEs, and data are unfortunately minimal, especially for marine species. A few chronic studies have suggested that PAEs are biologically active at concentrations well below acutely toxic concentrations. It has been suggested that PAEs in bottom sediments may affect bottom-dwelling macro- and microfauna. Further work is recommended on the chronic effects of PAEs.

11. Copper

Of 42 sediment samples from Puget Sound, only 14 had copper levels less than the 50 mg/kg "heavily polluted" classification by EPA for evaluation of dredged materials. Sediments with copper concentrations as high as 1600 mg/kg were found in Puget Sound. Ambient water concentrations of copper were not evaluated, and it is recommended that such evaluations be initiated. Saltwater invertebrates are particularly sensitive to copper and copper speciation. Data gaps identified include evaluation of copper speciation in Puget Sound waters and an evaluation of the effects of highly contaminated copper sediments on bottom-dwelling biota.

12. Lead

Many of the sediments of Puget Sound were heavily contaminated with lead, generally indicative of marine sediments in the vicinity of heavily urbanized and industrialized regions. Concentrations up to 790 mg/kg were found in Puget Sound sediments. Insufficient toxicity data exist on the effects of lead on marine organisms to evaluate the implications of the levels found in Puget Sound. Recent freshwater studies have shown that existing criteria for lead will have to be reconsidered and possibly lowered. Alkylation of lead may be of concern and there is a need to determine if this process occurs to any great extent in Puget Sound.

13. Mercury

Mercury concentrations in sediments from industrial areas of Puget Sound varied from 0.026 to 1.38 ppm. These levels may still be of biological importance, although mercury concentrations are probably decreasing in Puget Sound. Water and biota samples were not analyzed for mercury. Data requirements are contingent upon evaluation of existing concentrations in biota.

14. Selenium

Selenium levels in most Puget Sound sediments are much higher than expected background levels. Data gaps include the effect of selenium in sediments on bottom-dwelling biota, determination of the significance of selenium-methylation and whether methylated forms accumulate in biota as well as the implications to consumers of selenium-contaminated biota.

15. Silver

Silver was found at high levels in several Puget Sound sediments and biota. Low levels of silver dissolved in water have been shown to be very toxic to aquatic organisms, and determinations of silver levels in Puget Sound waters are recommended. Furthermore, the effects of silver-contaminated sediments on biota should be assessed.

Many compounds were classified not to be of concern on the basis of data on their persistence, toxicity, and concentrations in Puget Sound. Such contaminants included several halogenated aliphatic compounds, monocyclic aromatics, and various metals.

For many compounds, data on fate and effects were virtually absent. These compounds included halogenated cycloalkenes, halogenated alkenes, dibenzothiophenes, and the metals, gallium and germanium.

Another group of compounds was classified as "contaminants for which a hazard assessment cannot be provided." These are compounds which are toxic but identified at very low concentrations in sediments in confined areas or determined in one location at very high concentrations. Such compounds include nitrosamines, chlordane, heptachlor, lindane, several PAHs, tin, and polychlorinated terphenyls.

Four major research needs are recommended as a result of this study.

I. INTRODUCTION

The MESA Puget Sound Project was initiated to develop an understanding of the environmental impacts caused by human actions, primarily the introduction of chemical contaminants upon biological components of Puget Sound. Therefore, an integrated program of multidisciplinary research was designed to document the occurrence and fluxes of contaminants of special concern, the dynamic processes influencing their physical and chemical transport and fate, and their biological and ecological effects.

Prior to this study, 183 organic compounds were identified in the sediments, biota, and waters of Puget Sound; quantitative data were obtained for many of the compounds. A large number of the compounds were unspecified isomers. In addition, 37 inorganic ions have been quantified in sediments and biota. Table 1.1 lists the organic compounds and inorganic ions which were detected in Puget Sound. The table also lists the Chemical Abstracts Registry numbers and designates the environmental compartment in which the compounds and ions were detected. The category of concern for each compound is also designated. Abbreviations are explained at the end of the table.

The number of chemicals detected within the Sound are many and different physical, biological, and chemical processes influence the fate of each chemical. Therefore, a research program with finite resources cannot be expected to pursue and examine the fate and effects of each chemical identified within the Sound. E.V.S. Consultants Ltd. were contracted to undertake a project with the following specific objectives:

1. Select from the list of organic compounds and metal ions in Table 1.1, those contaminants of concern on the basis of their toxicity and distribution.

2. Document the present level of understanding of the following topics relative to the contaminants of concern: persistence in marine systems; bioavailability and tendency to accumulate in plant and animal tissues; metabolism and oxidation within organisms, including identification of metabolites; physical, chemical, and microbial degradation in marine systems; tendency to associate with suspended particulate matter, surface films, and pycnoclines; and physical fate.

3. Recommend a research strategy to define further the biogeochemical processes that influence the fate of selected toxic substances identified in Puget Sound.

Chemicals of concern were selected in accordance with procedures detailed in Chapter 2. Subsequently, computerized data systems (DIALOG and ORBIT) were used to collect information on literature relevant to the behavior, fate, and effects of the selected chemicals in the marine environment. Data bases which yielded much information included CHEMICAL ABSTRACTS, ENVIROLINE, OCEANIC ABSTRACTS, and POLLUTION ABSTRACTS. Manual searches for the actual documentation followed, using local academic facilities and interlibrary loans. In total, approximately 500 references were selected for review.

This report summarizes the results of the above review and addresses the existing state of knowledge with respect to contaminants selected to be of concern (Category I in Table I.I).

Table 1.1
Organic Contaminants and Inorganic Ions Detected in Puget Sound

Compound	CAS Number*	Category**	Compartment ***
Acenaphthene	83329	2	B,S
Acenaphthylene	208968	2	S
Acetate, methyl phenyl	122792	6	S
Aldrin	309002	5	S,B
Amine, N-nitroso dimethyl	62759	2	S
,N-nitroso phenyl	65759	2	S
,N-nitroso diphenyl	86306	2	S
,N-nitroso di-N-propyl	621647	2	S
Aniline, N-methyl	121697	6	S
,N,N, dimethyl	100618	2	S
Anthracene	120127	2	S,B,SS
benzo(a)anthracene	56553	1	S,B,SS
bromoanthracene	1564643	3	S
chloroanthracene	4985700 716530	3	S
dibenzanthracene	53703	1	S
dichloroanthracene	14381669 57472454 6406968 613070 605481	3	S
dichlorobenzo(a)anthracene	--	3	S
methyl (benzo(a)anthracene)	2498773 2498762 316494 2319962 316143 2541697 2381319 2381160 2381159	1	S

Table 1.1 (contd)

Compound	CAS Number *	Category**	Compartment ***
Anthracene			
tetrachloroanthracene	--	3	S
trichloroanthracene	--	3	S
Benzaldehyde	100527	6	S
Benzene	71432	6	S
,chloro	108907	5	S
,dichloro (m isomer)	25321226	4,5	S,B
,dichloro (o isomer)	95501	4,5	S,B
,dichloro (p isomer)	106467	4,5	S,B
,dinitro	99650 528290 100254	6	S
,ethyl	100414	6	S
,hexachloro	118741	1	S,B
,isopropyl	98828	6	S,B
,nitro	98953	6	S
,n-propyl	103651	6	S
,pentachloro	608935	5,6	?
,tetrachloro	95943 634602	5,6	S
,tetramethyl	488233 527537 95932	6	S
,trichloro	87616 120821 108702	5,6	S
,tri-isopropyl	--	6	S
Benzidene, 3,3,-dichloro	91941	2	S
Benzo(b)fluoranthene	205992	1	S,B
Benzo(g,h,i)fluoranthene	--	1	S
Benzo(i)fluoranthene	--	1	S,B
Benzo(k)fluoranthene	207089	1	S,B

Table 1.1 (contd)

Compound	CAS Number *	Category**	Compartment ***
Benzofuran	271896	3	S
dibenzofuran	52085468	3	S
	34734560		
hexachlorodibenzofuran	70648269	3	S
	67562407		
	55684941		
methyl dibenzofuran	60826622	3	S
	7320538		
pentachlorodibenzofuran	70872821	3	S
	69698573		
	69433007		
	67481225		
	58802167		
	58802156		
	57117416		
	57117314		
tetrachlorodibenzofuran	64126870	3	S
	64560174		
	57117405		
	30402143		
	57117370		
	57117369		
	51207319		
Benzothiophene			
benzo(b)thiophene	95158	2	S,B
benzonaphthothiophene	61523340	3	S
dibenzothiophene	--	2	S,B
methyl dibenzothiophene	--	2	S
Biphenyl	92524	2	S,B
,chloro	11141165	1	

Table 1.1 (contd)

Compound	CAS Number *	Category**	Compartment ***
Biphenyl			
,dichloro	53469219	1	S,B
,heptachloro	--	1	S,B
,hexachloro	--	1	S,B
,methyl	--	3	S
,nonachloro	--	1	S,B
,octachloro	--	1	S,B
,pentachloro	11696825	1	S,B
,tetrachloro	11097691	1	S,B
,trichloro	12672296	1	S,B
Butadiene			
,hexachloro	87683	1	S,B,W,SS
,pentachloro	55880778	1	S,B
	21484048		
	5659449		
	21400419		
	21484059		
,tetrachloro	921095	1	S,B
	1637316		
	18149763		
,trichloro	--	1	S,B
Butene, hexachloro	93089	3	SS
	18766875		
Carbazole	86748	3	S
Chlordane	57749	2	S,B
Chrysene	218019	2	S,B
dichlorochrysene	--	3	S
DDD	72548	1	S,B
DDE	72559	1	S,B
DDT	789026	1	S,B
Decalin	91178	6	S

Table 1.1 (contd)

Compound	CAS Number*	Category**	Compartment***
Dieldrin	60571	5	
Endrin	72208	5	S
Ethane			
,hexachloro	67721	6	?
,trichloro 1,1,1	71556	6	S
Ether			
,4-bromophenyl phenyl	101553	4	S
,bis (2-chloroethyl)	111444	4	S
,bis (2-chloroisopropyl)	108601	4	S
Ethylene			
,dichloro	540590	1	W
,tetrachloro	127184	1	S,W
,trichloro	79016	1	S,W
Fluoranthene	206440	1	S,B,W,SS
,chloro	25911577	3	S
,dibromo	--	3	S
,dichloro	--	3	S
,methyl	--	1	S
,pentachloro	--	3	S
,tetrachloro	--	3	S
,trichloro	--	3	S
Fluorene	86737	2	S,B
,dichloro	7012160 25023012	3	S
,methoxy	--	2	S
,methyl	--	2	S
Heptachlor	76448	2	S,B
Heptadiene, hexachloro	--	3	SS
Hexadiene, chlorocyclo	71432	3	SS
,heptachlorocyclo	--	3	SS
,cyclo	--	3	SS
,hexachlorocyclo	--	3	SS

Table 1.1 (contd)

Compound	CAS Number*	Category**	Compartment ***
Hexatriene; heptachloro	--	3	SS
;hexachloro	--	3	SS
Indan	496117	6	S,B
Lindane	58899	2	S,B
Methane			
Bis (2-chloroethoxy)	111911	4	S
chloro	74873	6	S
chlorodibromo	124481	6	W
dichloro	75092	6	S,W
tetrachloro	56235	6	S
tribromo	75252	6	S
trichloro	67663	6	S
Methyl phenyl acetate	122792	6	S
Naphthalene	91203	1	S,W,B,SS
,bi	--	1	S
,bromo	--	1	S
,chloro	25586430	1	S
,dichloro	28699889	1	S
,heptachloro	32241080 58863142 58863153	1	S
,hexachloro	17062872 1335871	1	S
,1,3 dimethyl	--	1	W,SS
,2,3 dimethyl	--	1	W,SS
,2,6 dimethyl	--	1	S,B,W,SS
,1-methyl	90120	1	S,B,W,SS
,2-methyl	91576	1	S,B,W,SS
,pentachloro	1321648	1	S
,phenyl	--	1	S
,tetrachloro	55720422 55720439	1	S

Table 1.1 (contd)

Compound	CAS Number*	Category **	Compartment***
Napthalene			
,tetrachloro (contd)	1335882	1	S
	53555649		
	53555638		
	51570457		
	31604281		
	20020024		
	3432573		
,trichloro	55720382	1	S
	55720359		
	55720348		
	55720337		
,2,3,5-trimethyl	--	1	S,B
,2,3,6-trimethyl	--	1	SS,W
Palmitic Acid	57103	6	S
Pentadiene, hexachloro	--	3	SS
,pentachloro	--	3	SS
Pentene, chlorocyclo	96402	3	SS
	930290		
,hexachlorocyclo	--	3	SS
,pentachlorocyclo	--	3	SS
Perylene	198550	2	S,B,SS
,methyl	--	2	S
,benzo(g,h,i)	191242	2	S
Phenanthrene	85018	2	S,B,W,SS
,bromo	573171	3	S
	715504		
	19462794		
	51958511		
	62162974		
,benzo	217594	2	S
,chloro	36472283	3	S
	947728		

Table 1.1 (contd)

Compound	CAS Number*	Category**	Compartment***
Phenanthrene (contd)			
,dichloro	17219942	3	S
,1-methyl	--	2	S,W,SS
,2-methyl	--	2	W,SS
,tetrachloro	--	3	S
,trichloro	--	3	S
Phthalate esters			
,bis (2-ethylhexyl)	117817	1	S
,butyl benzyl	85687	1	S
,di-n-butyl	84742	1	S
,diethyl	84662	1	S
,dimethyl	131113	1	S
,di-n-octyl	117840	1	S
Phytane	--	4	S,SS
Pristane	1921706	4	S,SS
Pyrene	129000	2	S,B,SS,W
,benzo(a)	50328	1	S,B
,benzo(c)	192972	1	S,B
,chloro	34244149	3	S
,dibromo	--	3	S
,dichloro	--	3	S
,indeno	193395	2	S
,methyl	--	2	S,SS
,pentachloro	--	3	S
,tetrachloro	--	3	S
,trichloro	--	3	S
Stearic Acid	57114	6	S
Terphenyl, para	92944	4	S
,tetrachloro	--	4	S
,trichloro	--	4	S
Toluene	108883	6	S

Table 1.1 (contd)

Compound	CAS Number*	Category**	Compartment***
Toluene (contd)			
,2,4 dinitro	121142	2	S
,2,6 dinitro	606202	2	S
Triphenylene	217594	2	S
Xylene	1330207	2	S,B
Inorganic Ions			
Aluminum		6	S,B
Antimony		2	S
Arsenic		1	S
Barium		6	S,B
Beryllium		6	S
Bismuth		6	S
Boron		6	S,B
Cadmium		1	S,B
Calcium		6	S,B
Chromium		6	S,B
Cobalt		6	S,B
Copper		1	S,B
Gallium		3	S
Germanium		3	S
Iron		6	S,B
Lead		1	S,B
Lithium		6	S,B
Magnesium		6	S,B
Manganese		6	S,B
Mercury		1	S
Molybdenum		6	S
Nickel		6	S,B
Phosphorus		6	S,B

Table 1.1 (contd)

Compound	Category**	Compartment***
Potassium	6	S
Scandium	6	S,B
Selenium	1	S
Silicon	6	S
Silver	1	S,B
Sodium	6	S
Strontium	6	S,B
Tin	4	S
Titanium	6	S
Tungsten	6	S,B
Vanadium	6	S
Ytterbium	6	S
Zinc	4	S,B
Zirconium	6	S

*CAS Numbers - Chemical Abstracts Registry Numbers

**Category Numbers

1 - Contaminant of concern selected for study.
2 - Of possible concern, hazard assessment difficult. Toxic, but found at very low concentrations.
3 - Of possible concern, but toxicity data minimal for evaluation purposes.
4 - Distribution localized. Source identification recommended.
5 - Analytical efforts minimal. Additional surveillance required.
6 - Contaminant not of concern.

***Compartment

S - Detected in sediment
B - Detected in biota
SS - Detected in suspended solids
W - Detected in water

2. RATIONALE FOR SELECTIONS OF CONTAMINANTS OF CONCERN WITHIN PUGET SOUND

Environmental agencies are actively involved in development of methodology for ecological hazard evaluation of environmental contaminants. Many hazard assessment schemes have been developed (Dickson et al., 1979). However, a common, internationally accepted scheme eludes the scientific community because of differences in scientific opinion which are in part due to many deficiencies in existing knowledge for hazard assessment. For example, on the basis of a workshop on hazard evaluation, Fetterolf et al. (1979) concluded that "research for improved test development should be an ongoing integral part of the overall effort to better understand the environmental consequences of today's chemicals."

The evaluation processes are becoming increasingly complex as a result of the increased sensitivity of analytical methodology for the detection of environmental contaminants. Detection levels for several contaminants have been lowered by factors of as much as one million (i.e., from mg/L to ng/L) in the past few years, and the environmental significance of such levels has been a subject of considerable scientific debate (i.e., Maugh, 1978).

While recognizing the deficiencies in existing knowledge, two simplistic schemes, one for organic compounds and one for inorganic ions, were used to provide a preliminary identification of contaminants of concern to Puget Sound. The schemes were used to evaluate the contaminants listed in seven reports provided to the contractor (Brown, 1978, 1979(a,b,c); Seattle METRO, 1980; Riley et al., 1980). The reports are summarized in Table 2.1. The data provided by Brown (1978; 1979 a,b,c) were later summarized in a report by Malins et al. (1980). While the data which were collected and provided for this study do not necessarily reflect the total diversity of chemicals likely occurring in Puget Sound, they do provide a first approximation based upon a relatively broad scale sampling and analytical scheme.

Table 2.1
Summary of Chemical Data Bases Provided for this Study

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1. Memorandum:
Subject: Analysis of Central Puget Sound Samples
Date: September 7, 1978
To: Ed Long, MESA, Puget Sound Project, NOAA/ERL, Seattle
From: Don Brown, National Analytical Facility, Northwest and Alaska Fisheries Center, Seattle

The memorandum summarized the result of analyses of sediment samples collected in June 1978 at 11 sites in Central Puget Sound.

Table 2.1 (contd)

The samples were analyzed for metals by plasma emission spectroscopy. Organic analyses were undertaken by gas-chromatography/mass spectrometry. All measurements were expressed as dry weight and identification of many organics was considered "tentative." Samples were taken near municipal and industrial areas and, therefore, likely reflected "worst case" situations. Some assessments of the results were provided in this memorandum.

2. Memorandum: Subject: Analyses of Four Central Puget Sound Sediment Samples
Date: March 15, 1979
To: Ed Long, MESA, Puget Sound Project, NOAA/ERL, Seattle
From: Don Brown, National Analytical Facility, Northwest and Alaska Fisheries Center, Seattle.

This memorandum supplements the September 7, 1978, memorandum. Four of the sediment samples collected in June 1978 (as per September 7 memorandum) were re-evaluated. Analyses included quantification of approximately 25 aromatic hydrocarbons and C_9 to C_{32} compounds. Also, 70 additional compounds were identified but not quantified. Compounds identified include volatile organics, n-alkanes, aromatic hydrocarbons, pesticides, sulfur compounds, and oxygenated compounds. Gas-chromatograms and mass spectra were provided. The memorandum indicates that many unidentified compounds probably exist in the sediments.

3. Data Sheets:
- Multielement analyses of 42 sediments, June 8, 1979) (Erich J. Gauglitz, Jr., Principal Investigator)
- Concentration of pesticides, PCBs, and 28 arenes in sediments and fish livers from Central Puget Sound (Memo to Bruce McCain from Don Brown, August 21, 1979).

Sediments were collected in May 1979 for chemical analyses. The results of the multielemental analyses by Gauglitz were presented in the form of a computer printout. Thirty-seven elements were quantified in 42 sediment samples.

The memorandum to McCain from Brown tabulated the quantities of pesticides, PCBs, and arenes in 42 sediment samples. Sixteen liver samples from rock sole and English sole were also analyzed for the same compounds, and the results are tabulated in the memorandum. Grain sizes of the 42 sediments were also indicated. No data interpretations were provided in either memorandum.

Table 2.1 (contd)

4.	Data Sheets:	- Multielemental analyses of tissues, September 25, 1979 (Erich J. Gauglitz, Jr., Principal Investigator). - Concentrations of organic compounds in fish and invertebrate tissues (Memo to Ed Long and Bruce McCain from Don Brown, October 19, 1979).

Tissue samples were collected in May 1979. The samples consisted of rock and English sole livers, crab hepatopancreas, polychaete worms, shrimp, and clams. The shrimp and clams were analyzed whole excluding shells. Some samples of shrimp and crab hepatopancreas were mixtures of different species. The results of the multielement analyses by Gauglitz were presented in the form of a computer printout which showed levels of 25 elements in 36 tissue samples.

The memorandum by Brown tabulated the quantities of pesticides, PCBs, and arenes in: 5 composited samples of shrimp; 5 composited samples of clams; 6 composited samples of crab hepatopancreas; 8 composite samples of worms; and 33 composite and 22 individual liver samples of English sole, rock sole, Pacific staghorn sculpin, and quillback rockfish. All results are reported on a dry weight basis and were not discussed nor summarized in the memoranda.

5.	Report:	"Chemical Contaminants and Biological Abnormalities in Central and Southern Puget Sound," by Donald C. Malins, Bruce B. McCain, Donald W. Brown, Albert K. Sparks, Harold O. Hodgins. NOAA Tech. Memo. OMPA-2. Boulder, Colorado, Nov., 1980.
6.	Data Sheets:	Preliminary results from Seattle METRO (1980) on the levels of 51 priority pollutants in sediments collected at or near some of the MESA stations.

The data sheets consisted of two tables which indicated the levels of 51 of the EPA's 129 Priority Pollutants in 18 sediment samples.

7.	Draft Report:	"Quantification of Pollutants in Suspended Matter and Water from Puget Sound," by R.G. Riley, E.A. Crecelius, D.C. Mann, K.H. Abel, B.L. Thomas, and R.M Bean of Battelle Pacific Northwest Laboratories. Prepared for NOAA/MESA, April 1980.

Table 2.1 (contd)

Suspended matter samples collected from nine sites in Puget Sound were analyzed for 22 metals, 19 aromatic hydrocarbons, saturated hydrocarbons, PCBs, and halogenated pesticides. A total ion mass chromatogram of an extract from suspended matter tentatively identified 26 halogenated organic compounds. Water samples were analyzed for saturate and aromatic hydrocarbons, PCBs, pesticides, and purgeable organic compounds. Metals were not quantitated. The report was later published as NOAA Technical Memorandum ERL MESA-49.

2.1 Evaluation of Organic Contaminants

Figure 2.1 outlines the sequential selection scheme used for the evaluation of organic contaminants. Two basic evaluation sequences were used.

2.1.1 First Evaluation Step: Toxicity

For the purposes of this study, the definition of "toxic substance" means a substance which can cause death, disease, behavioral abnormalities, cancer, genetic mutations, physiological or reproductive malfunctions, or physical deformities in any organism or its offspring, or which can become poisonous after concentration in the food chain or in combination with other substances. This definition was jointly derived by the Governments of Canada and the United States for the 1978 Great Lakes Water Quality Agreement.

The first evaluation step assessed the compound on the basis of prior information on whether the compound was highly toxic or, alternatively, the environmental levels in Puget Sound were such that biota or consumers of contaminated biota may be affected. The critical levels categorizing compounds as highly toxic, as shown in Figure 2.1, were adapted from recommendations by the State of Michigan (1978) Critical Materials Advisory Committee and the International Joint Commission's Human Health Aspects Committee (1979), who, in turn, based their recommended levels upon the deliberations of the National Academy of Sciences, Battelle Memorial Institute, the Federal Water Pollution Control Agency, and the Federal Hazardous Substances Labelling Act Title 15 Classifications.

Aquatic toxicity values (LC50 and chronic effects) were obtained by review of the EPA Quality Criteria for Water (1976) and by individual literature searches. Freshwater data were used only if data were unavailable for marine biota. Information on LD50 and carcinogenicity was obtained by review of the NIOSH (1979) Registry of Toxic Effects of Chemical Substances (RTECS). If the compounds were designated in RTECS as "carcinogenic" and were found within edible biota, they were considered to be of potential concern for purposes of this study regardless of their concentrations. This approach refrains from the controversial evaluation of carcinogenic risk of contaminants to the environment, i.e., whether "no-effect" levels exist or whether carcinogenic risk can be extrapolated to all levels of exposure (Maugh, 1978).

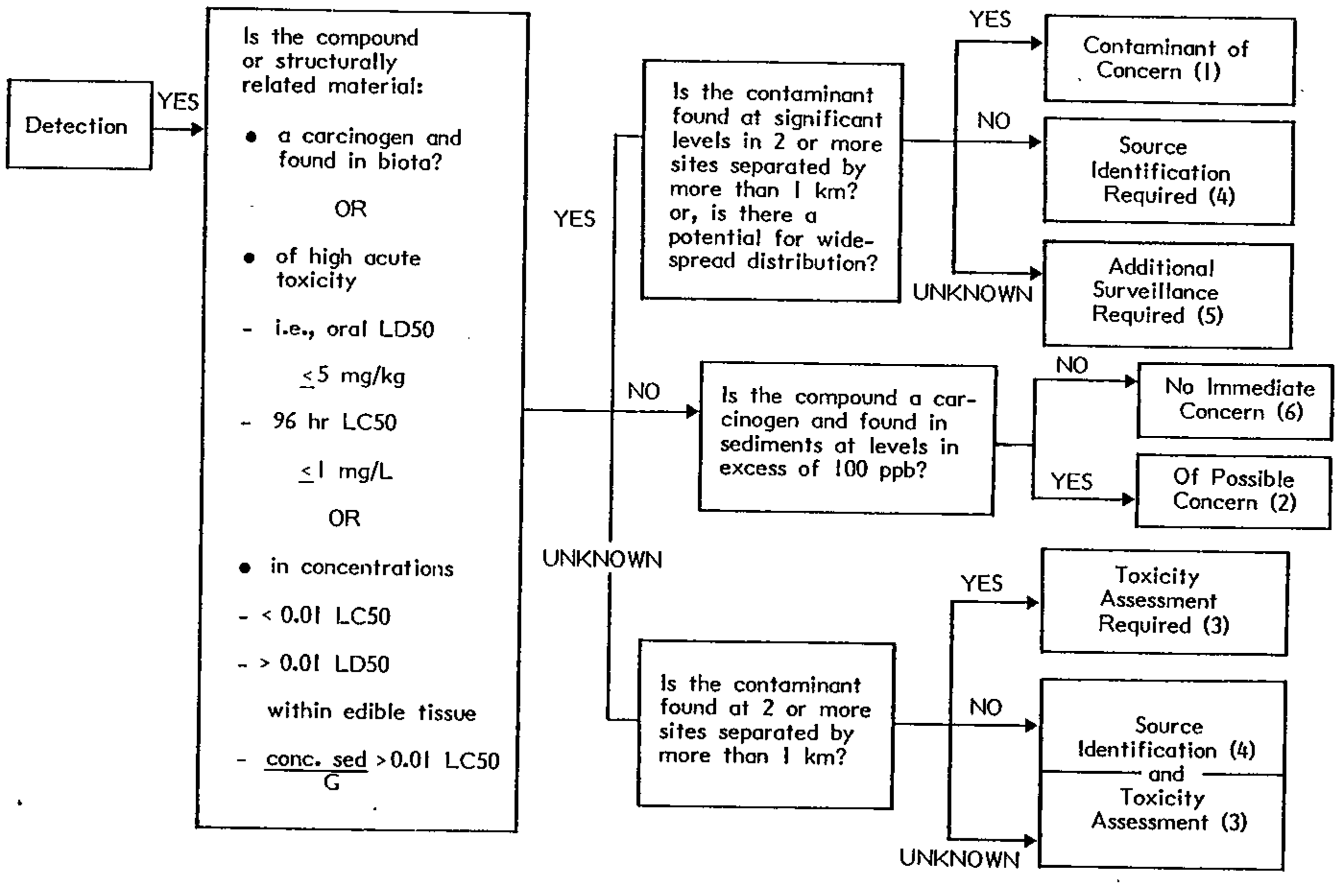


Figure 2.1

Scheme Used for Categorization of Organic Contaminants Detected in Puget Sound (numbers in parentheses refer to categories of compounds as noted in Table 1.1 and as described in Chapter 2)

Contaminants were also evaluated on the basis of comparisons of their concentrations in Puget Sound with LC50 (median lethal concentration) and LD50 (median lethal dose) literature values. If the levels in water were in excess of 0.01 of the LC50 of the most sensitive marine species, the contaminant was considered to be of concern. Likewise, a contaminant was considered to be of concern if it was found in any edible biota such as clams, shrimp, or crab at levels in excess of 0.01 LD50 for any test species noted within RTECS. The 100-fold safety factor was higher than the 20- and 50-fold factors used by EPA in its development of water quality criteria, but was necessary because analyses during the MESA program were carried out on an infrequent basis and may not have recorded maximum levels.

Many of the analyses were restricted to the quantification of contaminants in sediments. As a result, the levels of contaminants in sediments were considered to be of concern when concentration in sediments/G (partition coefficient soil/water) exceeded one one-hundredth of the LC50 to the most sensitive marine species. However, partition coefficients and LC50 values were not available for many compounds. In addition, it was uncertain whether low concentrations of carcinogenic compounds (i.e., 5-10 ppb) in sediments constituted a hazard to the environment.

Other difficulties were encountered in assessing many compounds because of the data bases provided for this study. For example, some compounds were only reported as tentative structures. The process of making an actual hazard evaluation of the many compounds to the Puget Sound ecosystem was therefore of concern and is identified in this report as a significant research need.

2.1.2 Second Evaluation Step: Distribution

Following the evaluation of toxicity, a sequential evaluation step based on distribution was undertaken.

If the toxicity of a compound appeared to be of concern and if it was found at significant levels in biota or water from two sites at least 1 km apart, it was designated as a "critical" compound for intensive investigation in this report. If analyses for the compound were restricted to sediments or suspended solids and found in at least two sites 1 km apart and at levels in excess of the levels determined by the previously described expression which used soil-water partition coefficients, the compound was likewise designated as critical. Where no partition coefficients were available, concentrations of toxic compounds in excess of 100 ppb were considered critical. Exceptions were made in the case of halogenated polyaromatic hydrocarbons and chlorinated dibenzofurans because of the potential toxicity of the compounds and because of the potential for widespread distribution of the compounds.

Category "I" of Table I.I and Figure 2.I represents the critical organic compounds. Five other categories are used for designating the remaining organic contaminants:

Category 2 - for compounds which were very toxic (usually carcinogenic) but with limited distribution and/or found at very low concentrations. The state-of-the-art for hazard assessment is inadequate to evaluate the implications of such compounds; hence, the compounds are considered as "of possible concern" and "difficult to evaluate."

Category 3 - for compounds for which there are minimal or no data on toxicity. If distribution of such compounds is extensive, there is an immediate need for toxicity studies.

Category 4 - for compounds which are toxic and are known to be distributed only in localized areas. Source identification is recommended.

Category 5 - for compounds which are toxic, but for which there is no information on distribution of their concentrations in Puget Sound.

Category 6 - for compounds which appear to be of no immediate concern to Puget Sound based on existing knowledge.

2.2 Evaluation of Inorganic Ions

All data on inorganic ion concentrations provided for this study were restricted to sediment, suspended solids, and biota analyses. Comparisons with EPA Quality Criteria for Water (1976) were not possible because no analyses of water were undertaken.

Concentrations of inorganic ions in Puget Sound sediments were considered of significance when in excess of average concentrations within the earth's crust (Bryan, 1976; Handbook of Physics and Chemistry) or in excess of values in deep sea sediments as reported by Bryan (1976). Subsequently, the toxicities of the inorganic ions found in excess of "normal levels" were evaluated. The toxicities of almost all such inorganic ions were such that they were considered to be of ecological concern (i.e., category I). An exception was the element tin, which was placed in the category "of potential concern." Tin in its ionic form is relatively non-toxic but it could be present due to release of the toxic organo-tins which are widely used in commerce.

Before elements were considered to be of "no concern," their distribution levels in Puget Sound biota were compared to "average" levels reported in marine biota by Bryan (1976). Aluminum was, for example, found in Puget Sound bivalves at concentrations much in excess of values reported by Bryan, and, therefore, placed in the category "of possible concern."

Figure 2.2 briefly outlines the scheme used to categorize inorganic ions detected in Puget Sound.

The categories are similar to those previously described for organic compounds:

Category 1 - inorganic ions found at concentrations above natural levels and which are known to be toxic to aquatic biota; therefore, ion is "of concern."

Category 2 - ions which are of "possible concern" because of unexpected levels of occurrence in biota or because of possible association with more toxic metallo-organic forms.

Category 3 - ions for which there are minimal or no data on toxicity.

Category 4 - ions for which distribution is localized.

Category 5 - ions which are toxic but for which there is minimal information on distribution or levels in Puget Sound.

Category 6 - ions which appear to be of no immediate concern to Puget Sound based on existing knowledge.

2.3 Additional Considerations

Several factors must be recognized during the selection of contaminants of concern in Puget Sound:

1. The MESA Puget Sound Project has to date conducted a research effort to determine what contaminants are present in the Sound. For many chemicals the levels of contamination were determined. Many qualitative and semi-qualitative data were also reported by analysts concerned with gaining a greater understanding of the extent and range of compounds contaminating Puget Sound. For example, many chlorinated polyaromatic hydrocarbons and several chlorinated five- and six-ring unsaturated hydrocarbons were reported. For many of these compounds, data are extremely limited, and few, if any, citations for the compounds were found within Chemical Abstracts. The citations generally had no relevance to environmental fate or toxicity.

2. Most data were from analyses of sediments.

3. Except for data provided by Seattle METRO, no specific attempt was made to look for compounds on the EPA's 129 Priority Pollutants List, nor for radioisotopes, organo-phosphates, etc.

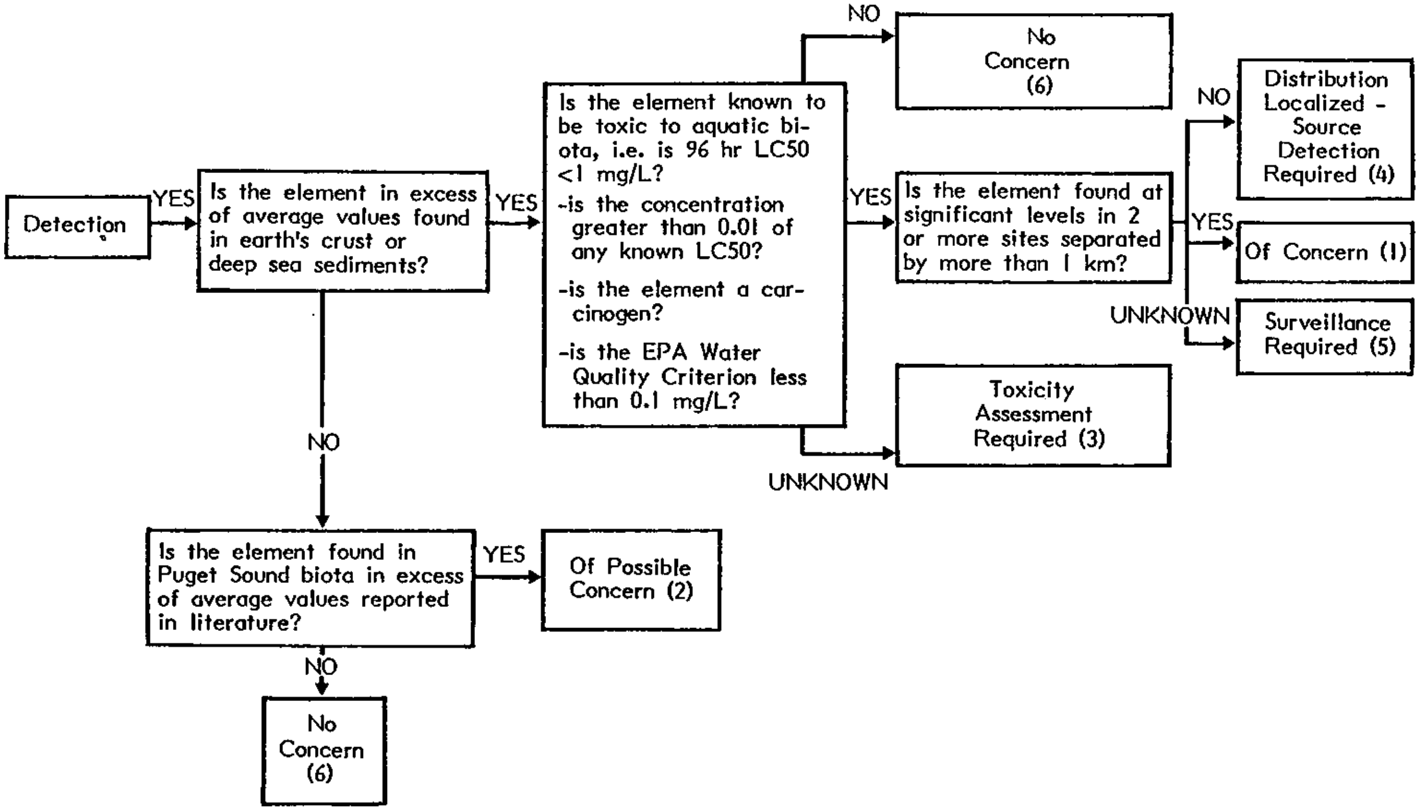


Figure 2.2

Scheme Used to Evaluate Inorganic Ions Detected in Puget Sound (numbers in parentheses refer to categories of ions as noted in Table 1.1 and as described in Chapter 2)

4. There were few analyses of particular compounds and elements within all compartments of the environment. For example, there are no analyses for mercury in biota or water. Assessments of distributions among compartments were difficult, and in this case, an evaluation could not be made of possible hazards of mercury to consumers of fish, such as birds, wildlife or man.

5. During the MESA Puget Sound Project, contaminant levels were determined on a restrictive basis, i.e., analyses of fish were restricted to dry weight livers and few data were available on the concentrations of contaminants in fish-tissue or whole-fish samples. Evaluations of the possible effects of consumption of Puget Sound biota were, therefore, difficult.

References

Brown, D. 1978. Memo to Ed Long, re: Analysis of Central Puget Sound Samples. (September 7, 1978). Environmental Conservation Division, Northwest and Alaska Fisheries Center, U.S. NOAA, Seattle.

1979(a). Memo to Ed Long, re: Analyses of Four Central Puget Sound Sediments (March 15, 1979). Environmental Conservation Division, Northwest and Alaska Fisheries Center, U.S. NOAA, Seattle.

1979(b). Memo to Bruce McCain, re: Central Puget Sound Data (August 21, 1979). Environmental Conservation Division, Northwest and Alaska Fisheries Center, U.S. NOAA, Seattle.

1979(c). Memo to Ed Long, Bruce McCain, re: Analyses of Puget Sound Samples (October 19, 1979). Environmental Conservation Division, Northwest and Alaska Fisheries Center, U.S. NOAA, Seattle.

Bryan, G.W. 1976. Heavy metal contamination in the sea. In: R. Johnston (ed.), Marine Pollution. Academic Press, London. pp. 185-302.

Dickson, K.L., A.W. Maki, and J. Cairns, Jr. 1979. Analyzing the Hazard Evaluation Process. Proceedings of the 1978 Workshop on the Application of Hazard Evaluation Programs for Chemicals in the Aquatic Environment. Amer. Fish. Soc., Washington, D.C.

Environmental Protection Agency. 1976. Quality Criteria for Water. Office of Water and Hazardous Materials, U.S. Environmental Protection Agency, Washington, D.C. 256 pp.

Fetterolf, C.M., W. Brungs, J.F. Jadlocki, and R. Parrish. 1979. Workshop Summary. Proceedings of the 1978 Workshop on the Application of Hazard Evaluation Programs for Chemicals in the Aquatic Environment. Amer. Fish. Soc., Washington, D.C.

Governments of United States and Canada. 1978. Great Lakes Water Quality Agreements of 1978.

International Joint Commission. Human Health Aspects Committee. 1979. Report within 1978 Great Lakes Water Quality Board Report to the International Joint Commission.

Malins, D.C., B.B. McCain, D.W. Brown, A.K. Sparks, and H.O. Hodgins. 1980. Chemical Contaminants and Biological Abnormalities in Central and Southern Puget Sound. NOAA Technical Memorandum OMPA-2. Office of Marine Pollution Assessment, Boulder, Colo. 295 pp.

Maugh, T.H. 1978. Chemical carcinogens: How dangerous are low doses. Science 202:37-41.

National Institute for Occupational Safety and Health (NIOSH). 1979. Registry of Toxic Effects of Chemical Substances (RTECS).

Riley, R.G., E.A. Crecelius, D.C. Mann, K.H. Abel, B.L. Thomas, and R.M. Bean. 1980. Quantitation of Pollutants in Suspended Matter and Water from Puget Sound. NOAA Technical Memorandum ERL MESA-49. Marine Ecosystems Analysis Program, Boulder, Colo. 99 pp.

Seattle METRO. 1980. Analyses of Seattle Harbor Sediments.

State of Michigan. (1978). Critical Materials Advisory Committee. Annual Report.

3. DESCRIPTION OF PUGET SOUND STUDY AREA AND SIGNIFICANT ENVIRONMENTAL PROCESSES

3.1 Description of the Puget Sound Study Area

The environmental fate and transport of contaminants is necessarily influenced by the physical as well as the chemical and biological characteristics of an environmental system. The purpose of this section is to define the Puget Sound study area and to outline, briefly, the main physical parameters characteristic of the Sound.

Puget Sound is located in the Pacific Northwest Region of the United States. It is bounded by the mountains of the Olympic Peninsula to the west, the mountains of Vancouver Island to the northwest, and the Cascade Mountains to the east. The northern end of the Sound opens to the Straits of Juan de Fuca and Georgia.

Puget Sound is divided into three main basins (Figure 3.1). The Northern Basin, usually referred to as the Whidbey Basin, extends from Possession Point to Deception Pass through Saratoga Passage; the Central or Main Basin extends south about 60 km from the Sound's major junction with Admirality Inlet near Possession Point to The Narrows; and the Southern Basin extends south of The Narrows to the head of the Sound.

3.1.1 Physical Characteristics

Puget Sound is a glacially modified lowland. It can be described as an estuary on the basis of Pritchard's (1967) definition: "a semi-enclosed body of water which has a free connection with the open sea and within which seawater is measurably diluted with freshwater derived from land drainage." The Sound has free connection with the Pacific Ocean through the Straits of Georgia and Juan de Fuca. Prominent points and embayments complicate the shoreline. Average depths within the steep-sided main channels range from 92 to 184 m with maximum depths to 276 m. The Main Basin and Southern Basin are separated by a sill (a cross channel ridge) at 44 m depth. This sill area is referred to as The Narrows (Figure. 3.1). Two sills are also found in Admiralty Inlet at 64 and 106 m (Barnes and Ebbesmeyer, 1976).

The study area of the MESA Puget Sound Project is confined to the Central and Southern Basins described above. Particular emphasis is placed on three urban subsystems: Elliott Bay, near Seattle; Commencement Bay, near Tacoma; and Sinclair Inlet, near Bremerton.

3.1.2 Hydrology and Circulation

Water circulation in Puget Sound is controlled by freshwater inflow, wind, and tides. Incoming marine water from the Pacific Ocean enters Juan de Fuca Strait at depths of 100 to 200 m and flows into Admiralty

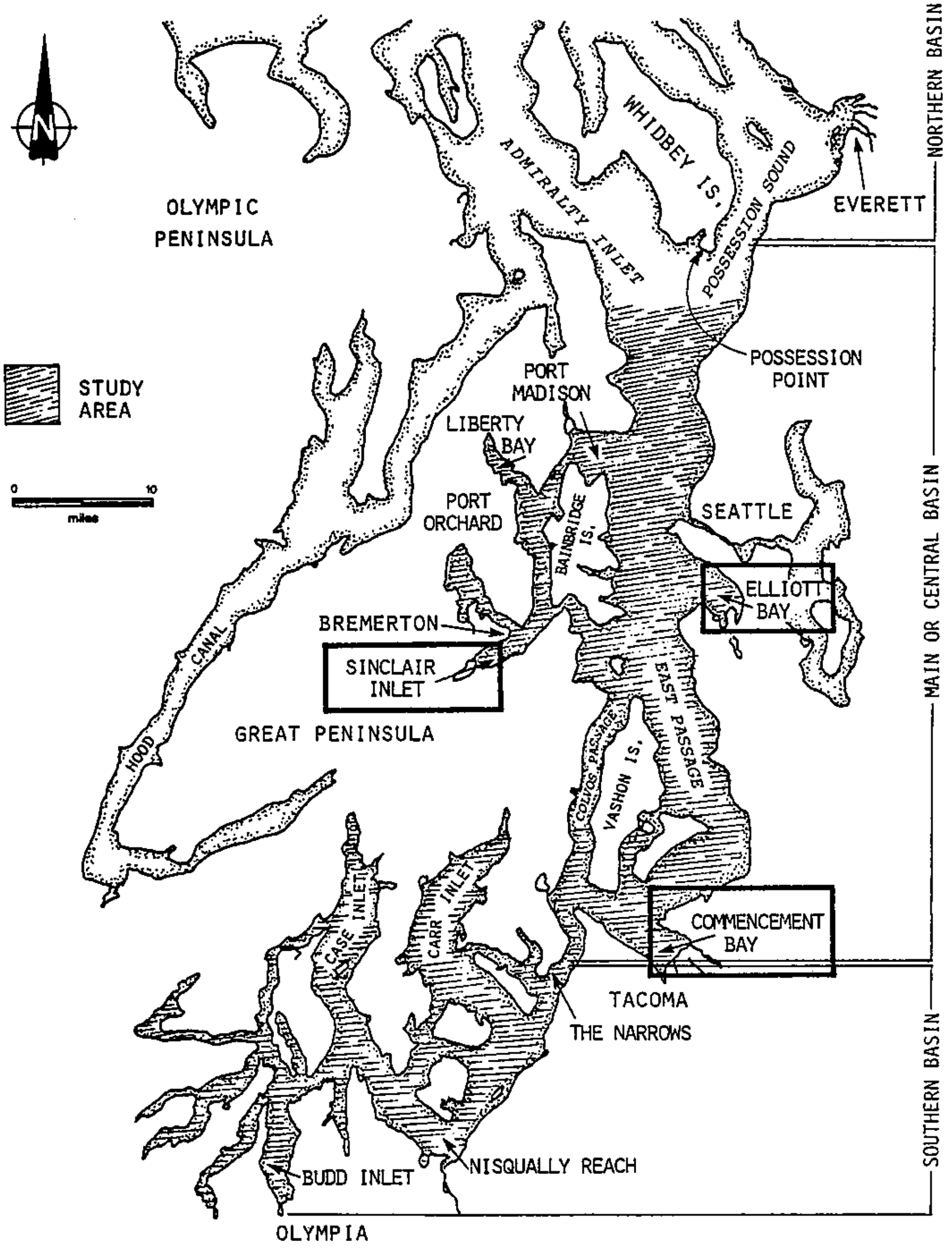


Figure 3.1

MESA Puget Sound Study Area

Inlet in the region of the two deep-lying sills. In this region the strength of the tidal currents acting against the sills is such that top-to-bottom mixing results. The presence of these shallow cross channel ridges in Admirality Inlet and The Narrows is an important feature of the Sound greatly influencing its water properties by reducing the extent of estuarine stratification.

Freshwater enters the Sound from various rivers, from local runoff, and from precipitation (Dawson and Tilley, 1972). The major rivers feeding Puget Sound are the Skagit, Snohomish, Cedar, Duwamish, Puyallup, Stilliguamish, and the Nisqually Rivers. The average daily freshwater discharge from the entire drainage basin (including the Northern Basin) to the Sound is 40,000-50,000 cubic feet per second. The Skagit and Snohomish Rivers account for one-third of the total discharge of freshwater into the Puget Sound Basin. The Stillaguamish and Puyallup Rivers each contribute 8% to the total flow.

Peak freshwater discharge in the Central and Southern Basins differs slightly from that of the Northern Basin. The northern drainage areas are higher mountainous regions where snow storage influences the timing of maximum runoff. The situation in the Northern Basin is not, however, as exaggerated as that associated with Fraser River discharge to the Strait of Georgia. In the Central and Southern Basins, maximum runoff occurrs from late fall through winter coinciding with heavy seasonal rainfall; whereas, the Northern Basin experiences a slight surge of freshwater discharge during June snowmelt.

Precipitation levels in the Puget Sound area are appreciable, varying from 58 cm to 104 cm. The eastern side of the Sound commonly receives a heavier rainfall by the rainshadow provided by the Olympic Peninsula Mountains to the west and the rain barrier formed by the Cascade Mountains to the east.

In addition to the surface outflows and the deep saline inputs from the Pacific Ocean, Puget Sound is subjected to significant tidal currents. Tides within Puget Sound are of the mixed semi-diurnal type characterized by two unequal high tides and two unequal low tides occurring during a single day. Average tidal range is 2.3 m. The tides control both the level of water and the rate of displacement of the upper mixed freshwater/seawater layer and the lower seawater layer.

Tidal pumping occurs between the Main and Southern Basins. Flood tides pump deep Main Basin water upward to mix with surface water in the region of the shallow sill (44 m) at the Tacoma Narrows. This mixed seawater floods into the Southern Basin and ebbing water returns variable amounts of river water, deep water, and Main Basin water (Barnes and Ebbesmeyer, 1976). Cannon et al. (1979) noted that the extremely high tidal currents through the Narrows appear to be capable of pumping deep water up from about twice the depth of the sill. This effect greatly assists the movement of deep water in Puget Sound. Seaward surface water circulation does not retrace the inflow route but goes out through Colvos Passage and into the portion of the Main Basin north of Vashon Island. Part may recirculate southward through East Passage and the rest continues northward (Barnes and Ebbesmeyer, 1978).

Cannon and Ebbesmeyer (1978) calculated an overall replacement rate of intermediate and deep water south of West Point in the Main Basin of about 9 days. Cannon et al. (1979) later approximated a deep water renewal rate of 1-2 weeks. These residence times of deep and intermediate waters appear to be much quicker than those calculated earlier by Friebertshauser and Duxbury (1972) of 2-10 months based on water property observations. Cannon et al. (1979) do not believe this apparent discrepancy is contradictory, reasoning that the results of Friebertshauser and Duxbury dealt with the total water column for the entire Puget Sound Basin including the slowly circulating Hood Canal. They also based their conclusions on monthly averages of water properties and did not make specific estimates for the Main Basin.

Wind may also have a role in affecting circulation patterns. Predominant wind directions within the Sound are from the northwest in spring, summer, and fall, and from the east and southeast in the winter. Average monthly velocities are approximately 10 knots (Vagners and Mar, 1972).

Variable circulation and displacement patterns may occur within the Sound. Collias et al. (1974) described the patterns in the following manner: "For some locations, such as the central portions of the major basins, short-term changes are relatively small and this portrayal can be considered quite representative of the water column. In other locations, as near the major constrictions in the channels or off the river mouths, the water properties fluctuate widely and rapidly with the tidal currents and may blur the longer period changes. In still other locations, such as the deeper waters of some basins, little change may occur for months, to be followed by rapid flushing which can be detected when all properties are considered."

3.1.3 Physical and Chemical Properties

3.1.3.1 Temperature

Surface temperatures follow the seasonal air temperatures with a variable time lag. Collias et al. (1974) stated that "in summer, surface temperatures generally are highest in the slowly circulating extremities of the various embayments and lowest in turbulent channels, while in winter, the lowest surface temperatures occur in the shallow, slowly circulating areas. The temperature at depth responds more quickly to advective processes than to local heat surface exchange and in some basins may be as much as 6 months out of phase with the surface temperature cycle. Top-to-bottom temperatures average lowest in March, lagging by 2 months the period of coldest regional weather."

Temperature ranges of surface waters are from 6.0 to 16.0°C (Collias et al., 1974). Bottom water temperatures are colder than surface water temperatures in the summer due to coastal upwelling. Bottom water temperatures range from 6 to 13°C. In the region of the sills, the temperature profile is fairly constant due to vigorous top-to-bottom mixing. Characteristically, stratified temperature regimes are found only in the deeper regions between sills.

3.1.3.2 Salinity

Surface salinity increases from near zero at river mouths to 31°/oo (parts per thousand) at Admiralty Inlet. Bottom salinity decreases from 33°/oo at Admiralty Inlet to approximately 28°/oo at the heads of the deeper arms due to top-to-bottom mixing at the Narrows. Inflowing ocean water is more saline in the summer at the peak of coastal upwelling, while surface water salinity is typically lower during peak river runoff periods, which occur from November to January (Collias et al., 1974).

3.1.3.3 Oxygen

Oxygen is supplied to the surface layer via gas exchange between the water and air surfaces, and photosynthesis. Oxygen decreases below the photosynthetic zone are probably due in part to the oxidation of organic compounds, mixing, and the lower oxygen content of inflowing ocean waters. Herlinveaux and Tully (1961), for example, reported that the lowest surface concentrations of dissolved oxygen were found in Juan de Fuca waters entering Puget Sound through Admiralty Inlet. Dissolved oxygen levels are lowest during periods of summer upwelling of deeper, more dense, oceanic water.

Collias et al. (1974) profiled the percentage saturation of oxygen within the Southern and Main Basins. General saturation levels varied from 50 to 110%. The profiles were not adequately detailed to indicate oxygen levels within localized areas.

3.1.3.4 pH

The pH levels of Puget Sound waters do not appear to change significantly with depth. In a water quality profile of waters sampled to 65 m depth, 0.3 km northwest of a West Point outfall, the pH range was 8.05 to 8.15 (Environmental Quality Analysts Inc., 1976). Such uniformity with depth substantiates an earlier observation that Puget Sound waters are well mixed in vertical profile, particularly in the region of the sills.

Thompson and Phifer (1936) recorded pH ranges from 7.9 to 8.4 in the surface waters of Puget Sound. Highest values were found at the head of Hood Canal, in Saratoga Passage, and in Skagit Bay.

3.1.3.5 Transparency

The depth to which one percent of incident light remains in Puget Sound waters varies from a maximum depth of 150 m to less than 50 m (Anderson, 1976). Nearshore areas would experience greater light attenuation at shallower depths due to a large suspended load. These waters absorb all wavelengths to a greater degree than clear ocean waters with the green-yellow wavelengths penetrating the farthest.

3.1.4 Sediment Characteristics

Sedimentation in estuaries may be very rapid when compared with rates for the open ocean because of the large input of suspended solids in estuaries by rivers. As a river enters an estuary the horizontal flow rates decrease, causing the suspended load to be deposited.

Sedimentation rates in Puget Sound range from 2 to 10.3 mm/yr depending on physical circulation of the water, distance from land, freshwater discharge, and bottom topography (Schell and Nevissi, 1977).

Sand and silt are the most common types of sediment in Sinclair Inlet and Commencement Bay. Clay was predominant under the Hylebos Bridge; shell and gravel were found at ASARCO. Elliott Bay sediments also consisted of mainly silt and sand, although clay was encountered at Harbor Island south and the Duwamish West Waterway (Malins et al., 1980).

The sand-to-mud ratio was less than 1 at most sampling stations; although Magnolia Bluff, West Point, Alki Point, Pier 42, the Tacoma Yacht Club, and the creek at the sewage plant in Commencement Bay were exceptions. In general, the percent organic carbon was highest in areas of low sand/mud ratio (Malins et al., 1980).

3.1.5 Biological Characteristics

3.1.5.1 Chlorophyll a

Chlorophyll a levels are a measure of the productivity of natural waters. The highest levels tend to be found in surface waters (less than 10 m depth), greater than 5 km from shore in the later spring and summer months. Increased levels of chlorophyll a coincide with the longest hours of sunshine, warmer surface water temperatures, and, hence, the largest phytoplankton blooms. Chlorophyll a levels decrease sharply at depths greater than 10 m due to light attenuation and nutrient decrease.

Chlorophyll a levels measured in Puget Sound surface waters ranged from 0.6 mg/m^3 in April to a high of 8.2 mg/m^3 in June (Anderson, 1976). These levels are indicative of algal growths which may be effective sinks for pollutants in the waters of Puget Sound.

3.1.5.2 Food Webs

Estuaries are among the most productive ecosystems supporting both abundant and diverse assemblages of organisms. Estuaries are very important juvenile-rearing grounds for anadromous fish species. The juvenile stage is extremely sensitive to suspended solid loads and contaminants in the water column. Abundant food sources, appropriate oxygen levels, and low contaminant levels must be ensured within the estuary for survival of these fish to reproductive age.

Important shellfish inhabiting the Puget Sound are oysters, crabs, hard shelled clams, shrimp, and scallops. Octopus and squid are also abundant. Anadromous fish found within the Sound include chinook, silver, sockeye, pink, and chum species of salmon, steelhead, sea-run cut throat trout, and Dolly Varden char. The saltwater fishery includes, rockfish, sole, flounder, black cod, truecod, sharks, rays, skates, ratfish, perch, anchovy, candlefish, halibut, herring, pilchard, smelt, turbot, greenling, and smaller fish not harvested for commercial fisheries.

The food web in these productive waters is necessarily complex. A detailed typical food web has been described by Chapman et al., (1979). Primary producers include phytoplankton (diatoms, dinoflagellates) and zooplankton (copepods, nauplii, and other planktonic forms of invertebrate species); in some nearshore and polluted areas, detritus-based food chains may be of significance.

Primary carnivorous and herbivorous species include bottom-dwelling shellfish such as molluscs, crustaceans, and annelids. Secondary carnivores include a large variety of fish species (demersal and nektonic).

3.1.6 Summary of Characteristics of Puget Sound

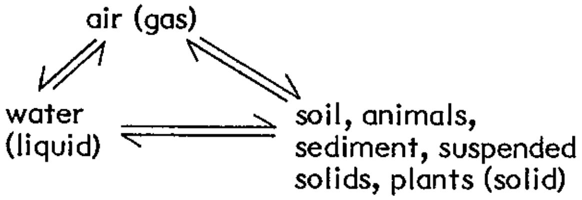
Puget Sound can be described as a water body which:

- is surrounded by a rural and urban population of greater than 2 million people;
- is a commercial and recreational resource;
- is a productive, biologically important ecosystem;
- is not exposed to severe variations in temperature, pH, or dissolved oxygen except on a localized basis; and
- is generally well mixed, with up to 2/3 of the Main Basin water that reaches Admiralty Inlet refluxed into the Puget Sound basins, while 1/3 exits through Admiralty Inlet.

3.2 Processes Affecting the Transport and Distribution of Chemical Contaminants in Puget Sound

3.2.1 Introduction

Chemicals in the Puget Sound ecosystem exist in gaseous, liquid, and solid phases in various ratios which are temperature, pressure, and solubility dependent. Within the ecosystem, a given chemical will be distributed between the three phases in accordance with the equilibrium diagram:



The relative distribution of a chemical among the three phases will be affected by several properties of the chemical which include its solubility in water and fat, its vapor pressure, and its ionic characteristics. In each phase, the chemical may undergo transformations by various reactions such as photolysis and biodegradation. This section reviews the processes and transformations which may affect the persistence and impact of chemicals in the environment.

3.2.2 Volatilization

The vapor pressure of a chemical will play a major role in the equilibrium of the chemical between the water body and the atmosphere. Vapor pressures, which are expressed in terms of mm Hg, may vary considerably for various compounds, i.e., 0.03 mm Hg for the parathion to 10^{-6}mm Hg for DDT.

Mackay and Leinonen (1975), Liss and Slater (1974), and Dilling (1977) have undertaken detailed studies of the rates of volatilization of gases from water bodies and have shown that the evaporation half life is approximately proportional to the square root of the molecular weight of organic compounds and inversely proportional to their vapor pressures. Higher temperatures will increase the rates of volatilization. Laboratory and theoretical calculations of volatility generally overestimate the actual volatility of a compound in the environment.

Volatilization rates of dissolved organic compounds in any given water body are enhanced by water turbulence, upwelling, and air currents. However, if the chemical is bound to suspended solids, volatility will be decreased appreciably. Suspended solid concentrations in the open waters of Puget Sound appear to be relatively low, implying that the volatilization process in the open waters would not be affected significantly.

Reference was made in several publications reviewed during this study to surface water microlayers, which are essentially thin layers of natural organic material capable of containing large quantities of lipophilic compounds such as DDT and PCB (Harvey and Steinhauer, 1975). The presence of this microlayer may enhance the volatility of organic compounds from the water layer to the atmosphere (Harvey and Steinhauer, 1975).

3.2.3 Photolysis

Photolysis, for the purposes of this study, refers to the process of stimulating chemical reactions or decompositions by absorption of visible or ultraviolet light from the sun. "Direct" photolysis implies light absorption by the affected chemical itself. Indirect or "sensitized" photolysis implies that photolytically activated forms of other substances react with the chemical. The photolysis rate depends chiefly on the intensity of light of the adsorbing wavelength.

The wavelengths and intensity of solar radiation available for photolysis of substances dissolved in water depends on the attenuation (weakening) of the light by both the atmosphere and the water medium.

The earth's atmosphere effectively reduces the intensity of light at wavelengths less than 290 nm. The water column will itself reduce the intensity of light in accordance with the Lambert-Beer Law Relationship shown below.

Lambert-Beer Relationship

$$\log \frac{I_o}{I} = a\,b\,c$$

where

I_o is the initial intensity of a particular wavelength of light
I is the intensity of light transmitted through the system

a is a coefficient indicative of absorption of a particular wavelength of light by a particular compound
b is the thickness of the medium
c is the concentration of an absorbing species (solute) in water

Specific wavelengths will transmit further into the water column than will others. For example, wavelengths indicative of yellow-green rays penetrate marine waters better than the low wavelength blue-violet rays. Zepp and Cline (1977) noted that attenuation of sunlight in oceans is primarily due to the water itself, but that in inland waters, absorption by dissolved organics is a major influence. Zepp and Cline

(1977) compared the attenuation of light in the photolytically-important, high energy 300-400 nm wavelength region, by pure water and by Savannah and Suwannee River water. The distances in the water column corresponding to 99% attenuation of light were, respectively, 15, 2 and 0.4 m. Anderson (1976) reported 99% attenuation of light in the open waters of Puget Sound at depths from 50 to approximately 150 m. Although Anderson's data appear to consider all wavelengths of light rather than just the 300-400 nm range, it does imply that the clarity of the open waters of Puget Sound is relatively pristine.

An absorption spectrum of a pollutant will determine the wavelengths which may potentially affect that pollutant. Absorption must occur to enable photodecomposition of a pollutant, although absorption does not necessarily imply that decomposition will occur. Decomposition may occur both within the water and the atmosphere.

The presence of suspended particulates and detritus near the surface, and dissolved organic material, will significantly reduce the transmission of sunlight and, consequently, the photolysis processes. This effect would probably be most frequent within nearshore areas.

Photodecomposition reactions are also promoted by the presence in water of oxygen, reducing agents, and nucleophilic ions; that is, these substances can be photolytically activated and the resultant species subsequently react with pollutants in water. Both saltwater and freshwater systems contain significant quantities of such species for reaction with pollutants (Crosby, 1972). There is also a remote chance of photolysis of chloride ion to form Cl_2^- and peroxide radicals which may degrade pollutants (Langmuir and Hayon, 1967). For example, Singmaster (1975) found rapid photodecomposition of DDT in seawater and relatively slow decomposition in distilled water. Additional photochemical studies in seawater are required to investigate this phenomenon.

3.2.4 Chemical Stability

There are three major solution processes which may affect the concentration of a pollutant: speciation (for inorganic pollutants), oxidation, and hydrolysis.

When a pollutant undergoes chemical change, the reaction products differ from the parent compound in toxicity, bioaccumulation, solubility, volatility, etc. Thus, such changes are of great importance in aquatic ecosystems.

3.2.4.1 Speciation

In the case of metals, speciation is the process by which a dissolved metal or metalloid reacts and equilibrates with other dissolved inorganic or organic substances. It also refers to changes in valence of a metal. For instance, a specific equilibrium state is reached when a known concentration of copper sulphate is added to natural waters containing known concentrations of chloride, carbonate and hydroxyl ions, humic acids, and other complexing organic species, at a defined temperature and reduction-oxidation (redox) potential. Equilibrium is rapidly reached and the equilibrium state would then be found to contain particular concentrations of such species as Cu^{2+}, $CuCl^{2+}$, $Cu(OH)^-$, Cu-humic acid complexes, and many other species. Each one of these species would probably have a different environmental impact. In fact, it is believed that the toxicity of copper-containing solutions can be largely ascribed to the Cu^{2+} form, with relatively low toxicity attributable to most others.

Models have been developed to predict the speciation of metals in natural waters. However, the presence of suspended particles and pelagic organisms will complicate these calculations. The former can selectively adsorb certain species, and the latter are capable of metabolizing ingested soluble forms and excreting organo-metallic or metal complex forms. In either case, the equilibrium state in the aqueous medium is affected.

There has been considerable attention recently to metal speciation in the environment. One reason is that water quality criteria on the basis of metal species rather than total metal content may be more meaningful to regulatory agencies and may lessen the burden on discharges of metals to the environment. A chemical analysis of metal speciation in environmental systems has been attempted by Batley and Florence (1976). Heavy metal solutions were analyzed according to their behavior with respect to anode stripping voltammetry (ASV), filtration, chelating capacity, and UV irradiation. It was possible to assay quantitatively seven different types of metal species in natural water samples on the basis of behavioral descriptions (such as "non-labile inorganic complexes dissociable by Chelex-100," a chelating resin), but not on specific chemical structures. The technique provided results in conflict with thermodynamic calculations (see the section on "Cadmium" in Chapter 4), and it is conceivable that the analytical procedures may disturb the equilibria. However, the technique is still relatively new, and future developments will be very useful for environmental applications.

In the case of organic compounds, speciation may refer to ionized and un-ionized species, such as phenols and phenates.

3.2.4.2 Oxidation

The oxidation of organic compounds in aqueous solution implies that the compounds combined with oxygen or that dehydrogenation of alcohols, for example, may have occurred.

Oxidation is known to occur in the atmosphere due to the presence of ozone and hydroxyl radicals resulting from solar radiation. Little is known about the significance of oxidation of organic compounds in the water column. Radding et al. (1977) have postulated that peroxy and alkoxy radicals may exist in aquatic systems resulting in the conversion of aromatic and aliphatic compounds to alcohols, ketones, and hydroperoxides.

For metals, oxidation would imply the conversion of a metal to a higher positive valence form. The process is dependent upon oxygen levels, pH, and the presence of other oxidizing and reducing agents.

The significance of oxidation to the fate of organic contaminants in Puget Sound is difficult to predict. Oxidation of metals is, however, an active and continuous process. The waters of Puget Sound are generally well oxygenated and, at various seasons and locales, are saturated or supersaturated near the surface (see Collias et al., 1974), thus favoring oxidative processes for metals.

3.2.4.3 Hydrolysis

The hydrolysis of an organic compound generally refers to the reaction of the compound with water to form a product with an initial functional group replaced by -OH, thus:

$$RX + H_2O \rightarrow ROH + HX$$

The reaction may be acid- or base-catalyzed and therefore generally pH-dependent.

As was the case with oxidation processes, hydrolysis rates also vary considerably depending upon the organic compound, presence or absence of metal ion catalysts, pH, and temperature (Mabey and Mill, 1978). Many of the organic compounds of concern within Puget Sound, such as PAHs, do not undergo hydrolysis.

3.2.5 Adsorption-Desorption

Adsorption is a general term indicating binding or association of dissolved material to suspended particles or to sediment. This process is of extreme significance in the transport, degradation, and bioavailability of pollutants. It has a significant effect on the relative distribution of pollutants within air, water, and solid phases.

Various factors will affect the adsorption of a pollutant to suspended particles or sediment. Adsorption will be affected by the characteristics of the pollutant, such as its polarity and water solubility, and by the characteristics of the particles or sediment, including surface area and organic content. The salinity of the water column will also affect adsorption. For example, increased salinity will enhance adsorption of organic pollutants to suspended particles. The most important variants for adsorption of organic pollutants appear to be the solubility of the pollutants in organic materials and the particle size and organic content of the solid phase.

A pollutant is distributed in accordance with an equilibrium coefficient (K) between adsorbed and solution phases, as in the expression:

$$K = \frac{\text{(conc. of pollutant in sorbent)}}{\text{(conc. of pollutant in water)}}$$

Baughman and Lassiter (1978) illustrated the significance of particle size on the K for several compounds. For example, K for pyrene distribution increased from 19,000 for a water-sand mixture to 122,000 for a fine silt-water mixture. Increases in organic content will also significantly increase the distribution constants.

Because organic content of sediments has a significant role in adsorption of organic pollutants, an experimental organic-water partition coefficient has often been used in the literature to predict adsorption of organics to sediments. The distribution of an organic compound between the organic solvent n-octanol and water is now widely used to predict the adsorption of organic compounds to the organic portion of sediments. The log of the distribution coefficient is referred to as "log P."

This factor is of extreme significance because many of the organic compounds of concern to Puget Sound have very high "log P's" or tendencies to associate with the organic phase. Because of such tendencies to associate with solids, the compounds will not be free to volatilize into the air. They may then sink to the bottom and/or they may be susceptible to microbial degradation by microbes associated with the solids.

The Freundlich equation describes adsorption equilibria and is frequently used in discussions of adsorption and desorption phenomena. The equation ($C_S = K(Cw)^{1/n}$) enables a prediction of the adsorption tendencies of a pollutant in water. C_S is the amount of adsorbed chemical per unit of adsorbent, Cw is the equilibrium solution concentration of the chemical, and K and n are constants. A high K implies a significant tendency of a pollutant to sorb to solids.

3.2.6 Bioaccumulation - Uptake and Depuration

The terms bioconcentration, bioaccumulation, and biomagnification have been inconsistently used in the literature. For the purposes of this report, bioconcentration refers to that process whereby chemical substances enter aquatic organisms through the gills or epithelial tissue directly from the water. Bioaccumulation is a process which includes bioconcentration and uptake of chemical residues from dietary sources. Biomagnification refers to a process by which tissue concentrations of bioaccumulated chemical residues increase as these materials pass up the food chain, through two or more trophic levels.

Bioaccumulation of metals is generally insignificant compared to bioaccumulation of organic chemicals. If a metal is present in solution simply as an uncomplexed ion, it will tend not to be lipid-soluble, and (in the case of fish) may accumulate in the gills rather than in internal organs. Accumulation may also occur as a result of diet. However, if the metal is present in a lipophilic organic form (such as a methyl mercury compound), then accumulation and migration in internal organs are enhanced. Filter feeders such as bivalve molluscs tend to accumulate metals through the adsorption of these metals to suspended particulates.

The bioaccumulation of dissolved organic molecules is greatest for highly lipophilic (or hydrophobic) substances. Much effort has been expended over the last decade or so in attempts to quantify this effect, particularly in the pharmaceutical industry, although attention was first drawn to the link between lipid solubility and biological effectiveness of organics at about the turn of this century (see Tute, 1971, for a review of this topic). The degree of bioaccumulation of organic compounds in animals has been shown to depend upon the lipid content of the animals, and organs with high lipid levels generally have the highest concentrations of organic compounds.

The common approach to a quantification of lipid solubility is to determine the experimental partition coefficient (P) of the organic compound between n-octanol and water, the alcohol being the model for biological lipid tissue. As an example, log P for trichloroethylene is 2.29 and for tetrachlorobiphenyl (PCB) is approximately 6. In other words, tetrachlorobiphenyl is one million times more soluble in n-octanol than in water. The American Institute of Biological Sciences (1978) Aquatic Hazards of Pesticides Task Group has recommended that compounds with log P greater than 3 be considered as of high bioaccumulation potential.

Generally speaking, if log P is unknown, it is assumed that the lower the solubility of a compound in water, the greater its log P. Good correlations have been shown to occur between log P and ecological magnification of compounds (Branson, 1975). As well, correlations have been indicated between the log Ps of families of organic compounds and their aquatic toxicity (Kopperman et al., 1974).

Currently, the state of the art is such that theoretical calculations of log P can be made solely from consideration of the structure of the organic molecule. The derived log P is expressed in terms of additive structural contributions from different parts of the molecule, using earlier experimental data as sources of log P contributions for these different molecular parts (Leo et al., 1971; Leo, 1975; Tute, 1971).

The overall performance of such theoretical estimates has been encouraging, but the application of experimentally or theoretically derived log P values for predicting environmental effects is not straightforward. Thus, Tulp and Hutzinger (1978) mention the following sources of uncertainty in applying log P estimates to environmental situations:

1. High salinity will decrease the water solubility (plus increase log P) of organics, by a "salting-out" effect. Therefore, high salinity areas of Puget Sound will increase the health hazard of soluble organics by enhancing their bioaccumulation, in comparison with the conditions in freshwater. Higher salinity areas in Puget Sound include the lower levels of the estuarine water column (so that benthic organisms would be more affected than pelagic organisms) and also shallow sites away from inflowing rivers. No log P values were found in the literature for organic-saltwater mixtures.

2. Many organics, particularly hydrocarbons, can exist in colloidal or particulate forms in appreciable quantities. For instance, chlorobiphenyls form stable emulsions in water. Hence, derived partition coefficients conceived in terms of "true" homogeneous solutions may provide misleading information on actual lipophilicity of the substance.

3. Many naturally occurring or anthropogenic organics present in trace amounts in rivers and estuaries can increase the solubility of non polar organics, thus decreasing biological uptake. Examples of such solubilizing substances are humic acids and artificial surfactants (detergents).

3.2.7 Biodegradation

Microorganisms are the principal biological agents for degradation of organic chemicals in the environment or transformation of metal ions to organo-metallic complexes. The rates of degradation will depend upon the strain of microorganisms, the populations of microorganisms, the availability of supplementary nutrients and, of course, temperature, and the nature of the chemical. Additional biodegradation or transformation of metals may occur as a result of metabolism of contaminants by, for example, fish and higher food chain organisms such as birds.

References

American Institute of Biological Sciences. 1978. Aquatic Hazards of Pesticides Task Group. In: J. Cairns, K.L. Dickson, and A.W. Maki (eds.), Estimating the Hazard of Chemical Substances to Aquatic Life. ASTM STP 657.

Anderson, G.C. 1976. Phytoplankton productivity and standing stock. In: A.C. Duxbury (ed.), Puget Sound Studies. Washington Sea Grant Report WSG-MR 76-3. University of Washington Press, Seattle. pp. 44-47.

Barnes, C.A. and C.C. Ebbesmeyer. 1976. Some Aspects of Puget Sound's Circulation and Water Properties. University of Washington, Seattle. NTIS (PB 274 655).

Barnes, C.A. and C.C. Ebbesmeyer. 1978. Some aspects of Puget Sound's circulation and water properties. In: B. Kjerfve (ed.), Estuarine Transport Processes. University of South Carolina Press, Columbia, S.C. pp. 209-228.

Batley, G.E. and T.M. Florence. 1976. A novel scheme for the classification of heavy metal species in natural waters. Analyt. Lett. 9:379-388.

Baughman, G.L. and R.R. Lassiter. 1978. Prediction of environmental pollutant concentration. In: J. Cairns, K.L. Dickson, and A.W. Maki (ed.), Estimating the Hazard of Chemical Substances to Aquatic Life. ASTM STP 657. pp. 35-54.

Branson, D. 1975. Predicting a bioconcentration potential of organic chemicals in fish from partition coefficients. In: G.D. Veith and D.E. Konasewich (eds.), Structure-Activity Correlations in Studies of Toxicity and Bioconcentration with Aquatic Organisms. International Joint Commission, Windsor, Ontario.

Cannon, G.A. and C.C. Ebbesmeyer. 1978. Winter replacement of bottom water in Puget Sound, In: B. Kjerfve (ed.), Estuarine Transport Processes. University of South Carolina Press, Columbia, S.C. pp. 229-230.

Cannon, G.A., N.P. Laird, and T.L. Keefer. 1979. Puget Sound Circulation: Final Report for FY77-78. NOAA Technical Memorandum ERL MESA-40. Marine Ecosystems Analysis Program, Environmental Research Laboratories, Boulder, Colo. 55 pp.

Chapman, P.M., D. Moore, and G.A. Vigers. 1979. Toxicant literature review and evaluation of Metro's experimental design. Prepared for the Municipality of Metropolitan Seattle, Wash. Prepared by E.V.S. Consultants Ltd., North Vancouver, B.C.

Collias, E.E., N. McGary, and C.A. Barnes. 1974. Atlas of Physical and Chemical Properties of Puget Sound and its Approaches. University of Washington Press, Seattle.

Crosby, D.G. 1972. The photodecomposition of pesticides in water. In: R.F. Gould (ed.), Fate of Organic Pesticides in the Aquatic Environment. Advances in Chemistry Series. Vol. 11. pp. 173-188.

Dawson, W.A. and L.J. Tilley. 1972. Measurement of salt-wedge excursion distance in the Duwamish River Estuary, Seattle, Washington, by means of the dissolved-oxygen gradient. U.S. Geological Survey Water-Supply Paper 1873-D, Washington, D.C.

Dilling, W.L. 1977. Interphase Transfer Processes. II. Evaporation rates of chloro methanes, ethanes, ethylenes, propanes and propylenes from dilute aqueous solutions. Comparisons with theoretical predictions. Environ. Sci. Technol. 11:405-409.

Duxbury, A.C. 1976. Puget Sound Studies. Washington Sea Grant Report WSG-MR 76-3. University of Washington, Seattle.

Environmental Quality Analysts, Inc. 1976. Water quality studies in the central basin. In: A.C. Duxbury (ed.), Puget Sound Studies. Washington Sea Grant Report. WSG-MR 76-3. University of Washington, Seattle. pp. 17-27.

Friebertshauser, M.A. and A.C. Duxbury. 1972. A water budget study of Puget Sound and its subregions. Limnol. Oceanog. 17:237-247.

Harvey, G.R. and D.G. Steinhauer. 1975. Biochemistry of PCB and DDT in the North Atlantic, In: J.O. Nriagu (ed.), Environmental Biogeochemistry: Vol. I. Elsevier/North Holland, Amsterdam.

Herlinveaux, R.H. and J.P. Tully. 1961. Some oceanographic features of Juan de Fuca Strait. J. Fish. Res. Board Can. 18:1027-1071.

Kopperman, H.L., R.M. Carlson, and R. Caple. 1974. Aqueous chlorination and ozonation studies. I. Structure-toxicity correlations of phenolic compounds to Daphnia magna. Chem. Biol. Interactions. 9:245-251.

Langmuir, M.E. and E. Hayon. 1967. Flash photolysis study of mercury (II) halide complexes in aqueous solution. Rates of reaction of X_2 radical anions. J. Phys. Chem. 71:3808-3814.

Leo, A. J. 1975. Calculation of partition coefficients useful in the evaluation of the relative hazards of various chemicals in the environment. In: G.D. Veith and D.E. Konasewich (eds.), Structure-Activity Correlations in Studies of Toxicity and Bioconcentration with Aquatic Organisms. International Joint Commission, Windsor, Ontario. pp. 151-176.

Leo, A.J., C. Hansch, and D. Elkins. 1971. Partition coefficients and their uses. Chem. Rev. 71:525-616.

Liss, P.S. and P.G. Slater. 1974. Flux of gases across the air-sea interface. Nature 247:181-184.

Mabey, W. and T. Mill. 1978. Critical review of hydrolysis of organic compounds in water under environmental conditions. J. Phys. Chem. Ref. Data 7:383-415.

Mackay, D. and P.J. Leinonen. 1975. Rate of evaporation of low solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 9:1178-1180.

Malins, D.C., B.B. McCain, D.W. Brown, A.K. Sparks, and H.O. Hodgins. 1980. Chemical Contaminants and Biological Abnormalities in Central and Southern Puget Sound. NOAA Technical Memorandum OMPA-2. Office of Marine Pollution Assessment, Boulder, Colo. 295 pp.

Pritchard, D.W. 1967. What is an estuary? In: G.H. Lauff (ed.), Estuaries. Am. Assoc. Adv. Sci. Pug. 83. pp. 3-5.

Radding, S. B., D.H. Liu, H.L. Johnson, and T. Mill. 1977. Review of the environmental fate of selected chemicals. Report No. EPA-560/5-77-003. U.S. Environmental Protection Agency.

Schell, W.R. and A. Nevissi. 1977. Heavy metals from waste disposal in central Puget Sound. Environ. Sci. Technol. 11:887-893.

Singmaster, J.A., III. 1975. Environmental behavior of hydrophobic pollutants in aqueous solutions. Ph.D. Thesis. University of California, Davis. 143 pp.

Thompson, T.G. and L.D. Phifer. 1936. The Plankton and Properties of the Surface Waters of the Puget Sound Region. University of Washington Press, Seattle.

Tulp, M.Th.M. and O. Hutzinger. 1978. Some thoughts on aqueous solubilities and partition coefficients of PCB, and the mathematical correlation between bioaccumulation and physico-chemical properties. Chemosphere 10:849-860.

Tute, M.S. 1971. Principles and practice of Hansch analysis: A guide to structure-activity correlation for the medicinal chemist. Adv. Drug Res. 6:1-77.

Vagners, J. and P. Mar. 1972. Oil on Puget Sound: An Interdisiplinary Study in Systems Engineering. University of Washington Press, Seattle.

Zepp, R.G. and D.M. Cline. 1977. Rates of direct photolysis in aquatic environment. Environ. Sci. Technol. 11:359-366.

4. REVIEW OF STATUS OF KNOWLEDGE ON TOXICITY AND BIOGEOCHEMICAL FATE OF SELECTED COMPOUNDS OF CONCERN

This chapter reviews the status of knowledge on toxicity and biogeochemical fate of 12 groups of organic compounds and seven metals which were chosen as being of concern in Puget Sound on the basis of the selection criteria outlined in Chapter 2. The organic compounds and metals are listed in Table 4.1:

Table 4.1
Chemicals Chosen to be of Concern in Puget Sound

1. DDT
   DDD
   DDE
2. Polychlorinated Biphenyls:
   - Chlorobiphenyl
   - Dichlorobiphenyl
   - Trichlorobiphenyl
   - Tetrachlorobiphenyl
   - Pentachlorobiphenyl
   - Hexachlorobiphenyl
   - Heptachlorobiphenyl
   - Octachlorobiphenyl
   - Nonachlorobiphenyl
3. Polychlorinated Dibenzofurans
4. Hexachlorobenzene (including other chlorinated benzenes)
5. Hexachlorobutadiene
   Pentachlorobutadiene
   Tetrachlorobutadiene
   Trichlorobutadiene
6. Dichloroethylene
   Trichloroethylene
7. Bis (2-ethylhexyl) phthalate
   Butylbenzyl phthalate
   Di-n-butyl phthalate
   Diethyl phthalate
   Dimethyl phthalate
   Di-n-octyl phthalate
8. Naphthalene
   - 1 methyl naphthalene
   - 2 methyl naphthalene
   - 1,3-dimethyl naphthalene
   - 2,3-dimethyl naphthalene
   - 2,6-dimethyl naphthalene
   - 2,3,5-trimethyl naphthalene
   - 2,3,6-trimethyl naphthalene
     - phenyl naphthalene
9. Benzo(a)Anthracene
   Dibenzanthracene
   Methyl (benzo(a)anthracene)
10. Fluoranthene
    - Benzo(b)fluoranthene
    - Benzo(g,h,i)fluoranthene
    - Benzo(i)fluoranthene
    - Methyl fluoranthene
    - Benzo(k)fluoranthene
11. Chlorinated naphthalene
12. Other halogenated polyaromatic hydrocarbons
13. Arsenic
14. Cadmium
15. Copper
16. Lead
17. Mercury
18. Selenium
19. Silver

The contaminants of concern are discussed in a format which stresses their potential impact on the biological communities of Puget Sound. As a result, contaminants are discussed initially in terms of their known aquatic toxicities and biological uptake. This approach is designed to emphasize the significance of each of these compounds to Puget Sound in the light of those environmental processes which affect the persistence of each compound.

4.1 DDT and its Metabolites

4.1.1 Introduction

DDT is a pesticide which has been suspended from production and use in the United States since 1972. It is a highly persistent chemical which has been detected throughout the world in water, sediment, air, and various biota, including man. Aquatic organisms are extremely sensitive to low concentrations (i.e., < 5 µg/L) of this pesticide. Fish-consuming birds are particularly sensitive to diets containing small quantities of DDT and its metabolites. The most common metabolites of DDT are referred to as DDE and DDD. Analytical results are frequently expressed as a total of DDT and its metabolites, DDD and DDE, and the total may be expressed in the literature as "t-DDT" or "DDT."

DDT and its metabolites, DDD and DDE, are on the EPA's 129 Priority Pollutant List. Despite its restricted use in North America, DDT was selected as a critical compound because of its low LC50 values, its distribution throughout the Sound, its relative inability to degrade in Puget Sound when compared to degradation rates observed in other marine environments, and because the levels of DDT and its metabolites in Puget Sound may constitute a hazard to some portion of the aquatic ecosystem.

4.1.2 Significance to Puget Sound

4.1.2.1 Review of Known Toxicity Data

The Environmental Protection Agency publication Quality Criteria for Water (1976) suggested that there should be no more than 0.001 µg/L of DDT (including its metabolites) in marine and freshwater to protect aquatic life. Some of the data upon which the criterion was based included that of Nimmo et al. (1970), whereby no survival of the shrimp, Penaeus duorarum, was observed at 0.12 µg/L after 28 days exposure and 30% mortality was observed at 0.05 µg/L after 56 days. Cox (1972) showed that DDT levels of 1 µg/L would inhibit photosynthesis by marine phytoplankton. The actual selection of the 0.001 µg/L criterion was based on the bioaccumulation potential of DDT and its major metabolite DDE within fish, and the effects of such bioaccumulated contaminant levels on fish-consuming birds. DDE levels have been associated with eggshell thinning for the brown pelican (Blus, 1972). Eggshell thinning has also been reported in the American kestrel after chronic feeding with 2.8 µg DDE/gram feed. Mallard ducks exhibited egg shell thinning with diets containing 2.8 µg DDE/gram feed.

Eggshell thinning has been shown to result in significant detrimental effects on reproduction of fish-consuming birds. As a result, the International Joint Commission (1977) recommended to the Governments of Canada and the United States that the "sum of concentrations of DDT and its metabolites in fish (wet weight) should not exceed 1.0 micrograms per gram (µg/g) for the protection of fish-consuming birds."

The EPA Quality Criteria for Water (1976) suggests that there should be a no-effect level from diets containing less than 0.2 µg of DDT and its metabolites per gram of fish.

Hom (1974) suggested that both DDE and PCB are associated with a high incidence of premature deaths among sea lions.

The United States Food and Drug Administration and the Canadian Food and Drug Directorate Administrative action guidelines for DDT in edible portions of fish are 5 µg/g.

4.1.2.2 Possible Effects of Levels Found in Puget Sound

Despite the ban on DDT usage, there still exists the probability that certain biota within Puget Sound may exceed either of the dietary suggested maximum levels of 0.2 or 1.0 µg/g. The dietary levels are, however, calculated on a "wet weight" basis, while all analytical levels provided for this study were calculated on a "dry weight" basis. Table 4.1.1 summarizes the levels of DDT and its metabolites which were found in biota and sediments of Puget Sound. Biota from Elliott Bay and Commencement Bay contain much higher levels of DDT and its metabolites than biota from other areas of Puget Sound, indicating that the contaminant levels are due to current or past localized sources rather than global non-point sources.

Due to decreasing levels of DDT and its metabolites in the North American environment, it is difficult to assess the comparative levels of t-DDT found in Puget Sound during 1979 with levels found in other areas of North America during, for example, 1974. Nonetheless, some values are reported herein to provide comparisons of degree of contamination within Puget Sound. Choi and Chen (1976) reported t-DDT levels of 0.12, 0.24, 0.30, 0.32, 0.35, 0.83 and 3.2 ppm in sediments from Los Angeles Harbor. The major components were p, p'-DDE (61-71% of the total) and p, p' -DDD (10-16.67, of the total). Levels of DDT were minimal, i.e., p, p'-DDT 2.8-7.7% of the total, and, o,p'-DDT 2.6-4.6% of the total. Marchand et al. (1976) reviewed DDT concentrations in mussels from various marine sites. Mussels from the Swedish coast contained no detectable amounts of DDT and small amounts of DDE and DDD. California coast mussels analyzed in 1965-1966 contained 19-34 ppb t-DDT and mussels from the northwest Mediterranean coast contained from 50 to 10,000 ppb t-DDT in 1973-1974, most of which was p,p'-DDT.

Butler and Schutzmann (1979) reported levels of t-DDT in livers from representative marine fish sampled in 1974 from the North Atlantic. Average wet weight values in livers of some of the fish were as follows: longhorn sculpin, 100 ppb; yellowtail flounder, 20 ppb; cod, 700 ppb; haddock, 320 ppb; and American plaice, 50 ppb. Goosefish contained the highest average values of t-DDT: 1,350 ppb. The predominant metabolic forms were DDE and TDE (tetrachlorodiphenyl ethane). Spiny dogfish contained large quantities of t-DDT (i.e., 4.76 ppm composite sample), of which 58% was DDT.

Table 4.1.1

Levels of DDT and Its Metabolites in Puget Sound

		Dry Weight (ppb)						
		DDT		DDE		DDD		
Site	Sample	o,p'	p,p'	o,p'	p,p'	o,p'	m,p'	p,p'*
Elliott Bay	Sediments	<.04-30	<.05-20	<.2-4	<.03-2	<.05-83	<.07-9	<.04-30
	Crab hep.		120	510	1900	50	460	510
	Worm		< 2-3	< 2-2	10-15	< 2-2	4-10	10-20
	Shrimp		<2	< 1	10	< 1	< 2-4	2-10
	Clams		< 10	< 10	10	< 10	5-10	1-4
	Liver - E. Sole		30-90	<10-5700	60-230	<10-10	<10-90	30-280
	Liver - R. Sole		< 40	< 20	130	< 30	< 50	<10
	Liver - Sculpin		20-40	10-20	290-870	10-20	<20-140	90-150
	Liver - Rockfish		10-290	10-30	150-1000	3-30	20-240	40-310
	English Sole Liver (Composites)	30-650	40-630	1-30	50-700	<2-40	10-290	30-650
	Rock Sole Liver (Composites)	20-90	30-130	<1-3	20-120	< 7	9-40	20-90
Commencement Bay	Sediments	<0.1-50	<0.05-70	<.04-20	<.01-30	<.02-6	<.05-10	<.1-50
	Crab hep.		40-80	20-80	1100-1500	10-20	240-730	120-320
	Clams	2-40	<2-80	<2	10-20	<3	3-10	2-40
	Worm		<4-4	<2-3	10-50	<2-4	5-10	3-20
	Shrimp		<5	<1-4	10-40	<1-10	<2-40	1-5
	Liver English Sole (Ind.)	50-270	20-340	<10-90	210-710	<4-10	<30-90	50-270
	Liver R. Sole (Composites)	<1-340	4-50	<10-340	2-10-180	<2-10	<4-30	<1-340
	Liver E. Sole (Composites)	50-110	10-190	120-620	160-460	<4-10	<40-140	50-110
	Liver Sculpin (Composites)		190-700	10-1400	50-800	<5-10	30-120	70-170
	Liver Rockfish (Composites)		360	30	710	10	70	60
	Liver Tom Cod (Composites)		310	30	490	<4	110	160

Table 4.1.1 (contd)

		Dry Weight (ppb)						
			DDT		DDE			DDD
Site	Sample	o,p'	p,p'	o,p'	p,p'	o,p'	m,p'	p,p'*
Sinclair Inlet	Sediments	1-9	0.9-4	.7-4	.2-2	.2-1	< 2	1-9
	Crab hep.		10	5	190	10	60	50
	Worm		< 5	< 3	10	< 3	10	10
	Shrimp		3	< 1	10	1	10	10
	Livers - E. Sole (Composite)		190	< 2	130	10	80	170
	Liver - R. Sole (Composite)		60	< 20	90	3	20	40
Port Madison	Sediments	0.1-0.3	0.1-0.6	< .04-.3	< .02-.2	< .04-.08	< .06-.1	.1-.3
	Livers - E. Sole (Composite)		60	< 10	100	3	10	40
	Livers - R. Sole (Composite)		30	< 10	70	2	10	20
	Worms		< 3	< 1	5	< 2	< 2	< 1
	Shrimp		< 2	< 1	4	< 1	2	1
	Clams		< 1	< 1	2	< .9	< 1	< 1
Case Inlet	Sediments	0.03-0.3	< .2	< .1	< .1	< .1	< .3	< .03-.3
	Livers - E. Sole (Composite)		30	< 10	60	1	10	30
	Livers - R. Sole (Composite)		10	< 3	30	.4	2	10
	Crab hep.		1	<.6	30	< 1	3	10
	Shrimp		2	< 1	10	< 1	< 2	< .5
	Clams		2	< 1	1	< 1	< 2	< 1
Budd Inlet	Sediments	< 0.6-1	<.08-1	< .1	< .04-.7	< .3	< .1-.2	<.6-1
	Liver - E. Sole (Composite)		30	< 10	80	2	10	30
	Liver - R. Sole (Composite)		20	< 10	60	1	5	20
	Crab hep.		4	2	140	< 1	20	20
	Shrimp		< 1	< 1	10	< 1	2	2
Madison Park (Seattle Harbor)	Sediments		3164		775			321.3

*Mixed - p,p'-DDD and o,p'-DDT

Comparisons of the Puget Sound dry weight tissue data prepared by Brown (1979) are difficult to compare with the wet weight values reported by Butler and Schutzmann (1979). Dry weight composition varied from 12 to 26 % of the total weight of various fish livers sampled during the MESA program. Nonetheless, some Puget Sound samples would greatly exceed the levels observed by Butler and Schutzmann (1979) following conversion to obtain approximate wet weight values. For example, individual sculpin livers from Commencement Bay contained from 540 to 1200 ppb t-DDT dry weight. Using the minimum concentration factor of four, the wet weight liver samples would have contained from 130 to 300 ppb t-DDT which are in excess of the 100 ppb t-DDT levels observed in North Atlantic sculpin livers.

4.1.3 Physical Properties of DDT and Its Metabolites

Technical DDT is a mixture of three isomers - p,p', o,p', and o,o' as shown in Figure 4.1.1. Gunther and Gunther (1971) analyzed several technical mixtures and found compositions which varied from 70 to 73% p,p'-isomer, 12 to 21% o,p'-isomer and less than 1% of the o,o'-isomer.

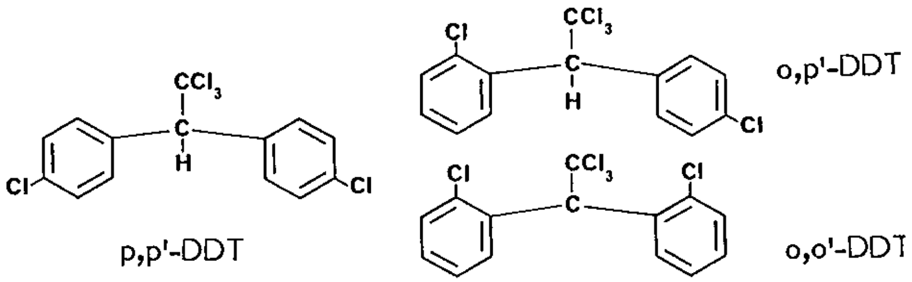


Figure 4.1.1
Isomers of DDT found within Technical Mixtures

DDD is also found within technical mixtures of DDT and the major isomer is p,p', as shown in Figure 4.1.2. It has also been shown that DDD is a metabolite of DDT. Commonly mentioned metabolites of DDD are DDMU and DDA, which are shown in Figure 4.1.2.

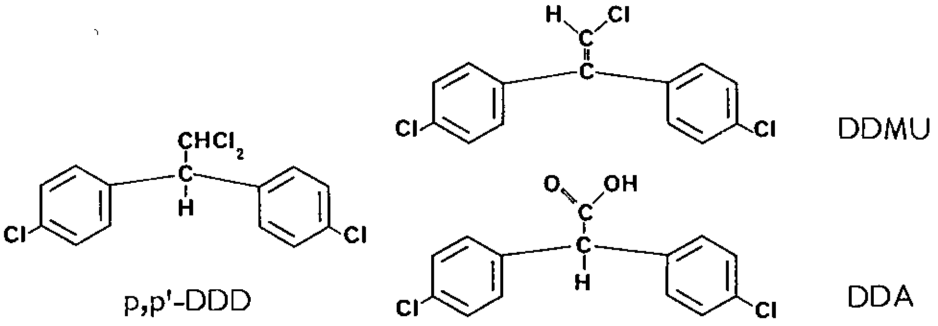
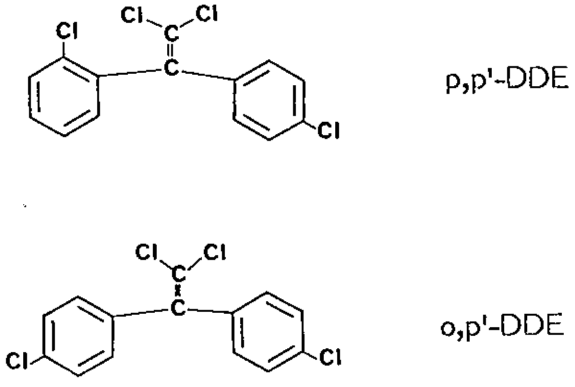


Figure 4.1.2
Structures of DDD, DDMU, and DDA

A major degradation product of DDT is DDE. Two isomers of DDE, namely, the o,p'- and p,p'-isomers are illustrated in Figure 4.1.3.



p,p'-DDE

o,p'-DDE

Figure 4.1.3
Structures of the o,p' - and p, p'-Isomers of DDE

Table 4.1.2 shows the physical properties of significance to the environmental fate of DDT and its metabolites. The properties indicate that: DDT and its metabolites are of low solubility in water; they are highly lipophilic (based on the log octanol/water partition coefficients) and, therefore, would tend to associate strongly with organic matter. Volatility would be minimal due to the very low vapor pressures.

4.1.4 Sources or Inputs

Due to the existing restrictions, DDT has not been used in the United States since 1972, except for extraordinary situations. One such situation was the application of DDT in Oregon and Washington in 1974 (Peakall, 1976). The highest levels of DDT and its metabolites in Puget Sound are found in the Elliott and Commencement Bay areas. This occurrence may be the result of past discharges into the rivers or transient inputs (i.e., spills, dumping of waste materials). Past or current residual chronic input, such as from land disposal sites, may also be responsible. No estimates of past or current inputs of DDT to Puget Sound were found in the literature.

4.1.5 Summary of Biogeochemical Fate Data in the Marine Environment

4.1.5.1 Bioaccumulation - Uptake and Depuration

Summary Statement: Bioaccumulation is an important fate process for DDT and its metabolites. Uptake of DDT occurs primarily via the gills of aquatic biota and there is little or no evidence for food chain magnification. Depuration rates are very slow compared to uptake

Table 4.1.2

Physical Properties of DDT and Its Metabolites*

	DDT		DDE		DDD		
	o,p'	p,p'	o,p'	p,p'	o,p'	m,p'	p,p'
Molecular Weight	354.5	354.5	318	318	320	320	320
Vapour Pressure (torr)	5.5×10^{-6}	1.5×10^{-7}	6.2×10^{-6}	6.5×10^{-6}	18.9×10^{-7}		10.2×10^{-7}
Solubility in Freshwater (µg/L)	26 85	5.5 25 1.2	140	14 120 40	100		20
Solubility in Saltwater							
Log Octanol/Water Partition Coefficient		3.98 to 6.19	5.78	5.69	6.08		5.99

*Callahan and Slimak (1979)

rates indicating that high bioaccumulation factors will occur. Generally fatty tissues such as hepatopancreas, egg masses and liver are the sinks for DDT and its metabolites within biota. However, exceptions have been shown. Bioaccumulated DDT may affect reproduction rates of Puget Sound organisms.

Review of Individual Studies: Many studies have been reported in the literature on the bioaccumulation of DDT. The studies of Hamelink et al. (1971) were the first to indicate that biological magnification via the food chain was not a major cause of the large levels of DDT observed in higher food chain organisms. Their work indicated that uptake of DDT by fish was a result of a respiratory process whereby DDT was absorbed from the water phase to the body system via the lipids within the fish gills. The investigators predicted that uptake would decrease in the presence of additional binding sites in the aquatic medium such as suspended matter (i.e., eutrophic or turbid waters) or sediments with high organic content. A bioconcentration factor for DDT (concentration in fish/concentration in water) of 10^6-10^7 was estimated. Jarvinen et. al. (1977) determined that clams reached equilibrium with trace quantities of DDT (1.8 µg/L) after 56 days exposure and with a 25,000-fold bioconcentration factor.

Harvey and Steinhauer (1975) found no evidence of food chain magnification of DDT among biota of the North Atlantic. High or low levels of t-DDT bore no relation to species trophic levels. Ratios of DDE to DDT increased with depth of habitat and with increasing trophic levels, indicating the greater ability of higher trophic levels to metabolize DDT. For example, the DDE/DDT ratio in shark liver was in excess of 100, while the ratio was 32 in brotulid liver.

However, the results of Macek et al. (1979) and Jarvinen et al. (1977) indicated that dietary uptake of radiolabelled DDT does occur. Contributions from the food chain (diet) to fish bioaccumulation levels were estimated to vary from 27 to 62%. Following uptake studies of various radiolabeled chemicals, Macek et al. (1979) concluded that DDT appeared to be the only chemical of the group with potential for uptake from the food chain. Dietary contributions for the other chemicals varied from 0.1% for kepone to 14% for diethyl hexyl phthalate. The estimated bioaccumulation factor for DDT in the fathead minnow was 133,000 (Macek et al., 1979).

Many studies have also attempted to determine the fate of DDT in aquatic organisms. For example, Guarino et al. (1974) used ^{14}C-labeled DDT to study the uptake, fate, and distribution of DDT in lobster. Seven days after injection, 90% of the injected radioactivity was found in the hepatopancreas. Likewise, 90% of radioactivity absorbed from diet and/or water was found in the hepatopancreas. The depuration half life of absorbed DDT was approximately 46 days. Analyses of commercial lobsters by Guarino et al. (1974) showed that egg masses had the highest concentrations of t-DDT (1 ppm) compared to hepatopancreas (0.4 ppm) and muscle (0.1 ppm). Guarino et al. (1974) speculated that such concentrations in egg masses could be of significance to reproduction.

Depuration half lives (t½) of DDT appear to be species dependent. For example, Nimmo et al. (1970) found that metabolism and depuration of DDT within shrimp occurred at a rapid rate with a half life of approximately 5 days. This observation may account for the relatively low levels of t-DDT found in shrimp of Puget Sound (Table 4.1.1). The half life (t½) represents the time it takes for an organism to excrete one-half of its bioaccumulated quantity of chemical after the organism is placed in clean water.

Macek et al. (1979) reported very slow depuration rates for fish. He calculated half lives of DDT from rainbow trout and lake trout in excess of 125 days.

Pritchard et al. (1973) applied intravenous injections of ^{14}C-DDT to winter flounder at levels equivalent to 0.1 mg/kg fish. Within the first 15 minutes, most of the pesticide was found in the plasma. After one hour, distribution occurred primarily in the carcass (muscle plus skin), liver, kidney, and plasma. After one week, the carcass which constituted 89% of the total weight of the fish, contained 80% of the pesticide. The liver, plasma, and other organs lost DDT, and the carcass acted as a sink. The initial uptake was not dependent upon the lipid content but rather upon the blood flow. Subsequent distribution was in accordance with lipid level. Urine accounted for a loss of 2% of the dose in one week, with 15-28% of the excreted dose being DDT and 50-70% converted to polar metabolites such as DDA and dichlorobenzophenone. Analyses of the carcass, plasma, and liver detected few metabolites. Only 2.6% of the DDT was converted to DDD and 1.3% to DDE. As a result of the observed time-dependent redistribution of DDT in body tissue, Pritchard et al. (1973) concluded that toxic effects of DDT may differ during long- or short-range tests because organs could be exposed to different concentrations at different time periods. Also, the investigators concluded that consumption of flounder flesh should be of concern because the residue burden was mainly within the muscle.

DDT may not be distributed similarly within all fish. Dvorchik and Maren (1972), for example, showed that dogfish, which has a large liver with a high lipid content, essentially retained most of the DDT. The liver was essentially the "sink." The flounder studies described by Pritchard et al. (1973) indicate that analyses for DDT and its metabolites in fish should not be restricted to the liver and that lipid contents in test species should be determined.

The rapid uptake and slow elimination of DDT by marine organisms, implies that low background levels of t-DDT may result in continued observed t-DDT levels in biota for many more years. Harding and Vass (1979), for example, found high first order uptake rate constants for euphausiids and copepods (0.7-1.21 x 10^4/day and 1.04-2.51 x 10^4/day, respectively) and low first order clearance rate constants (0.043/day and 0.048/day) respectively. Based on rate constants obtained from kinetic studies and on the current levels of t-DDT in natural planktonic crustaceans, Harding and Vass (1979) estimated that t-DDT in Atlantic seawater was considerably less than 0.1 ng t-DDT/L.

Hargrave and Phillips (1976) undertook a study of DDT distributions among various food chain levels in St. Margaret's Bay (Nova Scotia). With the ratio of p,p'-DDE to p,p'-DDT regarded as an index of metabolism, the investigators found that less than 50% of the t-DDT in benthic invertebrates (snails, holothurians, mussels, cumaceans, and four species of infauna) was p,p'-DDE. In all species of demersal fish, predatory starfish, and gastropods, 75% was p,p'-DDE. In the amphipod Ampelisca spp., only p,p'-DDE was detected. Highest t-DDT concentrations (on a lipid basis) for whole organisms were found in lobster, cod and plaice muscle, benthic lumbrinerid polychaetes, and the mollusc Crenella glandula. Benthic invertebrates such as amphipods, M. edulis and Littorina littorea, contained the lowest concentrations. No consistent relationship between DDT levels and lipid concentrations or trophic levels could be found. For example, carnivorous fish such as the thorny skate and Atlantic wolffish contained low t-DDT levels despite their high trophic positions. Hargrave and Phillips (1976) estimated that the background level of t-DDT within benthic invertebrates and demersal fish due to chronic contamination of the biosphere was 10.5 ± 8.8 ppb (grand mean - wet tissue). The low chronic supply of t-DDT may be the result of constant recycling - excretion and adsorption to particulate matter.

4.1.5.2 Metabolism

Summary Statement: The compound p,p'-DDT is metabolized to p,p'-DDD and p,p'-DDE by marine organisms however the degree of metabolism of p,p'-DDT may vary considerably among individual organisms. DDE is the predominant form found in tissue of aquatic biota indicating that DDT is gradually disappearing from the environment. However, DDT is found in greater quantities (relative to DDE) in Puget Sound than in other aquatic environments, indicating that, for some reason, metabolism of DDT in Puget Sound is much slower.

Review of Individual Studies: McKinney and Fishbein (1972) reported that formation of metabolites would depend upon the presence of appropriate enzymes and upon the degree of enzyme induction. Organisms conditioned with DDT (where enzyme induction was at a maximum), would predominantly metabolize DDT to unsaturated compounds such as DDE and DDMU. These unsaturated metabolites could in turn be converted to more polar and excretable metabolites such as DDA. Where preconditioning may not have occurred, saturated metabolites such as DDD are found.

Plankton and Invertebrates: Hargrave and Phillips (1976) noted that filter-feeding molluscs and snails feeding on suspended and sedimented particulate matter from epiphytic materials and seaweed debris contained higher portions of p,p'-DDT than other organisms. DDE and DDD were also virtually absent from zooplankton and Hargrave and

Phillips (1976) concluded that DDT in suspended particulate matter was essentially undegraded. Darrow and Harding (1975) found no metabolites in marine copepods which contained from 50-100 ppm DDT. However, other investigators have found evidence for some degree of metabolism of DDT by planktonic species. Bowes (1972) studied the ability of 7 marine phytoplankters to convert 80 ppb DDT to DDE, and noted a maximum conversion of 7.5%. Growth inhibition which occurred at higher DDT levels was attributed to inhibition of "noncyclic electron flow."

Fish: Temperature has been shown to have a significant effect on metabolism of DDT by fish. Zinck and Addison (1975) showed that the rate of p,p'-DDT degradation by brook trout, Salvelinus fontinalis, more than doubled during a temperature increase from 2 to 18°C. The half life of p,p'-DDT within the trout was estimated to be 2.95 years at 2°C, 1.79 years at 10°C, and 1.12 years at 18°C.

Marine fish have varying abilities to metabolize DDT. Butler and Schutzmann (1979) showed that New England coastal fishes less than four years old contained 70% of t-DDT as DDE, 19% as TDE, and 11% as DDT. Dogfish contained 29% of t-DDT as DDE, 13% as TDE and 58% as DDT. The authors suggested that there was significant attenuation in transmittal of the compounds to successive broods of the same female. Residues in dogfish were predicted to remain detectable for many more years. Their results also indicated that DDT was gradually disappearing from the environment and estuarine food web. Pooled samples of 25 estuarine yearling fish were analyzed annually from 1972-1976. In 1972, 97% of the samples contained more than 9 ppb t-DDT, of which 31% was DDT, 25% was TDE, and 44% was DDE. In 1976, 18% of the samples contained more than 9 ppb t-DDT, of which 0% was DDT, 18% was TDE, and 82% was DDE.

Results of other more recent fish sampling efforts have also shown the virtual absence of DDT. For example, Herdendorf et al. (1978) found that fish from Lake Erie sampled during 1976 and 1977 contained DDD and DDE, with fewer than 10% of the samples containing detectable quantities of DDT. These results differ from the Puget Sound data in that DDT is still detectable in Puget Sound biota in quantities which may even exceed DDE levels.

Microorganisms: Crosby (1973) in his review of metabolic processes of DDT, stated that microorganisms are a major factor in the conversion of DDT to DDE in the environment. Marei et al. (1978) incubated DDT in the presence of sewage sludge and found DDD to be the major metabolic product. Ware and Roan (1970), in their review of the interaction of pesticides with aquatic microorganisms, also showed that DDD was rapidly formed in anaerobic sludges with virtually no conversion to other metabolites. Porphyrins were noted to convert DDT to DDD under anaerobic conditions. DDD was also susceptible to further degradation to DDCO or bis-(p-chlorophenyl)-methane (Johnsen, 1976).

Under aerobic conditions DDT was found to be slowly degraded to DDE with no further degradation (Ware and Roan, 1970). However, no data were found to assess the rate of DDT transformation by microorganisms in aquatic environments. The rapid flushing conditions in Puget Sound probably ensure an aerobic environment within most areas of the Sound, and microbial degradation of DDT in Puget Sound may not be significant.

Higher Food Chain Organisms: Mammals can metabolize and excrete DDT as DDA or other oxygenated fragments including dichlorobenzophenone and p-chlorobenzoic acid (Crosby, 1973). The clearance rate is balanced by continuous intake and subsequent temporary storage. Metabolic pathways in humans and animals are illustrated in Figure 4.1.4.

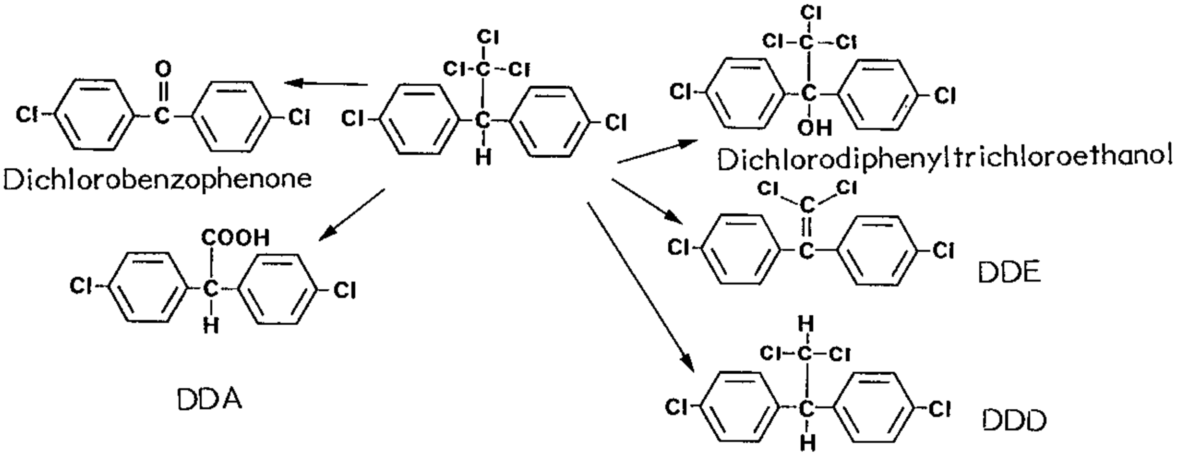


Figure 4.1.4
Metabolic Pathways for DDT in Mammals

Jansson et al. (1975) found hydroxylated metabolites of DDE in droppings of seal and guillemot from the Baltic, giving the first indication of DDE metabolites in higher food chain organisms.

The recent analytical programs indicated that of the concentrations of DDT and its metabolites in biota of Puget Sound, DDE was the predominant form. Quantities of DDD and DDT were similar to each other, but lower than DDE in most instances. Metabolic degradation of DDT is occurring in Puget Sound, however, at an apparently slower rate than in most other areas of the world.

4.1.5.3 Sorption and Sedimentation

Summary Statement: DDT and its metabolites have a high tendency to associate with sediment and suspended solids. Association is enhanced by increasing salinity. There is some evidence for uptake of adsorbed DDT by biota. DDT rather than DDE is the predominant form found in Puget Sound sediments, indicative of possible decreased metabolic conversion.

Review of Individual Studies: Many studies have shown that DDT and its metabolites are strongly adsorbed to sediments and suspended solids. For example, Cox (1972) found that most DDT residues recoverable from seawater were bound to particles less than 1-2 µm in diameter. Choi and Chen (1976) determined that p,p'-DDE accounted for 60-70% of the total chlorinated hydrocarbon content in sediments from Los Angeles Harbor. Predominant concentrations were found in particles less than 8 µm in size. Linear relationships existed between chlorinated hydrocarbon content and the organic carbon fulvic and humic acid fractions.

Picer et al. (1977) evaluated the effect of salinity on DDT adsorption to suspended solids. Lower salinities decreased DDT adsorption. For example, 45% of DDT in a 3.7^{o}/oo solution was adsorbed, while 70% of DDT in a 37^{o}/oo solution was adsorbed to suspended solids. Harding and Vass (1979) found that 50% of the organochlorines in seawater were associated with particles which were removed by a 0.22 µm filter. Partition coefficients for DDT between sediment and seawater were determined by Pierce et al. (1974) to be 4.8×10^4 compared to 8.6×10^3 determined by Hamelink and Waybrant (1973) in a freshwater system.

Jonas and Pfaender (1976) determined chlorinated pesticide levels at various depths (surface to 1000 m) of the North Atlantic Ocean. DDT concentrations were less than the detection level of 8 ng/L. The mean concentration of DDE was 3.8 ng/L in the North Atlantic waters with ranges from 0.1 to 18.1 ng/L. No systematic variation in pesticide concentration was observed with changes in depth or distance from shore. This type of distribution was attributed to uptake and transport of DDE on particulates in the sea.

Hom et al. (1974) analyzed sediment layers from the Santa Barbara Basin and showed that DDE first appeared in sediments about 1952. Estimated deposition rates of DDE in 1967 were 1.9×10^4 g/m /year. Following consideration of inputs to the Southern California Bight, the investigators concluded that a substantial portion of the chlorinated hydrocarbons were deposited in the sediments. DDE levels in the Bight sediments increased annually, from 24 ppb in 1955 to 160 ppb in 1967.

Despite the high log partition coefficients of DDT and its metabolites, and the high tendency of DDT to adsorb to sediments (i.e., Picer et al., 1977; Shin et al., 1970; and Huang and Liao, 1970), there is some evidence for uptake of DDT from sediments by biota. Burnett (1971) noted that the levels of t-DDT in the sand crab, *Emerita analoga*, increased following resuspension of particles in the water column during storms or periods of upwelling and mixing. In addition, DDE/DDT ratios increased in the sand crabs, indicating that the animals took up older residues which resulted from stirring of the sediments.

Compared to DDE/DDT ratios noted in marine sediments by investigators such as Choi and Chen (1976), the sediment DDE/DDT ratios in Puget Sound are indicative of either recent DDT inputs, or indicative of a lack of metabolic conversion in the natural system. DDT levels in sediment samples analyzed by Malins et al. (1980) were consistently higher than DDE levels. Analyses of sediments from Madison Park by Seattle METRO indicated 3164 ppb p,p'-DDT compared to 77.5 ppb p,p'-DDE.

4.1.5.4 Photolysis

Summary Statement: Most data were limited to results from studies of photolysis of DDT and its metabolites in vapor phase and in freshwater systems. Recent data indicate more rapid photodecomposition in seawater. DDE is more susceptible to photolysis than DDT or DDD. However, photolysis is not expected to be an important fate process because of the affinity of DDT, DDD and DDE to sediments.

Review of Individual Studies: There have been several efforts to study the photochemistry of DDT and DDE in natural systems, particularly by Zepp et al. (1976), Zepp (1978), Crosby and Moilanen (1977), and Singmaster (1975). No data were found for photolysis rates of DDD in natural systems.

DDT is normally quite resistant to photodecomposition (Crosby, 1973). A more appreciable decomposition would occur if DDT was in a vapor state. Zepp et al. (1976) calculated a direct photolysis half life within aqueous solutions of more than 150 years. Crosby and Moilanen (1977) estimated a mean residence time of 4 years for atmospheric DDT. Crosby (1973) stated that DDT may, however, be photosensitized in aqueous solutions by common natural products such as riboflavin, chlorophyll, and anthracene.

Singmaster (1975) presented results which differed from many previous investigators. With 7 days exposure to sunlight, 50% of DDT dissolved in water from San Francisco Bay was decomposed. The investigator could not detect DDE, DDD, or other related photoproducts. DDT in distilled water was unaffected.

DDE is more rapidly decomposed by sunlight than is DDT. Crosby and Moilanen (1977) indicated that photodecomposition is a dominant fate process for DDE. DDE decomposes slowly to DDMU and 4,4'-dichlorobenzophenone (DDCO). Figure 4.1.5 outlines the decomposition products. An ultimate product is dichlorobiphenyl.

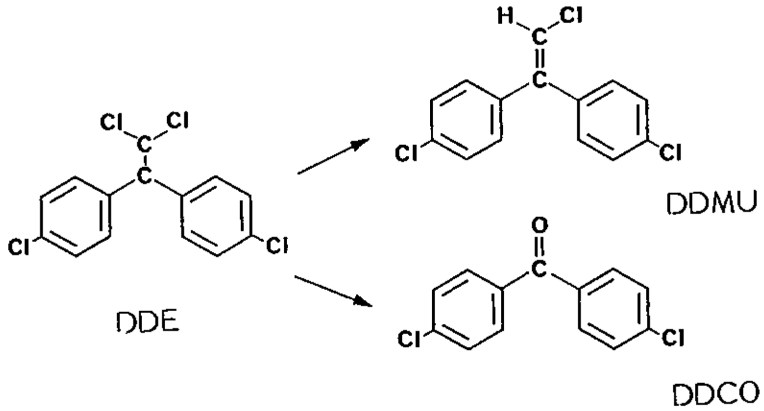


Figure 4.1.5
Photodecomposition Products of DDE

Zepp et al. (1976) and Singmaster (1975) calculated DDE photolytic half lives of 0.9 days (summer) and 1.1 days (unspecified season), respectively. The observed persistence of DDE in the environment may be a result of its high degree of sorption to sediments or biota, and, therefore, it may not be exposed to solar radiation.

Callahan and Slimak (1979) estimated that DDD is more resistant to photolysis than is DDT, and, therefore, photolysis of DDD in water is probably very slow. The studies of Singmaster (1975) in DDT dissolved in water from San Francisco indicated that photolytic decomposition in seawater may be enhanced in the presence of natural products or by the high chloride ion concentrations found in seawater. Photoproducts determined by Singmaster in seawater generally differed from products determined in distilled or fresh waters. As well, decomposition rates of DDT and DDE were equal to or greater in seawater than in distilled water. More intensive studies should be undertaken to further investigate photochemical reactions within seawater. Low wavelengths (i.e., less than 300 nm) were shown by Langmuir and Hayon (1967) to produce highly reactive Cl_2^-species in salt solutions. Anbar and Neta (1967) speculated that in the presence of air, an O_2^-species could be formed and this species could be an important environmental oxidant.

4.1.5.5 Volatilization

Summary Statement: Volatilization may be an important fate process for DDT and DDE. Actual quantification of the role of volatilization may be difficult because of competitive fate processes such as adsorption to solids.

Review of Individual Studies: Bidleman and Olney (1973) analyzed samples of the atmosphere and surface water in the Bermuda-Sargasso Sea. Atmospheric samples were initially passed through a glass fiber filter capable of removing 98% of the particles with radii greater than 0.015 µm and, subsequently, through polyurethene foam. Particles trapped in the glass fiber filter contained few chlorinated hydrocarbons. Most chlorinated hydrocarbons were found within the foam, suggesting that residues in the atmosphere may exist as vapors. However, some of the residues within the foam may have volatilized from the particles during sampling. The investigators also determined the relative concentrations of DDT in the surface microlayer and subsurface waters. Concentrations of p,p'-DDT in the microlayer varied from 0.2 to 0.7 ng/L and subsurface waters were all less than 0.15 ng/L (except for one sample of 0.5 ng/L). The o,p' isomer varied from less than 0.05 to 0.09 ng/L in the microlayer, and subsurface waters contained less than 0.05 ng/L. The relatively high concentrations of DDT in the surface microlayer indicated a larger than expected potential equilibrium between the atmospheric and water phases which would significantly influence the environmental fate of DDT.

There have been many other observations regarding the volatility of DDT in the environment. Hamelink et al. (1971), for example, estimated that 90% of the 5-15 ppb DDT in natural and artificial ponds was probably lost by "evaporation." This loss could not be accounted for by any other fate process. Crosby (1973) determined vapor levels above soils containing o,p'-DDT, p,p'-DDT and DDE. DDE was found to be more volatile than DDT. The vapor above a soil consisting of 75% p,p'-DDT, 21% o,p'-DDT, and 0.8% DDE was a mixture consisting of 41% p,p'-DDT, 43% o,p'-DDT, and 16% DDE.

Based on a model of a 1-m depth idealized aquatic system, Mackay and Leinonen (1975) calculated a volatilization half life for DDT of 73.9 hours. The half life of DDE would probably be considerably less. In an actual system, the half life would increase because of adsorption of DDT to suspended solids and sediments.

In Puget Sound, it is probable that volatilization may have an important role in determining the fate of DDT and its metabolites due to the continued mixing and turbulence of Puget Sound waters. The continued mixing, however, ensures that much of the DDT may be sorbed to suspended solids, hence decreasing the ability of DDT and DDE to volatilize.

4.1.5.6 Hydrolysis

In the presence of strongly basic conditions (i.e., pH 13) DDT will convert to DDE. This reaction is much slower at pH's less than 11 (Benson, 1969; Marei et al., 1978). Wolfe et al. (1977) evaluated the degradation rates of DDT and its degradation products at various pH's. Some of the results are shown in Table 4.1.3.

Table 4.1.3

Degradation Rates of DDT, DDE, and DDD Due to Hydrolysis

Compound	Conditions	Second-Order-Rate Constant k ($M^{-1} S^{-1}$)	Half Life $t_{1/2}$
DDT	pH9, 27°C	9.9×10^{-3}	81 days
DDD	pH9, 27°C	1.4×10^{-3}	570 days
DDT	pH5, 27°C	1.9×10^{-9}	12 yrs
DDE	pH5, 27°C	1.4×10^{-10}	120 yrs
DDD	pH5, 27°C	1.1×10^{-10}	190 yrs

The major product of DDT hydrolysis at pHs from 3 to 11 is DDE. Further degradation as a result of hydrolysis does not seem feasible. Although the hydrolysis rates are very slow, hydrolysis may have been a significant fate process in reduction of DDT levels in the environment since the ban of the use of DDT in 1972. However, the continued high levels of DDT in Puget Sound may be a result of low pHs in sediments and low reaction temperatures.

4.1.6 Overall Biogeochemical Fate Studies

Various freshwater microcosm studies have been conducted. The results of Hamelink and Waybrant (1973), which have been described previously, indicated that 90% of DDT added to ponds was lost by volatilization. The major residue in water after 90 days was DDD. Studies with DDE found 94% of the DDE associated with the bottom mud after 173 days.

Harvey and Steinhauer (1975) indicated that DDT was very unstable in the open marine environment due to decomposition by microorganisms, sunlight, and hydrolysis. Of the total DDT, a small fraction was incorporated in the food chain and converted to DDE. Within body lipids, DDT and its metabolites were relatively stable. Another fraction was sorbed with suspended solids without entering the food chain. The investigators considered t-DDT as only a minor hazard to the environmental quality of the Atlantic Ocean.

Woodwell et al. (1971) formulated a global model for DDT levels in the mixed layers of oceans and the atmosphere, based on DDT world production. Two scenarios were used, one assuming that DDT production would cease by 1974 and another that use would increase in accordance with previous production quantities. Vaporization was considered as one of the most important fate factors. Total quantities of DDT in soils, atmosphere, oceans, and biota were estimated. The model suggested that the worldwide pattern of movement of DDT residues was from the land through the atmosphere into the oceans and into the oceanic abyss. Furthermore, the model suggested that maximum concentrations of DDT residues should have occurred in air in 1966 and in the mixed layer of oceans in 1971 if world production ceased by 1974. Despite the findings of the model, the existing levels of DDT and its metabolites may still be of potential environmental concern.

In an assessment of environmental persistence by use of a computer model, Neely (1979) found that of 12 compounds studied, DDT was the second most persistent compound (after diethyl hexyl phthalate). The compound was calculated to have the highest bioconcentration factor which was several-fold higher than for two PCB mixtures. Calculations indicated a clearance half life of 915 hours. After 30 days, the following distributions in various compartments were calculated: water, 1.26%; soil, 67.5%; air, 28%; and fish, 2.4%.

4.1.7 Conclusions

Based upon the above review, the following observations relevant to DDT and its metabolites in Puget Sound can be made:

1. Predominant fate processes of DDT are adsorption, bioaccumulation, metabolism, and to a lesser extent, hydrolysis and volatilization. DDE is generally the predominant form found in the environment because of its increased resistance to metabolism and hydrolysis.

2. Data from other study areas indicated a predominance of DDE within marine sediments. Of the components of t-DDT in Puget Sound sediments, DDT itself was most predominant indicating either recent inputs of DDT to the Sound, depressed metabolic activity, and/or minimal hydrolysis of DDT within the sediments.

3. Despite a ban of DDT usage since 1972 in the United States, levels of DDT and its metabolites in Puget Sound may still be of ecological significance.

4.1.8 Research Needs

1. There is a need to determine the reason for the relatively high DDT/DDE ratios within Puget Sound, specifically addressing whether there are continuing inputs of DDT to the environment or whether conditions are such that degradation is less than observed in other marine areas.

2. There is a need to design an effective monitoring strategy for Puget Sound to accurately monitor the trends, persistence and possible effects of contaminants such as DDT. For example, analyses of estuarine yearling fish may be of significant value in determining trends.

3. An evaluation of the effects of t-DDT in Puget Sound crabs is recommended, particularly reproductive effects. Further efforts should be made to determine the possible sources of the high t-DDT levels observed in crabs, i.e., sediments or transmittal within egg masses.

4. Concern for DDT in North America arose as a result of its effects on wildlife, particularly, upon reproduction of birds. Data for residue levels in higher food chain species such as gulls, eagles, or herons, should be developed to determine if contaminant levels may be of concern.

References

Anbar, M. and P. Neta. 1967. Pulse radiolysis studies of aqueous sodium chloride solutions. J. Appl. Rad. Isotopes 18:493.

Benson, W.R. 1969. The Chemistry of Pesticides. Ann. N.Y. Acad. Sci. 160:7-29.

Bidleman, T.F. and C.E. Olney. 1973. Chlorinated hydrocarbons in the Sargasso Sea atmosphere and surface water. Science 183:516-518.

Blus, L.J. 1972. Further analysis of the logarithmic relationship of DDE residues to nest success. Nature 240:164.

Bowes, G.W. 1972. Uptake and metabolism of 2,2-bis-(p-chlorophenyl) - 1,1,1-trichloroethane (DDT) by marine phytoplankton and its effect on growth and chloroplast electron transport. Plant Physiol. 49:172-176.

Brown, D. 1979. Memoranda to Ed Long, September 1978; March, August, and October 1979.

Burnett, R. 1971. DDT residues. Distribution of concentrations in <u>Emerita analoga</u> (Stimpson) along coastal California. Science 174:606-608.

Butler, P.A. and R.L. Schutzmann. 1979. Bioaccumulation of DDT and PCB in tissues of marine fishes. *In:* L.L. Marking and K.A. Kimerle (eds.), Aquatic Toxicology, ASTM STP 667. American Society for Testing and Materials. pp. 212-220.

Callahan, M.A. and M.W. Slimak. 1979. Water-Related Environmental Fate of 129 Priority Pollutants. EPA 440/7-79-029.

Choi, W.W. and K.Y. Chen. 1976. Associations of chlorinated hydrocarbons with fine particles and humic substances in nearshore surficial sediments. Environ. Sci. Technol. 10:782-786.

Cox, J. L. 1972. DDT residues in marine phytoplankton. Residue Rev. 44:23-38.

Crosby, D.G. 1969. The nonmetabolic decomposition of pesticides. Ann. N.Y. Acad. Sci. 160:82-96.

Crosby, D.G. 1973. The fate of pesticides in the environment. Ann. Rev. Plant Physiol. 24:467-92.

Crosby, D.G. and K.W. Moilanen. 1977. Vapor-phase photodecomposition of DDT. Chemosphere 6:167-172.

Darrow, D.C. and G.C.H. Harding. 1975. Accumulation and apparent absence of DDT metabolism by marine copepods, *Calanus* spp., in culture. J. Fish. Res. Board 32:1845-1849.

Dvorchik, B.H. and T.H. Maren. 1972. The fate of p,p'-DDT (2,2-bis(p-chlorophenyl)-1,1,1-trichloroethanyl) in the dogfish, *Squalus acanthias.* Comp. Biochem. Physiol. 42A:205.

Environmental Protection Agency. 1976. Quality Criteria for Water. Office of Water and Hazardous Materials. U.S. Environmental Protection Agency, Washington, D.C. 256 pp.

Guarino, A.M., J.B. Pritchard, J.B. Anderson, and D.P. Rall. 1974. Tissue distribution of (C) DDT in the lobster after administration via intravascular or oral routes or after exposure from ambient seawater. Toxicol. Appl. Pharmacol. 29:277-288.

Gunther, F.A. and J.D. Gunther. 1971. Residues of pesticides and other foreign chemicals in foods and feeds. Residue Rev. 36:69-77.

Hamelink, J.L. and R.C. Waybrant. 1973. Tech. Rep. No. 44. Purdue University Water Resources Center, West Lafayette, Ind. p. 46.

Hamelink, J.L., R.C. Waybrant, and R. C. Ball. 1971. A proposal: Exchange equilibria control the degree chlorinated hydrocarbons are biologically magnified in lentic environments. Trans. Amer. Fish. Soc. 100:207-214.

Harding, G. and W.P. Vass. 1979. Uptake from seawater and clearance of p,p'-DDT by marine planktonic crustacea. J. Fish. Res. Board Can. 36:247-254.

Hargrave, B.T. and G.A. Phillips. 1976. DDT residues in benthic invertebrates and demersal fish in St. Margaret's Bay, Nova Scotia. J. Fish. Res. Board Can. 33:1692-1698.

Harvey, G.R. and W.G. Steinhauer. 1975. Biogeochemistry of PCB and DDT in the North Atlantic. In: J.O. Nriagu (ed.), Environmental Biogeochemistry Vol. I. Elsevier/North Holland, Amsterdam.

Herdendorf, C.E., C.L. Cooper, and M. Gessner. 1978. Lake Erie Water Quality Status Report for 1977 - Nearshore. Technical Report No. 80. Ohio State University Center for Lake Erie Area Research.

Hom, W., R.W. Risebrough, A. Soutar, and D.R. Young. 1974. Deposition of DDE and polychlorinated biphenyls in dated sediments of the Santa Barbara Basin. Science 184:1197-1199.

Huang, J.C. and C.S. Liao. 1970. Adsorption of pesticides by clay minerals. J. Sanit. Div., Amer. Soc. Civ. Eng. 96:1057-1078.

International Joint Commission. 1977. New and Revised Great Lakes Water Quality Objectives, Volume II.

Jansson, B., S. Jensen, M. Olsson, L. Renberg, G. Sundstrom, and R. Vaz. 1975. Identification by GC-MS of phenolic metabolites of PCB and p,p'-DDE isolated from baltic guillemot and seal. Ambio 4:93-97.

Jarvinen, A.W., M.J. Hoffman, and T.W. Thorslund. 1977. Long-term toxic effects of DDT food and water exposure on fathead minnows (Pimephales promelas). J. Fish. Res. Board Can. 34:2089-2103.

Johnsen, R.E. 1976. DDT metabolism in microbial systems. Residue Rev. 61:1-28.

Jonas, R.B. and F.K. Pfaender. 1976. Chlorinated hydrocarbon pesticides in western North Atlantic Ocean. Environ. Sci. Technol. 10:770-773.

Langmuir, M.E. and E. Hayon. 1967. Flash photolysis study of mercury (II) halide complexes in aqueous solution. Rates of reaction of X_2^- radical anions. J. Phys. Chem. 71:3808-3814.

Macek, K.J., S.R. Petrocelli, and B. H. Sleight III. 1979. Considerations in assessing the potential for, and significance of, biomagnification of chemical residues in aquatic food chains. In: L.L. Marking and R.A. Kimerle (eds.), Aquatic Toxicology, ASTM STP 667. American Society for Testing and Materials. pp. 251-268.

Mackay, D. and P.J. Leinonen. 1975. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 9:1178-1180.

Malins, D.C., B.B. McCain, D.W. Brown, A.K. Sparks, and H.O. Hodgins. 1980. Chemical Contaminants and Biological Abnormalities in Central and Southern Puget Sound. NOAA Technical Memorandum OMPA-2. Office of Marine Pollution Assessment, Boulder, Colo. 295 pp.

Marchand, M., D. Vas, and E.K. Duursma. 1976. Levels of PCBs and DDTs in mussels from the N.W. Mediterranean. Mar. Pollut. Bull. 7:65-69.

Marei, A.S.M., J.M.E. Quirke, G. Rinaldi, J. A. Zoro, and G. Eglinton. 1978. The environmental fate of DDT. Chemosphere 12:993-998.

McKinney, J.D. and C. Fishbein. 1972. DDE formation: dehydrochlorination or dehypochlorination. Chemosphere 2:67-70.

Neely, W.B. 1979. A preliminary assessment of the environmental exposure to be expected from the addition of a chemical to a simulated aquatic ecosystem. Intern. J. Environ. Studies 13:101-108.

Nimmo, D.R., A.J. Wilson, Jr., and R.R. Blackman. 1970. Localization of DDT in the body organs of pink and white shrimp. Bull. Environ. Contam. Toxicol. 5:333.

Peakall, D. B. 1976. DDT in rainwater in New York following application in the Pacific North-West. Atmos. Environ. 10:899-900.

Picer, N., M. Picer, and P. Strohal. 1977. The interaction of DDT with suspended particles in sea water. Water, Air, Soil Pollut. 8:429-440.

Pierce, R.H., Jr., C.E. Olney, and G.T. Felbeck, Jr. 1974. Geochim. Cosmochim. Acta 38:1061. (Cited in Picer et al. 1977).

Pritchard, J. B., A. M. Guarino, and W. B. Kintu. 1973. Distribution, metabolism, and excretion of DDT and Mirex by a marine teleost, the winter flounder. Environ. Health Perspec. 45-54.

Shin, Y.O., J.J. Chodan, and A.R. Wolcott. 1970. Adsorption of DDT by soils, soil fractions and biological materials. J. Agric. Food Chem. 18:1129-1133.

Singmaster, J. A., III. 1975. Environmental behavior of hydrophobic pollutants in aqueous solutions. Ph.D. Thesis, University of California, Davis. 143 pp. University Microfilms, Ann Arbor, Mich. Order No. 76-14, 237 (Diss. Abstr. Int. B 1976, 36(12, Pt.1): 6206-6207).

Ware, G.W. and C.C. Roan. 1970. Interaction of pesticides with aquatic microorganisms and plankton. Residue Rev. 33:15-45.

Wolfe, N. Lee, R.G. Zepp, D.F. Paris, G.L. Baughman, and R.C. Hollis. 1977. Methoxychlor and DDT degradation in water: rates and products. Environ. Sci. Technol. 11:1077-1081.

Woodwell, G.M., P.P. Craig, and H.A. Johnson. 1971. DDT in the biosphere: where does it go? Science 174:1101-1107.

Zepp, R.G. 1978. Quantum yields for reaction of pollutants in dilute aqueous solution. Environ. Sci. Technol. 12:327-329.

Zepp, R.G., N.L. Wolfe, J.A. Gordon, and R.C. Fincher. 1976. Light-induced transformation of methoxychlor in aquatic systems. J. Agric. Food Chem. 24:727-733.

Zinck, M. E. and R. F. Addison. 1975. The effect of temperature on the rate of conversion of p,p -DDT to p,p -DDE in brook trout (Salvelinus fontinalis). Can. J. Biochem. 53:636-639.

4.2 Polychlorinated Biphenyls

4.2.1 Introduction

Polychlorinated biphenyls (PCBs) are made by direct chlorination of biphenyl. The biphenyl molecule has 10 different possible sites at which chlorine atoms can be substituted. The substitution sites are designated in Figure 4.2.1.

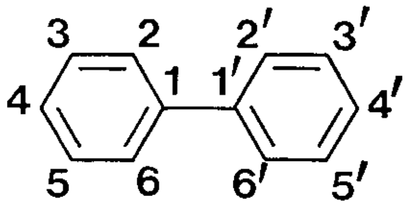


Figure 4.2.1.
Substitution Sites for Biphenyl

There are 209 possible compounds and isomers resulting from the chlorination of biphenyl with 1 to 10 chlorine atoms. In commercial PCB mixtures, about 100 individual compounds and isomers have been detected (Hutzinger et al., 1974).

PCB is no longer manufactured in the United States. The major producer of PCB mixtures in the United States was the Monsanto Company, which marketed PCB mixtures for closed electrical system applications under the Aroclor trademark. A numbering code was used to designate the Aroclor products. The first two digits, 12, indicated that the parent compound is biphenyl. The last two digits specified the percentage by weight of chlorine. As a result, Aroclor 1254 would contain biphenyls which are more chlorinated than biphenyls in an Aroclor 1221 mixture. The only exception to the designation scheme is Aroclor 1016, which retained its nomenclature as known during its development. Details of the composition of various Aroclor mixtures are described in the Proceedings of the National Conference on Polychlorinated Biphenyls (EPA, 1976) and by Callahan and Slimak (1979).

Analyses of sediments, biota, and waters of Puget Sound conducted by MESA determined the concentrations of polychlorinated biphenyls in terms of the degree of substitution, i.e., monochlorobiphenyl (one chlorine) to nonachlorobiphenyl (nine chlorines).

Polychlorinated biphenyls are one of the most widely distributed pollutants on earth. Their persistence is generally considered to be greater than that for most chlorinated pesticides. PCB residues are found in fat deposits of numerous warm- and cold-blooded animals, including man. In the aquatic environment PCBs have been detected in water, sediments, invertebrates, fish, and waterfowl with the highest levels being recorded in predatory organisms at the end of the food chain (IJC, 1977).

PCBs are among the chemicals listed in the EPA's 129 Priority Pollutants List. PCBs have been chosen for investigation in this report because of their: 1) widespread dispersion within Puget Sound; 2) continued persistence and significant levels in biota; and 3) possible effects on consumers of contaminated biota.

4.2.2 Significance to Puget Sound

4.2.2.1 Review of Known Toxicity Data

The EPA (1978) Ambient Water Quality Criteria recommended a maximum 24-hour average of 0.024 µg/L PCBs and a concentration of no more than 0.20 µg/L at any time within saltwater for the protection of marine biota. Hansen (1976) reviewed the toxicity of various Aroclor mixtures to estuarine organisms. Aroclors 1016, 1242, and 1254 had 48-96 hour LC50's of 9-32 µg/L for penaeid shrimp and 12-16 µg/L for grass shrimp. EC50's (reduction of shell growth) for oysters varied from 10 to 32 µg/L. Bioassays for periods longer than two weeks showed that Aroclor 1254 was toxic to shrimp (Penaeus spp. and Palaemonetes pugio) at concentrations of 1 µg/L. Shrimp exposed to PCBs were more sensitive to salinity stress and viral disease. Sheepshead minnow, an estuarine fish, suffered no apparent effects upon exposure to 0.1 µg/L Aroclor 1254. However, the survival of fry from eggs of exposed fish was diminished. Hansen (1976) noted Aroclor 1254 bioconcentration factors of 101,000-165,000 by oysters; 26,000 by shrimps; and 37,000 by fish. There are virtually hundreds of publications on the toxic aspects of PCBs. Table 4.2.1 briefly reviews some of the data which may be applicable to Puget Sound biota.

Currently, the U.S. guidelines for PCBs in fish used for human consumption specify a maximum level of 5 ppm wet weight and consideration is being given to 2 ppm which is the Canadian guideline. Studies by Allen and Norback (1976) have shown severe chronic effects at dietary intakes as low as 2.5 ppm in nonhuman primates. The total PCB intake over a period of 16-19 months for the primates was from 243 to 303 mg. A no-effect level for PCBs in nonhuman primates has not been established. Effects included conjunctivitis and reproductive dysfunctions, such as early abortions and stillbirths.

Wildlife may be susceptible to dietary intakes of PCBs. Two µg/g of PCBs in fish flesh have been shown to prevent survival of newborn ranch mink (Ringer et al., 1972), while reproduction was eliminated in mink which were fed a beef diet containing 0.64 µg/g Aroclor 1254 (Platonow and Karstad, 1973).

The most stringent limitation proposed for PCBs in the environment is that recommended by the International Joint Commission (1977) for the Great Lakes. The limitation which was written as an objective for the protection of fish-consuming birds and animals, recommended that the concentration of total polychlorinated biphenyls in fish tissue should not exceed 0.1 µg/g (whole fish, wet weight basis). "Based upon poorly defined bioconcentration factors" (The Commission) "concluded that PCBs in water should not exceed 0.001 µg/L."

4.2.2.2 Possible Effects of Levels Found in Puget Sound

PCBs were found in all compartments of Puget Sound. The PCB levels in Puget Sound biota are generally higher than the levels noted for other contaminants. The Puget Sound PCB levels are reviewed in Table 4.2.2. Table 4.2.3 provides a comparison of these levels from another Puget Sound study (Pavlou and Dexter, 1979). It should be noted that the authors reported detectable quantities of PCBs in all samples of water and suspended solids while similar samples for the MESA study indicated nondetectable levels. Table 4.2.4 outlines some of the values of PCBs noted in other areas of the world. Several dry weight analyses of tissues were reported by Malins et al. (1980). Muscle from three specimens of English sole contained from 3.8 to 4.6 µg/g PCBs and three liver samples yielded 26-120 µg/g PCBs (dry weight). Two samples of crab, Cancer gracilis, contained 0.06 and 0.4 µg/g PCBs in tissue, and 2.4 and 10 µg/g in hepatopancreas.

Although the PCB levels in Puget Sound fish muscle might not exceed the U.S. guidelines for human consumption (i.e., 5 ppm wet weight), the levels of PCBs in Puget Sound fish may be high enough to affect wildlife that consume the fish.

Table 4.2.1
Brief Review of Data on the Effects of PCBs on Aquatic Biota

Species	PCB Level in Water	Effects	Investigator
Juvenile pink Shrimp, Penaeus duorarum	0.1 mg/L Aroclor 1254	100% mortality 48 hours	Duke et al. (1970)
	0.01 mg/L	no effect-48 hours	Duke et al. (1970)
Oyster, Crassostrea virginica	1 µg/L	shell growth inhibited by 19%	Duke et al. (1970)
Marine diatom	0.1 mg/L Aroclor 1242	growth inhibited and diminished level of RNA and chlorophyll	Keil et al. (1971)
Nannoplankton <22 µ diameter	100 ng/L 2,2'-dichlorodiphenyl	photosynthetic rate reduced by 52%	McNaught (1978)
Netplankton >22 µ diameter	100 ng/L 2,2'-dichlorodiphenyl	No effect	McNaught (1978)

Table 4.2.2

Levels of PCBs Reported for the Puget Sound Project *

SAMPLES	Concentration Range - ng/gm (ppb) dry weight; N = Number of Chlorines								
Sediments N=	1	2	3	4	5	6	7	8	9
Elliott Bay	<	< .05-20	< .04-70	< .1-180	< .08-540	< .08-790	< .06-420	< .05-160	< .02-20
Commencement Bay	<	< .05-27	< .05-140	< .1-270	< .1-250	< .1-440	< .08-150	< .06-110	< .02-8.7
Sinclair Inlet	<	.01-.6	1-3	3-10	7-40	6-70	7-70	2-40	2-5
Port Madison	<	.1-.2	.4	1-2	1-2	.2-2	< .2-2	< .1-.4	< .04-.08
Case Inlet	<	.02-.2	.1-.5	.04-.9	.2-1.1	.1-.9	.05-<.3	<.04-<.1	<.02-<.1
Budd Inlet	<	.2-.3	.4-.6	2-4	.7-8	.6-5	< .3-3	< .2-.3	< .04-.08
<u>Biota</u>									
Fish liver (all sites)	<	2-310	10-2100	20-5900	50-9800	90-15,000	40-8900	10-2100	2-420
Budd Inlet: sole liver	<	10-30	10-20	80-120	290-450	430-640	310-490	70-160	10-30
crab hep.	<		10	210	480	470	200	30	<1
shrimp	<	10	4	30	80	80	20	2	<1
Elliott Bay: crab hep.	<	70	560	3800	7300	11,000	7800	1100	<3
worms	<	<4-10	10-60	110-350	190-500	280-550	130-250	30-60	<3
shrimp	<	<3-10	10-40	80-210	160-870	300-680	130-220	20	<1
clams	<	<10	<2	70-200	90-500	100-410	40-180	10-20	<5-2
fish liver	<	2-310	<10-1200	110-5900	380-9800	550-15,000	270-8900	20-1200	3-420
Sinclair Inlet:									
fish liver	<	10	30-70	230-490	820-2000	1600-3100	1100-2300	260-510	30-70
crab hep.	<	20	20	310	1200	1500	970	210	10
worms	<	<10	10	110	220	500	320	90	20
shrimp	<	10	N	30	170	280	160	30	<1
Port Madison:									
fish liver	<	10	20	140-190	440-730	700-1100	400-730	90-180	10
worms	<	<4	10	40	60	50	30	2	<2
shrimp	<	10	4	20	90	120	50	10	<1
clam	<	<3	<1	20	60	60	20	3	<1
Commencement Bay:									
crab hep.	<	50-60	190-640	340-1200	3600-11,000	2900-9200	1800-4900	350-1200	40-230
worms	<	<3-10	<1-20	60-120	130-450	110-440	50-160	10-40	2-10
shrimp	<	10	5-50	30-310	100-1400	110-930	40-290	10-40	<1-4
fish liver	<	<1-80	<3-2100	20-3700	50-9000	90-15,000	40-8500	10-2100	<2-410
clams	<	10	<2	30-220	100-310	130-240	50-80	10-20	4
Case Inlet:									
sole liver	<	20-30	10-20	50-140	120-360	200-520	110-400	30-120	5-20
crab hep.	<	N	10	70	160	160	70	10	<.6
shrimp	<	N	3	20	40	60	10	1	<1
clams	<	<2	<1	4	10	10	<1	<1	<1

<u>Water</u>

All Stations: none detected above detection limits of 0.5 - 1.0 ppt.

<u>Suspended Matter</u>

All Stations: none detected above detection limits of 2-4 ppb.

* Data are from the seven reports provided for this study as described in Chapter 2.

Table 4.2.3

Mean Total Polychlorinated Biphenyl Concentrations in Various Regions of Puget Sound*

Region	Water ng L^{-1}	SPM ng g^{-1}	Zooplankton µg $(g\text{-lipid})^{-1}$	Sediment ng g^{-1}	Surface Film ng L^{-1}
Duwamish River	22 ± 13 (60)[a]	1770 ± 540 (70)			116 ± 101 (5)
Elliott Bay	11 ± 13 (185)	920 ± 200 (87)	6.8 ± 3.1 (11)	637 ± 830 (4)	98 ± 83 (6)
Main Basin	4.3 (1)	104 ± 31 (3)	5.9 ± 4.4 (4)		12 (1)
Sinclair Inlet		168 ± 21 (4)	16 ± 7.0 (3)		
Whidbey Basin	4.4 ± 2.2 (15)	82 ± 37 (7)	3.7 ± 1.1 (12)	30 ± 14 (5)	
Northern Sound and Strait of Juan de Fuca	3.7 ± 1.7 (9)		1.3 ± 1.2 (3)	16 ± 13 (3)	
Southern Sound				8.0 ± 8.3 (6)	
Commencement Bay				28 ± 17 (8)	
Hood Canal	3.0 ± 2.2 (12)	88 ± 37 (3)		12 ± 3.0 (3)	

*Pavlou and Dexter (1979)

[a] Values in parentheses are the number of data points.

SPM = suspended particulate matter.

Table 4.2.4

Brief Summary of PCB Values Observed in Other Regions of the World

Region	Compartment and Level	References
North Atlantic	Water 1972 (2-150 ppt (ng/L)) Water 1973 (0.6-8 ppt) Water 1974-75 (0.4-7.7 ppt)	Harvey et al. (1974)
Global Hydrosphere	Upper 10-1000 meters (1-5 ppt)	Ballschmiter et al. (1978)
Sargasso Sea	Water 1973 4/8 stations (0.9 ppt) 4/8 stations (1-3.6 ppt)	Bidleman and Olney (1973)
Off Western Mexico	Water 1975 22 samples (.1 ppt) of these 11 samples (.05 ppt)	Risebrough (1976)
Gulf of Mexico	Sediments 2.0-330 ppb (μg/kg) in 31 of 157 samples	Dennis (1976)
Mediterranean - Italian Cost	Shrimp, *Nephrops norvegicus*, 4.4 - 55 ppb (μg/kg) Mussel, *Mytilus galloprovincialis*, 60.5 - 100.1 ppb	Amico et al. (1979)
North Sea	Phytoplankton, 3.5 ± 1.3 ppb Zooplankton, 20 ± 8 ppb Shrimp, *Crangon crangon*, 83 ± 12 ppb Mussel, *Mytilus edulis*, 237 ± 31 ppb	Ten Berge and Hillebrand (1974)

4.2.3 Physical Properties of Polychlorinated Biphenyls

Tulp and Hutzinger (1978) expressed a general concern about published physical properties of PCBs. For example, in the literature, solubility values are reported for Aroclor mixtures and for specific components of the mixtures. Solubility data vary considerably for individual isomers. For example, a review by Tulp and Hutzinger (1978) found published solubility values for 2-chlorobiphenyl that varied between 900 and 5,800 ppb and for 2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl the variation was from 0.016 to 15 ppb. Tulp and Hutzinger (1978) thus expressed their concerns about some of the methodologies used for determination of PCB solubilities. Several factors may influence aqueous solubility determinations. The presence of electrolytes will reduce the solubility of nonpolar compounds. Therefore, solubility studies in distilled water may not accurately simulate environmental solubilities. Detailed studies of PCBs in water have shown that some solutions are actually stable emulsions of chlorobiphenyl aggregates. Water soluble humic substances and surface active organic compounds may also increase concentrations of nonpolar compounds. Tulp and Hutzinger (1978) noted that the tendency of hydrophilic compounds such as PCBs to accumulate in air/water interfaces raises questions concerning the applicability of solubility studies done in distilled waters. Because of the wide ranges of solubilities reported in the literature, Tulp and Hutzinger (1978) concluded that "the true aqueous solubility of highly lipophilic compounds is still partly unknown."

In addition, Tulp and Hutzinger (1978) stated that most of the published solubility data on Aroclors is based on selective solubilization of the lower chlorinated components from the mixtures. If the solubilities of individual components of a mixture are not identical, the solubility of such a mixture in water cannot be defined as a physical constant. Therefore, they concluded that the reported aqueous solubilities of PCB mixtures are misleading.

The experimental solubilities of individual components and of PCB mixtures, as reported by various investigators, are outlined in Table 4.2.5.

Solubilities in seawater would be less than those reported for distilled or freshwater. Nonetheless, these values illustrate that the solubilities of PCB mixtures and their components are very low.

The partition coefficients of PCBs indicate that the components are extremely lipophilic. Where partition coefficients are reported for Aroclors, it should be noted that the more highly chlorinated compounds will more selectively partition within the n-octanol phase; therefore, partitioning will differ for each of the components of Aroclor mixtures. As a result, Tulp and Hutzinger (1978) concluded that log P values of PCB mixtures cannot be considered as physical constants. Many of the

Table 4.2.5

Reported Physical Properties of Polychlorinated Biphenyls*

Individual Isomers Chlorine Substitution	Solubility - Parts Per Billion: Distilled or Freshwater	Solubility - Parts Per Billion: Seawater	Vapor Pressure	Log of Octanol Water Coefficient
2	900-5,800			
3	1,300-3,600			
4	400-1,170			4.26
2,2'	790-1,440			4.04
2,4'	500-1,880			
4,4'	50-70			5.58
				5.18
2,2',5	16-640			
2,4,4'	85-260			
2,3,2',3'				4.63
2,2',5,5'	16-46			
3,3',4,4'	0.75-175			6.04
2,3,5,6				5.46
2,2',4,5,5'	4.2-28			6.11
3,3',5,5'				6.85
2,2',3,3',5'	4.5-23			6.72
2,2',4,4',5,5'	0.95-8.8			
2,2',3,3',4,4',5,5'	0.27-7.2			
2,2',3,3',4,4',5,5',6,6'	0.016-15			
Aroclor 1242	200 (Nisbet and Sarofim, 1972) 240 (MacKay and Leinonen, 1975) 340 ± 60 (Paris et al., 1978)		4.06×10^{-4}mm (MacKay)	
Aroclor 1248	100 (Nisbet and Sarofim, 1972) 54 (MacKay and Leinonen, 1975)		4.94×10^{-4}mm (MacKay)	
Aroclor 1254	50 (Nisbet and Sarofim, 1972) 12 (MacKay and Leinonen, 1975)	4 (Dexter and Pavlou, 1978) 56 (Haque et al., 1974)	7.7×10^{-5}mm (MacKay)	
Aroclor 1260	25 (Nisbet and Sarofim, 1972) 2.7 (MacKay and Leinonen, 1975)		4.05×10^{-5}mm (MacKay)	
Aroclor 1016	420 ± 80 (Paris et al., 1978)			

* from Callahan and Slimak (1979) unless otherwise noted

log P values have been calculated by the "Hansch pi values," within which the log Ps are determined without regard to the position of substituents. Tulp and Hutzinger (1978) noted that substituted positions do have significant effects and "erroneous" log P values can be obtained.

Although the data in Table 4.2.5 may not be entirely accurate in light of the concerns of Tulp and Hutzinger, the data nonetheless indicate that PCBs have low solubility in water, are extremely lipophilic (hence, very soluble in organic matter), and have decreasing vapor pressures with increasing degrees of chlorination.

4.2.4 Sources or Inputs

The uses and possible discharge sources of PCBs have been extensively reviewed in many publications including those by Nisbet and Sarofim (1972) and Peakall (1972). Considerable information is also found in the Proceedings of the National Conference on Polychlorinated Biphenyls (EPA, 1976) and the report of the Task Force on PCB to the Environmental Contaminants Committee of Environment Canada and Health and Welfare Canada (Environment Canada, 1976). The probable sources of PCB contamination are: leaks from transformers, heat exchangers, and hydraulic systems; vaporization from formulations; vaporization from poorly operated incinerators; and landfill leachates. The discharges may be direct (i.e., municipal and industrial discharges) or indirect (i.e., atmospheric fallout).

Pavlou et al. (1978), in an evaluation of chlorinated biphenyl distribution in Puget Sound, suggested that municipal marine outfalls probably do not constitute the major input of chlorinated biphenyls in the Sound; but, rather, indirect inputs associated with industrial activity in the major river watersheds, account for the predominant input load. Pavlou et al. (1978) were uncertain whether river PCB loads to Puget Sound are due to the discharge of industrial effluents or are the result of transient inputs (i.e., spills, dumping of waste materials, and residual chronic input).

The inputs of chlorinated biphenyls to Puget Sound as estimated by Pavlou et al. (1978) are shown in Table 4.2.6.

Table 4.2.6

Estimated Inputs of Polychlorinated Biphenyls To Puget Sound*

Source	Rate In (g CB day^{-1})	
<u>Major River Systems</u>		
Snohomish, Skagit, Stillaguamish Rivers	220	
Lake Washington (Ship Canal)	10	
Duwamish River	97	
Puyallup River	30	
<u>Outfalls</u>		
Westpoint	30	
Renton	3	
Combined Sewage Overflows	10	
TOTAL:	400	(1.44×10^5 g/yr)

*Pavlou et al. (1978)

4.2.5 Summary Of Biogeochemical Fate Data in the Marine Environment

4.2.5.1 Bioaccumulation - Uptake and Depuration

Summary Statement: Bioaccumulation of PCBs in aquatic organisms appears to occur primarily through direct uptake of PCBs from water and is strongly dependent upon lipid levels in organisms. Uptake rates increase and depuration rates decrease with increasing degrees of chlorination. PCBs are more rapidly depurated from biota than are DDT and metabolites of DDT. If PCB inputs to Puget Sound are eliminated, it is expected that PCBs with five or more substituted chlorine groups will continue to persist in biota for a long time.

Review of Individual Studies: Polychlorinated biphenyls have high partition coefficients and, hence, high lipophilic properties (high fat solubility). Their high bioaccumulation potential and stability, which will be discussed later, indicate their possible long-term persistence within organisms (Peakall, 1972). The strong tendency of PCBs to be bioaccumulated in Puget Sound biota is reflected in Table 4.2.2. For example, levels up to 15,000 ppb of a single isomer were detected in fish liver from Elliott Bay.

Uptake of PCBs is basically controlled by equilibrium partitioning between internal lipid pools of biota and ambient water, rather than by means of dietary uptake. For example, Zitko (1974) showed that with juvenile Atlantic salmon, the accumulation ratios of Aroclor 1254 from water and food were 600:0.629.

Clayton et al. (1977) recorded a 10^6 amplification of chlorinated biphenyls by zooplankton above the levels observed in Puget Sound waters. This amplification was considered a function of the lipid fraction in the organisms. Food chain biomagnification was determined not to be a controlling factor. The amplification factors were considered uniform over a wide range of temporal and spatial regimes, species composition, and lipid content of the organisms. Levels of trichlorobiphenyls in marine zooplankton reported by Clayton et al. (1977) varied from 0.08 ppm (Admiralty Inlet) to 1.57 ppm (Sinclair Inlet). Levels of biphenyls with five chlorines varied from 0.37 ppm (Admiralty Inlet) to 6.64 ppm (Sinclair Inlet). Ten Berge and Hillebrand (1974), found small differences in the content of organochlorine compounds among different biota (phytoplankton, zooplankton, shrimp, mussels, herring, and cod) when the concentrations were expressed in terms of lipid content.

Table 4.2.7 reviews uptake and bioconcentration data for various other marine species. Additional information can be found in Hansen's (1976) review on the effects and accumulation of PCBs in estuarine organisms.

Table 4.2.7

Review of Bioconcentration and Uptake Data for Various Marine Species

Species	Bioconcentration Factors (BCF) and Uptake Data	Investigator
Marine diatom, *Cylindrotheca closterium*	BCF: 470 in 0.01 ppm Aroclor 1242 BCF: 1092 in 0.1 ppm Aroclor 1242	Keil et al. (1971)
American oysters, *Crassostrea virginica*	BCF: 10^5 in 0.001 ppm Aroclor 1254 (25 weeks)	Lowe et al. (1972)
	12 weeks in clean water, no detectable residue (0.2 ppm)	
Grass shrimp, *Paleomonetes pugio*	BCF: 26,000 - Aroclor 1254 (1-3 months)	Nimmo et al. (1974)
	50-90% lost after 4-week depuration	Duke et al. (1970)
Mussels, *M. californianus*	BCF: 100,000 Aroclor 1254	McDermott et al. (1976)
Crab, *Cancer anthonyi*	Gonad tissue approximately 5-10 times greater than in muscle	McDermott et al. (1976)
Dover Sole, *Microstomus pacificus*	Liver 10-20 times greater than in muscle	McDermott et al. (1976)
Sandworm, *Nereis virens*	Dichlorobiphenyl: 58% of total dose accumulated when administered orally during 3 weeks (70% of trichloro- and 93% of pentachlorobiphenyl accumulated)	Goerke and Ernst (1977)
	Elimination ½ lives: dichloro - 3 weeks; trichloro - 1.8 weeks; pentachlorobiphenyl - 8.7 weeks	

Relative to DDT, PCBs appear to be depurated at a faster rate from tissue of aquatic biota. For example, Nealy (1979) calculated fish tissue clearance half lives of 228 hours for Aroclor 1254, 105 hours for Aroclor 1248, and 96 hours for 2,2', 5-trichlorobiphenyl, compared to 915 hours for DDT. However, Table 4.2.7 illustrates that the depuration rates of PCBs decrease with increasing chlorination and that PCBs with more than five substituted chlorine groups are very persistent.

There is uncertainty concerning the uptake mechanism for PCBs in benthic species such as clams, crabs, and polychaetes. Stainken and Rollwagen (1979) studied the uptake of PCBs by three species of bivalves (C. virginica, M. arenaria, and M. mercenaria) from sediments of lower New York Bay. No valid relationship could be found between sediment silt-clay content and sediment PCB content nor between tissue PCB content and sediment PCB content. Generally, tissue levels at all sites were greater than the residue values in sediments. Tissue levels of Aroclor 1016 and 1242 were most prevalent.

However, Malins et al. (1980) found that bottom-dwelling fish and benthic invertebrates sampled from areas in Puget Sound with the highest PCB levels in sediments had the highest tissue levels of PCBs. Uptake obviously does occur, but it is uncertain whether uptake occurred via absorption from interstitial waters or from ingestion of solid materials.

Elder et al. (1979) studied the uptake of Penaclor DP-S by the sediment dwelling polychaete, Nereis diversicolor. After an equilibrium period of 40-60 days, a bioconcentration factor of 3.5 was observed. The investigators were uncertain whether uptake occurred via absorption from ingested materials or by cuticular absorption from interstitial waters. Harvey and Steinhauer (1975) in their studies of waters, sediments and biota from the deep Atlantic (i.e., 5500-5800 m depth) observed that detritiphoric holothurians which depend upon sediments for food did not concentrate PCBs.

Despite the biological significance of PCBs, the amount of PCBs in the biological compartment is small compared to the amounts in other compartments such as the water column and the sediment layer (Nisbet and Sarofim, 1972). For example, Pavlou et al. (1977) have shown that the distribution of PCBs in zooplankton of Puget Sound accounts for no more than 4% of the total quantity estimated in the Sound. Harvey and Steinhauer (1975) estimated that only 0.1% of PCBs in the Northern Atlantic would be associated with organisms.

Although dietary intake does not appear to be important in the uptake of PCBs by fish and lower food chain organisms, higher food chain organisms appear to accumulate PCBs contained within diet. For example, Herman and Calambodikis (1978) reported a level of 38 ppm PCBs in blubber of a killer whale which was found washed ashore in 1977 in the Strait of Georgia (British Columbia). The reasons for the differences in uptake by fish versus uptake by higher food chain organisms such as whales and seals have not been found in the literature. Few, if any, direct, acute effects on aquatic organisms have been recorded as a result of PCB contamination in North America. However, PCBs do have sublethal effects on higher food chain organisms. Such effects include eggshell thinning of fish-consuming birds; behavioral alterations in birds; and reproductive failure and mortality of such wildlife as mink (Stendell, 1976).

4.2.5.2 Metabolism

Summary Statement: Mono-, di- and trichlorinated biphenyls are susceptible to some degree of metabolism by microbes and higher food chain organisms. The metabolites, if retained within the body system, may be of greater toxicity than the chlorinated biphenyls although minimal data exist on the toxicity of such metabolites. It does not appear that biphenyls with five or more chlorines are easily metabolized. However, there has been some evidence that mammals could metabolize small amounts of such isomers. There is no evidence of microbial degradation of PCBs in anaerobic sediments, while there is evidence for some degree of degradation in aerobic sediments.

The conclusions are substantiated by PCB levels recorded in biota of Puget Sound. The penta- and hexachlorobiphenyls are most predominant in fish liver, crab hepatopancreas, shrimp, and clams. Crabs appear to have the lesser degree of metabolic capability because samples contained the highest levels of the supposedly more biodegradable di- and trichlorobiphenyls. Trichlorobiphenyl was detected in all biota except clams.

Sediments in Elliott and Commencement Bays contain higher levels of di- and trichlorobiphenyls than sediments in Budd Inlet or Case Inlet, indicating higher degrees of anaerobic conditions in the Elliott and Commencement Bay sediments. It does not appear, therefore, that biodegradation plays a significant role in the removal of PCBs from Puget Sound.

Review of Individual Studies: Sundstrom et al. (1976) prepared an extensive review on biological metabolism of chlorobiphenyls. Generally speaking, biphenyls with four or fewer chlorine substitutions can be metabolized by a number of test organisms (i.e.,rats, birds). Metabolites of PCBs by mammalian species are predominantly monohydroxy and dihydroxy compounds, which are formed by means of arene oxide intermediates (Figure 4.2.2). Highly chlorinated compounds do not appear to be metabolized.

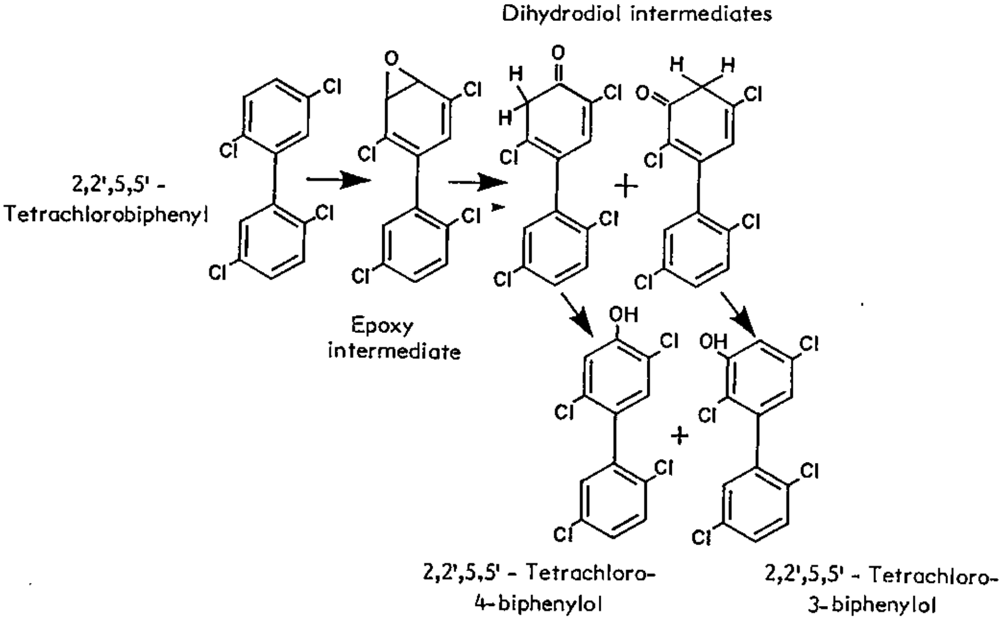


Figure 4.2.2
Metabolism of PCBs in Mammalian Species

The ease of metabolism of PCBs appears to decrease in the order mammals-birds-fish (Hutzinger et al., 1972). Bend et al. (1976), using lobster and dogfish, showed that marine species have some hepatic microsomal mixed function oxidase activity. However, this activity was considerably lower than that found in mammalian liver.

Metcalf et al. (1976) used a laboratory model ecosystem to determine biodegradation of tri-, tetra-, and penta-PCBs. Trichloro compounds were found to be degraded by all organisms including alga, snail, water flea, mosquito, and fish. However, a highly persistent and lipophilic degradation product was found to be stored within the test species. Hydroxylated PCB metabolites were suspected. Biodegradation of tetra- and pentachlorobiphenyls was minimal. Only one study was found regarding the toxicity of hydroxylated chlorobiphenyls during the literature review. Yoshimura and Yamamoto (1973) found that 3,4,4', 6-tetrachloro 3-biphenylol was four to five times more toxic to mice than the parent chlorinated biphenyl.

Jansson et al. (1975) detected numerous phenolic metabolites of PCBs in excreta of guillemot and grey seal from the North Sea Region. It appeared that molecules with both para positions chlorinated could not be hydroxylated by guillemot. In seals, PCBs with both para positions and one ortho position chlorinated were metabolized, indicating metabolic pathways which were different from guillemot.

Hydroxylated species of 4-chloro-, 4,4'-dichloro, and 2,2', 5,5'-tetrachlorobiphenyls were demonstrated as metabolites by Hutzinger et al. (1972) in feeding studies on rats and pigeons. Brook trout, however, did not produce any hydroxylated species.

There have been numerous studies with pure cultures of microorganisms which have indicated the ability of microbes to degrade PCBs, particularly the lower chlorinated species. Such studies include those of Yagi and Sudo (1980) using *Alcaligenes BMZ*; Ahmed and Focht (1973) using *Achromobacter* sp.; and Wallnofer et al. (1973) using the soil fungus, *Rhizopus japonicus*.

Tulp et al. (1978) studied the degradation of several chlorinated biphenyls by mixed cultures of bacteria isolated from activated sludge. If 4,4' dichlorobiphenyl was used as a sole carbon source, 4-chlorobenzoic acid and 4,4' dichloro-2,3-biphenyldiol were isolated. If other carbon sources were present with the 4,4' dichlorobiphenyl no metabolites were isolated. No metabolites were isolated if 2,4',5; 2,2',5,5'; 2,2',3,4,5; and 2,2',3,4,5,5' substituted chlorinated biphenyls were used as sole sources of carbon. Tulp et al. (1978) concluded that mixed bacterial populations do not degrade chlorobiphenyls with more than three chlorines, and degradation of such chlorobiphenyls by aerobic bacteria is not significant either in the environment or in sewage treatment.

Wong and Kaiser (1975) also indicated that bacterial degradation of lower chlorinated compounds is a possible pathway of breakdown but that the low concentration of PCBs in natural waters might not prompt bacteria to synthesize the necessary enzymes in their metabolism, unlike the bacterial response in artificial environments where PCB compounds are the only carbon source.

Carey and Harvey (1978) incubated seawater samples with Aroclor 1254 and mixed cultures of bacteria extracted from marine sediments. Neither changes in number nor relative heights of peaks were detected in gas chromatograms. When trichlorobiphenyl was incubated with seawater, approximately 1.4% was metabolized to what may have been a lactone acid (Figure 4.2.3).

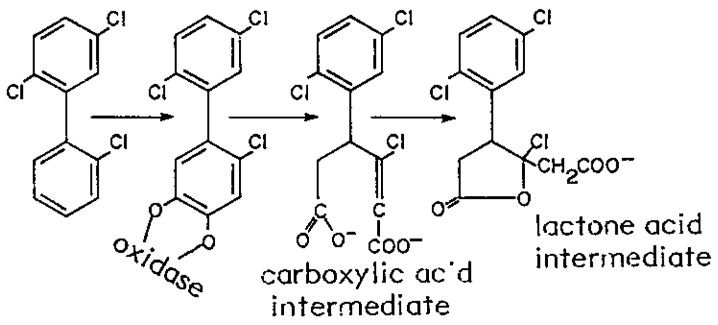


Figure 4.2.3
Proposed Pathway for Metabolism of 2,5,2'-Trichlorobiphenyl by Mixed Cultures of Marine Bacteria

Carey and Harvey (1978) found no evidence for metabolism of chlorobiphenyls in anaerobic marine mud, indicating that anaerobic environments may serve as long-term sinks for PCBs. These investigators suggested that metabolism studies with pure cultures minimized the chance of finding organisms capable of the initial ring opening and did not allow for the possibility that a suite of organisms might be required for metabolism. Eder (1976) found that the percentage of lower-chlorinated PCBs in anaerobic sediments of the Norwegian Depression was higher than in well-aerated marine sands suggesting a greater degree of biological degradation in the aerated sands, if the input ratios were identical for both areas.

4.2.5.3 Sorption and Sedimentation

Summary Statement: Adsorption is an important fate process for PCBs. Adsorption of PCBs to solids is enhanced by increasing salinity, increasing organic content of the solids, and by decreasing particle size. Release of PCBs from solids is marginal compared to uptake characteristics. However, there is evidence for some release upon resuspension of solids.

Review of Individual Studies: A number of studies have indicated that sediments and suspended matter have an important effect on the fate of PCBs in coastal waters. General studies of this nature and studies specifically dealing with Puget Sound are reviewed below.

Hiraizumi et al. (1979) conducted laboratory and field studies of PCB adsorption onto bed sediment, sand, and plankton. PCB adsorption was found to correlate well with the PCB concentration in brine water and could be described by a Freundlich isotherm. The PCB concentration factors of the adsorbents were found to be inversely related to particle size and linearly related to surface area of adsorbents. Organic content also influenced the PCB concentration factor. Concentration factors within media were: zooplankton, 10^4-0.5 x 10^5; suspended matter in the middle water layer and total plankton, 10^4-10^6; suspended matter in surface layer and phytoplankton, 0.5 x 10^5-10^5; suspended matter in bottom layer and fine sea mud, 10^3-0.2 x 10^5; and coarse sand and clay, 4 x 10^2-10^3. Equilibria were rapidly reached, i.e., phytoplankton reached their adsorption capacity within 100 minutes and zooplankton within 200 minutes. Desorption rates were much slower. During the first 24 hours, seabed mud released only 1% of the total adsorbed PCB and 0.8% during the next 5 days.

Studies by Weber et al. (1978) and Haque et al. (1974) have similarly shown that smaller particles and organic content will enhance absorptivity of PCBs. Wildish et al. (1980) studied the adsorption-desorption of Aroclor 1254 by various size fractions over a range of salinities. Adsorption was found to increase with increasing salinity. Concentration factors for 1 gram of silt-clay exposed to 0.2 µg/L Aroclor 1254 were: 810 for deionized water; 2710 for half strength seawater; and 4240 for full strength seawater. The concentration factors for desorption were greater than for adsorption, and adsorption of PCBs was considered relatively irreversible. The experiments by Wildish et al. (1980) indicated progressively less desorption with increasing salinity, but no conclusions were possible due to variations in results. Determination of an experimental Freundlich isotherm resulted in the relationship, $S = 430{,}000\ C^{1.1}$, whereby S is the equilibrium concentration of the Aroclor in the sediment (μg/kg) and C is the equilibrium concentration of Aroclor in the water. This equation could be used to determine the PCB concentrations in pore water of settled sediments.

Choi and Chin (1976) determined that natural fulvic and humic acid fractions could behave as potential adsorbents for chlorinated hydrocarbons. Paris et al. (1978) determined partition coefficients for bacteria, seston and sediments. For Aroclor 1016, partition coefficients were $5.5\text{-}6.4 \times 10^3$, $1.2\text{-}2.5 \times 10^3$, and $1.2\text{-}1.3 \times 10^3$ for bacteria, seston and sediment, respectively.

In addition to studies on adsorption and exchange dynamics between PCBs and suspended solids as described above, fate studies must consider the gravitational or vertical transport of solids. A study of the role of sedimentation in the flux of PCBs from the water column in the Sargasso Sea was undertaken by Harvey and Steinhauer (1975). Surveillance results showed that 2×10^{-3} g/m^2/yr of PCBs were lost from the upper 100 m of the water column. Concentration factors between PCBs in seawater and sediments varied from 1.1 to 3.4×10^5. Although partitioning to suspended solids may have accounted for some portion of the PCB decreases in water, the suspended solid concentrations were not sufficient to account for the observed flux. Grids placed at a depth of 2,150 m near the Bahamas showed a sedimentation flux rate of 4.9 μg PCBs/m^2/yr, and Harvey and Steinhauer (1975) concluded that less than 1% of the PCBs introduced in the North American Basin was transported to the sediment by sinking particles.

Munson et al. (1976) in Upper Chesapeake Bay found that chlorinated hydrocarbons were highest in particles with lowest size grain diameter. They speculated that resuspension of fine grain fractions by tidal scour is the major re-entry route for PCBs from bottom sediments.

Desorption of PCBs from sediments may continually release PCBs into the environment. Nimmo et al. (1971) reported transfer of PCBs from sediments to fiddler crab and pink shrimp. After 30 days exposure to contaminated sediments containing 1.4-61 ppm PCBs, pink shrimp and hepatopancreas of fiddler crabs contained 0.2-240 ppm and 3.2-80 ppm PCB, respectively. Grass shrimp caged downstream from an actual spill accumulated only 0.4 ppm in 3 months from sediments containing 5 ppm PCBs (Nimmo et al., 1974). Stout and Lewis (1977) exposed spot shrimp (Pandalus platyceros), sea cucumber (Parastichopus californicus), and mussels (Mytilus edulis) in cages in Elliott Bay close to a disposal area for disposal of PCB-contaminated sediments. No changes in PCB concentration were observed within these animals; however, the investigators admitted to some problems with their experimental design.

Pavlou et al. (1978) recorded increases in PCB levels in water immediately after disposal of contaminated dredged sediments in Elliott Bay. Background water levels (3 ng/L) were immediately increased to 3 µg/L. After one week, water levels had been reduced to 10 ng/L and after one month, predisposal concentrations existed. Analyses of interstitial waters showed approximate levels of 100 ng/L PCBs.

Additional discussions of the adsorption and distribution of PCBs in Puget Sound are found in Section 4.2.6 of this Chapter.

4.2.5.4 Photolysis

Summary Statement: Photolysis is not a significant fate process for PCBs. However, it may be the only fate process capable of any type of conversion of highly chlorinated PCBs.

Review of Individual Studies: No photolytic studies of PCBs with seawater as a medium were found during the literature search.

PCBs absorb light in the range of 280 to 320 nm. Photodegradation will, therefore, depend upon: the solar irradiance per unit time at 280-320 nm; the fraction of photons absorbed by PCB rather than by water or reflected from the surface; and the quantum yield of photodecomposition. Bunce et al. (1978) suggested a preferential loss of ortho chlorines in the photolysis of PCBs. Because it is difficult to simulate environmental conditions for photolysis experiments of PCBs, irradiations of thin films, gas phases, and aqueous suspensions have been used (Hutzinger et al., 1972). Irradiation of Aroclor 1254 in hydroxylic solvents have been shown by Hutzinger et al. (1972) to result in the formation of more polar carboxylic acid fractions and the addition of water to the PCB molecule. Irradiations of 2,2',5,5'-tetrachlorobiphenyl indicated "that dechlorination, formation of polymers and carboxylic products as well as hydroxylation, does occur."

Bunce et al. (1978) in studies of the photodecomposition of PCBs in Lake Erie water predicted that in shallow waters, up to 5% of lightly chlorinated PCBs might lose a chlorine atom each year and at least one chlorine atom from each highly chlorinated molecule would be lost annually. Adsorption to particulate material may reduce this degradation rate while concentration of PCBs within the surface film may increase decomposition.

The possible loss of one chlorine atom from highly chlorinated PCBs may have a significant effect on the decomposition of PCBs, because the lower chlorinated PCBs are more susceptible to biodegradation and because no other fate process is capable of degrading highly chlorinated PCBs. The reduction of chlorine substituents by photolysis will also result in species with increased susceptibility to vapor transport (Hutzinger et al., 1972).

4.2.5.5 Volatilization

Summary Statement: In the absence of suspended solids, volatilization may be an important fate process for PCBs. The role of volatilization in Puget Sound would be difficult to quantitate.

Review of Individual Studies: Harvey and Steinhauer (1975) accounted for the widespread distribution of PCBs within the North Atlantic by evaporative codistillation from surface waters. This concept, referred to as codistillation is, however, quite controversial (Tulp and Hutzinger, 1978). Harvey and Steinhauer described codistillation in the following manner: "Large fractions of PCBs are deposited on the sea surface by wet and dry fallout and by solvation from the atmosphere. Re-entrainment with the air mass may occur during periods of high evaporation and PCBs may then be transported to areas of high precipitation or condensed at colder high latitudes." Harvey and Steinhauer (1975) speculated that PCBs could be entrained by cold dense water and subsequently flow into deep waters without passing through intermediate depths. For example, in the Sargasso Sea, PCB maxima were found in surface water in September and in subsurface waters in February.

Theoretical calculations for PCB losses from waters with no suspended solids show that PCBs could be quite volatile. Paris et al. (1978) estimated that the half lives of Aroclors 1016 and 1242 in a volume of one cubic meter of surface water would be 9.9 and 11.2 hours, respectively. Volatilization rates would be affected by degradation and turbulence, and significantly reduced by sorption. Similar calculations were published by Mackay and Leinonen (1975) for Aroclors 1242 (12.1 hours); 1248 (9.53 hours); 1254 (10.3 hours); and 1260 (10.2 hours). High evaporation rates were attributed to the high activity coefficients of low solubility PCB compounds which subsequently resulted in high equilibrium vapor partial pressures.

Haque and Kohnert (1976) showed that vapor loss decreased with increasing quantities of chlorine atoms. One deviation was that of 4,4'-dichlorobiphenyl which had a rate loss less than 2,4,5,2',5'-pentachlorobiphenyl. The difference indicates that electronic distribution, position of chlorine atoms on the rings, and symmetry of the molecules may significantly affect vapor pressure. Haque and Kohnert (1976) also found that the vapor loss of Aroclor 1254 adsorbed to sand surfaces could be significant, but if bound to "soil" particles, the loss was very small. Loss of Aroclor 1254 was significantly affected by temperature: increasing the temperature from 26°C to 60°C enhanced loss by a factor of 40.

Because of the strong affinity of PCBs for suspended solids, it is difficult to quantitate the impact of volatilization on the environmental fate of PCBs. Oloffs et al. (1973) for example, recorded a volatilization loss of 67% from river water containing 100 µg/L Aroclor 1260. In the presence of suspended solids, the experimental half life of Aroclor 1260 was in the order of 1,260 hours, compared to the estimate of 10.2 hours by Mackay and Leinonen (1975) for a system in the absence of suspended particles.

In Puget Sound, volatilization will be affected adversely by the normally low water temperatures and adsorption to particulate matter, especially in the vicinity of urban areas. Volatilization may be enhanced by the consistent wave action and the virtual absence of suspended matter in the central area of Puget Sound. Therefore, it would be difficult to quantitate the role of volatilization on the fate of PCBs in Puget Sound.

4.2.6 Overall Biogeochemical Fate Studies

Nisbet and Sarofim (1972) attempted to assess the distribution of PCBs in the North American environment. They estimated that 5×10^3 tons of PCBs used in North America were transferred into the sea, 1.5×10^4 tons remained on terrestrial North America, 2×10^4 tons were transferred to lakes and rivers, and no more than "several hundred tons" were to be found in marine biota.

Harvey and Steinhauer (1975) found that rapid decreases in PCB levels occurred in the Sargasso Sea mixed layer in response to decreasing uses of PCBs. The losses could not be entirely explained by vertical and horizontal advection and diffusion, nor by association with descending particulate matter. Metabolism and accumulation by marine organisms was assumed to account for no more than 0.1% of the decrease. Consequently, Harvey and Steinhauer (1975) postulated that volatilization played a significant role with subsequent deposition of the PCBs within the colder, deeper low pressure trough. Dilution was assumed to be such that PCB levels or changes would be difficult to detect by current methodology.

Paris et al. (1978) concluded that volatilization of Aroclor 1016 and 1242 would be a significant transport pathway if sorption to sediments did not occur. When highly sorbed, the Aroclors were assumed to be transported in association with seston within the aquatic environment.

Whitmore (1977) developed an extensive model of the environmental fate of PCBs in Lake Michigan. He concluded that the major loss mechanisms would be evaporation from air-water interfaces and sorption to sediments. The half life of PCBs in the entire Lake Michigan system was calculated to be on the order of 25 years. Current data indicate that the PCB levels in fish are actually decreasing much more rapidly; however, there have been no efforts to evaluate the levels of PCBs in all components of the environment (International Joint Commission (1979) Surveillance Subcommittee). The discrepancy between the rapid losses in biota and the losses for the total system possibly indicate that sedimentation may serve to strongly bind PCBs, with little release to ambient water and biota.

Pavlou and Dexter (1979) examined the accumulation of PCBs in suspended phases and lower trophic level biota in Puget Sound. Their data suggested accumulation was predominantly governed by equilibrium partitioning. The partition coefficient of trichlorobiphenyl to suspended particulate matter was 4.36×10^4 and of heptachlorobiphenyl was 9.67×10^4. Zooplankton had partition coefficients varying from 0.9×10^6 for trichlorobiphenyl to 2.4×10^6 for hexachlorobiphenyl. During Pavlou and Dexter's 1979 study, the system appeared to be in equilibrium (i.e., receiving uniform input), in that the PCB concentrations in sediments of a system did not vary significantly from the suspended particulate matter concentrations. For example, sediments from the Duwamish River had PCB levels of 12.4×10^{-7} gm/gm while the SPM (suspended particulate matter) levels were $10.05 \pm 2.84 \times 10^{-7}$ gm/gm. Within the Main Basin, sediment levels were $0.82 \pm 0.03 \times 10^{-7}$ gm/gm and SPM levels were $0.7 \pm 0.09 \times 10^{-7}$ gm/gm. PCB levels at more than 25 m depths of Puget Sound were uniform, indicative of rapid mixing generated by tidal action. Levels within the Elliott Bay-Duwamish River system showed horizontal and vertical distribution which correlated with salinity levels.

Pavlou and Dexter (1979) estimated losses of PCBs in Puget Sound of 300 g/day by advection (based on freshwater flow) and 430 g/day by sedimentation. The amount by advection would include that adsorbed to suspended material and plankton. Volatilization was not considered in the calculations. Based on an assumed ambient concentration of 2 ng/L of PCBs in water, 0.34×10^6 grams were calculated to be in the water mass of Puget Sound and 1.33×10^6 grams were assumed adsorbed to the sediments. Pavlou and Dexter (1979) concluded that a large majority of the residues are retained within Puget Sound. They also state that it is not known whether sedimentation constitutes a complete loss to the system or merely temporary storage.

4.2.7 Conclusions

1. PCB levels in Puget Sound fish, crab, and clams, particularly those from Elliott and Commencement Bays, may affect consumers of such biota.

2. Many sediments of Puget Sound exceeded the maximum levels of 500 ppb total PCB recommended by Pavlou et al. (1978). The limits by Pavlou et al. were suggested to assure an ambient water level of total PCBs of no more than 5 ng/L.

3. A rapid decrease of PCB levels in the Puget Sound water column may be occurring. For example, during the MESA effort, Brown (1979) indicated high levels of PCBs in sediments, particularly sediments from Elliott and Commencement Bays, and Riley et al. (1980) indicated that PCB levels in suspended solids and water from the areas were below detection limits. Pavlou et al. (1977), in earlier studies, indicated that PCB levels in sediments and suspended solids in the water column of Puget Sound were quite similar in concentration, indicative of a system which was in equilibrium. These results may indicate that while PCBs are rapidly removed from the water column, PCB levels in biota may also be rapidly decreasing. PCBs in sediments would, however, decrease very slowly.

4. There are few data on physical chemical properties of PCBs in seawater and the effects of photolysis on PCBs in seawater.

5. Data on uptake of PCBs from sediments by biota do not conclusively indicate whether release from sediments is of environmental significance. This review suggests that PCBs must be released to the water column to enable subsequent uptake by biota. Annual monitoring of, for example, estuarine yearling fish may define the amount of release of PCBs from Puget Sound sediments in the apparent absence or decrease of additional inputs.

6. Environmental processes of significance to the fate of PCBs are dependent upon the degree of chlorination of the PCB molecules. Mono-, di- and trichlorobiphenyls appear to be metabolized to variable degrees by biota. Biphenyls with more than 5 substituted chlorines are not readily metabolized.

7. Sedimentation and adsorption to suspended matter is probably the most significant fate process for PCBs in Puget Sound. Adsorption to suspended matter would result in advection of PCBs from the sound on the basis of water transport. Volatilization may be of subsequent importance; however, quantification of its significance is difficult.

8. Metabolites of chlorinated biphenyls may be of ecological significance, due to their apparently higher degree of toxicity compared to parent PCB molecules.

4.2.8 Research Needs

1. There is a need to develop a meaningful ecological monitoring system within Puget Sound which would detect the possible effects, fates, and trends of contaminants such as PCBs.

2. There is a need to determine the existing sources of PCBs to Puget Sound.

3. Additional uptake studies of PCBs by marine biota from PCB contaminated sediments are required.

4. Additional evaluations of the effects of metabolites of PCBs are required.

References

Ahmed, M. and D.D. Focht. 1973. Oxidation of polychlorinated biphenyls by achromobacter pCB. Bull. Environ. Contam. Toxicol. 10:70-72.

Allen, J.R. and D.H. Norback. 1976. Pathobiological responses of primates to polychlorinated biphenyl exposure. In: Proceedings of the National Conference on Polychlorinated Biphenyls, November 19-21, 1975, Chicago. EPA-560/6-75-004. pp. 43-49.

Amico, V., G. Impellizzeri, G. Oriento, M. Piatelli, S. Sciuto, and C. Tringali. 1979. Levels of chlorinated hydrocarbons in marine animals from the central Mediterranean. Mar. Poll. Bull. 10:282-284.

Ballschmiter, K., M. Zell, and H.J. Nier. 1978. Persistence of PCB's in the ecosphere: Will some PCB-components "never" degrade? Chemosphere 2:173-176.

Bend, J.R., L.G. Hart, A.M. Guarino, D.P. Rall, and J.R. Fouts. 1976. Distribution and excretion of 14-C 2,4,5,2',5'-Pentachlorobiphenyl in the lobster (Homarus americanus) and the dogfish shark (Squalus acanthias). In: Proceedings of a National Conference on Polychlorinated Biphenyls, November 19-21, 1975. Chicago. EPA-560/6-75-004. pp. 292-302.

Bidleman, T.F. and C.E. Olney. 1973. Chlorinated hydrocarbons in the Sargasso Sea atmosphere and surface water. Science 183:516-518.

Brown, D. 1979. Memoranda to Ed Long, September 1978, March, August, and October 1979.

Bunce, N.J., Y. Kumai, and B.G. Brownlee. 1978. An assessment of the impact of solar degradation of polychlorinated biphenyls in the aquatic environment. Chemosphere 2:155-164.

Callahan, M. and M. Slimak. 1979. Water-Related Environmental Fate of 129 Priority Pollutants, Vol. I. EPA 440/4-79-029a.

Carey, A.E. and G.F. Harvey. 1978. Metabolism of polychlorinated biphenyls by marine bacteria. Bull. Environ. Contam. Toxicol. 20:527-534.

Choi, W-W and K.Y. Chin. 1976. Associations of chlorinated hydrocarbons with fine particles and humic substances in surficial sediments. Environ. Sci. Technol. 10:782-786.

Clayton, J.R., Jr., S.P. Pavlou, and N.F. Breitner. 1977. Polychlorinated biphenyls in coastal marine zooplankton: Bioaccumulation by equilibrium partitioning. Environ. Sci. Technol. 11:676-682.

Dennis, D.S. 1976. Polychlorinated biphenyls in the surface waters and bottom sediments of the major drainage basins of the United States. In: Proceedings of the National Conference on Polychlorinated Biphenyls, November 19-21, 1975. Chicago. EPA-560/6-75-004. pp. 183-194.

Dexter, R.N. and S.P. Pavlou. 1978. Mass solubility and aqueous activity coefficients of stable organic chemicals in the marine environment: polychlorinated biphenyls. Mar. Chem. 6:41-53.

Duke, T.W., J.I. Lowe, and A.J. Wilson. 1970. A polychlorinated biphenyl Aroclor 1254 in the water, sediment, and biota of Escambia Bay, Florida. Bull. Environ. Contam. Toxicol. 5:171-180.

Eder, G. 1976. Polychlorinated biphenyls and compounds of the DDT group in sediments of the central North Sea and the Norwegian Depression. Chemosphere 2:101-106.

Elder, D.L., S.W. Fowler, and G.G. Polikarpov. 1979. Remobilization of sediment-associated PCB's by the worm, Nereis diversicolor. Bull. Environ. Contam. Toxicol. 9:448-452.

Environment Canada. 1976. Background to the Regulation of Polychlorinated Biphenyls (PCB) in Canada. Technical Report. 76-1. 169 pp.

Environmental Protection Agency. 1976. Proceedings of the National Conference on Polychlorinated Biphenyls, November 19-21, 1975; Chicago. 472 pp.

Environmental Protection Agency. 1978. Ambient Water Quality Criteria: Polychlorinated Biphenyls. NTIS(PB 296 803).

Goerke, H. and W. Ernst. 1977. Fate of C-labelled di-, tri- and pentachlorobiphenyl in the marine annelid Nereis virens I. Accumulation and elimination after oral administration. Chemosphere 9:551-558.

Hansen, D. 1976. PCB's: Effects on and accumulation by estuarine organisms. In: Proceedings of the National Conference on Polychlorinated Biphenyls, November 19-21, Chicago. EPA-560/6-75-004. pp. 282-283.

Haque, R. and R. Kohnert. 1976. Studies on the vapor behavior of selected polychlorinated biphenyls. J. Environ. Sci. Health Bull. 3:253-264

Haque, R., D.W. Schmedding, and V.H. Freed. 1974. Aqueous solubility, adsorption, and vapor behavior of polychlorinated biphenyl Aroclor 1254. Environ. Sci. Technol. 8:139-142.

Harvey, G.R. and W.G. Steinhauer. 1975. Biogeochemistry of PCB and DDT in the North Atlantic. In: J.O. Nriagu (ed.), Environmental Biogeochemistry. Vol. I. Elsevier/North Holland, Amsterdam. pp. 203-221.

Harvey, G.R., W.G. Steinhauer, and H.P. Miklas. 1974. Decline of PCB concentrations in North Atlantic surface water. Nature 2522:387-388.

Herman, S.G. and J. Calambodikis. 1978. Personal Communication to Ed Long, MESA Project Office, Seattle.

Hiraizumi, Y., M. Takahashi, and H. Nishimura. 1979. Adsorption of polychlorinated biphenyl onto seabed sediment, marine plankton, and other adsorbing agents. Environ. Sci. Technol. 13:580-584.

Hutzinger, O., S. Safe, and V. Zitko. 1972. Photochemical degradation of chlorobiphenyls (PCB's). Env. Health Perspect. 1:15-20.

Hutzinger, O., S. Safe, and V. Zitko. 1974. The Chemistry of PCB's. Chemical Rubber Publishing Co., Cleveland, Ohio.

International Joint Commission. 1977. New and Revised Great Lakes Water Quality Objectives. Volume II.

International Joint Commission. 1979. Surveillance Subcommittee. Report on Great Lakes Water Quality. Windsor, Ontario.

Jansson, B., S. Jensen, M. Olsson, L. Renberg, G. Sundstrom, and R. Vaz. 1975. Identification by GC-MS of phenolic metabolites of PCB and p, p'- DDE isolated from Baltic guillemot, and seal. Ambio 4:93-97.

Keil, J.E., L.E. Priester, and S.H. Sandifer. 1971. Polychlorinated biphenyl (Aroclor 1242): Effects of uptake on growth, nucleic acids, and chlorophyll of a marine diatom. Bull. Environ. Contam. Toxicol. 6:156.

Lowe, J.I., P.R. Parrish, J.M. Patrick, Jr., and J. Forester. 1972. Effects of the polychlorinated biphenyl Aroclor 1254 on the American oyster, Crassostrea virginica. Mar. Biol. 17:209.

Mackay, D. and P.J. Leinonen. 1975. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 9:1178-1180.

Malins, D.C., B.B. McCain, D.W. Brown, A.K. Sparks, and H.O. Hodgins. 1980. Chemical Contaminants and Biological Abnormalities in Central and Southern Puget Sound. NOAA Technical Memorandum OMPA-2. Office of Marine Pollution Assessment, Boulder, Colo. 295 pp.

McDermott, D.J., D.R. Young and T.C. Heesen. 1976. PCB contamination of Southern California marine organisms. In: Proceedings of the National Conference on Polychlorinated Biphenyls, November 19-21, 1975. Chicago. EPA-560/6-75-004. pp. 209-217.

McNaught, D.C. 1978. Uptake rates and effects of PCBs on phytoplankton, and zooplankton. Results presented at a U.S. EPA Workshop on PCBs, April 3-4. Grosse Ile, Mich.

Metcalf, R.L., J.R. Sanborn, P-Y. Lu, and D. Nye. 1976. Laboratory model ecosystem studies of the degradation and fate of radio labelled tri-, tetra-, and pentachlorobiphenyl compared with DDE. In: Proceedings of the National Conference on Polychlorinated Biphenyls, November 19-21, 1975. Chicago. EPA-560/6-75-004.

Munson, T.O., H.D. Palmer, and J.M. Forns. 1976. Transport of chlorinated hydrocarbons in upper Chesapeake Bay. In: Proceedings of the National Conference on Polychlorinated Biphenyls, November 19-21, 1975. Chicago. EPA-560/6-75-004.

National Institute for Occupational Safety and Health (NIOSH). 1979. Registry of Toxic Effects of Chemical Substances (RTECS).

Nealy, W.B. 1979. A preliminary assessment of the environmental exposure to be expected from the addition of a chemical to a simulated aquatic ecosystem. Intern. J. Environ. Studies. 13:101-108.

Nimmo, D.R., P.D. Wilson, R.R. Blackman, and A.J. Wilson, Jr. 1971. Polychlorinated biphenyl absorbed from sediments by fiddler crabs and pink shrimp. Nature 231:50.

Nimmo, D.R., J. Forester, P.T. Heitmuller, and G.H. Cook. 1974. Accumulations of Aroclor 1254 in grass shrimp (Palaemonetes pugio) in laboratory and field exposure. Bull. Environ. Contamin. Toxicol. 11:303-308.

Nisbet, I.C.T. and A.F. Sarofim. 1972. Rates and routes of transport of PCBs in the environment. Environ. Health Perspect. 4:21-38.

Oloffs, P.C., L.S. Albright, S.Y. Szeto, and J. Lau. 1973. Factors affecting the behavior of five chlorinated hydrocarbons and their sediments. J. Fish. Res. Bd. Can. 30:1619.

Paris, D., W.C. Teen, and G.L. Baughman. 1978. Role of the physico-chemical properties of Aroclor 1016 and 1242 in determining their fate and transport in aquatic environments. Chemosphere 7:319-325.

Pavlou, S.P. and R.N. Dexter. 1979. Physical and chemical aspects of the distribution of polychlorinated biphenyls in the aquatic environment. In: L.L. Marking and R.A. Kimerle, (eds.), Aquatic Toxicology. ASTM STP 667. pp. 195-211.

Pavlou, S.P., R.N. Dexter, and W. Hom. 1977. Polychlorinated biphenyls (PCBs) in Puget Sound: Physical/chemical aspects and biological consequences. In: A.C. Duxbury (ed.), The Use, Study and Management of Puget Sound. University of Washington. Seattle. pp. 100-133.

Pavlou, S.P., R.N. Dexter, W. Hom, A.J. Hafferty, and K.A. Krogsulnd. 1978. Release and distribution of polychlorinated biphenyls induced by open water dredge disposal activities. DMRP Technical Report D-77-24.

Peakall, D. 1972. Polychlorinated biphenyls: Occurrence and biological effects. Residue Reviews 44:1-21.

Platonow, N.S. and L.H. Karstad. 1973. Dietary effects of polychlorinated biphenyls on mink. Can. J. Comp. Med. 37: 391-400.

Riley, R.G., E.A. Crecelius, D.C. Mann, K.H. Abel, B.L. Thomas, and R.M. Bean 1980. Quantitation of Pollutants in Suspended Matter and Water from Puget Sound. NOAA Technical Memorandum ERL MESA-49. Marine Ecosystems Analysis Program, Environmental Research Laboratories, Boulder, Colo. 99 pp.

Ringer, R.K., R.J. Aulerich, and M. Zabik. 1972. Effect of dietary polychlorinated biphenyls on growth and reproduction of mink. Amer. Chem. Soc. National Meeting, Preprints of Papers. 12: 149-154.

Risebrough, R.W. 1976. Recent studies of transport of PCBs to marine environments. In: Proceedings of the National Conference on Polychlorinated Biphenyls, November 19-21, 1975. Chicago. pp. 230-235.

Stainken, D., and J. Rollwagen. 1979. PCB residues in bivalves and sediments of Raritan Bay. Bull. Environ. Contam. Toxicol. 231:690-697.

Stendell, R.C. 1976. Summary of recent information regarding effects of PCBs on birds and mammals. In: Proceedings of a National Conference on Polychlorinated Biphenyls November 19-21, 1975. Chicago. EPA 560/6-75-009. pp. 262-267.

Stout, V.F. and L.G. Lewis. 1977. Aquatic disposal field investigations. Duamish Waterway disposal site, Puget Sound, Wash. Appendix B: Role of disposal of PCB-contaminated sediment in the accumulation of PCBs by marine animals. Dredged Material Research Program. Tech. Rep. D-77-24. U.S. Army Corps of Engineers.

Sundstrom, G., O. Hutzinger, and S. Safe. 1976. The metabolism of chloro biphenyls. Chemosphere 5:267-298.

Ten Berge, W.F. and M. Hillebrand. 1974. Organochlorine compounds in several marine organisms from the North Sea and the Dutch Wadden Sea. Netherlands Journal of Sea Research 8:361-368.

Tulp, M.Th.M. and O. Hutzinger. 1978. Some thoughts on aqueous solubilities and partition coefficients of PCB, and the mathematical correlations between bioaccumulation and physico-chemical properties. Chemosphere 7:849-860.

Tulp, M.Th.M., R. Schmitz, and O. Hutzinger. 1978. The bacterial metabolism of 4,4 -dichlorobiphenyl and its suppression by alternative carbon sources. Chemosphere 1:103-108.

Wallnofer, P.R., G. Englehardt, S. Safe, and O. Hutzinger. 1973. Microbial hydroxylation of 4-chlorobiphenyl and 4,4'-dichlorobiphenyl. Chemosphere 2:69-72.

Weber, W.J., Jr. J.D. Sherrill, and M. Pirbiazri. 1978. Transport and differential accumulation of PCB's in river-harbor-lake systems. Results presented at a U.S. EPA Workshop on PCB's, April 3-4, 1978. Grosse Ile, Mich.

Whitmore, F.C. 1977. A first order mass balance model for the sources, distribution, and fate of PCB's in the environment. EPA 560/6-77-006. 180 pp.

Wildish, D.J., C.D. Metcalfe, H.M. Akagi, and D.W. McLeese. 1980. Flux of Aroclor 1254 between estuarine sediments and water. Bull. Environ. Contam. Toxicol. 24:20-26.

Wong, P.T.S. and K.L.E. Kaiser. 1975. Bacterial degradation of PCB's: II. Rate Studies. Bull. Environ. Contam. and Toxicol. 13:249-255.

Yagi, O. and R. Sudo. 1980. Degradation of polychlorinated biphenyls by microorganisms. J. Water Poll. Control Fed. 52:1035-1043.

Yoshimura, H. and H. Yamamoto. 1973. Metabolic studies of polychlorinated biphenyls. I. Metabolic fate of 3,4,3 ,4 -tetrachlorobiphenyl in rats. Chem. Pharm. Bull. 21:1168.

Zitko, V. 1974. Uptake of chlorinated paraffins and PCB from suspended solids and food by juvenile Atlantic salmon. Bull. Environ. Contam. Toxicol. 12:406-412.

4.3 Polychlorinated Dibenzofurans

4.3.1 Introduction

Polychlorinated dibenzofurans (PCDFs) are structurally similar to chlorinated dibenzodioxins, which are among the most toxic chemicals known. The structures are shown in Figure 4.3.1 along with the numbering sequences for designation of positions of substituted chlorine. PCDFs are not produced intentionally for any purpose; however, they are either formed as by-products in manufacture of, or disposal of polychlorinated biphenyls (PCBs) or polychlorinated phenols.

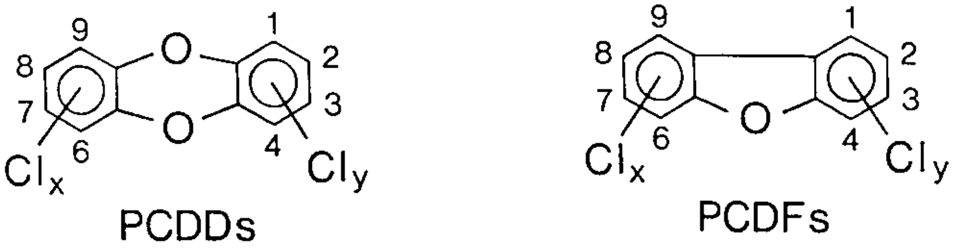


Figure 4.3.1
Structures and Polychlorinated Numbering Systems for
Dibenzofuran and Dibenzodioxin

During the MESA Program, PCDFs were detected as part of a special effort to identify compounds which are present, in addition to those for which routine monitoring efforts were underway. Three PCDFs were identified in sediments from Central Puget Sound (Malins et al., 1980).

Although the levels of PCDFs in Puget Sound have not been quantified, PCDFs have been chosen as compounds of possible concern to Puget Sound because of their high toxicity and because of their potential wide-spread distribution throughout the Sound.

4.3.2 Significance to Puget Sound

4.3.2.1 Review of Known Toxicity Data

There are few data on the toxicity of PCDFs to aquatic biota. Much of the data available are based on feeding studies to mammals and chickens. Chlorinated dibenzofurans are structurally similar to the chlorinated dibenzo-p-dioxins, some of which are both highly toxic and teratogenic. Several tetra- and penta- chlorinated dibenzofurans, particularly 2,3,7,8-tetra-CDF, are nearly as effective in inducing aryl hydrocarbon hydroxylase activity as is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), one of the most toxic known chemicals (Norstrom et al., 1976). PCDFs have been shown to be highly toxic to mammals and chickens. Goldstein et al. (1974, 1976) found that a dietary level of 5 µg/kg of 2,3,7,8-tetra-CDF was very toxic to chicks. McKinney et al. (1976) also fed tetra-CDF to chicks for 21 days and confirmed that a 5 µg/kg level in diet was fatal, producing liver edemas. However, a 1 µg/kg level produced no observable pathological effects.

Oishi et al. (1978) compared the toxicity of PCBs and dibenzofurans in rats by feeding them diets with either 100 ppm PCB, or 1 or, 10 ppm PCDF for 4 weeks. The diets with higher PCDF levels produced ear lesions within 3 weeks, markedly depressed body weight gain; and, significantly decreased thymus, ventral prostate gland and seminal vesicle weights. Both PCDF levels reduced hemoglobin and hematocrit values, increased serum cholesterol concentrations and cholinesterase activity, and decreased triglyceride concentrations and leucine aminopeptidase activity. The results suggested that PCDFs were more toxic to rats than PCBs when administered in the diet. PCDFs produced toxic effects on hematologic and thymic functions and the authors postulated that part of Yusho disease could be attributed to PCDF in rice oil contaminated with PCB.

Yusho is the name given to a mass food poisoning in western Japan in 1968, apparently caused by ingested PCBs in rice oil. However, recent findings suggest that small amounts of PCDFs found along with the PCBs in the rice oil may be one of the etiologic factors causing the symptoms of Yusho. Kuroki and Masuda (1978) examined PCDF residues persisting in the tissues of Yusho victims following death. Three PCDFs (tetra, penta, and hexa) were found in the tissue samples and pentachlorodibenzofuran was both most accumulated and most persistent (significant levels were still present in tissues after 9 years).

PCDF toxicity appears to be highly dependent on the positions and numbers of chlorine atoms on the dibenzofuran molecule (Morita et al. 1978). For example, Zitko et al. (1973) studied the acute toxicity of 2,8-dichlorodibenzofuran to immature brook trout and found no mortalities even with diets containing up to 122 mg/kg in a single case. The results suggested that this particular compound had a low acute toxicity possibly as a result of poor absorption in the gut and the possibility of excretion in the form of conjugated hydroxy derivatives. Fingerman and Fingerman (1977) studied the effects of both 1,2,3,4,5,6,7,8-octachlorodibenzofuran and Aroclor 1242 on moulting of the fiddler crab (<u>Uca pugilator</u>) by dissolving these compounds in acetone and then putting them in artificial seawater. They found that the PCB had a much more drastic effect on moulting than the octachloro-PCDF.

Firestone (1977) reviewed the approximate activity of 30 chlorinated dibenzofurans relative to 2,3,7,8-TCDD for chick embryo assay or induction of aryl hydrocarbonhydroxylase. The 2,8-dichloro DBF studied by Zitko et al. (1973) was considered "inactive" and the octachloro DBF studied by Fingerman and Fingerman (1977) had an activity of 0.002 of TCDD. As seen in Table 4.3.1, 1,3,6,7-tetrachloro DBF is inactive; 2,3,6,8-tetrachloro DBF is 0.005 as active as TCDD; and, 2,3,7,8 is 0.7 as active as TCDD. These data imply that a change in position of one chlorine atom may imply significant differences in toxicity, and thus illustrates the need for determination of the precise

Table 4.3.1

Dibenzofurans: Approximate Activity in Chick Embryo Assay for Induction of Aryl Hydrocarbon Hydroxylase*

Position of Substituted Chlorines	Approximate Activity to ^{a}TCDD
2,4	Inactive
2,8	Inactive
3,7	Inactive
2,3,4	0.001
2,3,6	0.001
2,3,7	-
2,3,8	0.001
2,3,9	-
2,4,6	-
2,4,8	0.001
1,4,6,8	-
1,2,7,8	-
1,3,6,7	Inactive
1,3,7,8	0.02
2,3,6,7	0.01
2,3,6,8	0.005
2,3,7,8	0.7
2,4,6,7	0.01
2,4,6,8	Inactive
3,4,6,7	0.01
1,2,3,6,7	0.2
1,2,3,7,8	0.2
1,2,4,7,8	-
1,3,4,7,8	0.005
2,3,4,6,7	0.1
2,3,4,7,8	0.7
2,3,4,6,7,8	0.2
2,3,4,7,8,9	0.3
1,2,3,4,6,7,8	0.2
1,2,3,4,6,7,8,9	0.002

*Firestone (1977)

[a] TCDD - tetrachlorodibenzodioxin

isomers of the chlorinated dibenzofurans which are found in Puget Sound.

4.3.2.2 Possible Effects of Levels Found in Puget Sound

No levels of PCDFs were determined in Puget Sound and possible effects can be only speculated. The most probable effects, if any, are on consumers of biota containing PCDFs.

4.3.3 Physical Properties of Chlorinated Dibenzofurans

There are 135 possible isomers of chlorinated dibenzofurans (Rappe et al. 1978). Figure 4.3.1 illustrates the structure and numbering system used to designate the isomers.

No information was found during this survey on the solubilities of any chlorinated dibenzofurans in water, however the solubilities are expected to be lower than 3.1 ppm, the solubility of dibenzofuran in freshwater at 25°C (Lu et al., 1978). On the basis of the log n-octanol/water partition coefficient of 4.12 for dibenzofuran (Leo et al., 1971), the tetra- and pentachlorodibenzofurans are theoretically very lipophilic with calculated partition coefficients (log P) which approach 7. This value implies that the chlorinated dibenzofurans have the ability for significant uptake by biota and for appreciable adsorption particularly to organic-containing sediments. Other known properties (Firestone, 1977) of chlorinated dibenzofurans include melting points (i.e., 185°C for dichlorodibenzofuran to 235°C for pentachlorobenzofuran) and vapor pressures (i.e., 7.3 x 10^{-6} mm for 2,4-dichlorodibenzofuran to 1.9 x 10^{-7}mm for octachlorodibenzofuran at 25°C). Volatilization is probably an insignificant fate process.

4.3.4 Sources or Inputs

Polychlorinated dibenzofurans (PCDFs) enter the global environment through a variety of avenues: as impurities of PCBs and chlorinated phenols (Norstrom et al., 1976); as by-products of coal conversion (Lu et al., 1978); from coal tar used as an anti-corrosion coating on public water systems (Alben, 1980); in fly ash and flue gases from municipal incinerators and industrial heating facilities; and, from the uncontrolled burning of PCBs (Buser et al., 1978; O'Keefe, 1978; Morita et al., 1978).

Any of the above sources could input chlorinated dibenzofurans to the Puget Sound ecosystem. In addition, a major manufacturer of pentachlorophenol (PCP) is located at Tacoma (Stanford Research Institute, 1979) and the product is widely used in the Pacific Northwest at sawmill facilities, lumber shipping terminals, and pulp and papermills. As well as being impurities of PCP formulations, PCDFs may also be formed during the burning of PCP contaminated hog fuel from sawmills.

4.3.5 Summary of Biogeochemical Fate Data in the Marine Environment

4.3.5.1 Bioaccumulation - Uptake and Depuration

Summary Statement: Few results were encountered in the literature concerning the bioaccumulation of polychlorinated dibenzofurans. Potential for uptake of the compounds is high. There are, however, indications that higher food chain organisms such as birds can depurate PCDFs rapidly. A sampling and analytical program for PCDFs in mussels, crabs, and other biota from Puget Sound should be initiated.

Review of Individual Studies: Few studies were found in the literature on bioaccumulation of PCDFs. Lu et al. (1978) followed the passage of tritiated dibenzofuran through a model aquatic system by applying this compound to sorghum leaves which, when eaten by salt marsh caterpillars, resulted in its release into water containing plankton, algae, *Daphnia*, snails, mosquito larvae, and mosquito fish. They found that the dibenzofuran was relatively water soluble, was not degraded, and exhibited substantial accumulation. An ecological magnification factor of 947 was determined for fish. All organisms accumulated dibenzofuran, with fish having a better ability to detoxify this compound through microsomal oxidations than algae or other organisms. The authors noted a good fit between log octanol/water partition coefficients and bioaccumulation by fish. A higher ecological magnification factor would be expected for chlorinated dibenzofurans. No bioconcentration studies (i.e., uptake direct from the water) were found in the literature. The log P's of chlorinated dibenzofurans indicate a potential for high levels of PCDFs in tissue of, for example, fish and shrimp. The relative absence of data on PCDFs in biota may be indicative of either limited analytical efforts or of the ability of aquatic organisms to rapidly depurate or metabolize PCDFs.

The other studies reported in the literature evaluated uptake via diets. Zitko et al. (1973) fed juvenile salmon (*Salmo salar*) dry fish food containing 2.7, 5.7, 2.8 and 9.1 µg/g wet weight of di-, tri-, tetra-, and octachlorodibenzofuran, respectively. Only the octa form was detected in fish tissues with levels in muscle and gut of 0.03 and 0.21 µg/g wet weight, respectively.

Norstrom et al. (1976) have shown that mallards eliminated over 97% of all PCDFs associated with Aroclor 1254 in long-term feeding experiments. Norstrom et al. (1976) speculated that PCDFs may be similar to chlorinated dibenzo-p-dioxins, which unlike DDE and the more highly chlorinated PCBs, are "less efficiently absorbed from the GI tract, and cleared from organisms more rapidly as the unchanged molecule." The authors also indicated that "a large body burden of PCBs may contribute to more rapid clearance of PCDFs by inducing a higher level of hydroxylase activity."

Lake et al. (1981) exposed caged mussels (Mytilus edulis) in various areas of Narragansett Bay, Rhode Island, and found from 643 to 1180 ppb (dry) of 2,4,8-trichlorodibenzofuran in the mussel tissues from the areas of the Bay described as highly polluted. Lobster hepatopancreas from the lesser polluted areas where mussels had a 52 ppb level of trichlorodibenzofuran, contained 1260 ppb trichlorodibenzofuran. The authors concluded that "the high toxicity generally associated with PCDFs calls for further documentation of their distributions throughout the coastal United States and for rapid identification and abatement of their sources." Assessments of similar biota in Puget Sound should be initiated.

Therefore, bioaccumulation studies of PCDFs are recommended to evaluate the potential for uptake of PCDFs in various species of aquatic biota, such as shrimp, crab, clams, and fish. Due to the toxicity of PCDFs, information on uptake is required to evaluate the ecological hazard associated with consumption of biota from PCDF contaminated areas.

4.3.5.2 Metabolism

Summary Statement: Polychlorinated dibenzofurans are probably not susceptible to metabolism to any appreciable extent. Information on metabolism of PCDFs was sparse.

Review of Individual Studies: Information on metabolism of PCDFs was sporadic. More studies on dibenzofuran and chlorinated dibenzodioxins were found in the literature and used in this report to assess the metabolism of PCDFs. Lu et al. (1978) found numerous degradation products of dibenzofuran following the exposure of a laboratory model ecosystem to dibenzofuran. Four of the compounds (designated as unknown) were substantially more polar than dibenzofuran and presumably represented ring hydroxylated compounds. However, much of the originally added dibenzofuran was not metabolized.

Zitko et al. (1973) found a hydroxy dichlorodibenzofuran in excreta of fish fed with 2,8-dichlorodibenzofuran. Cerniglia et al. (1979, 1980) reported that the marine fungi, Cunninghamella elegans, was capable of oxidizing dibenzofuran to metabolites which are quite similar to metabolites of mammalian enzyme systems. The predominant metabolites appeared to be hydroxylated forms of dibenzofuran.

Kearney et al. (1972) investigated the persistence of the structurally similar chlorinated dioxins (TCDD) and found that after one year approximately 60% of the originally applied 2,3,7,8-TCDD was recovered in two types of soils. The decrease due solely to microbial degradation was not determined.

Matsumura and Benezet (1973) found few microbial strains in nature which were able to degrade TCDD. About 100 microbial strains with the ability to degrade persistent pesticides were tested and only five showed the ability to degrade this compound.

In a study of the fate of ^{14}C-2,3,7,8-TCDD in lake water and sediments, Ward and Matsumura (1977) found that "TCDD is mostly bound with the lake sediment where it is stable and not very available for microbial degradation." Some metabolism in the aqueous phase was indicated. Under the conditions imposed in the experiment, the authors determined that the half life of TCDD in the sediment was about 590 days.

On the basis of structural similarity to dibenzofurans and TCDDs, it appears that chlorinated dibenzofurans would not be appreciably biologically degraded in the environment.

4.3.5.3 Sorption and Sedimentation

Summary Statement: On the basis of studies with the structurally related chlorinated dibenzo dioxins and on the basis of the apparent high log P of chlorinated dibenzofurans, it appears that sedimentation will be one of the most significant environmental fate processes for chlorinated dibenzofurans.

Review of Individual Studies: The lipophilic (high log n-octanol/water partition coefficients) properties of chlorinated dibenzofurans indicate potentially high adsorption to organic-containing sediments.

No publications were found relating to actual studies on adsorption-desorption of PCDFs. Studies, however, were found relating to chlorinated dibenzo-p-dioxins. In a review article, Helling et al. (1973) noted the investigations of the senior author (Helling, 1970) which evaluated the mobility of 2,7-dichlorodibenzo-p-dioxin and 2,3,7,8-tetrachlorodibenzo-p-dioxin in various soils. Both dioxins could not be leached from all soils tested including sandy loams, clay loam, and "muck."

Matsumura and Benezet (1973) attempted to leach 2,3,7,8-TCDD from a column of sandy loam. No mobility was observed. The investigations concluded that "the mode of translocation of TCDD in the environment would be limited to the movement of soil particles or dust-carried dispersion and biological transfer."

Arsenault (1976) composted sludges which contained octachlorodibenzodioxin (OCDD) and analysed the leachates. After 205 days, no significant migration of OCDD was observed.

4.3.5.4 Photolysis

Summary Statement: Photodecomposition of PCDFs in aqueous solutions is expected to be negligible.

Review of Individual Studies: Dibenzofurans can be formed photochemically from 2-chlorophenols. Crosby and Moilanen (1973) have also shown that 2-chlorodibenzofuran is a photolysis product of 2,5-dichloro- and 2,2',5,5'-tetrachlorobiphenyl. In addition, these authors found that 2,8-dichlorodibenzofuran undergoes dehalogenation by irradiation while 2-chlorodibenzofuran is almost unaffected by light. In the natural environment, dibenzofuran photolysis may be accelerated by natural and synthetic photosynthesizers (Crosby and Moilanen, 1973).

Hutzinger et al. (1973) observed that as in the case of chlorinated dibenzo-p-dioxins (Crosby et al., 1971), photolysis of 2,8-dichlorodibenzofuran and octachlorodibenzofuran in methanol and hexane solutions resulted in rapid dechlorination of the substrates with the eventual accumulation of unidentified resinous polymeric products.

However, due to the high adsorption of PCDFs to suspended solids and sediments, it is probable that as in the case of chlorinated dibenzo-p-dioxins (Crosby et al., 1971), photolysis will be hindered and photodecomposition in aqueous suspension will be negligible.

4.3.5.5 Volatilization

The estimated vapor pressures vary from a high of 7.3 x 10^{-6}mm (25°C) for 2,4-dichlorodibenzofuran to a low of 1.9 x 10^{-7} mm (25°C) for octachlorodibenzofuran (Firestone, 1977). Volatilization would be minimal. The Environmental Protection Agency (1978) in a report of its Environmental Health Advisory Committee estimated the rate of volatilization of chlorinated dibenzofurans from adsorbing surfaces and found rates which varied from 6.8 x 10^{-12}g/cm^2/S for dichlorodibenzofuran to 2.5 x 10^{-13}g/cm^2/S for octachlorodibenzofuran. The Committee concluded that volatilization of PCDFs would be minimal.

4.3.5.6 Hydrolysis

Firestone (1977) indicated that cyclic ethers such as dibenzo-p-dioxins and dibenzofurans are chemically stable. For example, OCDD distills unchanged at 350°C and can be recovered quantitatively from hot sulfuric acid.

Therefore, hydrolysis will be an insignificant fate process for chlorinated dibenzofurans.

4.3.6 Overall Biogeochemical Fate Studies

No overall fate studies were found for PCDFs and much of the data available are on the basis of studies with chlorinated dioxins and dibenzofurans.

4.3.7 Conclusions

1. Data are sporadic for physical-chemical properties, and distribution of chlorinated dibenzofurans in the environment.

2. Data on effects are minimal. Of the data available, none assess the effects of the more toxic isomers of PCDFs on aquatic biota. Effects on consumers of aquatic biota may be more significant.

3. The toxic properties of chlorinated dibenzofurans are highly dependent upon position of chlorine substitution and the number of chlorine substitutions. Determination of the isomers is essential for the evaluation of hazards to the environment.

4. Sedimentation and bioaccumulation are probably the most significant environmental fate processes for PCDFs in Puget Sound.

5. There are many potential sources of PCDFs and PCDDs in Puget Sound which are related to the use and disposal of polychlorinated biphenyls and polychlorinated phenols.

4.3.8 Research Needs

1. There is a need to further assess the presence of PCDFs and PCDDs in Puget Sound biota and sediments.

2. Contingent on the wide-spread detection of PCDFs and PCDDs in Puget Sound Biota and sediments,

    a. There is a need to assess the possible implications of PCDFs in sediments to bottom dwelling biota;

    b. There is a need for data on toxicity of PCDFs to marine species;

    c. There is a need for determination of sources of PCDFs and PCDDs in Puget Sound.

References

Alben, K. 1980. Gas chromatographic-mass spectrometric analysis of chlorination effects on commercial coal-tar leachate. Anal. Chem. 52:1825-1828.

Arsenault, R.D. 1976. Pentachlorophenol and contained chlorinated dibenzodioxins in the environment. In: Proceedings of the American Wood Preserving Association Annual Meeting. April 25-28, 1976. Atlanta, Ga.

Buser, H.R., H.R. Bosshardt, C. Rappe, and R. Lendahl. 1978. Identification of polychlorinated dibenzofuran isomers in fly ash and PCB pyrolyses. Chemosphere 5:419-429.

Cerniglia, C.E., R.L. Herbert, R.H. Dodge, P.J. Szaniszlo, and R.T. Gibson. 1979. Some approaches to studies on the degradation of aromatic hydrocarbons by fungi. pp.360-369. In: A.W. Bourquin, P.H. Pritchard (eds.), Proceedings of the Workshop: Microbial Degradation of Pollutants in Marine Environments. Gulf Breeze, Fla. EPA/600/9-79-012.

Cerniglia, C.E., R.H. Dodge, and D.T. Gibson. 1980. Studies on the fungal oxidation of polycyclic aromatic hydrocarbons. Bot. Mar. 23:121-124.

Crosby, D.G. and K.W. Moilanen. 1973. Photodecomposition of chlorinated biphenyls and dibenzofurans. Bull. Environ. Contamin. Toxicol. 10:372-377.

Crosby, D.G., A.S. Wong, J.R. Plimmer, and E.A. Woolson. 1971. Photochemical decomposition of chlorinated dibenzo-p-dioxins. Science 173:743-9.

Environmental Protection Agency. 1978. Report of the ad hoc study group on pentachlorophenol contaminants. Environmental Health Advisory Committee Science Advisory Board.

Fingerman, M. and S.W. Fingerman. 1977. Effects of a polychlorinated biphenyl and a polychlorinated dibenzofuran on moulting of the fiddler crab, Uca pugilator. Bull. Environ. Contamin. Toxicol. 18:138-142.

Firestone, D. 1977. Chemistry and analysis of pentachlorophenol and its contaminants. U.S. Food and Drug Admin. FDA By-lines No. 2, September, 1977. pp. 57-89.

Goldstein, J.A., J.D. McKinney, G.W. Lucier, J.A. Moore, P. Hickman, and H. Bergman. 1974. Effects of hexachlorobiphenyl isomers and 2,3,7,8-tetrachlorodibenzofuran (TCDF) on hepatic drug metabolism and porphyrin accumulation. Pharmacologist 16:239.

Goldstein, J.A., J.D. McKinney, G.W. Lucier, P. Hickman, H. Bergman, and J.A. Moore. 1976. Toxicological assessment of hexachlorobiphenyl isomers and 2,3,7,8-tetrachlorodibenzofuran in chicks. Toxicol. Appl. Pharmacol. 36:81-92.

Helling, C.S. 1970. Pesticide mobility in soils. II. Application of soil thinlayer chromatography. Soil. Sc. Soc. Am. Proc. 35:737-743.

Helling, C.S., A.R. Isensee, E.A. Woolson, P.D.J. Ensor, G.E. Jones, J.R. Plimmer, and P.C. Kearney. 1973. Chlorodioxins in pesticides, soils and plants. J. Environ. Qual. 2:171-178.

Hutzinger, O., S. Safe, B.R. Wentzell, and V. Zitko. 1973. Photochemical degradation of di- and octachlorodibenzofuran. Environ. Health Perspect. 5:267-271.

Kearney, P.C., E.A. Woolson, and C.P. Ellington, Jr. 1972. Persistence and metabolism of chlorodioxins in soils. Environ. Sci. Technol. 6:1017-1019.

Kuroki, H. and Y. Masuda. 1978. Determination of polychlorinated dibenzofuran isomers retained in patients with Yusho. Chemosphere 10:771-777.

Lake, J.L., P.F. Rogerson, and C.B. Norwood. 1981. A polychlorinated dibenzofuran and related compounds in an estuarine ecosystem. Environ. Sci. Technol. 15: 549-553.

Leo, A., C. Hansch and D. Elkins. 1971. Partition coefficients and their uses. Chemical Reviews 71:525-616

Lu, P.-Y., R.L. Metcalf, and E.M. Carlson. 1978. Environmental fate of five radiolabeled and conversion byproducts evaluated in a laboratory model ecosystem. Environ. Health Perspect. 24:201-208.

Malins, D.C., B.B. McCain, D.W. Brown, A.K. Sparks, and H.O. Hodgins. 1980. Chemical Contaminants and Biological Abnormalities in Central and Southern Puget Sound. NOAA Technical Memorandum OMPA-2. Office of Marine Pollution Assessment, Boulder, Colo. 295 pp.

McKinney, J.D., K. Chao, B.N. Gupta, J.A. Moore, and J.A. Goldstein. 1976. Toxicological assessment of hexachlorobiphenyl isomers and 2,3,7,8-tetrachlorodibenzofuran in chicks. I. Relationship of chemical parameters. Toxicol. Appl. Pharmacol. 36:65-80.

Matsumura, F. and H.J. Benezet. 1973. Studies on the bioaccumulation and microbial degradation of 2,3,7,8-tetrachlorodibenzo-p-dioxin. Environ. Health Perspect. 5:253-258.

Morita, M., J. Nakagawa, and C. Rappe. 1978. Polychlorinated dibenzofuran (PCDF) formation from PCB mixture by heat and oxygen. Bull. Environ. Contamin. Toxicol. 19:665-670.

Norstrom, R.J., R.W. Risebrough, and D.J. Cartwright. 1976. Elimination of chlorinated dibenzofurans associated with polychlorinated biphenyls fed to mallards (Anas platyrhynchos). Toxicol. Appl. Pharmacol. 37:217-228.

Oishi, S., M. Morita, and H. Fukuda. 1978. Comparative toxicity of polychlorinated biphenyls and dibenzofurans in rats. Toxicol. Appl. Pharmacol. 43:13-22.

O'Keefe, P.W. 1978. Formation of brominated dibenzofurans from pyrolysis of the polybrominated biphenyl fire retardant, Fire Master ff-1. Environ. Health Perspect. 23:347-350.

Rappe, C., A. Gara, and H.R. Buser. 1978. Identification of polychlorinated dibenzofurans (PCDFs) in commercial chlorophenol formulations. Chemosphere. 7:981-991.

Stanford Research Institute. 1979. Directory of Chemical Producers, United States of America. Chemical Information Services. Menlo Park, Calif.

Ward, C. and F. Matsumura. 1977. Fate of 2,4,5-T contaminant, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) in aquatic environments. Tech. Rept. Wis. WRC 77-01. University of Wisconsin Water Resources Center, Madison.

Zitko, V., D.J. Wildish, O. Hutzinger, and P.M.K. Choi. 1973. Acute and chronic oral toxicity of chlorinated dibenzofurans to salmonid fishes. Environ. Health Perspect. 5:187-189.

4.4 Hexachlorobenzene and Other Chlorinated Benzenes

4.4.1 Introduction

Hexachlorobenzene, monochlorobenzene, the three isomers of dichlorobenzene, and trichlorobenzene are among EPA's 129 Priority Pollutants.

Quantitative data were obtained for levels of hexachlorobenzene and dichlorobenzene in biota and sediments of Puget Sound (Malins et al., 1980). Dichlorobenzene levels were generally low, in many instances, below detection limits. Hexachlorobenzene on the other hand was one of the more predominant contaminants in many biota samples. Other chlorinated benzenes, namely chlorobenzene, dichlorobenzene, trichlorobenzene, and tetrachlorobenzene, were reported in "some sediment samples from Central Puget Sound" but were not quantitated.

Hexachlorobenzene (HCB) is used in agriculture for prevention of fungus disease, and is a starting material and by-product of the chemical industry. Other chlorinated benzenes may be components of chemical wastes (Safe et al., 1979) or formed by the chlorination of sewage effluents (Kopperman et al., 1976).

Chlorinated benzenes have been chosen as compounds of concern in Puget Sound because of their toxic properties and because of their levels of distribution in Puget Sound biota and sediments.

4.4.2 Significance to Puget Sound

4.4.2.1 Review of Known Toxicity Data

Chlorinated benzenes have varying effects on aquatic biota. For example, histological studies by Laseter et al. (1976) indicated changes after 10 days in kidney, liver, and gall bladder of bass exposed to 25 ppb HCB and in hepatopancreas of crayfish exposed to 36 ppb HCB. Hexachlorobenzene was not acutely toxic to pink shrimp and grass shrimp at 25 µg/L; however, both species were lethargic as compared to the controls and exhibited an uncharacteristic white hepatopancreas at the end of 96 hours exposure (Parrish et al., 1974).

Chlorinated benzenes have been designated as carcinogens (EPA, 1975) and the Food and Drug Administration has recommended no more than 0.3 ppm hexachlorobenzene be present in fat and dairy products (EPA, 1975). Courtney (1979) provided an extensive review of the toxicology and pathology of hexachlorobenzene. Much of the the medical data in the literature are a result of one unfortunate incident in Turkey where treated wheat seed was used for bread rather than for its intended purpose. The mortality rate was 10% and toxic symptoms in the survivors continue to the present day.

4.4.2.2 Possible Effects of Levels Found in Puget Sound

It is difficult to assess the potential ecological hazards of hexachlorobenzene and other chlorinated benzenes in Puget Sound.

The highest concentrations of HCB in Puget Sound were found in Hylebos Waterway and Southwest Commencement Bay, with maximum levels (dry weight in µg/g) of 1.3 in sediment, 3.7 in sole liver, 1.8 in crab hepatopancreas, 0.37 in whole worms, 0.08 in whole shrimp, and 0.13 in whole clams (Malins et al., 1980). No water analyses for HCB were attempted. Analyses of fish and crab indicated HCB levels in three sole muscle tissue samples from 0.04 to 0.2 µg/g (dry weight) and in two crab muscle tissue samples the levels varied from 0.01 to 0.05 µg/g (dry weight). The concentrations of HCB in liver for the above samples from sole were 0.4-1.6 µg/g (dry weight), and the levels in crab hepatopancreas were from 0.1 to 0.9 µg/g (dry weight).

Hexachlorobenzene was found in 59 of the 61 sediment samples taken in Puget Sound; it was not found in two samples from Pier 42 (Malins et al., 1980). Hexachlorobenzene levels ranged from 0.02 µg/kg to 1300 µg/kg, but did not exceed 1 µg/kg for samples taken outside of Commencement Bay. Highest HCB levels within Commencement Bay were located at Hylebos Waterway and in the Southwest Bay area. Comparison of HCB levels with sediment characteristics (Table D-7 of Malins et al., 1980) revealed no apparent relationships between HCB concentrations and grain size or sand/mud ratio.

Table 4.4.1 provides a comparison of HCB levels of HCB in Puget Sound biota with levels found in other areas of the world. It can be noted that the maximum levels of HCB in Puget Sound approach and/or exceed levels of HCB observed by Laska et al. (1976) in contaminated areas of the Mississippi River.

4.4.3 Physical Properties

Table 4.4.2 shows the known physical properties of chlorinated benzenes and it can be observed that increased chlorination results in decreasing vapor pressures, decreasing solubilities, and rapid increases in log octanol/water partition coefficients. Solubility values in marine waters were not found in the literature; however, solubility would be expected to be less in estuarine and marine waters than in freshwaters (Tulp and Hutzinger, 1978; Eganhouse and Calder, 1976).

4.4.4 Sources or Inputs

Hexachlorobenzene is not a naturally occurring compound (Steinwandter and Brune, 1977). It may be present in wastes from industries manufacturing other chlorinated hydrocarbons, and can enter the environment as a contaminant of the pesticides-diethyltetrachloroterephthalate and pentachloronitrobenzene. It is also a by-product in

Table 4.4.1

Hexachlorobenzene Levels in Sediments and Biota as Reported in the Literature

Investigators and Sample Evaluation	Location	Sample	HCB Levels (ppb)
Zitko (1971) (wet weight)	New Brunswick lakes and rivers	freshwater fish	3-12 (whole body)
	Nova Scotia banks	cod, plaice and ocean perch	ND
	Bay of Fundy	Mackerel and herring	1 ppb in one mackerel sample
Neuhaus (1973) (wet weight)	Australia	fish and shellfish	ND-9
Ten Berge and Hillebrand (1974) (wet weight)	North and Dutch Wadden Seas (offshore)	phytoplankton	0.06
		zooplankton	0.21
		shrimp	0.70
		mussel	0.53
		cod	1.0
		plaice	2.2, 3.0
		herring	8.3, 9.5
Laska et al. (1976) (wet weight)	Mississippi River (near industrial areas)	mosquito fish	72-380
		crayfish	22-194
Amico et al. (1979) (wet weight)	Central Mediterranean Sea	anchovy	0.1-2.2
		striped mullet	0.1-8.1
		tuna	0.1-0.2
		shrimp	0.1-0.6
		mussel	0.9-3.8
Malins et al. (1980) (dry weight)	Puget Sound	sole muscle	40-200
		crab muscle	10-50
		sole liver	up to 3700
		crab hepatopancreas	up to 1800
		whole worm	up to 370
		whole shrimp	up to 80
		whole clam	up to 130
Laska et al. (1976) (dry weight)	Mississippi River (near industrial areas)	Sediments	0.7-231.2
Malins et al. (1980; 1982) (dry weight)	Puget Sound	Sediments	max. level of 1300 ppb

ND = not detectable

Table 4.4.2

Physical Properties of Chlorobenzenes

	chlorobenzene	1,2-dichloro-benzene	1,3-dichloro-benzene	1,4-dichloro-benzene	1,2,4-trichloro-benzene	1,2,4,5-tetrachloro-benzene	penta-chloro-benzene	hexachloro-benzene
Molecular weight	112.56	147.01	147.01	147.01	181.5	215.9	250.36	284.79
Melting Point (^{o}C)	-45	-17.0	-24.7	53.1	16.95			230
Boiling Point (^{o}C @ 760 torr)	132	180.5	173	174	213.5			322
Vapour Pressure (torr @ 25^{o}C)	-	1.5	2.28	-	0.42			1.09×10^{-5}
Solubility with Water (mg/L @ 25^{o}C)	-	145	123	79	30	6	0.135	0.006 0.035^{a}
log octanol/water partition coefficient	2.84	3.38	3.38	3.39	4.26	4.67	6.19^{a} 4.94^{b}	6.18 6.23^{a}

From:

Callahan and Slimak (1979)
[a] Kenaga and Goring (1980)
[b] Veith et al. (1980)

the production of chlorine gas by the electrolysis of sodium chloride. HCB has been used in agriculture as a fungicide, and commerical formulations frequently contain small amounts of other toxic compounds such as lindane (National Academy of Sciences, 1975).

The highest levels of HCB in sediments, fish livers and invertebrate from South and Central Puget Sound were found in Commencement Bay (Tacoma) where industrial activities may be responsible for such levels.

No information on HCB inputs to Puget Sound was found in the literature review.

4.4.5. Summary of Biogeochemical Fate Data in the Marine Environment

4.4.5.1 Bioaccumulation-Uptake and Depuration

Summary Statement: Few data for bioaccumulation of chlorinated benzenes by marine biota were found in the literature. Studies with freshwater biota showed that bioaccumulation is a significant fate process for tetra-, penta-, and hexachlorobenzenes. Accumulations of mono-, di-, and trichlorobenzenes are low and the compounds are rapidly eliminated.

Results of Individual Studies: Veith et al. (1980) determined bioconcentration factors from 60 to 89 for three isomers of dichlorobenzene in bluegill sunfish during a 14-day test. Kopperman et al. (1976) exposed fathead minnows (Pimephales promelas) to water from two waste treatment plants. Although they found tetra- and pentachlorobenzenes in all fish raised in the sewage effluent, di-and trichlorobenzene levels were either at or below detection limits.

Lu and Metcalf (1975) used a model aquatic ecosystem consisting of a 3-liter flask containing Daphnia, mosquito larvae, snails, mosquito fish, and green algae, to study the uptake of radiolabeled chlorobenzene. After 48 hours exposures to 0.01 and 0.1 ppm levels of chlorobenzene, all organisms were found to contain the tracer. Hydroxylation was the predominant detoxifying mechanism for all organisms with the exception of the green alga, Oedogonium cardiacum.

Macek et al. (1977) investigated the relative significance of aqueous and dietary uptake of 1,2,4-trichlorobenzene using the water flea, Daphnia magna, as a food source for the bluegill sunfish, Lepomis macrochirus. Sunfish were subjected to one of three experiments with 1,2,4-trichlorobenzene: 3.0 µg/L in ambient water; fed D. magna which had been allowed to accumulate trichlorobenzene to equilibrium levels; or, both of the above. D. magna exposed to 3 µg/L in water accumulated up to 0.44 mg/kg in tissues. L. macrochirus accumulated to 0.53 mg/kg from water alone, 0.03 mg/kg from food alone, and 0.57 mg/kg from water and food. Thus, the authors concluded that the dietary contribution was insignificant.

Similar results were shown by Zitko (1977) in a freshwater study on juvenile Atlantic salmon (Salmo salar). Amounts adsorbed from water and from food were in the proportion 82.6%/17.4% indicating the importance of the water medium to bioaccumulation of HCB. Zitko (1977) reported an accumulation coefficient for HCB of 753 by salmon.

This literature survey found that bioconcentration factors of up to 44,000 have been reported for various organisms (Metcalf et al., 1972; Lu and Metcalf, 1975; Isensee et al., 1976; Branson et al., 1977; Laseter et al., 1976). Kenaga and Goring (1980) evaluated the relative bioconcentration factors of chlorinated benzenes in flowing water tests and their results are shown in Table 4.4.3.

Table 4.4.3
Bioconcentration Factors for Various Chlorinated Benzenes

Chemical	Octanol-Water Partition Coefficient	Bioconcentration Factor (flowing water)
Chlorobenzene	690	12
p-dichlorobenzene	2,450	215
1,2,4-trichlorobenzene	15,000	491
1,2,4,5-tetrachlorobenzene	47,000	4,500
Pentachlorobenzene	154,000	5,000
Hexachlorobenzene	168,000	8,600

The highest bioaccumulation value reported in the literature was 44,000, which was found by Laseter et al. (1976) for juvenile bass. In field experiments, Laseter et al. (1976) found that resident crayfish which were exposed to 44 ppb of HCB in natural waters had whole body levels of 1164 times this level. In another study in the same region (Laska et al., 1976) reported that whole body tissue extracts of mosquito fish contained HCB at levels 172 times the levels in ambient waters.

Depuration rates of bioaccumulated chlorinated benzenes are dependent upon the degree of substitution on the benzene ring. For example, Veith et al. (1980) showed that the half lives of dichlorobenzenes in tissue of bluegill sunfish were less than one day. Tetrachlorobenzene had a half life between 2 to 4 days and pentachlorobenzene had a half life greater than 7 days.

Parrish et al. (1974) reported that the estuarine species pinfish (Lagodon rhomboides), attained maximum residues of HCB in muscle which were 34,000 times greater than the measured concentration in water after 42 days exposure. The maximum HCB residue in liver was 47,000 times greater, and in the remainder of the fish, 56,000 times greater. Parrish et al. noted that HCB differed from many organochlorine compounds because the liver was the greatest site of accumulation for the compounds.

4.4.5.2 Metabolism

Summary Statement: Microbial biodegradation is not significant for any chlorinated benzenes. Large organisms are capable of biodegrading chlorinated benzenes to hydroxylated forms. Metabolism does not appear to be a significant fate process for chlorinated benzenes.

Results of Individual Studies: Ware and West (1977) noted that resistance to biodegradation generally increases as the degree of compound halogenation increases. Thus, the more highly chlorinated benzenes are less biodegradeable. Ware and West (1977) did demonstrate biodegradation of 1,2,4-trichlorobenzene under optimum conditions (e.g. activated sludge), but under environmental conditions biodegradation is expected to be slow.

Lu and Metcalf (1975) suggested that chlorobenzene is a persistent chemical which is not readily biodegraded unless the microorganisms present are already growing on another hydrocarbon source. Thom and Agg (1975) found 1,2- and 1,3-dichlorobenzene to be resistant to biodegradation. However, chlorobenzene was determined to be biodegradable by biological sewage treatment provided that suitable acclimatization could be achieved. Microbial biodegradation, therefore, is not a significant fate process for chlorinated benzenes.

As previously mentioned, Lu and Metcalf (1975) found that chlorobenzene was generally detoxified in aquatic organisms by hydroxylation. The model aquatic ecosystem studies of Metcalf et al. (1972) and Lu and Metcalf (1975) indicated that hexachiorobenzene was retained in biota primarily as hexachlorobenzene, but that pentachlorophenol was also produced and was excreted to the water. Stijve (1971) also reported pentachlorobenzene as a possible metabolite of hexachlorobenzene. Sanborn et al. (1977) showed that uptake and elimination of food containing 1 - 10 ppm HCB by the green sunfish, Lepomis cyanellus, resulted in the formation of pentachlorophenol as a metabolite.

Safe et al. (1979) also noted that chlorinated benzenes are metabolically degraded to hydroxylated and conjugated metabolites. These authors found that tetrachlorobenzene can form tetrachlorophenol in frogs and that, also in frogs, isomeric chlorobenzenes are metabolized to diverse phenolic products including some that are dechlorinated.

Pentachlorophenol is produced by rats and monkeys as a metabolite of HCB (Koss et al., 1977; Engst et al., 1976; Liu and Sweeney, 1975; Mehendale et al., 1975; Rozman et al., 1975). Koss and Koransky (1978) showed that half of the HCB taken up by rats was excreted in the form of metabolites, mainly pentachlorophenol, pentachlorotiophenol, and tetrachlorohydroquinone.

The metabolite, pentachlorophenol, is of potential concern whereby levels as low as 7 µg/L in waters have been shown to affect the development of larval stages of molluscs (Tagatz et al. 1977). In addition, pentachlorophenol appears to be widely dispersed in the Pacific Northwest (Vigers and Maynard, 1979). Because the compound is manufactured and used in the Puget Sound Basin, it may be difficult to estimate the amounts of pentachlorophenol in the environment which are a result of the metabolism of HCB.

4.4.5.3 Sorption and Sedimentation

Summary Statement: Theoretically sorption of chlorinated benzenes would increase with increasing levels of chlorination. The literature had little information on this subject, and no data were found for adsorption-desorption of chlorophenols in the marine environment.

Results of Individual Studies: The partition coefficients for the various chlorinated benzenes indicate moderate partitioning of mono-, di-, and trichlorobenzenes to sediments and strong partitioning of tetra-, penta-, and hexachlorobenzenes to sediments.

Only one soil adsorption coefficient was found for chlorinated benzenes, a value of 3,914 for hexachlorobenzene (concentration soil/concentration water) (Kenaga and Goring, 1980). Laseter et al. (1976) found that one day exposure to a regular flow of water with 8.3 µg/L HCB, concentrated HCB in soil to a level of 332 µg/kg resulting in a concentration factor of 40 times. After 4 days exposure, a level of 269 µg/kg was determined. Depuration of the sediment for 4 days in clean water showed that HCB concentrations did not decrease. Laska et al. (1976) reported dry weight levels of 107 and 135 µg/kg in sediments of the Mississippi River in areas of industrial contamination. HCB levels in water above the two sediment samples were 0.7 µg/L and 2.2 µg/L, respectively. No efforts were made to determine the organic content of the sediments, which would have aided in the evaluation of adsorption characteristics.

No data were found in the literature for adsorption-desorption of hexachlorobenzene from marine sediments.

4.4.5.4 Photolysis

The photolysis of chlorinated benzenes by sunlight is very low, but it is possible that the process could be enhanced by naturally occurring organic compounds (such as humic acids) acting as photosensitizers (Plimmer and Klingebiel, 1976).

In view of the tendency of the chlorinated benzenes to adsorb to suspended solids, it is not expected that they will be appreciably subjected to photolysis and photolysis is probably not a significant fate process.

4.4.5.5 Volatilization

Summary Statement: Volatilization of mono, di, and trichlorobenzenes may be an important fate process. Tetra-, penta-, and hexachlorobenzenes are not volatile due to their low vapor pressures and their high affinity to adsorb to solids.

Results of Individual Studies: The available data indicate that 1,2-dichlorobenzene is probably rapidly volatilized from the water column to the atmosphere. Garrison and Hall (1972) found that the following chlorobenzene concentrations were almost completely volatilized from aerated distilled water in 4 hours and from unaerated distilled water within 3 days: 100 mg/L 1,2-dichlorobenzene; 300 mg/L 1,4-dichlorobenzene; 300 mg/L chlorobenzene; and 100 mg/L 1,2,4-trichlorobenzene. However, these authors also found that when suspended solids (with high organic content) were added to the distilled water, the partitioning of these chlorobenzenes between water and suspended solids greatly reduced the rate of volatilization.

Evaporation rates would decrease with increasing chlorination. For example, Branson (1978) calculated the rates of evaporation at 25°C for several compounds from a hypothetical pond 1 m deep. Half lives of 6.03, 29.7, and 73.9 hours were calculated for chlorobenzene, HCB and DDT, respectively.

Volatilization of tetra, penta- and hexa- chlorobenzenes is probably insignificant due to the low vapor pressures of the compounds and their high affinity for suspended solids. Volatilization of the mono-, di-, and trichlorobenzenes may be an important fate process.

Chlorobenzenes may also be associated with surface microlayers and hence volatilization may be enhanced. However, the role of the surface microlayer in Puget Sound as a concentration medium for contaminants has not been assessed as of this writing.

4.4.5.6 Chemical Degradation

Chlorinated benzenes are very resistant to oxidation and hydrolysis (Fieser and Fieser, 1956; Patai, 1973; Leoni and D'Arca, 1976), and such processes are not expected to affect the fate of chlorinated benzenes significantly in Puget Sound.

4.4.6 Conclusions

1. Tetra-, penta-, and hexachlorobenzene in Puget Sound are expected to associate and persist in sediments and biota.

2. The degree of association of mono-, di-, and trichlorobenzenes with sediment and their accumulation by biota would be moderate. Volatilization is probably an important fate process for these compounds.

3. Data on the fate of chlorinated benzenes in the marine environment are minimal.

4. Low levels of hexachlorobenzene (i.e., 25 µg/L) have been shown to result in histological effects to freshwater biota. No data were found for effects on marine biota.

5. The levels of hexachlorobenzene in biota from certain areas of Puget Sound exceed levels reported in biota from other areas of the world and are equivalent to levels reported in the vicinity of industrial areas of the Mississippi River.

6. Metabolism by microbes and large animals is not an important fate process for chlorinated benzenes.

4.4.7 Research Needs

There is a need for information in the following areas:

1. to determine HCB concentrations in waters of Puget Sound;

2. to determine the source of high HCB levels in Commencement Bay;

3. to determine the effects of high levels of HCB in sediments to biota, (i.e., determine possible levels of HCB and determine whether uptake from sediments by benthic organisms occurs); and

4. to determine the role of the surface microlayer in concentrating organic contaminants such as HCB in Puget Sound.

References

Amico, V., G. Impellizzeri, G. Oriente, M. Piatelli, S. Scinto, and C. Tringali. 1979. Levels of chlorinated hydrocarbons in marine animals from the Mediterranean Sea. Mar. Pollut. Bull. 10:282-284.

Branson, D.R. 1978. Predicting the fate of chemicals in the aquatic environment from laboratory data, pp. 55-70. In: Cairns, Dickson, Maki (eds.), Estimating the Hazard of Chemical Substances to Aquatic Life. ASTM-STP 657, Philadelphia, Pa.

Branson, D.R., W.B. Neely, and G.E. Blau. 1977. Predicting a bioconcentration potential of organic chemicals in fish from partition coefficients. In: G.P. Veith and D.E. Konasewich (eds.), Structure-Activity Correlations in Studies of Toxicity and Bioconcentration with Aquatic Organisms. Symp. Proceedings Great Lakes Research Advisory Board, International Joint Commission. pp. 99-118.

Callahan, M.A. and M.W. Slimak. 1979. Water-Related Environmental Fate of 129 Priority Pollutants. EPA 440/4-79-029 b.

Courtney, K.D. 1979. Hexachlorobenzene: A review. Environ. Res. 20:225-266.

Eganhouse, R.P. and J.A. Calder. 1976. The solubility of medium molecular weight aromatic hydrocarbons and the effects of hydrocarbons co-solutes and salinity. Geochim. Cosmochim. Acta. 40:550-561.

Engst, R.R., R.M. Macholz, and M. Kujawa. 1976. The metabolism of hexachlorobenzene in rats. Bull. Environ. Contamin. Toxicol. 16:248-252.

Environmental Protection Agency. 1975. Preliminary Assessment of Suspected Carcinogens in Drinking Water. EPA-560/4-75-003. Office of Toxic Substances, Washington, D.C. 33 pp.

Fieser, L.M. and M. Fieser. 1956. Organic Chemistry. 3rd Edition. D.C. Heath and Co., Boston. 1112 pp.

Garrison, A.W. and D.W. Hall. 1972. Organic pollutants from mills persistent in downstream waters. Am Dyest. Rep. 21-25.

Isensee, A.R., E.R. Holden, E.A. Woolson, and G.E. Jones. 1976. Soil persistence and aquatic bioaccumulation potential of hexachlorobenzene. J. Agric. Food Chem. 24:1210-1214.

Kenaga, E.E. and C.A.I. Goring. 1980. Relationship between water solubility, soil sorption, octanol-water partitioning and concentration of chemicals in biota. In: J.G. Eaton, P.R. Parrish, and A.C. Hendricks (eds.) Aquatic Toxicology Proceedings of the Third Annual Symposium on Aquatic Toxicology. ASTM, Philadelphia.

Kopperman, H.L., D.W. Juehl, and G.E. Glass. 1976. Chlorinated compounds found in waste-treatment effluents and their capacity to bioaccumulate. N.T.I.S. PB 265 310.

Koss, G. and W. Koransky. 1978. Pentachlorophenol in different species of vertebrates after administration of hexachlorobenzene and pentachlorobenzene. In: R. Rao (ed.), Pentachlorophenol: Chemistry, Pharmacology, and Environmental Toxicology. Plenum Press. pp. 131-146.

Koss, G., J.J.T.W.A. Strek, and C.A. Kan. 1977. Metabolites of hexachlorobenzene in the excreta of different animal species. Abstract presented at the International Conference on in vivo Aspects of Biotransformation and Toxicity of Industrial Environmental Xenobiotics. Sept. 13-15, 1977. Prague.

Laseter, J.L., C.K. Bartell, A.L. Laska, D.G. Holmquist, D.B. Condie, J.W. Brown, and R.L. Evans. 1976. An Ecological Study of Hexachlorobenzene. EPA 560/6-76-009. Office of Toxic Substances, Washington, D.C. 62 pp.

Laska, A.L., C.K. Bartell, and J.L. Laseter. 1976. Distribution of hexachlorobenzene and hexachlorobutadiene in water, soil, and selected aquatic organisms along the lower Mississippi River, Louisiana. Bull. Environ. Contam. Toxicol. 15:535-542.

Leoni, V. and S.U. D'Arca. 1976. Experimental data and critical review of the occurrence of hexachlorobenzene in the Italian environment. Sci. Total Environ. 5:253-272.

Liu, H. and G.D. Sweeney. 1975. Hepatic metabolism of hexachlorobenzene in rats. FEBS Letters 51:225-226

Lu, P. and R.L. Metcalf. 1975. Environmental fate and biodegradability of benzene derivatives as studied in a model aquatic ecosystem. Environ. Health Perspect. 10:269-284.

Macek, K.J., S.R. Petrocelli, and B.H. Sleight. 1977. Considerations in assessing the potential for, and significance of biomagnification of chemical residues in aquatic food chains. Presented at: ASTM 2nd Symposium on Aquatic Toxicology, Oct. 31 - Nov. 1, Cleveland, Ohio.

Malins, D.C., B.B. McCain, D.W. Brown, A.K. Sparks, and H.O. Hodgins. 1980. Chemical Contaminants and Biological Abnormalities in Central and Southern Puget Sound. NOAA Technical Memorandum OMPA-2. Office of Marine Pollution Assessment, Boulder, Colo., 295 pp.

Malins, D.C., B.B. McCain, D.W. Brown, A.K. Sparks, H.O. Hodgins, and S. Chan. 1982. Chemical Contaminants and Abnormalities in Fish and Invertebrates from Puget Sound. NOAA Technical Memorandum (in press). Office of Marine Pollution Assessment, Boulder, Colo.

Mehendale, H.W., M. Fields, and H.B. Matthews. 1975. Metabolism and effects of hexachlorobenzene on hepatic microsomal enzymes in the rat. J. Agric. Food Chem. 23:261-264.

Metcalf, R.L., I.P. Kapoor, P. Lu, C.K. Schutch, and P. Sherman. 1972. Model ecosystem studies on the environmental fate of six organochlorine pesticides. Environ. Health Perspect. 4:35-44.

National Academy of Sciences. 1975. Principles for Evaluating Chemicals in the Environment. National Academy of Sciences, Washington, D.C. 454 pp.

Neuhaus, J. 1973. Mercury and organochlorine pesticides in fish. Med. J. Aust. 1:107-110.

Parrish, P.R., G.H. Cook, and J.M. Patrick, Jr. 1974. Hexachlorobenzene: Effects on several estuarine animals. In: Proceedings of the 28th Annual Conference of the Southeastern Association of Game and Fish Commissioners.

Patai, S. 1973. The Chemistry of the Carbon-Halogen Bond: Part 2. John Wiley Interscience, New York. 1215 pp.

Plimmer, J.R. and U.I. Klingebiel. 1976. Photolysis of hexachlorobenzene. J. Agric. Food Chem. 24:721-723.

Rozman, K., W. Mueller, M. Iatropoulos, F. Coulston, and F. Korte. 1975. Ausscheidung, Koerpervertilung and metabolisierurng von hexachlorobenzol nach oraler einzeldosis in ratten und rhesusaffen. Chemosphere 5:289-298.

Safe, S., C. Wyndham, A. Crawford, and J. Kohli. 1979. Metabolism: detoxification or toxification. In: Proceedings of Second International Symposium on Aquatic Pollutants, September 26-28, 1977. Amsterdam. pp. 299-307.

Sanborn, J.R., W.F. Childers, and L.G. Hansen. 1977. Uptake and elimination of (14C) hexachlorobenzene (HCB) by the freen sunfish, Lepomis cyanellus Raf., after feeding contaminated food. J. Agric. Food Chem. 25:551-553.

Steinwandter, H. and H. Brune. 1977. Kein naturliches vorkommen von hexachlorobenzol in der Ekosphere. Chemosphere 213:77-80.

Stijve, T. 1971. Determination and occurrence of hexachlorobenzene residues. Mitt. Geb. Lenensmittedunters. Hyg. 62:404-414.

Tagatz, M.E., J.M. Ivey, J.C. Moore, and M. Tobia. 1977. Effects of pentachlorophenol on the development of estuarine communities. J. Toxicol. Environ. Health. 3:501-506.

Ten Berge, W.F. and M. Hillebrand. 1974. Organochlorine compounds in several marine organisms from the North Sea and the Dutch Wadden Sea. Netherlands J. Sea Res. 8:361-368.

Thom, N.S. and A.R. Agg. 1975. The breakdown of synthetic organic compounds in biological processes. Proc. Roy. Soc. Lond. B. 189:347-357.

Tulp, M. Th. M. and O. Hutzinger. 1978. Some thoughts on aqueous solubilities and partition coefficients of PCB, and the mathematical correlation between bioaccumulation and physico-chemical properties. Chemosphere 10:849-860.

Veith, G.D., K.J. Macek, S.R. Petrocelli, and J. Carroll. 1980. An evaluation of using partition coefficients and water solubility to estimate bioconcentration factors for organic chemicals in fish. In: J.G. Eaton, P.R. Parrish, and A.C. Hendricks (eds.), Aquatic Toxicology. Proceedings of the Third Anual Symposium on Aquatic Toxicology. ASTM, Philadelphia.

Vigers, G.A. and A. Maynard. 1979. Monitoring Environmental Contamination from Chlorophenol Contaminated Wastes Generated in the Wood Preservation Industry. EPS Program Report 79-24. 66 pp.

Ware, S.A. and W.L. West. 1977. Investigation of Selected Potential Environmental Contaminants: Halogenated Benzenes. EPA/560/2-77-004. U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, D.C. 283 pp.

Zitko, V. 1971. Polychlorinated biphenyls and organochlorine pesticides in some freshwater and marine fishes. Bull. Environ. Contam. Toxicol. 6:464-470.

Zitko, V. 1977. Uptake and excretion of chlorinated and brominated hydrocarbons by fish. Fisheries and Marine Service Technical Report No. 737. Fisheries and Environmental Sciences Resource Branch, St. Andrews, New Brunswick. 14 pp.

4.5 Chlorinated Butadienes

4.5.1 Introduction

Chlorinated butadienes (CBD) are used or formed as by-products in a number of industrial processes including the manufacture of hexachlorobenzene and trichloroethylene. Hexachlorobutadiene, shown in Figure 4.5.1, affects behavior and causes histological damage in aquatic life at very low concentrations and is a known animal carcinogen. Hexachlorobutadiene is one of the EPA's 129 Priority Pollutants. Data on toxicities of other chlorobutadienes are limited, but toxicity is proportional to the degree of chlorine substitution of butadiene. Each of the less chlorinated forms can have a number of isomers. Data on the toxicity and environmental fate of chlorinated butadienes, particularly those with five or fewer chlorines are minimal. Generally, data on the less chlorinated butadienes are restricted to the Russian literature.

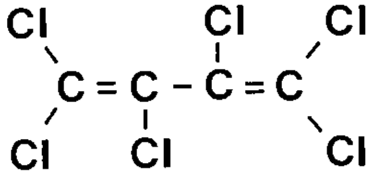


Figure 4.5.1
Structure of Hexachlorobutadiene

Chlorinated butadienes have been detected in all compartments of the Puget Sound ecosystem and are therefore chosen as compounds of concern.

4.5.2 Significance of Chlorinated Butadienes in Puget Sound

4.5.2.1 Review of Known Toxicity Data

There is currently no value for HCBD in the EPA (1978) Ambient Water Quality Criteria because of the lack of adequate toxicity data. Pearson and McConnell (1975) gave the following HCBD LC50's for marine organisms: dab (flat fish) (96 hours), 0.45 mg/L; barnacle nauplii (48 hours), 0.87 mg/L. Leeuwangh et al. (1975) found HCBD to be more toxic to some freshwater species. The Environmental Protection Agency (1978) compiled data which showed acute toxicity levels to freshwater organisms which varied from 90 to 210 µg/L.

Of greater concern are the chronic effects of chlorinated butadienes. Studies by Laseter et al. (1976) showed that respiration rates of bass and crayfish exposed to HCBD levels as low as 50 µg/L were affected. Levels of 5 µg/L had no effects. The same authors noted various other effects at low concentrations of HCBD:

a. bass exposed to 32.8 µg/L HCBD for 10 days showed histological damage to liver, kidney and gall bladder;

b. hepatopancreas of crayfish were affected upon exposure to HCBD levels as low as 3.7 µg/L in water;

c. low levels of HCBD (3.4 µg/L) elevated cortisol levels in bass;

d. exposure to 3 µg/L HCBD in water heightened the rate of mitosis in germination tips of hepatopancreas of crayfish.

Leeuwangh et al. (1975) reported that goldfish exposed to HCBD levels as low as 9.6 µg/L exhibited abnormal behavior, jumping, incoordination, and immobility (except for opercular movement). Furthermore, weight gain was affected and a specific influence on the regulation of enzyme synthesis was noted.

Experimental evidence from animal tests shows that HCBD is fetotoxic, neurotoxic, nephrotoxic, and carcinogenic (EPA, 1978). The National Institute for Occupational Safety and Health (NIOSH, 1979) and EPA (1978) provide the following data:

	LD50* mg/kg body weight Oral, Rat	Carcinogenic?
Hexa-CBD	90	Yes
2,3-dichloro -1,3-butadiene	422	Unknown
2-chloro -1,3-butadiene	1600	Suspected

* (exposure times not specified by NIOSH).

Since carcinogenicity is known or suspected for butadiene molecules with one to six chlorine atoms, it seems that molecules containing two to five chlorine atoms should be considered as potential carcinogens in the absence of data to the contrary. The LD50 data suggest that butadienes with three to five chlorine atoms would have systematic toxicity approaching that of HCBD.

4.5.2.2 Possible Effects of Levels Found in Puget Sound

Chlorinated butadienes have been identified in water, suspended matter, and biota in Puget Sound (Malins et al., 1980; Riley et al., 1980). Table 4.5.1 shows maximum sediment levels (ppb) noted for Puget Sound:

Table 4.5.1
Maximum Levels of Chlorinated Butadienes in
Puget Sound Sediments (µg/kg dry weight)*

	Hexa-CBD	Penta-CBD	Tetra-CBD	Tri-CBD
Elliott Bay	70	4	40	8
Commencement Bay	3300	2200	12,000	3900
Sinclair Inlet	10	10	50	20
Port Madison	0.3	0.4	2	0.5
Case Inlet	0.2	0.9	6	0.4
Budd Inlet	0.2	0.7	4	0.4

* Malins et al. (1980); Malins et al. (1982)

In Hylebos Waterway sediments at Tacoma, five isomeric forms of tri-CBD were found, five for tetra-CBD, one for penta-CBD and one for hexa-CBD. The highest concentrations in fish tissue were found in Commencement Bay (Hylebos) and reached the following maximum levels (ppb or µg/kg) in English sole livers:

	Hexa-CBD	Penta-CBD	Tetra-CBD	Tri-CBD
Hylebos	8600	410	220	10

In one set of experiments in Puget Sound, concentrations of HCBD in English sole muscle were 6-100 times less than concentrations in liver (Malins et al., 1980). Analyses for chlorinated butadienes in other biota showed that, in most cases, levels were nondetectable. However, positive values included 9 ppb (µg/kg) in clams from Commencement Bay Waterways, 60 ppb in clams from Hylebos Waterway, 200 ppb in shrimp from Hylebos Waterway and 70 ppb in crab hepatopancreas from Hylebos Waterway. Two samples of worms from Hylebos were found to have concentrations from 40 to 360 ppb.

HCBD levels up to 2.4 ng/L have been measured in waters from Blair and Hylebos Waterways (Riley et al., 1980). These levels were associated with up to 147.5 ppb (dry weight) HCBD in suspended matter; the suspended matter/water concentration ratios for HCBD were generally about four orders of magnitude. Distribution analyses showed that relative concentrations of HCBD between suspended matter and water varied from 0:100 to 70:30 (suspended matter:water).

The results of two distribution studies of chlorinated butadienes in other locations are presented for comparison purposes. Pearson and McConnell (1975) reported the results of analyses for chlorinated hydrocarbons in Liverpool Bay, and found sporadic distribution of HCBD. Average concentrations of HCBD in seawater were 4 ng/L with a maximum of 30 ng/L. Trace quantities of pentachlorobutadiene were reported. Sediment samples from the area contained HCBD levels up to 8 µg/kg (wet weight), with no correlation between water and sediment levels observed. Levels of HCBD in plankton from Liverpool Bay varied from nondetectable levels to 0.09 µg/kg. Most biota such as starfish, shrimp, and sea urchin had no detectable levels of HCBD, however, Mytilus edulis (mussels) from Liverpool Bay and Firth of Forth contained 3.2-3.8 µg/kg and 7 µg/kg HCBD, respectively. All analyses by Pearson and McConnell (1975) were reported on a wet weight basis. Of the few fish samples which contained HCBD, dab (Limanda limanda) from Liverpool Bay had 0.05-0.4 µg/kg in flesh and 0.3 to 2.0 µg/kg in liver. More frequent detections of HCBD were found in higher food chain organisms. For example, eggs from guillemot from the Irish Sea contained 1.6 to 9.9 µg/kg HCBD. Grey seal blubber had 0.4-3.6 µg/kg HCBD and one liver sample contained 0.8 µg/kg HCBD. The levels of HCBD in waters of Puget Sound are somewhat lower than those reported in Liverpool Bay which is surrounded by several major organochlorine plants. However, chlorinated butadienes are much more concentrated in sediments and biota of Puget Sound than they are in Liverpool Bay.

Laska et al. (1976) reported levels of HCBD within the industrialized area of the Mississippi River, between Baton Rouge and New Orleans. Levels of HCBD in water varied from 0.7 µg/L to 1.5 µg/L. Of seven sediment samples, two had detectable quantities of HCBD; 321.5 µg/kg and 21.6 µg/kg wet weight. Mosquitofish contained HCBD from 112.8 to 827.3 µg/kg (tissue - wet weight). No analyses for other chlorinated butadienes were reported.

The tri-, tetra-, and pentachlorobutadienes were generally detected at greater levels than HCBD in Puget Sound sediments. Considering that these lower chlorobutadienes would be more water soluble suggests that they may also be present in the water at much higher levels than HCBD.

The effects of chlorinated butadienes on Puget Sound biota are difficult to predict because of the lack of toxicity data. However, based on the studies of Laseter et al. (1976) and Leeuwangh et al. (1975) there is a possibility that histological and behavioral effects may occur, particularly in benthic species.

4.5.3 Physical Properties of Chlorinated Butadienes

Table 4.5.2 briefly reviews the known physical chemical properties of the chlorinated butadienes. The compounds have moderate bioaccumulation potential and on the basis of HCBD have low vapor pressure and water solubility.

Table 4.5.2

Review of Physical Chemical Properties of Chlorinated Butadienes [a]

	Hexa-CBD	Penta-CBD	1,2,3,4-Tetra-CBD	1,2,3-Tri-CBD
Molecular Weight	260.76	226.32	191.87	157.44
Vapor Pressure, 20°C, mm Hg	0.15			
Water solubility, 20°C, mg/l	2			
Log octanol/water partition coefficient	3.74	3.34 [b]	2.94 [b]	2.54 [b]
Melting point	-21°C			
Boiling point	215°C		188°C	
CAS Number	87-68-3			
Density	1.682(20°C)		1.516(15°C)	1.406(20°C)

[a] From Callahan and Slimak (1979)

[b] Calculated using method of Tute (1971)

4.5.4 Sources or Inputs

Hexachlorobutadiene is thought to be present in water as a significant by-product of production wastes from the manufacture of hexachlorobenzene (Laseter et al., 1976), tetrachloroethylene, trichloroethylene, and tetrachloromethane (EPA, 1975). It is used as a solvent for natural and synthetic rubber and other polymers, as a heat transfer liquid, transformer liquid and hydraulic fluid, and as a washing liquor for removing hydrocarbons (Verschueren, 1977).

The largest domestic users of HCBD are chlorine producers, which use it to recover chlorine from "snift" gas which is cleaned by passage through HCBD (EPA, 1978). It is known to be extensively used in Europe as a vineyard aphicide.

No information is available on sources of butadienes containing two to five chlorine atoms per molecule, although they may derive from the same sources as HCBD by-products. The compound 2-chloro-1,3-butadiene (Chloroprene) is used in the manufacture of the polymer Neoprene. The sources of the chlorinated butadienes in Puget Sound are uncertain, and will require identification.

4.5.5 Summary of Biogeochemical Fate Data in Marine Waters

4.5.5.1 Bioaccumulation - Uptake and Depuration

Summary Statement: Bioaccumulation factors up to 12,000 have been observed for hexachlorobutadiene in specific tissues of aquatic animals. Negligible uptake has been observed via contaminated food.

Review of Individual Studies: There does not appear to be a pattern of extensive bioaccumulation of HCBD in marine food chains (Pearson and McConnell, 1975). Confined uptake studies, such as laboratory or *in situ* studies in contaminated areas, have generally shown erratic bioconcentration factors. For example, Laseter et al. (1976) exposed crayfish in cages to waters and sediments contaminated with HCBD, and found that the bioconcentration factor varied from 7.8 to 300 among different test animals during the same time period. No explanations were suggested by the investigators.

The log P of chlorinated butadienes suggests moderate retention of the compounds by biota in the marine environment. Pearson and McConnell (1975) found that HCBD accumulated by factors of 7000 and 10,000 in livers of dab and plaice, respectively, after the fish were exposed to 1.6 µg/L HCBD over 39 days and 106 days, respectively. Negligible uptake was observed via contaminated food over a period of 88 days. The lack of bioaccumulation of HCBD via the food chain was also observed by Goldbach et al. (1976) and Leeuwangh et al. (1975).

Pearson and McConnell (1975) found that mussels exposed to 1.6 µg/L HCBD, bioconcentrated HCBD by factors of 900-2000 within a period of up to 50 days. The largest accumulation of HCBD occurred in the digestive gland and relatively less accumulation occurred in the foot of the mussel.

Laseter et al. (1976) showed that crayfish exposed to 2.97 µg/L HCBD concentrated the compound primarily in brain tissue (11,875 times) and the green gland (737 times). Concentration factors in hepatopancreas were 58; gills, 56; and muscle, 15. Bass exposed to 33 µg/L HCBD had highest concentrations of HCBD in its gut (1610 times) with lower concentrations in liver, kidney and brain. Laseter et al. (1976) also indicated that the green algae, Oedogonium cardiacum, concentrated HCBD by a factor of 160 after 7 days' exposure to 16.9 µg/L HCBD. It is uncertain if the lower concentrations of HCBD in liver of the test organisms was due to metabolism by the liver.

Caution is required in the interpretation of laboratory uptake studies with HCBD. Laska et al. (1976) for example, stated that one sample of commercial fish food used by laboratories to maintain fish stocks was contaminated with 88 ppb hexachlorobenzene and 60 ppb HCBD.

4.5.5.2 Metabolism

No experimental studies regarding biological metabolism of chlorinated butadienes were found in the literature.

4.5.5.3 Sorption and Sedimentation

Summary Statement: Sorption to suspended solids and sediments is an important fate process for chlorinated butadienes, and solids would therefore have the highest concentrations of the compounds of any compartment of the Puget Sound ecosystem.

Review of Individual Studies: Sediment concentrations of HCBD are generally several orders of magnitude higher than water concentrations (EPA, 1976; Leeuwangh et al., 1975). McConnell et al. (1975) noted that sediments rich in organic detritus adsorb much more chlorinated organics than do coarse gravels, although, particle size had no effect on the levels in sediments (Pearson and McConnell, 1975). Laseter et al. (1976) exposed sediments to 3.6 µg/L HCBD for 1 day and showed HCBD concentrations 201 times higher than concentrations in the water phase. After 4 days, levels of HCBD in sediments increased to 938 µg/kg. When the sediments were exposed to clean water, HCBD levels dropped to 632 µg/kg after 4 days.

Callahan and Slimak (1979) calculated a log P of 3.74 for HCBD using the procedures developed by Tute (1971). From these values, we estimated values of 3.34, 2.94, and 2.54 for penta-, tetra- and tri-CBD, respectively. As expected, lipophilicity increases with chlorine content, and the values indicate a tendency to associate with organic compartments even for tri-CBD. In fact, Pearson and McConnell (1975) described HCBD as being "tenaciously adsorbed" on sediment.

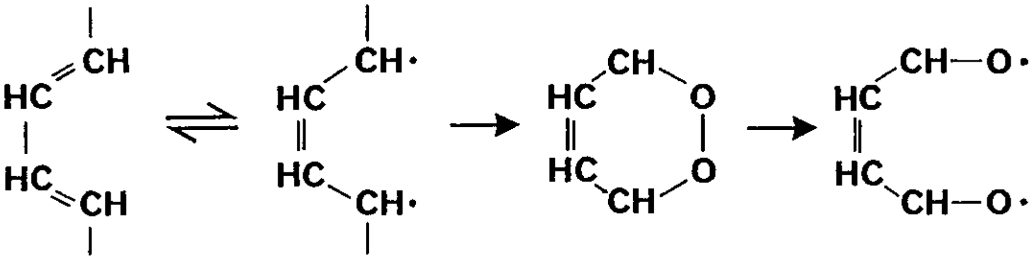
HCBD tends to be associated with Puget Sound suspended particles at concentrations about four orders of magnitude higher than the surrounding water (see Riley et al., 1980). This value indicates higher partitioning than observed in EPA (1976), Leeuwangh et al. (1975), or Laska et al. (1976). The reasons for this observation are uncertain; however, none of the studies in the literature correlated sorption with organic content of suspended solids.

4.5.5.4 Photolysis

Summary Statement: Chlorinated butadienes appear to be susceptible to cleavage and dimerization upon exposure to low wavelengths of light. Butadienes which are not adsorbed to solids and which are present near the water surface are probably photolyzed to other products.

Review of Individual Studies: HCBD in benzene solution is fairly rapidly photolyzed at a wavelength of 273 nm (EPA, 1976), which is a shorter wavelength than the window passed by atmospheric absorption processes. The effect of radiation at relevant wavelengths (290 nm) in aqueous media is not known, but it could produce slower photolysis. Pearson and McConnell (1975) reported that exposure of HCBD to xenon arc radiation filtered to remove wavelengths less than 290 nm resulted in a 95% conversion to hydrochloric acid. However, Laseter et al. (1976) indicated that irradiation of HCBD with ultraviolet light formed higher molecular weight products which were not identified. Data are lacking on photolysis of lower chlorinated forms; however, they are probably similarly susceptible to photolysis.

Conjugated dienes have been shown by Morrison and Boyd (1973) to undergo photo-initiated oxidation:



Initiation of a similar sequence involving photolytic cleavage of the relatively weak C-Cl bond (as is found in these chlorinated compounds) should occur even more readily. This sequence may form the higher molecular weight compounds reported by Laseter et al. (1976). It is not known whether the presence of dissolved oxygen would increase the rate of the removal process.

The photolysis process requires that the compound be present near the water surface for minimal attenuation of sunlight by the water column. The high tendencies to adsorb to suspended solids or sediment may remove the more highly chlorinated forms from these surface levels, and subsequently reduce the photolysis rates.

In the absence of adsorption to suspended solids, the chlorobutadienes may be photolyzed rapidly in the well-oxygenated waters that are common in Puget Sound.

4.5.5.5 Volatilization

Summary Statement: Volatilization appears to be an important fate process for HCBD, and the rate of volatilization will increase with decreasing numbers of substituted chlorines on the butadiene structure. Adsorption of the compounds to suspended solids will decrease the role of volatilization.

Review of Individual Studies: Pearson and McConnell (1975) determined a distilled water-air partition coefficient for HCBD of 0.97 at 20°C, indicating that HCBD is quite volatile. Theoretical half lives for volatilization for chlorinated butadienes as calculated by Dilling's (1977) procedure for water bodies with an average depth of one meter are 8.5 hours for hexachlorobutadiene and 3.0 hours for monochlorobutadiene. For means of comparison, the half life for volatilization of p, p'-DDT is more than 150 hours.

Volatilization may be a significant environmental process for HCBD. However, the adsorption of HCBD to suspended solids, as noted by Riley et al. (1980) may decrease the degree of volatilization for HCBD in Puget Sound.

4.5.5.6 Hydrolysis

The conjugated diene structure of butadiene molecules is generally quite stable and the presence of high levels of chlorinated butadienes in Puget Sound sediments indicates persistence. Based on published hydrolysis rates of organic compounds (Mabey and Mill, 1978), unsaturation and incomplete halogenation both enhance the hydrolysis rate. Therefore tri-, tetra- and pentachlorobutadiene may undergo some degree of hydrolysis.

No studies were found in this survey on the hydrolysis of chlorinated butadienes.

4.5.7 Conclusions

1. There is a high probability of chronic effects in biota which are exposed to very low levels of HCBD.

2. The relatively high quantities of pentachlorobutadiene in Puget Sound appear to be unique in the literature. There have been no previous references to the existence of penta-CBD in the environment, except for quantities relative to HCBD.

3. The literature indicates that highly chlorinated butadienes should tend to concentrate in sediment (and tissue) compartments because of their moderate lipophilic properties. However, photolysis in aerated water may degrade the many chlorinated butadienes near the water surface where there is minimal attenuation of solar radiation.

4. As the degree of chlorination of butadienes decreases, their ability to volatilize will increase because of their higher vapor pressures and lower tendency to associate with organic matter. They are also more susceptible to chemical degradation.

5. Uptake data for chlorinated butadienes by aquatic biota is restricted to HCBD, and those data are generally erratic for unexplained reasons.

6. Studies with chlorinated butadienes have been minimal, and these studies did not appear to carefully consider variable parameters such as lipid levels in biota, organic content in sediments, etc.

4.5.8 Research Needs

1. Chronic toxicity studies on chlorobutadienes should be undertaken for Puget Sound marine species to determine the effects of chlorobutadiene in water, suspended particles, and sediment.

2. Biodegradation and bioaccumulation studies at different trophic levels in a marine system should be considered, including assessing the uptake of chlorinated butadienes from sediments and degradation within sediments.

3. The sources of the chlorobutadienes present in Puget Sound should be determined.

References

Callahan, M.A. and M.W. Slimak. 1979. Water-Related Environmental Fate of 129 Priority Pollutants. EPA 440/4-79-029 a,b.

Dilling, W.L. 1977. Interphase transfer processes. II. Evaporation rates of chloro methanes, ethanes, ethylenes, propanes and propylenes from dilute aqueous solutions. Comparisons with theoretical predictions. Environ. Sci. Technol. 11:405-409.

Environmental Protection Agency. 1975. Survey of Industrial Processing Data. Task I - Hexachlorobenzene and Hexachlorobutadiene Pollution from Chlorocarbon Processing. EPA 560/3-75/003.

Environmental Protection Agency. 1976. An Ecological Study of Hexachloro-Butadiene. EPA 560/6-76-010.

Environmental Protection Agency. 1978. Ambient Water Quality Criteria: Hexachlorobutadiene. NTIS (PB 292 435).

Goldbach, R.W., H. van Genderen, and P. Leeuwangh. 1976. Hexachlorobutadiene residues in aquatic fauna from surface water fed by the river Rhine. Sci. Total Environ. 6:31-30.

Laseter, J.L., C.K. Bartell, A.L. Laska, D.G. Holmquist, D.B. Condie, J.W. Brown, and R.L. Evans. 1976. An Ecological Study of Hexachloro-Butadiene (HCBD). EPA 560/6-76-010.

Laska, A.L., C.K. Bartell, and J.L. Laseter. 1976. Distribution of hexachlorobenzene and hexachlorobutadiene in water, soil and selected aquatic organisms along the lower Mississippi River, Louisiana. Bull. Environ. Contam. Toxicol. 15:535-542.

Leeuwangh, P., H.J. Bult, and L. Schneiders. 1975. Toxicity of hexachlorobutadiene in aquatic organisms. In: Sublethal Effects of Toxic Chemicals on Aquatic Animals. Proceedings Swedish-Netherlands Symposium, September 2-5. Elsevier Scientific Publishing Co., New York.

Mabey, W. and T. Mill. 1978. Critical review of hydrolysis of organic compounds in water under environmental conditions. J. Phys. Chem. Ref. Data 7:383-415.

Malins, D.C., B.B. McCain, D.W. Brown, A.K. Sparks, and H.O. Hodgins. 1980. Chemical Contaminants and Biological Abnormalities in Central and Southern Puget Sound. NOAA Technical Memorandum OMPA-2. Office of Marine Pollution Assessment, Boulder, Colo. 295 pp.

Malins, D.C., B.B. McCain, D.W. Brown, A.K. Sparks, H.O. Hodgins, and S. Chan. 1982. Chemical contaminants and abnormalities in fish and invertebrates from Puget Sound. NOAA Technical Memorandum (in press). Office of Marine Pollution Assessment, Boulder, Colo.

McConnell, G., D.M. Ferguson, and C. R. Pearson. 1975. Chlorinated hydrocarbons and the environment. Endeavour 34:13-18.

Morrison, R. T. and R. N. Boyd. 1973. Organic Chemistry, 3rd edition. Allyn and Bacon, Inc., Boston. 1258 pp.

National Institute for Occupational Safety and Health (NIOSH). 1979. Registry of Toxic Effects of Chemical Substances (RTECS).

Pearson, C.R. and G. McConnell. 1975. Chlorinated C^1 and C^2 hydrocarbons in the marine environment. Proc. Royal Soc. London B 189:305-332.

Riley, R.G., E.A. Crecelius, D.C. Mann, K.H. Abel, B.L. Thomas, and R.M. Bean. 1980. Quantitation of Pollutants in Suspended Matter from Puget Sound. NOAA Technical Memorandum ERL MESA-49, Marine Ecosystems Analysis Program, Environmental Research Laboratories, Boulder, Colo.

Tute, M.S. 1971. Principals and practice of Hansch analysis: a guide to structure -activity correlation for the medicinal chemist. Adv. Drug Res. 6:1-77.

Verschueren, K. 1977. Handbook of Environmental Data on Organic Chemicals. Van Nostrand/Reinhold Press, New York. 659 pp.

4.6 Chlorinated Ethylenes

4.6.1 Introduction

The compounds, 1,2-dichloroethylene, trichloroethylene, and tetrachloroethylene have been measured in Puget Sound waters in varying concentrations. In particular, the Hylebos Waterway contains the highest levels of the compounds. Although the concentrations are much lower than the recommended limits specified in the EPA (1978) Ambient Water Quality Criteria, chlorinated ethylenes are selected for this study to enable an assessment of the state of knowledge on environmental fate and the possible environmental impact of volatile organic compounds such as chlorinated ethylenes in Puget Sound.

4.6.2 Significance to Puget Sound

4.6.2.1 Review of Known Toxicity Data

The toxicity of chlorinated ethylenes was reviewed by EPA (1978) for the development of water quality criteria. No data were found for acute or chronic toxicity of 1,2-dichloroethylene to marine biota. For freshwater species, 1,2-dichloroethylene was less toxic than 1,1- dichloroethylene. The 96-hour LC50 values of 1,1-dichloroethylene to marine biota are very high. For example, the LC50 for mysid shrimp is 224,000 µg/L. For tetrachloroethylene the 96-hour LC50 for the same species is 10,200 µg/L. No chronic toxicity values for dichloroethylenes were found for saltwater species. There was no effect of 1,1 dichloroethylene on the alga, Skeletonema costatum, at levels as high as 712,000 ppb.

Chronic and acute toxicity data on tetrachloroethylene have been reported for the mysid shrimp. The 96-hour LC50 value was 10,200 µg/L and the chronic value was 448 µg/L. Algal species were much more resistant to tetrachloroethylene than the mysid shrimp. EC50 values varied from 10,500 µg/L for Phaeodactylum tricornutum and 504,000 µg/L for Skeletonema costatum. The EPA (1978) Ambient Water Quality Criteria suggest a 24-hour average of no more than 310 µg/L and a maximum level of 700 µg/L in marine waters.

Many of the concerns about the effects of dichloroethylenes on human health are based upon the results of occupational exposure studies which have indicated that 1,1-dichloroethylene and tetrachloroethylene are potential carcinogens. EPA risk assessments of the dichloroethylenes in the environment are based upon possible human exposure via consumption of fish and shellfish. For a 10^{-7} level of lifetime cancer risk to humans, the EPA (1978) Ambient Water Quality Criteria recommended levels of no more than 0.21 µg/L and 0.07 µg/L of dichloroethylene and tetrachloroethylene, respectively, in the water column. For maximum protection of human life, a concentration of "zero" was recommended. No information was found on the possible carcinogenic effects of chlorinated ethylenes on marine biota.

4.6.2.2 Possible Effects of Levels Found in Puget Sound

The levels of chlorinated ethylenes in water and suspended solids from the Hylebos Waterway are greater than any reported in other marine environments. For example, Su and Goldberg (1976) summarized known values of chlorinated ethylene concentrations in marine water, freshwater, and precipitation samples throughout the world. Trichloroethylene concentrations in various marine environments were: 8.6 ± 4.3 ng/L in the open ocean of the East Pacific; 3.3 ± 0.5-9.4 ± 7.2 ng/L near the Scripps Institute of Oceanography pier; 8.2 ± 2.0 ng/L in the northeast Atlantic, and 0.3 ng/L in Liverpool Bay. The concentration of trichloroethylene in the Hylebos Waterway varied from 800 to 3000 ng/L (Riley et al., 1980). Tetrachloroethylene levels were: 2.0 ± 0.94 ng/L in the open ocean of the East Pacific; 5.5 ± 1.2-10.4 ± 6.7 ng/L near the Scripps Institute of Oceanography pier; 0.48 ± 0.22 ng/L in the northeast Atlantic; and, 0.12 ng/L in Liverpool Bay. The concentrations of tetrachloroethylene in Hylebos Waterway varied from 300 ng/L to 400 ng/L.

No analysis for chlorinated ethylenes in Puget Sound sediments and biota were attempted, and it is difficult to assess the implications of the compounds in Puget Sound. As will be seen later in this section, chlorinated ethylenes should not persist at concentrations reported by Riley et al. (1980) unless appreciable discharges of the compounds are occurring. On the basis of existing knowledge it is difficult to predict the possible effects of the observed levels of chlorinated ethylenes on marine biota and the consumers of the resident biota.

4.6.3 Physical Properties of Chlorinated Ethylenes

The chlorinated ethylenes are quite soluble in water, of high vapor pressure and have relatively low partition coefficients. Table 4.6.1 outlines some of the major physical properties of the chlorinated ethylenes.

Table 4.6.1
General Physical Properties of Chlorinated Ethylenes*

Compound	MW	CAS Number	Solubility ppm	log P	Vapor Pressure torr
1,2-trans dichloroethane	96.94	540590	600	1.48	200
trichloroethylene	131.39	79016	1,100	2.29	57.9
tetrachloroethylene	165.83	127184	150-400	2.88	14

*Callahan and Slimak (1979)

4.6.4 Sources or Inputs

The EPA (1980) Treatability Manual lists effluents from the following industries as sources of chlorinated ethylenes: paint and ink formulators, textile mills, auto and other laundries, and iron and steel manufacturing.

The principal isomer of industrial dichloroethylene is 1,1-dichloroethylene. Its 1976 U.S. production was approximately 120,000 tonnes (metric tons). It is used in the production of polyvinylidene chloride copolymers which are in turn used in the packaging industry (i.e., Saran). The polymers are also used for interior coatings of ship tanks, railroad cars, and fuel storage tanks. No analyses for the 1,1-isomer in Puget Sound were undertaken. Trichloroethylene is primarily used as a vapor degreaser of metal parts in industrial metal fabrication plants. Other uses include decaffeinating of coffee, and as cleaning solvents for paints. Tetrachloroethylene is used primarily as a solvent in the dry cleaning industry and as a degreasing solvent in metal industries.

4.6.5 Summary of Biogeochemical Fate Data in the Marine Environment

The high concentrations of chlorinated ethylenes are confined to the Hylebos Waterway. Therefore, a general rather than a detailed review of some of the environmental fate studies with chlorinated ethylenes is presented.

4.6.5.1 Global Model of Su and Goldberg (1976)

Su and Goldberg (1976) considered the production and uses, chemical and physical properties, and environmental concentrations and fluxes of several halocarbons including trichloroethylene and tetrachloroethylene. The U.S. production of trichloroethylene and tetrachloroethylene in 1973 was 205×10^9 grams and 320×10^9 grams, respectively. World production in 1975 was estimated to be 10^{12} grams of each, respectively. These large production figures were considered by Su and Goldberg (1976) to provide a significant potential for environmental pollution. Most aerosol samples obtained throughout the world showed detectable levels of both tri- and tetrachloroethylene although wide variations of chlorinated ethylene levels were reported by different investigators. Su and Goldberg (1976), for example, found trichloroethylene levels in marine air of 2.7×10^{-9} ml/ml, and levels in continental air from 1.5 to 3.5×10^{-9} ml/ml. The values are approximately 1,000 times less than those reported by Murray and Riley (1973). However, each group of investigators reported concentrations in marine air and continental air which were similar, implying a broad distribution of the compounds within the troposphere. The differences were probably due to sampling and analytical procedures. Mass balance calculations of Su and Goldberg (1976) indicated that the world production of halogenated hydrocarbons would remain primarily in the atmosphere with no evidence for any substantial destruction of any of the hydrocarbons.

4.6.5.2 Lake Zurich Model

Distribution studies for tetrachloroethylene were carried out at Lake Zurich, Switzerland. The results were reported by Schwarzenbach et al. (1979) and by Giger et al. (1978). The predominant elimination mechanism for tetrachloroethylene was found to be mass transfer to the atmosphere. It was noted that mass transfer coefficients determined in the laboratory were not applicable to natural conditions in the studies of tetrachloroethylene because hydrodynamics (and possibly the surface organic microlayer) were very significant in the transfer of volatile chlorinated hydrocarbons from surface waters to the atmosphere. The authors suggested that the mass transfer rates of organic compounds can be calculated from corresponding rates measured for gases such as radon or oxygen.

Slight depletions of trichloroethylene and tetrachloroethylene were noticed at the lake surface relative to waters below 20 m and the role of fate processes other than volatilization were also considered. Schwarzenbach et al. (1979) noted low partitioning of tetrachloroethylene to activated sludge, silica, or peat moss. The partition coefficient values were 0.23, 0.01, and 1.0, respectively. These low values were confirmed in the actual environment whereby no tetrachloroethylene could be detected in surface sediments except within sediments close to the outfall of treatment plants. No estimates of direct or indirect photolysis were possible. Because the molar extinction coefficients of tetrachloroethylenes are small, the authors considered direct photolysis in water to be insignificant. Microbial degradation was not considered responsible because the compounds persist in biologically treated sewage and concentrations were maximal at depths of maximal microbial activity (Giger et al., 1978). Evaporation was therefore reaffirmed as the major fate process.

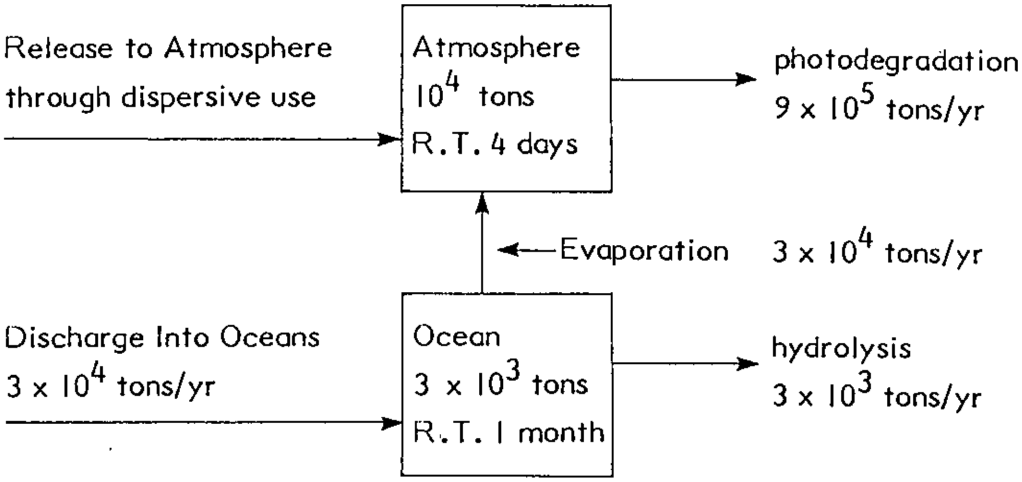
4.6.5.3 Assessment by the National Academy of Sciences

A review of the environmental fate of low-molecular-weight chlorinated hydrocarbons was prepared by the National Academy of Sciences (1975) Study Panel on Assessing Potential Ocean Pollutants.

The Panel indicated that in strongly mixed aqueous systems, half lives of low-molecular-weight chlorinated hydrocarbons due to volatility are in the order of minutes compared to half lives for biological degradation or hydrolysis which are in the order of days and months, respectively. The overall rate of loss across the air-sea interface is controlled by diffusion or mixing.

The Panel also reported results from Dow Chemical studies to evaluate evaporation rates for tri- and tetrachloroethylene. Evaporation half lives varied from 17 to 28 minutes for both compounds from freshwater, regardless of the presence of particulate matter such as clay and peat moss. A temperature decrease from 25°C to 1-2°C increased the half lives for both compounds to 37-42 minutes. The Dow Chemical studies also showed that exposure of tetra- and trichloroethylenes to sunlight decreased the half-lives of the compounds slightly. Bioaccumulation was considered to be an insignificant fate process. Factors of 10-40 have been measured or calculated for fish.

The Study Panel developed a global model to describe the overall fate of tetrachloroethylene in the environment. Assuming: a loss of 10% of total annual production; a mean concentration of 0.5 ng/L in the ocean surface layer; a mean residence time (R.T.) of 1 month in the ocean; and a time scale for degradation of 1 year, the model shown below was developed:



Under atmospheric conditions the chlorinated ethylenes would be photolyzed with half lives of the order of hours at high altitudes, versus days or longer at sea level. The major route for degradation of chlorinated ethylenes would be by photolysis in the atmosphere. The loss from oceans would be evaporation.

4.6.5.4. Studies of Distribution in Biota

Pearson and McConnell (1975) determined the levels of tri- and tetrachloroethylene within various trophic levels in the marine environment. Concentrations of trichloroethylene in tissues of fish liver, sea bird eggs, and sea seal blubber were approximately 100 times more than levels in water (i.e., 0.5 ppt water; 50 ppt tissues). Similar concentrations of tetrachloroethylene were also found. Separate experimentation by Pearson and McConnell (1975) indicated accumulation factors of less than 10 in flesh and more than 100 in liver of flatfish.

4.6.6 Conclusions

1. Several significant fate and distribution studies of chlorinated ethylenes have been reported in the literature and evaporation is the most important fate process.

2. The actual environmental impact of existing global levels appears to be minimal given the current knowledge about toxicity of the chlorinated ethylenes.

3. Based on EPA risk assessments in the EPA (1978) Ambient Water Quality Criteria, it could be suggested that the chlorinated ethylene levels in Hylebos Waterway exceed those levels which adequately protect human life and other consumers of Puget Sound biota.

4.6.7 Research Needs

1. The sources of chlorinated ethylenes in the Hylebos Waterway should be identified.

2. Chronic toxicity studies for marine biota should be conducted, especially for 1,2-dichloroethylene and trichloroethylene.

3. Levels of 1,1-dichloroethylene in the Hylebos Waterway should be assessed.

References

Callahan, M.A. and M.W. Slimak. 1979. Water-Related Environmental Fate of 129 Priority Pollutants. EPA 440/4-79-029.

Environmental Protection Agency. 1978. Ambient Water Quality Criteria-Tetrachloroethylene, NTIS (PB 292 445): Trichloroethylene, NTIS (PB 292-443).

Environmental Protection Agency. 1980. Treatability Manual. EPA 600/8-80-042.

Giger, W., E. Molnar-Kubica, and S. Wakeham. 1978. Volatile chlorinated hydrocarbons in ground and lake waters. In: O. Hutzinger, L.H. van Lelyveld and B.C.J. Zoetemann (eds.), Aquatic pollutants: Transformations and Biological Effects. Pergamon Press. pp. 101-123.

Murray, A.J. and J.P. Riley. 1973 . Occurrence of some aliphatic hydrocarbons in the environment. Nature 242:37-38

National Academy of Sciences. 1975. Assessing potential ocean pollutants. A Report of the Study Panel on assessing potential ocean pollutants to the Ocean Affairs Board, Commission on Natural Resources, National Research Council. ISBN 0-309-02325-4.

Pearson, C.R. and G. McConnell. 1975. Chlorinated C_1 and C_2 hydrocarbons in the marine environment. Proc. R. Soc. London B. 189: 305-332.

Riley, R.G., E.A. Crecelius, D.C. Mann, K.H. Abel, B.L. Thomas, and R.M. Bean. 1980. Quantitation of Pollutants in Suspended Matter and Water from Puget Sound. NOAA Technical Memorandum ERL MESA-49. Marine Ecosystems Analysis Program, Environmental Research Laboratories, Boulder, Colo. 99 pp.

Schwarzenbach, R.P., E. Molnar-Kubica, W. Giger, and S.G. Wakeham. 1979. Distribution residence time, and fluxes of tetrachloroethylene and 1, 4 dichlorobenzene in Lake Zurich, Switzerland. Environ. Sci. Technol. 13:1367-1373.

Su, C. and E.D. Goldberg. 1976. Environmental concentrations and fluxes of some halocarbons. pp. 353-374. In: H.L. Windom and R.A. Duce (eds.), "Marine Pollutant Transfer." D.C. Heath and Co. Lexington, Mass.

4.7 Phthalate Acid Esters

4.7.1 Introduction

Phthalate acid esters (PAEs) are used as plasticizers in the production of polyvinyl chloride. Over 5 x 10^8 kilograms of PAEs are manufactured annually in the United States. The high rate of production of PAEs and the detection of PAEs in the freshwater and marine environments has resulted in a significant amount of concern to environmental agencies. In particular, there is concern about the sublethal effects to aquatic biota at low PAE levels. In 1972 at a National Institute of Environmental Health Science symposium, scientists concluded that PAEs "do not appear to pose an imminent threat to human health" but that their apparent widespread distribution in the environment raised questions regarding the "possible subtle effects of persistent exposure" to those compounds (Marx, 1972). As a result phthalate acid esters have been classified within the EPA's 129 Priority Pollutants List.

PAEs are esters of benzene ortho dicarboxylic acid and can be characterized by the structure shown in Figure 4.7.1.

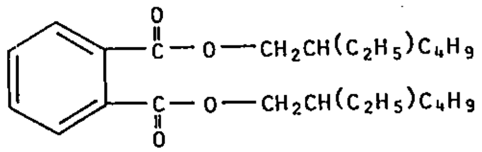


Figure 4.7.1
Structure of Bis or Di- (2-ethyl hexyl) Phthalate (DEHP)

Five different PAEs were reported within the sediment studies of Seattle METRO (1980). Diethyl hexyl phthalate (DEHP) was the most predominant PAE and it was detected at concentrations from 119 to 3219 ppb (μg/kg). There were no analyses of phthalate acid esters during the MESA Puget Sound Project, and phthalate acid esters were chosen as compounds of concern on the basis of the Seattle METRO data.

4.7.2 Significance to Puget Sound

4.7.2.1 Review of Known Toxicity Data

Phthalate acid esters have not been classified as carcinogens. However, Rubin (1979) recently published the results of in vitro mutagenic assays for various phthalate esters. Dimethyl and diethyl phthalates produced positive mutagenic responses which suggested the need for further evaluation of these compounds.

Acute toxicity values for PAEs imply that they are much less toxic than organochlorine compounds. For example, 96-hour LC50 values for sheepshead minnow were 445,000, 29,600, and 58,000 µg/L for butyl benzyl-, diethyl-, and dimethyl-phthalates, respectively. For the mysid shrimp 96-hour LC50 values were 9,630, 7,590, and 73,700 µg/L for butylbenzyl-, diethyl-, and dimethyl-phthalates, respectively.

Di-n-butyl phthalate was found by Wilson et al. (1978) to be the most toxic PAE to the marine dinoflagellate, Gymnodinium breve. EC50 ppm (µg/L) values were 0.0034-0.2 ppm for dibutyl phthalate, 3.0 - 6.1 ppm for diethyl phthalate and 54-96 ppm for dimethyl phthalate. DEHP showed no toxicity at 10% concentration.

Chronic long-term effects are, however, of greater concern. Chronic studies so far suggest that both DEHP and DBP (dibutyl phthalate) are biologically active at concentrations well below acutely toxic concentrations. McKim (1974) reported that growth of brook trout (Salvelinus fontinalis) was reduced significantly at a DBP concentration of 300 µg/L, but not at 90 µg/L.

Aquatic invertebrates appear to be more sensitive to PAEs than fish. Mayer and Sanders (1973) reported that reproduction in Daphnia magna was impaired by DBP and DEHP concentrations of 20 and 3-5 µg/L, respectively. The emergence of adult midges (Chironomus tentans) was reduced significantly at a DEHP concentration of 14 µg/L (Mayer and Rodgers, 1972).

The lower alkyl homologs appear to be more toxic; however, they are more susceptible to decomposition by bacteria and hydrolysis. Corcoran and Curry (1978) speculated that the toxicity of the group may be due to the hydrolysis product which was described as a toxic alcohol. Another concern is the possibility of phthalate-induced derangement of normal lipid metabolism in mammals (Bell and Nazir, 1976). It has been speculated that abnormal lipid metabolism may have a profound effect on oogenesis and other reproductive processes requiring rapid lipid synthesis and utilization.

4.7.2.2 Possible Effects of Levels Found in Puget Sound

There have been no analyses to determine whether PAE concentrations in Puget Sound waters approach the levels at which sublethal effects have been observed. The analyses are restricted to values reported by Seattle METRO (1979) for sediments from the vicinity of the Seattle Harbor. Measured di-n-octyl phthalate levels were 29-136.2 ppb (µg/kg); diethyl phthalates 4.1-62.1 ppb; dimethyl phthalate 1.4-12.6 ppb; di (2-ethyl hexyl) phthalate (DEHP) 119-1606 ppb; and butyl benzyl phthalate 4.0-246.7 ppb. The values are higher than those reported by

Giam et al. (1976) in sediments of the Gulf of Mexico. Their studies showed the mean levels in the Mississippi River Delta region were 116 ppb DEHP and 16 ppb DBP, while mean levels beyond the Delta dropped to 9 ppb DEHP and 3 ppb DBP. Levels in sediments of the Delta varied from 29 to 248 ppb DEHP and 5 to 52 ppb DBP. It has been suggested elsewhere that because of the low levels of PAE concentrations which result in chronic effects, the concentrations in bottom sediments may affect important bottom-dwelling macro- and micro fauna (International Joint Commission, 1977).

The higher levels of phthalate esters in sediments may have an impact on Puget Sound biota. For example, using soil-water partition coefficients determined by Gledhill et al., (1980) butyl benzyl phthalate concentrations as high as 4 µg/L may be present in interstitial waters in the presence of sediments containing 247 µg/kg of the compound. The level implies a minimal margin for elimination of chronic effects as described in Section 4.7.2.1.

4.7.3 Physical Properties of Phthalate Acid Esters

Individual phthalate acid esters vary considerably in solubility, vapor pressure, and partition coefficient. Each physical property is dependent upon molecular weight and upon the substituted alkyl or benzyl group. Table 4.7.1 outlines some of the significant physical properties of phthalate esters detected in Puget Sound.

Table 4.7.1
Physical Properties of Phthalate Esters*

Compound	MW	CAS Number	Solubility Water-25°C (ppm)	log P	Vapor Pressure (torr)
Dimethyl phthalate(DMP)	194	131113	4320	2.12	0.01(20°C)
Diethyl phthalate(DEP)	222	84662	896	3.22	0.05(70°C)
Di-n-butyl phthalate(DBP)	278	84742	13	5.2	0.1(115°C)
Butyl benzyl phthalate(BBP)	312	85687	2.9	4.8-5.8	8.6×10^{-6} (20°C)
Bis or Di-(2-ethyl hexyl) phthalate (DEHP)	391	117817	0.4	5.3-8.73	2×10^{-7} (20°C)

* Callahan and Slimak (1979)

4.7.4 Sources or Inputs

Phthalate esters have a variety of uses ranging from antifoam agents in the paper industry to perfume vehicles in cosmetic production. However, they are mainly used as plasticizers in the production of polyvinyl chloride. Within some plastic formulations, PAEs can comprise up to 60% of the total weight of plastic depending upon the degree of flexibility or workability required. The market for PAEs is, therefore, extremely diversified, and PAEs are used in the automobile, construction, clothing, home furnishings, medical, and packaging industries. Contamination of the environment by PAEs may occur by discharge of effluents from such industries, by incineration of plastics, or by leaching of PAE containing materials from land disposal sites (Giam et al., 1978(b); Johnson et al., 1977). As a result, there are many potential sources of PAEs in the Puget Sound area. It is probable that high levels of PAEs would be found in other areas of the Sound, such as the Hylebos Waterway.

4.7.5 Summary of Biogeochemical Fate Data in the Marine Environment

4.7.5.1 Bioaccumulation - Uptake and Depuration

Summary Statement: Bioaccumulation factors for phthalates such as DEHP are moderate. In waters free of phthalate esters, biota with bioaccumulated phthalate esters depurate the compounds rapidly.

Review of Individual Studies: In the marine environment, there have been few systematic studies of bioaccumulation of PAEs by biota. Giam et al. (1978a) attributed the lack of data to difficulties in analytical capabilities - some of which are due to contamination of dilution waters, reagents, and possibly equipment. Currently, many of the analytical problems have been recognized and apparently resolved, thus more data on accumulation levels of PAEs in the actual environment should be forthcoming.

One of the studies on PAE levels in marine biota was carried out by Giam et al. (1978a). DEHP levels were compared with levels of chlorinated hydrocarbons in organs and muscle tissues of biota from the Gulf of Mexico. In the Mississippi Delta area, for which sediment values were reported earlier in this section, starfish contained 135 ppb (µg/kg) DEHP compared to 1 ppb PCBs. Blue crab gills contained 20 ppb DEHP and 10 ppb PCBs. The relative concentrations of DEHP and PCBs in blue crab muscle were essentially reversed in that 3 ppb DEHP and 20 ppb PCBs were found. Spade fish had 20 ppb DEHP in muscle and 4 ppb in liver. PCB concentrations were higher in the liver (670 ppb) than in the muscle (35 ppb).

The mean levels of DEHP in the sediments of the region were 116 µg/kg and 63 ng/L in the waters (Giam et al., 1976). In all cases, PCB levels in sediments and waters were lower than DEHP levels. The PCB concentrations in biota were, however, higher than DEHP concentrations indicating a relatively lower bioaccumulation factor and/or rapid metabolism of the DEHP. The spade fish, for example, bioconcentrated DEHP approximately 300 times more than the water level (level tissue/level water = 20,000/63). This is much less than a 15,000 bioaccumulation factor observed for PCB.

All kinetic uptake studies of phthalate esters, found during this literature review, have used freshwater aquatic test organisms. Sanders et al. (1973) showed that ^{14}C-labeled DEHP was uptaken rapidly and bioaccumulation factors for six invertebrate species (including midge larvae, waterflea, scud, mayfly, grass shrimp and damsel fly) varied from 1900 to 6500 after equilibrium was reached, generally within 7 days. Laughlin et al. (1978) cautioned that these results were obtained on the basis of ^{14}C incorporation and some of the radioactivity in the tissue may have been due to metabolites. Furthermore, in another publication by the same authors and for the same test species, much lower bioconcentration factors were reported (Mayer and Sanders, 1973). Accumulation studies were apparently dependent upon the concentration of PAEs in water. For example, DEHP was bioconcentrated within scud by a factor of 13,400 using a water concentration of 0.1 µg/L and by a factor of 270 using a water concentration of 62.8 µg/L.

Biological elimination of accumulated PAEs was found by Sanders et al. (1973) to be rapid. Scud exposed to 0.1 µg/L of ^{14}C-DEHP accumulated 5.4 mg/kg in 3 days. Residual radioactivity decreased rapidly during 4 days in phthalate-free water to 20% of the initial activity.

Rapid depuration rates were also determined within bluegills, by Gledhill et al. (1980) who observed a bioconcentration factor of 663 at equilibrium (21 days) for butylbenzyl phthalate, based on ^{14}C-uptake. The depuration half life was less than 2 days.

Compared to DDT and PCBs, the bioaccumulation of phthalate acid esters by freshwater biota is not a significant fate process. Residues of PAEs in fish and invertebrates have not been correlated with adverse biological effects (Johnson et al., 1977). Data for bioaccumulation of PAEs by marine biota are sparse. Giam et al. (1978a) found low levels of PAEs in biota from the northwestern Gulf of Mexico (outside of the Mississippi River Delta). Average biota levels were 5 ppb (ug/kg) DEHP.

4.7.5.2 Metabolism

Summary Statement: All reports on the environmental persistence of PAEs which were retrieved during this literature search indicate that metabolism occurs and biodegradation is an important process for the destruction of PAEs in the environment. Data on metabolic rates are variable and sometimes conflicting. The PAE levels in Puget Sound indicate that degradation in Puget Sound sediments is either slower than expected or that inputs are appreciable.

Review of Individual Studies: Engelhardt et al. (1975) found that microbial strains capable of degrading phthalate esters are abundantly present in the environment and that microbial degradation of PAEs occurs much easier than for "classical" persistent organochlorine compounds such as PCBs. Furthermore, Engelhardt et al.(1975) identified many of the pathways for degradation and found that all steps did not occur with equal ease. Of the steps shown in (Figure 4.7.2) the formation of mono esters and the degradation of phthalic acid are readily carried out by most organisms. Subsequent hydrolysis was more difficult.

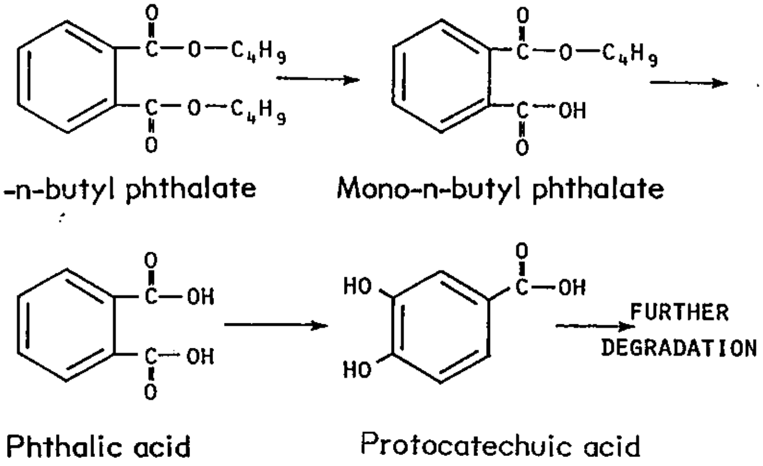


Figure 4.7.2
Bacterial Degradation of Di-n-butyl Phthalate

All bacterial organisms tested by Englehardt et al. (1975) were able to degrade other phthalate esters such as di-iso-butyl phthalate, di-n-octyl phthalate, and di(2-ethyl hexyl) phthalate. Dimethyl phthalate could function as a carbon source for only two of the bacterial populations used. Mixed populations of bacteria were suggested as the most effective means of microbial degradation.

Saeger and Tucker (1976) reported similar results in studies of biodegradation of five phthalic acid esters in river water and activated sludge samples. Rapid primary degradation was observed. Acclimated sludge degraded 70% of added DEHP within 24 hours, and 93% of added butyl benzyl phthalate during the same time frame. In river water, 5% of the butyl benzyl phthalate remained after 5 days and 40% of the DEHP was present after 5 weeks. Despite Saeger and Tucker's findings, the Lake Michigan Toxic Substances Committee Report (1974) found DEHP residues sludges from 54 treatment plants in concentrations from 17 to 884 µg/kg (dry weight). Johnson et al. (1977) suspected that these concentrations are a result of large quantities of PAEs in sewage, rather than the inability of organisms to degrade these PAEs.

Microbial degradation of PAEs will be significantly reduced under anaerobic conditions. For example, Johnson and Lulves (1975) found that 46% of ^{14}C-DBP was degraded to mono-n-butyl phthalate sediment samples incubated aerobically and after 5 days nearly 98% of the DBP disappeared. In the absence of oxygen, the degradation rate was reduced by a factor of six. Fourteen days were necessary for 50% of ^{14}C-DEHP to degrade in aerobic sediments and no degradation of DEHP occurred after 30 days anaerobic incubation.

Degradation of PAEs will also occur in aquatic biota such as plankton, clams, and snails; however, the degradation rate is very slow. Metcalf et al. (1973) found that 95% or more of DEHP in snail, clam, Daphnia and Elodea remained as DEHP after 48 hours. However, guppies had within 48 hours converted all but 37% of the DEHP to polar metabolites, phthalic acid, phthalic anhydride, and one additional unidentified compound. These results differ from those of Sanborn et al. (1975), who indicated that of the DEHP accumulated by the water flea, Daphnia, only 2% was present as the unmetabolized ester. This degree of metabolism was suspected by Laughlin et al. (1978) to occur in larvae of the grass shrimp, Palaemonetes pugio.

Data on marine bacterial degradation or metabolism by marine organisms of PAEs are restricted to data obtained by Giam et al. (1978a) who found low levels of phthalates in biota in the Gulf of Mexico despite elevated levels of phthalates in water and sediments. This observation was attributed to rapid metabolism by the organisms. Also, concentrations in liver were lower relative to muscle levels indicating the presence of metabolic degradation of PAEs.

The distribution of PAEs in waters of the Gulf of Mexico differed significantly from DDT and PCBs (Giam et al., 1978a). For example, coastal waters had generally higher levels of DEHP and DBP than waters at the mouth of the Mississippi River. The authors suggested this difference may be due to: other pollution sources such as ocean dumping or atmospheric transport; more enriched bacterial populations and nutrient levels within the Mississippi River estuary; and/or the reduced ability of marine bacteria to degrade PAEs. The mean concentrations in the coastal region were 112 ng DEHP/L and 87 ng DBP/L. In the lower Mississippi, levels were 63 ng DEHP/L and 14 ng DBP/L. Levels in sediments were much lower in areas beyond the river delta. Corcoran and Curry (1978) observed that concentrations of all esters found in surface sediments decrease rapidly with depth, disappearing within the first 0.5 m of sediment. This observation was attributed by the investigators to degradation by anaerobic bacteria and hydrolysis of the ester linkage. This conclusion differs from the conclusions of Johnson and Lulves (1975) described previously, which indicated that anaerobic decomposition of phthalate esters did not occur.

Hattori et al. (1975) reported that 25 mg/L concentrations of DBP, DMP, and DEP were completely decomposed in seawater within 4-10 days. DEHP was only partially decomposed after 2 weeks.

The high PAE levels noted in sediments of the Seattle Harbor suggest that biodegradation in Puget Sound sediments is very slow and/or that discharge levels from wastewater treatment plants (both municipal and industrial) are significant. Phthalate ester levels in West Point effluents have been found to vary from 10 to 20 ppb (µg/L) DEHP, 1 to 5 ppb DBP, 1 to 8 ppb DEP, and 0.2 to 0.4 ppb butyl benzyl phthalate (Chapman et al., 1979); and it is uncertain whether the observed sediment levels could be attributed solely to the observed effluent levels.

4.7.5.3 Sorption and Sedimentation

Summary Statement: High molecular weight phthalate esters will associate with organic particulates in water. Other phthalate esters such as dimethyl phthalate will have minimal tendencies to adsorb the particulates.

Review of Individual Studies: The partition coefficients for various phthalate esters vary considerably as shown in Table 4.7.1, implying proportional variations in the ability of the phthalate esters to adsorb to organic fractions in sediments and suspended solids. For example, dimethyl phthalate with a log P of 2.12, will have less tendency to adsorb to sediment than DEHP which has a partition coefficient of 8.73. This relationship was confirmed by Corcoran and Curry (1978), who detected DEHP within sediments from the Gulf of Mexico, but no dibutyl phthalates could be detected.

DEHP and DBP have been shown to form complexes with fulvic acid, a fraction found in high organic particulates in water (Ogner and Schnitzer, 1970). Studies with butyl benzyl phthalate (BBP) have shown that BBP has a moderate potential to adsorb to sediment (Gledhill et al., 1980). A log n-octanol/water partition coefficient of $5.9 \pm 4.3 \times 10^4$ and soil-water partition coefficients from 68 to 350 were determined for BBP. Adsorption coefficients calculated from both the ratio of the mean and geometric mean sediment concentrations of BBP to water concentrations were 571 and 389, respectively.

Sedimentation thus appears to be a significant environmental fate process for phthalate esters such as di-n-butyl phthalate, butyl benzyl phthalate and bis (2-ethyl hexyl) phthalate (DEHP). Studies in the Lake Michigan Toxic Substances Committee Report (1974) found settleable solids with residues from 1 to 75 ppm (dry weight) of phthalate esters within tributaries, suggesting that PAEs may be adsorbed to particulate materials in streams and ultimately deposited in bottom sediments.

4.7.5.4 Photolysis

Photolysis does not appear to affect the persistence of phthalate esters in the environment. Gledhill et al. (1980) exposed samples of butyl benzyl phthalate (BBP) in quartz tubes to sunlight for a period of one month. No measurable decrease in BBP was observed. No other studies of the effect of light on phthalate esters were found in the literature.

4.7.5.5 Volatilization

The vapor pressures of phthalate esters at 20°C vary from 0.01 torr (dimethyl phthalate) to 2×10^{-7} torr for DEHP. Using Neely's (1976) suggested calculations, the volatilization half lives of phthalate esters at 25°C in a pond 1 m deep would vary from 3140 hours for dimethyl phthalate to 132,600 hours for DEHP. Volatilization half lives for PCB and DDT calculated by Neely (1976) were 46 and 73.9 hours, respectively.

4.7.5.6 Hydrolysis

At normal environmental pH levels, the hydrolysis of phthalate esters is expected to be minimal. Gledhill et al. (1980) indicated that hydrolysis is not a major degradation pathway for butyl benzyl phthalate. Callahan and Slimak (1979) calculated the hydrolysis half lives of various phthalate esters at pH 7. The hydrolysis half life for dimethyl phthalate was 3.2 years; diethyl phthalate, 18.3 years; di-n-butyl phthalate, 10 years; and bis (2-ethyl hexyl) phthalate, 2000 years.

On the basis of these calculations, volatilization should not be an important fate process for phthalate esters. Nevertheless, detectable quantities were reported in air samples over the Gulf of Mexico. Giam et al. (1976) reported DEHP levels of 0.4 ng/m^3 and 0.3 ng/m^3 for DBP compared to 0.4 ng/m^3 for PCBs and 0.04 ng/m^3 for t-DDT.

4.7.6 Overall Biogeochemical Fate Studies

Several integrated assessments of the possible fate and effects of phthalate esters have been reported in the literature, with variable conclusions on the implications of the compounds in the environment.

Gledhill et al. (1980) reported the results of an environmental safety assessment of butyl benzyl phthalate (BBP). Their results indicated that: BBP is relatively insoluble in water and will partition to suspended solids and sediment; partitioning from water to air is unlikely; biodegradation is the controlling rate process for the environmental degradation of BBP; and rates of photolysis and hydrolysis appear to be too slow to affect the environmental concentrations of BBP. On the basis of the above findings and on the basis of current environmental levels of BBP, Gledhill et al. (1980) concluded that "BBP under its present use and disposal patterns does not constitute a hazard to safety and well being of the aquatic environment."

At least three papers have been published by Giam et al. (1976, 1978(a), 1978(b)) on the concentrations and fluxes of phthalates in the Gulf of Mexico. One of their observations was that the distribution of concentrations of phthalates in the analyzed components of the marine environment appear to be quite different from those of the chlorinated hydrocarbons. DDT and PCBs were most concentrated in biota, and phthalates were more concentrated in sediment that biota samples. Giam et al. (1976) indicated that "since DEHP, DDTs and PCBs are hydrophobic compounds with a high affinity for surfaces, the concentration differences are probably due to dissimilar routes and rates of uptake, metabolism, and excretion rather than selectivity in sediment absorption" and that "the higher levels of PCBs than phthalates in biota but lower in water and sediment, and the lower levels of phthalates in liver than in muscle samples suggest that phthalates may be readily metabolized in open-ocean biota samples." One of the major concerns expressed by Giam et al. (1976) was that the input sources of phthalate esters to the Gulf of Mexico, which would relate to the calculated quantities within the Gulf, could not all be identified. The Mississippi River, which was assumed to be the major source of organic contaminants to the Gulf, only contributed 0.04 x 10^6 kg/yr of the calculated 0.2 x 10^6 kg/yr flux of DEHP to the Gulf. Similarly, calculations for dibutyl phthalate indicated a flux of 0.09 x 10^6 kg/yr with only 0.01 x

10^6 kg/yr contributed by the Mississippi River. Other possible sources include disposal sites of plastics and atmospheric transport. In a later publication, Giam et al. (1978b) indicated that the current use and disposal patterns of phthalates (as plastics) may be producing an environmental reservoir of phthalates which is being slowly leached and thus expressed the concern about the possibility of reproductive effects on the marine biota.

Studies on phthalate esters within the Gulf of Mexico were also carried out by Corcoran and Curry (1978). Of all the phthalate esters, DEHP was the most prevalent ester in water and sediment. Total concentrations of PAEs in river water decreased rapidly within the salt wedge resulting from the mixture of water from the Gulf of Mexico with the Mississippi River. Concentrations of PAEs in the sediment appeared to be independent of the distributions and the concentrations found in the overlying water. The major concern of Corcoran and Curry (1978) related to the actual hazard of PAEs to the marine environment and they suggested that the environment is being constantly exposed to a "yet unknown health hazard."

4.7.7 Conclusions

1. The concern for phthalate acid esters in the environment is a result of the high production of the compounds and their subsequent release into the environment. Considerable resources are being utilized to determine the magnitude of dispersion of the compounds within the environment. On the basis of the literature, there is conflicting evidence as to whether phthalate esters deserve the attention or perhaps the priority they are receiving.

2. The major concern appears to be the possible chronic effects of low concentrations of PAEs. In this instance, data are unfortunately minimal, especially for marine species. If more efforts could be placed to determine the chronic effects of PAEs on aquatic biota, more appropriate assessments could be made of the actual potential hazard, if any, that PAEs pose to the environment.

3. Very high concentrations of PAEs are required before acute toxic effects on aquatic biota are observed.

4. Natural mixed bacteria populations appear to be capable of degrading PAEs. Fish likewise appear to metabolize PAEs to seemingly non toxic metabolites.

5. Elimination of PAEs from biota appears to occur readily.

6. Another concern, illustrated in this review, is that relevant data are sometimes conflicting. For example, there appears to be a discrepancy in observations about anaerobic decomposition of PAEs. Significantly different bioconcentration factors are also reported.

4.7.8 Research Needs

1. Chronic studies to determine long-term effects of PAEs on the marine biota are necessary.
2. On the basis of the high PAE levels in the Seattle Harbor sediments, a limited surveillance program of PAE levels in bottom-dwelling biological species is recommended.
3. There is a need to evaluate the presence of PAEs elsewhere in Puget Sound, particularly in the Tacoma area.

References

Bell, F.P. and Nazir, D.J. 1976. Effect of dietary di-2-ethyl hexyl phthalate on lipid biosynthesis in selected tissues from the rat, in vitro. Lipids. 11:216.

Callahan, M.A. and M.W. Slimak. 1979. Water-Related Environmental Fate of 129 Priority Pollutants. Vol. II. EPA 440/4-79-0296.

Chapman, P.M., D. Moore, and G.A. Vigers. 1979. Toxicant literature review and evaluation of METRO'S experimental design. E.V.S. Consultants Ltd. report prepared for Municipality of Metropolitan Seattle.

Corcoran, E.F. and R.W. Curry. 1978. Phthalic acid esters in the marine environment. Rev. Biol. Trop. 26:125-133.

Engelhardt, G., P.R. Wallnofer, and O. Hutzinger. 1975. The microbial metabolism of di-n-butyl phthalate and related dialkyl phthalates. Bull. Environ. Contam. Toxicol. 13:342-347.

Giam, C.S., H.S. Chan, and G.S. Neff. 1976. Concentrations and fluxes of phthalates DDT, and PCBs to the Gulf of Mexico. In: H.L. Windom and R.A. Duce (eds.), Marine Pollutant Transfer, Lexington, Mass. D.C. Heath and Co. pp. 375-386.

Giam, C.S., H.S. Chan, and G.S. Neff. 1978(a). Phthalate ester plasticizers, DDT, DDE and polychlorinated biphenyls in biota from the Gulf of Mexico. Mar. Poll. Bull. 9:249-251.

Giam, C.S., H.S. Chan, G.S. Neff, and E.L. Atlas. 1978(b). Phthalate ester plasticizers: a new class of marine pollutant. Science 199:419-420.

Gledhill, W.E., R.G. Kaley, W.J. Adams, O. Hicks, P.R. Michael, V.W. Saeger, and G.A. LeBlanc. 1980. An environmental safety assessment of butyl benzyl phthalate. Environ. Sci. Technol. 14:301-305.

Hattori, Y., Y. Kuge and S. Nakagawa. 1975. Microbial decomposition of phthalate esters in environmental water. Cited in Chemical Abstracts 85:8304 3v.

International Joint Commission. 1977. New and Revised Great Lakes Water Quality Objectives. Vol. II.

Johnson, B.T., D.L. Stalling, J.W. Hogan, and R.A. Schoettger. 1977. Dynamics of phthalic acid esters in aquatic organisms. Adv. Environ. Sci. Technol. 8:283-300.

Johnson, B.T. and W. Lulves. 1975. Biodegradation of dibutyl phthalate and di-2-ethylhexyl phthalate in freshwater hydrosoil. J. Fish. Res. Board Can. 32:333-339.

Lake Michigan Toxic Substances Committee Report. 1974. U.S. Environmental Protection Agency, Chicago.

Laughlin, R.B., J.M. Neff, Y.C. Hrung, T.C. Goodwon and C.S. Giam. 1978. The effects of three phthalate esters on the larval development of grass shrimp Palaemonetes pugio. Water, Air, Soil Pollut. 9:323-336.

Marx, J.L. 1972. Phthalate acid esters: biological impact uncertain. Science 178:46-7.

Mayer, F.L., Jr. and C.A. Rodgers. 1972. Residue dynamics of di-2-(ethyl hexyl) phthalate in fathead minnows. U.S. Fish and Wildlife Service, Fish-Pesticide Research Laboratory, Columbia, Mo., Annual Progress Report 1972:24-25.

Mayer, F.L., Jr. and H.O. Sanders. 1973. Toxicity of phthalate esters in aquatic organisms. Environ. Health Perspectives 3:153.

McKim, J. 1974. Personal communication listed in IJC report to Governments on "New and Revised Great Lakes Water Quality Objectives".

Metcalf, R.L., G.M. Booth, C.K. Schuth, D.L. Hansen, and P.Y. Lu. 1973. Uptake and fate of di-2-ethylhexyl phthalate in aquatic organisms and in a model system. Environ. Health Perspectives 4: 27-34.

Neely, W.B. 1976. Predicting the flux of organics across the air/water interface. In: Proceedings of the 1976 National Conferences on Control of Hazardous Materials Spills. New Orleans, La.

Ogner, G. and M. Schnitzer. 1970. Humic substances: fulvic and dialkyl phthalate complexes and their role in pollution. Science 170:317-318.

Rubin, R.J. 1979. Ames mutagenic assay of a series of phthalate acid esters: positive response of the dimethyl and diethyl esters in TA100. Abstract. Soc. Toxicol. Annual Meeting, March 11, New Orleans.

Saeger, V.W. and E.S. Tucker. 1976. Biodegradation of phthalic esters in river water and activated sludge. Appl. and Environ. Microbiol. 31:29-34.

Sanborn, J.J., R.L. Metcalf, C.-C. Yu, and P.-Y. Lu. 1975. Plasticizers in the environment: fate of di-n-octyl phthalate (DOP) in two model ecosystems and uptake and metabolism of DOP by aquatic organisms. Arch. Environ. Contamin. Toxicol. 3:244-255.

Sanders, H.O., F.L. Mayer, Jr. and D.F. Walsh. 1973. Toxicity, residue dynamics, and reproductive effects of phthalate esters in aquatic invertebrates. Environ. Res. 6:84-90.

Seattle METRO. 1980. Unpublished data.

Taylor, B.F. 1975. Degradation of o-phthalic acid and some of its esters by marine bacter. Annual Meeting of American Soc. Microbiol. (Abstracts):212.

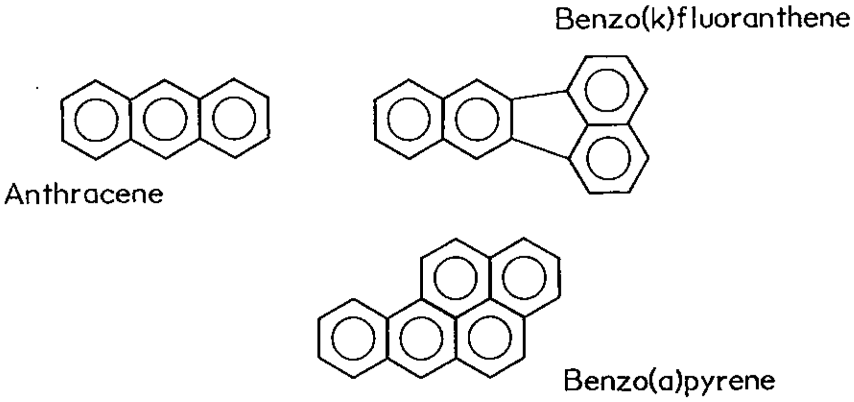
Wilson, W.B., C.S. Giam, T.E. Goodwin, A. Aldrich, V. Carpenter, and Y.C. Hrung. 1978. The toxicity of phthalates to the marine dinoflagellate <u>Gymnodinium breve</u>. Bull. Environ. Contam. Toxicol. 20:149-154.

4.8 Polyaromatic Hydrocarbons: General Description

4.8.1 Introduction

Referral to polyaromatic hydrocarbons (PAHs) implies compounds which consist of two or more fused benzene rings in linear, angular or cluster arrangements. Other terms commonly used for these compounds are "polycyclic hydrocarbons" or "polynuclear hydrocarbons."

The compounds are ubiquitous in nature. Youngblood and Blumer (1975) estimated that "in many ancient sediments and in fossil fuels we encounter thousands, if not hundreds of thousands of homologous and isomeric aromatics." As a result, oil discharges and burning of fossil fuels are some of the sources of polyaromatic hydrocarbon contaminants which have been found in the marine environment. For example, Hites et al. (1977) measured PAH levels in core samples from Buzzard's Bay, Massachusetts, and found that phenanthrene, fluoranthrene, and pyrene started to increase significantly in sediment layers indicative of the period 1850 to 1900. Combustion of coal and wood was assumed to be the major source of the compounds. The structures of some common PAHs are shown in Figure 4.8.1.


Benzo(k)fluoranthene

Anthracene

Benzo(a)pyrene

Figure 4.8.1
Structures of Common PAHs

There is appreciable concern about the distribution of polyaromatic hydrocarbons in the environment. Many are potent carcinogens. Of the EPA's 129 Priority Pollutants, 16 are polyaromatic hydrocarbons. The World Health Organization (1970) has recommended a limit of 0.2 ppb PAHs in drinking water. As a result, there have been considerable efforts recently to evaluate the fate and effects of PAHs in the environment. Many of these studies have simultaneously considered several PAHs. In particular, toxicity (and carcinogenicity) and uptake studies have attempted to correlate relationships of effects and uptake with structure.

This report, therefore, presents some general observations regarding the fate and effects of PAHs and subsequently, several PAHs will be considered individually.

4.8.2 Significance to Puget Sound

Polyaromatic hydrocarbons are found, in especially high concentrations, in sediments of Elliott and Commencement Bays. Approximate total PAH levels in Elliott Bay varied from 150 ppb (ug/kg) to 63,000 ppb. Concentrations of the identified carcinogens, benzo(a)pyrene and benzo(a)anthracene in sediments varied from 6 to 4,000 ppb, and from 10 to 8400 ppb, respectively. Sediments from Port Madison, Budd Inlet, Case Inlet, and Sinclair Inlet contained much lower concentrations of PAHs. Levels of PAHs in fish livers were often below detection limits; however, PAH levels in other biota such as crab, worms, shrimp, and clams were significant. Of the biota, clams generally contained the highest levels of PAHs. For the sake of comparison, the levels of PAHs found in Puget Sound biota are tabulated with a summary review provided by Pancirov and Brown (1977) of PAH levels in biota from other locations in North America (Table 4.8.1). Comparisons are difficult because contaminants are expressed inconsistently in terms of dry weight or wet weight. Assuming a dry weight concentration factor of 5, (Brown, 1980) it appears that the levels of PAHs in Puget Sound are much higher than levels reported by Pancirov and Brown (1977).

On the basis of the high concentrations of PAHs in biota and sediments of Puget Sound and on the basis of categorization of some as carcinogens, PAHs in general are considered to be contaminants of concern within Puget Sound. The fate and effects of all PAHs could not be reviewed within the scope of this study. Therefore, naphthalenes, benzo(a)anthracenes, fluoranthenes, and benzo(a)pyrene have been selected for individual review as representative PAHs. The following section provides some general comparisons of properties of various PAHs.

4.8.3 Physical Properties - Solubility and Partition Coefficients

Solubilities and partition coefficients of PAHs in freshwater and seawater are generally dependent upon molecular weight. Alkylation of a parent aromatic compound will decrease solubility and increase lipophilic properties. For example, Table 4.8.2 shows that the addition of two methyl groups decreased the solubility of naphthalene from 20 ppm (mg/L) to 2.4 ppm in seawater (Rossi and Neff, 1978). Addition of a third methyl group decreased the solubility to 1.7 ppm. Positions of the added groups may also affect solubility. Hollifield (1979) showed that 9 methyl benzo(a)anthracene was approximately three times more soluble than 10 methyl benzo(a)anthracene.

Table 4.8.1

Polyaromatic Hydrocarbons (ppb, μg/kg)[a]

Location of Sample	Marine Tissues	BaA	BaP	Pyrene	Methylpyrene	Other Individual PAHs
Long Island Sound	Oyster	8	2	58	11	2-15
Chincoteague, Va.						
Black Point	Oyster	0.1	0.2	0.5	0.1	0.5-0.7
Little Toms Cove	Clam	0.3	0.3	1.0	0.2	0.1-0.9
Darien, Conn., Scott's Cove	Clam	1	1	12	2.5	1.3
Fish Market, Linden, N.J.	Clam	1	1	3	1	0.5-3.0
Chesapeake Bay	Crab	1.5	0.5	0.2	0.2	0.3-1.2
Raritan Bay	Crab	2	3	6	1.6	1-2
	Menhaden	0.3	1.5	0.3	0.6	0.3-1.0
Atlantic Ocean						
Long Branch, N.J.	Flourider	1	2	1	0.6	1-2
South of Long Island (40°27',73°06'W)	Flounder	1	1	2	0.5	1
Falmouth, Mass.						
Little Sippewissett	Mussell	0.2	0.5	2	0.5	0.2-0.3
Wild Harbor	Mussell	0.6	0.5	4	1.5	0.5-1.2
Palacios, Tex.	Shrimp	0.2	1	0.3	0.3	0.3-1.0
Atlantic Ocean,25 mi. off Toms River, N.J. (39°57'N,73°35'W)	Codfish	2	1	0.5	2	0.5-5.0
Lake Muskinonge, Ont., Canada	Lake trout	0.5	1	0.3	0.6	0.5-1.5
Puget Sound[c]						
Elliott Bay	Crab	60	20	20		
	Shrimp	20-80	10	60-150		
	Clam	280-1000	100-230	510-980		
Commencement Bay	Crab	<20-90	5-10	40-70		
	Shrimp	50-120	<10-50	90-390		
	Clam	140-730	20-250	280-1300		

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[a] All values are expressed as wet weight, except for Puget Sound data.

[b] Includes chrysene, triphenylene, benzo(b)fluoranthene, benzo(e)pyrene, and benzo (g,h,i) perylene

[c] Analyses of crab used crab hepatopancreas

Table 4.8.2

Comparison of Some Physical Properties of PAHs

PAH	MW	Solubility [a] Seawater ppm	Solubility Freshwater ppm	log P
Naphthalene	128	20 ± 2(22)[c]	31.3[b]	3.3[c]
2-methyl naphthalene	142	(f)	(f)	4.1[c]
1,5-dimethyl naphthalene	156	2.4 ± 0.5	2.74[b]	4.9[e]
2,6-dimethyl naphthalene	156	(f)	1.30[b]	4.9[e]
Trimethyl naphthalene	170	1.7 ± 0.6	(f)	5.7[e]
Fluorene	116	0.8 ± 0.2	1.69-1.89[d]	4.2[d]
Phenanthrene	178	0.6 ± 0.1(.71)[b]	1.07	4.4[c]
Methyl phenanthrene	192	0.3 ± 0.1	(f)	5.2[e]
Fluoranthene	202	0.01 ± 0.06	0.26[d]	5.3[d]
Benzo(a)pyrene	252	(f)	0.0038[d]	6.0[d]
Dibenzanthracene	278	(f)	0.0005[d]	6.0[d]
Benzo(a)anthracene	228	(f)	0.044(g)	5.6[c]
9 methyl - benzo(a)anthracene	242	(f)	0.037(g)	6.4[e]
10 methyl - benzo(a)anthracene	242	(f)	0.011(g)	6.4[e]
9,10 dimehtyl - benzo(a)anthracene	256	(f)	0.055(g)	7.2[e]

[a] results of Rossi and Neff (1978)

[b] results of Eganhouse and Calder (1976)

[c] results of Southworth et al. (1978)

[d] Callahan and Slimak (1979)

[e] estimated

(f) no data available

(g) Hollifield (1979)

Eganhouse and Calder (1976) found that mixtures of hydrocarbons (i.e., tertiary and quaternary systems) may affect the solubilities of various PAHs. For example, naphthalene and phenanthrene enhance the solubility of acenaphthene. The presence of 2-methyl naphthalene and phenanthrene results in mutual reductions of solubilities. On the other hand, the solubility of naphthalene is essentially unaffected by the presence of other PAHs. Aromatic hydrocarbons are "salted out" by increasing concentrations of inorganic salts, as observed in Table 4.8.2 where solubilities in saltwater were lower than in freshwater systems. Such changes in equilibrium conditions will affect the eventual environmental fate of PAHs.

4.8.4 Toxicity

For the purpose of this study PAHs were evaluated in terms of both acute aquatic toxicity and carcinogenic properties. Although the toxicities of individual compounds are discussed later in the subsequent chapters, there are a few generalities regarding PAH toxicity which were found in the literature:

1. The degree of sensitivity of aquatic organisms to PAHs is appreciably affected by salinity. For example, Laughlin and Neff (1979) found that zoeae of the mud crab, Rhithropanopeus harrisii, had the highest mortality rates when exposed to phenanthrene and naphthalene at low salinities. The authors speculated that estuaries might be the most biologically sensitive areas to contamination by PAHs.

2. PAHs are metabolized by most biota. The degradation products (or metabolites) may have more impact on biota than the parent compounds. For example, Calder and Lader (1976) studied the effects of dissolved petroleum hydrocarbons on nonhydrocarbon degrading bacteria. Although growth rates and maximum cell density decreases were noted for all PAHs tested, the greatest toxic effects observed were due to a degradation product - dihydroxynaphthalene.

   Also, the carcinogenic properties of PAHs have been attributed primarily to metabolites of PAHs rather than the actual PAH molecules themselves (Co and Kwiram, 1979; Gibson, 1976). The initial oxidation products are arene oxides which due to their electrophilic character can bind to nucleophilic sites in cells. Arene oxides and subsequent oxygenated products bind to DNA and are powerful mutagens (Gibson, 1976). Examples of the products are shown in Figure 4.8.2. Malins (1980) described the work of Varanasi et al. (1980), who found that English sole can extensively metabolize benzo(a)pyrene to intermediates that interact with DNA. Such interactions are believed to initiate possible tumor formation.

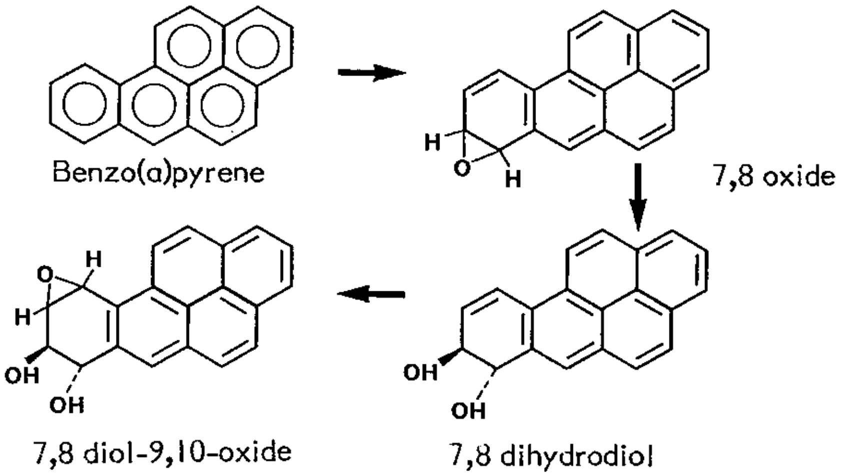


Figure 4.8.2
Metabolic Formation of Arene Oxides from Benzo(a)pyrene

3. In some instances, the toxicity of PAHs to aquatic organisms is directly proportional to molecular weight. For example, Rossi and Neff (1978) reported 96-hour TLm values for the polychaete, Neanthes arenaceodentata, exposed to 10 PAHs. For naphthalene, 2,6-dimethyl naphthalene, and 2,3,6-trimethyl naphthalene, the TLm values were 3.8, 2.6, and 2.0 ppm, respectively. Higher molecular weight compounds such as phenanthrene had lower 96-hour TLm values.

4.8.5 Metabolism

Microbes in water-sediment interfaces effectively degraded PAHs. However, the higher molecular weight PAHs were degraded more slowly (Lee, 1977). Different oxygenation mechanisms exist among various organisms. Bacteria apparently do have the potential to carry out ring cleavage and subsequently degradation to CO_2 (Lee, 1976). However, Gibson (1976) stated that for PAHs with more than three rings, microbial degradation is difficult and only oxidation may occur, i.e., formation of dihydrodiols as shown in Figure 4.8.3.

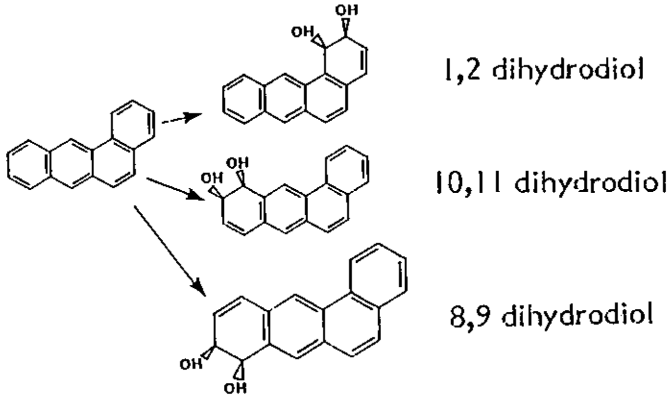


Figure 4.8.3
Microbial Degradation Products of Benzo(a)anthracene

The introduction of two hydroxyl groups into the aromatic nucleus is an essential requirement for subsequent fission of the benzene ring (Gibson, 1976).

The extent of microbial biodegradation will depend on several factors. Temperature will increase the rate considerably (Lee, 1977). Roubal and Atlas (1978) found that low levels of nutrients, such as after spring-summer algal blooms, could severely limit the degradation of petroleum hydrocarbons. Exposure to the sediment-water interfaces also can increase the rate of microbial degradation of PAHs. Roubal and Atlas (1978) found that microbial hydrocarbon utilizers are found in high concentrations in sediments. Activity by benthic animals also affected degradation rates by reworking of sediments so that hydrocarbons adsorbed to sediments would be more exposed to microbial action (Lee, 1976).

Within mammalian tissues, it has been well established that the metabolism of PAHs is accomplished by the microsomal enzyme complex of mixed function oxidases, termed aryl hydrocarbon hydroxylases. This enzyme complex, which is mainly found in the liver, is responsible for metabolic detoxification of PAHs and also has the capability for activation of PAHs to toxic and carcinogenic metabolites (Marquardt, 1977).

4.8.6 Uptake and Bioconcentration

Higher molecular weight PAHs are generally bioaccumulated to a greater extent by aquatic biota and are retained for longer periods of time. Equilibrium levels are reached more quickly with lighter molecular weight PAHs. For example, Roesijadi et al. (1978) found that the benthic deposit feeder Macoma inquinata concentrated phenanthrene from water by a factor of 10.3; chrysene by 694; dimethyl benzo(a)anthracene by 1349, and benzo(a)pyrene by 861. Phenanthrene levels in the bivalve rapidly reached equilibrium with the ambient levels in water, and benzo(a)pyrene levels in the bivalve still did not reach equilibrium with ambient levels in water after 60 days.

Southworth et al. (1978) observed similar trends for PAH bioconcentration within Daphnia pulex. After 24 hours, the following bioconcentration factors were observed: naphthalene, 134; phenanthrene, 325; anthracene, 917; 9-methyl anthracene, 4583; pyrene, 2702; benzo(a)anthracene, 10,409; and perylene, 2194. Uptake and elimination rate constants varied considerably with no discrete pattern. Naphthalene, however, had the lowest uptake rate and the highest elimination rate.

4.8.7 Sorption

Adsorption to sediments and suspended solids is an important fate process for higher molecular weight PAHs (Lee, 1977). Detrital particles, which are a mixture of organic matter, bacteria, and clay, have a high affinity for PAHs. Karickhoff et al. (1979) showed that sorption of PAHs to sediments was directly proportional to organic content of the sediments and the partition coefficients of the compounds. Some of the values of sediment partition coefficients (Kp sed/organic content) are as follows: naphthalene, 1.3×10^3; 2-methyl naphthalene, 8.5×10^3; anthracene, 2.6×10^4; 9 methyl anthracene, 6.5×10^4; and phenanthrene, 2.3×10^4. Within saline solutions, no adsorption of durene and acenaphthalene to a common clay, smectite, was observed after 48 hours exposure. Adsorptions of pyrene and anthracene were 19% and 46%, respectively (Meyers and Oas, 1978).

4.8.8 Volatilization

Southworth (1979) observed that volatilization of low molecular weight PAHs such as naphthalene may be substantial. Volatilization of higher molecular weight PAHs with more than four rings is probably insignificant. Volatilization half lives of benzo(a)anthracene and benzo(a)pyrene were calculated to be in excess of 100 hours.

Henry's Law constants (H) which are the ratio of molar concentration in air to molar concentration in water, decrease with increasing molecular weight. Some of the H values calculated by Southworth (1979) were: naphthalene, 2.26×10^{-2}; anthracene, 2.66×10^{-3}; phenanthrene, 2.24×10^{-3}; pyrene, 7.64×10^{-4}; benzo(a)anthracene, 3.28×10^{-4}; and, benzo(a)-pyrene, 1×10^{-4}.

4.8.9 Overall Fate

Lee et al. (1978) reported the distributions of various PAHs in water, zooplankton, oysters, and bottom sediments in controlled ecosystem enclosures which were located in Saanich Inlet, British Columbia. Microbial degradation and evaporation were found to be primary removal processes for lower molecular weight aromatics such as naphthalenes, anthracene and phenanthrene. Higher molecular weight PAHs such as chrysene, benzanthracenes, and benzopyrenes were affected primarily by sedimentation and photochemical oxidation.

Concentrations of the introduced PAHs in water in the enclosures decreased at an exponential rate. After 17 days, 39% of benzo(a)pyrene and benzo(a)anthracene was found in sediments. Only 11% or less of the low molecular weight PAHs were found within the sediments. Large quantities of the higher molecular weight compounds were also found adsorbed to suspended solids.

Rapid uptake and release of naphthalene was observed by oysters and zooplankton. Half lives of PAHs within exposed oysters, which were subsequently removed to clean waters, were: anthracene, 3 days; benzo(a)anthracene, 9 days; and benzo(a)pyrene, 18 days.

Lee et al. (1978) also found that phytoplankton blooms were found to remove PAHs from the water column rapidly.

4.8.10 Conclusions and Research Needs

PAHs have different chemical-physical, toxicological and biogeochemical properties, and it was necessary to review several PAHs in detail. The particular PAHs were chosen on the basis of their distribution and possible effects within Puget Sound.

Conclusions and research needs are, therefore, defined after discussion of each of the selected PAHs in Sections 4.9 to 4.12.

References

Brown, D. 1980. Personal Communication.

Calder, J.A. and J.H. Lader. 1976. Effect of dissolved aromatic hydrocarbons on the growth of marine bacteria in batch culture. Appl. Environ. Microbiol. 37:95-101.

Callahan, MA. and M.W. Slimak. 1979. Water-Related Environmental Fate of 129 Priority Pollutants. EPA 440/4-79-0296.

Co, T-T and A.L. Kwiram. 1979. Effect of methyl substituents on the triplet state properties of benz(a)anthracene. Photochem. Photobiol. 29:1021-1023.

Eganhouse, R.P. and J.A. Calder. 1976. The solubility of medium molecular weight aromatic hydrocarbons and the effects of hydrocarbon co-solutes and salinity. Geochim. Cosmochim. Acta. 40:555-561.

Gibson, D.T. 1976. Microbial degradation of carcinogenic hydrocarbons and related compounds. In: Proceedings of the Symposium on the Sources, Effects, and Sinks of Hydrocarbons in the Aquatic Environment, August 9-11. Washington, D.C.

Hites, R.A., R.E. LaFlame, and J.W. Farrington. 1977. Sedimentary polycyclic aromatic hydrocarbons. The historical record. Science 198:829-831.

Hollifield, H.C. 1979. Rapid nephelometric estimate of water solubility of highly insoluble organic compounds of environmental interest. Bull. Environ. Contam. Toxicol. 23:579-586.

Karickhoff, S.W., D.S. Brown, and T.A. Scott. 1979. Sorption of hydrophobic pollutants on natural sediments. Water Res. 13:241-248.

Laughlin, R.B., Jr. and J.M. Neff. 1979. Interactive effects of salinity, temperature and polycyclic aromatic hydrocarbons on the survival and development rate of larva of the mud crab Rhithropanopeus harrisii. Mar. Biol. 53:281-291.

Lee, R.F. 1976. Metabolism of petroleum hydrocarbons in marine sediments. In: Proceedings of the Symposium on Sources, Effects, and Sinks of Hydrocarbons in the Aquatic Environment, August 9-11. Washington, D.C.

Lee, R.F. 1977. Fate of petroleum components in estuarine waters of the Southeastern United States. In: Proceedings of the 1977 Oil Spill Conference. American Petroleum Institute, Washington, D.C. pp. 611-616.

Lee, R.F., W.F. Gardner, J.W. Anderson, J.W. Blaylock, and J. Barwell-Clarke. 1978. Fate of polycyclic aromatic hydrocarbons in controlled ecosystem enclosures. Environ. Sci. Technol. 123:832-838.

Malins, D.C. 1980. Pollution of the marine environment. Environ. Sci. Techol. 14:32-37.

Marquardt, H. 1977. Mutagenitaets - vorteste auf carcinogene wirkungen von umweltchemikalien. In: Recent Advances in the Assessment of the Health Effects of Environmental Pollution. III. Luxembourg: Commission of the European Communities. Directorate General Scientific and Technical Information and Information Management. pp. 1607-1611.

Meyers, P.A. and T.G. Oas. 1978. Comparisons of associations of different hydrocarbons with clay particles in simulated seawater. Environ. Sci. Technol. 12:934-937.

Pancirov, R.J. and R.A. Brown. 1977. Polynuclear aromatic hydrocarbons in marine tissues. Environ. Sci. Technol. 11:989-992.

Roesijadi, G., J.W. Anderson, and J.W. Baylock. 1978. Uptake of hydrocarbons from marine sediments contaminated with Prudhoe Bay oil: Influence of feeding type of test species and availability of polycyclic aromatic hydrocarbons. J. Fish. Res. Board Can. 35:608-614.

Rossi, S.S. and J.M. Neff. 1978. Toxicity of polynuclear aromatic hydrocarbons to the polychaete Neanthes arenoceodentata. Mar. Pollut. Bull. 9:220-223.

Roubal, G. and R.M. Atlas. 1978. Distribution of hydrocarbon-utilizing microorgaisms and hydrocarbon biodegradation potentials in Alaskan continental shelf areas. Appl. Environ. Microbiol. 35:897-905.

Southworth, G.R., J.J. Beauchamp, and P.K. Schmiedev. 1978. Bioaccumulation potential of polycyclic aromatic hydrocarbons in Daphnia pulex. Water Res. 12:973-977.

Southworth, G.R. 1979. The role of volatilization in removing polycyclic aromatic hydrocarbons from aquatic environments. Bull. Environ. Contamin. Toxicol. 21:507-514.

Varanasi, U., D. Gmur, and P. Treseler. 1980. In: Malins, D.C. 1980. Environ. Sci. Technol. 14:32-37.

World Health Organization. 1970. European Standards for Drinking Water, 2nd ed. Revised. Geneva.

Youngblood, W.W. and M. Blumer. 1975. Polycyclic aromatic hydrocarbons in the environment: Homologous series in soils and recent marine sediments. Geochim. Cosmochim. Acta. 39:1303-1304.

4.9 Naphthalene and Substituted Naphthalenes

4.9.1 Introduction

Naphthalene is the most abundant single constituent of coal tar. It is used as an intermediate in production of dye compounds and in the formulation of solvents, lubricants, and motor fuels. One of its principal uses is as a feedstock for synthesis of phthalate anhydride which is subsequently used for the manufacture of alkyd and polyester resins, dyes, pharmaceuticals and insecticides. In 1976, the U.S. production of naphthalene was 48,720 metric tons (EPA, 1978).

When crude and refined oils are mixed with water, naphthalene and methylated naphthalene are the major hydrocarbons detected in water (Lee, 1977). Analyses of four American Petroleum Institute reference oils (two crude and two refined) by Anderson et al. (1974a) showed the presence of 400 to 4000 ppm naphthalene. The analyses of water soluble fractions of crude and refined oils by Anderson et al. (1974a) showed that naphthalenes were the most prevalent soluble hydrocarbons. For example, following the mixing of 1.5 liters of Louisiana crude oil with 13.5 liters $20^{o}/oo$ seawater, the water column contained 120 ppb naphthalene, 60 ppb 1-methyl naphthalene, 50 ppb 2-methyl naphthalene, 60 ppb dimethyl naphthalenes and 8 ppb trimethyl naphthalenes. Mixing of Number 2 fuel oil with seawater resulted in a water layer with 840 ppb naphthalene, 340 ppb methyl naphthalene, 480 ppb 2-methyl naphthalene, and 240 ppb dimethyl naphthalene. The higher naphthalene levels in refined oils probably result in higher toxicity of the oils to aquatic biota (Anderson et al., 1974a).

Naphthalene and numerous substituted forms of naphthalene have been detected during the surveillance efforts of the MESA Puget Sound program. Naphthalene, seven methylated forms of naphthalene, ethyl naphthalenes and propyl naphthalenes have been quantified in sediments and biota of Puget Sound. In addition, phenyl naphthalene and binaphthalene have been identified but not quantified in certain sediment samples.

Naphthalene is one of the EPA's 129 Priority Pollutants. It is moderately toxic to aquatic biota. However, the alkylated forms of naphthalene and metabolites of naphthalene are much more toxic to aquatic biota. Naphthalene is currently being tested as a carcinogen. Naphthalene, its derivatives and its metabolites are, therefore, considered to be of concern to Puget Sound.

4.9.2 Significance to Puget Sound

4.9.2.1 Review of Known Toxicity Data

No criterion for naphthalene levels in either fresh or saltwater was specified within the EPA (1978) Ambient Water Quality Criteria, because of "minimal toxicity data."

Much of the data available in the literature assess the acute toxicity of naphthalene and various substituted naphthalenes. Ott et al. (1978) found that alkyl naphthalenes are one of the more toxic and persistent groups of hydrocarbons to marine life. For the estuarine copepod, *Eurytemora affinis*, the 24-hour LC50 values decreased with increasing methylation. The following LC50 values were reported: naphthalene, 3798 µg/L; 2-methyl naphthalene, 1499 µg/L; 2,6-dimethyl naphthalene, 852 µg/L; and, 2,3,5-trimethyl naphthalene, 316 µg/L. Similar trends were noted for estuarine shrimp. Anderson et al. (1974b) found the following 24-hour LC50 values for *Palaemonetes pugio* (brown shrimp): 2.6 ppm (mg/L) naphthalene; 1.7 ppm methyl naphthalene; and 0.7 ppm dimethyl naphthalene. Ninety-six-hour LC50 values for the same species and the same compounds were 2.4 ppm, 1.1 ppm, and 0.7 ppm respectively (Tatem et al., 1978).

The zoeal stages of mud crab, *Rhithropanopeus harrissii*, were apparently not affected by naphthalene levels up to 500 ppb (Laughlin and Neff, 1979). Decreases in salinity to 5^{o}/oo did, however, slightly reduce the survival rates at 500 ppb.

Sanborn and Malins (1977) found that naphthalene at 8-12 ppb in flowing seawater produced 100% mortality in 24-36 hours for newly hatched Dungeness crab (*Cancer magister*) zoeal and stage I and V spot shrimp (*Pandalus platyceros*). The authors raised concern about the possible sublethal effects of even lower hydrocarbon concentrations.

Calder and Lader (1976) studied the effects of several dissolved aromatic hydrocarbons on non-hydrocarbon degrading marine bacteria. During batch culture growth experiments, 2-methyl and 2,6-dimethyl naphthalene were considerably more toxic than naphthalene. Toxicity effects were observed at 10 ppm naphthalene, 2.7 ppm 2-methyl naphthalene, and 0.2 ppm 2,6-dimethyl naphthalene. The most significant effects were observed with the bacterial metabolite, dihydroxynaphthalene. The authors speculated that "because of its more polar structure, the dihydroxy compound can achieve concentrations high enough to cause complete cessation of growth. If partial oxidation products were to build up in an environment, the impact of an oil spill may be significantly increased."

Armstrong et al. (1979) determined the concentrations of naphthalenes in Trinity Bay (Texas) sediments in the vicinity of an oil separator platform and their effects on the benthic fauna. An inverse correlation existed between benthos populations (total individuals) and concentrations of naphthalenes in sediments. Sediments with more that 18-21 ppm naphthalenes were apparently devoid of benthos. Armstrong et al.(1979) suggested that naphthalene levels as low as 2 ppm in sediments can affect biota. Naphthalenes were, therefore, considered to be of considerable use in tracing oil pollution in marine waters.

Chronic effects are observed at levels much lower than the experimentally determined acute toxicity levels. Ott et al. (1978) exposed the estuarine copepod, Eurytemora affinis, to separate 10 µg/L solutions of naphthalene, 2-methyl naphthalene, 2,6-dimethyl naphthalene, and 2,3,5-trimethyl naphthalene. Within 29 days, which is the average duration of the adult life, reductions were observed in life span, total nauplii produced, and brood size. The magnitude of the effects could be correlated with the degree of methylation.

Chronic studies of four generations of the marine polychaeta, Neanthes arenaceodentata, were conducted by Rossi and Anderson (1978). Water soluble fractions from No. 2 fuel oil were used and effects were noted and expressed in terms of total naphthalenes. With low levels of total naphthalenes, i.e., 0.03 ppm, no disruption was noted of normal growth in larval or juvenile polychaetes. Reproduction of Neanthes was nonetheless sensitive to the low concentrations of naphthalenes. Inhibitions of larval and juvenile growth observed for higher naphthalene concentrations were found to be reversible upon transfer of the larvae or juveniles to hydrocarbon-free water.

Anderson et al. (1974b) found that water soluble fractions of oil increased the respiratory response of the sheepshead minnow, while the respiratory rate of crustaceans decreased. Respiratory rates returned to normal after the test species were returned to clean seawater.

Malins (1980) noted that because alkyl naphthalenes enhance the carcinogenic effects of benzo(a)pyrene in mammals, it is possible that similar effects could occur within marine organisms.

4.9.2.2 Possible Effects of Levels Found in Puget Sound

The levels of total naphthalene within Puget Sound sediments may approach the 18-21 ppm levels reported by Armstrong et al. (1979) which appeared to affect benthos populations. For example, using the highest naphthalene level detected in Commencement Bay (Table 4.9.1), the total naphthalene concentration was 4 ppm.

The maximum concentrations of naphthalenes in Puget Sound waters were in the order of 0.1 µg/L (Riley et al., 1980). The levels are therefore lower than the published acute and chronic toxicity values. In the case of chronic effects, a safety factor of no more than 100 exists. The widespread distribution within Puget Sound of the naphthalenes as shown in Table 4.9.1 and the possible chronic and carcinogenic effects of the naphthalenes and/or their metabolites, imply their selection as "compounds of concern" within Puget Sound.

Table 4.9.1

Ranges in Concentrations of Naphthalene in Sediment and Biota from Puget Sound in ppb (ng/g) Dry Weight*

Location	Sediments	Fish Livers	Shrimp	Worms
Elliott Bay	5 - 680	< 10 - < 410	10 - 120	30 - < 80
Commencement Bay	30 - 4000	< 10 - < 340	< 20	30 - 70
Sinclair Inlet	40 - 360	< 10	30	< 50
Budd Inlet	30 - 80	20	20	-
Case Inlet	3 - 20	< 5	40	-
Port Madison	8 - 30	< 10	< 20	< 30
Port Susan	8.7 - 14	-	-	-

*from Malins et al. (1980, 1982)

4.9.3 Physical Properties of Naphthalenes

Naphthalene consists of two conjugated aromatic rings. Figure 4.9.1 indicates the numbering designations for substituted naphthalenes:

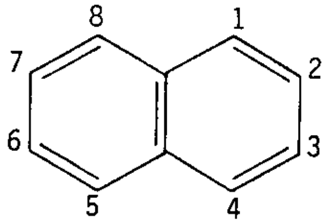


Figure 4.9.1
Structure and Numbering System for Naphthalene

Table 4.9.2 indicates some of the known general physical properties of the naphthalenes detected in Puget Sound. The compounds have moderate lipophilic properties and low solubilities in seawater. The solubilities are, however, higher than the solubilities of chlorinated insecticides and chlorinated biphenyls.

Table 4.9.2

Known Significant Physical Properties of Naphthalenes

Compound and Registry Number	Molecular Weight	Solubility (Seawater)	log P	Vapor Pressure
Naphthalene 91203	128.19	20-22 ppm	3.395(a)	0.0492 torr
1-Methyl naphthalene 90120	142.21		2.870(a)	
2-Methyl naphthalene 91576	142.21	2.4±.5	3.864(a)	
1,3-Dimethyl naphthalene	156.23		4.421(a)	
2,3-Dimethyl naphthalene	156.23		4.396(a)	
2,6-Dimethyl naphthalene	156.23	1.3 (freshwater)	4,313(a)	
2,3,5-Trimethyl naphthalene	170.25			
2,3,6-Trimethyl naphthalene	170.25			
Phenyl naphthalene	204.22			
Ethyl naphthalene	156.21			
C_3 substituted naphthalene				
Binaphthalene	254.36			

Krishnamorthy and Wasik (1978)

4.9.4 Sources or Inputs

Based on the observed sediment levels in Table 4.9.1, Commencement and Elliott Bays are contaminated with high levels of naphthalenes. The diversity of alkylated naphthalenes found within Puget Sound indicate that contamination by crude and refined oil is occurring. Furthermore, there are several plastic and resin manufacturers in the Seattle and Tacoma areas who may use naphthalene as a feedstock (Stanford Research Institute, 1978). EPA has also identified various industrial wastewaters within the United States which contain appreciable quantities of naphthalene. The more significant sources are wastewaters from timber products processing, paint and ink formulation facilities and, iron and steel manufacturing plants. The EPA survey found naphthalene levels in timber product processing levels up to 45,000 ppb. Other plant effluents were below detection levels and the median level was 3,500 ppb.

No estimates of naphthalene inputs to Puget Sound were found.

4.9.5 Summary of Biogeochemical Fate Data in the Marine Environment

4.9.5.1 Bioaccumulation - Uptake and Depuration

Summary Statement: Equilibrium between levels of naphthalenes in water and in tissue of aquatic biota is rapidly attained. Bioaccumulation factors are generally low (i.e., 100 fold) and depuration occurs readily for naphthalene. The presence of alkyl groups enhances bioaccumulation and depuration rates decrease. Uptake for all species occurs primarily through the water phase. The brain is susceptible to bioaccumulated levels possible resulting in sublethal effects.

Review of Individual Studies: As noted in Section 4.8.6, equilibrium tissue levels of aquatic biota are reached quickly for lighter molecular weight PAHs such as naphthalene relative to higher molecular weight PAHs such as benzo(a)pyrene (Roesijadi et al., 1978). Partitioning is proportionate to tissue lipid levels.

Southworth et al. (1978) determined the Daphnia pulex reached equilibrium with naphthalene levels in water in 2 hours, compared to 24 hours for benzo(a)anthracene. Daphnia pulex bioconcentrated naphthalene by a factor of 134. The uptake and elimination rate constants were 197 hr^{-1} for naphthalene and 1.667 hr^{-1} for benzo(a)anthracene.

Using the oceanic and estuarine copepods, Calanus helgolandicus and Eurytemora affinis, Harris et al. (1977) found that body levels of ^{14}C-naphthalene reached equilibrium levels after 8 days. Copepods exposed to low naphthalene levels (1 µg/L and 0.2 µg/L) achieved dry weight concentrations of 50 ppm and 0.1 ppm, respectively. When the copepods were transferred to uncontaminated seawater, initial depuration rates were rapid. After 24 hours, Calanus helgolandicus lost 86% of its accumulated ^{14}C-naphthalene. Exposure to higher concentrations of naphthalene resulted in higher levels of naphthalene in tissues. Nonetheless, steady state conditions were achieved.

Anderson et al. (1974b) found a rapid uptake of naphthalene and methylated naphthalenes by the brown shrimp, Penaeus aztecus. A 0.02-0.03 ppm solution of dimethyl naphthalene resulted in 0.4 ppm in the shrimp tissue after 30 minutes exposure. Methyl naphthalenes were accumulated to the greatest extent by the shrimp. A 0.2-0.3 ppm solution of methyl naphthalene resulted in a 3 ppm level in tissue. When removed to hydrocarbon-free water, complete depuration occurred within 600 minutes. The rapidity of exchange between tissue and environmental levels was also observed for the sheepshead minnow which accumulated 205 ppm 1-methyl naphthalene and 60 ppm naphthalene from a seawater solution of 1 ppm of both compounds after 4 hours exposure. After 29 hours in clean seawater, the levels in tissue dropped to 10 ppm naphthalene and 30 ppm 1-methyl naphthalene, respectively (Anderson et al., 1974b).

Sanborn and Malins (1977) found a 100-fold accumulation of naphthalene within spot shrimp which could be entirely depurated in 24 to 36 hours. Metabolic products were, however, strongly resistant to depuration.

Lee et al. (1972) found rapid uptake of ^{14}C-naphthalene from seawater by the common marine mussel, Mytilus edulis. The hydrocarbon was taken up by gill tissue, then eventually transferred to the hepatopancreas rapidly. Evidence of metabolism of naphthalene was not found, and it was assumed that the hepatopancreas of the mussel may lack the hydroxylating enzymes present in vertebrate liver. After four hours exposure a bioconcentration factor of 218 was observed, based on dry weight analyses. Two hours after transfer to uncontaminated seawater, whole mussel levels of ^{14}C-naphthalene were reduced by approximately 40%.

The results of another benthic uptake study of naphthalene were reported by Roesijadi et al. (1978). Phascolosoma agassizii, Macoma inquinata, and Protothaca staminea were exposed to oil contaminated sediments for 60 days. After 40 days, the deposit feeders P. agassizii and M. inquinata both accumulated the hydrocarbons to a greater extent than P. staminea. After 60 days, more intrinsic differences in the ability of the three species to accumulate hydrocarbons were apparent. Equilibrium levels were not evident after 60 days' exposure of M. inquinata nor P. staminea to the contaminated sediments. In addition, the authors indicated that the hydrocarbons present in the interstitial water were a prime source of contamination rather than the hydrocarbons associated with particulate matter. Methylation appeared to enhance the bioconcentration of naphthalene within the clams. For example, methyl naphthalene levels after 40 and 60 days were 0.06 and 0.27 ppm, respectively, in M. inquinata. Dimethyl naphthalene levels were 0.89 and 2.39 ppm after 40 and 60 days, respectively.

Rossi (1978) found that the polychaete, Neanthes arenaceodentata, did not accumulate naphthalene from sediments containing as much as 9 μg naphthalene per gram sediment. Uptake did occur from water. A 40-fold increase was determined after 24 hours exposure to a solution of 0.15 ppm ^{14}C-naphthalene. Rapid release to uncontaminated waters was also observed, with levels in the polychaete decreasing to less than 0.05 ppm after 300 hours.

Naphthalenes were found in very low levels within liver of fish from Puget Sound implying the probability of metabolism within the liver, the lack of uptake of naphthalenes, and/or the possibility of accumulation in other organs of the fish. Dixit and Anderson (1977) studied the uptake and distribution of ^{14}C-naphthalene within the estuarine fish Fundulus similus. After 8 hours, only 3% of the totally orally administered ^{14}C-naphthalene could be recovered. During the 8-hour period and especially during the first 4 hours, much of the accumulated ^{14}C-naphthalene was found in the liver, gall bladder, heart, and brains.

Gross behavioral abnormalities were observed for fish exposed to 2 ppm naphthalenes in water. Analyses of the affected fish implied that accumulation and long retention of naphthalenes in the brain may be responsible for the behavior. Fish transferred to clean seawater were found to recover rapidly.

Uptake of naphthalenes by fish was also studied by McCain and Malins (1979) who exposed flatfish for up to 4 months to sediments which contained petroleum hydrocarbons. Of the hydrocarbons, 2-methyl naphthalene, 1-methyl naphthalene, and 2,6-dimethyl naphthalene were predominant. After 29 days exposure, muscle tissue of flatfish accumulated approximately 300 ppb 2-methyl naphthalene from sediments which contained 2200 ppb and 1800 ppb 2-methyl naphthalene at 14 and 29 days, respectively. The ratios of tissue to sediment levels were less than 0.15. No uptake of 2,3,5-trimethyl naphthalene was observed; however, after 29 days the compound was not detectable in sediments.

Lawler et al. (1978) found that mallard ducks exposed to crude oil primarily accumulated naphthalene, methyl naphthalene, and dimethyl naphthalene within the skin and underlying adipose tissue. The aromatics were also detected in the brain, suggesting the possibility of sublethal effects on the nervous system.

All the biological species analyzed in Puget Sound appear to have the ability to rapidly depurate naphthalenes from their systems. The occurrence of naphthalenes in Puget Sound biota is, therefore, reflective of a rapid equilibrium between concentration in water and sediments. Analyses of most fish liver samples indicated levels of naphthalenes below detection limits. Considering the ability of liver to metabolize naphthalenes, reliance solely on liver analyses to evaluate uptake of naphthalenes appears to be inadequate. Bottom dwellers such as crabs, clams, worms, and shrimp from Elliott and Commencement Bays have variable amounts of naphthalene and substituted naphthalene which are indicative of an equilibrium between sediments and interstitial waters.

4.9.5.2 Metabolism

Summary Statement: Microbial degradation is an important fate process for naphthalene and substituted naphthalene. Marine animals such as crabs and fish can only hydroxylate naphthalenes and cannot cleave the ring structure. It has been suggested that the hydroxylated metabolites may be of ecological concern.

Review of Individual Studies: An extensive review of metabolism of polyaromatic hydrocarbons has been prepared by Cripps and Watkinson (1978). Microbial metabolism of naphthalene appears to occur via a cis-dihydrodiol metabolite with eventual accumulation of salicylate as shown in Figure 4.9.2.

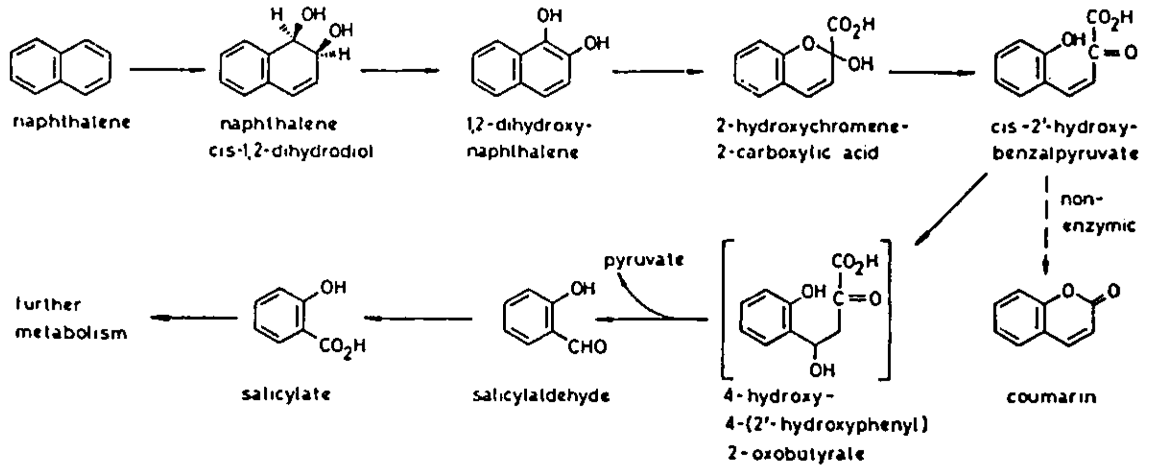


Figure 4.9.2
Pathway of Metabolism of Naphthalene by Pseudomonads

Substituted naphthalenes also degrade by pathways analogous to those outlined in Figure 4.9.2. Therefore, 1-methyl and 2-methyl naphthalene would be oxidized to 3-methyl and 4-methyl salicylic acid, respectively. Further metabolism may occur to form 3-methyl and 4-methyl catechol.

A range of products can be formed as a result of the oxidation of dimethyl naphthalenes. For example, Cripps and Watkinson (1978) described studies which showed that Pseudomonas putida, which is found in soil, can convert 1,8 dimethyl naphthalene to 1-methyl-8-hydroxymethyl naphthalene, 1-methyl-8-naphthoic acid, 1,8-hydroxymethyl naphthalene and 1,8-napthalene dicarboxylic acid.

Lee (1977) studied the degradation rates of naphthalene and methyl naphthalene in natural marine waters. Rapid degradation of a 30 µg/L solution of naphthalene occurred in estuarine waters (0.87 µg/L/day) relative to degradation in coastal waters (0.33 µg/L/day) and in the Gulf Stream (0.01 µg/L/day). A degradation rate of 0.25 µg/L/day was noted for a 30 µg/L solution of methyl naphthalene placed in estuarine waters, and no degradation was observed in coastal or Gulf Stream waters. The higher degradation rate in estuarine waters was attributed to a larger standing stock of bacteria and elevated nutrient concentrations. Temperature also has a significant effect on degradation rates. For example, the degradation rate of 30 µg/L naphthalene dissolved in Skidaway River water during the summer (average 24°C) was 0.68 µg/L/day and during the winter (average 13°C) was 0.07 µg/L/day.

Lee's (1977) studies indicate the microbial degradation of naphthalene and methyl naphthalenes may be an important fate process in estuarine areas and a minor process in coastal areas of Puget Sound.

Most aquatic animals with possible exceptions (e.g. mussels) contain the necessary enzyme systems for initiating the bioconversion of aromatic hydrocarbons. The enzymes, aryl hydrocarbon mono-oxygenases, operate in unison with the election transport system. Oxygen from the electron transport system combines with the aromatic nucleus to form an epoxide which is then converted to mono- and dihydric alcohols. Additional conversions may then occur.

Malins (1980) described a study which found that flatfish readily converted naphthalene into a variety of oxygenated metabolites that remain in tissue for extended periods of time. The metabolites included 1,2-dihydro-1,2-dihydroxynaphthalene, 1-naphthol and 2-naphthol. The physiological implications of these metabolites is not known, but fish exposed to oil contaminated sediments have increased lipid accumulations in liver, weight losses and higher mortalities (Malins, 1980).

Malins et al. (1979) found eight polar derivatives in liver of salmonids (coho salmon and rainbow trout) exposed to naphthalene. Two nonconjugates (1-naphthol and 1,2 dihydro-1,2-dihydroxy naphthalene) and three conjugates (1-naphthyl glucuronic acid, 1-naphthyl sulfate and 1-naphthyl glucoride) were identified.

Lee (1976) compared the metabolism of PAHs by microbes and by marine animals. Although bacteria were found to carry out ring cleavage, metabolism by marine animals involved only hydroxylation but no ring cleavage. No hydrocarbon metabolism was evident in bivalve molluscs; however, their burrowing activities may expose deeper sediments to water-sediment interfaces where there is more microbial activity.

Lee et al. (1976) found that a large fraction of naphthalene and methyl naphthalene bioaccumulated by the blue crab, Callinectes sapidus, was metabolized in the hepatopancreas. The metabolites were highly polar dihydroxy-compounds and their conjugates. Subsequently, the metabolites were identified primarily in excreted material, blood, and in the hepatopancreas. Storage of hydrocarbons in tissue was minimal. Depuration studies showed rapid release of PAHs from the tissues, however the metabolites were generally retained within the hepatopancreas.

Burns (1976), using the fiddler crab, Uca pugnax, as a test species, found that the species does have a microsomal mixed function oxidase system. Nevertheless, the uptake of hydrocarbons occurred at a faster rate in the crabs than the metabolic and excretion rates.

The distribution of metabolites of naphthalene may be of ecological concern. The possible effects of the metabolites in biota as suggested by Malins (1980) and the actual aquatic toxicity of metabolites as noted by Calder and Lader (1976) implies the need for identification, fate, and effects of such metabolites within Puget Sound.

4.9.5.3 Sorption and Sedimentation

Summary Statement: Naphthalene has a rapid flux rate to sediments; concentrations as low as 2 ppm in sediments have been suggested to be able to restrict many species of biota. Fecal pellets furnish a prime mode of introduction of PAHs to sediments.

Review of Individual Studies: There is some evidence that sediment associated naphthalenes are biologically available to various marine species. Armstrong et al. (1979) in their studies of effects of oilfield brine effluents in Trinity Bay, Texas, found inverse correlations between abundance of benthos and relative concentrations of naphthalenes in the sediments. Sediments with 18-21 ppm naphthalenes were completely devoid of benthos. The authors speculated that a low (possibly 2 ppm) persistent concentration of naphthalenes is capable of restricting many species and suggested that "it would not appear that sediment-sorbed naphthalenes have only limited bioavailability to deposit-feeding benthic animals." Rossi and Anderson (1978) showed that the polychaete, *Neanthes arenaceodentata*, can take up detritus-bound methyl naphthalene.

Naphthalenes may reach bottom sediments by adsorptive partitioning to suspended solids and by association with zooplankton fecal pellets. The degree of adsorptive partitioning will depend upon the degree of methylation of the naphthalenes. For example, Lee (1977) showed that 0.7% and 6% of 30 μg/L naphthalene and methyl naphthalene solutions, respectively, were adsorbed to particles in estuarine waters.

Sediment-water partition coefficients for naphthalene are 1.3×10^3 and for methyl naphthalene, 8.5×10^3 (Karickhoff et al., 1979). Lee et al. (1978) found that naphthalenes, particularly dimethyl naphthalenes, were found in bottom sediments within the first seven days while the heavier weight aromatics were slower to reach the sediment. This observation suggested that naphthalenes reached the bottom via a different mechanism than heavier PAHs.

It was suggested that naphthalenes could be taken up by living phytoplankton cells which subsequently sank to the bottom. Another possible mechanism was uptake by particulates, subsequent consumption of the particulates by the zooplankton, and excretion of fecal pellets which rapidly settle through the water column and accumulate in the sediments. Prahl and Carpenter (1979) measured the annual flux of individual PAHs in sediment traps within Dabob Bay, Puget Sound. Although naphthalenes were not measured, the flux rate ($ng/cm^2/yr$) of PAHs was inversely proportional to molecular weight. For example, phenanthrene flux to sediments via fecal pellets was greater than for benzo(a)anthracene. On this basis naphthalene would have the most rapid flux rate. The investigators found quantitative agreement between sediment trap and actual sediment calculated PAH fluxes. The findings indicated that the compounds did not undergo significant degradation during sediment deposition and that vertically transported fecal pellets furnish the primary mode of introduction to these sediments, for the PAH studied.

The naphthalene levels in Puget Sound sediments, as noted in Table 4.9.1, indicate that sedimentation may be an important fate process in Puget Sound. Lee et al. (1978) showed low recoveries of naphthalene and methyl naphthalenes (11 and 7%, respectively) and high recoveries of dimethyl naphthalenes (32%) in sediments of a "controlled ecosystem enclosure" study. The low recoveries were probably due to biodegradation. Considering the high levels of naphthalene noted in Table 4.9.1, it appears that the input rates of naphthalenes to Puget Sound are appreciable.

4.9.5.4 Photolysis

Photooxidation of naphthalenes was not considered by Lee et al. (1978) to be of importance in the removal of naphthalenes from a "controlled ecosystem enclosure." However, adsorption of solar radiation by dissolved naphthalenes is theoretically feasible. Radding et al. (1976) suggested that direct photolysis may be of significance, particularly because the solubility of naphthalene is high. The literature search did not retrieve any studies which reported on possible photolytic products of naphthalene.

Compared to degradation, adsorption and volatilization processes, photolysis probably has an insignificant role regarding the fate of naphthalene in the environment.

4.9.5.5 Volatilization

Summary Statement: Volatilization is probably of significance to the fate of naphthalenes in the environment, however, its actual significance is uncertain because of differences between field and laboratory data.

Review of Individual Studies: Lee et al. (1978) indicated that evaporation and microbial degradation were the most important fate processes for naphthalene. Relative to many other PAHs, naphthalene is considered to readily volatilize from water. Southworth (1979) calculated a Henry's Law constant of 2.26×10^{-2} for naphthalene. The constant is the ratio of molar concentration in air to molar concentration in water.

Mackay and Leinonen (1975) presented a hypothetical half life of 7.5 hours for naphthalene found in the top one meter of a body of water. For naphthalene in depths greater than one meter, the half life would increase significantly.

Gordon et al. (1975) produced results which indicated that naphthalenes do not readily evaporate. In evaluating the fate of crude oil spilled on seawater, the investigators found that medium molecular weight aromatics readily entered the water column and sediments, and these persisted for a long time. Naphthalenes persisted at least 17 days in the surface film and 3 months or more in the water column which was contrary to other results which indicated the naphthalene should dissipate from slicks within a matter of hours. The observations of Gordon et al. (1975) indicate the importance of studies which relate actual situations (i.e., naphthalene inputs via crude and refined oil spills) versus studies which solely utilize pure components (i.e., naphthalene). The results also imply the significance of in situ versus laboratory studies.

4.9.6 Overall Fate Studies

Lee and Anderson (1977), and Lee et al. (1978) studied the fate of naphthalene and methyl naphthalenes in controlled ecosystem enclosures. The investigators added 2 gm naphthalene, 4 gm methyl naphthalene and 4 gm dimethyl naphthalene to a 68,000-liter enclosure, and observed reductions of 50% within 24 hours in the water column. Concentrations in the water column gradually decreased to the background levels during the next 20 days (Lee and Anderson, 1977). Most of this decrease was attributed to adsorption to sinking phytoplankton and microbial degradation. The sediments became enriched in methyl naphthalene and dimethyl naphthalenes with minor quantities of naphthalene. Microbial degradation rates of naphthalene in the water column increased from 0.04 µg/L/day to 3.3 µg/L/day after 3 days. Slower microbial degradation rates were observed for methyl and dimethyl naphthalenes. The increase in the biodegradation rate after 3 days was presumed due to the time needed for selection of hydrocarbon-degrading microbes. During the study of Lee and Anderson (1977), it was noted that the ctenophore, Pleurobrachia pileus, suffered heavy mortality while the copepod, Calanus plumchrus, was not affected.

Similar results were obtained by Lee et al. (1978) for methyl naphthalene within similar enclosures. A degradation rate of 0.5 µg/L/day was observed, indicating that 5% of the naphthalenes could be biodegraded daily. Uptake rates of naphthalenes were determined for oysters within the enclosures. Naphthalenes were rapidly accumulated, then rapidly released. There were no detectable quantities in oysters 23 days after initiation of depuration.

Harris et al. (1977) found no evidence for photooxidation of naphthalene in seawater. When mercuric chloride was added to inhibit microbial activity, no decreases in naphthalene concentrations were observed in samples exposed to light or dark conditions. Higher degradation rates were observed in inshore waters than in offshore waters. For example, more than 90% of the naphthalene was degraded within inshore waters over 24 hours and 17-40% was degraded over the same time period in offshore waters. Of the radioactivity remaining, the dissolved portion in the water column was still present as ^{14}C-naphthalene, and only 3.1% in the particulate material was unchanged, implying that suspended solids serve as degradation sites for naphthalene in the environment.

4.9.7 Conclusions

1. On the basis of the literature review, naphthalene appears to be readily biodegraded in water and sediments. The high concentrations of naphthalene in sediments of Elliott and Commencement Bays implies that there are constant inputs of naphthalenes to these areas.

2. The prevalence of naphthalenes within Puget Sound may have an effect on the fauna. Sublethal effects of low levels of naphthalenes are possible for species such as the ctenophore, Pleurobrachia pileus, zoea of the crab, Cancer magister, and various stages of the spot shrimp, Pandalus platyceros.

3. Of particular concern are the effects of metabolites of the naphthalenes. Some have been shown to be extremely toxic and others have been suggested as possible carcinogens.

4. Fecal pellets of zooplankton furnish a primary mode of introduction of PAHs to sediments.

4.9.8 Research Needs

1. Source identification on naphthalenes to Puget Sound is required.

2. The ecological effects of naphthalenes to Puget Sound should be carefully assessed using community structure and population analyses.

3. The identification, distribution, and eventual fate of metabolites of napthalenes in biota and subsequently in the environment should be of high priority.

References

Anderson, J.W., J.M. Neff, B.A.Cox, H.E. Tatem, and G.M. Hightower. 1974a. Characteristics of dispersions and water-soluble extracts of crude and refined oils and their toxicity to estuarine crustaceans and fish. Mar. Biol. 27:75-88.

Anderson, J.W., J.M. Neff, B.A. Cox, H.E. Tatem, and G.M. Hightower. 1974b. The effects of oil on estuarine animals: toxicity, uptake and depuration, respiration. In: F.J. Vernberg and W.B. Vernberg (eds.), Pollution and the Physiology of Marine Organisms. Academic Press. N.Y. pp. 285-310.

Armstrong, H.W., K., Fucik, J.W. Anderson, and J.M. Neff. 1979. Effects of oilfield brine effluent on sediments and benthic organisms in Trinity Bay, Texas. Mar. Environ. Res. 2:55-69.

Burns, K.A. 1976. Hydrocarbon metabolism in the intertidal fiddler crab *Uca pugnax*. Mar. Biol. 36:5-11.

Calder, J.A., and J.H. Lader. 1976. Effect of dissolved aromatic hdyrocarbons on the growth of marine bacteria on batch culture. Appl. Environ. Microbiol. 32:95-101.

Cripps, R.E. and R.J. Watkinson. 1978. Polycyclic aromatic hydrocarbons: metabolism and environmental aspects. *In*: R.J. Watkinson (ed.), Developments in Biodegradation of Hydrocarbons, Applied Science Publishers, Ltd., London.

Dixit, D. and J.W. Anderson. 1977. Distribution of naphthalenes within exposed *Fundulus similus* and correlations with stress behavior. *In*: *1977 Oil Spill Conference*. American Petroelum Institute. Publication 4284. pp. 633-636.

Environmental Protection Agency. 1978. Ambient Water Quality Criteria: Naphthalene. NTIS (PB 296 786).

Gordon, D.C., Jr., P.D. Keizer, W.R. Hardstaff, and D.G. Aldous. 1975. Fate of crude oil spilled on seawater contained in outdoor tanks. Environ. Sci. Technol. 10:580-585.

Harris, R.P., V. Berdugo, S.C.M. O'Hara, and E.D.S. Corner. 1977. Accumulation of^{14}C-1-Naphthalene by an oceanic and an estuarine copepod during long term exposure to low-level concentrations. Mar. Biol. 42:187-197.

Karickhoff, S.W., D.S. Brown, and T.A. Scott. 1979. Sorption of hydrophobic pollutants on natural sediments. Water. Res. 13:241-248.

Krishnamorthy, T. and S.P. Wasik. 1978. Fluorometric determination of partition coefficients of naphthalene homologues in octanol-water mixtures. J. Environ. Sci. Health. A13:595-602.

Laughlin, R.B., Jr., and J.M. Neff. 1979. Interactive effects of salinity, temperature and polycyclic aromatic hydrocarbons on the survival and development rate of the mud crab, *Rhithropanopeus harrisii*. Mar. Biol. 53:281-291.

Lawler, G., W.-A. Loong, and J.L. Laseter. 1978. Accumulation of aromatic hdyrocarbons in tissues of petroleum-exposed mallard ducks (*Anas platyrhynchos*). Environ. Sci. Technol. 12:51-54.

Lee, R.F. 1976. Metabolism of petroleum hydrocarbons in marine sediments. *In*: Sources, Effects and Sinks of Hydrocarbons in the Aquatic Environment. American Institute of Biological Sciences. Washington, D.C. pp. 334-343.

Lee, R.F. 1977. Fate of petroleum components in estuarine waters of the southeastern United States. pp. 611-616. *In*: Proceedings of the 1977 Oil Spill Conference. American Petroleum Institute, Washington, D.C.

Lee, R.F., R. Sauerheber, A.A. Benson. 1972. Petroleum hydrocarbons: Uptake and discharge by the marine mussel Mytilus edulis. Science 177:344-346.

Lee, R.F., C. Ryan, and M.L. Neuhauser. 1976. Fate of petroleum hydrocarbons taken up from food and water by the blue crab Callinectes sapidus. Mar. Biol. 37:363-370.

Lee, R.F. and J.W. Anderson. 1977. Fate and effect of naphthalenes: controlled ecosystem pollution experiment. Bull. Mar. Sci. 27:127-134.

Lee, R.F., W.S. Gardner, J.W. Anderson, J.W. Blaylock, J. Barwell-Clarke. 1978. Fate of polycyclic aromatic hydrocarbons in controlled ecosystem enclosures. Environ. Sci. Technol. 12:832-833.

MacKay, D. and P.J. Leinonen. 1975. Rate of evaporation of low-solubility contaminants from water bodies to atmosphere. Environ. Sci. Technol. 9:1178-1180.

Malins, D.C. 1980. Pollution of the marine environment. Environ. Sci. Technol. 14:32-37.

Malins, D.C., T.K. Collier, L.C. Thomas, and W.T. Roubal. 1979. Metabolic fate of aromatic hydrocarbons in aquatic organisms: analysis of metabolites by thin-layer chromatography. Inter. J. Environ. Anal. Chem. 6:55-66.

Malins, D.C., B.B. McCain, D.W. Brown, A.K. Sparks, and H.O. Hodgins. 1980. Chemical Contaminants and Biological Abnormalities in Central and Southern Puget Sound. NOAA Tech. Memo. OMPA-2. Office of Marine Pollution Assessment, Boulder, Colo.

Malins, D.C., B.B. McCain, D.W. Brown, A.K. Sparks, H.O. Hodgnis, S. Chan. 1982. Chemical Contaminants and Biological Abnormalities in Fish and Invertebrates from Puget Sound. NOAA Tech. Memo. (in press). Office of Marine Pollution Assessment, Boulder, Colo. 295 pp.

McCain, B.B. and D.C. Malins. 1979. Uptake, fate and effects of aromatic hydrocarbons on selected fish and crustaceans from the Northeast Pacific Ocean. Presented at the Marine Ecosystems Analysis (MESA) - New York Bright Meeting, June, 1979. New York, N.Y.

Ott, F.S., R.P. Harris, and S.C.M. O'Hara. 1978. Acute and sublethal toxicity of naphthalene and three methylated derivatives to the estuarine copepod Eurytemora affinis. Mar. Environ. Res. 1:49-58.

Prahl, F.G. and R. Carpenter. 1979. The role of zooplankton fecal pellets in the sedimentation of polycyclic aromatic hydrocarbons in Dabob Bay, Washington. Geochim. Cosmochim. Acta 43:1959-1972.

Radding, S.B., T. Mill. C.W. Gould, D.H. Lui, H.L. Johnson, D.C. Baumberger and C.V. Fojo. 1976. The Environmental Fate of Selected Polynuclear Aromatic Hydrocarbons. EPA 560/5-75-009.

Riley, R.G., E.A. Crecelius, D.C. Mann ,K.H. Abel, B.L. Thomas, R.M. Bean. 1980. Quantitation of Pollutants in Suspended Matter and Water from Puget Sound. NOAA Technical Memorandum. ERI MESA-49. Marine Ecosystems Analysis Program, Environmental Research Laboratories, Boulder, Colo., 99 pp.

Roesijadi, G., G.W. Anderson, and J.W. Blaylock. 1978. Uptake of hydrocarbons from marine sediments contaminated with Prudhoe Bay crude oil: influence of feeding type of test species and availability of polycyclic aromatic hydrocarbons. J. Fish. Res. Bd. Can. 35:608-614.

Rossi, S.S. and J.W. Anderson. 1978. Effects of No. 2 fuel oil water-soluble-fractions on growth and reproduction in Neanthes arenaceodentata. Water, Air, Soil Pollut. 9:155-170.

Sanborn, H.R. and D.C. Malins. 1977. Toxicity and metabolism of naphthalene: a study with marine larval invertebrates. In: Proceedings of the Society for Experimental Biology and Medicine 154:151-155.

Southworth, G.R., J.J. Beauchamp, and P.K. Schieder. 1978. Bioaccumulation potential of polycyclic aromatic hydrocarbons in Daphnia pulex. Water Res. 12:973-977.

Southworth, G.R., 1979. The role of volatilization in removing polycyclic aromatic hydrocarbons from aquatic environments. Bull. Environ. Contamin. Toxicol. 21:507.

Stanford Research Institute. 1978. Directory of Chemical Producers - United States of America. Chemical Information Services, Menlo Park, Calif.

Tatem, H.E., B.A. Cox, and J.W. Anderson. 1978. The toxicity of oils and petroleum hydrocarbons to estuarine crustaceans. Estuar. Coastal Mar. Sci. 6:365-373.

4.10 Benzo(a)anthracene
Methyl Benzo(a)anthracene
Dibenzo(a,h)anthracene

4.10.1 Introduction

Benzo(a)anthracene is a polycyclic aromatic hydrocarbon which contains four aromatic rings in the configuration shown in Figure 4.10.1.

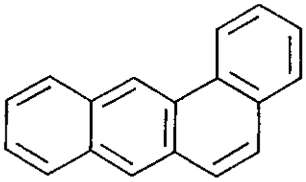


Figure 4.10.1
Benzo(a)anthracene (benzanthracene)

This chapter combines discussions on the possible fate and effects of benzo(a)anthracene, methyl benzo(a)anthracene, and dibenzo(a,h)-anthracene because of structural similarities.

Probable sources of the compounds are engine exhaust, cigarette smoke, coal-tar pitch, and soot and smoke of industrial and domestic origin. Environmental contamination of benzo(a)anthracene, for example, is widespread. It has been detected in North American drinking waters at levels from 1 to 23 ng/L (ppt) and in industrial and municipal effluents at levels from 25 to 10,360 ng/L (Radding et al., 1976).

All three forms of benzanthracene have been detected at high levels in areas of Puget Sound with significant industrial activity. Benzo(a)-anthracene and dibenzo(a,h)anthracene are two of the EPA's 129 Priority Pollutants.

4.10.2 Significance to Puget Sound

4.10.2.1 Review of Known Toxicity Data

Benzo(a)anthracene, 7-methyl benzo(a)anthracene and dibenzo(a,h)-anthracene are listed in the tentative carcinogen list of the Occupational Safety and Health Administration. All compounds (including each isomer of methyl benzo(a)anthracene) are categorized as carcinogens and/or neoplastigens in the NIOSH (1979) Registry of Toxic Effects of Chemical Substances. The methylated forms have variable carcinogenicity. For example, 1-methyl benzo(a)anthracene is considered "weakly carcinogenic", 12-methyl benzo(a)anthracene is more potent and 1,12-dimethyl benzo(a)anthracene is categorized "inactive" (Jones and Sowden, 1979). Coombs et al. (1976) categorized 7-methyl benzo(a)anthracene as a strong carcinogen and 7,12 -dimethyl benzo(a)-anthracene as a very strong carcinogen.

4.10.2.2 Possible Effects of Levels Found in Puget Sound

Benzo(a)anthracene was detected in edible biota (clams, crab, shrimp) from Puget Sound. Analyses of fish liver, however, indicated that the compound was usually at concentrations less than detection limits. The dry weight levels are summarized within Table 4.10.1. Levels of benzo(a) anthracene in the biota of Puget Sound were much higher than those reported by Pancirov and Brown (1977) in biota from the Atlantic Ocean and from the Gulf of Mexico where ppb wet weight levels in oysters were 0.1-8; in clam, 0.3-1; in crab, 1.5-2; and shrimp, 0.2. Flounder and codfish from the Atlantic Ocean contained less than the 1 ppb detection limit for benzo(a)anthracene.

Concentrations of benzo(a)anthracene in water from all sampling sites in Puget Sound were less than the detection level of 1 ng/L.

Benzo(a)anthracene levels in sediments of Central Puget Sound varied from 1 to 13,000 ppb (µg/kg). The higher levels were found in sediments from Elliott Bay, Commencement Bay, and Sinclair Inlet. Measurable quantities of the contaminant were detected within the sediments of Port Madison which was considered as a reference area. The effects of the high levels of benzo(a)anthracene on benthic biota are not known.

Analyses for dibenzo(a,h)anthracene and methyl benzo(a)anthracene were more limited. Dibenzo(a,h)anthracene was positively confirmed by Brown (1979) in sediment samples from the vicinity of Pier 54 and Hylebos. Sediments from Upper Sinclair and Duwamish East Waterways did not contain dibenzo(a,h)anthracene above the detection limits. Sediment samples analyzed by Seattle METRO (1979) indicated concentrations from 14.2 to 113.5 ppb of dibenzo(a,h)anthracene. No analyses for dibenzo(a,h) anthracene in biota, water or suspended solids were reported during the MESA Puget Sound surveillance program.

Eight isomers of methyl (benzo(a)anthracene) were detected by Brown (1979) in sediments obtained from the vicinity of Pier 54. Four isomers were reported in sediments of Upper Sinclair and five isomers in sediments of the Hylebos Waterway. No quantitative analyses were attempted.

The benzanthracenes are selected for review in this report because of their carcinogenic and/or neoplastic potential and the widespread distribution of benzo(a)anthracene in sediments and biota of Puget Sound.

4.10.3 Physical Properties of Benzanthracenes

Generally speaking, benzanthracenes have low solubility, low vapor pressure, and high log n-octanol/water partition coefficients. Table 4.10.2 and 4.10.3 show the structures of the compounds, their chemical registry numbers, and their basic physical properties.

Table 4.10.1

Concentration in µg/g (ppm) of Benzo(a)anthracene Found at Various Locations in Central Puget Sound *

Subarea	Sediment Avg.(#samples)[a] (Range)	Fish Livers[b] Avg.(#samples)[a] (Range)	Crab Hepato-pancreas	Worm Avg.(#samples)[a] (Range)	Shrimp	Clam	Suspended Solids
Case Inlet	0.022 (2) (0.040,0.0030)	<0.010 (2)	0.010 (1)	-c	0.16 (1)	<0.030 (1)	
Port Madison	0.045 (2) (0.070,0.020)	<0.030 (2)	-	0.020 (1)	0.010 (1)	0.020 (1)	0.01
Sinclair Inlet	0.72 (4) (2.1,0.14)	<0.040 (2)	0.070 (1)	0.050 (1)	0.12 (1)	0.45 (1)	0.02
Budd Inlet	0.080 (3) (0.11,0.050)	<0.010 (2)	<0.020 (1)	-	0.040 (1)	-	.01
Duwamish Waterway	1.1 (6) (1.4,0.10)	<0.090 (6)	0.060 (1)	1.3 (1)	0.080 (1)	1.0 (1)	
Seattle Waterfront	2.4 (6) (13,0.030)	<0.040 (2)	-	-	-	0.28 (1)	(0.08,0.03)
Outer Elliott Bay	0.13 (4) (0.29,0.010)	<0.050 (1/4)	-	0.22 (2) (0.25,0.19)	0.020 (1)	-	
West Point	4.8 (1)	<0.11 (2)	-	-	-	-	
Hylebos Waterway	1.2 (5) (3.2,0.060)	0.14 (2/11) (0.22,0.060)	<0.020 (1)	1.6 (2) (3.0,0.20)	0.12 (1)	0.14 (1)	0.01-0.43
Commencement Waterways	1.2 (5) (4.7,0.010)	-	0.090 (1)	0.53 (1)	-	0.73 (1)	0.01-0.34
Southwest Commencement Bay	0.72 (3) (2.1,0.020)	0.050 (1/4)	-	-	-	-	
Brown's Point	0.040 (1)	0.0030(1/2)	-	-	0.050 (1)	-	

[a] Where nondetectable levels of material were observed, a ratio of the number of samples with detectable levels to the total number of samples was substituted.

[b] English and rock sole species

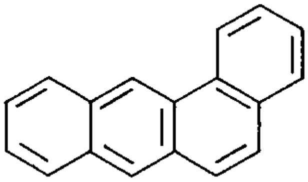
[c] Signifies that no sample was taken

*Malins et al. (1980)

Table 4.10.2

Structures and Chemical Abstracts Registry Numbers (CAS No.) Benzanthracenes

Benzo(a)anthracene



CAS No.: 56553

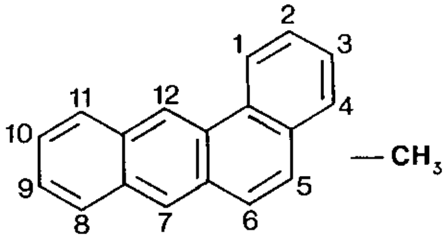
Alternative Names

1,2-Benzanthracene

tetraphene

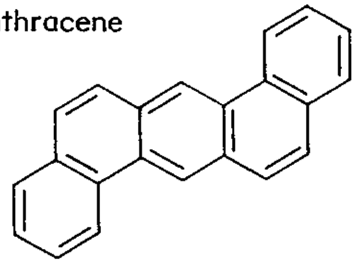
naphthanthracene

Methyl (benzo(a)anthracene)



Isomer	CAS No.	Isomer	CAS No.
1 methyl	2498773	7 methyl	2541697
2 methyl	2498762	8 methyl	2381319
3 methyl		9 methyl	2381160
4 methyl	316494	10 methyl	2381159
5 methyl	2319962	11 methyl	6111780
6 methyl	316143	12 methyl	2422799

Dibenzo(a,h)anthracene



CAS No: 53703

Alternative Name

1,2,5,6-Dibenzanthracene

Table 4.10.3

Physical Properties of Benzanthracenes

Physical Property	Benzo(a)-anthracene	Dibenzo(a,h)-anthracene	Methyl benzo(a)-anthracene
Molecular Weight	228	278	242
Vapor Pressure	5×10^{-9} torr @ 20°C (Smith et al., 1978)	10^{-10} torr @ 20°C (Callahan and Slimak, 1979)	
Solubility in Water	Freshwater 0.014 mg/L @ 25°C(Callahan) and Slimak, 1979) 5.7 ± .5 mg/L @ 20°C (Smith et al., 1978)	Freshwater 0.0005 mg/L @ 25°C(Davis and Parke, 1942)	
	Seawater	Seawater .005-0.01 mg/L @ 22°C (Rossi and Neff, 1979)	
Log Octanol/Water Coefficient	5.61(Radding et al., 1976) 5.60 (Leo et al., 1971)	5.97 (Callahan and Slimak, 1979)	6.4 (estimated)

4.10.4 Sources or Inputs

Based on the distribution of the benzanthracenes in Puget Sound, industrial and domestic sources appear to be the major input sources. There is no information on actual loadings of benzanthracenes to Puget Sound. Inputs may originate as a result of low level chronic inputs of petroleum hydrocarbons and fossil fuel combustion products. Other inputs of benzo(a)anthracene include wastewaters from foundries, coil coating, timber products processing, iron and steel manufacturing, and nonferrous metals manufacturing.

4.10.5 Summary of Biogeochemical Fate Data in the Marine Environment

4.10.5.1 Bioaccumulation - Uptake and Depuration

Summary Statement: Benzanthracenes accumulate in biota at levels as much as 18,000 times greater than concentrations in water. Metabolic conversion of bioaccumulated PAHs may result in compounds which may be of concern.

Review of Individual Studies: The partition coefficients shown in Table 4.10.2 indicate that the three compounds should have a high affinity for uptake by biological organisms and for adsorption to suspended solids and sediments containing organic carbon.

Oysters which were suspended in enclosures for 8 days were found by Lee et al. (1978) to have accumulated benzo(a)anthracene at a level 18,000 times greater than the ambient water concentration. When the oysters were transferred to uncontaminated waters, benzo(a)anthracene was slowly released and its half life in the oysters was 9 days.

Roesijadi et al. (1978) exposed the benthic species Macoma inquinata to marine sediments contaminated with Prudhoe Bay crude oil and found that dimethyl benzo(a)anthracene was bioconcentrated by a factor of 1349 above concentrations in water. Dimethyl benzo(a)anthracene had the highest bioconcentration factor of the PAHs studied, which included phenanthrene, chrysene, and benzo(a)pyrene.

The ratio of benzo(a)anthracene levels in Daphnia pulex to water concentration was found by Southworth et al. (1978) to be 10,109 ± 507 after 24 hours exposure. The uptake rate constant for benzo(a)anthracene was 669 ± 90/h and the elimination rate constant was 0.14 ± 0.02/h. The findings of these studies suggested that the Daphnia-PAH bioaccumulation factor was explainable primarily in terms of lipid/H_2O PAH partitioning.

Studies of the bioaccumulation of the benzanthracenes in higher aquatic organisms are complicated by the presence of metabolic elimination/detoxification mechanisms. For example, Varanasi et al. (described in Malins, 1980) found that dietary radio-labeled naphthalene can be readily converted by flatfish into a variety of oxygenated metabolites that remained in tissues for extended periods.

Because of the carcinogenic properties of the benzanthracenes, there is a need to understand the uptake and elimination (and hence persistence) of the compounds within biota, such as crabs, clams, and shrimp, and a need to identify and evaluate the metabolic products, if any, within such organisms. More extensive analyses of fish tissue are likewise required to determine the metabolic products to enable subsequent evaluations of the implications to consumers of such biota.

4.10.5.2 Metabolism

Summary Statement: Microbial degradation rates of benzanthracenes are very slow, but may be enhanced in sediments containing polychaete worms. Dihydroxy and catechol compounds may result upon metabolism. Nonetheless, biodegradation is not an important fate process for benzanthracenes.

Review of Individual Studies: Polyaromatic hydrocarbons can be metabolized by various levels of biological organisms. The mechanisms and efficiencies may, however, differ. Gibson (1976) stated that "mammals initiate the oxidation of aromatic hydrocarbons by the enzymatic incorporation of one atom of molecular oxygen to form physiologically-reactive arene oxides." Further metabolism would result in trans-dihydrodiols. In contrast, bacteria incorporate both atoms of molecular oxygen into aromatic hydrocarbons and cis-dihydrodiols are formed. Further oxidation may occur, with subsequent enzymatic fission of the aromatic nucleus (Figure 4.10.2).

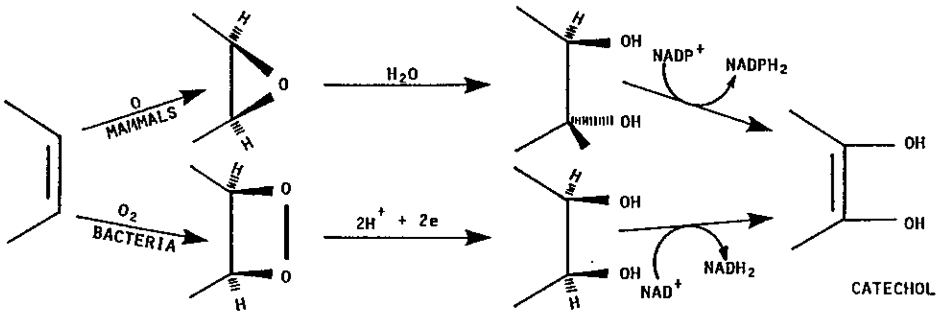


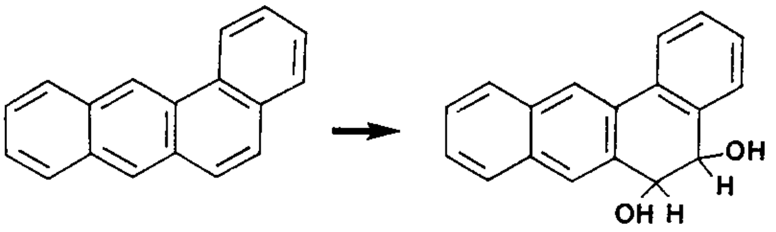
Figure 4.10.2
Mechanisms for Metabolic Oxidation of Aromatic Hydrocarbons

Several studies have been reported on the metabolism of benzo(a)anthracene. Three cis-dihydrodiols of benzo(a)anthracene were detected by Gibson (1976) as a result of metabolism by a mutant strain of the bacteria, Beijerinckia. A 30% conversion by the mutant bacteria was estimated for benzo(a)anthracene to the cis-dihydrodiols. Gibson (1976) speculated that the diol is probably metabolized further, but was uncertain whether metabolism would proceed beyond one ring.

Groenewegen and Stolp (1975) found that benzo(a)anthracene was susceptible to microbial attack in soil percolators. Their results indicated that microbial degradation of benzo(a)anthracene in natural systems, would probably occur at sediment-water interfaces.

Gardner et al. (1979) used a laboratory (20°C) flowing seawater system to study the effects of microbes and polychaete worms on the degradation of benzo(a)anthracene. Microbial degradation rates of benzo(a)-anthracene were 1.5-1.8% per week in coastal sand sediments and 1.4% per week in coastal marsh sediments. In the presence of the benthic polychaete worm, Capitella capitata, which is associated with areas of high oil input, degradation rates were increased to 2.7-3.0% per week in sand sediments and 1.8% in the marsh sediments. Two reasons were postulated for the increased degradation in the presence of the polychaete: 1) the worms improved conditions in the sediments for microbial degradation (i.e., mixing the sediment distributes nutrients to subsurface areas); and/or, 2) the worms metabolically degraded the compounds.

Lee et al. (1972) showed that cell free extracts of Capitella capitata have aryl hydrocarbon hydroxylase activity and benzo(a)anthracene can be taken up from sediment with subsequent metabolism to trans 5,6-dihydro, 5,6-dihydroxybenzo(a)anthracene (Figure 4.10.3). The same metabolite was also produced by large polychaetes such as Nereis succinea and Nereis virens (Lee et al., 1972). No further ring cleavage by the polychaetes was observed.



Trans 5,6-dihydro, 5,6-dihydroxybenzo(a)anthracene

Figure 4.10.3
Dihydroxy Metabolite of Benzo(a)anthracene

Short-term field tests with benzo(a)anthracene have not shown detectable microbial degradation. Lee et al. (1978), in experiments with C-14 labeled benzo(a)anthracene, found no $^{14}CO_2$ produced after 72 hours exposure in the waters of "controlled ecosystem enclosures" located in Saanich Inlet. Smith et al. (1978) failed to obtain enrichment cultures capable of degrading benzo(a)anthracene within a 6 week time frame in a freshwater system. As a result, a biodegradation rate of zero was assumed within the one compartment model of Smith et al. (1978). The investigators speculated that the enrichment procedures did not provide enough available benzo(a)anthracene for the organisms to utilize this substrate for growth, and they cautioned that their results should not "necessarily classify benzo(a)anthracene as a recalcitrant compound."

The low levels of benzo(a)anthracene in livers of Puget Sound fish indicate that the compound is metabolized to a high degree by fish. Other biological organisms have variable capabilities of metabolizing bioaccumulated benzo(a)anthracene; however, the overall role of metabolism by biota in reducing benzo(a)anthracene levels in the environment will be minimal.

No specific data for metabolism of dibenzo(a,h)anthracene or any isomer of methyl benzo(a)anthracene was found in the literature. Similar metabolic compounds would probably be obtained considering the similarities of the parent structures.

4.10.5.3 Sorption and Sedimentation

Summary Statement: Benzanthracenes are strongly adsorbed to sediments and suspended solids which contain organic material. Sorption is a major fate process for benzanthracenes.

Review of Individual Studies: The high log n-octanol/water partition coefficient for benzo(a)anthracene (log P = 5.6) indicates that the compound would be strongly adsorbed to sediments and suspended solids containing organic material. Lee (1977) determined that most of the benzo(a)anthracene within the waters from the Skidaway River estuary was adsorbed to organic detrital particles which were essentially a mixture of clay, phytoplankton and zooplankton remains, as well as dead and living bacteria. Very little adsorption to pure clay particles and free-floating bacterial or phytoplankton cells was observed. During a separate laboratory experiment, 53% of a 10 µg/L solution of benzo(a)anthracene was adsorbed to the particles after 3 hours exposure. In "controlled ecosystem enclosures" located in Saanich Inlet, Lee et al. (1978) recovered 39% of benzo(a)anthracene in sediments 17 days after addition to the water column. Benzo(a)anthracene was presumably carried there by particles originally in the water column.

Smith et al. (1978) evaluated the partition coefficients for benzo(a)-anthracene between water and several sediments with organic carbon levels from 0.6-3.8%. The partition coefficient varied from 10^4 for sediments of 0.6% organic carbon; 2 x 10^4 for 3.8% organic carbon sediments; and 2.8 x 10^4 for 1.4% organic carbon sediments.

Sorption of benzo(a)anthracene to bacterial cells could also be of significance. Smith et al. (1978) determined sorption coefficients of benzo(a)anthracene with bacterial cultures which varied from 2.5 to 3.9 x 10^4. Sorption to bacterial cells may be important in biomagnification.

Benzo(a)anthracene was found in suspended solids of Puget Sound at various levels. Riley et al. (1980) recorded benzo(a)anthracene levels in suspended solids from Hylebos Waterway which varied from <0.01 to

0.43 mg/kg (ppm). Levels in suspended solids from Blair Waterway varied from 0.01 to 0.34 ppm. Suspended solids from Budd Inlet and Port Madison contained less than 0.01 ppm benzo(a)anthracene. These levels are less than the levels reported in sediments from the same areas. On the basis of the work by Lee (1977) and Smith et al. (1978), such differences would not be expected because both investigators determined the sediments and suspended solids to contain similar levels of benzo(a)anthracene. It is possible that equilibrium conditions may not exist within Puget Sound.

4.10.5.4 Photolysis

Summary Statement: Benzanthracenes found in the photic zones of waters may photolyze to an undetermined degree. Photolysis is not expected to be an important fate process for benzanthracenes.

Review of Individual Studies: Benzo(a)anthracene strongly absorbs solar light from the near ultraviolet range (i.e., 297.5 nm to 390 nm). Absorption coefficients range from 3200 to 7930 M^{-1} cm^{-1} within the wavelength range from 297.5 nm to 330 nm. At 390 nm the coefficient drops to 417 M^{-1} cm^{-1} and at 400 nm the coefficient is 17.2 M^{-1} cm^{-1} (Smith et al., 1978).

The near ultraviolet wavelengths have limited penetration in ocean waters. Penetration will be affected by suspended solid concentrations, phytoplankton blooms, and by other dissolved organic compounds.

Benzo(a)anthracene molecules found in the first 1-2 m of the ocean layer may upon absorption of near ultraviolet light be converted to other compounds. McGinnes and Snoeyink (1974) and Smith et al. (1978) identified benzo(a)anthracene -7,12-quinone (Figure 4.10.4) as one photoproduct of benzo(a)anthracene. Of the benzo(a)anthracene molecules which did photolyze, 25% were converted to the quinone and 74% formed unknown products.

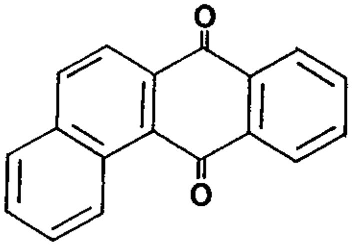


Figure 4.10.4
Structure of Benzo(a)anthracene 7,12- Quinone

Smith et al. (1978) calculated a photolytic half life of benzo(a)anthracene of approximately 1-2 hours (mid-day) and 3 hours (cloudy day) within the photic zone of a freshwater system. If suspended solids were in greater concentrations such as in the case of a eutrophic lake, the photolytic half life of benzo(a)anthracene would increase to 50 hours.

In a larger and deeper body of water such as Puget Sound, the role of photolysis would be much less than for the systems studied by Smith et al. (1978). The large quantities of benzo(a)anthracene in sediments of Puget Sound indicate that if photodegradation did occur, either its effect was not of significance or concentrations of benzo(a)anthracene were originally high.

4.10.5.6 Oxidation

Summary Statement: Free radicals may oxidize benzanthracenes. However, there is minimal information on the formation of free radicals in seawater and on the effects of the free radicals on organic compounds.

Review of Individual Studies: The Ocean Affairs Board of the National Research Council (1975) suggested that free radicals may form in the environment as a result of catalysis by light or metal ions and may play an important role in the destruction of oil slicks. Several investigators (Andelman and Snodgrass, 1974; Larson et al., 1976; and Nagata and Kondo, 1977) have suggested that benzo(a)anthracene is subject to photochemical oxidation in slicks or near surface waters.

Smith et al. (1978), using 4, 4'-arobis (4 cyano valeric acid) as a source of free radicals, attained oxidation of benzo(a)anthracene at a rate of $5 \times 10\ M^{-1} sec^{-1}$. With a consistent source of free radicals, the half life of benzo(a)anthracene in a one compartment model due to photo-oxidation would be in the order of 38 hours. No in-situ studies with benzo(a)anthracene were attempted. Studies by Lee et al. (1978) with benzo(a)pyrene in "controlled ecosystem enclosures", suggested that as much as 50% of the benzo(a)pyrene was photo-oxidized. No attempt was made to determine the reaction products.

The role of free radical reactions within a marine system may be significant. Currently, it is difficult to predict the possible effects of this process on contaminants in Puget Sound.

4.10.5.7 Volatilization

Summary Statement: Volatilization is probably not of significance for the fate of benzanthracenes.

Review of Individual Studies: Southworth (1979) determined the relative volatility of two to five ring PAH structures in water and attempted to estimate the function of volatilization in removing PAHs from aquatic environments. On the basis of a Henry's Law constant of 3.28 ± 0.46 x 10^{-4}, volatilization half lives were calculated under varying conditions of wind and current velocity in a stream 1.0 m in depth (Figure 4.10.5).

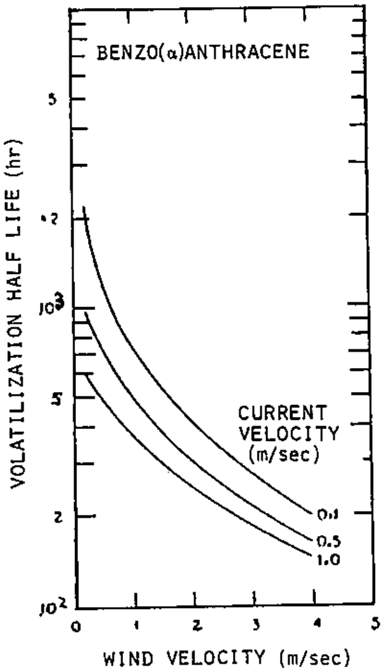


Figure 4.10.5
Effect of Wind and Current Velocity
in Volatilization of Benz(a)anthracene

Southworth (1979) cautioned that the calculations yielded maximum volatilization rates. Bulk fluid mixing and phenomena such as stratification and adsorption to sediments would affect volatilization. The volatilization rates for Puget Sound would therefore be lower (and the half lives higher) than those noted within Figure 4.10.5.

Smith et al. (1978) predicted volatilization half lives in excess of 1,000 hours for benzo(a)anthracene in eutrophic and oligotrophic lakes. A volatization rate constant of 0.0016 ± .0006 kv^{o} was calculated. Compared to the other fate processes, volatilization was not considered to be of significance for benzo(a)anthracene. This observation probably also holds true for Puget Sound.

4.10.6 Ecosystem Fate Studies

There are several papers in the literature which report the results of efforts to determine the relative effects of environmental processes on benzo(a)anthracene concentrations. Lee (1977) reported no observable degradation rate of benzo(a)anthracene within 48 hours in estuarine waters of the Skidaway River which drains into the Gulf Stream.

Lee et al. (1978) published the results of a "controlled ecosystem" study whereby benzo(a)anthracene and two other PAHs were added to suspended enclosures located in Saanich Inlet near Sidney, British Columbia. The enclosures enabled the determination of: degradation rates of the PAHs; adsorption rates by the sediments; and uptake rates by plankton. The concentrations of benzo(a)anthracene appeared to be primarily affected by sedimentation and photochemical oxidation.

The results of a more extensive marine microcosm study were reported by Hinga et al. (1980). Carbon-14 labeled benzo(a)anthracene was added to a microcosm. Observations were made of: the fate of the parent compound; the production of metabolites; and $^{14}CO_2$ over a period of 230 days. The following observations were made:

1. After 216 days, 21% of the total ^{14}C-activity initially added as ^{14}C benzo(a)anthracene remained as benzo(a)anthracene, 29% was converted to $^{14}CO_2$ and 22% was present in the form of intermediate products.

2. The labeled intermediate products were believed to be a result of microbial and photochemical processes.

3. After 220 days, 1% of the ^{14}C-activity initially added was found in the water column and from 19-44% was found in the sediment.

4. Once incorporated into sediments, the benzo(a)anthracene and its metabolites were mixed deeper into the sediments by benthic animal activity.

5. Measurable $^{14}CO_2$ production took place in sediments and no production occurred in water.

6. Most of the ^{14}C-labeled metabolites were found in the top centimeter of sediment, indicating the possible need for oxidizing conditions. Anoxic conditions will decrease degradation rates appreciably.

7. Local patchiness of chemical distributions was observed in sediments indicating the effects of varying feeding and burrowing strategies.

8. Depending upon temperature, half lives of benzo(a)anthracene on the environment may vary from 1.2 to 3 years.

9. Concern was expressed about the possible environmental effects of metabolites and reaction products of PAHs.

Benzo(a)anthracene was also carefully studied within a freshwater system by Smith et al. (1978). The conclusions of this investigation were similar to those of Lee et al. (1978) and Hinga et al. (1980) in that photolysis and sorption dominate the transformation and removal processes.

No overall fate studies of dibenzanthracene or methyl benzo(a)-anthracene were found in this literature review.

4.10.7 Conclusions

1. On the basis of the literature review, the environmental compartment most susceptible to contamination by benzo(a)anthracene, methyl benzo(a)anthracene and dibenzanthracene is the bottom sediment phase.
2. Benzo(a)anthracene bioaccumulates readily in biota; however, its persistence on biota may be affected by metabolic processes.
3. Metabolites may be formed which may be as toxic and/or as persistent as the parent compound itself.
4. Other fate processes do not appear to be significant, although the degree of photochemical degradation in a large body of water such as Puget Sound is uncertain.
5. The levels of the benzanthracenes in biota of Puget Sound are higher than most other areas reported in the literature. The persistence and widespread distribution of the compounds implies a need for efforts to evaluate the "real" hazards of the compounds to the environment

4.10.8 Research Needs

1. There is a need to identify and quantitate levels of metabolites of benzo(a)anthracene within edible portions of biota and to evaluate the toxicities of the metabolites.
2. There is a need for chronic and acute toxicity data to determine the effects of benzo(a)anthracene and dibenzo(a)anthracene levels in water and sediments.

References

Andelman, J.B. and J.E. Snodgrass. 1974. Incidence and significance of polynuclear aromatic hydrocarbons in the water environment. CRC Critical Rev. Environ. Control 4:69-83.

Brown, D. 1979. Memo to Ed Long, Bruce McCain, re: Analyses of Puget Sound samples (October 19, 1979).

Callahan, M.A. and M.W. Slimak. 1979. Water-Related Environmental Fate of 129 Priority Pollutants. EPA 440/4-79-0296.

Coombs, M.M., C. Dixon, and A.M. Kissonerghis. 1976. Evaluation of mutagenicity of compounds of known carcinogenicity, belonging to the benzo(a)-anthracene, chrysene, and cyclopenta(a)phenanthrene series, using Ame's test. Cancer Res. 36:4525-4529.

Davis, W.W. and T.V. Parke, Jr. 1942. Determination of solubilities of extremely low order. J. Amer. Chem. Soc. 64:101-107.

Gardner, W.S., R.L. Lee, K.R. Tenore, and C.W. Smith. 1979. Degradation of selected polycyclic aromatic hydrocarbons in coastal sediments: importance of microbes and polychaete worms. Water, Air, Soil Pollut. 11:339-347.

Gibson, D.T. 1976. Microbial degradation of carcinogenic hydrocarbons and related compounds. In: Sources, Effects and Sinks of Hydrocarbons in the Aquatic Environment. American Institute of Biological Sciences, Washington, D.C. pp. 224-238.

Groenewegen, D. and H. Stolp. 1975. Microbial degradation of polycyclic aromatic hydrocarbons. Erdoel Kohle, Erdgas, Petrochem. Brennst. Chem. 28:206.

Hinga, R., M.E.Q. Pilson, R.F. Lee, J.W. Farrington, K. Tjessem, and A.C. Davis. 1980. Biogeochemistry of benzanthracene in an enclosed marine ecosystem. Environ. Sci. Technol. 14:1136-1143.

Jones, D.W. and J.M. Sowden. 1979. Shapes of carcinogenic benz(a)anthracenes: the crystal molecular structure of 1-methylbenz(a)anthracene. Cancer Biochem. Biophys. 4:43-47.

Larson, R.A., D.W. Blankenship, and L.L. Hunt. 1976. Toxic hydroperoxides: photochemical formation from petroleum constituents. In: Sources, Effects and Sinks of Hydrocarbons in the Aquatic Environment. American Institute of Biological Sciences, Washington, D.C. pp. 298-308.

Lee, R.F., R. Sauerherber, and G.H. Dobbs. 1972. Uptake, metabolism, and discharge of polycyclic aromatic hydrocarbons by marine fish. Mar. Biol. 17:201-208.

Lee, R.F. 1977. Metabolism of Petroleum Hydrocarbons in the Aquatic Environment. American Institute of Biological Sciences, Washington, D.C.

Lee, R.F., W.F. Gardner, J.W. Anderson, J.W. Blaylock and J. Barwell-Clark. 1978. Fate of polycyclic aromatic hydrocarbons in controlled ecosystem enclosures. Environ. Sci. Technol. 123:832-838.

Leo, A., C. Hansch and D. Elkins. 1971. Partition coefficients and their uses. Chem. Rev. 71:525-616.

Malins, D. 1980. Pollution of the marine environment. Environ. Sci. Technol. 14:32-37.

Malins, D.C., B.B. McCain, D.W. Brown, A.K. Sparks, and H.O. Hodgins. 1980. Chemical Contaminants and Biological Abnormalities in Central and Southern Puget Sound. NOAA Technical Memorandum OMPA-2. Office of Marine Pollution Assessment, Boulder, Colo. 295 pp.

May, W.E. and S.P. Wasik. 1978. Determination of the solubility behavior of some polyaromatic hydrocarbons in water. Anal. Chem. 50:997-1000.

McGinnes, P. and V.L. Snoeyink. 1974. Determination of the fate of polynuclear aromatic hydrocarbons in natural water Systems. Illinois Water Resources Research Report No. 80. 60 pp.

Nagata, S. and G. Kondo. 1977. Proceedings 1977 Oil Spill Conference. American Petroleum Institute, Washington, D.C. pp. 617-625.

National Institute for Occupational Safety and Health (NIOSH). 1979. Registry of Toxic Effects of Chemical Substances (RTECS).

Ocean Affairs Board of the National Research Council. 1975. Assessing potential ocean pollutants.

Pancirov, R.J. and R.A. Brown. 1977. Polynuclear aromatic hydrocarbons in marine tissues. Environ. Sci. Technol. 11:989-992.

Radding, S.B., T. Mill, C.W. Gould, D.H. Liu, H.L. Johnson, D.C. Bomberger, and C.V. Fojo. 1976. The Environmental Fate of Selected Polynuclear Aromatic Hydrocarbons. EPA 560/5-75-009. 122 pp.

Riley, R.G., E.A. Crecelius, D.C. Mann, K.H. Abel, B.L. Thomas, and R.M. Bean. 1980. Quantitation of Pollutants in Suspended Matter and Water from Puget Sound. NOAA Technical Memorandum ERL MESA-49. Marine Ecosystems Analysis Program, Environmental Research Laboratories, Boulder, Colo. 99 pp.

Roesijadi, G., J.W. Anderson, and J.W. Blaylock. 1978. Uptake of hydrocarbons from marine sediments contaminated with Prudhoe Bay crude oil: Influence of feeding type of test species and availability of polycyclic aromatic hydrocarbons. J. Fish. Res. Bd. Can. 35:608-614.

Rossi, S.S. and J.M. Neff. 1978. Toxicity of polynuclear aromatic hydrocarbons to the polychaete Neanthes arenaceodentata. Marine Pollut. Bull. 9:220-223.

Seattle METRO. 1979. Unpublished data submitted to contractor.

Smith, J.H., W.R. Mabey, N. Bohonos, B.R. Holt, S.S. Lee, T.-W. Chou, D.C. Bomberger, and T. Mill. 1978. Environmental Pathways of Selected Chemicals in Freshwater Systems; Part II: Laboratory Studies. EPA 600/7-78-074.

Southworth, G.R. 1977. Transport and Transformation of Anthracene in Natural Waters: Process Rate Studies. U.S. Dept. of Energy, Oak Ridge National Lab., Tenn. 26 pp.

Southworth, G.R., J.J. Beauchamp, and P.K. Schmiedev. 1978. Bioaccumulation potential of polycyclic aromatic hydrocarbons in Daphnia pulex. Water Res. 12:973-977.

Southworth, G.R. 1979. The role of volatilization in removing polycyclic aromatic hydrocarbons from aquatic environments. Bull. Environ. Cotnam. Toxicol. 21:507.

4.11 Fluoranthenes

4.11.1 Introduction

Fluoranthene consists of three aromatic rings which are fused and bridged as shown in Figure 4.11.1. Fluoranthene, methyl fluoranthene, and several benzofluoranthenes were detected in Puget Sound.

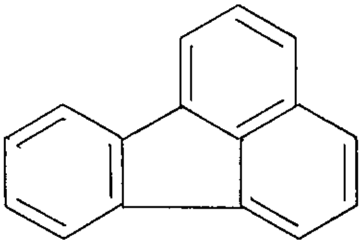


Figure 4.11.1
Structure of Fluoranthene

NIOSH (1979) Registry of Toxic Effects, lists fluoranthenes as co-carcinogens and/or carcinogens. Biota appear to be quite sensitive to small quantities of fluoranthene in water. The data search did not retrieve much information on the environmental fate of fluoranthenes and discussions are, therefore, relatively brief.

The concentrations of fluoranthenes were generally less than detection limits in most biota samples from Puget Sound; however, the levels in sediments were extremely high. In many samples, for example, fluoranthenes and benzofluoranthenes were the most dominant PAHs.

4.11.2 Significance to Puget Sound

4.11.2.1 Review of Known Toxicity Data

EPA (1978) Ambient Water Quality Criteria suggest a 24-hour average marine concentration of 0.30 µg/L of fluoranthene with a maximum concentration of 0.69 µg/L for the protection of saltwater organisms. The criteria are based on several toxicity tests which included tests with mysid shrimp for which 40 µg/L was acutely toxic and 16 µg/L was chronically toxic. A measured bioconcentration factor is unavailable for fluoranthene. However, the EPA during its development of the Ambient Water Quality Criteria, used a calculated log n-octanol/water partition coefficient of 79,000 to estimate a bioconcentration factor of 3,100 for aquatic organisms which have a lipid content of 8%.

Fluoranthene has been labeled as a potent cocarcinogen in the EPA (1978) Ambient Water Quality Criteria Document. Fluoranthene will enhance the yield of benzo(a)pyrene induced carcinogens in mice. At high feeding concentrations to test species, fluoranthene has exhibited positive tumorigenic activity; however, it is not currently categorized by NIOSH as a carcinogen. One of the methylated forms, 2-methyl fluoranthene, is labeled with NIOSH as an active carcinogen. Alkylation appears to enhance the carcinogenicity of the fluorene molecule considerably.

Benzo(b)fluoranthene and benzo(j)fluoranthene are listed as positive carcinogens for animals in the NIOSH (1979) Registry of Toxic Effects. Benzo(k)fluoranthene has been shown to act as a tumorigenic agent in mice. EPA Ambient Water Quality Criteria are unavailable for benzofluoranthene.

4.11.2.2 Possible Effects of Levels Found in Puget Sound

Tables 4.11.1 and 4.11.2 summarize the levels of fluoranthene and benzofluoranthenes detected in various environmental compartments of Puget Sound. The levels of fluoranthene in sediments of the Seattle and Tacoma Harbors were much higher than the 0.11-0.79 ppm (µg/g) levels reported in sediments of Buzzard's Bay, Massachussets, by Giger and Blumer (1974). The effects of the sediment-associated fluoranthenes on Puget Sound biota are not known. Assuming that fluoranthene with a log P of 5.3, has similar soil to water distribution factors (i.e., 104) as benzo(a)anthracene which has a log P of 5.6, then it may be estimated that fluoranthene levels in interstital waters may go as high as 1.4 µg/L, which is in excess of the EPA (1978) Ambient Water Quality Criteria. This value was obtained by dividing the maximum observed concentration in sediment (i.e., 14,000 µg/kg) by the 104 distribution coefficient.

The fluoranthenes were selected as contaminants of concern on the basis of their positive carcinogenic activity, their potential chronic effects, and widespread distribution in Puget Sound.

4.11.3 Physical Properties of Fluoranthenes

Table 4.11.3 outlines some of the known physical properties of the fluoranthenes. The compounds are characterized by low solubility, low vapor pressure, and high partition coefficients.

Solubility data could only be found for fluoranthene. Hollifield (1979) reported a solubility of 0.12 mg/L in distilled water. Solubilities of methyl fluoranthene and the benzofluoranthenes will be less than the value reported for fluoranthene. Rossi and Neff (1978) reported a solubility of fluoranthene in seawater as 0.1 ± 0.06 ppm. The EPA in its derivation of Water Quality Criteria suggested that the presence of fluoranthene can be increased through micelle (a molecular aggregate that constitutes a colloidal particle) formation by optimum synthetic detergent concentrations and by the action of certain organic solvents.

Table 4.11.1

Dry Weight Concentration in µg/g (ppm) of Fluoranthene Found at Various Locations in Central Puget Sound*

	Sediment Avg.(Range)	Suspended Solids	Water (ppt)	Fish Livers	Crab Hepatopancreas	Worms	Shrimp	Clam
Case Inlet	0.054 (.007-0.1)	-	<1	<.006	<.02	-	0.27	<.01
Port Madison	0.055 (0.03-0.08)	0.15	<1	<.009	-	.04	.03	.04
Sinclair Inlet	0.8 (.16-2.3)	0.54	<1	<008	.04	.08	0.2	0.28
Budd Inlet	0.12 (0.08-0.16)	0.08	25±35	<.005	<.03	-	.07	0.28
Duwamish Waterway	1.93 (.16-3.7)	0.36	<1	<0.02	0.03	1.5	0.14	1.3
Seattle Waterfront (incl. Harbor Isl.)	7.0 (.03-14)	0.31 (0.25-.37)	<1	<0.02	-			0.10
Outer Elliott Bay	.02	-	<1	-	-	0.05-.08	.04	-
West Point	6.1	-	<1	-	-	-	-	-
Hylebos Waterway	4.05 (1.7-6.4)	0.83	<1	<.01-.120	0.10	0.18-2	0.28	0.28
Commencement Bay Waterways	3.06 (0.03-6.1)	2.9 (2.34-3.45)	<1	<.190	0.03	0.38	-	0.79
Brown's Point	.09	-	<1	-	-	-	0.08	-
SW Commencement Bay	0.065 (0.04-.09)	-	<1	-	-	-	-	-

*from Malins et al. (1980), Riley et al. (1980), and Brown (1978)

Table 4.11.2

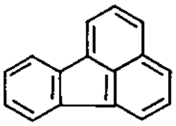
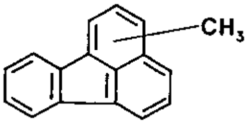
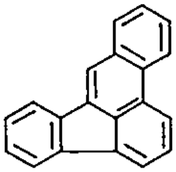
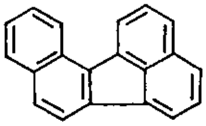
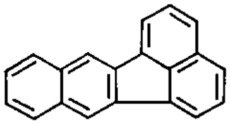
Benzofluoranthene Levels in Puget Sound*
(Benzo(i,b and k)fluoranthenes) (ug/kg) (ppb) dry weight

Sampling Location	Sediment	Fish Livers	Crab	Worm	Shrimp	Clam
Elliott Bay						
Magnolia Bluff	130	<1				
Pier 54	4700					240
Harbor Island	2500	< 40				
West Point	6800	< 30-<70				
Alki Point	20					
Duwamish(lower)	1360			<10	<10	230
Duwamish W.	8400					
Duwamish E.	730		<5			
Pier 86	1300					
Central Elliott Bay	570	< 1.0-<50		<20-<30	<10	
Pier 42	30-40					
Corps Dumpsite	260					
Pier 70	480					
Commencement Bay						
Hylebos Turning Basin	2900					
Hylebos	11,000	< 1-<70	<10	<20-2910	80	< 90
Blair	720					
Sitcum	200					
City	6600			330		
Puyallup	4.0					
Between Blair & Hylebos	70					
NE Bay	1800					
Old Tacoma	1100					
Outer Bay	70	< 2-<170				
Brown's Point	70	< 30-<50			< 10	
Port Madison	40-80	<20		<10	< 10	<30
Budd Inlet	70-120	<8	<10		< 5	
Case Inlet	7-60	<9	<10		170	<40
Sinclair Inlet	290-1800	<20	<5	<10	30	240

* Malins et al. (1980)

Table 4.11.3

Some Physical Properties of Fluoranthenes*

Compound	CAS Number	Molecular Weight	Solubility (ppm)	log P	Vapor Pressure (torr)
Fluoranthene 	206440	202.3	0.12	5.33	10^{-6}-10^{-4}
Methyl fluoranthene  	2-methyl 33543316	216.29			
	3-methyl 1706010	216.29			
Benzo(b)fluoranthene 	205992	252.32		6.57	10^{-11}-10^{-6}
Benzo(i)fluoranthene 		252.32			
Benzo(k)fluoranthene 	207089	252.32			959 x 10^{-11}

*Callahan and Slimak (1979)

4.11.4 Sources or Inputs

Both natural and man-made sources appear to be responsible for fluoranthene levels in the environment. Man-made sources appear to be shipping and harbor oil discharges and industrial effluents from oil refineries, coke production industries, plastic and dyestuff industries, and industries using high temperature furnaces. Borneff and Kunte (1965) indicated that road runoff can be a source of fluoranthene as a result of bituminous road surfaces, car tire wear, and vehicle exhausts.

The EPA review of fluoranthene levels in discharges indicates that timber products processing is a significant source of fluoranthenes. Median levels of 1,600 ppb were found in such effluents with maximum levels up to 35,000 ppb.

4.11.5 Summary of Biogeochemical Fate Data in the Marine Environment

Only two papers were found which described any aspect of biogeochemical fate of fluoranthene or benzofluoranthene.

Prahl and Carpenter (1979) studied the sedimentary fluxes of fluoranthene, benzo(b)fluoranthene and benzo(k)fluoranthene within Dabob Bay, Puget Sound. Concentrations of fluoranthene in sediments and vertically transported particulates were 64 ng/g and 82 ng/g, respectively. Using concentration values normalized to organic carbon content, the authors reported that the fluoranthenes were "chemically refractory despite significant recycling of total organic carbon by benthic respiration." Similar concentrations were found in studies with $HgCl_2$ poisoned sediment traps and unpoisoned surface sediments implying that biodegradation of the fluoranthenes in sediments was not significant.

Prahl and Carpenter (1979) found that PAH levels were similar in plankton, zooplankton fecal pellets, and sediments, and concluded that transported fecal pellets furnish the primary mode of introduction of PAHs to sediments. Seasonal fluctuations were observed and correlated to deposition of the PAH via carbon particles from atmospheric aerosols or to association with eroded material. Sorption is, therefore, an important fate process for fluoranthene.

Fluoranthene was one of the PAHs added to the controlled ecosystem enclosures by Lee et al. (1978). Fluoranthene was observed to reach the sediments via sinking phytoplankton. Within 10 days, the concentration in water at 3 m decreased from 6.2 ppb to 0.1 ppb. After 17 days, 10% of the fluoranthene added was found in the sediment.

Oysters exposed to PAHs in the enclosure bioaccumulated 5 ppm fluoranthene in 2 days from water containing 7.2 ppb fluoranthene. After 23 days depuration time, 0.4 ppm fluoranthene remained in the tissue. A half life of 5 days was calculated.

Lee et al. (1978) suggested that photo-oxidation and sedimentation would be the more significant fate processes for fluoranthene. Photo-oxidation was assumed to be a significant process on the basis of publications by Nagata and Kondo (1977) and by Larson et al. (1976). The publications investigated photo-oxidation of PAHs, and fluoranthenes were not studied. However, applicability of the results are questionable. Nagata and Kondo (1977), for example, exposed high concentrations of PAHs dissolved in water-organic solvents to several hours of irradiation by a high pressure UV lamp, the conditions of which are much different from natural exposure to sunlight.

4.11.6 Conclusions

1. The fluoranthenes are the most predominant PAHs (in terms of concentration) within Puget Sound.

2. Despite their high partition coefficients, fluoranthene concentrations in biota are in most cases low, indicative of possible rapid metabolism.

3. Sorption is an important fate process.

4. Microbial biodegradation of fluoranthenes and benzofluoranthenes is probably minimal within the marine environment.

4.11.7 Research Needs

1. Uptake studies and identification of metabolites, if any, within biota would aid considerably in the evaluation of the environmental hazard of fluoranthenes and benzofluoranthenes in Puget Sound.

2. Studies are required on possible chronic effects of high concentrations of fluoranthenes in sediments on benthic species.

References

Borneff, J. and H. Kunte. 1965. Carcinogenic substances in water and soil: About the origin and evaluation of PAH in water. Arch. Hyg. Bakt. 149:226.

Brown, D. 1978. Memorandum to E. Long, MESA Puget Sound Project.

Callahan, M.A. and M.W. Slimak. 1979. Water-Related Environmental Fate of 129 Priority Pollutants. EPA 440/4-79-0296.

Environmental Protection Agency. 1978. Ambient Water Quality Criteria: Fluoranthene. NTIS (PB 292 433).

Giger, W. and M. Blumer. 1974. Polycyclic aromatic hydrocarbons in the environment: Isolation and characterization by chromatography visible, ultraviolet and mass spectrometry. Anal. Chem. 46:1163-1171.

Hollifield, H.C. 1979. Rapid nephelometric estimate of water solubility of highly insoluble organic chemicals of environmental interest. Bull. Environ. Contamin. Toxicol. 23:579-586.

Larson, R.A., D.W. Blankenship, and L.L. Hunt. 1976. Toxic hydroperoxides: photochemical formation from petroleum constituents. In: Sources, Effects, and Sinks of Hydrocarbons in the Aquatic Environment. American Institute of Biological Sciences, Washington, D.C. pp. 298-308.

Lee, R.F., W.F. Gardner, J.W. Anderson, J.W. Blaylock, and J. Barwell-Clarke. 1978. Fate of polycyclic aromatic hydrocarbons in controlled ecosystem enclosures. Environ. Sci. Technol. 123:832-838.

Malins, D.C., B.B. McCain, D.W. Brown, A.K. Sparks, and H.O. Hodgins. 1980. Chemical Contaminants and Biological Abnormalities in Central and Southern Puget Sound. NOAA Technical Memorandum OMPA-2. Office of Marine Pollution Assessment, Boulder, Colo. 295 pp.

Nagata, S. and G. Kondo. 1977. Proceedings of the 1977 Oil Spill Conference. American Petroleum Institute. Washington, D.C. pp. 617-625.

National Institute for Occupational Safety and Health (NIOSH). 1979. Registry of Toxic Effects of Chemical Substances (RTECS).

Prahl, F.G. and R. Carpenter. 1979. The role of zooplankton fecal pellets in the sedimentation of polycyclic aromatic hydrocarbons in Dabob Bay, Washington. Geochim. Cosmochim. Acta. 43:1959-1972.

Riley, R.G., E.A. Crecelius, D.C. Mann, K.H. Abel, B.L. Thomas, and R.M. Bean. 1980. Quantitation of Pollutants in Suspended Matter and Water from Puget Sound. NOAA Technical Memorandum ERL MESA-49. Marine Ecosystems Analysis Program, Environmental Research Laboratories, Boulder, Colo. 99 pp.

Rossi, S.S. and J.M. Neff. 1978. Toxicity of polynuclear aromatic hydrocarbons to the polychaete Neanthes arenaceodentata. Mar. Pollut. Bull. 9:220-223.

4.12 Benzo(a)pyrene

4.12.1 Introduction

Benzo(a)pyrene (BaP) is a recognized carcinogen (NIOSH, 1979). It is found in low levels in crude and refined oils and has been identified in combustion products of wood, peat, coal, and petroleum (Johnston, 1976). Furthermore, it has been identified in the marine environment as a result of leaching from creosote treated pilings or timbers (Dunn, 1976).

Benzo(a)pyrene has been identified in sediments of Puget Sound at levels as high as 4 mg/kg and it appears to be widely dispersed throughout Puget Sound. Levels of the compound in biota were, however, quite low (Malins et al., 1980).

Benzo(a)pyrene has already been discussed to some extent in Section 4.8. Its properties in the environment are quite similar to those of benzo(a)anthracene, and many of the research needs already outlined for PAHs are applicable to benzo(a)pyrene. As a result, only a brief review of the biogeochemical fate of benzo(a)pyrene in the marine environment is provided.

Benzo(a)pyrene is widely distributed in the environment as a result of both natural and anthropogenic sources. It is found in many foodstuffs, cigarettes and alcoholic beverages. Risk assessment to consumers of contaminated biota must therefore address the question of how much extra dietary intake constitutes a level of "unacceptable" risk. Furthermore, risk assessment must address the question of whether a chemical which is a carcinogen to humans, is a potential carcinogen to aquatic biota. Benzo(a)pyrene is one of the EPA's 129 Priority Pollutants.

4.12.2 Significance to Puget Sound

4.12.2.1 Review of Known Toxicity Data

As noted previously, benzo(a)pyrene is a recognized carcinogen (NIOSH, 1979). The implications of the presence of benzo(a)pyrene in the marine environment are difficult to assess. Ishio et al. (1970) implied that polyaromatic hydrocarbons appeared to be responsible for cancerous growths in the tissue of the seaweed Porphyra tenera growing in the proximity of wastes from the Japanese coal chemical industry. Shimkin et al. (1951) detected benzo(a)pyrene in barnacles from the coast of California. Extracts from the barnacles injected into mice produced subcutaneous carcinomas. Malins et al. (1980) reported that the incidence of liver lesions in fish from Puget Sound was generally highest in fish from areas in Commencement and Elliott Bays with the highest levels of sediment-associated contaminants (particularly PAHs and certain metals). The contributions of individual contaminants such as benzo(a)pyrene to the incidence of liver lesions could not be isolated because of the large number of other contaminants detected within the areas.

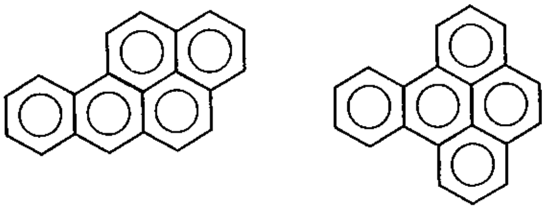
4.12.2.2 Possible Effects of Levels Found in Puget Sound

Table 4.12.1 reviews the levels at which benzo(a)pyrene has been detected in biota and sediments of Puget Sound. Table 4.8.1 provides comparisons of levels of benzo(a)pyrenes detected in Puget Sound biota with levels in biota from other areas in North America. It can be noted that the levels of benzo(a)pyrene in clams, crabs, and shrimp from Commencement and Elliott Bays are appreciably higher than levels detected in clams from ocean waters of the eastern United States.

Consumption of benzo(a)pyrene contaminated biota may imply some degree of risk to wildlife and man. Such risk assessment is beyond the current state of the art. It is, therefore, essential to develop an appropriate risk assessment program for Puget Sound which could be continually updated in view of newly developed information.

4.12.3 Physical Properties of Benzo(a)pyrene

Benzo(a)pyrene consists of five conjugated aromatic rings as shown in Figure 4.12.1. Benzo(e)pyrene, a non-carcinogenic structure, is also shown for comparative purposes.



Benzo(a)pyrene

Benzo(e)pyrene

Figure 4.12.1

Structures of Benzo(a)pyrene and Benzo(e)pyrene

A vapor pressure of 10^{-10}torr was calculated for benzo(a)pyrene (Callahan and Slimak, 1979). Its solubility in freshwater is approximately 0.004 mg/L (MacKay and Shui, 1977), and its log n-octanol/water partition coefficient is 6.04 (Radding et al., 1976). These physical properties would imply that benzo(a)pyrene is highly susceptible to uptake by biota, highly susceptible to adsorption to organic-containing sediments, and subject to minimal, if any, volatilization.

Table 4.12.1

Concentration in µg/g (ppm) Dry Weight of Benzo(a)pyrene Found at Various Locations in Central Puget Sound*

Subarea	Sediment avg. (# samples)[a] (range)	Fish Livers[b]	Crab Hepato-pancreas	Worm	Shrimp	Clam
Case Inlet	0.019 (2) (0.030, 0.0070)	< 0.0090 (2)	<0.010 (1)	-[c]	0.090 (1)	<0.010 (1)
Port Madison	0.020 (2) (0.030, 0.0090)	< 0.020 (2)	-	<0.010 (1)	<0.010 (1)	<0.010 (1)
Sinclair Inlet	0.30 (4) (0.83, 0.070)	< 0.020 (2)	< 0.0050 (1)	< 0.010 (1)	0.070 (1)	0.12 (1)
Budd Inlet	0.027 (3) (0.040, 0.010)	< 0.0070 (2)	< 0.010 (1)	-	0.030 (1)	
Duwamish Waterway	0.56 (6) (1.5, 0.040)	< 0.040 (6)	0.020 (1)	0.35 (1)	<0.010 (1)	0.23 (1)
Seattle Waterfront	0.52 (6) (2.2, 0.010)	< 0.030 (2)	-	-	-	0.10 (1)
Outer Elliott Bay	0.077 (4) (0.18, 0.0060)	< 0.090 (4)	-	< 0.030 (2)	<0.010 (1)	-
West Point	4.0 (1)	0.070 (2)	-	-	-	-
Hylebos Waterway	0.53 (5) (1.7, 0.020)	0.37 (1/11)	< 0.010 (1)	0.73 (1/2)	0.050 (1)	<0.020 (1)
Commencement Waterways	0.58 (5) (2.6, 0.0020)	-	< 0.0050 (1)	0.25 (1)	-	0.25 (1)
Southwest Commencement Bay	0.12 (3) (0.34, 0.0060)	< 0.080 (3/4)	-	-	-	-
Brown's Point	0.010 (1)	0.21 (1/2)	-	-	< 0.010 (1)	

*Malins et al. (1980)

[a] Where nondetectable levels of material were observed, a ratio of the number of samples with detectable levels to the total number of samples was substituted.

[b] English and rock sole species

[c] - signifies that no sample was taken

4.12.4 Sources or Inputs

As mentioned in the introduction, benzo(a)pyrene (BaP) has been identified in combustion products of wood, peat, coal, and petroleum, and in crude and refined oils. Mix and Schaffer (1979) in their studies of BaP levels in mussels in Yaguina Bay, Oregon, could not pinpoint the sources of BaP; however, they indicated that creosote treated pilings, marinas, fish processing factories, and boat traffic were probable sources. Dunn (1976) found there was a marked correlation between the presence of human activity in coastal areas and the contamination of mussels by BaP. Harrison et al. (1975) showed that storm runoff is a source of BaP, as are slashburned areas of watersheds.

Dunn (1976) found wet-weight averages of 0.55 µg/kg benzo(a)pyrene in mussels from shorelines designated as "outer Vancouver Harbor" (British Columbia, Canada), 1.78 µg/kg in mussels from a moderate sized marina and 49.2 µg/kg in mussels from creosote treated pilings.

The EPA (1980) Treatability Manual lists two industrial wastewaters as major sources of BaP: timber products processing; and auto and other laundries. Similar sources of BaP within the Puget Sound area are possible.

4.12.5 Summary of Biogeochemical Fate Data in the Marine Environment

4.12.5.1 Bioaccumulation - Uptake and Depuration

Summary Statement: Bioaccumulation studies of benzo(a)pyrene by fish have been complicated by the rapid metabolism of the compound and its conversion to unknown products. Invertebrates such as clams will bioaccumulate BaP from the water phase.

Review of Individual Studies: Biological uptake studies of benzo(a)-pyrene have predominantly utilized invertebrate test species possibly because vertebrate species, such as fish, metabolize polyaromatic hydrocarbons, hence, complicating interpretation of uptake data.

Roesijadi et al. (1978) exposed the bivalve *Macoma inquinata* for 7 days to oil contaminated sediments and found that the concentration factor for benzo(a)pyrene uptake from sediment was 0.09 compared to an uptake concentration factor from water of 861 (i.e., a seawater concentration of 0.04 µg/L and final tissue level of 37 µg/kg). Long-term exposure of *M. inquinata* to contaminated sediments showed continuing increases of benzo(a)pyrene within the bivalves despite decreasing quantities of BaP in the sediments, indicating that equilibrium was not quickly reached with benzo(a)pyrene and that benzo(a)pyrene would be relatively persistent in tissue of exposed bivalves (Roesijadi et al., 1978).

Mix and Schaffer (1979) showed that seasonal trends of benzo(a)pyrene bioaccumulation are possible. Several possible explanations were offered, including: decreases in August and September as a result of decreases in BaP because of photo-oxidation; BaP body burden could depend upon degree of gonadal maturation; or increased levels of BaP could be the result of reduced temperatures. Levels of BaP in bivalves from some sites varied from 1.9 to 170 µg/kg over a 2-year sampling period.

Freshwater studies by Lu et al. (1977) found that fish metabolize benzo(a)pyrene about "as fast as it is adsorbed and converts it to unextractable products." However, the authors noted minimal degradation of BaP in snail, with a 2177-fold concentration observed after 3 days. Therefore, studies of uptake of benzo(a) pyrene indicate that it is rapidly metabolized in fish livers, explaining the low values of BaP found in fish livers during the Puget Sound studies (Table 4.12.1). Nonetheless, metabolites may remain in fish tissue and possibly affect physiological processes (Malins, et al., 1980).

Bioaccumulation of BaP will be evident within bivalves, and the literature indicates that appreciable accumulation may occur over long time exposure to BaP in the water phase.

4.12.5.2 Metabolism

Summary Statement: Metabolites of BaP are formed by mammalian and vertebrate species. The implications of the metabolites are unknown. Evidence for microbial degradation is minimal.

Review of Individual Studies: As mentioned in Section 4.8.4, the carcinogenic properties of PAHs are due to the formation of arene oxides during metabolic reactions in mammalian and vertebrate species. The arene oxides are shown in Figure 4.8.2. Subsequently, trans-dihydrodiols would be formed. The physiological implications of such metabolites are not understood. Anderson (1978) showed that the American oyster, Crassostrea virginica contains an aryl hydrocarbon hydroxylase which may catalyze the formation of dihydrodiols, quinones, and hydroxy derivatives, with quinones as the major metabolites.

The bacteria, on the other hand, could degrade BaP to cis-9,10-dihydroxy 9,10-dihydrobenzo(a)pyrene (Gibson, 1976). In the actual environment, tests have shown minimal evidence for biodegradation of benzo(a)pyrene. Lee et al. (1978), for example, found no evidence for biodegradation of benzo(a)pyrene within "controlled ecosystem enclosures."

Other studies on the metabolism of benzo(a)pyrene also showed that biodegradation of BaP in the aquatic environment is slow. The toxicity of the metabolites to aquatic biota may be of concern, particularly in areas of continual contamination.

4.12.5.3 Sorption and Sedimentation

Adsorption to sediments containing organic carbon is probably the major fate process for benzo(a)pyrene. Smith et al. (1978), for example, reported a suspended matter-water partition coefficient of 150,000 for benzo(a)pyrene. The sediment used by Smith et al. (1978) contained 5% organic carbon.

Similar conclusions were reached by Lee et al. (1978), who found that 39% of benzo(a)pyrene added to an ecosystem enclosure was recovered in sediments within 7 days. The recovery in sediment of benzo(a)pyrene was higher than that for any of the other polyaromatic hydrocarbons studied.

4.12.5.4. Photolysis

Benzo(a)pyrene will adsorb solar radiation (Radding et al., 1976). Smith et al. (1978) determined half lives of 1.1 and 0.7 hours for benzo(a)-pyrene as a result of photolysis in winter. The products appeared to be a mixture of quinones. It is unknown whether the products are a result of photolysis or photo-oxidation. Stevens and Algar (1968) suggested that singlet oxygen resulting from photolysis is responsible for quinone formation.

The effectiveness of photolysis as an environmental fate process will be inversely dependent upon the concentration of ambient dissolved organic content levels and/or suspended solid levels. Smith et al. (1978) found that the presence of humic acids would decrease the rate of photolysis of BaP significantly, and McGinnes and Snoeyink (1974) observed inhibition when benzo(a)pyrene was adsorbed in kaolinite clay. No studies were found regarding photolysis of benzo(a)pyrene in seawater.

4.12.5.5 Volatilization

Volatilization does not appear to be a significant fate process for benzo(a)pyrene. As mentioned in Section 4.8.8, Southworth (1979) observed that volatilization of higher molecular weight PAHs (with more than four rings) is probably insignificant. Lee et al. (1978), for example, failed to detect any volatile radioactivity in an aquatic microcosm containing ^{14}C-labeled benzo(a)pyrene.

4.12.6 Conclusions

1. Sorption to suspended solids and sediments is a major fate process for benzo(a)pyrene.
2. Degradation by bacterial action would be minimal.

3. Metabolites from vertebrate species may be of environmental concern. The uptake of benzo(a)pyrene may result in *in vivo* metabolites which may act as carcinogens within biota.

4. The effects of sediment-associated benzo(a)pyrene on benthic species are not known.

4.12.7 Research Needs

1. An ecological risk assessment scheme should be developed for Puget Sound to assess the relative implications of the presence of contaminants such as benzo(a)pyrene.

2. The products of metabolism and photolysis of benzo(a)pyrene should be identified and evaluated with regard to environmental hazard.

3. The effects of high concentrations of benzo(a)pyrene in sediments to biota should be evaluated as a single substituent.

References

Anderson, R.S. 1978. Benzo(a)pyrene metabolism in the American oyster (*Crassostrea virginica*). EPA 600/3-78-009. 18 pp.

Callahan, M.A. and Slimak. 1979. Water-Related Environmental Fate of 129 Priority Pollutants. EPA 440/4-79-029b.

Cowell, E.B. 1976. Oil pollution of the sea. *In:* R. Johnston (ed.)., Marine Pollution. Academic Press, London. pp. 353-401.

Dunn, B.P. 1976. Techniques for determination of benzo(a)pyrene in marine organisms and sediments. Environ. Sci. Technol. 10:1018-1021.

Environmental Protection Agency. 1980. Treatability Manual. 5 Vols. EPA-600/8-80-042.

Gibson, D.T. 1976. Microbial degradation of carcinogenic hydrocarbons and related compounds. *In:* Proceedings of a Symposium on Sources, Effects and Sinks of Hydrocarbons in the Aquatic Environment. The American Institute of Biological Sciences. pp. 224-238.

Harrison, R.M., R. Perry and R.A. Wellings. 1975. Review paper - polynuclear aromatic hydrocarbons in raw, potable and waste waters. Water Res. 9:331.

Ishio, S., T. Yano, and R. Natagena. 1970. Algal cancer and causal substances in wastes from the coal chemical industry. In: S.H. Jenkins (ed.), Adv. Water Poll. Vol. 2. Pergamon Press, Oxford. pp 11-18.

Johnston, R. 1976. Mechanisms and problems of marine pollution in relation to commercial fisheries. In: R. Johnston (ed.), Marine Pollution. Academic Press, London. pp. 3-156.

Lee, R.F., W.S. Gardner, J.W. Anderson, J.W. Blaylock, and J. Barwell-Clarke. 1978. Fate of polycyclic aromatic hydrocarbons in controlled ecosystem enclosures. Environ. Sci. Technol. 12:832-838.

Lu, P., R.L. Metcalf, N. Plummer, and D. Mandel. 1977. The environmental fate of three carcinogens: benzo(a)pyrene, benzidine, and vinyl chloride evaluated in laboratory model ecosystems. Arch. Environ. Contam. Toxicol. 6: 129-142.

MacKay, D. and W.Y. Shui. 1977. Aqueous solubility of polynuclear aromatic hydrocarbons. Chem. Eng. Data 22:399-402.

Malins, D.C., B.B. McCain, D.W. Brown, A.K. Sparks, and H.O. Hodgins. 1980. Chemical Contaminants and Biological Abnormalities in Central and Southern Puget Sound. NOAA Technical Memorandum OMPA-2. Office of Marine Pollution Assessment, Boulder, Colo. 259 pp.

McGinnes, P. and V.L. Snoeyink. 1974. Determination of the fate of polynuclear aromatic hydrocarbons in natural water systems. Illinois Water Resources Research Report No. 80. 60 pp.

Mix, M.C. and R.L. Schaffer. 1979. Benzo(a)pyrene concentrations in mussels (Mytilus edulis) from Yaquina Bay, Oregon during June 1976 - May 1978. Bull. Environ. Contam. Toxicol. 23:677-684.

National Institute for Occupational Safety and Health (NIOSH). 1979. Registry of Toxic Effects of Chemical Substances (RTECS).

Radding, S.B., T. Mill, C.W. Gould, C.H. Liu, H.L. Johnson, D.C. Bomberger, and C.V. Fogo. 1976. The Environmental Fate of Selected Polynuclear Aromatic Hydrocarbons. EPA 560/5-75-009. 122 pp.

Roesijadi, G.J., J.W. Anderson, and J.W. Blaylock. 1978. Uptake of hydrocarbons from marine sediments contaminated with Prudhoe Bay crude oil: influence of feeding type of test species and availability of polycyclic aromatic hydrocarbons. J. Fish. Res. Board Can. 35: 608-614.

Shimkin, M.B., B.K. Koe, and L. Zechmeister. 1951. An instance of the occurrence of carcinogenic substances in certain barnacles. Science 113:650-651.

Smith, J.H., W.R. Mabey, N. Bohonos, B.R. Holt, S.S. Lee, T.W. Chou, D.C. Bomberger, and T. Mill. 1978. Environmental Pathways of Selected Chemicals in Freshwater Systems; Part II: Laboratory Studies. EPA 600/7-78-074. 432 pp.

Southworth, G.R. 1979. The role of volatilization in removing polycyclic aromatic hydrocarbons from aquatic environments. Bull. Environ. Contam. Toxicol. 21: 507-51.

Stevens, B. and B.E. Algar. 1968. Photoperoxidation of unsaturated organic molecules. II. Autoperoxidation of aromatic hydrocarbons. J. Phys. Chem. 72:3468-3474.

4.13 Chlorinated and Bromo- Naphthalenes

4.13.1 Introduction

Polychlorinated naphthalenes (PCNs) were widely used industrial compounds. They have similar physical properties to PCBs (Chu, 1977; Cooke et al., 1979). Brinkman and Reymer (1976) provided an extensive review of PCNs and noted that they were chiefly used in the electrical industry as separators in storage batteries, as capacitor impregnants, and as heat-resistant seals for condensers and coils. They were also used to provide water, heat, and insect-resistant properties to wood, cable, and textiles and serve as plasticizers and oil additives. Chlorinated naphthalenes have been reported as contaminants in foreign PCB formulations (EPA, 1978). The production of PCNs in the United States has decreased drastically in the past few years.

Bromonaphthalene may be an impurity of commercial chlorinated naphthalene mixtures or as a result of chlorination of waters containing polyaromatic hydrocarbons (Alben, 1980). Bromine is a common impurity of chlorine gas.

There have been few studies of the toxicity of chlorinated naphthalenes to marine biota; however, both lethal and sublethal effects have been noted at low concentration levels. Metabolic studies with chlorinated naphthalenes indicate that arene oxides and hydroxylated metabolites are formed. Similar metabolites have been identified with the carcinogenic properties of naphthalene (see Section 4.9).

Naphthalene is one of the EPA's 129 Priority Pollutants. Section 4.9, Naphthalenes and Substituted Naphthalenes, discussed the toxicity and distribution of naphthalenes in Puget Sound. The identification of chlorinated and bromo- naphthalenes in Puget Sound is, therefore, of concern.

4.13.2 Significance to Puget Sound

4.13.2.1 Review of Known Toxicity Data

Brinkman and Reymer (1976) in reviewing the toxicity of PCNs note that exposure to PCNs may result in:

1. chloracne, a form of dermatitis, in humans through external contact;
2. liver damage, through ingestion, to a variety of organisms including humans;
3. X-disease in cattle; and
4. mortality or growth suppression in some species of marine phytoplankton.

Toxicity tests with chlorinated naphthalenes have shown that increasing the degree of chlorination does not necessarily imply increasing toxicity. Green and Neff (1977), for example, found that Halowax 1099 (trichloro-and tetrachloronaphthalene) was slightly more toxic to grass shrimp than Halowax 1013, which is a mixture of tetrachloronaphthalene and pentachloronaphthalene. They attributed this difference to a more rapid uptake of Halowax 1099 and to the relative inability of the grass shrimp to metabolize or excrete the components of Halowax 1099. The observed 96-hour LC50 values for grass shrimp were as follows: Halowax 1000 (monochloro- and dichloronaphthalene), 440 µg/L for post larvae, 325 µg/L for adults; Halowax 1013 (tetrachloro- and pentachloronaphthalene), 74 µg/L for post larvae; and Halowax 1099 (trichloro- and tetrachloronaphthalene), 68 µg/L for post larvae and 90 µg/L for adults. The lowest 96-hour LC50 value found in the literature for chlorinated naphthalenes was 7.5 µg/L for brown shrimp (EPA, 1976). A bioaccumulation factor of 2,300 was noted in this study.

Laughlin and Neff (1979) reported that Halowax 1099 concentrations as low as 20 µg/L resulted in a number of sublethal effects to juvenile mud crabs (*Rhithropanopeus harrisii*). Mean respiratory rates were found to increase above control values with the largest increases occurring in waters of lower salinity, i.e., 5^{o}/oo. There was evidence that chlorinated naphthalenes interfere with hyperosmotic repullation and reduce the efficiency of metabolic compensation for hyposmotic shock. Laughlin and Neff (1979) speculated that field populations of mud crabs would be very sensitive to the presence of chlorinated naphthalenes because the crabs are generally subjected to wide fluctuations in salinity from surface runoff into estuarine habitats. Decreased growth and smaller brood sizes in reproducing adults might also occur.

The EPA (1978) Ambient Water Quality criteria for 1-chloronaphthalene to protect saltwater aquatic life stipulates that levels should not exceed 2.8 ppb as a 24-hour average, nor exceed 6.4 ppb at any time.

To evaluate the possible implications of the presence of contaminants in the environment to mammals (including man), environmental agencies have in many instances, used industrial hygiene data. The American Industrial Hygiene Association (1966) recommends appreciable care in the use of chlorinated naphthalenes. The Association noted that several deaths due to acute atrophy of the liver and a number of nonfatal cases of liver disease have been reported in workers repeatedly exposed to fumes of chlorinated naphthalenes. In every case but one, penta- or hexachloronaphthalenes were involved. Also, the Association (1966) reported that "although ingestion of harmful amounts of the chloronaphthalenes is not likely to be a serious industrial hazard, cattle have been severely poisoned as a result of consuming pelleted feed processed in machinery lubricated with a chloronaphthalene-containing oil."

Cornish and Block (1958) found that rabbits can metabolize naphthalene, 1-chloronaphthalene, and dichloronaphthalene. Tetrachloronaphthalene was metabolized to a lesser extent. The more highly chlorinated naphthalenes (i.e., octachloro-, heptachloro-, and pentachloro-) were found to be toxic and the toxicity was attributed to the inability of the animal to metabolize and excrete these compounds.

4.13.2.2 Possible Effects of Levels Found in Puget Sound

No concentrations of chlorinated naphthalenes were reported during the MESA Puget Sound Project. They were noted to have been identified (with many other chlorinated polyaromatic hydrocarbons) in "sediments of Central Puget Sound". Naphthalenes containing from one to seven substitute chlorine groups were reported (Malins et al., 1980). Only mono-substituted bromonaphthalene was reported.

Variable toxic effects may occur in Puget Sound as a result of the presence of chlorinated naphthalenes. Low levels (i.e., 7 to 20 μg/L) of mono- and dichloronaphthalenes may result in acute and chronic toxic effects to aquatic species such as grass shrimp and mud crabs. The more highly chlorinated naphthalenes are more toxic to mammalian species.

4.13.3 Physical Properties of Chlorinated Naphthalenes

A summary of several physical properties of chloronaphthalenes is shown in Table 4.13.1.

Table 4.13.1
Significant Physical Properties of Chloronaphthalenes*

	Monochlor-	Tri- Tetrachlor-	Tetra- Pentachlor-	Penta- Hexachlor-	Octachlor-
Chlorine content, %	22	52	56	62	70
Specific gravity	1.20	1.59	1.67	1.78	2.00
Initial boiling point, °C	250	315	328	344	-
Melting point, °C	-25	102	120	137	185
Flash point, °C	121	141	180	180	-
Maximum UV absorbance	230	235	239	245	274
Peaks in hexane, mu	285	-	306	314	324

*From American Industrial Hygiene Association (1966)

The high boiling points imply probable low vapor pressures. Callahan and Slimak (1979) calculated the vapor pressure of 2-chloronaphthalene to be 0.017 torr at 20°C, the solubility as 6.7 ng/L at 25°C, and the log n-octanol/water partition coefficient to be 4.12.

Increased chlorination will result in decreased vapor pressures and solubilities, and increased log n-octanol/water partition coefficients. For example, the log n-octanol/water partition coefficient for dichloronaphthalene would be approximately 4.52 and tetrachloronaphthalene would be approximately 5.3. Uptake of chloronaphthalenes by biota could be of appreciable significance because of their lipophilic (high log n-octanol/water partition coefficients) properties.

4.13.4 Sources or Inputs

Chlorinated naphthalenes are prepared by the chlorination of naphthalene in the presence of a catalyst such as ferric or antimony chloride. The result is a mixture of chlorinated naphthalenes which are produced and marketed commercially as Halowaxes in the United States, as Nibren waxes in Germany, Seekay waxes in Great Britain, and Clonacire waxes in France. The compositions of the mixtures are shown in Brinkman and Reymer (1976). The composition of Halowaxes vary from a mixture of 95% monochloronaphthalene and 5% dichloronaphthalene (Halowax 1031) to a mixture of 90% octachloronaphthalene and 10% heptachloronaphthalene (Halowax 1051).

During World War I, chlorinated naphthalenes were used in place of rubber. During World War II, they were used extensively in the United States as heat resistant electrical insulation. Their usage appears to be decreasing annually and there is only one manufacturer of the product in the United States. In 1972, 2,300 tons (metric tons) were produced in the United States, and in 1979 less than 270 tons were projected. Tri- and tetrachloronaphthalenes are the most commonly used PCNs and they are used in automobile capacitors. Because of their chemical stability, chlorinated naphthalenes were used in cutting oil additives, capacitor dielectrics, fabric dyeing processes, and engine cleaning operations.

Possible sources appear to be leaching from disposal sites, discarded capacitors, and cable insulation. PCNs are also found in waters and sediments adjacent to point sources or in areas of heavy PCB contamination. Some PCB formulations have been found to contain PCNs in various quantities. Crump-Wiesner et al. (1973) reported large quantities of chlorinated naphthalenes in sediments (1250-5000 ppb) and water (5-7 ppb) near an airplane engine overhaul facility. Other studies, however, have shown infrequent occurrence of chlorinated naphthalenes (PCN) in the environment. Law and Goerlitz (1974), for example, detected PCN in only 1 of 39 sediment samples within San Francisco Bay.

Carlson et al. (1978) suggested that polyaromatic hydrocarbons can be chlorinated during conditions encountered during chlorination of drinking water. Chlorination of 1-methyl naphthalene, for example, resulted in 1-chloro-4-methyl naphthalene.

4.13.5 Summary of Biogeochemical Fate Data in the Marine Environment

4.13.5.1 Bioaccumulation - Uptake and Depuration

Summary Statement: Bioaccumulation of chlorinated napthalenes, particularly those with four or more chlorine substitutes, is probably a significant environmental fate.

Review of Individual Studies: Green and Neff (1977) exposed adult grass shrimp, *Palaemonetes pugio*, to 40 ppb (µg/L) levels of each of Halowax 1099, 1013, and 1000 for periods up to 16 days. Halowax 1000 (monochloro- and dichloronaphthalene) was accumulated by a factor of 63; Halowax 1013 (tetrachloro- and pentachloronaphthalene) by a factor of 187; and Halowax 1099 (trichloro- and tetrachloronaphthalene) by a factor of 257. In each case accumulation was rapid in the first 3 days. Depuration was rapid in clean water; tissue levels were generally reduced to 1 mg/kg or less within 5 days.

The bioconcentration factors reported by Green and Neff (1977) for grass shrimp are much lower than the 2300 factor reported by the EPA (1976) for brown shrimp. Halowax 1014, a mixture of tetra-, penta- and hexa- chloronaphthalene, was used for the EPA (1976) studies and the increased number of substituted chlorines may have contributed to increased bioaccumulation levels in these studies.

4.13.5.2 Metabolism

Summary Statement: Naphthalenes with five or more substituted chlorines cannot be metabolized. Metabolites of naphthalenes with fewer substituted chlorines may result in physiological effects to biota.

Review of Individual Studies: Mammalian species have been shown to easily metabolize monochloro-and dichloronaphthalene to chlorinated naphthols. Such metabolites were detected by Cornish and Block (1958) during feeding studies using rabbits as test species, and by Ruzo et al. (1975) who used pigs for test purposes. The EPA (1978) in its review of chlorinated naphthalenes reported that metabolism decreases with increasing chlorine levels. No metabolism of naphthalenes with five or more substituted chlorines was observed.

Chu (1977) fed rats a 400 mg/kg oral dose of (1,4,5,8-^{14}C)-1,2-dichloronaphthalene in corn oil. Blood samples were taken over various time periods and after 7 days the rats were sacrificed and levels of PCNs in tissues were measured. PCN was found in blood samples initially. After 7 days only a small percent was left in the skin and adipose tissue. The liver and intestines were the initial sites of uptake and most of the PCN was eliminated via urine and feces. The data of Chu (1977) indicated that, following rapid absorption by the gastrointestinal tract, the dichloronaphthalene was metabolized to dihydrodiol; 42% was excreted unchanged via the feces; and 35% was excreted in urine as a dihydrodiol.

Cornish and Block (1958) conducted a comparative study of metabolic end products of naphthalene and chlorinated naphthalenes (di-, tetra-, penta-, hepta-, and octa-forms) on rabbits. These compounds were fed directly to the rabbits by stomach tube and it was noted that metabolism was reduced with an increasing degree of chlorination. The lower chlorinated naphthalenes were broken down to a glucosiduronic acid whereas the penta-, hexa-, and octa-forms were not significantly metabolized.

Safe et al. (1977) reported the presence of an arene oxide intermediate during the metabolism of chlorinated naphthalenes by frogs. The production of this intermediate (Figure 4.13.1) may imply that metabolites such as those described for naphthalene (Section 4.8.6) may be present within the aquatic species. Malins et al. (1980) have speculated that these metabolites, which included dihydroxynaphthalenes and naphthol, may have physiological effects on fish. The presence of a chlorine group among such intermediates will enhance uptake by tissue within an organism and subsequently result in more evident physiological effects. Safe et al. (1977) noted that arene oxides are associated with chemical carcinogenesis.

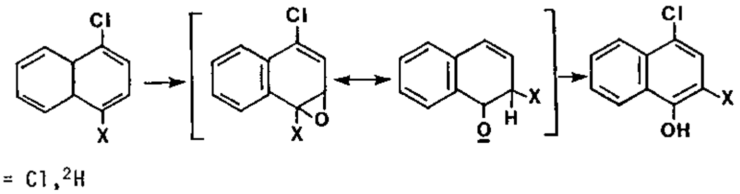


Figure 4.13.1
The NIH Shift of Chlorine and Deuterium in Chloronaphthalene Metabolism

Naphthalene by itself appears to be readily biodegraded by bacteria in water and sediments (see Section 4.9.5.2). Similar degradation probably occurs for naphthalene with four or less substituted chlorines. No degradation studies were found in the literature for chlorinated naphthalenes in water; however, Walker and Wiltshire (1955) found that soil bacteria could degrade 1-chloronaphthalene to 8-chloro-1,2-dihydroxynaphthalene and 3-chlorosalicylic acid.

4.13.5.3 Sorption and Sedimentation

Summary Statement: In Section 4.9.7 it was concluded that sedimentation is a significant fate process for naphthalene. Since chlorinated naphthalenes would have higher partition coefficients than naphthalenes, adsorption and sedimentation would be expected to constitute a significant fate process for chlorinated naphthalenes.

Review of Individual Studies: Crump-Wiesner et al. (1973), in a study of PCB distributions in the aquatic environment, found mixtures of PCNs in a Southern Florida drainage ditch at levels ranging from 1,250 to 5,000 µg/kg in sediments; whereas overlying water contained an average of only 5.7 µg/L. Thus, the evidence suggests that these compounds are strongly adsorbed to suspended particulates, particularly in association with organic matter.

4.13.5.4 Photolysis

Ruzo et al. (1975) reported that photochemical degradation of chlorinated aromatic hydrocarbons may be more efficient than metabolic degradation within the environment. As the degree of chlorination increased, more efficient absorption of light may occur resulting in faster degradation rates of the higher chlorinated components of Halowaxes. A wide range of products were formed by photolysis, most being the result of dechlorination and/or dimerization. Small quantities of methoxylated naphthalenes and methoxylated dimers were also observed. Photolysis will therefore decrease the degree of chlorination, resulting in increased susceptibility to biodegradation. Adsorption of PCNs to suspended solids will reduce the rate of photolysis.

4.13.5.5 Volatilization

Summary Statement: No data were available to assess the role of volatilization as a fate process for PCNs.

Discussion: Measured volatilization rates for chlorinated or bromonaphthalenes were not found in the literature. Southworth (1979) measured the evaporation rate of naphthalene and concluded that evaporation of naphthalene will only be substantial in clear, rapidly flowing shallow streams. In contrast, Lee (1977) found naphthalene to be rather volatile when present as part of an oil spill.

Because volatilization rates of naphthalenes determined from laboratory and in situ studies differ significantly (see Section 4.9.5.5), it is not possible to assess the actual extent of naphthalene volatilization in the environment, although it is probably a significant fate process.

Chlorination of naphthalene would decrease its vapor pressure, hence reducing the rate of volatilization relative to that of naphthalene. No studies were found in the literature on the volatilization of chlorinated naphthalenes and it is not possible to assess the role of this process to the fate of the compounds.

4.13.5.6 Hydrolysis

PCNs do not contain groups amenable to hydrolysis, thus hydrolysis is not thought to be a significant fate process (Callahan and Slimak, 1979).

4.13.6 Conclusions

1. Sublethal effects are caused by low levels of chlorinated naphthalenes in the marine environment and include increased respiration rates, and a possible interference with the ability of marine biota to compensate for hyposmotic shock. Consequently, field populations may be adversely affected.

2. Industrial usage of chlorinated naphthalenes appears to be decreasing. However, long-term leaching from disposal sites may assure continuing levels of chlorinated naphthalenes in the environment. Another source may be chlorinated wastewater treatment effluents.

3. The sediments are probably the major sink for chlorinated naphthalenes. Bacteria within sediments and water appear to be capable of degrading napthalenes with fewer than 5 chlorines to hydroxylated derivatives.

4. Metabolism of chlorinated naphthalenes in mammalian species and upper food chain biota may result in toxic metabolites. Arene oxide intermediates derived from metabolism are known to be associated with chemical carcinogenesis. The metabolites of chlorinated naphthalenes are probably of greater concern than the metabolites of naphthalenes because of the chlorine substitutions. These substitutions will result in greater lipophilic properties, hence greater probability of uptake by cells. No carcinogenesis studies of chlorinated naphthalenes have been found in the literature.

4.13.7 Research Needs

1. The levels of chlorinated naphthalenes in sediments and biota of Puget Sound should be quantified. Because metabolism may have occurred within biota, analyses of biota should include determination of hydroxylated metabolites.

2. There is a need to evaluate the carcinogenicity of chlorinated naphthalenes.

3. There is a need to further evaluate the chronic effects of chlorinated naphthalene on representative Puget Sound biota.

4. There is a need to evaluate whether chlorinated naphthalenes result from sewage disinfection.

References

Alben, K. 1980. Gas chromatographic - mass spectrometric analyses of chlorination effects on commercial coal-tar leachate. Anal. Chem. 52:1825-1828.

American Industrial Hygiene Association. 1966. Chloronaphthalenes. In: Hygienic Guide Ser. Jan.-Feb. pp. 89-91.

Brinkman, U.A. and H.G.M. Reymer. 1976. Polychlorinated naphthalenes. J. Chromatogr. 127:203-243.

Callahan, M.A. and M.W. Slimak. 1979. Water-Related Environmental Fate of 129 Priority Pollutants. EPA 440/4-79-029a.

Carlson, R.M., R. Caple, A.R. Oyler, K.J. Welch, D.L. Bodenner, and R. Liukkonen. 1978. Aqueous chlorination products of polynuclear aromatic hydrocarbons. In: Proceedings Conf. Water Chlorination: Environmental Impact and Health Effects. Ann Arbor Science Publishers, Ann Arbor, Mich.

Chu, I. 1977. Metabolism of chloronaphthalenes. J. Agric. Food Chem. 25:881.

Cooke, M., G. Nickless, A. Povey, and D.J. Roberts. 1979. Polychlorinated biphenyls, polychlorinated naphthalenes and polynuclear aromatic hydrocarbons in Severn Estuary (U.K.) Sediments. Sci. Tot. Environ. 13:17-26.

Cornish, H.H. and W.D. Block. 1958. Metabolism of chlorinated naphthalenes. J. Biol. Chem. 231:583-588.

Crump-Wiesner, H., R. Feltz, and M.L. Yates. 1973. A study of the distribution of polychlorinated biphenyls in the aquatic environment. U.S. Geol. Sur. J. Res. 1:603-607.

Environmental Protection Agency. 1976. Semi-annual report, April-September, 1976. Environmental Research Lab., Gulf Breeze, Fla.

Environmental Protection Agency. 1978. Ambient Water Quality Criteria: Chlorinated Naphthalenes. NTIS (PB 292 426).

Green, F.A., Jr. and J.M. Neff. 1977. Toxicity, accumulation, and release of three polychlorinated naphthalenes (Halowax 1000, 1013, 1099) in postlarval and adult grass shrimp, Palaemonetes pugio. Bull. Environ. Contamin. Toxicol. 17:399-407.

Laughlin, R.B., Jr. and J.M. Neff. 1979. The respiratory response of juvenile mud crabs, Rhithropaneus harrisii to variations in salinity and following short-term exposure to Halowax 1099, a polychlorinated naphthalene. Mar. Environ. Res. 2:275-286.

Law, L.M. and D.F. Goerlitz. 1974. Selected chlorinated hydrocarbons in bottom material from streams tributary to San Francisco Bay. J. Pesticides Monitoring. 8:33-36.

Lee, R.F. 1977. Fate of petroleum components in estuarine waters of the southeastern United States. In: Proceedings of the 1977 Oil Spill Conference American Petroleum Institute. Washington, D.C. pp. 611-616.

Malins, D.C., B.B. McCain, D.W. Brown, A.K. Sparks, and H.O. Hodgnins. 1980. Chemical Contaminants and Biological Abnormalities in Central and Southern Puget Sound. NOAA Technical Memorandum OMPA-2. Office of Marine Pollution Assessment, Boulder, Colo. 295 pp.

Ruzo, L.O., N.J. Bunce, S. Safe, and O. Hutzinger. 1975. Photodegradation of polychloronaphthalenes in methanol solution. Bull. Environ. Contamin. Toxicol. 14:341-345.

Safe, S., C. Wyndam, A. Crawford, and J. Kohli. 1977. Metabolism: detoxification or toxification. Presented at the International Symposium on Aquatic Pollutants. Amsterdam.

Southworth, G.R. 1979. The role of volatilization in removing polycyclic aromatic hydrocarbons from aquatic environments. Bull. Environ. Contamin. Toxicol. 21:507-514.

Walker, N. and G.H. Wiltshire. 1955. Decomposition of 1-chloro and 2-bromo naphthalene by soil bacteria. J. Gen. Microbiol. 12:478-483.

4.14 Other Halogenated Polyaromatic Hydrocarbons

4.14.1 Introduction

In addition to chlorinated naphthalenes, 25 other halogenated polyaromatic hydrocarbons were reported in sediment samples from Central Puget Sound (Malins et al., 1980). These compounds are named in Table 4.14.1. No quantitative data were provided.

Several polyaromatic hydrocarbons were identified as compounds of concern in Puget Sound because of their possible environmental effects and their persistence in the environment. The presence of halogens on the aromatic structures will probably accentuate their environmental effects and persistence. There is very little information on the halogenated polyaromatic hydrocarbons shown in Table 4.14.1. For example, computer searches using the Chemical Abstracts data base retrieved very few publications for any of the compounds under the sections of "environmental toxicology" and "pollution." As a result many deductions were made in this section which were based on known effects of chlorine or bromine substitution on properties of organic compounds such as partition coefficients, sedimentation, and volatilization.

4.14.2 Significance to Puget Sound

4.14.2.1 Review of Known Toxicity Data

In Puget Sound, halogenated derivatives of seven polyaromatic hydrocarbons were identified: fluorene, phenanthrene, anthracene, pyrene, fluoranthene, chrysene, and benzo(a)anthracene. All parent compounds have been documented to be of environmental concern. For example,

- 1-methyl benzo(a)anthracene (Jones and Sowden, 1979) and benzo(a)anthracene (Co and Kwiram, 1979) have been specifically documented as carcinogenic. Coombs et al. (1976) tested a total of 29 cyclo-penta(a)phenanthrenes, 11 chrysenes and 14 benzo(a)-anthracenes by the Ames' tests and found that all were positively mutagenic.

- Calder and Lader (1976) found that phenanthrene (and two other PAHs) decreased the growth rate and maximum cell density of marine bacteria in batch cultures.

- The EPA (1978) lists fluoranthene as an ubiquitous carcinogen.

- Calder and Lader (1976) found that pyrene (and two other PAHs) decreased the growth rate and maximum cell density of marine bacteria in batch cultures.

Table 4.14.1

Identification and Physical Properties of Halogenated Polyaromatic Hydrocarbons*

Compound	Solubility	Log P	Vapor Pressure
Fluorene	1.69-1.89 mg/L	4.18	10^{-3}-10^{-2} torr
Dichlorofluorene		(5.60)**	
Phenanthrene	1.0-1.29 mg/L	4.46	6.8×10^{-4} torr
Bromophenanthrene		(5.32)	
Chlorophenanthrene		(5.17)	
Dichlorophenanthrene		(5.88)	
Trichlorophenanthrene		(6.59)	
Tetrachlorophenanthrene		(7.30)	
Anthracene	0.045-0.073 mg/L	4.45	1.95×10^{-4} torr
Bromoanthracene		(5.31)	
Chloroanthrancene		(5.16)	
Dichloroanthracene		(5.87)	
Trichloroanthracene		(6.58)	
Tetrachloroanthracene		(7.29)	
Pyrene	0.14 mg/L	5.32	6.85×10^{-7} torr
Dibromopyrene		(7.04)	
Chloropyrene		(6.03)	
Dichloropyrene		(6.74)	
Trichloropyrene		(7.45)	
Tetrachloropyrene		(8.16)	
Pentachloropyrene		(8.87)	
Fluoranthene	0.26 mg/L	5.33	10^{-6}-10^{-4} torr
Dibromofluoranthene		(7.05)	
Chlorofluoranthene		(6.04)	
Dichlorofluoranthene		(6.75)	
Trichlorofluoranthene		(7.46)	
Tetrachlorofluoranthene		(8.17)	
Pentachlorofluoranthene		(8.88)	
Chrysene	0.002 mg/L	5.61	10^{-11}-10^{-6} torr
Dichlorochrysene		(7.03)	
Benz(a)anthracene	0.009-0.014 mg/L	5.61	5×10^{-9} torr
Dichlorobenz(a)anthracene		(7.03)	

* All values from Callahan and Slimak (1979) except for estimated log P values

**( ) estimated values, based on method of Tute (1971)

The addition of halogens to organic compounds increases their partition coefficients and enhances their uptake by organisms. Correlations between the toxicities of organic compounds (within specific classes) and their partition coefficients have been shown by several investigators. For example Addison and Cote (1973) found a linear relationship between the acute toxicity of C_7-C_{11} alkylhydroxamic acids to juvenile Atlantic salmon and the partition coefficients of the acids. Kopperman et al. (1974) obtained a similar relationship between acute toxicity of several phenols to Daphnia magna and various parameters associated with partitioning of phenolic compounds. Green and Neff (1977) found that tetra- and pentachloronaphthalene mixtures were more toxic than mixtures of mono- and dichloronaphthalene.

As noted in sections 4.8 to 4.12, carcinogenic properties of PAHs have been attributed primarily to metabolites of PAHs rather than the actual PAH molecules themselves. The metabolites, arene oxides, have been presumed capable of binding to DNA and are powerful mutagens (Gibson, 1976). Chlorine derivatives of the metabolites would be more lipophilic and binding to cells may be enhanced, subsequently resulting in more adverse effects. However, studies are required to evaluate the biological effects of halogenated polyaromatic hydrocarbons.

4.14.2.2 Possible Effects of Levels Found in Puget Sound

Quantifications of chlorinated PAHs in Puget Sound sediments and biota are recommended. Halogenated polyaromatic hydrocarbons have been chosen as "compounds of concern" in Puget Sound because of their potential adverse effects.

4.14.3 Physical Properties of Other Halogenated Polyaromatic Hydrocarbons

Table 4.14.1 outlines some of the known physical properties of the parent polyaromatic hydrocarbons. On the basis of the known partition coefficients of parent PAH molecules, partition coefficients of the halogenated polyaromatic hydrocarbons were calculated. In general, the solubilities of the compounds are low, the partition coefficients are high, and the vapor pressures will probably be low.

4.14.4 Sources or Inputs

Polycyclic aromatic hydrocarbons (PAHs) enter the aquatic environment from many sources, including: high temperature industrial processes and coal liquefaction; coal tar used as an anti-corrosion coating on public water systems; and sewer overflows and runoff of crankcase oil from metropolitan streets.

There is limited information on the possible sources of the halogenated derivatives of PAHs. Alben (1980) investigated the effects of chlorination on the composition of coal-tar leachate to determine the types of compounds formed in public water supply, storage tanks, and pipes coated with coal-tar. The compounds identified by Alben (1980) were generally mono-substituted PAHs, and included chloronaphthalene, chlorofluorene, chlorodibenzofuran, chlorophenanthrene, bromonaphthalene, bromofluorene and bromodibenzofuran. Oxygen-substituted PAHs such as dibenzofuran were found in relatively large quantities.

A major study on the products of aqueous chlorination reactions of PAHs has been under way at the University of Minnesota (Duluth) and some of the results were published by Oyler et al. (1978). Monochlorinated PAHs were detected, particularly when chlorination occurred at low pHs. For example, the yield of monochlorofluorene at pH 3.35 was 52%, and 73±4% fluorene remained unreacted at pH 7.0. Polar products appeared to be formed simultaneously but these were not identified.

The results of Oyler et al. (1978) and Alben (1980) indicate that chlorination of PAHs with more than one substituted chlorine may be difficult under normal chlorination conditions such as during water purification. The formations of di-, tri-, tetra- and pentachloro- PAHs, which have been found in Puget Sound, appear to require more drastic chlorination procedures and sources with such procedures have not been identified.

4.14.5 Summary of Biogeochemical Fate Data in the Marine Environment

Because no environmental fate data were found for any of the "other halogenated polyaromatic hydrocarbons," the biogeochemical fates of the parent compounds are reviewed and the possible fate of the halogenated derivatives are inferred.

4.14.5.1 Fluorene and Dichlorofluorene

Lu et al. (1977) studied the passage of tritiated fluorene through an aquatic microcosm by applying the labeled fluorene to sorghum leaves which were eaten by salt marsh caterpillars, thus allowing transfer of the tracer (via feces) into water containing plankton, alga, Daphnia, snails, mosquito larvae and mosquito fish. The authors found that fluorene was relatively water soluble and was accumulated to high levels by all organisms. Alcohol and ketone analogs were formed through metabolism.

In a review of polycyclic aromatic hydrocarbons, Callahan and Slimak (1979) inferred that fluorene will probably adsorb strongly onto suspended particulates and biota but, dissolved in the water column, it may undergo direct photolysis. These reviewers felt that oxidation by chlorine and ozone could be a significant fate process when sufficient quantities of oxidants were available. Hydrolysis was not considered to be significant, nor was volatilization. Biodegradation was suggested as the ultimate fate process for fluorene.

Dichlorofluorene, which was found in Puget Sound, has a calculated log P of 5.60 and, therefore, the degree of uptake by biota would be more appreciable than for fluorene. On the basis of studies by Cornish and Block (1958) with chlorinated naphthalenes it may be inferred that chlorination will decrease metabolism of chlorinated PAHs; however, with the presence of only two substituted chlorines, the decrease will not be significant.

Therefore, biodegradation and adsorption to suspended solids may be the significant fate processes for dichlorofluorene. If the compound is found to be widely dispersed throughout Puget Sound, fate studies should be undertaken to evaluate its fate and effects.

4.14.5.2 Phenanthrene and its Halogenated Derivatives

In a review by Callahan and Slimak (1979), environmental fate data specific for phenanthrene were sparse. Sorption and movement via sediment and biodegradation were considered to be the important fate processes. Bioaccumulated phenanthrene was assumed to undergo rapid metabolism. The significant fate processes are apparent from the data provided by Malins et al. (1980) for Puget Sound. Phenanthrene concentrations in Puget Sound biota were generally low. Levels up to 0.51 ppm (dry weight) were found in worms and crab hepatopancreas from Duwamish and Hylebos Waterways (Malins et al., 1980). Sediments from the vicinity of Tacoma and Seattle Harbors had phenanthrene levels up to 7.3 ppm.

As many as four substituted chlorines were found among the halogenated phenanthrenes detected in Puget Sound, implying that bioaccumulation rates may be enhanced significantly and metabolic rates would be reduced, in comparison to phenanthrenes themselves. Sorption would be an important fate process on the basis of the log P of 7.30 for tetrachlorophenanthrene (Table 4.14.1).

4.14.5.3 Anthracene and its Halogenated Derivatives

Callahan and Slimak (1979) implied there is insufficient information in the literature to permit assessment of the aquatic fate of anthracene. Fate processes which were considered of possible significance were: volatilization, sorption and movement via sediment, and biodegradation. Rapid metabolism of bioaccumulated anthracene was presumed. Elliott Bay sediments contained from 3 to 2400 ppb (dry weight) anthracene, and sediments from Commencement Bay had 8 to 2200 ppb anthracene (Malins et al. 1980). Anthracene was virtually absent in fish livers from Elliott Bay, but present in crab, worms, shrimp, and clams at levels from < 10 to 210 ppb. Similar results were observed for biota from Commencement Bay, although fish livers did contain more frequent detections of anthracene.

Some of the halogenated anthracenes found in Puget Sound have very high partition coefficients (Table 4.14.1). For example, trichloroanthracene has a log P of 6.58 and tetrachloroanthracene has a log P of 7.29. Bioaccumulation of such compounds may be much more significant than that observed for anthracene and metabolism of the compounds in biota may be reduced appreciably.

4.14.5.4 Pyrene and its Halogenated Derivatives

Pyrene itself has a higher partition coefficient and lower vapor pressure than fluorene, phenanthrene, and anthracene. Callahan and Slimak (1979) predicted that sorption to sediments and biodegradation would be the most significant fate processes for pyrene. Bioaccumulated pyrene was assumed to be susceptible to metabolism by biota.

In Puget Sound, pyrene was one of the more predominant PAHs found in biota and sediments. Levels in Elliott Bay sediments varied from 20 to 11,000 ppb (dry weight), and levels in Commencement Bay sediments varied from 20 to 10,000 ppb. Levels in fish livers from Elliott Bay varied from less than 8 ppb to 570 ppb (dry weight), and levels in worms, crab, shrimp, and clams from Elliott Bay varied from 20 to 1600 ppb. Many fish livers contained less than detection values of pyrene. This information indicates that sorption to sediments is a significant fate process for pyrene. In most instances, fish appeared more able to metabolize pyrene than other organisms.

Table 4.14.1 shows that mono- to penta- chlorinated forms of pyrene were detected in Puget sound sediments, and all have high log P's which are indicative of high bioaccumulation potential and high adsorption to sediments. Metabolism of such chlorinated pyrenes would probably be reduced appreciably.

4.14.5.5 Fluoranthene and its Halogenated Derivatives

Section 4.11 reviews the biogeochemical fate of fluoranthenes. Sorption and biodegradation appear to be significant fate processes. Fluoranthenes are widely distributed in Puget Sound sediments with levels as high as 14,000 ppb. Levels in biota were generally low, although a few of the worm and clam samples had levels up to 2000 ppb (dry weight).

Table 4.14.1 shows that fluoranthenes with one to five substituted chlorines have been found in Puget Sound sediments, with calculated partition coefficients up to log P = 8.88. Sorption and bioaccumulation will probably be important fate processes. Degradation will probably decrease as a result of halogenation (Ware and West, 1977).

4.14.5.6 Chrysene and Dichlorochrysene

Callahan and Slimak (1979) indicated that sorption and biodegradation are important fate processes for chrysene. Dichlorochrysene will probably bioaccumulate to a more appreciable degree than chrysene. Metabolism within the organisms will probably remain significant.

4.14.5.7 Benzo(a)anthracene and Dichlorobenzo(a)anthracene

Section 4.10 of this report indicates that sedimentation is an important fate process for benzo(a)anthracene. Benzo(a)anthracene levels in sediments of Puget Sound varied from 1 to 13,000 ppb. The levels of benzo(a)anthracene in Puget Sound biota, other than fish, were higher than expected. Concern was also expressed for the effects of the metabolites of benzo(a)anthracene.

The persistence of benzo(a)anthracene will be enhanced by the addition of two chlorine groups, with a log P increase from 5.61 to 7.03.

4.14.6 Conclusions

1. Halogenated PAHs are of potential concern to Puget Sound. The compounds will be more persistent and possibly more toxic than the parent compounds.
2. Information on the dispersal in Puget Sound, toxicity and individual properties of halogenated PAHs is minimal.

4.14.7 Research Needs

1. There is a need to determine the amounts of halogenated PAHs in sediments and biota of Puget sound.
2. Of the predominant halogenated PAHs, there will be a need to evaluate their toxicities, metabolites and environmental fates.
3. There is a need to determine the sources of halogenated PAHs, particularly the multihalogenated derivatives.

References

Addison, R. and R.P. Cote. 1973. Variation with chain length in acute toxicity of alkylhydroxamic acids to salmon (Salmo salar) fry. Lipids 8:493.

Alben, K. 1980. Gas chromatographic - mass spectrometric analysis of chlorination effects on commercial coal-tar leachate. Anal. Chem. 52:1825-1828.

Calder, J.A. and J.H. Lader. 1976. Effect of dissolved aromatic hydrocarbons on the growth of marine bacteria in batch culture. Appl. Environ. Microbiol. 32:95-101.

Callahan, M.A. and M.W. Slimak. 1979. Water-Related Environmental Fate of 129 Priority Pollutants. EPA 440/4-79-029.

Co, T.-T. and A.L. Kwiram. 1979. Effect of methyl substituents on the triplet state properties of benzo(a)anthracene. Photochem. Photobiol. 29:1021-1023.

Coombs, M.M., C. Dixon and A.-M. Kissonerghis. 1976. Evaluation of the mutagenicity of compounds of known carcinogenicity, belonging to the benzo(a)anthracene, chrysene and cyclopenta(a)phenanthrene series, using Ames test. Cancer Res. 36:4525-4529.

Cornish, H.H. and W.D. Block. 1958. Metabolism of chlorinated naphthalenes. J. Biol. Chem. 251:583-588.

Environmental Protection Agency. 1978. Ambient Water Quality Criteria: Fluoranthene. NTIS (PB 292 433).

Gibson, D.T. 1976. Microbial degradation of carcinogenic hydrocarbons and related compounds. In: Proceedings of a Symposium on Sources, Effects and Sinks of Hydrocarbons in the Aquatic Environment. The American Institute of Biological Sciences. pp. 224-238.

Green F.A. and J.M. Neff. 1977. Toxicity, accumulation and release of three polychlorinated naphthalenes (Halowax 1000, 1013, 1099) in postlarval and adult grass shrimp, Palaemonetes pugio. Bull. Environ. Contam. Toxicol. 17:399-407.

Jones, D.W. and J.M. Sowden. 1979. Shapes of carcinogenic benzo(a)anthracenes: the crystal and molecular structure of 1-methylbenzo(a)anthracene. Cancer Biochem. Biophys. 4:43-47.

Kopperman, H.L., R.M. Carlson, and R. Caple. 1974. Aqueous chlorination and ozonation studies. I. Structure - toxicity correlations of phenolic compounds to Daphnia magna. Chem.-Biol. Interactions 9:245-251.

Lu, P., R.L. Metcalf, N. Plummer, and D. Mandel. 1977. The environmental fate of three carcinogens: benzo(a)pyrene, benzidine, and vinyl chloride evaluated in laboratory model ecosystems. Arch. Environ. Contam. Toxicol. 6:129-142.

Malins, D.C., B.B. McCain, D.W. Brown, A.K. Sparks, and H.O. Hodgins. 1980. Chemical Contaminants and Biological Abnormalities in Central and Southern Puget Sound. NOAA Technical Memorandum OMPA-2. Office of Marine Pollution Assessment, Boulder, Colo. 295 pp.

Oyler, A.R., D.L. Bodenner, K.J. Welch, R.J. Luikkonen, R.M. Carlson, H.L. Kopperman, and R. Caple. 1978. Determination of the aqueous chlorination reaction products of polynuclear aromatic hydrocarbons by reversed phase high performance liquid chromatography - gas chromatography. Anal. Chem. 50:837-842.

Ware, S.A. and W.L. West. 1977. Investigation of Selected Potential Environmental Contaminants: Halogenated Benzenes. EPA 560/2-77-004. 283 pp.

4.15 Arsenic

4.15.1 Introduction

Arsenic, a naturally occurring element, is found in the aquatic environment as a result of the weathering of igneous rocks, shale, sandstone, and lime and as a result of man's activities which include the burning of coal and smelting of copper ore.

Arsenic is classified as moderately toxic to plants (Bowen, 1966), highly toxic to animals and a cumulative poison (Fenwick, 1972). Arsenic is one of the EPA's 129 Priority Pollutants.

Puget Sound has a major anthropogenic source of arsenic - a large copper smelter located near Tacoma (Crecelius et al., 1975). This smelter has been in operation since 1890 and it produces as a by-product almost all the arsenic trioxide sold in the United States. Crecelius et al. (1975) reported that sediments in the vicinity of the smelter contain up to 10,000 ppm (µg/g) arsenic. The Puget Sound MESA project reported values between 57 and 640 ppm arsenic in six sampling sites (Malins et al., 1980). The highest levels (640 and 472 µg/g) were found in West Duwamish Waterway and Sitcum Waterway (Commencement Bay). The other values, 84, 95 and 282 µg/g, were found in the Duwamish Waterway, and 57 and 140 µg/g were found in Budd Inlet sediments. Values from 3 to 15 µg/g arsenic were considered by Crecelius et al. (1975) to represent "background levels" for Puget Sound. Minimal information was found in the literature about the potential environmental effects of elevated arsenic levels in marine sediments.

Arsenic is either a carcinogen or a cocarcinogen with a latent period of 20 to 30 years (Health and Welfare Canada, 1980). Arsenic has, therefore, been selected as a contaminant of concern within Puget Sound.

4.15.2 Significance to Puget Sound

4.15.2.1 Review of Known Toxicity Data

The EPA (1978) in developing Ambient Water Quality Criteria expressed concern about the "paucity of marine toxicity data" for arsenic. Of the studies available, none distinguished the arsenic oxidation states during the biological testing programs. During the review of toxicity data with freshwater test species, the Agency concluded that toxicity would depend upon the oxidation state of arsenic. Furthermore, the EPA stated that the toxicity data available were inadequate to assess comparative sensitivity among a variety of species, life stages or the effect of physical/chemical parameters such as temperature and salinity.

From the marine toxicity data available, the acute toxicity of arsenic in seawater does not appear to be of significant concern. For example, the 96-hour LC50 for the American oyster (Crassostrea virginica) determined by Calabrese et al. (1973) was 4,330 µg/L. The 48-hour LC50 of sodium arsenite to chum salmon (Oncorhynchus keta) was about 11,000 µg/L (Alderdice and Brett, 1957).

Only one chronic test has been conducted with arsenic, that being for the freshwater species, Daphnia magna (Biesinger and Christensen, 1972). A chronic level of 853 µg/L was reported.

The EPA criterion, based upon the above results, is that to protect saltwater aquatic life, arsenic should not exceed 24 µg/L as a 24-hour average and the concentration should not exceed 67 µg/L at any time.

Following review of the toxicity of arsenic to laboratory animals, Health and Welfare Canada (1980) concluded that trivalent arsenic compounds are more toxic than pentavalent arsenicals because they are readily absorbed from the gut and distributed throughout the body. Pentavalent compounds are poorly absorbed and most are quickly eliminated.

The biological effects of arsenic have received much attention in studies of human health. Clinical, occupational, and population studies have demonstrated that both ingestion and inhalation exposures to arsenic compounds increase the risk of cancer induction in the tissues of the lung and skin and possibly other sites (EPA, 1978). Arsenic is unusual in that, while there is little question that it is a human carcinogen on the basis of industrial hygiene and epidemiological studies, there has been a general failure to demonstrate this effect in any animal model (EPA, 1978). A review by Health and Welfare Canada (1980) of clinical and epidemiological studies suggested that arsenic is either a carcinogen or a cocarcinogen with a latent period of 20 to 30 years.

The EPA (1978) Ambient Water Quality Criteria, suggested that for zero risk of cancer, humans should not be exposed to arsenic. However, recognizing that exposure will occur, the Agency has calculated various lifetime risk levels of cancer incidence based on consumption of 18.7 grams per day of fish and shellfish on the basis of known concentration factors of arsenic. For a lifetime risk level of 10^{-7}, a maximum water concentration of 0.01 µg/L was recommended; for a risk of 10^{-6}, a water concentration of 0.1 µg/L was recommended. A risk of 10^{-6} implies a probability of one additional case of life-time cancer for every million people exposed.

4.15.2.2 Possible Effects of Levels Found in Puget Sound

The applicability of the EPA risk analyses to Puget Sound is quite limited. "Natural" seawater levels of arsenic in accordance with EPA calculations, imply an associated risk in the order of 10^{-5}. Nonetheless, the calculations do imply that discharges should be limited as much as possible to minimize effects on human health.

Arsenic is undoubtedly added to Puget Sound from anthropogenic sources (Crecelius et al., 1975). The following data indicate the degrees of contamination which have been reported in the literature:

- Puget Sound surface sediments contained levels of arsenic which ranged from 2.9 to 10,000 ppm (dry weight). The largest concentrations were found in the Tacoma area (Crecelius et al., 1975).
- Surface seawater flowing out Admiralty Inlet was measured as 1.48 ± 0.12 ppb (μg/L) total arsenic (Crecelius et al., 1975).
- Unfiltered rain and snow collected in the Seattle area averaged 17 ± 8 ppb (μg/L) of arsenic, compared to 0.4 ± 0.2 ppb detected west of the Olympic Mountains (Crecelius et al., 1975).
- Levels of arsenic reported in Puget Sound sediments varied from 57 to 640 μg/g in 1979 (Malins et al., 1980).
- Up to 66,000 mg/L arsenic were found in bank seepage water collected along the Tacoma Waterways (EPA unpublished data, 1981).

It is somewhat difficult to evaluate the implications of these levels based on current knowledge.

4.15.3 Sources or Inputs

Arsenic ranks twentieth in elemental abundance in the earth's crust. It is frequently associated with sulfur-containing minerals. In igneous rocks it is fairly uniformly distributed at an average concentration of about 2 ppm. In sedimentary rock, arsenic is less uniformly distributed; however, its levels are significantly higher than its levels in igneous rocks.

Arsenic is present in all soils at an average level of 5-6 ppm, with wide variations in different geographical areas. Soils associated with underlying sulfide ores may contain arsenic at levels in the 10 ppm range. Arsenic may also be loosely bound to organic matter in soil. It is associated with sediments carried by runoff waters to the sea, frequently absorbed to clays, phosphorite, and hydrous oxides of iron and manganese.

Arsenic is formed as a by-product of smelting of nonferrous ores, particularly those of lead, zinc, and copper. It is used in insecticides, herbicides, feed additives, wood preservatives, war gases and riot control agents, and in drugs. It is also used as a crop desiccant, and in ceramics, glass, and semiconductors.

There are many possible sources of arsenic inputs to Puget Sound, and the major inputs were identified during a mass balance study for arsenic in Puget Sound (Crecelius et al., 1975). The following inputs and outputs were calculated:

- The copper smelter at Tacoma released 2 x 10^5 kg/yr of As_2O_3 as stack dust into the air, 2-7 x 10^4 kg As/yr dissolved in liquid effluent, and 1.5 x 10^6 kg/yr in crystalline slag particles dumped directly into the sound.
- Arsenic in deep waters flowing into Puget Sound through Admiralty Inlet averaged 1.51 ± 0.15 µg/L. A volume of 3.8 x 10^{11} m^3/yr entering the Sound implied a total of 5.8 ± 0.6 x 10^5 kg/yr of arsenic from incoming seawaters.
- The total influx of arsenic from rivers was calculated to be 3 ± 1 x 10^4 kg/yr.
- The upper limit for arsenic via precipitation to the Sound was 7.7 ± 3.6 x 10^4 kg/yr.
- The Seattle METRO sewage plant was estimated to contribute 7 x 10^2 kg As/yr and drydock operations contributed 9 x 10^2 kg As/yr.
- Outputs of arsenic from Puget Sound via Admiralty Inlet were calculated to be 0.6 x 10^5 kg/yr.

The budget developed by Crecelius et al. (1975) indicated that less than 30% of the arsenic entering the Sound accumulated within the sediments and that discharge to the Strait of Juan de Fuca was the major sink of arsenic. The mass balance studies did not consider volatilization.

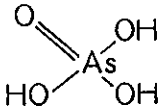
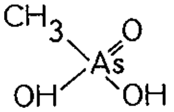
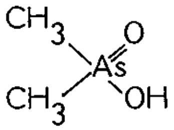
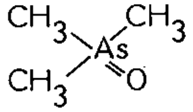
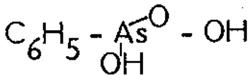
4.15.4 Speciation of Arsenic

The chemistry of arsenic in aquatic systems is very complex, with four possible oxidation states (+5, +3, 0, -3). Each valence will have different properties with regard to toxicity, complexation, adsorption, and precipitation. For example, the +3 form is much more toxic than the +5 form. At low pH, low Eh and low dissolved oxygen, lower oxidation forms such as arsenite (+3) and arsine (-3) are favored. Furthermore, arsenic can be methylated in the environment to several forms, each with different physical properties and toxicities.

Several studies of speciation of arsenic in marine waters were found in the literature. Of the arsenic species detected in seawater samples taken off Southern California, arsenate (+5) was the dominant form with arsenite (+3), monomethyl arsonic acid and dimethyl arsinic acid found in varying quantities (Andreae, 1978). The structures of these and other common arsenic compounds are shown in Table 4.15.1.

Table 4.15.1

Arsenic Acids Detected in the Marine Environment

Arsenic acid	
Arsenous acid	$O = As - OH$
Methyl arsonic acid	
Dimethyl arsinic acid	
Trimethyl arsine oxide	
Phenyl arsonic acid	 $C_6H_5 - \underset{OH}{\overset{O}{As}} - OH$

Arsenic speciation in the California coastal waters was significantly influenced by biological activity, and arsenite (+3) and methylated arsenicals were predominant in the euphotic zone. In waters below the euphotic zone, arsenate concentrations increased with depth, suggesting regeneration of the arsenate species (Andreae, 1978). Depending upon biological activity the natural arsenite/arsenate concentration ratios in oxygenated seawaters could range from 0.1 to 10 (Braman, 1976).

Arsenic compounds can also be reduced and converted by anaerobic bacteria to give dimethyl arsine and trimethyl arsine, which are extremely toxic and volatile. The biological cycle for arsenic is shown in Figure 4.15.1. Biological processes influence the speciation of arsenic associated with estuarine suspended particulates (Waslenchuk and Windom, 1978). A dimethyl arsine maximum was observed at mid-estuary, reflecting dimethylation of inorganic arsenic.

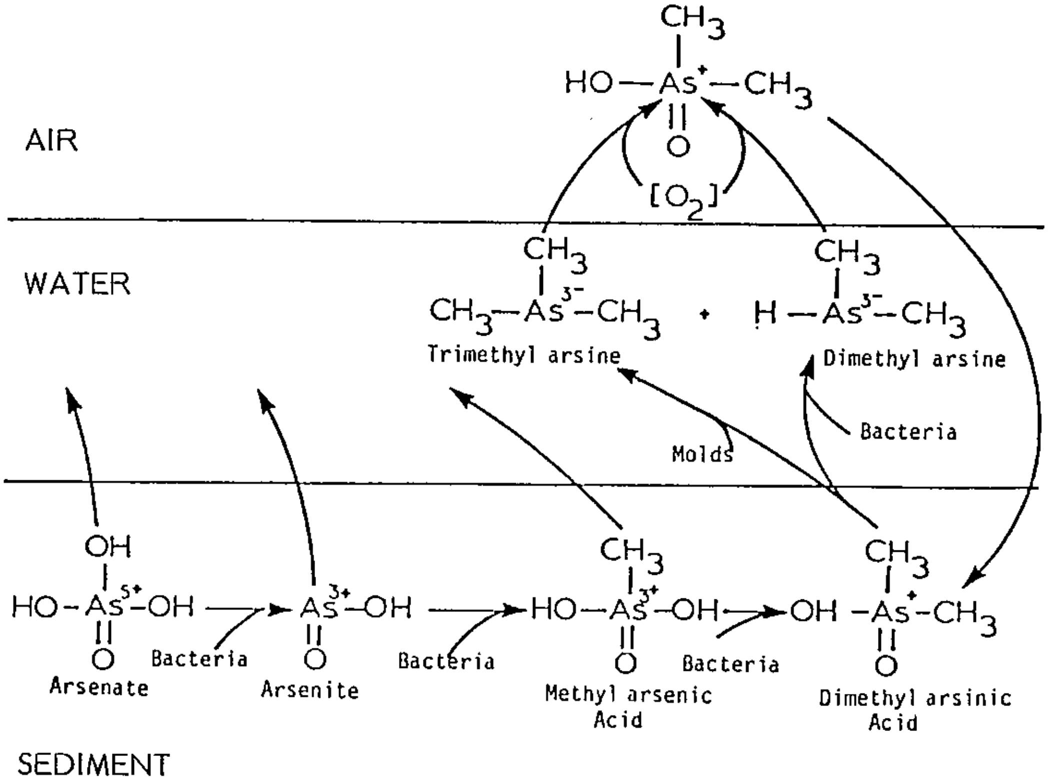


Figure 4.15.1
The Biological Cycle for Arsenic

Braman (1976) reported the relative levels of arsenic species in nearshore areas of Tampa Bay and in seawater from the Sargasso Sea. Relative concentrations (ppb) of the arsenic species As (+3), As (+5), methyl arsonic acid (MAA), and dimethyl arsinic (DMAA) acid were as follows: Tampa Bay Causeway - 0.12, 0.45, <0.02, 0.2; tidal flat - 0.62, 1.29, 0.08, 0.29; McKay Bay - 0.06, 0.35, 0.07, 1.00; Alafia River (brackish) - 0.72, N.D., 0.16, trace; and Sargasso Sea - 0.24, N.D., <0.02, trace. Relative concentrations (ppm) of arsenic species in sargassum weed from the Bermuda area were 1.8 (As + 3), 17.7 (As + 5), 0.01 (MAA), and 0.184 (DMAA). Analyses of shrimp, barnacles, and fish from the vicinity of the analyzed sargassum weed indicated the presence of small amounts of methyl arsenic compounds. Braman's (1976) data show the variations in dominant arsenic species. In the case of Tampa Bay Causeway, As (+5) was dominant; in McKay Bay, dimethyl arsonic acid was dominant; and in the Alafia River and Sargasso Sea the more toxic As (+3) was dominant.

Because of the difference in toxicity of As (+3) and As (+5), it is recommended that speciation studies of arsenic be undertaken within contaminated areas of Puget Sound. Furthermore, the toxicity of the methylated arsenic forms should be evaluated.

4.15.5 Summary of Biogeochemical Fate Data in the Marine Environment

4.15.5.1 Bioaccumulation - Uptake and Depuration

Summary Statement: Marine biota bioaccumulate arsenic and uptake via the water column appears to be more important than uptake via the food chain. Methylated arsenic compounds are readily bioaccumulated. Studies of arsenic levels in Puget Sound biota are recommended.

Review of Individual Studies: Kennedy (1976) found higher arsenic concentrations in marine shrimp of Northern Newfoundland and Southern Labrador than in either their potential prey (zooplankton), the mud in their habitat, or their predators (fish). The mean arsenic concentrations (ppm wet weight) found were: shrimp muscle, 17.7; shrimp eggs, 10.2; zooplankton (4 species), 1.4 to 6.6; fish (4 species), 0.8 to 4.4; and mud (2 sites), 3.5 and 4.6. No quantitative water levels were reported due to a lack of analytical sensitivity but levels were reported to be "in the ppb range." Since arsenic levels in fish were lower than in shrimp, Kennedy (1976) concluded that there was no evidence of increasing arsenic concentrations through successively higher levels of the food chain. Giddings and Eddlemon (1977) reached the same conclusion for a freshwater ecosytem.

High concentrations of arsenic in tissues of fish obtained off West Greenland were reported by Bohn (1975). Average dry weight concentrations in American plaice muscle and turbot tissue were 80 ppm and 77 ppm, respectively. Bohn (1975) found no statistically significant differences between values for liver and muscle.

Fowler and Unlu (1978) found that uptake of sodium arsenate by the benthic marine shrimp, Lysmata seticaudata, varied inversely with salinity. Accumulation was slow and derived chiefly from food. Concentration factors were less that 10 and influenced by molting.

The similarity between dimethyl mercury and dimethyl arsine suggests that the latter may undergo bioaccumulation in the aquatic food chains, principally by partitioning within fatty tissues of organisms. Isensee et al. (1973) studied the uptake of two arsenic based herbicides, dimethyl arsinic acid (cacodylic acid), and dimethyl arsine, by aquatic organisms in a model ecosystem using radiotracers. After 32 days exposure to concentrations of 4 to 10 ppb of the test arsenic compounds, bioaccumulation factors of 1248 to 1635 were observed in algae, 299-419 in snails, 736-2175 in water fleas, and 19-49 in fish. After 16 days of depuration in clean water, snail bioaccumulation factors decreased to values between 110 and 176. The authors speculated that surface adsorption may have accounted for much of the activity, particularly within algae. Feeding experiments showed that fish and snails accumulated 2-10 times more dimethyl arsinic acid from water than from food.

No analyses for arsenic levels in Puget Sound biota were undertaken during the MESA study. The fact that marine biota bioaccumulate arsenic compounds implies the need for assessment of arsenic levels within representative biota of Puget Sound, particularly species such as shrimp and plaice.

4.15.5.2 Adsorption-Desorption

Summary Statement: Adsorption-desorption processes to and from particulates do not appear to be significant for arsenic in estuarine or marine environments. In the presence of hydrous oxides of iron and manganese, arsenic is strongly adsorbed. No information was found on the release of arsenic from highly contaminated sediments.

Review of Individual Studies: Waslenchuk and Windom (1978) found that arsenic associated with particulates which entered estuaries from rivers apparently remained so and accumulated in the sediments. If the arsenate was in solution within the river, it remained as such within the estuary. In the presence of low molecular weight material, soluble arsenic complexes were formed which prevented adsorptive and coprecipitative interactions with the sediments (Waslenchuk, 1979).

In the absence of low molecular weight material, arsenic has a strong affinity for hydrous oxides of iron and manganese. Neal et al. (1979) reported that most of the arsenic in North Atlantic deep sea sediments is associated with iron or iron oxides. Gupta and Chen (1978) found that As (+3) and As (+5) had minimal affinity for clay particles under saline conditions and, hence, are likely to remain dissolved.

Studies of adsorption and desorption of arsenic within Puget Sound are limited to those of Crecelius et al. (1975). These investigators found that minimal changes in levels of arsenic adsorbed to, or desorbed from, river particulates entering the Sound occurred, and that adsorption to particulate phases in the open waters of Puget Sound was much less important for arsenic than for other metals such as mercury and lead. Crecelius et al. (1975) concluded that sediments accumulated less that 30% of the arsenic entering the Sound.

High concentrations of arsenic (10,000 ppm) were found in sediments from 3 of 42 sampling sites in the Tacoma area. This result implies a rapid precipitation, adsorption and/or discharge of arsenic in insoluble forms to account for such a limited dispersal of arsenic. Crecelius et al. (1975) noted that the major component of the total arsenic content in Tacoma smelter effluent is the more toxic arsenite species and its rate of oxidation under natural conditions in Puget Sound is not known.

4.15.5.3 Volatilization

As mentioned previously, arsenic can be methylated within the marine environment as a result of biological activity. Braman (1976), for example, has observed the presence of methylated arsenic compounds "out-of-doors" (author's terminology). However, levels were not reported. Trimethyl arsine which is quite resistant to oxidation in the aqueous environment has been shown to be very volatile at room temperature with a vapor pressure of 322 torr (Parris and Brinckman, 1976).

Volatilization may have a significant impact on the fate of arsenic compounds in Puget Sound.

4.15.6 Conclusions

1. Arsenic is a major pollutant of Puget Sound.
2. There are minimal toxicological data to enable an assessment of the possible biological effects arsenic would have on marine biota in Puget Sound.
3. The levels of arsenic in Puget Sound biota and water have not been determined; however, the levels may be of concern for the protection of human health.
4. A mass balance study indicated that discharge through the Strait of Juan de Fuca (water phase) was a major sink for arsenic in Puget Sound.
5. Sedimentation was predicted to have a relatively minor role in the fate of arsenic.
6. The role of volatilization of arsenic in Puget Sound has not been evaluated.

4.15.7 Research Needs

1. A simultaneous assessment of total arsenic levels in water, biota, and sediments from Puget Sound is required.
2. Arsenic speciation in Puget Sound should be evaluated, since speciation will affect toxicity, bioaccumulation, and general distribution and transport of arsenic in the Sound.
3. Acute and chronic toxicity tests are required to assess the effects of various arsenic species on representative Puget Sound biota.
4. The effects of sediment-associated arsenic levels on bottom-dwelling biota should be evaluated.
5. The role of volatilization in the fate of organo-arsenic species should be assessed.

References

Alderdice, D.F. and J.R. Brett. 1957. Toxicity of sodium arsenite to young chum salmon. Fish. Res. Bd. Can., Prog. Rep. 108:27-29.

Andreae, M.O. 1978. Distribution and speciation of arsenic in natural waters and some marine algae. Deep-sea Res. 25:391-402.

Biesinger, K.E. and G.M. Christensen. 1972. Effect of various metals on survival, growth, reproduction and metabolism of Daphnia magna. J. Fish. Res. Bd. Can. 29:1691-1700.

Bohn, A. 1975. Arsenic in marine organisms from West Greenland. Mar. Pollut. Bull. 6:87-89.

Bowen, H.J.M. 1966. Trace Elements in Biochemistry. Academic Press, London.

Braman, R.S. 1976. Molecular forms of arsenic in the environment. In: R.W. Andrew, P.V. Hodson, and D.E. Konasewich (eds.), Proceedings of a Workshop on Toxicity to Biota of Metal Forms in Natural Waters. International Joint Commission. Windsor, Ontario.

Bryan, G.W. 1976. Heavy metal contamination in the sea. In: R. Johnston (ed.), Marine Pollution. Academic Press, Inc., London. pp. 185-290.

Calabrese, A. R.S. Collier, D.A. Nelson and J.R. MacInnes. 1973. The toxicity of heavy metals to embryos of the American oyster, Crassostrea virginica. Mar. Biol. 18:162-166.

Crecelius, E.A., M.H. Bothner, and R. Carpenter. 1975. Geochemistries of arsenic, antimony, mercury and related elements in sediments of Puget Sound. Environ. Sci. Technol. 9:325-333.

Environmental Protection Agency. 1978. Ambient Water Quality Criteria: Arsenic. NTIS (PB 292 420).

Fenwick, P.D. 1972. The use of selected metals and metallic compounds by industry in the Great Lakes basin. (Unpublished). Canada Centre for Inland Waters, Burlington, Ontario.

Fowler, S.W. and M.Y. Unlii. 1978. Factors affecting bioaccumulation and elimination of arsenic in the shrimp Lysmata seticaudata. Chemosphere 9:711-720.

Giddings, J.M. and G.K. Eddlemon. 1977. The effects of microcosm size and substrate type on aquatic microcosm behavior and arsenic transport. Arch. Environ. Contam. Toxicol. 6:491-505.

Gupta, S. and K.Y. Chen. 1978. Arsenic removal by adsorption. J. Water Pollut. Control Fed. 50:493-506.

Health and Welfare Canada. 1980. Guidelines for Canadian Drinking Quality 1978. Supporting Documentation. Minister of Supply and Services Canada. 738 pp.

Isensee, A.R., P.C. Kearney, E.A. Woolson, G.E. Jones, and V.P. Williams. 1973. Distribution of alkyl arsenicals in model ecosystem. Environ. Sci. Technol. 7:841-845.

Kennedy, V.S. 1976. Arsenic concentrations in some co-existing marine organisms from Newfoundland and Laborador. J. Fish. Res. Bd. Can. 33:1388-1393.

Malins, D.C., B.B. McCain, D.W. Brown, A.K. Sparks, and H.O. Hodgins. 1980. Chemical Contaminants and Biological Abnormalities in Central and Southern Puget Sound. NOAA Technical Memorandum OMPA-2. Office of Marine Pollution Assessment, Boulder, Colo. 295 pp.

Neal, C., H. Elderfield, and R. Chester. 1979. Arsenic in sediments of the North Atlantic Ocean and the Eastern Mediterranean Sea. Mar. Chem. 7:207-219.

Parris, G.E. and F.E. Brinckman. 1976. Reactions which relate to the environmental mobility of arsenic and antimony. II. Oxidation of trimethylarsinc and trimethylstibine. Environ. Sci. Technol. 10:1128-1134.

Waslenchuk, D.G. and H.L. Windom. 1978. Factors controlling the estuarine chemistry of arsenic. Estuarine Coastal Mar. Sci. 7:455-464.

Waslenchuk, D.G. 1979. The geochemical controls on arsenic concentrations in southeastern United States rivers. Chem. Geol. 24:315-325.

4.16 Cadmium

4.16.1 Introduction

Cadmium is a heavy metal which occurs naturally as a sulphide, usually in association with lead and zinc sulphides. It is a by-product of zinc mining (Lymburner, 1974). Cadmium has various industrial uses such as electroplating and manufacture of storage batteries (EPA, 1978). Cadmium is one of the EPA's 129 Priority Pollutants.

Salts of cadmium have been classified as carcinogenic, teratogenic, and neoplastic (NIOSH, 1979). When present in water at very low levels (i.e., 5 µg/L) cadmium may cause chronic effects to various marine species (Calabrese et al., 1975). In addition, cadmium contaminated sediments have been shown to cause behavioral changes in benthic invertebrates (McGreer, 1979; Wentsel et al., 1977).

Cadmium is environmentally mobile, owing to its tendency to readily dissolve and transport in the water medium. Cadmium, therefore, is accessible to all forms of biota in Puget Sound waters, and it may pose a potential hazard to the Puget Sound ecosystem.

4.16.2 Significance to Puget Sound

4.16.2.1 Review of Known Toxicity Data

There is a general lack of information on the acute toxicity of cadmium to marine biota. The 96-hour LC50 values for marine fish are generally quite high, i.e., for larval Atlantic silversides, the LC50 was 1600 µg/L and for juvenile mummichog, the LC50 was 114,000 µg/L (EPA, 1978). Gastropod molluscs are generally quite insensitive with LC50 values above 1,500 µg/L. However, other invertebrates are more sensitive, with the LC50 for the mysid shrimp being 15.5 µg/L. Inhibition of growth rate of the alga, Skeletonema costatum, was observed at 175 µg/L (EPA, 1978).

Low levels of cadmium are capable of causing various chronic effects. Nimmo et al. (1977) reported that mysid shrimp exposed to 6.4 µg/L cadmium exhibited 48-hour delays in brood formation and a 57% decrease in the number of young born per female. No effects were observed at 4.8 µg/L. Calabrese et al. (1975) demonstrated significant alterations in gill-tissue respiration rates measured in vitro after 60 days exposure to 5 µg/L of cadmium. The significance of this observation has not been evaluated.

It has been suggested that because of its chemical kinship to zinc, cadmium may displace zinc in certain enzymes, thereby disrupting normal metabolic functions (Callahan and Slimak, 1979).

Wentsel et al. (1977) demonstrated a linear relationship between concentrations of cadmium in sediments and avoidance of the sediments by the midge larva (Chironomus tentans). McGreer (1979) showed that burrowing behavior of the marine bivalve, Macoma balthica, was affected by cadmium contaminated sediments. Dry weight cadmium concentrations in sediments during McGreer's (1979) tests were from 0.4 to 1.4 mg/kg.

4.16.2.2 Possible Effects of Levels Found in Puget Sound

The sediment dry weight levels of cadmium in Puget Sound varied from 3.1 to 18.3 ppm (Malins et al., 1980). These levels are much higher than the levels reported by McGreer (1979) which affected burrowing in Macoma balthica. They are also higher than the 0.6 mg/kg maximum allowable level for ocean dumping as recommended by the Canadian Department of Fisheries and Oceans (Swiss et al., 1980). Most values (26 of 42) exceed the "heavily polluted" designation of 6 mg/kg for Great Lakes harbors (International Joint Commission, 1979). Cadmium levels in Puget Sound waters have not been determined, but concentrations may be of significance.

4.16.3 Sources or Inputs

Cadmium is used in metallurgical applications (alloys, solders), plating, paint and varnish, battery manufacture, fungicides, fertilizers, rubber tires and motor oils. Cadmium can be released to the atmosphere from fuel combustion, smelting operations of zinc, copper, and lead ores, and other sources related to the above uses (Biosystems Environmental Consultants, 1977). The EPA (1980) Treatability Manual notes that industrial wastewaters with the highest cadmium levels include those of foundries, iron and steel manufacturing, nonferrous metals manufacturing, porcelain enameling, and rubber processing. Anthropogenic sources can transport significant amounts of cadmium by air emission over large distances (Duce et al., 1976) and the effects of cadmium emission from metallurgical activities are widely dispersed rather than localized.

No estimates were found in the literature concerning cadmium inputs to Puget Sound.

4.16.4 Speciation of Cadmium

There is considerable variability in published data for the toxicity of cadmium to estuarine and marine organisms. The variability may be due to cadmium speciation in such systems, particularly with regard to chloride equilibria (Engel and Fowler, 1979). For example, the toxicity of cadmium to estuarine shrimp and larval fish is a function of free cadmium ion concentration, which is largely controlled by chloride content (in essence, salinity). The cadmium-chloride complexes formed at higher salinities reduce free cadmium ion levels and lower the solution toxicity (Engel and Fowler, 1979; Sunda et al., 1978).

Sunda et al. (1978) determined the dependence of the free cadmium ion concentration on salinity (Figure 4.16.1), and also demonstrated the critical nature of free cadmium ion on toxicity for the grass shrimp Palaemonetes pugio (Figure 4.16.2).

Cadmium is always found in the +2 valence state in water. Speciation studies of the cadmium present in typical freshwater and seawater mixtures (Sibley and Morgan, 1977) showed that the major anionic species associated with cadmium in these mixtures were chloride and carbonate. Free cadmium ion was the major form in freshwaters with no more than 1% seawater and a chloride complex was the major form in even slightly saline mixtures. The level of cadmium adsorbed to particulates declines as freshwater is diluted by saltwater, in common with the behavior of many other metals. The release of adsorbed cadmium may imply that estuarine biota are subject to high levels of dissolved cadmium.

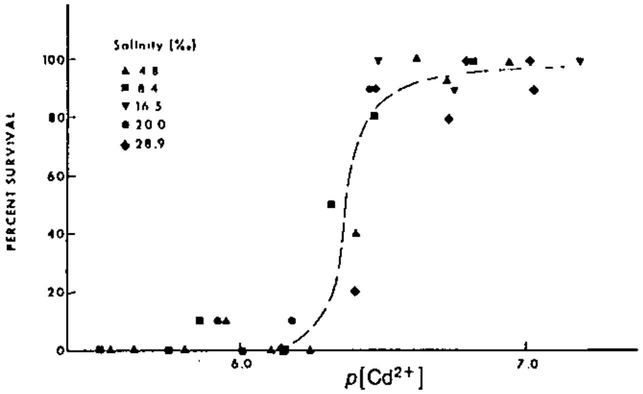


Figure 4.16.1

Relationship between 4-Day Survival of P. pugio and Negative Log of Measured Free Cadmium Ion Concentration ($p[Cd^{2+}]$) (Sunda et al., 1978)

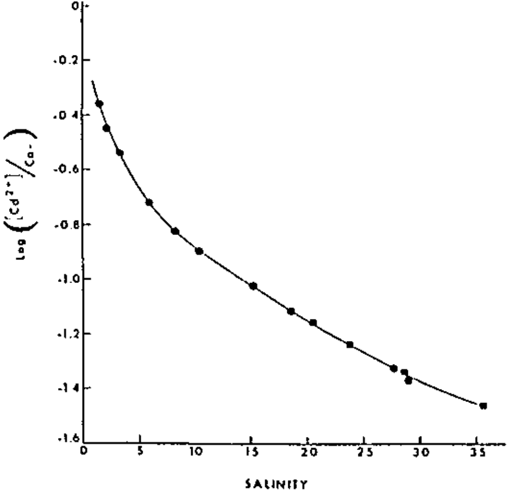


Figure 4.16.2

Log of Fraction of Total Cadmium Present as Free Cadmium Ion (Sunda et al., 1978) as a Function of Salinity at 22°C

In reducing conditions such as highly polluted sediments, cadmium may form an insoluble sulphide (Huang et al., 1977).

The presence of organic complexing agents does not appear to affect the distribution of inorganic cadmium species in marine waters. Mantoura et al. (1978) calculated that levels of humic-cadmium complexes would be very low even in predominantly freshwater systems. Likewise, Stumm and Brauner (1975) modeled the effect of organic complexing agents and concluded that the distribution of inorganic cadmium species was not affected by the presence of organic functional groups at the concentrations normally found in seawater. Excessive quantities of organics in water may, however, result in the formation of complexed ligands. If organic colloids are present, experiments by Batley and Florence (1976) have shown that cadmium may be loosely adsorbed, minimizing the impact of organic pollution on cadmium availability.

Cadmium is not known to be methylated. As a result, its chemistry in seawater is relatively simple when compared with that of other inorganic elements such as mercury or selenium.

In situ studies off the coast of California by Martin et al. (1976) indicated that levels of cadmium were higher nearshore than offshore and higher cadmium levels were found at subsurface depths nearshore. These authors noted that cadmium, like nutrients, may be taken up by phytoplankton in ocean surface water and transported to deeper waters. Thus, cadmium has a relatively short residence time at the surface and tends to be enriched in deeper waters. In addition, cadmium and phosphorus concentrations were apparently correlated in both seawater and plankton, although the reason for this correlation was unclear. Because of the natural downward migration of cadmium, upwelling becomes an important transport mechanism.

4.16.5 Summary of Biogeochemical Fate Data in the Marine Environment

4.16.5.1 Bioaccumulation - Uptake and Depuration

Summary Statement: Bioaccumulation is an important fate process for cadmium. Accumulation occurs slowly and steadily for long time periods. Depuration rates are slow. Bioaccumulation over the long-term may result in toxic effects to the organism.

Review of Individual Studies: Cadmium is actively accumulated by marine organisms. There are, however, significant differences in the literature concerning the degree of accumulation. Chapman et al. (1968) reported bioaccumulation factors of cadmium within marine invertebrates as high as 250,000. The EPA (1978) indicated that bivalve molluscs most actively accumulated cadmium and a bioconcentration factor of 2600 was observed after 280 days exposure. Vernberg et al. (1977) reported 700-fold bioaccumulation of cadmium by grass shrimp and Nimmo et al. (1977) reported a 57-fold bioaccumulation by pink shrimp.

Cadmium uptake studies require long-term experimentation. Frazier (1979) in his studies with the American oyster, Crassostrea virginica, found continuing cadmium accumulation even after 280 days exposure. Uptake is affected by speciation; an inverse relationship exists between tissue level accumulation and water salinity (Frazier, 1979; Engel and Fowler, 1979). Uptake is also affected by ambient water temperature with increased uptake at higher temperatures. Depuration rates are slow. Greig and Wenzloff (1978) and Zaroogian (1979) found no decrease in cadmium concentration in C. virginica when transferred from metal impacted waters to cleaner waters or in a declining temperature regime. However, the latter worker found that both concentration and weight of the oysters declined during depuration. Although the cadmium concentration stayed the same, the total amount of cadmium in the organism decreased.

In a study of the relationship between toxicity and bioaccumulation in aquatic invertebrates, Spehar et al. (1978) found that the 28-day LC50 values for cadmium-exposed snails and lead-exposed amphipods were 11 and 4 times lower than the 7- and 4-day LC50 values for these metals, respectively. The results indicate that effects could occur at lower concentrations during longer exposure periods. Data are not available on the relationship between toxicity and accumulated body burdens of metals in aquatic invertebrates and research into this area is required for marine species. Since concerns over ecological impacts of heavy metal contamination are commonly developed from environmental surveys that identify contaminant levels in biological tissues, relationships between toxic effects and metal burdens in major body organs must be established. Such information would provide much needed fundamental data for the development of environmental contaminant criteria.

Uptake levels of cadmium in biota of Puget Sound may be of potential concern. The ranges in wet weight concentrations in Puget Sound were 0.56 to 1.49 ppm in fish livers and 0.38 to 53.4 ppm in crab hepatopancreas (Malins et al., 1980).

4.16.5.2 Photolysis

Due to the stability of the cadmium ion, photolysis would not be expected to result in changes in valence, nor result in changes to the predominant cadmium chloride complexes in seawater.

4.16.5.3 Volatilization

Cadmium is not known to methylate in the environment. It is, therefore, not expected that cadmium would volatilize from the aquatic environment.

4.16.5.4 Adsorption-Desorption

Summary Statement: In the marine environment, the formation of soluble Cd-Cl complexes enhances the release of sediment-associated cadmium. Adsorption of cadmium to solids is weak compared to adsorption by other metals. Organics enhance adsorption of cadmium. The release of cadmium from Puget Sound sediments may impact the well-being of Puget Sound benthic biota.

Review of Individual Studies: The rate and amount of cadmium sorption by sediments and suspended solids will depend on such factors as the presence of natural organic compounds and hydroxylated forms of various metals. Cadmium is generally a weak competitor for adsorption sites on hydrous metal oxides (Kinniburgh et al., 1977). Huang et al. (1977) found that strength of adsorption of divalent metal ions decreased in the order: Copper/zinc/lead/cadmium for several hydrous oxides and soils, and also that the extent of adsorption was pH-dependent with highest adsorption at high pH. Some anions promote heavy metal adsorption at low pH, in the order: humic acid/nitriloacetate/ d-glycine/tartrate/phosphate. Gardner (1974) concluded that the main component responsible for cadmium adsorption to naturally occurring suspending solids was humic acid. The affinity of cadmium to associate with organic sediment-suspended solid matrix is considered significant in its transfer to detritus-eating benthic organisms (EPA, 1977).

Food or particulate material is frequently a significant source of metal enrichment for marine organisms. Differences in the availability of metals in foodstuffs depends upon many factors such as the ease with which the material is digested, the chemical form of the metal, the relative binding capacities of the animal, and the products of digestion. Luoma and Jenne (1975a, 1975b) have shown that the type of geochemical fractionation of metals in the sediment affected the accumulation of trace metals within the deposit feeding clam, Macoma balthica. Very little uptake of radioactive cadmium occurred through ingestion of either labeled organic detritus or labeled particulate hydrous iron oxides that were coated with organics. However, the clam picked up radioactive cadmium if the iron oxides lacked the organic coating (Luoma and Jenne, 1975a). In contrast to cadmium, the metals, silver, cobalt, and zinc, were all taken up when bound to detrital organics (Luoma and Jenne, 1975b).

The form of cadmium within sediments (i.e., stable solid, adsorbed, or dissolved) is dependent upon redox conditions. Thus, under reducing conditions, sulphide formation regulates the amount of dissolved cadmium, by the formation of sulphide complexes which are generally insoluble species. Under oxidizing conditions, carbonate formation is the governing process, and chlorides are the major soluble complexes.

Khalid et al. (1978) subjected reduced sediment suspensions containing cadmium, sulphides, and other inorganics to streams of oxygenated gas mixtures. They found that the oxygen flow lowered sediment pH and raised the redox potential, with the result that gas mixtures with high and low oxygen contents solubilized more lead, cadmium, and copper than gases with an intermediate oxygen content. Their explanation was that a low oxygen regime favored metal solubilization by organics; a high oxygen regime supported conversion of insoluble sulphides to soluble sulphates as the redox potential increased from -170 mV to +600mV, and the concomitant decrease in pH promoted the formation of more soluble cadmium species. Khalid et al. (1978) also suggested that hydrous oxides of iron and manganese acted not only as scavengers for dissolved cadmium but could also release adsorbed soluble cadmium as sediments became slightly acidic and oxidizing.

When river particulates enter a saline estuary, adsorbed cadmium is probably released to the water compartment. For example, Rohatgi and Chen (1975) observed that of the total quantity of cadmium associated with suspended particulates of wastewater effluents, sludge, or dry weather flow from the Los Angeles River, up to 95% was released upon discharge to the ocean. The rate of release increased with higher proportions of seawater in the system. The species of $CdCl+$ and $CdCl_2$ were predominant and it was suggested that complex formation is more important than adsorption in determining the fate of cadmium.

Montgomery and Price (1975) found that cadmium (along with chromium, copper, nickel, lead, and zinc) was leached and mobilized from sewage sludge by flowing seawater. The largest resulting net uptake of metals occurred in the "fouling organisms" (i.e.,algae, worms, barnacles, weeds) where cadmium, lead, and zinc uptake closely paralleled loss of these metals from the sewage sludge. Valiela et al. (1974) also noted the lability of cadmium in sediment, and its ready uptake by salt marsh biota.

In a survey of Southern and Central Puget Sound, Malins et al. (1980) found cadmium levels in sediment to vary from 3 to 18 ppm (dry weight). Levels greater than 9 ppm were found at Hylebos and Sitcum Waterways (Commencement Bay); at three locations in Duwamish Waterway (Elliott Bay); and at the south end of Entrance Channel and Olympia Shoal in Budd Inlet. These seven sites were apparently also heavily contaminated with other metal pollutants, particularly arsenic, lead, copper, zinc, selenium, and chromium.

Comparison of cadmium levels with sediment characteristics indicates an apparent tendency for cadmium to be associated with fine-grained sediment and with high organic carbon levels (Malins et al., 1980). Armstrong et al. (1976) noted a correlation between copper, zinc, and lead with fine-grained sediments and organic carbon, but analytical difficulties frustrated their attempts to similarly assess cadmium correlations.

The release of cadmium from sediments appears to occur readily in marine waters, and may be of importance to the health of Puget Sound biota.

4.16.6 Conclusions

1. Cadmium levels in the sediments of Puget Sound are highly elevated when compared to regulatory criteria for classifying sediments. The probable sources are metallurgical operations, particularly smelting.

2. The major fate processes of cadmium in marine waters are the formation of soluble chloride complexes and sorption to solids with high organic content.

3. Cadmium has significant sublethal effects at very low (i.e., 5 µg/L) levels in seawater. Levels of cadmium in Puget Sound sediments are potentially high enough to affect behavioral patterns of bottom-dwelling species.

4. Biota tend to strongly accumulate and retain cadmium in their tissues.

4.16.7 Research Needs

1. There is a need to evaluate the concentrations of cadmium in ambient and interstitial waters in Puget Sound, particularly in more highly polluted areas.

2. There is a need to determine the sources of cadmium in Puget Sound.

3. There is a need to evaluate the sublethal and behavioral effects of cadmium-contaminated sediments on representative bottom-dwelling biota from Puget Sound.

4. There is a need to identify the relationships between toxic effects and metal burdens in major body organs of representative Puget Sound biota.

References

Armstrong, P.B., G.M. Hanson, and H.E. Gandette. 1976. Minor elements in sediments of Great Bay estuary, New Hampshire. Environ. Geol. 1:207-214.

Batley, G.E. and T.M. Florence. 1976. Determination of the chemical forms of dissolved cadmium, lead and copper in seawater. Marine Chem. 4:347-363.

Biosystems Environmental Consultants. 1977. Cadmium: Criteria for developing drinking water standards. D.G. Stevens, R.W. Steele, and L. Hermametz (eds.), for the Dept. of Natl. Health and Welfare, Ottawa, Ontario.

Calabrese, A., F.P. Thurberg, M.A. Dawson, and D.R. Wenzloff. 1975. Sublethal physiological stress induced by cadmium and mercury in winter flounder. In: J.H. Koeman and J.J.T.W.A. Strik (eds.), Sublethal Effects of Toxic Chemicals in Aquatic Animals. Elsevier Publications, New York. pp. 15-21.

Callahan, M.A. and M.W. Slimak. 1979. Water-Related Environmental Fate of 129 Priority Pollutants. EPA 440/4-79-029a.

Chapman, W.H., H.L. Fisher, and M.W. Pratt. 1968. Concentration factors of chemical elements in edible aquatic organisms. UCRL-50564. University of California, Livermore. Lawrence Radiation Lab. 50 pp.

Duce, R.A., G.L. Hoffman, B.J. Ray, I.S. Fletcher, G.T. Wallace, J.L. Fasching, S.R. Piotrowicz, P.R. Walsh, E.J. Hoffman, J.M. Miller, and J.L. Heffter. 1976. Trace metals in the marine atmosphere: sources and fluxes. In: H.L. Windom and R.A. Duce (eds.), Marine Pollut. Transfer. D.C. Heath and Co., Lexington, Mass.

Engel, D.W. and B.A. Fowler. 1979. Factors influencing cadmium accumulation and its toxicity to marine organisms. Environ. Health Persp. 28:81-88.

Environmental Protection Agency. 1977. Behavior of Mercury, Chromium and Cadmium in Aquatic Systems. EPA 600/3-77-023.

Environmental Protection Agency. 1978. Ambient Water Quality Criteria: Cadmium. NTIS (PB 292 423).

Environmental Protection Agency. 1980. Treatability Manual. Office of Research and Development, Washington, D.C.

Frazier, J.M. 1979. Bioaccumulation of cadmium in marine organisms. Environ. Health Persp. 28:75-79.

Gardner, J. 1974. The chemistry of cadmium in natural waters - II. The adsorption of cadmium on river muds and naturally occurring solids. Water Res. 8:157-164.

Greig, R.A. and D.R. Wenzloff. 1978. Metal accumulation and depuration by the American oyster, Crassostrea virginica. Bull. Environ. Contam. Toxicol. 20:499-504.

Huang, C.P., H.A. Elliott, and R.M. Ashwood. 1977. Interfacial reactions and the fate of heavy metals in soil-water systems. J. Water Pollut. Control Fed. 49:745-756.

International Joint Commission. 1979. Interim Report of the Dredging Subcommittee to the Great Lakes Water Quality Board. December 13, 1979. Windsor, Ontario.

Khalid, R.A., W.H. Patrick, Jr. and R.P. Gombrell. 1978. Effect of dissolved oxygen on chemical transformations of heavy metals phosphorus and nitrogen in an estuarine sediment. Estuar. Coastal Mar. Sci. 6:21-35.

Kinniburg, D.G., K. Sridhar, and M.L. Jackson. 1977. Specific adsorption of zinc and cadmium by iron and aluminum hydrous oxides. In: Biological Implications of Metals in the Environment, ERDA Symp. Ser: 42. Conf. #750929/77. pp. 231-239.

Luoma, S.N., E.A. Jenne. 1975a. Factors affecting the availability of sediment-bound cadmium to the estuarine, deposit-feeding clam, (Macoma balthica). Radioecology and Energy Resources, Ecol. Soc. Amer., Special Pub. No. 1:283.

Luoma, S.N. and E.A. Jenne. 1975b. The availability of sediment-bound cobalt, silver and zinc to a deposit-feeding clam. In: Symp. Biological Implications of Metals in the Environment, Hanford, Wash.

Lymburner, D.B. 1974. Environmental Contaminants Inventory Study No. 2. The Production, Use and Distribution of Cadmium in Canada, Report Series No. 39, Canada Center for Inland Waters, Inland Waters Directorate.

McGreer, E.R. 1979. Sublethal effects of heavy metal contaminated sediments on the bivalve, Macoma balthica(L.). Marine Poll. Bull. 10:259-262.

Malins, D.C., B.B. McCain, D.W. Brown, A.K. Sparks, and H.O. Hodgins. 1980. Chemical Contaminants and Biological Abnormalities in Central and Southern Puget Sound. NOAA Technical Memorandum OMPA-2. Office of Marine Pollution Assessment, Boulder, Colo. 295 pp.

Mantoura, R.F.C., A. Dickson, and J.P. Riley. 1978. The complexation of metals with humic materials in natural waters. Estuar. Coastal Mar. Sci. 6:387-408.

Martin, J.H., K.W. Bruland, and W.W Broenkow. 1976. Cadmium transport in the California current. In: H.L. Windom and R.A. Duce (eds.), Mar. Pollut. Transfer. D.C.Heath and Co. Lexington, Mass. pp. 159-184.

Montgomery, J.R. and M.T. Price. 1975. Release of trace metals by sewage sludge and the subsequent uptake by members of a turtle grass mangrove ecosystem. Harba Branch Foundation Inc., Contribution No. 115.

Nimmo, D.R., L.H. Bahner, R.A. Rigby, J.M. Sheppard, and A.J. Wilson, Jr. 1977. Mysidopsis bahia: An estuarine species suitable for life-cycle toxicity tests to determine the effects of a pollutant. In: F.L. Mayer and J.L. Hamelink (eds.), Aquatic Toxicol. Hazard Eval. ASTM STP 634. pp. 109-116.

National Institute for Occupational Safety and Health (NIOSH). 1979. Registry of Toxic Effects of Chemical Substances. (RTECS).

Rohatgi, N. and K.Y. Chen. 1975. Transport of trace metals by suspended particulates on mixing with seawater. J. Water Poll. Control Fed. 47:2298-2316.

Sibley, T.H. and J.J. Morgan. 1977. Equilibrium speciation of trace metals in freshwater:seawater mixtures. In: T.C. Hutchinson (ed.), International Conference on Heavy Metals in the Environment, Vol. I, Symp. Proceedings (Oct. 1975) Toronto.

Spehar, R.L., R.L. Anderson, and J.T. Fiandt. 1978. Toxicity and bioaccumulation of cadmium and lead in aquatic invertebrates. Environ. Pollut. 15:195-208.

Stumm, W. and P.A. Brauner. 1975. Chemical speciation. In: J.P. Riley and G. Skirrow (eds.), Chemical Oceanography, 2nd edition. Academic Press, New York.

Sunda, W.G., D.W. Engel, and R.M. Thuotte. 1978. Effect of chemical speciation on toxicity of cadmium to grass shrimp, Palaemonetes pugio: Importance of free cadmium ion. Environ. Sci. Technol. 12:409-413.

Swiss, J.J., D.W. McLeese, J.F. Payne, and R.F. Addison. 1980. Regulated levels of Schedule I substances in the Ocean Dumping Control Act - a review. Department of Fisheries and Oceans, Gov't. of Canada. 73 pp.

Valiela, I., M.D. Banus, and J.M. Teal. 1974. Response of salt marsh bivalves to enrichment with metal-containing sewage sludge and retention of lead, zinc and cadmium by marsh sediments. Environ. Pollut. 7:149-157.

Vernberg, W.B., P.J. DeCoursey, M. Kelly, and D.M. Johns. 1977. Effects of sublethal concentrations of cadmium on adult Palaemonetes pugio under static and flow through conditions. Bull. Environ. Contamin. Toxicol. 17:16-24.

Wentsel, R., A. McIntosh, W.P. McCafferty, G. Atchison, and V. Anderson. 1977. Avoidance response of midge larvae (Chironomus tentans) to sediments containing heavy metals. Hydrobiologia 55:171-175.

Zaroogian, G.E. 1979. Studies on the depuration of cadmium and copper by the American oyster Crassostrea virginica. Bull. Environ. Contam. Toxicol. 23:117-122.

4.17 Copper

4.17.1 Introduction

Copper is a heavy metal which is found in all compartments of the ecosystem. It is an essential element in the respiratory pigments of some saltwater species, especially crustaceans. Saltwater plants have enzymes containing copper which are necessary for photosynthesis.

However copper may be of appreciable concern when it is found at concentrations in excess of ambient levels because it is one of the most toxic metals to marine organisms. For example, a large amount of copper sulphate, dumped illegally on a shore near Moordwijk in the Netherlands, contaminated a large water mass and affected an area of the coast approximately 100 km in length (Roskan, 1965, cited in Bryan 1976). Fish, plankton, and mussel beds were observed dead or dying throughout the area. Effects were lessened after 2 weeks by strong winds which accelerated the mixing and dilution process.

In aquatic ecosystems, copper tends to associate strongly with particulates and organic matter. However, transfer between environmental compartments can be accomplished by relatively small changes in pH, redox potential, salinity, the presence of chelating agents, and several other physico-chemical factors. Consequently, the biological impact of this element and its compounds are both complex and variable.

Copper is found in Puget Sound sediments at levels from 10 to 1600 mg/kg (dry weight). EPA guidelines for classifying sediments within the Great Lakes consider sediments with levels in excess of 50 mg copper/kg sediment (dry weight) as "heavily polluted." Of 41 sediment samples from Puget Sound, only 13 samples had copper levels less than 50 mg/kg. The impact of the high copper levels in Puget Sound thus requires evaluation.

4.17.2 Significance to Puget Sound

4.17.2.1 Review of Known Toxicity Data

It is difficult to assess the impacts of copper in the environment because the toxicity of copper is highly dependent upon its speciation within the aqueous environment (Andrew, 1976). Toxicity tests are generally carried out by the addition of specific quantities of copper salts to water and such tests may not simulate the actual species of copper which exist in the environment. Nonetheless, to illustrate the degree of toxicity of copper, the following data are presented:

- The adjusted 96-hour LC50 values of copper ranged from 5 to 47 µg/L for the calanoid copepod, Acartia tonsa (EPA, 1978).

- Adjusted 96-hour LC50 values for embryos of summer flounder were 21 µg/L and for Florida pompano, adjusted LC50 values varied from 197 to 278 µg/L (EPA, 1978).

- copper at 5 µg/L inhibited 50% of photosynthesis or growth (EC50) of the alga, Thalassiosiria pseudonana and Scrippsiella faeroense (EPA, 1978).

- Zaroogian (1979) showed that exposure to 5 µg/L of copper resulted in 100% mortality of bay scallops within 119 days.

The EPA (1978) Ambient Water Quality Criteria for copper in saltwater is 0.79 µg/L (24 hour average). The Agency recommended that levels not exceed 18 µg/L at any time.

Marine species may vary considerably in their sensitivity to copper. Shuster and Pringle (1969) found that American oyster (Crassostrea virginica) could concentrate copper by a factor of 30,000 after 20 weeks exposure to 50 µg/L copper. Although the tissue was bluish-green in color, mortalities were no different than mortalities observed in the controls.

The toxicity of copper is affected by temperature. Eisler (1977) indicated that the sensitivity of Mya arenaria varied in accordance to seasonal temperature, with copper toxicity at least 100 times greater at summer temperatures (22°C) than toxicity observed at winter temperatures (4°C).

4.17.2.2 Possible Effects of Levels Found in Puget Sound

Determination of copper levels in 41 Puget Sound sediment samples, showed that 13 samples contained less than 50 mg/kg Cu, 16 samples had levels from 50 to 100 mg/kg, nine samples had levels from 100 to 200 mg/kg, two samples contained from 200 to 300 mg/kg, and one sample had 1600 mg Cu/kg sediment (dry weight).

Suspended matter from Puget Sound contained from 47 to 484 mg/kg (dry weight) copper with the higher values found in the Tacoma and Seattle harbors (Riley et al., 1980). No determinations of dissolved copper concentrations were made during the MESA program. Concentrations of copper in tissues of bottom-dwelling and filter-feeding biota approached or exceeded 100 ppm in many cases.

It is difficult to predict the possible biological effects of high copper levels observed in Puget Sound sediments. The effects will probably depend upon the interstitial water copper concentrations and the forms of copper within the sediments. For example, inhibition of burrowing behavior of clams (Venerupis decussata) exposed to sublethal concentrations (0.01 ppm) of copper was demonstrated by Stephenson and Taylor (1975) but no significant differences in burrowing behavior were observed when copper was added in the presence of excess ethylenediaminetetra-acetic acid (EDTA). McGreer et al. (1980) found that the aqueous phase copper concentrations above mine tailings had little relationship to the solid phase copper concentrations. The biological uptake of copper from the mine tailings was highly dependent upon the metal-binding associations within the tailings. As a result, no generalizations can be made about the effects of high concentrations of copper in marine sediments.

4.17.3 Sources or Inputs

Copper enters marine systems by a number of natural processes including runoff, geothermal sources, and airborne particles. Copper also enters the environment as a result of industrial activities such as smelting and the employment of antifouling paints, algicides, and pesticides (Lewis and Cave, 1979).

Loadings of copper to Puget Sound have been quantified by Schell and Nevissi (1977), and natural rather than man-made sources appear to contribute most of the trace elements to Puget Sound. The relative values of input quantities (metric tons per year) to Puget Sound as determined by Schell and Nevissi (1977) were: rivers, 787; Seattle METROs West Point Plant, 29; other municipalities, 22; atmospheric input, 450; vessels' protective measures, 360-590; urban runoff, 15; and advective transport, 306. Copper smelting in Tacoma may be the cause of the relatively high levels detected at stations in Commencement Bay (Schell and Nevissi, 1977).

4.17.4 Speciation of Copper

Copper discharged into aquatic environments may be present as soluble species (copper ions, copper complexes with inorganic ligands, copper complexes with organic ligands), insoluble particles (colloidal particulates of copper complexes or aggregates of hydrous metal oxides, and metal complexes adsorbed on organic or inorganic particulates), or as soluble or insoluble copper species contained within biomass (Mancy and Allen, 1973; Chynoweth et al., 1976).

Copper is a transition metal having two oxidation states (not including the metallic form) in solution and solid phases: cuprous (Cu^+) and cupric (Cu^{2+}). In aerated solutions the latter form (or a compound or complex of it) predominates but, in anaerobic conditions such as in sediments, the cuprous form may become stabilized. Speciation is therefore dependent on oxidizing or reducing conditions (measured by the redox potential, Eh) that prevail in the system.

An appreciation of the different forms of copper present in aquatic ecosystems is essential to understanding its toxicology, mobility and ultimate fate. The most toxic form of copper is the soluble Cu^{2+} (cupric) ion (Andrew, 1976). Copper toxicity is reduced by the addition of various organic or inorganic species which remove Cu^{2+} via complex formation (Takata and Nishikawa, 1969; Pagenkopf et al., 1974; Sunda and Guillard, 1976; Andrew, 1976). Reduction in toxicity of copper may be related to the stability of the complex (Chynoweth et al., 1976).

Sibley and Morgan (1975) calculated the relative quantities of species of copper in freshwater-seawater mixtures and found major changes in speciation at low seawater concentrations (Figure 4.17.1). The chloride form becomes predominant and the amount of copper adsorbed to particulates decreases with increasing salinity. Levels of the free cupric ion decrease with increasing salinity.

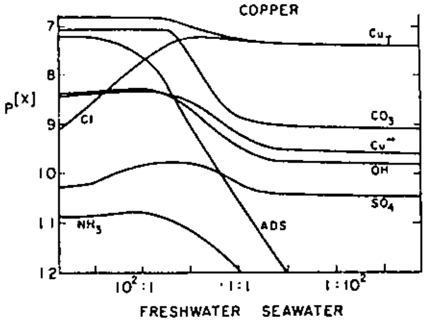


Figure 4.17.1
Speciation of Copper in Various Freshwater-Seawater Mixtures

The presence in the aquatic environment of naturally-occurring organic molecules containing relatively strong ligand groups (carbonyl, carboxyl, amino or sulphydryl) will affect speciation, and therefore toxicity, via complex formation with copper. Stumm and Brauner (1975) calculated the degree of copper-complex formation in seawater containing naturally-occurring organic solutes. They concluded that organic ligands are able to compete successfully with inorganic anions for Cu^{2+}even at low concentrations and that this competition would be most successful in interstitial water where levels of organic compounds tend to be highest.

Anode stripping voltammetry has been used to determine the amount of labile copper, free Cu^{2+} ions, and labile organic and inorganic complexes present in solution, and to subsequently relate the quantities of the various species to toxicity (Young et al., 1979). Gillespie and Vaccaro (1978) determined "copper chelation capacity" by use of a bacterial bioassay and an EDTA complexing technique for waters from Saanich Inlet (British Columbia), Vineyard Sound (Massachussetts), and the Sargasso Sea. EDTA forms particularly stable complexes with metals and therefore may not be representative of organic ligands present in seawater. However, the results with EDTA showed that, "The difference in chelation capacities (3-40 µg/L) among different water masses suggests that the biological impact of copper and other toxic metals may be site-specific and regulated by the dissolved oxygen content. Copper concentrations as low as 2 µg/L could be significantly toxic in areas of low chelation capacity such as the Sargasso Sea, whereas much higher levels would be necessary to produce a comparable effect in organically richer nearshore waters."

Although it is expected that the complexing materials of a water body would be related to its dissolved organics, Chau and Wong (1976) found "no correlation between complexing capacity with either dissolved organic carbon or dissolved organic nitrogen or both together."

4.17.5 Summary of Biogeochemical Fate Data in the Marine Environment

4.17.5.1 Bioaccumulation - Uptake and Depuration

Summary Statement: Bioaccumulation of copper occurs in benthic invertebrates to a much greater extent than in fishes. Depuration does occur; however, it is affected by many factors.

Review of Individual Studies: Uptake of soluble copper species can take place through gills of marine biota leading to concentration and passage into the bloodstream, from where it may collect in the liver, kidney, spleen, and intestine. Uptake from water is reduced by any speciation process which lowers the availability of Cu^{2+} ion. For example, high levels of chelating agents will reduce the bioavailability of copper (McGreer and Vigers, 1979). Precipitating anions and adsorption to suspended matter or sediment are also effective in reducing uptake.

Cross et al. (1975) monitored copper flux in three fish species from the Newport River estuary and found that copper ingested with suspended particulates was not significantly retained but was excreted in the feces.

Many studies have been published on bioaccumulation of copper by marine biota. Accumulation factors for Cu increased with increasing Cu concentrations for several phytoplankton species, suggesting that planktonic uptake may be a regulatory mechanism for Cu concentrations in seawater (Knauer and Martin, 1973; Saward et al., 1975). Uptake by phytoplankton may also be the major pathway for entry of the solubilized metal into the food web (Schmidt, 1978).

Although copper uptake by phytoplankton is an active process, adsorption is an important method of copper accumulation by seaweeds and polychaete worms. However, for the majority of marine animals, dietary sources are a very important route for copper accumulation (Schmidt, 1978).

Bioaccumulation factors of copper by other biological species are species dependent. Horne (1969) quoted a copper bioconcentration factor of 80 for fish, and 3,000 and 4,300 for the bottom-dwellers, scallops and nudibranches, respectively. Mussels and oysters had concentration factors of 3,000 and 13,700. Ayling (1974) suggested that the high uptake of copper by oysters may be a result of ingestion of copper adsorbed to particulates (Ayling, 1974; Halcrow et al., 1973).

Bindra and Hall (1977) found that trace metals in benthic organisms were not related to total trace metals in the sediments. The exchangeable and easily reducible phases of copper appeared to be most important in regulating bioaccumulation of this metal.

Shuster and Pringle (1969) found that oysters with high copper content were able to reduce body burdens of copper to normal levels 116 days after their transfer to clean waters. Mandelli (1975) noted that copper depletion in the oyster, <u>Crassostrea virginica</u>, occurred more quickly in winter than in summer, whereas Shuster and Pringle (1969) reported slower metal depuration at seawater temperatures of 4-12° than at 20°C. Shuster and Pringle (1969) also noted that depuration was affected by salinity, duration of metal exposure and, physiological condition and activity of the shellfish.

Bioaccumulation of copper by Puget Sound biota is evident. The following ranges of copper levels in Puget Sound biota were reported by Malins et al. (1980):

	ppm Cu
Rock and English sole (livers)	3.06-17.6
Crab (hepatopancreas)	34.9-223
Polychaete worms, shrimp, and clams (whole)	2.58-79.7

The blood and hepatopancreas of crustaceans generally contain the highest tissue copper levels (Bryan, 1968; Wright, 1976); thus, the above values would be higher than concentrations found in muscle tissue of the biota.

The bioavailability of copper to Puget Sound biota is apparently greater in non-urban areas. Of the samples analyzed during the MESA Project, Sinclair Inlet had the highest copper levels in clams. Case Inlet had the highest levels in crab hepatopancreas, and Port Madison had the highest levels in sole liver. The concentrations of copper in biota from the above areas exceeded concentrations observed in similar species from Commencement and Elliott Bays. Sediment copper levels in the "non-urban" areas were not notably high.

4.17.5.2 Adsorption-Desorption

Summary Statement: Adsorption to particulate matter and sediments is an important fate process for copper in marine waters. The adsorption-desorption processes are affected by many physical, chemical, and biological parameters. Release of copper from sediments may occur in the presence of aerobic conditions.

Review of Individual Studies: Adsorption of dissolved trace metals by clays and hydrous oxides is an important process in estuarine and coastal environments (Grieve and Fletcher, 1976; Batley and Gardner, 1978), and both copper ions and copper complexes may be thus removed from solution (Batley and Gardner, 1978; Davis and Leckie, 1978). Copper removal by a variety of naturally occurring substances (including clays, terrestrial soils, marine sediments, polymers produced by film-forming bacteria and water extracts of humic acid, and diatoms) results in reduction in toxicity (Lewis et al., 1972; Corpe, 1975).

Common divalent cations adsorb to clays with the following orders of stability (Farrah and Pickering, 1977):

illite	Pb > Cu > Zn > Ca > Cd > Mg
kaolinite	Pb > Ca > Cu > Mg > Zn > Cd
montmorillonite	Ca > Pb > Cu > Mg > Cd > Zn

This order indicates that copper can compete successfully for clay adsorption sites with most of the divalent ions found in estuarine and coastal waters.

Adsorption of dissolved copper on iron and manganese oxides may be an important coastal process (Parks, 1967), and is dependent on Eh, pH and concentrations of copper, other metal ions, and organic-complexing agents (Jenne, 1968). Adsorption may also occur on flocculated dissolved organic and inorganic matter which results during the mixing of river and seawater (Sholkovitz, 1976).

Hem (1975) indicated the conditions of Eh and pH over which a number of solute and solid species are stable in $Cu-H_2O-C-S$ systems. The solubility of copper in water at a given pH is highly dependent upon Eh. Also, copper ion solubility drops sharply as mildly reducing conditions are encountered due to the cuprous solids being much less water-soluble than their cupric analogues.

There are two important consequences of Hem's (1975) data. First, the reducing conditions that tend to prevail in anaerobic sediment will promote deposition of copper compounds. Second, a half-reaction between two different copper oxidation states (Cu^{2+}, Cu^{+}, or Cu^{0}) can couple with a half-reaction involving another transition metal. For instance, Cu^+ - Cu^0 reduction can couple with Fe^{2+}- Fe $(OH)_3$ oxidation so that ferrous ion can be an effective copper ion scavenger. Such a reaction would be feasible on the surface of ferrous-containing solids in suspension or in sediment.

Desorption of sediment-associated copper species might occur as a result of upwelling of sediment to aerated levels, dredging, and the spilling of oxidizing pollutants. Forstner et al. (1978) described other mechanisms for desorption of "immobilized" sediment-associated heavy metals, which included increased salinity, lowering of pH, increased levels of organic degradation products and synthetic complexing agents, microbial activity, and physical effects such as erosion and bioturbation.

The leachability and flux of sediment- and particulate-bound copper in the marine environment was discussed by Schmidt (1978). Copper content was highly correlated to the amount of sediment material less than 60 μm grain size, as well as to organic content and to the presence of clays and hydrous oxides.

In Saguenay fjord (Quebec), Loring (1976) found that 80% of the copper in sediment was found within the detrital (acetic acid-insoluble) fraction, the remainder within the non-detrital (acid-soluble) fraction. The amount of detrital fraction was strongly correlated with the presence of mud and organic carbon, indicating that copper accumulation was directly related to the deposition of fine grained inorganic and organic matter.

A multi-element analysis of sediments and tissues (Malins et al., 1980) sampled at 47 stations in Puget Sound indicated a wide variation in copper sediment levels. High sediment copper levels in Puget Sound were generally found in areas with high ratios of mud and/or organic carbon indicating that copper tends to associate with organic sediment material and/or that copper is discharged to Puget Sound in areas which are subject to considerable organic discharges.

Riley et al. (1980) showed that five metals, including copper, were present at higher levels in suspended matter from Elliott and Commencement Bays than at control sites, and tentatively concluded that copper contamination was high in industrial harbors of Puget Sound. Metal levels in suspended matter appeared to correlate with the presence of fine-grained sediment.

In Puget Sound, upwelling may be an important process in freeing and possibly oxidizing copper associated with sediments. Time-lapse photography and a hydraulic model have demonstrated that eddies are formed downstream from promontories during major flood and ebb tides (McGary and Lincoln, 1977), and that pollutants discharged in or near tidal eddies at depth may be upwelled and circulated toward shore (Ebbesmeyer et al., 1977). Important sites of possible pollutant upwelling are West Point (Ebbesmeyer et al., 1977) and Alki Point (Rattray and Lincoln, 1955).

Redox potentials in Elliott Bay sediment (Baumgartner et al., 1978) show a rise from a winter low of about -0.15 V to an early summer high of 0 to +0.3 V depending on station. Over the same period, sediment pH changed from 7.5 ± 0.2 to 7.0 ± 0.3. The winter Eh-pH values would correspond to lower oxidation states for copper (Cu(I) and Cu(0)), whereas the summer values suggest a significant proportion of Cu(II) in the solution phase. Cu(II) formation in summer would be significant for bottom-dwelling organisms and their predators in view of the greater toxicity of solubilized Cu(II). In the aqueous phase above the sediment, aerobic conditions will additionally favor Cu(II) formation.

Dissolved oxygen levels and salt wedge penetrations in Duwamish River estuary show diurnal and seasonal variations which could affect copper mobilization and dissolution from sediment, particularly at the "toe" of the wedge where salinity is increased (Dawson and Tilley, 1972).

4.17.6 Conclusions

1. In the marine environments copper is generally associated with particulates (sediments and suspended solids).
2. The most toxic species of copper is Cu^{2+}, the levels of which are diminished by the presence of ligands or several anions including chloride.
3. Copper is extremely toxic to marine biota with 96-hour LC50 values as low as 5 µg copper/L.
4. It is not possible to predict the effects of copper-contaminated sediments on biota, because of the complexity of metal-binding associations within the sediment. Individual studies are required to assess those effects.
5. Copper release for sediments may occur, dependent upon various conditions including changes in pH, Eh, oxygen levels, microbial activity, etc.
6. Copper bioaccumulates particularly within invertebrates.

4.17.7 Research Needs

1. There is a need to assess the dissolved copper levels in the waters of Puget Sound.
2. There is a need to assess the possible effects of copper-contaminated sediments on representative biota of Puget Sound.

3. If dissolved copper levels are in excess of the EPA (1978) Ambient Water Quality Criteria, or if the copper levels in sediments are found to impact Puget Sound biota, then:

    a. There is a need to describe the ability of Puget Sound waters to chelate copper. Low chelation capacity indicates that copper will be available to bottom dwellers; high capacity indicates that it could be available to pelagic biota if the complex is water-soluble. Analytical techniques such as anode stripping voltammetry, copper selective ion electrode, and bacterial bioassay should be considered.

    b. There is a need to monitor physico-chemical changes that may occur at upwelling sites, since sediment copper may become available to susceptible biota.

    c. There is a need to determine the cause of elevated copper levels in biota at Port Madison and Case Inlet.

    d. There is a need to assess equilibrium conditions for copper speciation in the presence of seawater/freshwater/organic compounds known to be present in Puget Sound, including involvement of temperature and pressure conditions representative of those in the Sound (not at STP) and incorporating relevant pH and Eh values. This assessment should include both aqueous and sediment/water heterogeneous sytems.

    e. There is a need to evaluate the influence of kinetic constraints on the attainment of copper speciation equilibrium, particularly for sediment processes and clearance by biota.

References

Andrew, R.W. 1976. Toxicity relationships to copper forms in natural waters. In: R. Andrew, P. Hodson, D. Konasewich (eds.), Toxicity to Biota of Metal Forms in Natural Water. Proceedings Workshop at Duluth Minnesota, October 7-8. 1975. International Joint Commission, Windsor, Ontario. pp. 127-143.

Ayling, G.M. 1974. Uptake of cadmium, zinc, copper, lead and chromium in the Pacific oyster *Crassostrea gigas* grown in the Tomar River, Tasmania. Water Res. 8:729-738.

Batley, G.E. and D. Gardner. 1978. A study of copper, lead and cadmium speciation in some estuarine and coastal marine waters. Estuar. Coastal Mar. Sci. 7:59-70.

Baumgartner, D.J., D.W. Schults, and J. B. Carkin. 1978. Aquatic disposal field investigations, Duwamish Waterway disposal site, Puget Sound, Washington. Appendix D. Chemical and physical analyses of water and sediment in relation to disposal of dredged material in Elliott Bay. Final Report. Dept. of the Army.

Bindra, K.S. and K.J. Hall. 1977. Effect of physical and chemical factors in water and sediments on the release of selected trace metals. Department of Civil Engineering, University of British Columbia. 65 pp. (unpublished manuscript).

Bryan, G.W. 1968. Concentrations of zinc and copper in the tissues of decopod crustaceans. J. Mar. Biol. Assn. U.K. 48:303-321.

Bryan, G.W. 1976. Heavy metal contamination in the sea. In: R. Johnston (ed.), Marine Pollution. Academic Press, London.

Chau, Y.K. and P.J.S. Wong. 1976. Complexation of metals in natural waters. In: R.W. Andrew, P.V. Hodson, D.E. Konasewich (eds.), Toxicity to Biota of Metal Forms in Natural Water. Proceedings Workshop at Duluth, Minnesota, October 7-8. 1975. International Joint Commission, Windsor, Ontario. pp. 187-196.

Chynoweth, D.P., J.A. Block, and K.H. Mancy. 1976. Effects of organic pollutants on copper toxicity to fish. In: R.W. Andrew, P.V. Hodson, D.E. Konasewich (eds.), Toxicity to Biota of Metal Forms in Natural Water. Proceedings Workshop at Duluth, Minnesota, October 7-8. 1975. International Joint Commission, Windsor, Ontario. pp. 145-157.

Collias, E.E., N. McGary, and C.A. Barnes. 1974. Atlas of Physical and Chemical Properties of Puget Sound and Its Approaches. University of Washington Press. 235 pp.

Corpe, W.A. 1975. Metal-binding properties of surface materials from marine bacteria. Develop. Indust. Microbiol. 16:249-255.

Cross, F.A., J.N. Willis, L.H. Hardy, N.Y. Jones, and J.M. Lewis. 1975. Role of juvenile fish in cycling of Mn, Fe, Cu and Zn in a coastal plain estuary, In: L. E. Cronin (ed.), Estuarine Research, Vol. 1. Academic Press, New York. pp. 45-63.

Davis, J.A. and J.O. Leckie. 1978. Effect of absorbed complexing ligands on trace metal uptake by hydrous oxides. Environ. Sci. Technol. 12:1309-1315.

Dawson, W.A. and L.J. Tilley. 1972. Measurement of salt-wedge excursion distance in the Duwamish River estuary, Seattle, Washington, by means of the dissolved oxygen gradient. Geological Survey Water Supply Paper 1873-D.

Ebbesmeyer, C.C., J.M. Helseth, C.A. Barnes, J.H. Lincoln, and W.P. Bendiner. 1977. On nearshore trappings of pollutants by tidal eddies downstream from points in Puget Sound, Washington. In: The Use, Study and Management of Puget Sound (a symposium). University of Washington. pp. 134-146.

Eisler, R. 1977. Acute toxicities of selected heavy metals to the softshell clam, (*Mya arenaria*). Bull. Environ. Contam. Toxicol. 17:137-145.

Environmental Protection Agency. 1978. Ambient Water Quality Criteria: Copper. NTIS (PB 296 791).

Farrah, H. and W. F. Pickering. 1977. Influence of clay solute interactions of aqueous metal ion levels. Water, Air, Soil Pollut. 9:189-198.

Forstner, U., G. Muller, and P. Stoffers. 1978. Heavy metal contamination in estuarine and coastal sediments: sources, chemical association and diagenetic effects. In: Biogeochemistry of Estuarine Sediments (Workshop proceedings). UNESCO. pp. 49-69

Gillespie, P.A. and R.F. Vaccaro. 1978. A bacterial bioassay for measuring the copper-chelation capacity of seawater. Limnol. Oceanogr. 23:543-548.

Grieve, P. and W.K. Fletcher. 1976. Heavy metals in deltaic sediments of the Fraser River, British Columbia, Canada. Can. J. Earth Sci. 13:1683-1693.

Halcrow, W., D.W. MacKay, and I. Thornton. 1973. The distribution of trace metals and fauna in the Firth of Clyde in relation to the disposal of sewage sludge. J. Mar. Biol. Assoc. U.K. 53:721.

Hem, J.D. 1975. Discussion paper. In: P. A. Krenkel (ed.), Heavy Metals in the Aquatic Environment. Pergammon Press. pp. 149-153.

Horne, R.A. 1969. Marine Chemistry: The Structure of Water and the Chemistry of the Hydrosphere. Wiley-Interscience Publishers.

Irving, H. and R.J.P. Williams. 1948. Order of stability of metal complexes. Nature 162:746

Jenne, E.A. 1968. Controls on Mu, Fe, Co, Ni, Cu and Zn concentrations in soils and water: the significant role of hydrous Mu and Fe oxides. In: R. A. Baker (ed.), Trace Inorganics in Water. Amer. Chem. Soc., Washington, D.C. pp. 337.

Johnson, D.L. 1978. Biological mediation of chemical speciation. I. Microcosm studies of the diurnal pattern of copper species in sea water. Chemosphere 8:641-644.

Knauer, G.A. and J.H. Martin. 1973. Seasonal variations of cadmium, copper, manganese, lead and zinc in water and phytoplankton in Monterey Bay. California. Limnol. Oceanogr. 18:597-604.

Lewis, A.G. and W.R. Cave. 1979. The biological importance of copper in the sea. Final Report. International Copper Research Assoc., Inc. (Incra) Project No. 223.

Lewis, A. G., P. H. Whitfield, and A. Rammarine. 1972. Some particulate and soluble agents affecting the relationship between metal toxicity and organism survival in the calanoid copepod Euchaeta japonica. Mar. Biol. 17:215-221.

Loring, D.H. 1976. The distribution and partition of zinc, copper and lead in the sediments of the Saguenay fjord. Can. J. Earth Sci. 13:960-971.

Malins, D.C., B.B. McCain, D.W. Brown, A.K. Sparks, and H.O. Hodgins. 1980. Chemical Contaminants and Biological Abnormalities in Central and Southern Puget Sound. NOAA Technical Memorandum. OMPA-2. Office of Marine Pollution Assessment, Boulder, Colo. 295 pp.

Mancy, K.H. and H.E. Allen. 1973. Physical and chemical aspects of copper toxicity to fishes. Environmental Protection Agency. Contract No. 14-12-591. Final Report.

Mandelli, E.F. 1975. The effect of desalivation brines on Crassostrea virginica. Water Res. 9: 287-296.

McGary, N. and J.H. Lincoln. 1977. Tide Prints, a Surface Current Atlas of Puget Sound. Sea Grant Pub. W5G 77-1.

McGreer, E.R. and G.A. Vigers. 1979. Identification of heavy metals in organisms within an area of the Fraser River estuary receiving a major municipal, industrial and stormwater discharge. E.V.S. Consultants report to the Dept. of Fisheries and Environment.

McGreer, E.R., B.J. Reid, and G.A. Vigers. 1980. Availability of metals from inorganic particulates (mine tailings) for uptake by marine invertebrates. Report prepared for Department of Fisheries and Oceans by E.V.S. Consultants Ltd., North Vancouver, B.C. 15 pp.

Pagenkopf, G.K., R.C. Russo, and R.V. Thurston. 1974. Effect of complexation on toxicity of copper to fishes. J. Fish. Res. Board Can. 31:462-465.

Parks, G.A. 1967. Aqueous surface chemistry of oxides and complex oxide minerals: isoelectric point and zero point of charge. In: W. Stumm (ed.), Equilibrium Concepts in Natural Water Systems. American Chemical Society, Washington, D.C.

Rattray, J., Jr. and J.H. Lincoln. 1955. Operating characteristics of an oceanographic model of Puget Sound. Trans. Amer. Geophys. Union 36:251-261.

Riley, R.G., E.A. Crecelius, D.C. Mann, K.H. Abel, B.L. Thomas, and R.M. Bean. 1980. Quantitation of Pollutants in Suspended Matter and Water from Puget Sound. NOAA Technical Memorandum ERL MESA-49. Marine Ecosystems Analysis Program, Environmental Research Laboratories, Boulder, Colo. 99 pp.

Roskan, R.T. 1965. I.C.E.S.C.M. Papers and Reports, Section C - Hydrographical Committee No. 40.

Saward, D., A. Stirling, and G. Topping. 1975. Experimental studies on the effects of copper on a marine food chain. Mar. Biol. 29:351.

Schell, W.R. and A. Nevissi. 1977. Heavy metals from waste disposal in central Puget Sound. Environ. Sci. Technol. 11:887-893.

Schmidt, R.L. 1978. Copper in the marine environment - Part II. CRC Critical Reviews in Environmental Control. 247-291.

Sholkovitz, E.R. 1976. Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater. Geochim. Cosmochim. Acta 36:825-865.

Shuster, C. and B.H. Pringle. 1969. Trace metal accumulation by the Eastern American oyster, Crassostrea virginica. Proc. Nat. Shellfish Ass. 59:91-103.

Sibley, T.H. and J.J. Morgan. 1975. Equilibrium speciation of trace metals in freshwater:seawater mixtures. In: T.C. Hutchinson (ed.), International Conference on Heavy Metals in the Environment. Vol. I. Symp. Proceedings, October 27-31, 1975. Toronto, Ontario.

Stephenson, R.R. and D. Taylor. 1975. The influence of EDTA on the mortality and burrowing activity on the clam (Venerupis decussata) exposed to sublethal concentrations of copper. Bull. Environ. Contam. Toxicol. 14:304-308.

Stumm, W. and P.A. Brauner. 1975. Chemical Speciation. In: J.P. Riley and G. Skirrow (eds.), Chemical Oceanography. Academic Press, New York.

Sunda, W. and R.R.L. Guillard. 1976. The relationship between cupric ion activity and the toxicity of copper to phytoplankton. J. Mar. Res. 34:511-529.

Takata, K. and K. Nishikawa. 1969. The toxicity of heavy metals to aquatic animals and factors which decrease the toxicity. V. A trial to decrease the toxicity of heavy metal ions by the addition of complexing agents. Bull. Tokai. Reg. Fish. Res. Lab. 58:255-264.

Wright, D.A. 1976. Heavy metals in animals from the north east coast. Mar. Pollut. Bull. 7:36-38.

Young, J.S., J.M. Gurtisen, C.W. Apts, and E.A. Crecelius. 1979. The relationship between the copper complexing capacity of seawater and copper toxicity in shrimp zoeae. Marine Environ. Res. pp. 265-273.

Zaroogian, D. 1979. Studies on the depuration of cadmium and copper by the American oyster Crassostrea virginica. Bull. Environ. Contam. Toxicol. 2:117-122.

4.18 LEAD

4.18.1 Introduction

Lead inputs to Puget Sound are the result of natural erosion and anthropogenic sources. Lead has a variety of uses for its metallic, inorganic and organic forms. Metal products constitute the greatest use of lead. The most widely used organo-lead compounds are tetramethyl- and tetraethyl-lead as anti-knock additives in automobile fuel. Lead is also used extensively in paint pigments and dyes. Lead is one of the EPA's 129 Priority Pollutants.

Many of the sediments sampled from Puget Sound were found to contain elevated levels of lead which may be of environmental concern.

4.18.2 Significance to Puget Sound

4.18.2.1 Review of Known Toxicity Data

The data base for the toxicity of lead to saltwater organisms is quite limited when compared to data available on its toxicity to freshwater species. The available toxicity data for saltwater organisms deal almost exclusively with invertebrate species. Only one toxicity study on saltwater fish was noted where the effect of lead on cholinesterase inhibition in shiner perch was studied. LC50 values for saltwater invertebrates ranged from 2,450 µg/L for oyster larvae (Calabrese et al., 1973) to 22,869 µg/L for soft shell clam adults (Eisler, 1977). Benijts-Claus (1975) found that 50 µg/L lead delayed larval development of the mud crab, Rhithropanopeus harissii. Lead was reported to be acutely toxic to freshwater invertebrates at concentrations as low as 450 µg/L and chronically toxic at concentrations less than 100 µg/L.

Shellfish have been shown to bioconcentrate lead many times the ambient water concentrations. Schulz-Baldes (1972) reported a bioconcentration factor of 2,576 for Mytilus edulis, and in a later study (Schulz-Baldes, 1976) showed bioconcentration factors of 1,050 and 933 for a marine diatom and phytoplankter, respectively. Schulz-Baldes (1974) found that Mytilus edulis may take up 23.5% of the lead available in food organisms (such as diatoms and phytoplankton) as compared to 29% of the lead available in the water.

Table 4.18.1 lists bioconcentration factors which have been reported for a number of marine invertebrates. It is important to note that variable bioconcentration factors have been reported for a single organism (e.g., Mytilus edulis). Bioconcentration of a contaminant is affected seasonally, by differences in the weight of individuals, length of exposure to metal, water temperature, experimental design, and chemical form of metal in seawater (EPA, 1978).

Table 4.18.1

Reported Bioconcentration Factors of Lead

Organism	Bioconcentration Factor*	Exposure Time(days)	Reference
Oyster, *Crassostrea virginica*	536	140	Zaroogian, Manuscript
Oyster, *Crassostrea virginica*	68	49	Pringle, 1968
Oyster, *Crassostrea virginica*	1,400	70	Schuster and Pringle, 1969
Mussel, *Mytilus edulis*	650	40	Schulz-Baldes, 1972
Mytilus edulis	2,568	130	Schulz-Baldes, 1972
Mytilus edulis	2,077	130	Schulz-Baldes, 1972
Quahaug, hard clam, *Mercenaria mercenaria*	175	56	Pringle, 1968
Soft shell clam, *Mya arenaria*	112	70	Pringle, 1968
Diatom, *Phaeodactylum tricornutum*	1,050	1/24	Schulz-Baldes, 1976
Phytoplankton, *Platymonas subcordiformis*	933	1/24	Schulz-Baldes, 1976

* ratio of concentration of lead in organism after exposure period to concentration of lead in ambient water

The organolead compounds detected in the environment are tetramethyl and tetraethyl lead. Saltwater toxicity data were not found for tetramethyl- and tetraethyl lead compounds. Tetraethyl lead is toxic at concentrations less than 1 ppm to small animals (NIOSH, 1979) and the compound was selected for carcinogenic bioassay by the National Cancer Institute in September, 1979. Tetramethyl lead is believed to be less toxic than tetraethyl lead.

The EPA has been unable to derive a criterion for lead and lead-containing compounds in saltwater organisms due to insufficient toxicity data (i.e., no chronic studies have been conducted with lead and saltwater organisms). Therefore, only freshwater criteria are available which are based on a plot of total hardness versus lead concentration. For example, for water with a hardness of 20 μg/L a 24-hour average of no more than 2.5 μg/L of lead is recommended. This approach is not applicable to the marine environment.

Recent toxicity studies with lead have shown that the EPA water quality criteria may have to be reconsidered. The studies showed that symptoms of lead toxicity to fish and snails occurred at 22 μg/L and 17 μg/L concentrations, respectively (International Joint Commission, 1980). These toxicity values are much lower than those considered by the EPA for the development of its criteria.

There has been some renewed interest in lead as a contaminant of concern in the Mediterranean and the Great Lakes. Lead levels in herring gull eggs from Lake Erie were found to be of 0.55 μg/g (wet weight). The consequences of the concentrations are not known (International Joint Commission, 1979). Vannuchi et al. (1978) reported lead levels as high as 40 ppm (μg/g) in kidney, 11 ppm in muscle and 30 ppm in brain of seagulls from the Mediterranean. These levels were higher than those of any other heavy metal, including mercury.

4.18.2.2 Possible Effects of Levels Found in Puget Sound

Schell and Nevissi (1977) reported lead levels in Central Puget Sound waters from 0.2 to 1 μg/L. Other measurements by Schell and Nevissi (1977) indicated levels as high as 7 μg/L; however, there were uncertainties about these measurements. Open sea levels generally contain between 0.1 to 0.2 μg lead/L (Bryan, 1976).

Lead concentrations in the sediments of Puget Sound range from 8 to 790 ppm (mg/kg) (Malins et al., 1980). The highest levels were found in Elliott Bay-Duwamish Waterway and Commencement Bay-Sitcum Waterway. Lead in the sediments of Raritan and Lower New York Bays, adjacent to heavily urbanized and industrialized regions, varied from 7-990 ppm (Waldhauer et al., 1978). Lead levels in sediments of the Saguenay River and fjord adjacent to the moderately urbanized and industrialized area were between 14-66 ppm. The following ranges are used to classify lead-containing sediments from Great Lakes Harbors (EPA):

Nonpolluted	< 40	ppm
Moderately polluted	40-60	ppm
Heavily polluted	> 60	ppm

In this context some sediments of Puget Sound appear to be heavily polluted with lead. Their effect on marine benthic biota cannot be predicted on the basis of current knowledge and individual tests are required for assessment.

The concentrations of lead detected in biota ranged from undetectable levels to 22.9 μg/g (wet weight) in clams from Commencement Bay-City Waterway (Malins et al., 1980). Positive detections and quantifications were made in samples of crab hepatopancreas, worms, shrimp, and clams.

4.18.3 Sources or Inputs

Nriagu (1978) estimated global anthropogenic lead emissions during the period 1974/75. He calculated that of 2.8×10^{10}tons of anthropogenic lead released during this period, 61% was contributed by the combustion of leaded gasoline, 21% was attributed to steel and base metal production, the mining and smelting of lead accounted for 8%, and the non-automotive burning of fossil fuels was responsible for the remaining 5%. Lead additives appear to be the major contributers to atmospheric lead according to a number of authors (Chow and Earl, 1970).

The major sources of lead input into the Puget Sound are listed in Table 4.18.2. Atmospheric input was calculated to be the largest source.

Table 4.18.2
Sources and Input Quantities of Lead to Puget Sound *

Source	Pb (metric tons/yr)
Rivers (Lake Washington Ship Canal included)	2032
Metro's West Point Plant	9
Atmospheric Input	2730
Vessels' protective measures and fuel consumption	9-12
Urban Runoff (Seattle)	350
Advective Transport	1640
Other Municipalities in Puget Sound Area	16

* Schell and Nevissi (1977)

Other study areas have also indicated the significance of atmospheric inputs of lead. Patterson et al. (1976) found that the atmospheric deposition of lead into a 12,000 km area of the Southern California Bight accounted for about 45% of the lead input, the remaining 55% being from wastewater, storm runoff, and river input. Duce et al. (1975) in a study over the New York Bight, estimated that approximately 13% of the input of pollutant lead to a 10,000 km area of the Bight was from atmospheric fallout - the rest was attributed to barge dumping, runoff, sewage and river input.

4.18.4 Speciation of Lead

The fate and transport of lead in the aquatic environment are dependent on its chemical species. Speciation may also have direct bearing on toxicity and availability to biota (Robinson et al., 1979; Chau et al., 1980; Whitfield and Lewis, 1976; Waldhauer et al., 1978). Alkylation may make lead particularly toxic (Beijer and Jernelov, 1978).

Lead may exist in the aquatic environment in several soluble and particulate forms (Beijer and Jernelov, 1978):

1. Soluble - free hydrated ion; complex and chelated ions with inorganic ligands (OH, CO_3^{2-}, Cl^-) or organic ligands (amines, proteins, humic and fulvic acids); or alkylated forms.

2. Particulate - in colloidal complexes such as hydrated oxides; adsorbed onto particles; precipitated, for example, as metal coatings on particles, incorporated into biota; or part of a structural lattice in crystalline detrital mineral particles.

The composition of these species in the aquatic environment varies with pH, Eh, and substrate composition. Temperature, pressure, concentration of suspended solids, and biological activity may also alter the dominant chemical form of lead in the aquatic environment. In freshwater-seawater mixtures, the parameters affecting lead speciation are ionic strengths, co-concentrations of adsorbing surfaces in seawater, concentration of lead, and concentrations of major cations and ligands.

Sibley and Morgan (1977) found that free ion concentrations of lead increase gradually in going from freshwater to a 1:1 mixture of freshwater and seawater. Two reasons were given. Firstly, desorption increases the concentration of dissolved metal and causes a corresponding increase in free ion. Second, with increased ionic strength, the free ion concentration will be higher relative to most complexes. The net effect is an approximate doubling in concentration of free ion lead. Figure 4.18.1 shows the shift of dominant forms of lead in freshwater-seawater mixtures with changing pH. The particulate-adsorbed lead decreases with higher seawater concentration due to desorption from solid surfaces. Beyond 1:1 ratios of seawater to freshwater, free lead ion decreases. Sibley and Morgan (1977) suggested that because free metal ion levels are highest at 1:1 seawater to freshwater ratios, the most severe toxic effects would occur in this range (i.e., in an estuary).

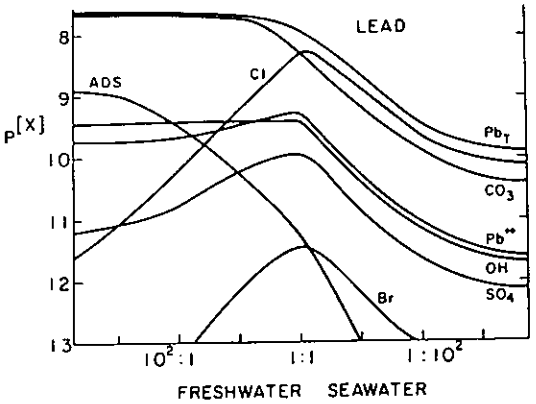


Figure 4.18.1
Lead Chemical Speciation in Seawater-Freshwater Mixtures
(from Sibley and Morgan, 1977)

Long and Angino (1977) constructed a pH-dependent model for the speciation of lead in seawater using estimated thermodynamic stability constants and ion activity coefficients. Their model is shown in Figure 4.18.2

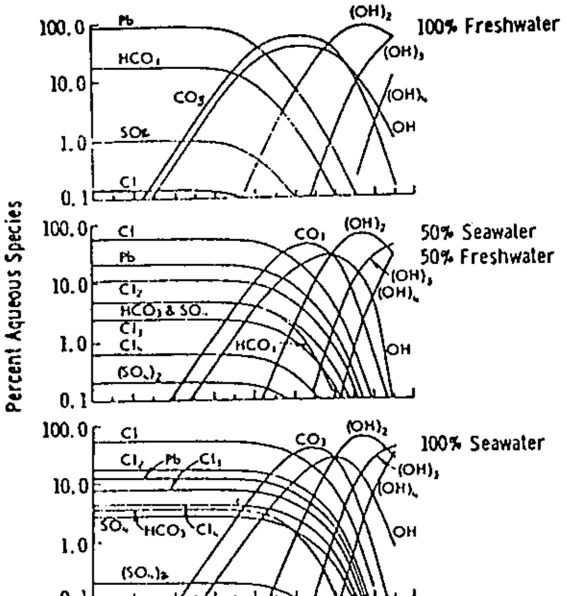


Figure 4.18.2
Calculated Distributions of the Chemical Species of Lead in Seawater at 25°C and 1 Atmosphere as a Function of pH (from Long and Angino, 1977)

Long and Angino's (1977) scheme of lead speciation shown in Figure 4.18.2 indicates that lead complexation with the chloride ion increases significantly with addition of seawater. At pH values between 7.5 and 8.5 (ambient Puget Sound levels) lead is present predominantly as free lead, $PbCl^+$, $PbCO_3$, and $PbCl_2$. Although the concentration of free lead ion appears to decrease with the addition of seawater in the Long and Angino (1977) model, Sibley and Morgan (1977) reported maximal free ion concentrations of lead in 50:50 mixtures of seawater and freshwater.

Natural organic compounds that can form stable complexes with lead ions fall into two categories:

1. amino acids, organic acids, peptides, proteins, polyphenols, and polysaccharides (soluble),
2. fulvic and humic acids (insoluble).

Such complexes would be important in estuaries with high carbon loadings and would decrease the availability of lead to biota.

Other significant forms of lead in the environment are the alkylated species. Wong et al. (1975) showed that microorganisms in lake sediments could convert lead nitrate, lead chloride and tetravalent lead in the form of $(CH_2)_3PbOAc$, to tetramethyl lead. Thompson and Crerar (1980) reported that methylation may not be as important in marine sediments. Only 0.03% of lead added as lead nitrate underwent methylation in marine sediments. However, the studies were restricted to sediments containing large quantities of mine tailings. Robinson et al. (1979) studied the interaction of tetraethyl lead, which is still important as an anti-knock agent in automobile fuels, and seawater. Tetraethyl lead (TEL) was found to be only slightly soluble in seawater, but its solubility increased with time. In seawater, TEL is known to produce triethylchloro-lead ($PbEt_3Cl$) which is very soluble and is approximately 100 times more toxic (Millar et al., 1972; Maddock and Taylor, 1977) than TEL. Robinson et al. (1979) reported that TEL and $PbEt_3Cl$ in seawater appeared to reach an equilibrium state with $PbEt_3Cl$ being dominant. TEL was also found to be converted by the liver of biota to $PbEt_3Cl$ (Robinson et al., 1979).

Urban runoff is responsible for the discharge of 350 metric tons lead/year into Puget Sound (Schell and Nevissi, 1977). Soluble lead tends to constitute only a small fraction of total lead content in urban runoff waters (Oliver et al., 1974). Most of the soluble lead will be complexed with inorganic ligands (Hem, 1976; Rickard and Nriagu, 1978) with a small portion present as soluble alkylleads.

4.18.5 Summary of Biogeochemical Fate Data in the Marine Environment

4.18.5.1 Bioaccumulation - Uptake and Depuration

Summary Statment: Phytoplankton and shellfish bioaccumulate lead to a much greater extent than do fish. Adsorption to phytoplankton and consumption of phytoplankton and bottom debris by shellfish are possible mechanisms of uptake. Organo-lead is bioaccumulated by fish, but studies on uptake of organo-lead are minimal.

Review of Individual Studies: Bioaccumulation studies have shown that marine plants and invertebrates accumulate lead more rapidly and to a greater extent than do marine fish. Bioconcentration factors in lead have been previously summarized in Table 4.18.1.

Phytoplankton accumulate large quantities of lead from solutions (International Joint Commission, 1980; Rickard and Nriagu, 1978). The accumulation may be due to adsorption by the relatively large surface areas of algal cells, or to ion exchange (National Academy of Sciences and National Academy of Engineering, 1973). Leland and McNurney (1974) studied total lead concentrations in biota from urban and rural Illinois streams and found that lead concentrations were highest in small planktonic or sestonic organisms with a high surface to body weight ratio. Adsorption was suggested as a major uptake mechanism.

Adsorption was also evident during studies by Canterford et al. (1978) on the accumulation of heavy metals by the marine diatom Ditylum brightwellii. The concentration of lead in the organism increased with increased concentrations of lead in the culture medium.

The adsorption of lead by phytoplankton implies that herbivorous fish may have higher lead concentrations that carnivorous fish (I.J.C., 1980). Boothe and Knauer (1972) studied bioaccumulation of lead by the herbivorous crustacean Pugettia producta (adult kelp crab) with the brown alga, Macrocystis pyrifera, as a sole food source. Lead was found to be concentrated in the feces with a concentration 5.4 times greater than that found in algae. Poplikarov (1966) found evidence that planktonic primary consumers concentrate certain metals in their feces, including lead. Fecal material is a possible food source of marine organisms, especially detrital feeders (Harvey, 1945; Cushing, 1959; Jorgensen, 1962; Newell, 1965; Johannes and Satomi, 1966). However, little information is available on whether fecal material is a final "sink" of heavy metals and/or serves to transfer metals to other biota.

In addition to dependence on the dissolved species of lead, uptake of lead will also depend upon other factors such as life stages of the biota. For example, Ray (1978) compared the relative lead levels in tissues of two age groups of Atlantic salmon, Salmo salar, the parr (juvenile salmon) and grilse (mature, undersized, male salmon returning to freshwater to spawn for the first time). The levels were highest for parr in all tissues. Ray (1978) postulated that the lower metal content in grilse tissues may be due to rapid growth of fish while the metal load remains the same (e.g., stepped up metabolism). The liver and kidney tissues accumulated the lead selectively.

Alkylated lead species would probably have high partition coefficients and, therefore, have potential for bioconcentration within fatty tissues of organisms. Data on uptake of alkylated lead species are, however, minimal. The presence of tetraalkyl lead compounds in fish was first reported by Sirota and Uthe (1977). They found high ratios of alkyl lead to lead in fish products from Halifax, Nova Scotia. Mor and Beccaria (1977) reported high tetraalkyl lead concentrations in mussels sampled in the Adriatic Sea near the S.S. Cavat incident where a shipload of anti-knocking compounds was sunk. The inability to metabolize the tetraalkyl lead was believed responsible for the elevated concentrations found in the mussels. Chau et al. (1980) carried out a study in which environmental samples (fish, vegetation, sediment, and water) were analyzed for the presence of tetraalkyl lead compounds. They were unable to detect tetraethyl lead in water, vegetation, or sediment. However, 17 of the 107 fish samples analyzed contained tetraalkyl lead compounds. Generally, the concentration of tetraethyl lead was low, representing less that 10% of the total lead.

4.18.5.2 Adsorption-Desorption

Summary Statement: Adsorption is an important fate process for lead. Release to the water column may occur under oxidizing conditions.

Review of Individual Studies: The partitioning of metals in the surface sediments (i.e., 1 cm deep) is of consequence in understanding adsorption/desorption mechanisms as well as transport, toxicity, and biological availability of lead in this environmental compartment. The sediment compartment includes both the sediment and interstitial pore waters. Lead can exist in the pore waters as either free or complexed ions, or it can be loosely adsorbed on solids. Possible mechanisms for the migration of soluble trace metals between the sediment/seawater interface are: chemical transformation, bio-oxidation, sorption, dissolution, precipitation, complexation, diffusion, and redox mix.

Speciation of lead varies with the redox condition of sediments and pH. In an estuarine environment the sediment may be anoxic due to large terrestrially-derived organic carbon loadings from industrial and municipal effluents. During the transport of lead either as a free ion or associated with suspended matter, it is usually in an oxidizing environment. The chemical environment in sediments are usually anoxic and typically lower in pH. The predominant species within an anoxic environment will be the sulfide solids (PbS). Metal migration will occur if the overlying water is aerobic. PbS has a high oxidation rate and will readily form more soluble compounds such as $PbCO_3$ and $Pb(OH)_2$ in the presence of an oxygenated environment.

Upon entering the marine environment from rivers, lead adsorbed to particulates will be subjected to two major processes:

1. As ionic strength increases, desorption of lead from river particulates, particularly river clays, increases due to competitive exchange in the electrical double layer.

2. Salting out of the large, molecular weight organic fractions (usually of terrestrial origin) and flocculation of inorganic matter results in particles which will then adsorb some of the dissolved lead and move to the sediment (Sibley and Morgan, 1977).

Patterson et al. (1976) found that 11% of the lead adsorbed to particulate matter from sewage effluent was released when exposed to seawater. Additional exposure did not, however, result in further release. Lu and Chen (1977) found that the release of lead from polluted sediment in seawater increased as the redox conditions became more oxidizing.

The levels of lead in Puget Sound sediments indicate, however, that adsorption to sediments is a significant fate process. The literature indicates that substantial release may occur under appropriate environmental conditions, implying that the water column may have lead levels of concern.

4.18.5.3 Photolysis

Photolysis of lead compounds in the atmosphere determines the form of lead entering the marine environment via the atmosphere. In urban areas, automobile emissions would be of particular importance.

Lead halides are the main forms of lead from automobile exhausts. These compounds are photochemically decomposed by ultraviolet light resulting in the release of free halogen (bromine and chlorine) (Nriagu, 1978). Pierrand (1969) believed lead oxide to be the end product of the photolysis of lead halides in the atmosphere. However, it was also stated that an appreciable portion of the lead halides are converted to lead carbonate and lead sulphate (International Joint Commission, 1980).

Tetraalkyl lead compounds are stable in air at ambient temperatures but at elevated temperatures or in the presence of light they are decomposed to lead metal and free organic radicals (Rickard and Nriagu, 1978). Organic end products may include ethane, ethylene, propylene, hydrogen, butane, and some higher hydrocarbons. No publica tions were found in the literature of the effects of sunlight on inorganic lead or organic lead in marine waters.

4.18.5.4 Volatilization

Summary Statement: Volatilization is an important fate process for alkylated lead compounds. However, the extent of alkylation of lead in the marine environment is not known.

Results of Individual Studies: Transient volatile species of lead may result from anthropogenic sources, such as fossil fuel combustion and other high temperature industrial processes, as well as natural processes, such as volcanism and biological methylation.

Both tetraethyl lead and tetramethyl lead are relatively volatile with respective vapor pressures of 0.15 mm and 22.5 mm at 20°C (Verschueren, 1977). Robinson et al. (1979) performed a study on volatilization of tetraethyl lead (TEL) by placing 200 μL TEL in a flask containing 25 ml of seawater. The flask was stoppered and covered with aluminum foil to exclude light. Analysis of the gas phase indicated that, in an open system, TEL would diffuse very rapidly through the seawater.

Chau et al. (1980) reporting on the occurrence of tetraalkyl lead compounds in aquatic environments, found ppb levels of these compounds in fish but none in the water column, vegetation, or sediments of the lake studies. They attributed the lack of tetraalkyl lead compounds in all environmental compartments but biota to the high vapor pressure and susceptibility to volatilization of these compounds.

The extent to which lead alkylates in the marine environment is questionable; thus, there is inadequate information at this time to evaluate the significance of volatilization as a fate process for lead.

Duce et al. (1972) found the surface microlayer of the ocean surface (top 150-300 μm) to be significantly enriched with respect to particulate lead compared to water 20-40 cm below. They believed that enrichment of the surface layer resulted from migration of particulate trace metals from subsurface water to the surface via bubble flotation. It is uncertain whether this phenomenon is significant to the fate of lead in Puget Sound.

4.18.6 Conclusions

1. Lead concentrations in some Puget Sound sediments are very high and require individual assessment to determine if the levels are of concern.

2. Data on toxicity of lead to saltwater biota are insufficient. However, studies have indicated that lead levels as low as 50 µg/L delayed larval development of mud crab.

3. Shellfish, diatoms, and phytoplankton generally contain higher concentrations of lead than do fish.

4. High levels of lead have been found in wildlife in other areas of the world, resulting in renewed concern about lead.

5. Data are sparse on the formation of alkyl lead compounds in the marine environment. The compounds are probably very toxic to biota.

6. Free lead ion concentrations may be maximal at 50:50 mixtures of freshwater and seawater indicating that biota in estuaries may be very sensitive to lead.

7. Predominant fate processes are adsorption to solids and complexation with organic ligands and inorganic ions.

4.18.7 Research Needs

1. There is a need to perform toxicity studies on the effects of lead on biota in seawater and freshwater-seawater mixtures.

2. There is a need to determine if the process of alkylation of lead occurs in the marine environment.

3. There is a need to assess lead levels and lead species in higher food chain organisms of Puget Sound, particularly birds.

References

Beijer, K. and A. Jernelov. 1978. Sources, transport and transformation of metals in the environment. In: Toxicology of Metals, Volume III. EPA-600/1-78-016.

Benijts-Claus, C. and F. Benijts. 1975. The effect of low lead and zinc concentrations on the larval development of the mud-crab *Rhithropanopeus harrisii.* Gould. In: J.H. Koeman and J.J.T. W.A. Strik (eds.), Sublethal Effects of Toxic Chemicals on Aquatic Animals. Elsevier Publishing Co., Amsterdam. pp. 43-52.

Boothe, P.N. and G.A. Knauer. 1972. The possible importance of fecal material in the biological amplification of trace and heavy metals. Limnology and Oceanography 17:270-274.

Bryan, G.W. 1976. Some aspects of heavy metal tolerance in aquatic organisms. In: A.P.M. Lockwood (ed.), Effects of Pollutants on Aquatic Organisms. 2 Cambridge Press, Great Britain. pp. 7-34.

Calabrese, A., R.S. Collier, D.A. Nelson, and J.R. MacInnes. 1973. The toxicity of heavy metals to embryos of the American oyster Crassostrea virginica. Mar. Biol. 18:162-166.

Canterford, G.S., A.S. Buchanan, and S.C. Ducker. 1978. Accumulation of heavy metals by the marine diatom, Ditylum brightwelli (West) Grunow. Aust. J. Mar. Freshwater Res. 29:613-622.

Chau, Y.K. P.T.S. Wong, O. Kramar, G.A. Bengert, R.B. Cruz, J.O. Kinrade, J. Lye, and J.C. van Loon. 1980. Occurrence of tetraalkyllead compounds in the aquatic environment. Bull. Environ. Contam. Toxicol. 24:265-269.

Chow, T.J. and J.L. Earl. 1970. Lead aerosols in the atmosphere - increasing concentrations. Science 169:577-580.

Cushing, D.H. 1959. The seasonal variation in oceanic production as a problem in population dynamics. J. Cons., Cons. Perm. Int. Explor. Mer. 24:455-464.

Duce, R.A., J.G. Quinn, C.E. Olney, S.R. Piotrowicz, B.J. Ray, and T.L. Wade. 1972. Enrichment of heavy metals and organic compounds in the surface microlayer of Narragansett Bay, Rhode Island. Science 176:161-163.

Duce, R.A., G.L. Hoffmann, and W.H. Zoller. 1975. Atmospheric trace metals at remote northern and southern hemisphere sites - pollution or natural? Science 187:59-61.

Eisler, R. 1977. Acute toxicities of selected heavy metals to the soft shell clam, Mya arenaria. Bull. Environ. Contamin. Toxicol. 17:137.

Environmental Protection Agency. 1978. Ambient Water Quality Criteria: Lead. NTIS (PB 292 437).

Harvey, H.W. 1945. The Chemistry and Fertility of Seawater. Cambridge Press. Cambridge, Great Britain. 224 pp.

Hem, J.D. 1976. Inorganic chemistry of lead in water. In: T.G. Lovering (ed.), Lead in the Environment; Professional Paper 957., U.S. Geological Survey, Washington, D.C.

Johannes, R.E. and M. Satomi. 1966. Composition and nutritive value of fecal pellets of a marine crustacean. Limnol. Ocean. 11:191-197.

Jorgensen, C.B. 1962. The food of filter-feeding organisms. Rapp. Proces. - Verb. Reunions. Cons. Perm. Int. Explor. Mer. 153:39-47.

International Joint Commission. 1979. Great Lakes Water Quality Board Report.

International Joint Commission. 1980. Report of the Aquatic Ecosystem Objectives Committee. Great Lakes Science Advisory Board, Windsor, Ontario.

Leland, H.V., and J. McNurney. 1974. Lead transport in a river ecosystem. In: Proceedings of the International Conference on: Transport of Persistent Chemicals in Aquatic Ecosystems. University of Ottawa, May 1-3, Ottawa, Ontario. pp. III17-I I123.

Long, D.T. and E.E. Angino. 1977. Chemical speciation of cadmium, copper, lead and zinc in mixed freshwater, seawater and brine solutions. Geochim. Cosmochim. Acta 41:1183-1191.

Lu, J.C.S. and K.Y. Chen. 1977. Migration of trace elements in interfaces of seawater and polluted surficial sediments. Environ. Sci. Technol. 11:174-182.

Maddock, B.G. and D. Taylor. 1977. The acute toxicity of and bioaccumulation of some lead alkyl compounds in marine animals. Presented at the International Experts Discussion Meeting on: Lead- Occurrence, Fate and Pollution in the Marine Environment, October 18-22. Rovinj, Yugoslavia.

Malins, D.C., B.B. McCain, D.W. Brown, A.K. Sparks, and H.O. Hodgins. 1980. Chemical Contaminants and Biological Abnormalities in Central and Southern Puget Sound. NOAA Technical Memorandum OMPA-2. Office of Marine Pollution Assessment, Boulder, Colo. 295 pp.

Millar, J.A., G.G. Thompson, A. Goldberg, P.S.I. Barry, and E.H. Lowe. 1972. British J. Ind. Med. 29:317-320.

Mor, E.D. and A.M. Beccaria. 1977. A dehydration method to avoid loss of trace elements in biological samples. Presented at the International Experts Discussion on: Lead-Occurrence, Fate and Pollution in the Marine Environment. Rovini, Yugoslavia, October 18-22.

National Academy of Sciences and National Academy of Engineering. 1973. Water Quality Criteria 1972. Ecological Research Series. EPA-R3-073-033, Washington D.C.

Newell, B. 1965. The role of detritus in the nutrition of two marine deposit feeders, the prosobrach Hyrobia ulva and the bivalve Macoma balthica. Proc. Zool. Soc. London. 144:25-45.

National Institute for Occupational Safety and Health (NIOSH). 1979. Registry of Toxic Effects of Chemical Substances (RTECS).

Nriagu, J.O. 1978. Properties and the biogeochemical cycle of lead. In: J.O. Nriagu (ed.), The Biogeochemistry of Lead in the Environment. Part A. Elsevier/North Holland Biomedical Press, New York.

Oliver, B.G., J.B. Milne, and N. LaBarre. 1974. Chloride and lead in urban snow. J.W.P.C.F. 46:766-771.

Patterson, C., D. Settle, and B. Glover. 1976. Analysis of lead in polluted coastal seawater. Mar. Chem. 4:305-319.

Pierrand, J.M. 1969. Photochemical decomposition of lead solids from automobile exhaust. Environ. Sci. Technol. 3:48-51.

Poplikarov, G.G. 1966. Radioecology of Aquatic Organisms. North Holland Press. 314 pp.

Pringle, B.H. 1968. Trace metal accumulation by estuarine mollusks. Proc. Am. Soc. Civil Eng., J. San. Eng. Div. SA3:455-475.

Ray, S. 1978. Bioaccumulation of lead in Atlantic salmon (Salmo salar). Bull. Environ. Contamin. Toxicol. 19:631-636.

Rickard, D.T. and J.O. Nriagu. 1978. Aqueous environmental chemistry of lead. In: J.O. Nriagu, (ed.), The Biogeochemistry of Lead in the Environment. Part A. Ecological Cycles. Elsevier/North Holland Biomedical Press, New York.

Robinson, J.W., E.L. Kiesel, and I.A.C. Rhodes. 1979. Studies of the interactions between tetraethyllead and seawater using GC-AA. J. Environ. Sci. Health. A14:65-85.

Schell, W.R. and A. Nevissi. 1977. Heavy metals from waste disposal in central Puget Sound. Environ. Sci. Technol. 11:887-893.

Schulz-Baldes, M. 1972. Toxizitat und anreicherung von blei bei der miesmuschel Mytilus edulis in labor experiment. Mar. Biol. 16:266.

Schulz-Baldes, M. 1974. Lead uptake from seawater, food and lead loss in the common mussel, Mytilus edulis. Mar. Biol. 25:177.

Schulz-Baldes, M. 1976. Lead uptake in two marine phytoplankton organisms. Biol. Bull. 150:118.

Schuster, C.N. and B.H. Pringle. 1969. Trace metal accumulation by the Eastern Amerian Oyster Crassostrea virginica. Proc. Natl. Shellfish Assoc. 59:91.

Sibley, T.H. and J.J. Morgan. 1977. Equilibrium speciation of trace metals in freshwater, seawater mixtures. In: T.C. Hutchinson (ed.), Symposium Proceedings: International Conference on Heavy Metals in the Environment, Volume I. October 27-31. Toronto, Ontario. pp. 319-338.

Sirota, G.K. and J.F. Uthe. 1977. Determination of tetraalkyllead compounds in biological materials. Anal. Chem. 49:823-825.

Thompson, J.A.J. and J.A. Crerar. 1980. Methylation of lead in marine sediments. Mar. Pollut. Bull. 11:251-253.

Vannucchi, C., S. Sivieri and M. Ceccanti. 1978. Residues of chlorinated naphthalenes, other hydrocarbons and toxic metals (Hg, Pb, Cd) in tissues of Mediterranean seagulls. Chemosphere 6:483-490.

Verschueren, K. 1977. Handbook of Environmental Data on Organic Chemicals. Van Nostrand Reinhold Company, London.

Waldhauer, R., A. Matte, and R.E. Tucker. 1978. Lead and copper in the waters of Raritan and Lower New York Bays. Mar. Pollut. 9:38-42.

Whitfield, P.H. and A.G. Lewis. 1976. Control of the biological availability of trace metals to a calanoid copepod in a coastal fjord. Estuarine and Coastal Mar. Sci. 4:255-266.

Wong, P.T.S., Y.K. Chau, and P.L. Luxon. 1975. Methylation of lead in the environment. Nature 253:263-264.

Zaroogian, G.E., EPA. Environmental Research Lab., Narragansett, R.I. (Manuscript).

4.19 Mercury

4.19.1 Introduction

Mercury compounds have been known to pose a health hazard since Roman times. The first recorded description of industrial mercury poisoning was in 1557 (D'Itri, 1972). However, it was not until the mass poisonings of Minamata (in 1953) and Nigata, Japan (in 1965) that world-wide attention was focused on the hazards of mercury contamination in the environment. The local people of the area consumed fish and shellfish which had concentrated 50 to 30,000 times the levels of methylmercury present in the waters they were exposed to (D'Itri and D'Itri, 1977). In 1972, the most severe mercury poisoning incident occurred in Iraq. Farmers ingested wheat seed treated with mercurial fungicides instead of planting it. The government subsequently put a ban on the possession and sale of the seeds and the farmers disposed of them in nearby rivers and lakes. The result of this incident cost the lives of an estimated 5,000 to 50,000 people and the permanent disability of more than 100,000 people (Bakir et al., 1973).

As a result of these and other less publicized accounts, regulatory and research agencies have paid considerable attention to the environmental mercury problem. Many studies have been published on the fate and effects of mercury in the environment (Kanzantzis, 1971; Hartung and Dinman, 1972). In addition, the finding that certain microorganisms have the ability to convert inorganic and organic forms of mercury to the highly toxic methyl- or dimethylmercury have been of particular concern to the environment (Jensen and Jernelov, 1969).

Efforts have been made to reduce the discharge of mercury to the environment. For example, chlorine production facilities have eliminated or reduced the usage of mercury.

Mercury remains on the list of EPA's 129 Priority Pollutants. Efforts to restrict the use and therefore reduce the discharge of mercury may have abated its pollution threat to Puget Sound. However, several sediments of Puget Sound still contain levels of mercury which may be of environmental significance.

4.19.2 Significance to Puget Sound

4.19.2.1 Review of Known Toxicity Data

Mercury is one of the most hazardous heavy metals present in the environment. The toxicity of mercury varies greatly with its chemical form (Luckey et al., 1975). Monovalent mercury is relatively nontoxic due to the low solubility of its salts. However, tissues and erythrocytes can oxidize monovalent mercury to highly toxic divalent forms. Organic mercurials are also highly toxic. Elemental mercury, both in liquid and vapor form, is equally toxic due to its lipid solubility and lack of ionic charge which enhance its membrane permeability. Schroeder (1974) described mercury as about five times as toxic as lead and about as toxic as cadmium and antimony.

Alkyl or methylmercury poisoning differs somewhat from inorganic mercury poisoning. Symptoms may be dormant for weeks or months after acute exposure, and if brain damage occurs, effects may be irreversible. Alkyl mercury poisonings have caused permanent neurological damage resulting in impaired vision and hearing, sensory loss in limbs, ataxia, and tremor. Neurological disorders such as mental retardation and convulsive cerebral palsy have occurred in infants whose mothers were exposed to methylmercury during pregnancy. Fetal nerve tissue may be especially sensitive to methylmercury (Grant, 1971).

The EPA (1978) Ambient Water Quality Criteria recommended an upper limit of 0.19 µg/L inorganic mercury (mercuric chloride) as a 24-hour average and a maximum concentration of 1.0 µg/L at any time for the protection of saltwater life. The criterion for methylmercury is more stringent with 0.025 µg/L as a 24-hour average and a maximum concentration of 2.6 µg/L at any time. Invertebrate animal species, especially at early life stages, are noted to be more sensitive to inorganic mercury than are fish species.

The EPA recommended a maximum permissible tissue concentration of 1 ppm for protection of wildlife. The present U.S. Food and Drug Administration and Canadian Food and Drug Directorate (in: IJC, 1977) administrative guidelines for protection of human health are 0.5 µg/g mercury in edible portions of fish. Concentrations of mercury in fish that have been killed by chronic exposure to methylmercury ranged from 9.5 to 23.5 µg/g (McKim et al., 1975).

Wildlife which feed on mercury contaminated biota are particularly sensitive. Stoewsand et al. (1971) reported egg shell thinning in one study of Japanese quail at 1 µg/g of mercuric chloride in the diet. The most sensitive effects recorded are the effects on hatchling survival in mallards which were fed mercury-contaminated diets of 3 µg/g (Heinz, 1974). Fish-eating birds should be protected from sublethal and toxic effects if the concentration of total mercury in whole fish does not exceed 0.5 µg/g.

4.19.2.2 Possible Effects of Levels Found in Puget Sound

The MESA Puget Sound Project did not analyze biota for mercury concentrations. Schell (1976) reported wet weight mercury levels in biota from the Puget Sound area. The ranges reported in biota were: Ulva (seaweed), 5-9 ppb; Fucus (seaweed), 3-8 ppb; Mytilus edulis, 15-18 ppb; and clams, 10-18 ppb. The highest values were consistently reported in biota sampled from West Point. The levels reported by Schell (1976) were much lower than EPA (1978) Ambient Water Quality Criteria and U.S. Food and Drug Administration guidelines (in: IJC, 1977).

Levels of mercury in Puget Sound waters were not determined during the MESA Project. Baseline total mercury concentrations in seawater throughout the world range from 0.03 µg/L to 2.0 µg/L, depending on area and depth (EPA, 1978).

The ranges of total (dry weight) mercury content in sediments determined during the MESA Project are given below (Malins et al., 1980):

Elliott Bay	0.026 ppm	-	1.38 ppm
Commencement Bay	0.063 ppm	-	1.0 ppm
Sinclair Inlet	0.32 ppm	-	1.20 ppm
Budd Inlet	0.12 ppm	-	0.33 ppm
Case Inlet	0.02 ppm	-	0.12 ppm

The sediment levels may still remain of potential environmental significance. For example, the EPA Region V has designated sediments with greater than 1 ppm total mercury content to be of possible concern to the health of the aquatic ecosystem, and the Canadian Government has recommended that levels of 0.5 ppm be of concern.

If mercury is widely dispersed within biota of Puget Sound, it may be of significant concern. A more complete surveillance effort is required. Mercury is chosen as a contaminant of concern because of its toxicity to aquatic life and because of its possible effects on consumers of aquatic life.

4.19.3 Sources or Inputs

The oceans receive in excess of 10,000 metric tons of mercury per year, derived in approximately equal portions from natural and man-made processes (Klein and Goldberg, 1970). Natural sources of mercury in aquatic systems include direct deposition following volcanic activity, and groundwater transport following erosion and leaching of natural mercury deposits. Anthropogenic sources include pollution from a number of industrial processes, particularly the manufacture of electrical apparatus, chlorine, caustic soda, paint, pharmaceuticals, pulp, paper, fungicides, amalgams, cement, smelting, and fossil fuels (Sherbin, 1979; D'Itri, 1972).

Possible sources of mercury in Puget Sound are chlor-alkali plants and municipal sewage treatment plants, in particular the Seattle METRO West Point sewage treatment plant, which discharged about 420 kg of mercury per year prior to 1973. Crecelius et al. (1975) reported that the most significant industrial source of mercury to Puget Sound was a mercury cell chlor-alkali plant in Bellingham which discharged from 4.5-9 kg of mercury per day between 1965 and 1970. Since 1970, the discharge was reduced to about 0.1 kg/day. Other sources mentioned by Crecelius et al. (1975) were stack dust from a smelter and industrial inputs to the Duwamish River.

4.19.4 Speciation of Mercury

Mercury may exist in the environment as either its elemental form, mercurous ion (Hg^{+1}), or the mercuric ion (Hg^{+2}). In oxygenated seawater, the predominant forms are charged mercuric chloride complexes (Garvis and Ferguson, 1972). Under mildly reducing conditions, such as in anoxic sediments, ionic mercury is generally precipitated as a relatively insoluble sulfide.

Of greater significance to the environment are the methylated forms of mercury which are formed in sediments by bacterial action. The inorganic forms of mercury may be methylated by at least two mechanisms (Ladner, 1971; Wood et al., 1968). The extent and rates of methylation are affected by many factors including concentration of mercury ions, availability of mercury ions, growth rate, and metabolic activity of the methylating organisms, temperature, and pH (Bisogni and Lawrence, 1973). Methylmercury may also be demethylated by bacteria in sediments (Spangler et al., 1973). Thus, the amount of methylmercury found in the environment at any one time is dependent on the combined reaction kinetics of the methylating and the demethylating processes. Consequently, the combination of the available mercury concentrations and the operations of both transformation processes are significant. These processes are shown in Figure 4.19.1. Fish concentrate methylmercury preferentially over the other forms of mercury, and excrete methylmercury very slowly. They are therefore a good indicator of long-term trends of the net methylation rate in an environment. Crayfish also accumulate significant amounts of methylmercury (Armstrong and Hamilton, 1973). Because of their shorter life cycles, crayfish may be suitable to measure intermediate term trends in the net methylation rate.

Methylation is actually a form of detoxification within bacteria involving the conversion of Hg^{2+} to methyl- and dimethylmercury. The reactions and enzymes required to make these conversions are described by Wood (1974). Dimethylmercury is synthesized from CH_3Hg^+ and the rate of synthesis of dimethylmercury is about 6,000 times slower than that for methylmercury.

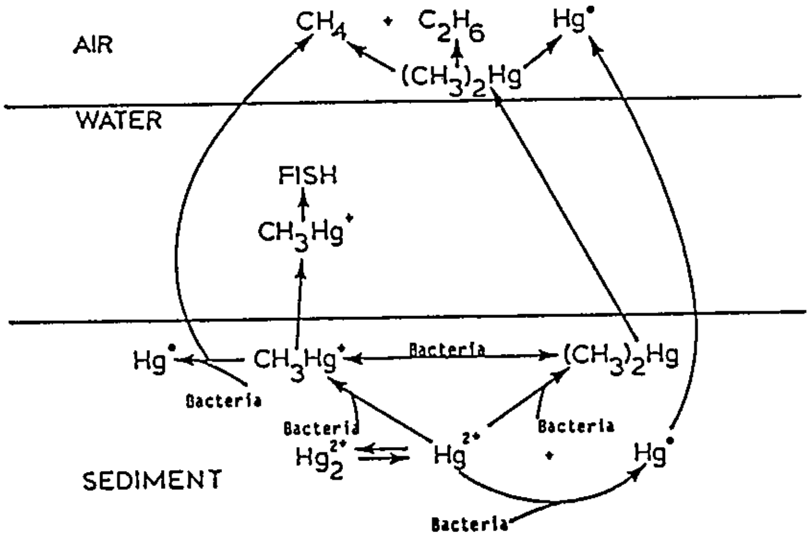


Figure 4.19.1
The Biological Cycle for Mercury (Wood, 1974)

Interconversions of mercury compounds occur in a dynamic system with reversible reactions which lead to steady state concentrations of methylmercury in the sediment. Windom et. al. (1976) studied methylmercury production and transfer of mercury in a salt marsh ecosystem in Georgia. Mercury had a great affinity for particulate matter and was present primarily in the form of an insoluble sulfide. Bacterial methylation in sediments increased mercury mobility but the rate of methylmercury production was very slow in a normal marsh community. The annual production of methylmercury was calculated to be 50 µg for each gram of total mercury. Residence time of methylmercury in the sediments was speculated to be very short as no detectable quantities could be measured.

The relationship of bacterial numbers in the sediment to production of methylmercury and its subsequent availability to organisms higher in the food chain has not been studied. However, this may be an important consideration in areas receiving sewage effluent where the density of bacteria in the sediments is exceedingly high.

4.19.5 Summary of Biogeochemical Fate Data in the Marine Environment

4.19.5.1 Bioaccumulation - Uptake and Depuration

Summary Statement: Uptake of mercury by biota occurs readily via intake of food and via the water column. Organo-mercury compounds are rapidly bioconcentrated. Uptake and release of mercury are affected by seasonal factors and the life-state of the organisms.

Results of Individual Studies: Fish have been shown to accumulate mercury compounds more than other aquatic organisms, both directly from seawater and indirectly through the food chain. Concentrations of mercury up to 9.8 ppm have been recorded from fish taken from contaminated environments (Keckes and Miettinen, 1972). The position of the fish in the food chain was found to be an important factor in relation to its mercury content. Ratkowsky et al. (1975) found that in the Derwent estuary, Tasmania, approximately 50% of the fish species whose diet consisted predominantly of other fish had mercury concentrations in excess of 0.5 mg/kg wet weight. In contrast, 24% of invertebrate predators and only 7% of individuals of herbivorous habit had mercury concentrations above the 0.5 mg/kg level. A similar correlation between the mercury concentrations and feeding habits was reported for fishes in the lower Fraser River (Northcote et al., 1975). Mercury levels in piscivorous fishes (i.e., northern squawfish and prickly sculpins) were greater than mercury levels in benthic feeders, which in turn were greater than levels found in planktonic and surface feeders.

Methylmercury is the form of mercury most readily bioconcentrated by estuarine fish. It has a long biological half life, i.e., 400-700 days for flounder in brackish water (Keckes and Miettinen, 1972).

Table 4.19.1 outlines some of the published bioconcentration factors of mercury obtained in studies with the inorganic form and the organo-mercury forms. Uptake and bioconcentration of organo-mercury occurs much more readily than for inorganic mercury. Uptake of organo-mercury, particularly methylmercury, can be effectively modeled by relatively simple kinetic equations. Hartung (1976), using experimental data of Jarvenpaa et al. (1970), found that uptake of methylmercury by fish could be modelled by zero-order input kinetics. As a result, Hartung (1976) calculated that elimination half lives of methylmercury in pike and eel were in the order of 600 to 1,030 days, thus illustrating the persistence of bioaccumulated methylmercury.

Uptake and bioconcentration of mercury is dependent upon various factors. Studies on rainbow trout (MacLeod and Pessah, 1973; Uthe et al., 1973) have shown that temperature affects the uptake rate of mercury into fish muscle. Increases in temperature from 10°C to 20°C increased the biological magnification factor (mercury concentration in fish divided by the mercury concentration in water) from 10 to 22 times (MacLeod and Pessah, 1973), and that rapid uptake of mercury occurred during the first warm summer months (Uthe et al., 1973). Luoma (1977) showed that the total mercury concentrations in biota from a small Hawaiian estuary, fluctuated over nearly two orders of magnitude during one year. Shrimp (Palaemon debilis) rapidly concentrated soluble mercury which periodically entered the estuary from storm runoff. Between rainstorms, minimal mercury remaining in the estuary was available. The net loss in mercury in tissues was slow relative to the rate of uptake, and long periods of time were necessary to lower the levels of mercury accumulated during the short rain storms.

Table 4.19.1

Bioconcentration Factors for Mercury

Organism	Bioconcentration Factor	Exposure Time(days)	Reference
	Inorganic Mercury Mercuric Chloride		
Alga, *Chaetoceros galvestonensis*	7,400	4	Hannan et al., 1973(b)
Alga, *Aoomonas salina*	853	2	Parrish and Carr, 1976
Agla (mixed), *Asterionella japonica* + *Digeros* sp.	3,467	8	Laumond et al., 1973
Alga, *Phaeodactylum tricornatum*	7,120	4	Hannan et al., 1973(a)
Oyster (adult), *Crassostrea viginica*	2,800	45	Cunningham and Tripp, 1973
Oyster (adult), *Crassostrea virginica*	10,000	74	Kopfler, 1974
	Organo-mercuric Compounds Methylmercuric Chloride		
Oyster (adult), *Crassostrea virgnicia*	40,000	74	Kopfler, 1974
	Phenylmercuric Chloride		
Oyster (adult), *Crassostrea virginica*	40,000	74	Kopfler, 1974

Luoma (1976) studied the uptake and inter-organ distribution of mercury in the carnivorous crab (Thalamita crenata). The rate of increase of mercury in muscle vs. uptake in the viscera was used as in indication of the relative importance of the source of mercury (i.e., from water or food) to the crab. High mercury levels in crab gills were observed after rainstorms. The body muscle-chela muscle partioning of mercury changed seasonally from the wet to the dry season, which suggested a considerable lag time in translocation of mercury from the environment to some slowly exchanging tissues. Luoma (1976) suggested that because of the lag in metal translocation, short-term laboratory experiments may underestimate the potential for contamination of such tissues.

McGreer (1981) reported seasonal variation in concentration of mercury from crabs on Roberts Bank (Strait of Georgia). The lowest concentrations were reported from winter and spring sampling occasions, while higher concentrations were reported in samples taken in late summer to fall.

Based on studies of uptake with mercury, it can be seen that all field studies on contaminants should assure standardization of the sex, size, and age of the organism, period of collection, and analytical methods to assess the rates of accumulation and changes in body burdens over a period of time. It is also important to recognize the mechanisms of excretion and regulation of heavy metals in various marine organisms (Bryan, 1976). For example, in studies of the role of metal regulation in the accumulation of mercury in body tissues of Dungeness crab, the destruction or blocking of enzyme pathways in the excretory organs was suggested as a mechanism leading to progressively reduced ability to eliminate free mercury in the crabs (Sloan et al., 1974). Deterioration of excretory capability after chronic exposure to mercury would lead to higher concentrations in the oldest, largest animals.

Marine invertebrates have some protection from low level chronic heavy metal pollution by a detoxification mechanism involving metal binding proteins. The low molecular weight protein metallothionein is present in several species of marine invertebrates from Sturgeon Bank (Brown et al., 1977) and is instrumental in providing protection against high body burdens of metals.

Selenium offers another protection mechanism to marine biota against inorganic and organic mercury compounds. Selenium exerts its influence when it is available prior to or in conjunction with mercury exposure. Although the action of the selenium appears to be similar to that of sulphur-containing compounds, the precise nature of the mercury-selenium interactions is still unclear (Parizek et al., 1974). In ocean fish with mercury concentrations of about 1 ppm (i.e., tuna), selenium is present in approximately equimolar concentration. However, in fish contaminated with mercury compounds from nearshore pollution, mercury levels are elevated but not selenium levels. Selenium-mercury ratios may therefore provide an indication of the relative pollutant loading on coastal systems, as well as an indication of the tolerance of organisms to mercury body burdens.

The term biomagnification refers to a specific phenomenon in which a compound is concentrated through consumption by progressively higher food chain organisms, and results in a net increase in the tissue concentration at each successive trophic level. Compared to other metals such as copper, zinc, or cadmium, mercury is unique in its ability to readily undergo biomagnification in both aquatic and terrestrial food chains.

Biomagnification of mercury occurs, especially, in long-lived predatory fish species such as swordfish, tuna, and pike. In this way, even relatively low concentrations of mercury in the environment can be built up through the food chain to mercury levels exceeding the 0.5 ppm wet weight concentration considered safe for human consumption.

Numerous laboratory systems have been designed to study the transport of materials through food chains (e.g., Metcalf et al., 1971) and they have provided limited information on biomagnification. Both bioconcentration and biomagnification occur simultaneously under the same conditions and it is usually not possible to separate the contribution by each process. Terhaar et al. (1977) recently designed a system to evaluate and compare both bioaccumulation and biomagnification through successive trophic levels in an aquatic ecosystem over extended periods of time. Inorganic mercury was tested in a freshwater system with algae (*Scenedesmus* sp.), zooplankton (*Daphnia magna*), mussels (*Ligumia* sp. and *Margaritisera* sp.), and the fathead minnow (*Pimephales promelas*). Results showed that mercury was bioconcentrated by lower trophic level organisms. Fish clearly displayed biomagnification of mercury and the data offered strong support for the experimental design employed.

Williams and Weiss (1973) found concentrations of mercury in clam tissue 5.8 to 26 times the levels in the sediments. In turn, the levels in flounder were 1.2 times greater than levels in tissue of the clam *M. balthica* which is a deposit-feeding clam and is known to feed to a large extent on bacteria attached to sand grains (Tunnicliffe and Risk, 1977). Flatfish feed upon bottom-dwelling invertebrates including the clam *M. balthica* (Risk and Craig, 1976). In so feeding, the flatfish produce feeding pits 3-5 cm deep and 2-3 cm in diameter as they strike downward at clam siphons and burrowing crustaceans. The characteristic shape of flatfish feeding traces as described by Risk and Craig (1976) have also been identified from sites on Sturgeon Bank. It is probable that a major source of mercury contamination to flatfish may be from feeding on contaminated *M. balthica*.

4.19.5.2 Adsorption-Desorption

Summary Statement: Sedimentation is an important fate process for mercury, particularly in the presence of high organic-containing sediments. However, rapid decreases in mercury levels in Puget Sound sediments have been documented indicating loss by methylation and/or dissolution.

Results of Individual Studies: Mercury released into a river may be initially dissolved, as an inorganic species, and is usually rapidly adsorbed by river particulates. When these particulates enter the more saline estuary, some adsorbed mercury compounds may dissolve to form tetrachloride complexes and eventually associate with organic ligands. Subsequently, the ocean or tidal effects will dilute the dissolved mercury. The overall result is that dissolved mercury tends to be higher in concentration in the estuary than in the inflowing river or in the receiving ocean (Jernelov, 1975; Cranston and Buckley, 1972; So 1979; Windom, 1975). More than half of the dissolved mercury in coastal waters may be associated with organic matter (Fitzgerald and Lyons, 1973), which may resemble the fulvic matter of soils (Andren and Harriss, 1975).

In estuarine sediments, mercury is associated with fine particles, the result of prior adsorption on sedimenting particulate matter (Cranston, 1976) or possibly adsorption to flocculated dissolved organic and inorganic matter in the estuary (Sholkovitz, 1976). Crecelius et al. (1975) also noted that mercury in Bellingham Bay sediments was associated with fine particles, and that organic matter was more important than surface area in controlling the mercury contents of the sediments.

Crecelius et al. (1975) noted that the sediments were not a permanent sink for mercury. The results of monitoring mercury disappearance from polluted sediments in Bellingham Bay indicated a first-order rate loss of mercury with a half life of about 1.3 years in sediments. Although Crecelius et al. (1975) noted that many other workers had reported a correlation between organic matter and mercury in sediments, the mercury-total carbon correlation for surface sediments of Puget Sound was considered by the investigators to be "only fair." Nonetheless, more than 80% of the mercury recovered from sediments was found to be bound to organic matter of Puget Sound sediments. Mercury loss from Ottawa River sediments were calculated by Akagi et al. (1979) to be in the order of 1 year. This loss and the loss noted in Puget Sound may be due to biological methylation or redissolution processes.

Adsorption-desorption of mercury in the marine environment may also be affected by several other parameters. Clay particles would apparently adsorb very small quantities of mercury (Farrah and Pickering, 1977). Insoluble mercuric sulfides may be formed within anoxic sulfur-containing sediments (Eganhouse et al., 1978). Craig and Bartlett

(1978) however, found that the insoluble mercuric sulfide could be methylated by appropriate microorganisms. Akagi et al. (1979) showed that sediments containing high organic content are more apt to produce organic mercury species.

4.19.5.3 Photolysis

Summary Statement: Photolysis may have an effect on the lifetime of organo-mercurial compounds. Limiting factors would include light transmission and association of the mercury organic compounds with particulates.

Review of Individual Studies: Photolysis may also be a significant fate process for organo-mercurials. Wolfe et al. (1972) found that dimethylmercury and CH_3Hg X compounds were not photodegraded by sunlight for X = Cl, OH and the ionic form CH_3Hg . Some degradation was noted for X = Br, and a great deal of degradation for CH_3HgI. Phenyl mercuric salts are photolyzed to inorganic mercury by sunlight. Zepp et al. (1973) deduced half lives for a number of such salts which were in the range 14 to 20 hours; the half life of diphenylmercury itself was 8.5 hours.

4.19.5.4 Volatilization

Summary Statement: Volatilization is probably an important fate process for mercury, in particular for methylmercury.

Review of Individual Studies: Loss of elemental mercury and some of its stable organic and inorganic compounds to the atmosphere is an important fate process. Johnson and Braman (1974) monitored the distribution of atmospheric mercury species near ground in a metropolitan area bordering Tampa Bay (Florida), and found that airborne mercury was predominantly "volatile" (mercury, methylmercury, and elemental mercury compounds) with a small amount of the "particulate" form. They suggested that the volatile methylated forms may have originated from biomethylation processes in sediments and water.

Wolfe et al. (1972) suggested that, because of the high vapor pressure of dimethylmercury (50 mm. Hg at 20.5°C) and because dimethylmercury does not dissociate in solution, evaporation may be an important process. Dimethylmercury evaporation occurred at about the same rate as oxygen diffusion and a theoretical half life of 12 hours was calculated for the system. It was estimated that elemental mercury had 2.3 times the evaporation rate of dimethylmercury for the river site under examination.

Quantitative data are limited on the subject of the volatilization of mercury compounds from natural waters; therefore, the impact of volatilization on the overall fate of mercury in the marine environment is not known. Nonetheless, the process is probably significant.

4.19.5.5 Hydrolysis

Methylated forms of mercury undergo hydrolysis at the pH of natural waters. At 25°C and a pH of 5, the half life would be about 33 years. Diphenylmercury is much less stable at pH 5 and its half life may be measured in hours under such conditions (Bisogni and Lawrence, 1975).

4.19.6 Conclusions

1. Mercury is one of the most toxic heavy metals present in the environment. Alkylated forms of mercury are more toxic than inorganic forms.
2. Consumers of mercury-contaminated fish, are particularly sensitive to mercury poisoning.
3. Mercury discharges to Puget Sound are probably decreasing; however, some sediments contained mercury at levels in excess of levels designated by environmental agencies to be of concern.
4. Speciation of mercury in the aquatic ecosystem controls the fate and effects of mercury. Conversion to organo-mercurials results in toxic but volatile compounds. Reducing environments may produce HgS which precipitates and constitutes a major sink.
5. Bioaccumulation occurs both via the diet and water phase. Uptake of organo-mercury compounds is rapid and elimination is very slow.
6. Sedimentation is an important fate process, and is strongest in the presence of sediments with high organic content.
7. Other fate processes which may be of importance include volatilization and photolysis.

4.19.7 Research Needs

There have been extensive efforts in the past years with regard to the biogeochemical fate of mercury in the aquatic environment. Recommendations on research needs regarding mercury in Puget Sound will depend upon an assessment of whether mercury is significantly distributed within the waters and biota of Puget Sound. The prime recommendation is therefore:

1. To assess the levels of mercury in biota of Puget Sound, particularly the levels in tissue of edible biota such as flounder and crab.

If levels are in excess of FDA levels, research will be required to:

2. identify the sources and routes of entry of mercury in Puget Sound.

3. Evaluate the rates of uptake, elimination and accumulation, and the seasonal factors affecting the rates of bioaccumulation within commercial food organisms in Puget Sound. Standardization of the sex, size, age of the organism, period of collection, and analytical methods will be required to assess the rates of accumulation and changes in body burdens.

References

Akagi, H., D.C. Mortimer, and D.R. Miller. 1979. Mercury methylation and partition in aquatic systems. Bull. Environ. Contam. Toxicol. 23:372-376.

Andren, A.W. and R.C. Harriss. 1975. Observations on the association between mercury and organic matter dissolved in natural waters. Geochim. Cosmochim. Acta 39:1253-1257.

Armstrong, F.A.J. and A.L. Hamilton. 1973. Pathways of mercury in a polluted northwestern Ontario lake, In: P.C. Singer (ed.), Trace Metals and Metal-Organic Interactions in Natural Waters. Ann Arbor Science, Ann Arbor, Mich.

Bakir, F., S. F. Damluji, L. Amin-Zaki, M. Murtadha, A. Khalid, N.Y. Al-Rawi, S. Tikrite, H.I. Dhahil, T.W. Clarkson, J.C. Smith, and R.A. Doherty. 1973. Methyl mercury poisoning in Iraq. Science 181:230-241.

Bisogni, Jr., J.J. and A.W. Lawrence. 1975. Kinetics of mercury methylation in aerobic and anaerobic aquatic environments. J. Water Pollut. Contr. Fed. 47:135-152.

Brown, D.A., C.A. Bawden, K.W. Chatel, and T.R. Parsons, 1977. The wildlife community of Iona Island jetty, Vancouver, B.C. and heavy metal pollution effects. Environ. Conserv. 4:213-216.

Bryan, G.W. 1976. Some aspects of heavy metal tolerance in aquatic organisms. In: A.P.M. Lockwood, (ed.), Effects of Pollutants on Aquatic Organisms, 2: Cambridge Press, Great Britain. pp. 7-34.

Craig, P.J. and P.D. Bartlett. 1978. The role of hydrogen sulphide in environment transport of mercury. Nature 275:635-637.

Cranston, R.E. 1976. Accumulation and distribution of total mercury in estuarine sediments. Estuar. Coastal Mar. Sci. 4:695-700.

Cranston, R.E. and D.E. Buckley. 1972. Mercury pathways in a river and estuary. Environ. Sci. Technol. 6:274-278.

Crecelius, E.A., M.H. Bothner, and R. Carpenter. 1975. Geochemistries of arsenic, antimony, mercury and related elements in sediments of Puget Sound. Environ. Sci. Technol. 9:325-333.

Cunningham, P.A. and M.A. Tripp. 1973. Accumulation and depuration of mercury in the American oyster, *Crassostrea virginica*. Mar. Biol. 20:14.

D'Itri, F.M. 1972. The Environmental Mercury Problem, Cleveland, CRC.

D'Itri, P.A. and F.M. D'Itri. 1977. Mercury contamination: A human tragedy. John Wiley and Sons, New York.

Eganhouse, R.P., D.R. Young, and J.N. Johnson. 1978. Geochemistry of mercury in Palos Verdes Sediments. Environ. Sci. Technol. 12:1151-1157.

Environmental Protection Agency. 1978. Ambient Water Quality Criteria: Mercury. NTIS (PB 297 925).

E.V.S. Consultants Ltd. 1979. Identification of heavy metals in organisms within an area of the Fraser River estuary receiving a major municipal industrial and stormwater discharge. Prepared for Dept. of Fisheries and Environment.

Farrah, H. and W.F. Pickering. 1977. The sorption of mercury species by clay minerals. Water, Air, Soil Pollution. 9:23-31.

Fitzgerald, W.F. and W.B. Lyons. 1973. Organic mercury compounds in coastal waters. Nature 242:452-453.

Gavis, J. and J.F. Ferguson 1972. The cycling of mercury through the environment. Water Res. 6:1193-1202.

Grant, N. 1971. Mercury in man. Environment. 13:2.

Hannan, P.J. et al. 1973(a). Hg as tracer on pigments of Phaeodactylum tricornutum. Int. Jour. Appl. Radiat. Isotopes. 24:665.

Hannan, P.J. et al. 1973(b). Measurements of mercury sorption by algae. U.S. Naval Res. Lab., Washington, D.C.

Hartung, R. 1976. Pharmokinetic approaches to the evaluation of methylmercury in fish. In: R.W. Andrew, P.V. Hodson, D.E. Konasewich (eds.), Toxicity to Biota of Metal Forms in Natural Water (workshop proceedings). 1975. Great Lakes Reg. Off. International Joint Commission, Windsor, Ontario. pp. 233-248.

Hartung, R. and B.D. Dinman (eds.). 1972. Environmental Mercury Contamination. Ann Arbor Science Publishers, Inc., Ann Arbor, Mich.

Heinz, G. 1974. Effects of low dietary levels of methylmercury on mallard reproduction. Bull. Environ. Contamin. Toxicol. 11:386-392.

International Joint Commission. 1977. The Waters of Lake Huron and Lake Superior. Volume II (Part B). Windsor, Ontario.

Jarvenpaa, T., M. Tillander, and J.K. Miettinea. 1970. Methylmercury: half-time of elimination in flounder, pikes and eel. Paper presented at the FAO Technical Conference on Marine Pollution and its Effect on Living Resources and Fishing. Rome. December 9-18, 1970.

Jensen, S. and A. Jernelov. 1969. Biological methylation. Nature 223:753.

Jernelov, A. 1975. Microbial alkylation of metals. In: T.C. Hutchinson (ed.), Symposium Proceedings: International Conference on Heavy Metals in the Environment. Volume II, Part 2. October 27-31, Toronto, Ontario.

Johnson, D.L. and R.S. Braman. 1974. Distribution of atmospheric mercury species near ground. Environ. Sci. Technol. 8:1003-1009.

Kanzantzis, G. 1971. The poison chain for mercury in the environment. Intern. J. Environ. Studies. 1:301-306.

Keckes, S. and J.K. Miettinen. 1972. Mercury as a marine pollutant. In: M. Ruivo (ed.), Marine Pollution and Sea Life, FAO, Fishing News (Books) Ltd., London.

Klein, D.H. and E.D. Goldberg. 1970. Mercury in the marine environment. Environ. Sci. Technol. 4:765-768.

Kopfler, F.C. 1974. The accumulation of organic and inorganic mercury compounds by the eastern oyster (Crassostrea virginica). Bull. Environ. Contam. Toxicol. 11:275.

Ladner, L. 1971. Biochemical model for the biological methylation of mercury suggested from methylation studies in vitro with Neurospora crassa. Nature 230:252-253.

Laumond, F., et al. 1973. Experimental investigations, at laboratory, on the transfer of mercury in marine trophic chains. In: 6th Int. Symp. Medicale Ocean., September 26-30. Portoroz, Yugoslavia.

Luckey, T.D., B. Venngopal, and D. Hutcheson. 1975. Heavy Metal Toxicity, Safety and Hormonology. Academic Press, New York.

Luoma, S.N. 1976. The uptake and interorgan distribution of mercury in a carnivorous crab. Bull. Environ. Contam. Toxicol. 16:719-723.

Luoma, S.N. 1977. The dynamics of biologically available mercury in a small estuary. Estuar. Cstl. Mar. Sci., 5:643-652.

Malins, D.C., B.B. McCain, D.W. Brown, A.K. Sparks, and H.O. Hodgins. 1980. Chemical Contaminants and Biological Abnormalities in Central and Southern Puget Sound. NOAA Technical Memorandum OMPA-2. Office of Marine Pollution Assessment, Boulder, Colo. 295 pp.

MacLeod, J.C. and E. Pessah. 1973. Temperature effects on mercury accumulation, toxicity and metabolic rate in rainbow trout (Salmo gairdneri). J. Fish. Res. Board Can. 30: 485-492.

McGreer, E.R. 1981. Factors affecting the distribution of the bivalve (Macoma balthica) (L.) on a mudflat receiving sewage effluent Fraser River estuary, British Columbia. Marine Environmental Research (in press).

McKim, J.M., G.F. Olson, G.W. Holcombe, and E.P. Hunt. 1975. Long term effects of methyl-mercuric chloride on three generations of brook trout (Salvelinus fontinalis): toxicity, accumulation, distribution, and elimination. (Manuscript). Environmental Protection Agency, Environmental Research Laboratory, Duluth, Minn.

Metcalf, R.L., G.K. Sangha, and I.P. Kapoor. 1971. Model ecosystem for the evaluation of pesticide biodegradability and ecological magnification. Environ. Sci. Technol. 5:709-713.

Northcote, T.G., N.T. Johnston, and K. Tsumura. 1975. Trace Metal Concentrations in Lower Fraser River Fishes. Westwater Research Centre Tech. Rept. No. 7: 41 pp.

Parizek, J., J. Kalouskova, A. Babicky, J. Benes, and L. Pavlik. 1974. Interaction of selenium with mercury, cadmium and other toxic metals. In: W.G. Hockstra (ed.), Trace Element Metabolism in Animals. Park Press, New York.

Parrish, K.M. and R.A. Carr. 1976. Transport of mercury through a laboratory two-level marine food chain. Mar. Pollut. Bull. 7:90.

Ratkowsky, D.A., T.G. Dix, and K.C. Wilson. 1975. Mercury in fish in the Derwent estuary, Tasmania and its relation to the position of the fish in the food chain. Aust. J. Mar. Freshwater. Res. 26:223-231.

Risk, M.J., and H.D. Craig. 1976. Flatfish feeding traces in the Minas Basin. Sed. Petrology 46:411-413.

Schell, W.R. 1976. Heavy metals in Central Puget Sound. In: Alyn C. Duxbury, (ed.), Puget Sound Studies. Div. of Marine Resources, University of Washington.

Schroeder, H.A. 1974. The Poisons Around Us. University Press, Bloomington, Ind.

Sherbin, I.G. 1979. Mecury in the Canadian Environment. Environmental Protection Service Report 3-EC-79-6.

Sholkovitz, E.R. 1976. Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater. Geochim. Cosmochim. Acta 40:831-845.

Sloan, J.P., J.A.J. Thompson, and P.A. Larkin. 1974. The biological half-life of inorganic mercury in the Dungeness crab (Cancer magister). J. Fish. Res. Board Canada 31:1571-1576.

So, C.L. 1979. Mercury-water interactions in the estuarine environment. Mar. Pollut. Bull. 10:334-337.

Spangler, W.J., J.L. Spigarelli, J.M. Rose, and H.M. Miller. 1973. Methylmercury bacterial degradation in lake sediments. Science 180:192-193.

Stoewsand, G.S., J.L. Anderson, W.H. Guntenmann, C.A. Bache, and D.J. Lisk. 1971. Eggshell thinning in Japanense quail fed mercuric chloride. Science 173:1030-1031.

Terhaar, C.J., W.S. Ewell, S.P. Dziuba, W.W. White, and P.J. Murphy. 1977. A laboratory model for evaluating the behavior of heavy metals in an aquatic environment. Water Res. 11:101-110.

Tunnicliffe, V., M.J. Risk. 1977. Relationships between the bivalve (Macoma balthica) and bacteria in intertidal sediments: Minas Basin, Bay of Fundy. J. Mar. Res. 35:499-507.

Uthe, J.F., F.M. Atton, and L.M. Royer. 1973. Uptake of mercury by caged rainbow trout (Salmo gairdneri) in the South Saskatchewan River. J. Fish. Res. Board Can. 30:643-650.

Williams, P.M. and H.V. Weiss. 1973. Mercury in the marine environment: concentration in seawater and in a pelagic food chain. J. Fish. Res. Board Can. 30:293-295.

Windom, H.L. 1975. Heavy metal fluxes through salt marsh estuaries. In: L.E. Cronin, (ed.), Estuarine Research Vol. 1: Academic Press, New York. pp. 137-152.

Windom, H.L., W.S. Gardner, W.M. Dunstan, and G.A. Paffenhofer. 1976. Cadmium and mercury transfer in a coastal marine ecosystem. In: H.L. Windom and R.A. Duce (eds.), Mar. Pollut. Transfer. D.C. Heath and Co., Lexington, Mass. pp. 135-157.

Wolfe, N.L., R.G. Zepp, J.A. Gordon, and G.L. Baughman. 1972. Chemistry of phenyl mercury compounds in the aquatic environment. Chemosphere 6:273-278.

Wood, J.M., F.S. Kennedy, and C.G. Rosen. 1968. Synthesis of methylmercury compounds by extracts of a methanogenic bacteria. Nature 220:173-174.

Wood, J.M. 1974. Biological cycles for toxic elements in the environment. Science 183:1049-1052.

Zepp, R.G., N.L. Wolfe, and J.A. Gordon. 1973. Photodecomposition of phenyl mercury compounds in sunlight. Chemosphere 3:93-99.

4.20 Selenium

4.20.1 Introduction

Selenium is a common element which appears in the earth's crust. Selenium is extracted mainly as a by-product of copper and lead refining. Commercially, selenium is used in electronics for rectifiers, photocells, and photocopying; in steel; and in pigments for paints, glass, and ceramics (Cooper, 1967).

Selenium is one of the EPA's 129 Priority Pollutants. It is moderately toxic to marine biota with the lowest observed chronic effect level being 135 µg/L for mysid shrimp (EPA, 1978).

The International Joint Commission (1977) expressed its concern about the effect of high dietary selenium concentrations on fish-eating birds and wildlife. Barnhart (1958) reported a case of fish mortality in a Colorado reservoir caused by selenium from bottom deposits which had passed through the food chain to accumulated levels of 300 µg/g. Koeman et al. (1973) expressed concern about the 46 to 134 µg/g selenium levels found in livers of seals from the Wadden Sea.

Selenium levels in Puget Sound are much higher than average levels reported in the earth's crust and in deep-sea sediments. Selenium is, therefore, chosen as a contaminant of concern in Puget Sound.

4.20.2 Significance to Puget Sound

4.20.2.1 Review of Known Toxicity Data

Selenium is essential in trace amounts for growth and fertility in animals and for prevention of some specific diseases. At higher levels, chronic selenosis may be manifested in animals resulting in dullness, listlessness, and damage to joints. In cases of acute poisoning, animals experience abdominal pain, become blind, and die. The toxicity of selenium may be due to replacement of SH (thiol) groups by SeH groups (Forstner and Wittmann, 1979). Selenium is teratogenic, but there are insufficient data to decide whether it is carcinogenic (EPA, 1978).

The 96-hour LC50's of selenium to marine biota indicate a moderate toxicity of the element. For example, the 96-hour LC50's for sheepshead minnow and mysid shrimp are 3668 and 51 µg/L, respectively (EPA, 1978). The EPA guidelines specify a maximum acute value of 10 µg/L for saltwater biota and a maximum 24-hour average concentration of 4.4 µg/L. Algae are less sensitive to selenium. A 96-hour EC50 of 8000 µg/L has been reported for Skeletonema costatum (EPA, 1978).

More serious concerns are related to the toxic effects of selenium on higher food chain species. Schroeder (1967) reported that a diet of 3 µg/g of selenium, as selenite, is toxic to rats over their lifetime. In addition to the data provided in Section 4.20.1, no information was found on the effects of high dietary selenium concentrations on fish-eating birds or mammals.

4.20.2.2 Possible Effects of Levels Found in Puget Sound

No analyses of selenium levels in biota were reported within the Puget Sound MESA studies; however, the reported dry weight sediment levels (22-113 μg/g) indicate a need for evaluation of their potential effects. The average continental crust levels of selenium are 0.05 μg/g and deep-sea clays have levels of 0.17 μg/g (Bryan, 1976).

4.20.3 Sources or Inputs

Non-anthropogenic sources of selenium in air include volcanoes, plants, animals, and soil. Volatile forms of selenium include dimethyl selenide and diselenide. Major industrial emission sources are mining, milling, smelting, and refining operations on copper, lead, zinc, phosphates, and uranium; the manufacture of glass and ceramics, semi conductors, iron and steel alloys, pigments, and duplicating; and fossil fuel combustion (EPA, 1978).

The average concentration of selenium in the earth's crust has been estimated to be from 0.03 to 0.8 ppm, with reports of 100 ppm levels in some limestones and sandstones. Selenium tends to be present in sulfur-rich deposits because of the chemical similarity of the two elements. Selenium content of soil can be deduced by plant analysis, which has indicated that soil in the Pacific Northwest has one of the lowest selenium contents in the United States (Kubota et al., 1967). It would therefore appear that the selenium levels found in Puget Sound are unlikely to have been derived from coastal soil.

Selenium has also been found at 0.2 mg/kg (ppm) levels in paper pulps, and it has been suggested that these levels may be a major health concern to pulp workers (Anderson and Acs, 1974).

4.20.4 Speciation of Selenium

Selenium can exist in +6 (selenate), +4 (selenite), 0 (the elemental form) and -2 (selenide) oxidation states. The thermodynamically favored state in any given situation will depend on the chemical composition of the surroundings, including pH, salinity, and redox potential. Changes in oxidation state greatly affect the toxicity and transport of selenium in aquatic systems, and so selenium speciation is an essential facet of its environmental impact.

Both selenium +6 and +4 states exist in coastal and open oceanic waters (Sillen, 1961; Sugimura et al., 1976). Selenite (+4) has been shown to be much more toxic to zebra fish larvae than selenate (+6) (Niimi and LaHam, 1975). No comparable studies on saltwater species are known.

The predominant form of selenium in oxygenated seawater is selenite (SeO^{2-}). Under reducing conditions, elemental Se is the stable form and relatively high concentrations of Se occur in euxinic sediments.

Selenite is strongly adsorbed by iron hydroxides (Geering et al., 1968), and tends to be less soluble than selenates (EPA, 1976). Consequently, selenite may not be a long-lived dissolved species in the aquatic environment. In the northeast Atlantic Ocean, selenite was found in deep water where it was deduced to persist as a result of vertical transport and biological reduction of the more thermodynamically favored selenate (Measures and Burton, 1980). Since selenite is more toxic than selenate, at least for some freshwater species, deep water and benthic organisms may be more affected than pelagic organisms in Puget Sound.

The sensitivity of selenium speciation (and consequent toxicity and bioaccumulation) to environmental changes (i.e., Eh and pH) means that it is essential to define the selenium species present. Determination of the selenium species can be made either directly by analysis or indirectly by determining the Eh, pH, salinity, and other parameters which define the species present. However, the state-of-the-art of the latter option is inadequately defined, particularly with regard to the effects of salinity on speciation. Sugimura et al. (1976) found variations in the selenate (+6) to selenite (+4) ratios in seawater at various depths in the western North Pacific which could not be attributed solely to changes in salinity, temperature or dissolved oxygen. Biochemical reactions were suggested as a cause for some of the changes. Measures and Burton (1980) found that within estuaries, total dissolved selenium decreased with increasing salinity. Parallel decreases in selenium (+4) levels were also observed.

Fluxes among relative quantities of various inorganic species of selenium obviously do occur, but the literature indicates that there is an inadequate understanding of selenium speciation in the marine environment.

Selenium is known to be methylated biologically and Chau et al. (1976) have demonstrated methylation of sodium selenite, sodium selenate, selenocystine, selenourea, and seleno-DL-methionine by microbial action in lake sediments. All sediments that demonstrated microbial action were capable of methylating selenite and/or selenate. Three compounds, mono-, and dimethyl selenide, and an unknown were produced. Since bacterial action may have produced an unknown selenium compound of high toxicity to fish, Niimi and LaHam (1975) recommended that the environmental significance of selenium methylation should be more completely understood.

4.20.5 Summary of Biogeochemical Fate Data in the Marine Environment

4.20.5.1 Bioaccumulation - Uptake and Depuration

<u>Summary Statement</u>: Food appears to be the main source of selenium uptake. Speciation of selenium plays an important role in bioaccumulation and the selenite form is preferably bioaccumulated. No data were found on uptake of methylated forms.

Review of Individual Studies: Uptake and bioaccumulation of selenium will depend upon the species of selenium in the environment. Most bioaccumulation studies have utilized inorganic forms of selenium and/or an organic form, selenomethionine. No uptake studies with methylated forms of selenium were found in the literature survey.

Fowler and Benayoun (1976a) reported that selenite (+4) was the preferential form of selenium accumulated in mussels. Similar results for preferential uptake of selenite (+4) were reported by Fowler and Benayoun (1976b) who also determined bioconcentration factors of 46 for a 2 gm mussel and 13 for a 21.8 gm mussel.

Bioconcentration factors for selenium in marine biota are generally quite low. The EPA (1978) reported bioconcentration factors of 5 for saltwater fish, 150 for saltwater molluscs, and 5 for saltwater decapods. These values are lower than those of Chapman et al. (1968) who reported bioconcentration factors of 800 for marine plants, and 400 for both marine invertebrates and fish.

It has been suggested that the major pathway for accumulation of selenium appears to be through the food chain rather than the aquatic medium (Sandholm et al., 1973; Fowler and Benayoun, 1976b, 1976c). Wrench (1979) found that marine phytoplankton and other microorganisms were able to fix inorganic selenium along the same metabolic pathways as sulfur, thus producing selenium analogues of the sulfur amino acids. However, higher species (such as oysters) cannot fix selenium by this means, and filter-feeding shellfish appear to acquire selenium amino acids from their food and not from water. The biological half lives of selenium in mussels and shrimp moved to clean waters are in the order of 60-80 days, indicating that selenium is significantly persistent (Fowler and Benayoun, 1976a).

Fish also appear to absorb selenium principally from food. Sandholm et al. (1973) found little direct uptake of selenium from inorganic and organic forms in water by fish. A survey of fish obtained from a wide range of locations in fresh and ocean water indicated wet-weight levels from 0.16 to 0.6 µg/g within tissue (Sandholm et al., 1973). Selenium levels in excess of 3 µg/g are of probable concern because laboratory animals have been shown to be affected at these levels.

Thus, selenium is both an essential element for living organisms at low concentrations and a very toxic element at high concentrations. It is noteworthy that selenium has also been shown to exert a protective influence against mercury poisoning. For example, Kim et al. (1977) found that creek chubs previously immersed in water with selenium were less susceptible to mercury levels in water than untreated individuals. Selenium exerts its influence in this respect either prior to or in conjuction with mercury exposure. Although the action of selenium appears to be similar to that of sulphur-containing compounds, the precise nature of the mercury-selenium interactions is still unclear (Parizek et al., 1971). In ocean fish with mercury concentrations of about 1 ppm (i.e., tuna), selenium is present in approximately equimolar concentrations. However, in fish contaminated with mercury compounds from nearshore pollution, mercury levels are elevated while selenium levels are not. This difference suggests that selenium-mercury ratios may provide an indication of the tolerance of organisms to mercury body burdens.

It is essential to evaluate the levels of selenium in biota of Puget Sound to ascertain whether selenium uptake is occurring, and whether the uptake levels are such that concern is necessary.

4.20.5.2 Adsorption-Desorption

Summary Statement: Selenium is known to adsorb strongly to iron and manganese hydroxides. Puget Sound data suggest association with organic-rich sediments.

Review of Individual Studies: A review of the summary data provided by Malins et al. (1980) indicates that higher concentrations of selenium in Puget Sound sediments were favored by small grain sizes, low sand/mud ratios, and high organic carbon. A cluster analysis by Malins et al. (1980) showed an apparent association of high selenium levels with high organic, cadmium and arsenic levels at three stations in Elliott Bay and two in Budd Inlet. The organic-rich sediment may imply an anaerobic environment which may lead to the formation of the more reduced forms of selenium. Of these reduced forms, H_2Se and methylated compounds may volatilize but selenite would remain.

Few systematic studies exist on the adsorption and desorption of selenium in sediments or suspended solids. Sediments and suspended solids in an unpolluted environment are generally clays with small portions of organic material and iron or manganese hydroxides. Kharkar et al. (1967) found that selenium is strongly adsorbed to iron and manganese hydroxides which are found in varying fractions of suspended particles and sediments. Desorptions from the hydroxides would thus be minimal. On the other hand, clays weakly adsorb selenium under natural environmental pH's (Frost and Griffin, 1977). Kharkar et al. (1967), therefore, concluded that of the dissolved fraction of selenium within the ocean waters, 10% or less would be a result of desorption from solids, and selenium is transported within the environment as a dissolved species. It therefore appears probable that the high levels of selenium observed in Puget Sound are accompanied by high ferric or manganese hydroxide concentrations, which are generally found in areas of industrial and municipal discharges.

No data were found on the uptake of sediment-absorbed selenium by aquatic organisms.

4.20.5.3 Photolysis

To determine total selenium concentrations, analysts irradiate samples with UV light to convert the various oxidation states to selenium (+4), which is then directly determined (Measures and Burton, 1980). It is, therefore, likely that selenium (+6) within the upper layer of the ocean may convert to selenium (+4) as a result of solar radiation. However, the effects of photolysis cannot be properly quantified due to the effects of such variables as biological processes, oxygen levels, salinity, etc.

4.20.5.4 Volatilization

Volatilization may be an important fate process for selenium.

Under reducing conditions, selenium can be converted to a volatile form, H_2Se. Such conditions may exist within Elliott and Commencement Bays, particularly in the vicinity of industrial and municipal outfalls. For example, Baumgartner et al. (1978) reported redox potentials within Elliott Bay as low as -0.15 V in the winter, which may result in reduction of selenium.

The results of Chau et al. (1976) showed that volatile organic selenium can be produced by microbes within sediments, and biomethylation with subsequent volatilization may be a significant fate process for selenium.

4.20.6 Conclusions

1. Consumers of selenium-contaminated biota may suffer toxic effects. Consumers of concern include birds, seals, and man.

2. It appears that the water column is the major compartment for the distribution of selenium in the environment.

3. Sediments and suspended solids will have a significant role in binding selenium if high concentrations of iron and manganese hydroxides are present.

4. Biomethylation of selenium can occur within sediments, but it is uncertain whether the methylated forms can be taken up by aquatic biota.

5. Bioaccumulation of selenium appears to be dependent upon dietary sources. Thus, it is essential that levels of selenium in Puget Sound biota be determined to evaluate whether upper food-chain organisms such as mammals or fish-consuming birds may be affected.

4.20.7 Research Needs

1. The effects of high dietary concentrations of selenium on fish-eating birds and wildlife should be evaluated by use of feeding studies;
2. Uptake of selenium from sediments and/or detrital material by commercially important benthic organisms, such as crabs and clams, should be evaluated;
3. Studies should be undertaken of the uptake and depuration of methylated forms of selenium by aquatic biota.

References

Anderson, L.W. and L. Acs. 1974. Selenium in North American paper pulps. Environ. Sci. Technol. 8:462-464.

Barnhart, R.A. 1958. Chemical factors affecting the survival of game fish in a western Colorado reservoir. Colorado Co-operative Fisheries Research Unit, Quarterly Report, 4:25-28.

Baumgartner, D.J., D.W. Schults, and J.B. Larkin. 1978. Appendix D: Chemical and physical analyses of water and sediment in relation to disposal of dredged material in Elliott Bay. Dredged Material Research Program, Tech. Rept. D-77-24. U.S. Army, Corps of Engineers, Vicksburg, Miss.

Bryan, G.W. 1976. Heavy Metal Contamination in the Sea. In: R. Johnston, (ed.), Marine Pollution. Academic Press, London. pp. 185-302.

Chapman, W.H., H.L. Fisher, and M.W. Pratt. 1968. Concentration Factors of Chemical Elements in Edible Aquatic Organisms. Lawrence Radiation Laboratory, Livermore, Calif. 46 pp.

Chau, Y.K., P.T.S. Wong, B.A. Silverberg, P.L. Luxon, and C.A. Bengert. 1976. Methylation of selenium in the aquatic environment. Science 192:1130-1131.

Copper, W.C. 1967. Selenium toxicity in man. In: O.H. Muth, J.E. Oldfield, P.H. Weswig (eds.). Avi Pub. Co., Westport, Connecticut.

Environmental Protection Agency. 1976. Selenium. National Research Council, Washington D.C. EPA 600/1-76/014.

Environmental Protection Agency. 1978. Ambient Water Quality Criteria: Selenium. NTIS (PB 292 440).

Forstner, U., G. Muller, and P. Stoffers. 1978. Heavy metal contamination in estuarine and coastal sediments: sources, chemical association and diagenetic effects. In: Biochemistry of Estuarine Sediments, UNESCO, Paris. pp. 49-69.

Forstner, U. and G.T.W. Wittmann. 1979. Metal Pollution in the Aquatic Environment. Springer-Verlag, New York.

Fowler, S.W. and A. Benayoun. 1976a. Influence of environmental factors on selenium flux in two marine invertebrates. Mar. Biol. 37:59-68.

Fowler, S.W. and A. Benayoun. 1976b. Accumulation and distribution of selenium in mussel and shrimp tissues. Bull. Environ. Contam. Toxicol. 16:339-346.

Fowler, S.W. and A. Benayoun. 1976c. Selenium kinetics in marine zooplankton. Mar. Sci. Commun. 2:43-67.

Frost, R.R. and R.A. Griffin. 1977. Effect of pH on adsorption of arsenic and selenium from landfill leachate by clay minerals. Soil Sci. Soc. Amer. Journ. 41:53-57.

Geering, H.R., E.E. Cary, L.H.P. Jones, and W.H. Allaway. 1968. Soil Sci. Soc. Amer. Proc. 32:35-40.

International Joint Commission. 1977. New and Revised Great Lakes Water Quality Objectives. Volume II. Windsor, Ontario.

Kharkar, D.P., K.K. Tarekian, and K.K. Bentine. 1967. Stream supply of dissolved silver, molybdenum, antimony, selenium, chromium, cobalt, rubidium and cesium to the oceans. Geochim. Cosmochim. Acta. 32:285-298.

Kim, J.H., E. Birks, and J.F. Heisinger. 1977. Protective action of selenium against mercury in Northern Creek chubs. Bull. Environ. Contam. Toxicol. 17:132-136.

Koeman, J.H., W.H.M. Peeters, C.H.M. Koudstaal-Hol, P.S. Tjioe, and J.J.M. de Geoij. 1973. Mercury-selenium correlation in marine mammals. Nature 342:385-386.

Kubota, J., W.H. Allaway, D.L. Carter, E.E. Cary, and V.A. Lazar. 1967. Selenium in crops in the United States in relation to selenium-responsive diseases of animals. J. Agric. Food Chem. 15:448-453.

Malins, D.C., B.B. McCain, D.W. Brown, A.K. Sparks, and H.O. Hodgins. 1980. Chemical Contaminants and Biological Abnormalities in Central and Southern Puget Sound. NOAA Technical Memorandum OMPA-2. Office of Marine Pollution Assessment, Boulder, Colo. 295 pp.

Measures, C.I. and J.D. Burton. 1980. The vertical distribution and oxidation states of dissolved selenium in the northeast Atlantic Ocean and their relationship to biological processes. Earth Planetary Sci. Lett. 46:385-396.

Niimi, A.J. and Q.N. LaHam. 1975. Selenium toxicity on the early life stages of zebrafish, Brachydanis rerio. J. Fish. Res. Bd. Can 32:803-806.

Parizek, J., I. Ostadalova, J. Kalouskova, A. Babicky, and J. Benes. 1971. The detoxifying effects of selenium interrelations between compounds of selenium and certain metals. In: W. Mertz and W.E. Corvatzer (eds.), Newer Trace Elements in Nutrition. Pub. Dekker, N.Y. pp. 85-112.

Sandholm, M., H.E. Oksanen, and L. Pesonen. 1973. Uptake of selenium by aquatic organisms. Limnol. Oceanogr. 18:496-499.

Schroeder, H.A., 1967. Effects of selenate, selenite, and tellurite on the growth and early survival of mice and rats. J. Nutr. 92:334.

Sillen, J.G. 1961. The physical chemistry of seawater. In: M. Sears (ed.), Oceanography, Amer. Assoc. for the Advan. of Sci., Washington, D.C. pp. 549-581.

Sugimura, Y., Y. Suzuki, and Y. Miyake. 1976. The content of selenium and its chemical form in seawater. J. Oceanogr. Soc. Jpn. 32:235-241.

Wrench, J.J. 1979. Uptake and metabolism of selenium by oysters. Mar. Sci. Commun. 5:47-59.

4.21 Silver

4.21.1 Introduction

Silver is biologically a nonessential, and nonbeneficial element. It is extremely toxic to aquatic organisms at relatively low concentrations (<1 mg/L) and has been cited as the most toxic of heavy metals to aquatic organisms with the exception of mercury (Birge et al., 1977).

Silver is used principally in photographic materials, electroplating, as a conductor, in dental alloys, solder, paints, jewelry, silverware, coinage, and mirror production (Smith and Carson, 1977). Silver is an antibacterial agent and is used as such to sterilize drinking water supplies.

Silver is one of the EPA's 129 Priority Pollutants, and is chosen as a contaminant of concern on the EPA's basis of concentrations detected in Puget Sound sediments.

4.21.2 Significance of Silver to Puget Sound

4.21.2.1 Review of Known Toxicity Data

Very low levels of silver have been shown to be toxic to aquatic organisms. Concentrations as low as 0.004 ppm silver are toxic to adult sticklebacks, causing death within 7 days (Cooper and Jolly, 1970).

Silver is more toxic to organisms at earlier life stages. For example, the 96-hour LC50 for American oyster (Crassostrea virginica) larva is 5.8 ppb (Calabrese et al., 1973). However, Thurberg (1974) on tests with adult American oysters found only a significant increase in oxygen consumption at 100 ppb silver. Chinook salmon fry exposed to 0.04 ppb silver (as $AgNO_3$) survived only 48 hours (McKee and Wolfe, 1963).

Silver has been tested for carcinogenicity in laboratory animals (mice and rats). Several authors have reported the carcinogenic effects of silver foil, pellets, and dental alloys implanted under the skin of laboratory animals (Oppenheimer et al., 1956; Fujita, 1972; Habu, 1968). However, Cannon and Hopps (1971) believe that silver may act as a nonspecific irritant rather than a specific carcinogen.

The current EPA (1978) Ambient Water Quality Criteria for silver to protect salt water aquatic life is 0.26 µg/L as a 24-hour average concentration not exceeding a concentration 0.58 µg/L at any time.

4.21.2.2 Possible Effects of Levels Found in Puget Sound

Silver levels in the sediments of Puget Sound ranged from 1.2 to 11 ppm (dry weight) (Malins et al., 1980). The highest levels were encountered in sediment from the southwest end of Sinclair Inlet and the Sitcum and City Waterways of Commencement Bay. The levels are higher than those reported by Bruland et al. (1974) who noted that the silver content in marine sediments receiving Los Angeles city sewage has increased from 1.5 to 3.5 ppm silver since about 1920. Silver levels in Puget Sound are widely distributed; hence, they are of concern.

Waters of Puget Sound were not analyzed for silver during the MESA Project and comparisons with EPA Water Quality Criteria are not possible.

The concentration of silver detected in the biota of Puget Sound ranged from 0.23 to 6.07 ppm wet weight silver (Malins et al., 1980). The highest levels were reported in crab hepatopancreas from Sinclair and Case Inlets. The lowest levels were found in shrimp and clams. Neither whole body nor fish livers were analyzed for silver content.

4.21.3 Speciation in the Estuarine and Marine Environments

The particular physico-chemical forms of silver are of importance in determining the bioavailability of this contaminant in the estuarine and marine environments (Jenne and Luoma, 1977).

Ionic silver is present in the aqueous medium as the univalent ion (Ag^+) although it may also form compounds in the divalent and trivalent states (Cotton and Wilkinson, 1972).

Sibley and Morgan (1977) calculated the equilibrium speciation of silver in freshwater-seawater mixtures. In freshwater, the adsorbed species is more important than in seawater due to the abundance of particulate material relative to seawater. The principal species of dissolved silver in freshwater is the free ion, Ag^+. The silver-chloride complex may also account for up to 5% of the dissolved silver. Jenne et al. (1978) also found the complex, AgSH, to be a significant species, exceeding the activity of $Ag^+$and AgCl approximately 10 fold. In seawater, the adsorbed and dissolved free ion species are neglibible. The chloride ligand appears to control the speciation of dissolved silver in seawater.

Parameters which influence the speciation of dissolved inorganic silver in the aqueous environment include: pH, oxidation-reduction state, different ionic strengths, concentration of adsorbing surfaces in seawater, concentration of silver, and the concentrations of ligands and other cations. Figure 4.21.1 illustrates the change in dominant species in various freshwater and seawater ratios (Sibley and Morgan, 1977).

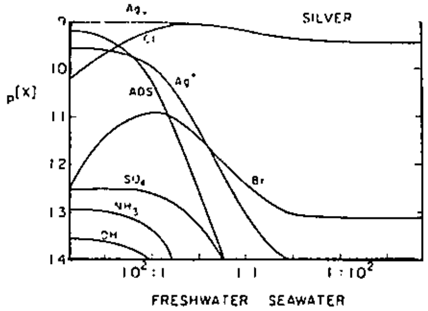


Figure 4.21.1

Speciation of Silver in Various Freshwater - Seawater Mixtures (Sibley and Morgan, 1977)

4.21.4 Summary of Biogeochemical Fate Data in the Marine Environment

4.21.4.1 Bioaccumulation - Uptake and Depuration

Summary Statement: Dissolved silver, rather than silver-contaminated food, appears to be the major mechanism for uptake of silver by aquatic biota. Depuration rates are slow.

Review of Individual Studies: Luoma and Cain (1979) studied the fluctuations of metals (including silver) in clams from south San Francisco Bay. They suggested that the discharge of freshwater into the Bay may affect the concentration of trace metals available to organisms in several ways:

1. During the rainy season river, stream and sewer discharge may carry elevated concentrations of dissolved and particulate bound metals into the estuary.

2. Land-derived sediments entering the estuary would, due to the physico-chemical differences from estuarine sediments, affect both the partitioning of metals between particulate and dissolved states and the ability of particulate feeding organisms to accumulate metals.

3. Flushing may reduce the concentrations of solute metals and change the chemistry of the sediments.

4. Variable salinity of estuarine waters may affect metal uptake by organisms (Phillips, 1977).

Several authors have shown that silver can be accumulated by aquatic organisms (Greig and Wenzloff, 1978; Luoma and Cain, 1979; Luoma and Jenne, 1977; Callahan and Slimak, 1979). Greig and Wenzloff (1978) in a study on the uptake and depuration by the oyster, *Crassostrea virginica*, concluded that the oysters did not obtain silver directly from the sediment. Silver was found to depurate very slowly with little decrease in silver concentration in oysters occurring over the 40-week study period.

Luoma and Cain (1979) found that freshwater discharge rates into south San Francisco Bay were important in determining the degree of clam (*Macoma balthica*) contamination. Silver was noted to accumulate in the clams as rainfall increased in frequency through the summer and fall, suggesting that local runoff was primarily responsible for input of silver into the Bay.

Freeman (1979) in a study on silver kinetics in an alpine lake found a significant portion of the silver associated with the sediments, rather than water. He noted that silver concentrations in chironomid larvae paralleled sediment trends in a year of study, while levels in plankton reflected the concentration of silver in water.

Terhaar et al. (1972) in a study on the toxicity of photographic processing effluents to fish, found algae, Daphnia, freshwater mussels, and fathead minnows capable of accumulating silver from water. However, they did not find food to be a significant source of silver for organisms of higher trophic levels.

Luoma and Jenne (1977) determined uptake of silver bound to various sediment types by a deposit feeding clam, Macoma balthica. They found that uptake was dependent on the type of sediment to which silver was bound, as well as the rate of desorption of silver. Silver was taken up from both biogenic carbonates (crushed shells) and synthetic calcites to a greater degree than from iron oxides or detrital organics. The authors noted that the solid forms of silver, which could contribute to a significant portion of a deposit feeder's silver levels, were taken up at a slower rate than solute forms (Jenne and Luoma, 1977). A significant portion of the silver taken up by the clams was deposited in the shell of the animals.

4.21.4.2 Sorption/Desorption

Summary Statement: Silver can be strongly sorbed to clays and organic-containing sediments. Exposure to seawater, however, enhances the release of silver from sediments.

Review of Individual Studies: The sorption/desorption of silver in sediments is a very important factor controlling the bioavailability of this metal to deposit and detritus feeding organisms (Luoma and Jenne, 1977).

Adsorption of silver to river particulates is a signficant process in freshwater systems. However, as the freshwater is diluted with seawater there is a general desorption of silver due to association with the chloride ion and displacement of silver by other cations.

Little data are available on the sorption mechanisms of silver in estuarine and marine waters. Bruland et al. (1974) found that in the sediments of the Southern California Coastal Basin, silver existed mainly as the insoluble sulfide or bound to the organic phase.

Kharkar et al. (1968) attempted to estimate the supply of soluble and adsorbed heavy metals in streams and degree of desorption on contact with seawater. They studied the adsorption of silver on clay minerals: montmorillonite, illite, and kaolinite, and on three hydrous metal oxides: freshly precipitated $Fe(OH)_3$, manganese oxide, and reagent Fe_2O_3. The affinity of these adsorbing surfaces for silver decreased in the order: MnO_2 > freshly precipitated $Fe(OH)_3$ > montmorillonite > illite > kaolinite > Fe_2O_3. Transfer of these minerals to seawater resulted in the desorption of 20-30% of the adsorbed silver. The authors suggested that the release of the adsorbed silver is a result of the displacement of the silver ions by magnesium or sodium ions in seawater. Therefore, stream-supplied particulates, rather than acting as binding sites for silver in seawater, actually contribute dissolved silver to the oceans.

Freeman et al. (1979) found a correlation of silver content and organic matter in sediments. He also noted that silver was present in higher concentrations in the finer fractions of the lake sediment.

4.21.4.3 Photolysis

No data were found pertaining to photolysis of silver in the environment.

4.21.4.4 Volatilization

Studies on the volatilization of silver compounds were not encountered in the literature. The formation of biogenic alkyl silver compounds is not an important process (Cotton and Wilkinson, 1972), and volatilization is probably not an important fate process for silver in the Puget Sound marine environment.

4.21.5 Conclusions

1. Silver is very toxic to organisms at earlier life stages.
2. Silver levels in Puget Sound sediments are very high in some areas and efforts are required to evaluate the implications of such levels.
3. Major fate processes for silver in marine waters are: complexation with chloride and bromide ions in the water phase; and adsorption to sediments with high organic content, or with high iron and manganese hydroxide content.
4. Bioaccumulation predominantly occurs by uptake via the water phase rather than from the diet.

4.21.6 Research Needs

1. Levels of silver in waters of Puget Sound should be determined because of the sensitivity of aquatic biota to low levels of silver.
2. Adsorption-desorption processes of silver from Puget Sound sediments should be studied to enable assessment of possible ecological impact on benthic organisms.
3. Point sources should be identified.

References

Birge, W.J., J.A. Black, and A.G. Westerman. 1977. The evaluation of aquatic pollutants using fish and amphibian eggs as bioassay organisms. In: International Symposium on the Pathology of Environmental Pollution-Animal Models and Wildlife as Monitors, University of Connecticut, Storrs, Conn., June 1-3. Armed Forces Institute of Pathology, Northeast Research Center for Wildlife Diseases.

Bruland, J.W., K. Bertine, M. Koide, and E.D. Goldberg. 1974. History of metal pollution in Southern California Coastal Zone. Environ. Sci. Technol. 8:425.

Calabrese, A., R.S. Collier, D.A. Nelson, and J.R. MacInnes. 1973. The toxicity of heavy metals to embryos of the American oyster Crassostrea virginica. Mar. Biol. 18:162-166.

Callahan, M.A., and M.W. Slimak. 1979. Water-Related Environmental Fate of 129 Priority Pollutants. EPA 440/4-79-029a.

Cannon, H.L. and H.C. Hopps (eds.). 1971. Environmental Geochemistry in Health and Disease. The Geological Society of America, Inc., Boulder, Colorado.

Cooper, C.F. and W.C. Jolly. 1970. Ecological effects of silver iodide and other weather modification agents: A review. Water Resources Res. 6:88-98.

Cotton, F.A. and G. Wilkinson. 1972. Advanced Inorganic Chemistry. Interscience Publishers, N.Y. 1145 pp.

Environmental Protection Agency. 1978. Ambient Water Quality Criteria: Silver. NTIS (PB 292 441).

Freeman, R.A. 1979. Ecological kinetics of silver in an alpine lake ecosystem. In: L.L. Marking and R.A. Kimerle (eds.), Aquatic Toxicology. ASTM Special Technical Publication 667. pp. 342-358.

Fujita, S. 1972. Silver-palladium-gold alloys carcinogenicity and acid mucopolysaccharides in the induced tumors. Shika Igaku. 34:918-932.

Greig, R.A. and D.R. Wenzloff. 1978. Metal accumulation and depuration by the American oyster Crassostrea virginica. Bull. Environ. Contamin. Toxicol. 20:499-504.

Habu, T. 1968. Histopathological effects of silver-palladium-gold alloy implantation on the oral sub-mucous membranes and other organs. Shika Igaku. 31:17-48.

Jenne, E.A. and S.N. Luoma. 1977. Forms of trace elements in soils, sediments, and associated waters: An overview of their determination and biological availability. In: H. Drucker and R. Wildung (eds.), The Biological Implications of Metals in the Environment. Proc. 15th Ann. Hanford Life Sci. Symp, September 29-October 1, 1975, Richland, Wash. CONF-750929.

Jenne, E.A., D.C. Girvin, J. W. Ball, and J.M. Birchard. 1978. Inorganic speciation of silver in natural water-fresh to marine. In: D.A. Klein (ed.), Environmental Impacts of Artificial Ice Nucleating Agent. Dowden, Hutchinson, and Ross, Inc. Stroudsburg, Penn. pp. 41-63.

Kharkar, D.P., K.K. Turekian, and K.K. Bertine. 1968. Stream supply of dissolved silver, molydenum, antimony, selenium chromium, cobalt, rubidium, and cesium to the oceans. Geochim. Cosmochim. Acta 32:285-208.

Luoma, S.N. and E.A. Jenne. 1977. The availability of sediment-bound cobalt, silver and zinc to a deposit feeding clam. In: H. Drucker and R. Wildung (eds.), Biological Implications of Metals in the Environment. Proc. 15th Ann. Hanford Life Sci. Symp. at Richland, Wash. Sept. 29-Oct. 1, 1975. CONF -750929.

Luoma, S.N. and D.J. Cain. 1979. Fluctuations of copper, zinc, and silver in Tellenid clams as related to freshwater discharge - South San Francisco Bay. In: San Francisco Bay: The Urbanized Estuary. The Pacific Division of the American Association for the Advancement of Science. California Academy of Sciences, San Francisco.

Malins, D.C., B.B. McCain, D.W. Brown, A.K. Sparks, and H.O. Hodgins. 1980. Chemical Contaminants and Biological Abnormalities in Central and Southern Puget Sound. NOAA Technical Memorandum OMPA-2. Office of Marine Pollution Assessment, Boulder, Colo. 295 pp.

McKee, J.E. and H.W. Wolfe (eds.). 1963. Water Quality Criteria, 2nd edition. Publication 3-A. California State Water Resources Control Board (Reprint January 1973).

Oppenheimer, B.S., E.T. Oppenheimer, I. Danishefsky, and A.P. Stout. 1956. Carcinogenic effect of metals in rodents. Cancer Res. 16:439-441.

Phillips, D.J.H. 1977. The common mussel Mytilus edulis as an indicator of pollution by zinc, cadmium, lead and copper. I. Effects of the environmental variables on uptakes of metals. Mar. Biol. 38:59-69.

Sibley, T.H. and J.T. Morgan. 1977. Equilibrium speciation of trace metals in freshwater:seawater mixtures. In: Symposium Proceedings International Conference on Heavy Metals in the Environ. Vol. I, October 27-31, 1975. Toronto, Ontario.

Smith, I.C. and B.L. Carson. 1977. Trace Metals in the Environment - Silver. Ann Arbor Science Publishers, Inc. Ann Arbor, Mich.

Terhaar, C.J., W.S. Ewell, S.P. Dziuba, and D.W. Fassett. 1972. Toxicity of photographic processing chemicals to fish. Photograph. Sci. Eng. 16:370-377.

Thurberg, F.P. 1974. Effects of silver on oxygen consumption of bivalves at various salinities. In: F.J. Vernberg and W.B. Verburg (eds.). Pollution and Physiology of Marine Organisms. Academic Press, N.Y. pp. 67-68.

5. REVIEW OF ADDITIONAL CONTAMINANTS IDENTIFIED WITHIN PUGET SOUND

Based on the scheme described in Chapter 2, contaminants identified in Puget Sound have been characterized in Table 2.1 as:

Category - "critical" and of concern

Category 2 - "of possible concern and difficult to evaluate" - i.e., compounds which are toxic but found at very low concentrations

Category 3 - compounds for which there are minimal or no data on toxicity

Category 4 - "source identification required" - i.e., compounds which are toxic and known to be distributed only in localized areas

Category 5 - compounds which are toxic but for which there is minimal information on their distribution or levels in Puget Sound

Category 6 - compounds which appear to be of no immediate concern

Chapter 4 described the fate and effects of contaminants considered as critical to Puget Sound. This chapter reviews the data which resulted in the selection of the remaining contaminants within categories other than "critical."

5.1 Contaminants Considered to be of No Immediate Concern Based on Existing Knowledge (Category 6)

5.1.1 Organic Contaminants - Category 6

Organic contaminants in this category are not of high acute toxicity (i.e., oral LD50 >5 mg/kg or 96-hour LC50 >1 µg/L), nor were they detected in Puget Sound water in excess of 1% of any known LC50 concentration for marine species, nor were they detected in Puget Sound marine biota in concentrations in excess of 1% of any known LD50. Generally, they are not carcinogens. If they are, they were not detected in Puget Sound biota nor do they have the potential to bioconcentrate within biota. Sediment concentrations were below the levels at which equilibrium water levels would have exceeded 1% of any known LC50 for marine species.

5.1.1.1 Halogenated Aliphatic Compounds

The following halogenated aliphatic compounds were considered to be of no immediate concern based upon existing knowledge:

Chloromethane: Detected in one Puget Sound sediment sample at 0.1 ng/g (Seattle METRO). Low toxicity, e.g., 96-hour LC50 for silversides = 256 ppm (EPA, 1978).

Trichloromethane: Detected in sediment samples at levels from 0.3-0.9 ppb (Seattle METRO). Low toxicity, e.g., 96-hour LC50 for bluegill = 115 ppm (EPA, 1978).

Tetrachloromethane: Detected in one sediment sample at 0.26 ppb (Seattle METRO). Low toxicity, e.g., 96-hour LC50 for bluegill = 27-125 ppm (EPA, 1978).

Chlorodibromomethane: Detected in one of 15 water samples at 0.2 ppb (Riley et al., 1980). Low toxicity assumed, based on toxicity data for other halomethanes.

Tribromomethane: Detected once in sediment samples at 0.26 ppb (Seattle METRO). Low toxicity, e.g., 96-hr LC50 for mysid shrimp = 24 ppm (EPA, 1978).

1,1,1-Trichloroethane: Detected in one sediment sample at 6 ppb (Seattle METRO). Not a carcinogen (NIOSH, 1979).

There is no evidence that the chlorinated aliphatics listed above persist in the environment or are bioaccumulated to any appreciable degree. Most of these compounds have high vapor pressures and volatilize readily. For example, chloromethane which has been detected within West Point sewage effluents at levels from 18-65 µg/L (Chapman et al., 1979) has a calculated volatilization half life of 27 minutes. A similar half life was calculated for trichloromethane which was detected by Seattle METRO at levels between 3-19 µg/L in West Point effluents. Environmental concerns related to trace quantities of halogenated aliphatic compounds are based mainly upon their intake via drinking water, which will not be a concern in the marine environment.

5.1.1.2 Monocyclic Aromatics

The following monocyclic aromatics were considered to be of no immediate concern based upon levels and areal distribution of these compounds in Puget Sound:

Benzene: Detected in three sediment samples at levels from 0.6 to 15.2 ppb (Seattle METRO). Toxicity to marine biota is low, e.g., 96-hour LC50 values for several species = 5-100 ppm (EPA, 1978).

Ethyl Benzene: Detected in 4 of 18 sediment samples at 0.3 to 1.0 ppb (Seattle METRO). Low oral toxicity, LD50 rat = 3500 mg/kg (NIOSH, 1979). LC50 for sheepshead minnow = 275 ppm (EPA, 1978).

N-Propyl Benzene: Not detectable in most samples. Analytical problems render any positive detections doubtful (Brown, 1980). Low toxicity, LD50 for rat = 4830 mg/kg (NIOSH, 1979).

Isopropyl Benzene: Not detectable in most samples. Analytical problems render any positive detections doubtful (Brown, 1980). Low toxicity, LD50 for rat = 2910 mg/kg (NIOSH, 1979).

Tri-isopropyl Benzene: Listed in tables submitted for study. Not detected in Puget Sound.

Methyl Benzene (Toluene): Detected in 4 of 18 sediment samples at 2.3-7.6 ppb (Seattle METRO). Saltwater species 96-hour LC50's = 3.7-74 ppm (EPA, 1978).

Tetramethyl Benzene: Detected in most sediments from 0.1 to 10 ppb (Brown, 1978, 1979a,b,c). Low toxicity, e.g., LD50 for rat = 6408 mg/kg (NIOSH, 1979).

Benzaldehyde: Detected in one sediment sample (Brown, 1979a). Very low toxicity, actually a narcotic (Merck and Co., 1976). Oxidizes in air to benzoic acid which would not be toxic to biota.

N-methyl Aniline: Detected in one sediment sample (Brown, 1978), at 20 ppb. Low toxicity, e.g., LD50 for rabbits = 280 mg/kg (NIOSH, 1979).

Methyl Phenyl Acetate: Detected in one sediment sample at 30 ppb (Brown, 1978). Low toxicity, e.g., LD50 for rat = 1630 mg/kg (NIOSH, 1979).

The monocyclic aromatics listed above are generally low in toxicity. The majority of water and/or sediment samples examined contained nondetectable levels of these compounds. Bioconcentration factors for these compounds are low; partition coefficients are all less than 3.5.

5.1.1.3 Additional Organic Compounds

The following additional organic compounds were also considered not to be of concern:

Palmitic Acid: Detected in 2 of 4 sediment samples (Brown, 1978). Toxicity unknown, but toxicity of similar fatty acids is low, e.g., oleic acid 96-hour LC50 for trout = 8.2 ppm (B.C. Research, 1977).

Stearic Acid: Identified in sediment samples but levels not quantified (Brown, 1978). Toxicity unknown, but that of similar fatty acids is low, e.g., 96-hour LC50 oleic acid for trout = 8.2 ppm (B.C. Research, 1977).

Indan: Detected at trace levels in biota and sediment (Brown, 1978, 1979a,b,c). Low toxicity, e.g., LDLo (lowest dose of a substance reported to have caused death in animals) for rat = 5000 mg/kg (NIOSH, 1979).

Decalin: Identified in one sediment sample (Brown, 1978). Low toxicity, e.g., LD50 for rat = 4170 mg/kg (NIOSH, 1979).

5.1.2 Metals - Category 6

Metals were considered to be of concern if they were detected in sediments of Puget Sound in excess of average concentrations reported within the continental crust or deep sea clays and were known to be toxic. All "background" values in this chapter were obtained from Bryan (1976). Based on the above criteria, the following metals were considered to be of no concern:

Barium: Detected in Puget Sound sediments at levels between 11.7 to 283 ppm. Average levels in the earth's crust, 250 ppm.

Beryllium: Detected in Puget Sound sediments at levels between 0.16 to 1.1 ppm. Average levels in earth's crust, 6 ppm.

Bismuth: Detected in Puget Sound sediments at levels from 22 to 150 ppm. Average levels in earth's crust 0.2 ppm. Not toxic in the aquatic environment (NAS/NAE, 1972).

Boron: Detected in Puget Sound sediments at levels between 12.0 to 99.6 ppm. Average levels in earth's crust, 3 ppm; in continental shelf, 20-80 ppm, in Black Sea sediments, 114 ppm (Perkins, 1973).

Calcium: Detected in Puget Sound sediments at levels from 2300 to 20,000 ppm. Average levels in earth's crust 36,300 ppm.

Chromium: Detected in Puget Sound sediments at levels between 20.9 to 160 ppm. Average levels in earth's crust, 100 ppm; in deep sea clay, 90 ppm.

Cobalt: Detected in Puget Sound sediments at levels between 5.3 to 280 ppm. Average levels in earth's crust, 25 ppm; in deep sea clay, 74 ppm.

Iron: Detected in Puget Sound sediments at levels between 11,120 and >50,000 ppm. Average levels in earth's crust, 56,300 ppm; in deep sea clay, 65,000 ppm.

Lithium: Detected in Puget Sound sediments at levels between 7.2 to 26.8 ppm. Average levels in earth's crust, 65 ppm.

Magnesium: Detected in Puget Sound sediments at levels between 3533 to 12,961 ppm. Average levels in earth's crust, 20,900 ppm.

Manganese: Detected in Puget Sound sediments at levels between 141 to 1500 ppm. Average levels in earth's crust, 950 ppm; in deep sea clay, 6,700 ppm.

Molybdenum: Detected in Puget Sound sediments at levels between 6.0 to 29.7 ppm, although two values of 56 and 114 ppm were reported. Average levels in earth's crust, 1.5 ppm; in deep sea clay, 27 ppm. Toxicity to aquatic life not known to be of concern (NAS/NAE, 1972).

Nickel: Detected in Puget Sound sediments at levels between 13 to 130 ppm. Average levels in earth's crust, 75 ppm; in deep sea clay, 225 ppm.

Phosphorus: Detected in Puget Sound sediments at levels between 303 to 1,474 ppm. Average levels in earth's crust, 1,180 ppm.

Scandium: Detected in Puget Sound sediments at levels between 2.89 to 16.1 ppm. Average levels in earth's crust, 5 ppm. NIOSH (1979) toxicity data indicates salts not of significant concern.

Silicon: Detected in Puget Sound sediments at levels between 88 to 3800 ppm. Average levels in earth's crust, 277,200 ppm.

Sodium: Detected in Puget Sound sediment at levels between 3100 to >20,000 ppm. Average levels in earth's crust, 28,300 ppm.

Strontium: Detected in Puget Sound sediments at levels between 26.4 to 513 ppm. Average levels in earth's crust, 300 ppm.

Titanium: Detected in Puget Sound sediments at levels between 640 to 1,931 ppm. Average levels in earth's crust, 4,400 ppm.

Vanadium: Detected in Puget Sound sediments at levels between 28.0 to 107 ppm. Average levels in earth's crust, 135 ppm; in deep sea clay, 120 ppm.

Yttrium: Detected in Puget Sound sediments at levels between 3 to 18.1 ppm. Average levels in earth's crust, 28 ppm.

Zirconium: Detected in Puget Sound sediments at levels between 2 to 13 ppm. Average levels in earth's crust, 220 ppm.

5.2 Contaminants For Which There Are Insufficient Toxicological Data for Evaluation - Category 3

Compounds such as halogenated linear and cycloalkenes, dibenzofurans and thiophenes have rarely been reported as environmental contaminants. Studies of the fate and effects of these compounds were generally not found in the literature search.

The chlorinated linear and cycloalkenes identified in suspended matter of Hylebos Waterway may be of concern, although no specific marine toxicity data are available. One closely related structure, hexachlorocyclopentadiene, is extremely toxic to freshwater organisms; 96-hour LC50 values for fathead minnow vary from 7 to 104 ppb with chronic effects observed at 2.6 ppb (Spehr, cited in EPA, 1978).

The contaminants for which there are insignificant toxicity data are shown in Table 5.1. Gallium and germanium are inorganic elements which could not be evaluated because of minimal toxicity data. Toxicity evaluations of these compounds and elements are recommended.

5.3 Contaminants for Which an Ecological Hazard Evaluation Could not be Provided - Category 2

During the evaluation procedure, several contaminants could not readily be classified as definitely "of concern" or "not of concern." For example, although N-nitrosodimethyl amine is a carcinogen which is acutely toxic at very low concentrations, it was detected at very low concentrations (14-32 µg/kg) in sediments in a confined area of Puget Sound (Seattle METRO). While the source of this and other contaminants should obviously be identified, it is questionable whether N-nitrosodimethyl amine presently poses a hazard to the Puget Sound ecosystem at the observed concentrations.

5.3.1 Nitrosamines

N-nitrosodimethyl amine
N-nitrosodiphenyl amine
N-nitrosodi-N-propyl amine
N-nitrosophenyl amine

The nitroso-amines are designated within NIOSH (1979) Registry of Toxic Effects of Chemical Substances as potent or possible carcinogens. Toxicity data relevant to marine biota are minimal. There is no information on bioaccumulation; however, the low partition coefficients for these compounds (0.06 for N-nitrosodimethyl amine to 2.57 for N-nitrosodiphenyl amine) suggest neither bioaccumulation nor uptake by sediments are significant fate processes. Concentrations of these compounds in sediments were below 60 ppb (Seattle METRO).

Table 5.1 .

Contaminants Detected in Puget Sound of Possible Concern For Which There Are Minimal Toxicity Data

hexachlorobutene
pentachloropropene
pentachlorocyclopentene
pentachloropentadiene
hexachlorocyclopentene,
hexachloropentadiene
hexachloroheptatriene,
hexachlorocycloheptadiene
heptachlorocyclohexadiene,
heptachlorohexatriene
heptachlorocyclohexadiene,
heptachlorohexatriene
heptachlorocyclohexadiene,
heptachlorohexatriene
hexachlorocyclohexadiene,
hexachlorohexatriene
carbazole
biphenyl
dibenzofuran
methyl dibenzofuran
benzothiophene
benzonaphthothiophene
dibenzothiophene
methyl dibenzothiophene
gallium
germanium

5.3.2 N,N-Dimethyl Aniline

This compound is moderately toxic to humans; toxic effects have been observed at dosages of 50 mg/kg (NIOSH, 1979). However, this compound was observed at only one site (Duwamish East) and at a level of 1,800 ppb (Brown, 1978). The partition coefficient was calculated to be 2.6, which implies that partitioning to sediments may not be significant and that levels in the water column may be high.

5.3.3 3,3-Dichlorobenzidene

This compound is categorized as a carcinogen (NIOSH, 1979). Levels of 29-39 ppb were reported in sediments (Seattle METRO), but the significance of these levels in Puget Sound cannot be predicted on the basis of current knowledge. Biota levels are expected to be low on the basis of the compound's partition coefficient of 3.0 (Tute, 1971).

5.3.4 Chlordane

The use of chlordane is currently restricted due to the issuance of a registration suspension notice by EPA. Some commercial use is allowed primarily for termite control (EPA, 1978).

This compound is extremely toxic; the 96-hour LC50 for pink shrimp is 0.4 μg/L (EPA, 1978). The EPA (1978) Ambient Water Quality Criteria recommend that levels in water not exceed 0.06 μg/L at any one time and 24 hour averages not exceed 0.004 μg/L. Bioconcentration factors for marine biota vary from 3200 to 18,700 (EPA, 1978). Levels of chlordane in the biota and sediments of Puget Sound were generally very low. With the exception of Commencement Bay, chlordane levels in Puget Sound sediments were generally less than 1 μg/kg. Levels in Commencement Bay sediments varied from 0.9 to 20 μg/kg, and levels in biota were generally less than 20 μg/kg. Occasionally, fish liver samples showed higher chlordane levels; for example, up to 180 μg/kg were detected in samples of fish liver from Elliott Bay (Brown, 1979b).

Chlordane is not widely dispersed in Puget Sound and levels in excess of 100 μg/kg were restricted to several fish liver samples. While it is recognized that the compound is very toxic, it is uncertain whether chlordane is a hazard to the Puget Sound environment because of its restricted usage and because of its limited distribution.

5.3.5 Heptachlor

Heptachlor is extremely toxic to marine biota. 96-hour LC50's for pink and spot shrimp are 0.11 μg/L and 0.85 μg/L, respectively (EPA, 1978). Since 1975, however, there has been a dramatic decrease in the use of the compound as a result of a voluntary restriction in production by the sole producer. Minimal commercial usage still occurs (EPA, 1978).

Heptachlor was generally not detected in biota and sediment samples from the Main Basin of Puget Sound. However, it was occasionally detected in sediment and fish liver samples from Elliott Bay and Commencement Bay. It is uncertain whether heptachlor is a hazard to the Puget Sound environment.

5.3.6 Lindane

Lindane is toxic to marine biota at very low levels. For example, 96-hour LC50's for pink and grass shrimp are 0.17 µg/L and 4.4 µg/L, respectively (EPA, 1978). Lindane was infrequently detected at quantifiable levels in Puget Sound biota and sediments. However, one fish liver sample contained 100 ng/g lindane. It is probable, but not certain, that lindane is not a problem in Puget Sound, based on the low levels measured.

5.3.7 Dinitrotoluene

Dinitrotoluene has been identified by NIOSH (1979) as a carcinogen, and it is moderately toxic to aquatic biota. 96-hour LC50 values for mysid shrimp are 590 µg/L, and EC50 values for the alga, <u>Skeletonema costatum</u>, are approximately 400 µg/L (EPA, 1978). Two dinitrotoluene isomers (2,4 and 2,6) have been identified in sediment samples by Seattle METRO, with levels varying from 1.4 to 50.4 µg/kg.

The relatively low partition coefficient of dinitrotoluene (log P = 2) suggests that bioconcentration in biota may be minimal. The effects of such carcinogens on aquatic biota are not known.

5.3.8 Polyaromatic Hydrocarbons

Some PAHs have been specifically identified in this report as compounds of concern. However, a large number of other PAHs identified within Puget Sound could not be adequately evaluated. These compounds are:

- Acenaphthalene
- Acenaphthene
- Anthracene
- Chrysene
- Fluorene
  - methyl fluorene
  - methoxy fluorene
- Indeno (1,2,3 -c,d) pyrene
- Perylene
  - methyl perylene
  - benzo(g,h,i) perylene
- Phenanthrene
  - benzo phenanthrene
  - methyl phenanthrene

Acenaphthalene was found in sediment samples throughout Puget Sound at concentrations from < 0.1 to 310 µg/kg. Levels in biota were often generally less than detection limits; however, detectable levels were reported, particularly in crabs (Malins et al., 1980). Derivatives such as nitro-acenaphthalene are known to be carcinogenic. An evaluation of this compound by the International Joint Commission (1980) designated this compound not to be of concern to human health. Similar evaluations of the effects of acenaphthalene on aquatic biota have not been undertaken.

Acenaphthene was found in most sediment samples of Puget Sound at levels from 0.1 to 1,300 µg/kg (Brown, 1979b,c; Seattle METRO, 1980). It was generally detected at low levels in biota. Acenaphthene has been shown to affect plants through improper nuclear division, and microorganisms may be similarly affected (EPA, 1978). Acute toxicity determinations, although limited in number, have shown 96-hour LC50 values of 2,230 µg/L for sheepshead minnow and 970 µg/L for mysid shrimp (EPA, 1978). The potential effects of acenaphthalene on Puget Sound biota require additional assessment.

Anthracene is listed within NIOSH (1979) as a possible carcinogen although; compared to other PAHs, its carcinogenicity is of less concern (International Joint Commission, 1980). It was found to be widely distributed in Puget Sound sediments at levels from 0.3 to 6400 µg/kg (Brown, 1978, 1979b,c). Anthracene was not detected at quantifiable levels in the majority of biota samples examined; however, Elliott and Commencement Bays' biota such as crab and clams contained up to 270 µg/kg anthracene. Anthracene may require additional evaluation with regard to its presence in Puget Sound.

Chrysene, which is listed in NIOSH (1979) as a positive carcinogen, was detected in all sediment samples with particularly high levels in sediments of Commencement and Elliott Bays (9-6,000 µg/kg) (Malins et al., 1980). The carcinogenicity of chrysene is not of similar concern as other PAHs (International Joint Commission, 1980). Fish livers generally contained low levels of chrysene, and biota such as shrimp, clams and worms contained levels up to 3500 µg/kg. The effects of chrysene on marine biota and consumers of chrysene-contaminated biota are not known.

There is no evidence for carcinogenicity of fluorene (NIOSH, 1979) and aquatic toxicity data are minimal. Fluorene was found in most sediment samples at concentrations from 0.4 to 2400 µg/kg (Malins et al., 1980; Seattle METRO, 1980). Fluorene was not detected at quantifiable levels in most samples of biota; however, Elliott Bay crab, shrimp, worms, and clams contained detectable quantities. Riley et al. (1980) detected fluorene in two water samples from the Seattle and Tacoma areas (30 ± 8 and 3 ± 2 ng/L, respectively) and found between 0.01 to 0.07 mg/kg of fluorene in suspended solids.

Indeno (1,2,3- c,d) pyrene is listed by NIOSH (1979) as a carcinogen. It was widely dispersed within Puget Sound sediments (0.4-2500 µg/kg); but detected at low levels in biota (Malins et al., 1980; Seattle METRO, 1980). It is uncertain whether concern for this compound is necessary.

Perylene is not considered a carcinogen (NIOSH, 1979). It was found in Puget Sound sediments at concentrations varying from 2 to 7600 µg/kg (Malins et al., 1980). Concentrations in suspended solids varied from 0.01 to 3.58 ng/kg (Riley et al., 1980). Levels in biota were generally below the detection limits, although up to 1300 ng/g dry weight were found in some samples. Methyl perylene and benzo(g,h,i)perylene were also detected in sediments (Brown, 1979a; Seattle METRO, 1980). The biological implications of the presence of perylene and associated compounds is not known.

Phenanthrene is widely distributed throughout Puget Sound with concentrations in sediments which varied from 1 to 11,000 µg/kg (Malins et al., 1980; Seattle METRO, 1980; Riley et al., 1980). Biota samples generally contained phenanthrene at levels below the detection limits; however, some biota samples contained appreciable levels of phenanthrene. Crabs from Commencement Bay, for example, contained between 100 and 500 µg/kg phenanthrene (Brown, 1979c) and clams had levels up to 410 µg/kg. Water from all sampling sites in Puget Sound contained from 1 to 24 ng/L and suspended solids contained from 0.08 to 0.65 mg/kg phenanthrene. The 1-methyl and 2-methyl forms of phenanthrene were found in high concentrations in water samples from all sites; the former was found at levels from 25 and 274 ng/L, the latter at 22-59 ng/L (Riley et al., 1980). Phenanthrene is not a known carcinogen; however, its metabolites may imply the need for concern similar to that of naphthalene.

5.4 Contaminants Which are Toxic but for Which Additional Information on Distribution, Form, or Levels is Required - Category 5

5.4.1 Tin

Levels of tin measured in Puget Sound sediments (9.6 to 70 ppm) are greater than the average levels in the earth's crust and deep sea sediments (2 ppm and 1.5 ppm, respectively) (Bryan, 1976). Although tin as an ion does not appear to be of concern (EPA, 1978), organo-tin, which may comprise a portion of the total tin in Puget Sound sediments, may be of concern.

Organo-tins are used commercially as heat stabilizers, PVC stabilizers, curing agents for silicone rubbers, biocides (molluscicides, fungicides, insecticides and rodent repellents), and preservatives for wood, textiles, paper, leather, and glass (Piver, 1973). Acute and chronic toxicity studies show that organo-tins are very toxic to rats. Triethyl tin sulfate, for example, has an oral LD50 of 5.7 mg/kg body weight of rat

(Stoner, 1955). The molluscicide, tributyl tin oxide, can cause lesions to the cornea of fish at a concentration of 5 µg/L (Center for Overseas Pest Research, 1974). Although tin has not been categorized as a contaminant of concern in Puget Sound, further studies are needed to evaluate whether it is present in tissues of biota, and to evaluate the forms of tin within the sediments.

5.4.2 Polychlorinated Terphenyls

Two PCTs (trichloroterphenyl and tetrachloroterphenyl) have been detected in sediment samples from Central Puget Sound. However, levels were not quantified.

Polychlorinated terphenyls (PCTs) are industrial chemicals with similar applications to PCB s (Chittim et al., 1977). The production of these compounds peaked in 1970-1971 and was halted in the United States in April, 1972 (Lincer et al., 1976). However, the compounds continue to be produced in France, Italy, Japan, and Germany (Jamieson, 1977). PCTs serve in a variety of uses: plasticizers in synthetic resins and adhesives; as lubricants; in investment casting waxes, printing inks, sealants, and caulking compounds; as fire-retardants in paperboards and fabrics; and as components of adhesives, lacquers, varnishes, and paints.

Data on toxicity of PCTs in the marine environment or information on mutagenicity or carcinogenicity of PCTs are sparse. PCTs are, however, very similar to PCBs in structure and their effects may be similar. The following summary gives some of the data retrieved on PCTs:

- Kinter et al. (1972) found that juvenile rainbow trout exposed to terphenyl compounds experienced swimming and postural difficulties. Yap et al. (1971) found that Aroclor 5460 (a mixture of terphenyls) inhibited Na^+- K^+ATPase activity in the brain and liver of trout.

- Studies of PCT toxicity are largely restricted to laboratory studies with mammals and birds. Sosa-Lucero et al. (1973) orally dosed rats with Aroclor 5460 for 7 days and found residues of this PCT in all rat tissues analyzed, with the greatest concentration in the liver. Although there were no observable acute effects at 10 ppm levels, the liver showed a significant increase in size.

- No specific information was obtained on the solubility, partition coefficients, rates of volatilization, or photolysis of PCTs. Information was also not available on the possible sorption or sedimentation of these compounds. However, Doguchi (1977) stated that PCTs are much less volatile and less soluble than PCBs. This author noted that PCTs were rare in the Japanese environment and, if found, were only present at very low levels.

- PCTs have been shown to accumulate in rat tissues following oral dosing (Sosa-Lucero et al., 1973).

- Addison et al. (1972) tube fed cod (Gadus morphua) with herring oil containing 1 gm Aroclor 5460 and found that excretory efficiency was poor and in some cases this PCT remained in cod tissues for over 70 days following dosing.

- PCTs have been detected in herring gulls and wildlife samples from Western Europe (Renberg et al., 1978). Freudenthal and Greve (1973) detected mean PCT concentrations in Rhine River waters of 0.07 ppb and concentrations of 0.2 and 0.4 ppm in oysters and eels from these waters. Levels to 0.8 ppm were also detected in two of four human fat samples.

- Hassell and Holmes (1977) measured PCT levels in livers of British birds and determined the following maximal levels (in mg/kg): kestrels, 0.9; barn owls, 0.5; sparrowhawk, 1.2; heron, 0.2; long-eared owl, 0.05; and kingfisher, 0.08.

- Renberg et al. (1978) examined PCTs in Swedish white-tailed eagles and grey eagles and found maximum levels in the fat of these species to be 17.2 µg/g and 1.0 µg/g, respectively. The authors noted that these levels were low, comprising only 1 to 2% of the PCB content in the same fat tissues, and they suggested that PCT accumulation should follow the same trend as shown by PCBs and DDT: the higher the trophic levels, the higher the levels of PCTs in tissues. This suggestion appears to be confirmed by various authors (Nishimoto et al., 1973; Doguchi et al., 1973; Minagara et al., 1974; Doguchi and Fukano, 1975; Fukano and Doguchi, 1977) who have shown substantial amounts of PCTs in human fat and blood in Japan. Doguchi (1977) found levels of PCTs in human fat and blood to be almost equivalent to PCB levels, although he could not establish significant PCT levels in the Japanese environment nor in food stuffs.

There is a need, therefore, to determine the levels and extent of distribution of PCTs in Puget Sound.

5.4.3 Dieldrin

Analyses are reported for aldrin but not for dieldrin in Puget Sound sediments and biota (Brown, 1979b,c). Levels of aldrin were generally lower than detection limits. However, aldrin is metabolized to dieldrin, a compound which tends to persist in the freshwater and marine environment (Konasewich et al., 1978). Thus, it is recommended that levels of dieldrin, particularly within Puget Sound biota, be determined. Dieldrin is extremely toxic, with LC50's to stonefly naiads of 0.2 µg/L (20-30 days) (EPA, 1978).

5.4.4 Endrin

This compound is highly toxic to aquatic biota with LC50's as low as 0.09 µg/L for juvenile striped bass. No analyses were conducted for endrin in the aquatic biota of Puget Sound even though endrin has a high bioconcentration factor (log partition coefficient 5.6). A brief sampling program is recommended to determine whether endrin is present in Puget Sound biota.

5.5 Toxic Contaminants Distributed Only in Localized Areas and for Which Source Identification Is Necessary - Category 4

The following compounds and elements are known to have potential toxic effects and have been reported in localized areas of Puget Sound:

- methylene chloride
- terphenyl
- phytane
- pristane
- bis (2-chloro ethyl) ether
- bis (2-chloro isopropyl) ether
- bis (2-chloro ethoxy) methane
- 4-bromophenyl phenyl ether
- dichlorobenzene
- zinc

The concentrations and/or the toxicities of these contaminants are such that source identification should be undertaken to enable efforts to minimize their localized effects.

Methylene chloride was found at levels from 26 to 508 ng/g in sediments (Seattle METRO). Levels in water varied from 3.8 to 109.4 µg/L (Riley et al., 1980). Although the levels in water are below the recommended EPA guidelines of 1,900 µg/L in saltwater at any one time, efforts should be made to determine the discharges of methylene chloride to Puget Sound.

Terphenyl was detected in Upper Sinclair sediments (Brown, 1979a). Chlorination of terphenyl is possible if found within effluent discharges, resulting in a compound with high bioconcentration potential whose environmental effects would be similar to PCBs. Thus, the source(s) of terphenyl to Puget Sound should be identified.

Phytane and pristane are long chain alkanes which are used as lubricants and as transformer and anti-corrosion agents (Merck, 1976). The toxicities of the compounds are questionable, i.e., within NIOSH (1979), pristane is reported to cause neoplasms, but only at levels of 1300 ng/kg body weight. Elevated levels were detected in suspended solids from Puget Sound: 1.9-50.6 mg/kg for pristane and from 0.2 to 2.5 mg/kg for phytane (Riley et al., 1980).

Chlorinated ethers have been detected in sediments from the Seattle METRO area at low concentrations (i.e., less than 3 µg/kg). Nonetheless, these compounds are all classified as carcinogens or possible carcinogens (NIOSH, 1979). The sediment phase is not predicted to be the "sink" of chlorinated ethers and the levels in water may be of concern. Source identification is therefore recommended.

Dichlorobenzene was detected mainly within the sediments of Commencement Bay (Brown, 1979b,c; Seattle METRO) at levels as high as 78 µg/kg. Dichlorobenzene is generally quite toxic to marine biota. For example, the EPA recommended guidelines for 1,4-dichlorobenzene list a maximum 24-hour average concentration of 15 µg/L in marine waters. Source identification is therefore recommended.

High levels of zinc were occasionally reported in Commencement Bay sediments (up to 1720 mg/kg). The sources of the elevated zinc levels should be identified.

References

Addison, R.F., G.L. Fletcher, S. Ray, and J. Doane. 1972. Analysis of a chlorinated terphenyl (Aroclor 5460) and its deposition in tissues of cod (Gadus morhua). Bull. Environ. Contamin. Toxicol. 8:52-60.

B.C. (British Columbia) Research. 1977. Identification of the Toxic Materials in Sulphite Pulp mill effluents. Environment Canada - Forestry Division. 56 pp.

Brown, D. 1978. Memo to Ed Long, re: Analyses of Central Puget Sound Samples. (September 7, 1978).

1979(a) Memo to Ed Long, re: Analyses of Four Central Puget Sound Sediments. (March 15, 1979).

1979(b) Memo to Bruce McCain, re: Central Puget Sound Data. (August 21, 1979).

1979(c) Memo to Ed Long, Bruce McCain, re: Analyses of Puget Sound Samples. (October 19, 1979).

Brown, D. 1980. Personal communication.

Bryan, G.W. 1976. Heavy metal contamination in the sea. In: R. Johnston (ed.), Marine Pollution. Academic Press, London. pp. 185-302.

Center for Overseas Pest Research. 1974. Report for January, December. College House Wrights Lane, Kensington, London.

Chapman, P.M., D. Moore, and G. Vigers. 1979. Toxicant literature review and evaluation of Metro's experimental design. Prepared for the Municipality of Seattle.

Chittim, B., S. Safe, L.O. Ruzo, O. Hutzinger, and V. Zitko. 1977. Synthesis and spectroscopic and gas chromatographic behavior of isomeric chlorinated terphenyls. J. Agric. Food Chem. 25:323-326.

Doguchi, M. 1977. Polychlorinated terphenyls as an environmental pollutant in Japan. Ecotoxicol. Env. Safety. 1:239-248.

Doguchi, M. and S. Fukano. 1975. Residue levels of polychlorinated terphenyls, polychlorinated biphenyls and DDT in human blood. Bull. Environ. Contamin. Toxicol. 13:57-63.

Doguchi, M., S. Fukano, and F. Ushio. 1973. Polychlorinated terphenyls in the human fat. Bull. Environ. Contamin. Toxicol. 11:157-162.

Environmental Protection Agency. 1978. Ambient Water Quality Criteria.

Freudenthal, J. and P.A. Greve. 1973. Polychlorinated terphenyls in the environment. Bull. Environ. Contamin. Toxicol. 10:108-111.

Fukano, S. and M. Doguchi. 1977. Polychlorinated terphenyls, polychlorinated biphenyls and pesticide residues in human fat and blood. Bull. Environ. Contamin. Toxicol. 17:613-617.

Hassell, K.D. and D.C. Holmes. 1977. Polychlorinated terphenyls in some British birds. Bull. Environ. Contamin. Toxicol. 17:618-621.

International Joint Commission (IJC). 1980. Annual Report of the Committee on the Assessment of Human Health Effects of Great Lakes Water Quality. Windsor, Ontario. 34 pp.

Jamieson, J.W.S. 1977. Polychlorinated terphenyls in the environment. Economic and Technical Review Report (Canada). EPS-3-EC-77-22. 71 pp.

Kinter, W.B., C.S. Merkens, R.H. Janicki, and A.M. Guarino. 1972. Studies on the mechanism of toxicity of DDT and polychlorinated biphenyls (PCBs): Disruption of osmoregulation in marine fish. Environ. Health Perspect. Exp. Issue 1:169-173.

Konasewich, D., W. Traversy, and H. Zar. 1978. Status report on organic and heavy metal contaminants in the Lake Erie, Michigan, Huron and Superior Basins. International Joint Commission. Windsor, Ontario. 338 pp.

Lincer, J.L., M.E. Haynes, and M.L. Klein. 1976. The Ecological Impact of Synthetic Organic Compounds on Estuarine Ecosystems. EPA 600/3-76-075.

Malins, D.C., B.B. McCain, D.W. Brown, A.K. Sparks, and H.O. Hodgins. 1980. Chemical Contaminants and Biological Abnormalities in Central and Southern Puget Sound. NOAA Tech. Memo. OMPA-2. Office of Marine Pollution Assessment, Boulder, Colorado. 295 pp.

Merck and Co., Inc. 1976. The Merck Index. 9th Edition. Merck and Co., Inc. Rahway, N.J.

Minagawa, K., Y. Takigawa, H. Sakai and I. Sesagawa. 1974. Polychlorinated terphenyls in human fat and mother's milk. Nippon Eseigaku Zasshi. 28:543-547.

National Academy of Sciences, National Academy of Engineering. 1972. Water Quality Criteria. U.S. Government Printing Office, Wash., D.C. (1974).

National Institute for Occupational Safety and Health (NIOSH). 1979. Registry of Toxic Effects of Chemical Substances (RTECS).

Nishimoto, T., M. Udea, S. Taue, H. Chikazawa, and T. Nishigama. 1973. PCT (polychlorinated terphenyl) in human adipose tissue and mother's milk. Igaku No Ayumi. 87:264-265.

Norbank, D.H. and J.R. Allen. 1972. Chlorinated terphenyl induced extensions of the hepatic endoplasmic reticulum. Proc. Soc. Exp. Biol. Med. 139:1127-1131.

Perkins, E.J. 1973. The Biology of Estuaries and Coastal Waters. Academic Press, London.

Piver, W.T. 1973. Organotin compounds: Industrial applications and biological investigation. Env. Health Perspect. 4:61-67.

Renberg, L., G. Sundstrom, and L. Reutergardh. 1978. Polychlorinated terphenyls (PCT) in Swedish white-tailed eagles and in grey seals - a preliminary study. Chemosphere 6:477-482.

Riley, R.G., E.A. Crecelius, D.C. Mann, K.H. Abel, B.L. Thomas, and R.M. Bean. 1980. Quantitation of Pollutants in Suspended Matter and Water from Puget Sound. NOAA Technical Memorandum ERL MESA-49. Marine Ecosystems Analysis Program, Environmental Research Laboratories, Boulder, Colo. 99 pp.

Seattle METRO: Analyses of Seattle Harbor Sediments.

Sosa-Lucero, J.C., F.A. de la Iglesia, and G.H. Thomas. 1973. Distribution of a polychlorinated terphenyl (PCT) (Aroclor 5460) in rat livers and effect on hepatic microsomal mixed function oxidases. Bull. Environ. Contamin. Toxicol. 10:248-256.

Stoner, H.B. 1955. Studies on the toxicity of alkyltin compounds. Brit. J. Phamacol. 10:16.

Tute, M.S. 1971. Principles and practice of Hansch analysis: a guide to structure-activity correlation for the medicinal chemist. Adv. Drug Res. 6:1-77.

Yap, H.H., D. Desarah, L.K. Cutkomp, and R.B. Koch. 1971. Sensitivity of fish ATPases to polychlorinated biphenyls. Nature 233:61-62.

6. CONCLUSIONS

The study described in this report attempted to identify the contaminants of concern to the Puget Sound ecosystem, and to document the existing knowledge on the fate and effects of those contaminants of concern. The findings of the study suggested that:

- Concentrations of many contaminants (such as PAHs, phthalate esters, DDT) in Puget Sound sediments and biota were much higher than concentrations reported in other areas of the world.

- A very low rate of microbial degradation of compounds such as DDT, phthalate esters and the lower chlorinated biphenyls is evident in Puget Sound.

- Fate and effects information for many contaminants are confined to data from freshwater studies rather than marine studies.

- It is difficult to predict potential ecological hazards of contaminants on the basis of toxicity data obtained from laboratory tests.

- The results of this study indicate that the chemicals of greatest concern to Puget Sound are probably: polychlorinated dibenzofurans and their possible precursors, tetra- and pentachlorophenol; chlorinated butadienes; several PAHs and their halogenated derivatives; arsenic; and, cadmium. Also of concern are: DDT; PCBs; hexachlorobenzene; chlorinated ethylenes; phthalate acid esters; copper; lead; mercury; selenium;and, silver.

7. RECOMMENDED RESEARCH NEEDS

The purpose of this section is to recommend general research strategies that will lead to a definition of biological, physical, and chemical processes and mechanisms that influence the fate and effects of environmental contaminants in Puget Sound. Recommended research needs for specific chemical compounds of concern are outlined in Section 4 of this report.

7.1 Research Need 1

Develop and implement a coordinated surveillance plan to assess trends and fate and effects of pollutants in Puget Sound.

Comment:

The MESA Project showed that the Puget Sound ecosystem is contaminated by many chemicals which are produced and used by man. Many of the chemicals by themselves are potentially harmful to the ecosystem and the effects of combinations of chemicals cannot be predicted on the basis of existing knowledge. A continual coordinated cost-effective surveillance plan will be required to detect ecological trends in Puget Sound arising from abatement programs or continued pollutant discharge. Surveillance guidelines utilizing biological, chemical, and physical expertise must be developed. Furthermore, the effort must enable the development of a standard of consistency and quality in sampling and analytical methodology and in data storage and retrieval.

Work Tasks:

1. Identify environmental compartments the; analysis of which will provide the most meaningful results with regard to trends, fate, and impact of specific types of contaminants. This task will require:

    a. identification of contaminants of concern which include the chemicals identified as such in this report, as well as chemicals which will be identified in the future;

    b. identification of actual species of biota (including birds and mammals) which are good indicators for monitoring trends, either by bioaccumulation of the chemicals or by their susceptibility to the chemicals;

    c. identification of sampling and analytical procedures for all compartments (including specification of sampling periods, identification of tissues for analyses, etc.); and

    d. identification of physical-chemical parameters which must be determined during the sampling of water, sediment and biota (i.e., pH, particle size, temperature).

2. Develop protocols to assure compatibility in sampling, preparatory, analytical, and reporting methodologies.

3. Assure continual assessment and interpretation of the data.

7.2 Research Need II

Develop an ecological hazard assessment scheme for Puget Sound.

Comment

Data regarding the toxicity of all compounds detected in Puget Sound are based on exposure of test organisms to concentrations of chemicals which were much higher than the concentrations normally detected *in situ*. In many instances, the concentrations observed in sediments and biota were extremely low, i.e., µg/kg. Some of the compounds were recognized as carcinogens based on laboratory test data with terrestrial species (rats, mice, etc.). However, the relevance to aquatic biota is not known and methodology and information to assess the ecological significance of contaminants at such levels was not available. The capabilities of analysts to detect low concentrations of contaminants and to detect "previously unidentified" contaminants is improving immensely due to new technology. As a result, there is a need to assess the significance of low level contaminants to an ecosystem.

Work Tasks

1. Define and, if necessary, develop tests which enable assessment of the ecological hazard of contaminants found in Puget Sound. Tests should consider the use of species indigenous to Puget Sound and should attempt to simulate the range of environmental conditions found within the Sound. For example, the release of metals from sediments should be tested under both reducing and oxidizing conditions. Higher food chain organisms should be included, such as fish-consuming birds and mammals.

2. Using the results of the above study, a protocol for defining contaminants of concern to Puget Sound should be developed.

3. Assess the relevance of carcinogenicity data obtained from laboratory test animals to the assessment of effects on aquatic biota, i.e., does categorization of a compound as a carcinogen to terrestrial species imply a problem to the health of Puget Sound biota?

7.3 Research Need III

Establish the relationship between levels of contaminants in sediments and benthic biota and the consequent acute and chronic, lethal, and sublethal effects of these levels on the biota.

Comment

Despite a great deal of work by previous research teams, a relationship between sediment contaminant levels and availability to biota has not been established for many chemicals. Although a precise relationship may be difficult to obtain, a greater understanding of the effects of physical-chemical characteristics of sediments on contaminant release may provide a greater predictive capability. Furthermore, the effects of bioaccumulated levels of contaminants on biota remain virtually unknown. For example, this study found that exchange among various tissues in biota could occur over long-term periods resulting in effects which were not observed during short-term toxicity studies.

Work Tasks

Using representative contaminants such as PAHs, chlorinated biphenyls, arsenic, and cadmium the following tasks are recommended:

1. The effects of physical-chemical characteristics of sediments on release of contaminants should be further defined to aid in situ evaluations.

2. Time series studies at known dumpsites or other heavily contaminated sites should be undertaken to evaluate impacts and changes in baseline chemical, physical, and biological features at the sites.

3. Additional long-term laboratory studies (including life-cycle studies) should be undertaken to evaluate the effects of low levels of contaminants which are steadily bioaccumulated in biota.

7.4 Research Need IV

Develop additional basic information on the behavior and fate of chemicals in the marine and estuarine environments.

Comment

Information on the chemical behavior of many organic pollutants in aqueous media is restricted to freshwater systems. Thus, data on partition coefficients, solubilities, oxidation, photolysis, and sorption-desorption phenomena need to be derived for many organic compounds in the marine and estuarine environments, in particular for conditions relevant to Puget Sound. In addition, there is a need to further the understanding of various physical processes in the marine environment.

For example, Singmaster (1975) showed rapid photolysis of DDT in seawater and virtually no photolysis in distilled water, indicating the possibility of photolytic catalysis by seawater or formation of photolytic species in seawater with oxidative capacities. Another example of a process in seawater which may affect the fate of pollutants is the formation of marine snow, a white precipitous matter which has been observed in many marine waters at depths greater than 50 meters. The composition of the matter and its effects on benthos is not known.

Work Tasks

1. Develop protocols to obtain physical-chemical data in marine waters. These protocols may be attained jointly with the ongoing efforts of The American Society for Testing Materials.

2. Obtain required physical-chemical data for compounds identified to be of concern to Puget Sound.

3. Initiate studies on fate processes in the marine environment to further knowledge on photolysis, adsorption-desorption, precipitation reactions, and volatilization.

7.5 Research Need V

Determine the unique aspects of Puget Sound relevant to particular pollutants.

Comment

There is a need to provide insight into certain inconsistencies of pollutant levels in Puget Sound. The most glaring of these inconsistencies is the fact that DDT is present in extremely high levels in Puget Sound sediments as compared to levels of DDE, its degradation product. Since these measurements run counter to those taken at various areas around the world, either DDT is still being discharged to the Sound, which is unlikely, or this persistence is due to some unique combination of circumstances peculiar to the Sound. Similar observations of possibly reduced microbial degradation rates in Puget Sound sediments have been suggested in this report for phthalate acid esters and PCBs with 2 or 3 substituted chlorines. In general, additional mass balance studies are also required to further define the fate of pollutants in Puget Sound.

Work Tasks

1. Assess the microbial degradation processes in sediments of Puget Sound and evaluate the possibility of effects on microbial activity.

2. Undertake mass balance studies of contaminants such as DDT and copper within a confined area of Puget Sound, to further define the parameters which are affecting the fate of these pollutants and to refine the input-output parameters for pollutants. This information would enable more detailed assessment of hazards associated with contaminants in Puget Sound.

7.6 Research Need VI

Define sources, amounts and availability of pollutant inputs.

Comment

Chemical pollutants may originate from point source discharges (e.g., industrial or municipal effluent outfalls or non-point sources such as strom-water, landfill leachates, or, atmospheric fall-out. It is particularly important that sources and amounts of inputs of the identified compounds of concern be defined to determine whether corrective measures can be taken. Futhermore, it is not known whether the particular discharges contain pollutants which are available or potentially available to biota. For example, it is uncertain whether the large quantities of copper and arsenic present in smelter slag discharged to the Sound are released to the environment.

Work Tasks

1. Characterize and quantify discharges to Puget Sound with regard to the identified contaminants of concern.
2. Undertake a survey existing industries in Puget Sound to determine the input of additional contaminants to Puget Sound, which analysts may not have attempted to determine.
3. Survey previous and current landfill sites to determine potential leachate sources.
4. Evaluate the biological availability of pollutants contained within each type of discharge.

Reference

Singmaster, J.A., III. 1975. Environmental behavior of hydrophobic pollutants in aqueous solutions. Ph.D. Thesis. University of California, Davis. 143 pp.

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