

NOAA Technical Memorandum NOS OMA 7

Chemical Pollution of the Hudson-Raritan Estuary

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December 1984



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Ronald J. Breteler,
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ABSTRACT. This report contains statements of issues and conclusions prepared for a workshop held in late 1981-1982 to assess the relative threats to human health and ecosystem well-being posed by toxic pollutants in the Hudson-Raritan Estuary. The workshop considered more than 50 toxic metals, petroleum hydrocarbons, and halogenated hydrocarbons. These were classified on the basis of their toxicity, bioavailability, and concentrations in the environment of the Hudson-Raritan Estuary. Separate assessments were made of the significance of pollutants to ecosystem well-being and to human health.

Materials were divided into three categories: contaminants that pose an immediate threat and require continued study (Class A), contaminants that are potentially significant threats, for which additional data must be collected and evaluated (Class B), and contaminants that do not require priority attention at this time (Class C). Of the substances considered, ten were identified as Class A contaminants with respect to ecosystem well-being, and eleven were identified as Class A contaminants with respect to human health. The report suggests that additional effort is required to evaluate the prevalence of constituent polycyclic aromatic hydrocarbons (PAH) and selected halogenated hydrocarbons in the Hudson-Raritan Estuary environment. The report also suggests that it may be possible, through the use of "carcinogenic potency factors," derived by the U.S. Environmental Protection Agency, to quantify, at least crudely, the increased lifetime risk of human cancer associated with ingesting seafood contaminated with these toxicants.

1. INTRODUCTION AND SUMMARY OF FINDINGS

Ronald J. Breteler

1.1 Background

After centuries of use as waterway, sewer, fishing ground, and dumping ground, the Hudson-Raritan Estuary is seriously contaminated with many types of pollutants. The present quality of the estuary's water is documented by Mytelka et al. (in press), and Mueller et al. (1982) discuss the quantities of pollutants entering the Hudson-Raritan Estuary from a variety of sources, including tributaries and municipal and industrial waste discharges. Numerous local sources have contaminated estuarine sediments and waters with a variety of pollutants such as toxic metals, polynuclear aromatic hydrocarbons (PAH), and polychlorinated biphenyls (PCB). Excessive nutrient and carbon loadings and pathogenic bacteria and viruses further degrade the condition of the estuary. The integrated effects of this contamination are

evidenced by several types of environmental degradation: diseased fishes, turbid and oily waters, noxious odors, pathogen contamination of bathing waters and shellfish beds, degraded benthic communities, restricted distribution of fishes, and fishes and shellfish tainted with petroleum hydrocarbons. Other manifestations of the contamination may not be visible, but could have severe consequences such as pollution-induced changes in estuarine food webs, accumulation of toxic materials in the flesh of food organisms, behavioral modifications of fishes caused by high pollutant concentrations and oxygen depletion, and the decline of economically important fish and shellfish stocks.

1.2 Scope and Methods

A two-part workshop sponsored by the Hudson-Raritan Estuary Project (HREP) of the National Oceanic and Atmospheric Administration (NOAA) was held on November 16 and 17, 1981, and January 20, 1982. The workshop brought together a team of 17 specialists (Appendix) in the fields of marine chemistry, geochemistry, toxicology, ecology, and human health and included several participants with extensive knowledge of the nature and volume of contaminant input to the Hudson-Raritan Estuary.

The workshop was intended to identify and rank the contaminants that occur in the portion of the lower Hudson-Raritan Estuary illustrated in Figure 1. The following guidelines, in order of descending importance, were proposed for evaluating the contaminants:

- o potential hazards to human health, either directly or through consumption of contaminated fish or shellfish;
- o potential hazards to fish and shellfish resources of commercial or recreational importance;
- o potential hazards to other organisms or biological communities inhabiting the estuary.

The workshop participants were divided into three panels, each focused on a specific class of contaminants: metals, petroleum hydrocarbons, and halogenated hydrocarbons. Each panel was composed of three or four specialists who provided information on toxic effects, geochemical behavior, pollutant concentrations in the estuary, and other relevant issues. Specific information relating to contaminant inputs and human health and ecological effects was provided by a number of workshop participants who contributed to the deliberations of all three panels.

Early in the workshop, the participants evaluated the information available on each contaminant in order to apply the ranking criteria. A consensus emerged that the data base was inadequate to allow a precise ranking of all contaminants but was sufficient to permit a general categorization of the materials. The following categories were proposed:

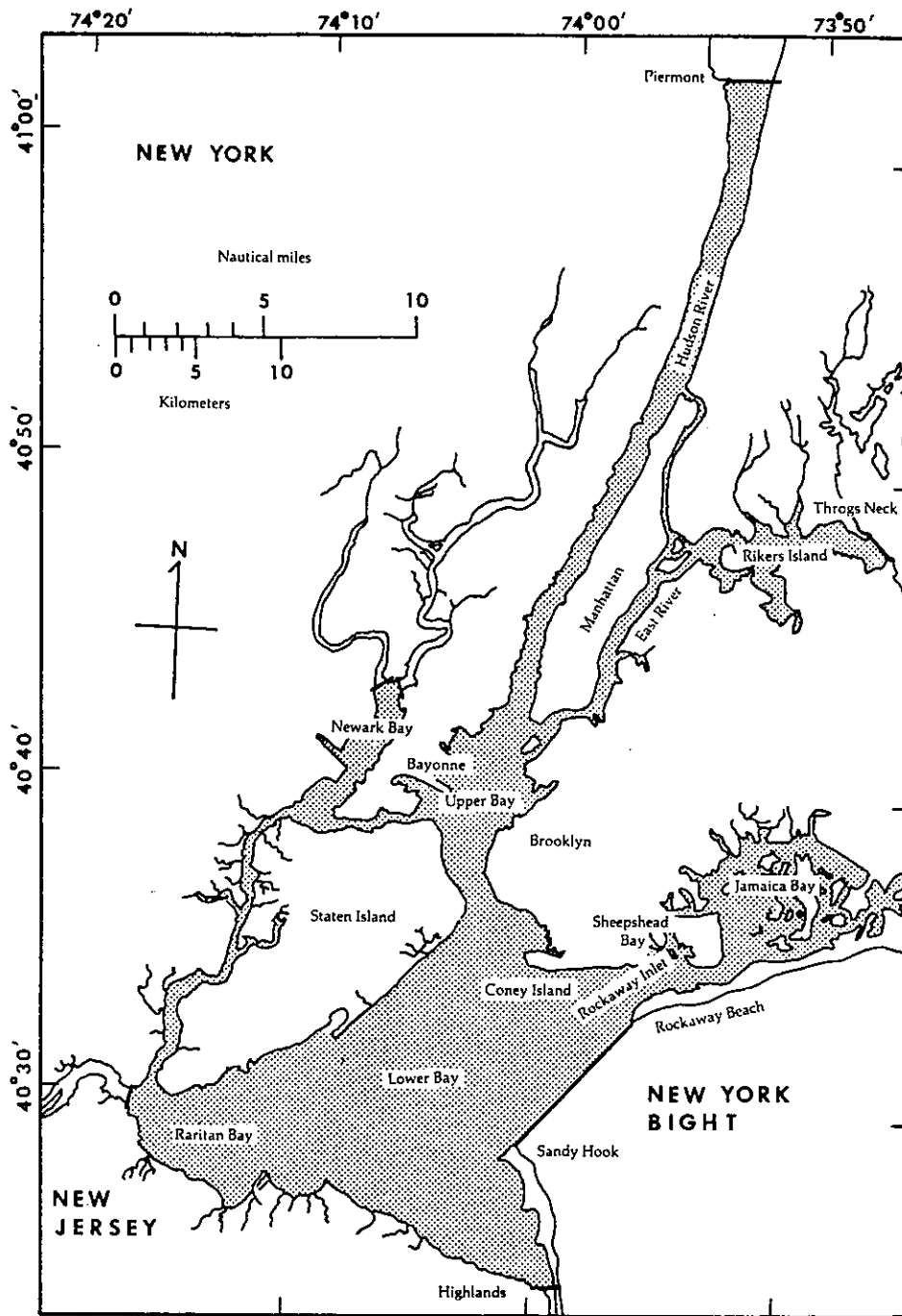


Figure 1. Geographical area of the Hudson-Raritan Estuary considered in this report

Class A: Contaminants that pose an immediate threat and require continued study.

Class B: Contaminants that are potentially significant threats, but for which additional data must be collected and evaluated.

Class C: Substances that do not require priority attention at present.

The participants agreed to evaluate each contaminant with regard to its potential threat to human health and to ecosystem well-being. Where substantive data were lacking, the panelists agreed to make subjective judgements (i.e., experts' best guesses) regarding the position of individual contaminants in the classification system, recognizing that as data become available, contaminants may have to be reassigned from one class to another. Contaminants were assigned to one of the classes above after evaluation of their toxicity to aquatic biota or to humans, their occurrence in the sediments and in waters of the estuary, and their bioavailability. Each panel settled upon its own method(s) for assigning a relative weighting value to each of these factors and used independent criteria for evaluating its scoring procedure. Despite this systematic approach, the inputs to the scoring process and the interpretation of results often were subjective: they represent the best professional opinion of the panel.

1.3 Summary of Findings

The conclusions of the three workshop panels are summarized in Table 1, with contaminants listed alphabetically within each class. The classification is based upon the probable severity of the impact of individual contaminants. Although the combined effects of contaminants may be greater than individual effects, no attempt was made to assess impacts of contaminant combinations. Existing information is inadequate to assess the potential significance of such combinations.

Relatively little information is available on the distribution and abundance of many of the toxic organic compounds considered in this report. It is likely that some of the substances are present in the estuary in higher concentrations than suspected. Many contaminants for which substantive data were not available were placed in Class C. More reliable concentration estimates may justify the categorization of some pollutants as more serious threats. The workshop recommended that broad-scan analyses for toxic but "nontraditional" organic compounds be undertaken on samples of major waste inputs, suspended particulates, bottom sediments, and biota from the estuary. The halogenated hydrocarbon subpanel further recommended limited monitoring, on a trial basis, of certain highly toxic insecticides characterized by inhibition of acetylcholinesterase in invertebrates.

Table 1. Classification of contaminants of the Hudson-Raritan Estuary with respect to ecosystem and human health concerns

Contaminant	Ecosystem concern	Human health concern
<u>Metals</u>		
Arsenic	C	B
Cadmium	B	A
Chromium	C	B
Copper	A	C
Lead	B	A
Mercury	A	A
Nickel	C	B
Selenium	C	C
Silver	B	C
Zinc	B	C
<u>Petroleum Hydrocarbons</u>		
Alkanes	C	C
Polycyclic aromatic hydrocarbons	A	A
Total hydrocarbons (oil and grease)	A	B
<u>Pesticides</u>		
Aldrin	C	C
α -BHC	C	B
Chlordane	A	A
Dieldrin	A	A
DDT and metabolites	A	A
Endosulfan	C	A
Endrin	C	C
Heptachlor	A	B
Heptachlor epoxide	B	B
Kepone	B	A
Lindane (γ -BHC)	C	C
Mirex	B	A
Trans-nonachlor	C	C
Toxaphene	A	A
2,4-D	C	C
2,4,5-T	C	C

Table 1. Continued

Contaminant	Ecosystem concern	Human health concern
<u>Halogenated Hydrocarbons</u>		
Brominated benzenes	C	C
Brominated diphenyl ethers	C	C
Chlorinated anilines	C	C
Chlorinated benzenes	C	C
Chlorinated dibenzodioxins	B	B
Chlorinated dibenzofurans	B	B
Chlorinated diphenyl ethers	C	C
Chlorinated ethanes	C	C
Chlorinated ethylenes	C	C
Chlorinated methanes	C	C
Chlorinated paraffins	C	C
Chlorinated phenols (other)	C	C
Chlorinated styrenes	C	C
Chloronitrobenzenes	B	B
Dechloranes	C	C
1,2 dibromo-3-chloropropane	C	C
Dichlorobenzidine	C	C
Halogenated alkyl esters	C	C
Hexabromobenzene	C	C
Hexachlorobenzene	B	B
Hexachlorobutadiene	C	C
Hexachlorocyclopentadiene	C	C
Pentabromotoluene	C	C
Pentachlorophenol	C	C
Polybrominated biphenyls	C	C
Polychlorinated biphenyls	A	A
Polychlorinated naphthalenes	C	C
Polychlorinated terphenyls	C	C

2. CONTAMINANT INPUTS TO THE HUDSON-RARITAN ESTUARY

J.A. Mueller and C.E. Werme

2.1 Introduction

The Hudson-Raritan Estuary receives wastes from the densely populated, highly industrial New York-New Jersey metropolitan area. Direct sources of contaminants to the estuary include:

- municipal and industrial wastewater discharges;
- tributaries including the Hudson River, the Raritan River Basin, the Passaic River Basin, the Hackensack River, the Elizabeth River, and the Rahway River Basin;
- urban runoff;
- accidental spills;
- atmospheric fallout;
- landfill leachate.

Data on the loadings from these sources have been obtained from numerous federal, state, county, and municipal sources and have been documented by Mueller et al. (1982). Their findings are briefly summarized below and in Table 2. A large data base was available for some contaminants, including the heavy metals. For other contaminants, such as the toxic organics, data were scarce, and many estimates are based on nationwide data.

In general, wastewater discharges are the largest source of contaminants in the estuary. Tributaries, urban runoff, and accidental spills also are important, particularly for selected classes of pollutants. Atmospheric fallout and leachate are relatively minor contributions to the overall loadings of the estuary.

2.2 Sources of Contaminants

2.2.1. Wastewater Discharges

Wastewater discharges are the greatest source of contaminants to the estuary. They contribute 40-90 percent of the heavy metals loads, half the oil and grease, and about 40 percent of the PCBs. Upper New York Bay and the East River receive the greatest loads of heavy metals from these discharges.

Table 2. Hudson-Raritan total mass loads a

Constituent	Total mass load (metric tons/day)	Percent contributed by each source					Landfall leachate
		Wastewater	Tributaries	Urban runoff	Atmospheric	Accidental spills	
Oil and grease	350	48	12	34	- b	6 c	0.4
Di-n-butylphthalate	56-61	82-89	-	10-11	0.35-8.2	-	-
Diethylphthalate	20	80	-	20	-	-	-
Anthracene	29	-	-	100	-	-	-
Phenanthrene	20.5	12	-	88	-	-	-
Pyrene	37	-	-	100	-	-	-
Tetrachloroethylene	530	99.8	-	-	-	-	0.2
Toluene	280	88	-	3.5	-	3.3	5.3
Trichloroethylene	300	95	-	-	-	3.6	1.1
Aldrin	0-1.0	-	* d	-	-	100-97	0-3
Lindane (γ-BHC)	0.46-4.3	6.0-57	*	-	43-94	-	-
Chlordane	0.13-0.33	30-77	*	-	23-61	-	0-9
DDT	1.0-1.1	-	*	97-91 e	2.9-9	-	-
Heptachlor	0.2-4	-	*	-	100	-	-
PCB	11-14	34-44	*	8.9-6.8 e	1.9-14	-	0-4.1
Toxaphene	0.1-1.3	-	41-45	-	-	100-76	0-24
Benzene	170	96	-	0.6	-	-	3.6
1,1,1-trichloroethane	370	99.9	-	-	-	-	0.1
1,1,2,2-tetrachloroethane	6.3	-	-	-	-	-	100
Chloroform	140	92	-	4.4	-	-	3.9
1,2-dichlorobenzene	49	99.9	-	-	-	-	0.1
1,1-dichloroethylene	15	99.9	-	-	-	-	0.1
1,2-transdichloroethylene	21	99.9	-	-	-	-	0.1
Ethylbenzene	66	96	-	-	-	-	3.8
Fluoranthene	50	-	-	100	-	-	-
Methylene chloride	930	99	-	0.6	-	-	0.4

Table 2. Continued

Constituent	Total mass load (metric tons/day)	Percent contributed by each source						Landfall leachate
		Wastewater	Tributaries	Urban runoff	Atmospheric	Accidental spills		
Dichlorobromomethane	3.2-3.3	97-99	-	-	-	-	1-3	
Trichlorofluoromethane	5.2	-	-	100	-	-	-	
Dichlorodifluoromethane	27	-	-	-	-	-	100	
Naphthalene	35	49	-	-	-	51	-	
Pentachlorophenol	26	100	-	-	-	-	-	
Phenol	70	80	-	11	-	-	9	
Bis(2-ethylhexyl)phthalate	350-355	76-77	-	23	0.1-1.4	-	-	
Butylbenzylphthalate	41	73	-	27	-	-	-	
Antimony	1,100	100	-	-	-	-	-	
Arsenic	190-210	47-51	49-51	-	0.1-1.4	-	0.2-1.2	
Beryllium	41-43	91-96	3.7-8.9	-	-	-	0.23-0.25	
Cadmium	130-190	38-56	12-39	22-30	1.6-1.1	-	0.5-0.7	
Chromium	2020-2040	50	37	12	0.5	-	0.2	
Copper	3,400	52	28	20	-	-	0.19	
Cyanide	990	99.8	-	-	-	-	0.20	
Lead	2,800	39	29	29	3.5	-	0.26	
Mercury	62-92	60-89	8.9-37	2.6-3.2	-	-	0.2-0.3	
Nickel	1,700	55	20	23	1.2	-	0.3	
Selenium	120-160	65-49	34-51	-	-	-	0.3-0.4	
Silver	65-78	80-95	4.8-19	-	-	-	0.2-1.2	
Thallium	350	100	-	-	-	-	-	
Zinc	9,400	60	19	19	2.1	-	0.3	

a Data from Mueller et al. (1982).

b Dashes indicate no data available, except for wastewater, where constituents detected less than 90 percent of the time were excluded.

c Petroleum hydrocarbons.

d Asterisks indicate negligible or zero loads were estimated from sediment data; water column data not available.

e New York data unavailable; estimates based on Los Angeles information.

In some cases, significant point sources of contaminants can be identified. For example, as much as 91 percent of the total mercury load to the estuary has been attributed to a municipal sewage treatment system that discharges into Upper Bay. This system receives the bulk of its mercury from a single industrial source. High zinc concentrations in the effluent from another municipal plant contribute 29 percent of the wastewater zinc load to Raritan Bay. Many municipal sewage treatment plants are being upgraded and, depending on degree of pretreatment, should discharge fewer contaminants in the future.

2.2.2 Tributaries

The Hudson, Raritan, and Passaic Rivers contribute 98 percent of the gauged water flow and most of the tributary contaminant load to the estuary. PCB concentrations are particularly high in the Hudson River because of upstream contamination. Heavy metal loads also are highest from the Hudson River as a result of its relatively high flow (87 percent of the total). Lead and cadmium loads are high from the rivers in New Jersey. In general, contaminant loads are positively correlated with water flow and are lowest in the summer.

2.2.3 Urban Runoff

Urban runoff from nonpoint sources contributes as much as 10 to 30 percent of the total load of heavy metals (for which a large data base is available) to the estuary. Metropolitan New York, which encompasses about one-half of the total area considered by Mueller et al., contributes more than 90 percent of the runoff load of oil and grease, cadmium, copper, lead, nickel, and zinc as a result of flow through storm sewers and combined storm-sanitary sewers. Data on concentrations of DDT in runoff are not available for the New York area, but estimates based on Los Angeles data indicate that despite the ban on DDT use, runoff may be a major source of DDT to the estuary.

2.2.4 Accidental Spills

The New York Bay region of the estuary receives at least 90 percent of the volume of accidental spills, with residual fuel oil and diesel oil being the primary constituents of the spills. For some contaminants, spills are the major source to the estuary.

2.2.5 Atmospheric Fallout

Data on atmospheric loads are sparse, and fallout is not considered an important source of contaminants to the estuary. The fallout that does occur comes chiefly from urban areas. Urban surface area is far greater than rural surface area in the lands surrounding the estuary, and urban flux (load per unit area) is frequently two to five times higher than flux from rural areas. Concentrations of atmospheric metals decrease significantly from the densely populated mid- and lower-Manhattan areas to the estuarine regions of the New Jersey coast and out into the New York Bight.

2.2.6 Landfill Leachate

The quantity of landfill leachate produced and the amount of leachate that ultimately reaches estuarine waters are unknown; consequently, the figures in Table 2 are best-guess estimates. Among the metals, zinc has the highest loading rate through leachate, but its load to the estuary through leachate is insignificant compared to the load contributed by other sources. Toluene and dichlorodifluoromethane are the dominant toxic organics in leachates.

3. METALS SUBPANEL REPORT

R.J. Breteler, J.W. Rachlin, D.W. Engel

3.1 Introduction

Throughout the past century, the Hudson-Raritan Estuary has received large amounts of heavy metals from sources that include tributaries, waste water outfalls, and urban runoff. Waste water discharges contribute 40-60 percent of the loads of heavy metals for which good data bases are available (i.e., for cadmium, chromium, copper, lead, nickel, and zinc). Approximately 20-40 percent of heavy metal loads is from tributaries, and 10-39 percent is input through urban runoff. Atmospheric input contributes less than 5 percent, and landfill leachates add less than 1 percent (Mueller et al., 1982).

Trace metals are of ecological and toxicological interest because of their roles as micronutrients (iron, zinc, copper, manganese, cobalt, molybdenum) and as toxicants (copper, mercury, silver, chromium, cadmium, zinc, nickel, lead). Some metals, such as copper and zinc, can act in either a stimulatory or inhibitory mode depending on their availability to organisms. The potential effects of trace metals on aquatic organisms and on human health have been recognized as a significant problem because of continued anthropogenic inputs into aquatic systems. The question of how much metal contamination can occur before damaging an ecosystem is pertinent, especially since existing environmental levels of some trace metals, such as copper, can be toxic to selected organisms (Anderson and Morel, 1978; Sunda and Ferguson, 1983). In such instances, increases above natural concentrations may have deleterious effects on estuarine food chains.

In the Hudson-Raritan Estuary, heavy metals are partitioned among three reservoirs--water, sediment, and biota. Although the relevance of the biotic reservoir to human health is apparent, the quantity of metals contained in this reservoir is small compared to that found in the water, which in turn is much smaller than that contained in the sediment reservoir. In general, there exists a flux of metals across the sediment-water interface, whose direction is dependent on ambient conditions. Thus, sediments may concentrate metals from the water or release metals to the water (Meyerson et al., 1981), but the predominant tendency is attraction of metals to fine particulates and subsequent rapid accumulation in sediments (Olsen et al., 1978).

In the aquatic environment trace metals exist in a variety of chemical forms, including free ions, inorganic and organic complexes, and metals adsorbed on or incorporated into particulate matter (Stumm and Brauner, 1975). The chemical forms of a metal in aqueous media are dependent upon the chemical properties of the individual metals and the chemical composition of the natural waters. Recent research has demon-

strated that metal toxicity and bioavailability are highly dependent on chemical speciation of the metal (Anderson and Morel, 1978; Sunda and Guillard, 1976; Sunda et al., 1978; Anderson et al., 1978; Breteler et al., 1981). These investigations have shown that bioavailability and biological response to dissolved trace metals are a function of the concentration of free metal ions, which in turn is determined by the total dissolved concentration and pH and by the extent of metal complexation to both organic and inorganic ligands. In the Hudson-Raritan Estuary, therefore, measurements of dissolved and particulate metal levels and enumerations of the chemical characteristics of the system contribute greatly to the ability to predict or forecast the relative health of the system. Since such information exists neither for most natural environments nor for the area of concern to this report, the metals subpanel used existing data to provide first-order approximations of conditions as they currently exist. This reflects the state of the art of heavy metal monitoring in natural systems.

The metals considered by the subpanel include those that are known to be toxic to man and/or to aquatic biota and for which data relating to the Hudson-Raritan Estuary were available to the panel members. These metals are lead, cadmium, copper, mercury, zinc, chromium, silver, arsenic, selenium, and nickel.

3.2 Classification Methods

Two independent approaches were used to assess and classify the implications of the presence of heavy metals in the Hudson-Raritan Estuary: "the minimum tolerance approach" and "the matrix approach." While the two methods have elements in common (i.e., the evaluation of ambient metal concentrations, bioaccumulation potential, and toxic effects), they differ primarily in the manner in which estimates of toxicity are derived and in the degree of subjectivity implied in characterizing the metals, in terms of seriousness of potential effects. The distinction in methods reflects the difficulty of objectively classifying metals. Both approaches are explained here fully. Where discrepancies exist in the results of these approaches, the subpanel deliberated to determine final classifications.

3.2.1 Minimum Tolerance Approach

Ambient Metal Concentrations. The primary data base for water column metal values was derived from the reports of the Interstate Sanitation Commission (ISC) (Interstate Sanitation Commission, 1979; Mytelka et al., in press). Sediment data were derived from the published literature (Greig and McGrath, 1977; Bryan, in press); and from ongoing research of geochemists active in the region whose work was known to the members of the metals subpanel (J.E. Nadeau, personal communication). These data are summarized in Tables 3, 4, 5, and 6.

Table 3 presents the high and low water column values, converted to moles/liter, for metals evaluated by the ISC during the 1978-1979 sampling season. Tables 4 and 5 present ISC metal values, converted to moles/liter, for the 1979-1980 sampling season. The measure of moles

Table 3. Water column metal concentrations (total) in the HREP study area, 1978/1979, in moles per liter ^a

Metal	Lower Hudson River	Western Long Island Sound	East River	Harlem River	Upper Bay	Lower Bay
	Cu-low	6.3x10 ⁻⁸	<1.8x10 ⁻⁸	6.3x10 ⁻⁸	2.1x10 ⁻⁷	4.7x10 ⁻⁸
Cu-high	6.6x10 ⁻⁷	4.2x10 ⁻⁷	1.2x10 ⁻⁶	1.2x10 ⁻⁶	3.4x10 ⁻⁶	1.4x10 ⁻⁶
Zn-low	<1.5x10 ⁻⁸	1.2x10 ⁻⁷	1.5x10 ⁻⁷	4.6x10 ⁻⁷	3.7x10 ⁻⁷	3.7x10 ⁻⁷
Zn-high	8.1x10 ⁻⁷	1.5x10 ⁻⁶	2.5x10 ⁻⁶	9.6x10 ⁻⁷	1.5x10 ⁻⁶	2.9x10 ⁻⁶
Pb-low	<2.4x10 ⁻⁸	<2.4x10 ⁻⁸	<2.4x10 ⁻⁸	4.8x10 ⁻⁸	<2.4x10 ⁻⁸	<2.4x10 ⁻⁸
Pb-high	7.2x10 ⁻⁸	1.9x10 ⁻⁷	9.7x10 ⁻⁸	7.2x10 ⁻⁸	7.2x10 ⁻⁸	1.9x10 ⁻⁷
Ni-low	<8.5x10 ⁻⁸	<8.5x10 ⁻⁸	<8.5x10 ⁻⁸	<8.5x10 ⁻⁸	<8.5x10 ⁻⁸	<8.5x10 ⁻⁸
Ni-high	6.0x10 ⁻⁷	6.8x10 ⁻⁷	6.8x10 ⁻⁷	3.4x10 ⁻⁷	7.7x10 ⁻⁷	7.7x10 ⁻⁷
Cd-low	<4.5x10 ⁻⁹	<4.5x10 ⁻⁹	<4.5x10 ⁻⁹	<4.5x10 ⁻⁹	<4.5x10 ⁻⁹	<4.5x10 ⁻⁹
Cd-high	1.8x10 ⁻⁸	4.0x10 ⁻⁸	2.2x10 ⁻⁸	3.1x10 ⁻⁸	4.5x10 ⁻⁸	1.0x10 ⁻⁷
Hg-low	5.0x10 ⁻¹⁰	<5.0x10 ⁻¹⁰	<5.0x10 ⁻¹⁰	1.5x10 ⁻⁹	<5.0x10 ⁻¹⁰	<5.0x10 ⁻¹⁰
Hg-high	1.5x10 ⁻⁹	7.0x10 ⁻⁹	2.0x10 ⁻⁹	1.5x10 ⁻⁹	1.5x10 ⁻⁹	2.0x10 ⁻⁹
As-low	<2.7x10 ⁻⁸	<2.7x10 ⁻⁸	<2.7x10 ⁻⁸	<2.7x10 ⁻⁸	<2.7x10 ⁻⁸	<2.7x10 ⁻⁸
As-high	4.0x10 ⁻⁸	2.7x10 ⁻⁸	5.3x10 ⁻⁸	2.7x10 ⁻⁸	1.5x10 ⁻⁷	<2.7x10 ⁻⁸
Cr-low	<1.9x10 ⁻⁸	<1.9x10 ⁻⁸	1.9x10 ⁻⁸	7.7x10 ⁻⁸	<1.9x10 ⁻⁸	1.9x10 ⁻⁸
Cr-high	1.7x10 ⁻⁷	4.8x10 ⁻⁷	3.5x10 ⁻⁷	1.7x10 ⁻⁷	1.5x10 ⁻⁷	8.7x10 ⁻⁷
Ag-low	<9.3x10 ⁻⁹	<9.3x10 ⁻⁹	<9.3x10 ⁻⁹	9.3x10 ⁻⁹	9.3x10 ⁻⁹	9.3x10 ⁻⁹
Ag-high	9.3x10 ⁻⁹	1.4x10 ⁻⁷	9.3x10 ⁻⁹	9.3x10 ⁻⁹	9.3x10 ⁻⁹	5.6x10 ⁻⁸

^a Interstate Sanitation Commission (1979).

Table 4. Water column metal concentrations total (tot.) and soluble (sol.) in the HREP study area in moles per liter ^a

Metal	Western				East River	Harlem River	Newark Bay	Arthur and Kill Kill Van Kull
	Lower Hudson River	Long Island Sound						
Cu-tot	6.3x10 ⁻⁸	1.9x10 ⁻⁷	5.4x10 ⁻⁷	9.4x10 ⁻⁸	6.8x10 ⁻⁷	9.3x10 ⁻⁷		
Cu-sol	1.6x10 ⁻⁸	9.4x10 ⁻⁸	7.9x10 ⁻⁸	<1.6x10 ⁻⁸	1.4x10 ⁻⁷	3.3x10 ⁻⁷		
Zn-tot	3.4x10 ⁻⁷	6.1x10 ⁻⁷	1.4x10 ⁻⁶	3.2x10 ⁻⁷	1.2x10 ⁻⁶	1.2x10 ⁻⁶		
Zn-tot	1.8x10 ⁻⁷	3.5x10 ⁻⁷	5.7x10 ⁻⁷	2.9x10 ⁻⁷	1.1x10 ⁻⁶	1.1x10 ⁻⁶		
Pb-tot	4.8x10 ⁻⁸	4.8x10 ⁻⁸	9.7x10 ⁻⁸	4.8x10 ⁻⁸	9.7x10 ⁻⁸	7.2x10 ⁻⁸		
Pb-sol	2.4x10 ⁻⁸	<2.4x10 ⁻⁸	<2.4x10 ⁻⁸	2.4x10 ⁻⁸	2.4x10 ⁻⁸	2.4x10 ⁻⁸		
Ni-tot	1.5x10 ⁻⁷	1.2x10 ⁻⁷	3.4x10 ⁻⁷	1.0x10 ⁻⁷	3.4x10 ⁻⁷	2.6x10 ⁻⁷		
Ni-sol	<8.5x10 ⁻⁸	<8.5x10 ⁻⁸	8.5x10 ⁻⁸	<8.5x10 ⁻⁸	2.2x10 ⁻⁷	1.7x10 ⁻⁷		
Cd-tot	<4.5x10 ⁻⁹	4.5x10 ⁻⁹	4.5x10 ⁻⁸	<4.5x10 ⁻⁹	8.9x10 ⁻⁹	8.9x10 ⁻⁹		
Cd-sol	<4.5x10 ⁻⁹	<4.5x10 ⁻⁹	6.2x10 ⁻⁹	<4.5x10 ⁻⁹	<4.5x10 ⁻⁹	<4.5x10 ⁻⁹		
Hg-tot	1.0x10 ⁻⁹	1.5x10 ⁻⁹	5.0x10 ⁻⁷	2.0x10 ⁻⁹	3.0x10 ⁻⁹	2.0x10 ⁻⁹		
Hg-sol								

-----No reported values-----

^a Median values only (Mytelka et al., in press).

Table 5. Water column metal concentrations total (tot.) and soluble (sol.) in the HREP study area, 1979/1980, in moles per liter ^a

Metal	Upper Bay	Raritan and Sandy Hook Bays	Lower Bay (east)	Lower Bay (west)	Jamaica Bay
Cu-tot	8.2x10 ⁻⁷	5.5x10 ⁻⁷	9.6x10 ⁻⁷	6.1x10 ⁻⁷	5.2x10 ⁻⁷
Cu-sol	3.3x10 ⁻⁷	2.0x10 ⁻⁷	4.9x10 ⁻⁷	2.2x10 ⁻⁷	2.7x10 ⁻⁷
Zn-tot	9.0x10 ⁻⁷	9.2x10 ⁻⁷	1.0x10 ⁻⁶	7.2x10 ⁻⁷	8.3x10 ⁻⁷
Zn-sol	7.0x10 ⁻⁷	6.4x10 ⁻⁷	8.6x10 ⁻⁷	6.0x10 ⁻⁷	5.2x10 ⁻⁷
Pb-tot	4.8x10 ⁻⁸	7.2x10 ⁻⁸	7.2x10 ⁻⁸	7.2x10 ⁻⁸	7.2x10 ⁻⁸
Pb-sol	<2.4x10 ⁻⁸	2.4x10 ⁻⁸	2.4x10 ⁻⁸	2.4x10 ⁻⁸	2.4x10 ⁻⁸
Ni-tot	1.4x10 ⁻⁷	1.9x10 ⁻⁷	1.4x10 ⁻⁷	1.4x10 ⁻⁷	1.4x10 ⁻⁷
Ni-sol	8.5x10 ⁻⁸	1.4x10 ⁻⁷	8.5x10 ⁻⁸	8.5x10 ⁻⁸	1.2x10 ⁻⁷
Cd-tot	<4.5x10 ⁻⁹	<4.5x10 ⁻⁹	<4.5x10 ⁻⁹	5.3x10 ⁻⁹	<4.5x10 ⁻⁹
Cd-sol	<4.5x10 ⁻⁹	<4.5x10 ⁻⁹	<4.5x10 ⁻⁹	<4.5x10 ⁻⁹	<4.5x10 ⁻⁹
Hg-tot	1.0x10 ⁻⁹	1.5x10 ⁻⁹	1.5x10 ⁻⁹	1.0x10 ⁻⁹	1.5x10 ⁻⁹
Hg-sol					

-----No reported values-----

^a Median values only (Mytelka et al., in press).

Table 6. Average sediment metal concentration from the HREP study area and from a non-HREP area, and calculated bioavailability of metals to aquatic organisms

Metal	HREP area a		Non-HREP area b		Calculated bioavailability b (see Table 12)
	mg/kg	moles/kg	mg/kg	moles/kg	
Silver	---	No reported values---	16.0	1.5×10^{-4}	14.9
Arsenic	---	No reported values---	24.0	3.2×10^{-4}	1.0
Cadmium	5.0	4.5×10^{-5}	7.7	6.9×10^{-5}	3.2
Chromium	180.0	3.5×10^{-3}	380	7.3×10^{-3}	0.04
Copper	500.0	7.9×10^{-3}	550.0	8.7×10^{-3}	0.9
Mercury	3.5	1.7×10^{-5}	3.5	1.7×10^{-5}	1.2
Nickel	40.0	6.8×10^{-4}	102.0	1.7×10^{-3}	0.16
Lead	300.0	1.5×10^{-3}	449.0	2.2×10^{-3}	0.25
Selenium	---	No reported values---	---	---	---
Zinc	500.0	7.7×10^{-3}	1853.0	28.4×10^{-3}	2.5

a Greig and McGrath (1977); H.G. Multer and J.E. Nadeau (unpublished data).

b Bryan (in press).

per liter, rather than parts per million (ppm), was used because it reflects atomic weights of individual metals and therefore allows better comparison of the acute toxicity values of these metals. Tables 4 and 5 present data as both total and soluble values and provide median values in each case. The median values were considered conservative estimates of water column metal burdens in the Hudson-Raritan Estuary and were selected for use in later steps of this analysis.

Sediment data for the study area are presented in Table 6. No sediment measurements of silver and arsenic were available from the Hudson-Raritan Estuary. Consequently, it was proposed that values presented by Bryan (Bryan, in press) from southwest England be used as estimates of these concentrations. Bryan's data are presented in the column labeled "Non-HREP area" of Table 6. An examination of this table shows that the values of metals common to both the Hudson-Raritan Estuary and southwest England are comparable. The subpanel therefore felt that the silver and arsenic values from Bryan's data base were appropriate first approximations of the concentrations of these metals in the Hudson-Raritan Estuary.

Metal Toxicity. In order to evaluate the potential toxicity to biota of existing metal loadings in the study area and in order to categorize the metals into three groups (Class A--major perceived threat, Class B--potential threat, and Class C--no threat at present), the subpanel examined metal toxicity data for those organisms or life stages considered to be most sensitive to metal poisoning (i.e., planktonic eggs and larvae and phytoplankton). The data representing concentrations reported to cause mortality or abnormal development in embryos and larvae of representative taxa are presented in Table 7. The average of these values, for each metal of concern, was used as an index of the metal's toxic potential to sensitive stages in the life histories of animal members of the Hudson-Raritan Estuary ecosystem. Data on the toxic potential of metals to the phytoplankton community are presented in Table 8. Averages are provided of the lowest values for metals reported in the literature to have produced measurable inhibitions of photosynthesis, reductions in carbon fixation, or reductions in growth.

To provide conservative estimates of the overall toxicity of metals to biota of the Hudson-Raritan Estuary ecosystem, values for each metal in Tables 7 and 8 were averaged; the results are presented in Table 9. On the basis of the molar values derived in Table 9, the following toxic hierarchy of metals of concern to the estuarine ecosystem emerged:

Hg>Cu>Ag>Pb>Zn>Cd>As>Ni>Cr>Se

Implications for the Ecosystem. The relative threat posed to the Hudson-Raritan Estuary ecosystems by the metals listed above was evaluated by comparing the toxicity levels reported in moles/liter in Table 9 with the water column concentration values presented in Tables 3, 4, and 5. If the toxic level for a given metal was equaled or exceeded by the water column concentration at any location within the study area, the metal was nominated for placement in Class A. If the toxic level was not equaled, but was of the same order of magnitude as the water

column concentration, the metal was nominated for placement in Class B. If water column concentrations of the metal were found to be at least one order of magnitude lower than the average toxic level, the metal was suggested for placement in Class C.

An examination of the water column concentration data and the toxicity data reveals that copper is the one metal for which the toxic level was consistently equal to or exceeded by water column concentrations in the study area. It therefore was proposed as a Class A material. Mercury was found in concentrations in excess of its toxic level on only one occasion (Table 4, East River), and this data point was labeled questionable in the ISC data base. In all other areas, water column values for total mercury are significantly below the toxic level. Since only total mercury levels were measured rather than levels of the more toxic methylated form, it is not unreasonable to propose mercury as a Class B metal. Zinc and silver were the only other metals whose water column concentrations were of the same order of magnitude as the toxic levels; therefore, they also were proposed for Class B. Water column concentrations of all the other metals (cadmium, lead, arsenic, nickel, chromium) were found to be consistently lower, by at least one order of magnitude, than their toxic levels. These metals were therefore suggested for Class C. Selenium also was placed in Class C, in the absence of any water column data, because its toxicity level is so low that it is not considered a threat to aquatic life in the concentrations anticipated in the estuary.

The determinations above are based solely on water column data. A second analysis was undertaken to factor sediment loadings into the ranking process. The subpanel used sediment metals data presented in Table 6, metals toxicity data indicated in Table 9, and information on average bioavailability for typical benthic organisms from Bryan (in press). Bryan's bioavailability factors represent average values derived from animal/sediment metal ratios for two bivalves and one polychaete (see Table 13 for details). The following index was calculated for each metal to quantify the relationships between metal concentrations in benthic organisms and sediments, and the mobility and toxicity of metals:

$$\text{Index} = \frac{\text{SC} \times \text{BF}}{1000 \text{ ATL}},$$

where:

SC = sediment concentration (moles/kg),
BF = bioaccumulation factor,
ATL = average toxic levels (moles/l).

Results are presented in Table 10. On the basis of the index results, it is possible to order the metals as follows:

Cu>Ag>Zn>Hg>Pb>As>Cd>Ni>Cr

Table 7. Level of toxic effect of metals to larval stages of aquatic invertebrates ^a

Metal	48h EC 50 µg/l <u>Crassostrea</u> <u>gigas</u> embryos	48h EC 50 µg/l <u>Mytilus</u> <u>edulis</u> embryos	96h LC 50 µg/l <u>Cancer</u> <u>magister</u> zoa	48h LC 50 µg/l <u>Crassostrea</u> <u>virginica</u> average	µg/l average	Moles/l average
Hg	6.7	5.8	8.2	5.6	6.6	3.3x10 ⁻⁸
Ag	22	14	55	5.8	22	2.2x10 ⁻⁷
Cu	5.3	5.8	49	103	41	6.4x10 ⁻⁷
Cd	611	1200	247	3800	1465	13.0x10 ⁻⁶
Pb	755	476	575	NRV ^b	603	2.9x10 ⁻⁶
Zn	119	175	456	310	265	4.1x10 ⁻⁶
As	326	>3000	232	NRV	1186	15.8x10 ⁻⁶
Ni	349	891	4360	1180	1695	28.9x10 ⁻⁶
Cr	>4538	4469	3440	NRV	4149	79.8x10 ⁻⁶
Se	>10000	>10000	>10000	NRV	>10000	>126.7x10 ⁻⁶

^a Data from Saila and Segar (1979) and Martin et al. (1981).

^b NRV: no reported value.

Table 8. Average of lowest metal values producing measurable effects in phytoplankton: inhibition of photosynthesis, reduction of carbon fixation, or growth reduction ^a

Metal	µg/l	Moles/l
Mercury	1.0	5.0x10 ⁻⁹
Silver	83.3	7.7x10 ⁻⁷
Copper	2.8	4.4x10 ⁻⁸
Cadmium	1566.6	13.9x10 ⁻⁶
Lead	313.3	1.5x10 ⁻⁶
Zinc	943.3	14.4x10 ⁻⁶
Arsenic	-----No reported values-----	
Nickel	1000	17.0x10 ⁻⁶
Chromium	1900	36.5x10 ⁻⁶
Selenium	-----No reported values-----	

^a Data from Davis (1978), Leland et al. (1979), and Rai et al. (1981).

Table 9. Average toxic levels of metals calculated from data of Tables 7 and 8

Metal	$\mu\text{g/l}$	Moles/l
Mercury	3.8	1.9×10^{-8}
Silver	53.6	5.0×10^{-7}
Copper	21.8	3.4×10^{-7}
Cadmium	1515	13.5×10^{-6}
Lead	458	2.2×10^{-6}
Zinc	604	9.2×10^{-6}
Arsenic	1186	15.8×10^{-6}
Nickel	1347	23.0×10^{-6}
Chromium	3024	58.2×10^{-6}
Selenium	>10000	$>126.7 \times 10^{-6}$

Table 10. Indexed value for sediment metals calculated from data of Tables 6 and 9

Metal	Indexed value ^a
Silver	4.5
Arsenic	0.02
Cadmium	0.01
Chromium	0.002
Copper	21
Mercury	1.1
Nickel	0.005
Lead	0.17
Zinc	2.1

^a All sediment values except silver and arsenic are taken from Hudson-Raritan Estuary data.

The data in Table 10 are consistent with the evaluation of metals based on water column data alone. Copper, with an index value of 20.9, remains a candidate for placement in Class A; silver and zinc, with respective index values of 4.5 and 2.1, may be placed in Class B along with mercury, which has an index value of 1.1. The remaining metals (lead, arsenic, cadmium, nickel, and chromium) all have index values below 1.0 and may be grouped into Class C.

Implications to Humans. Existing data on human health concerns (Mytelka et al., in press; Kazantzis and Lilly, 1979; Waldron, 1980; Lucier and Hook, 1981) and on the potential for dietary accumulation of metals led the panel to conclude that cadmium, lead, and mercury be proposed for Class A. While human absorption of arsenic, chromium, nickel, silver, copper, selenium, and zinc from aquatic food sources has not been firmly documented (Mytelka et al., in press; Kazantzis and Lilly, 1979; Waldron, 1980; Lucier and Hook, 1981), the potential for toxicity to humans and carcinogenicity suggests that arsenic, chromium, and nickel be placed in Class B and that silver, copper, selenium, and zinc be placed in Class C.

3.2.2 Matrix Approach

A matrix method to categorize metals was developed by one of the panel members and subsequently was adopted by the metals subpanel as an alternate approach. The matrix considered five criteria:

1. toxicity of metals to humans;
2. acute toxicity of metals to marine organisms;
3. bioaccumulation potential of sediment-bound metals by marine benthic invertebrates;
4. ambient concentrations of metals in the sediments of the Hudson-Raritan Estuary, as compared to those in clean estuaries;
5. ambient concentrations of metals in the water column of the Hudson-Raritan Estuary, as compared to those in clean estuaries.

Other considerations, such as uptake dynamics of soluble metals by planktonic organisms and the potential for subsequent biological transfer along marine trophic levels, were recognized as being of importance. However, the general difficulty of obtaining quantitative data for these considerations precluded their use.

Toxicity to Marine Biota. The toxicity of heavy metals to marine invertebrates and phytoplankton has been studied extensively during the past decades. Generally, toxicity data are reported as LC₅₀ values for 48- or 96-hr exposures. The acute toxicity of heavy metals depends largely upon the experimental organisms used, the length of exposure, and the experimental conditions (e.g., salinity, temperature, dissolved oxygen content, and pH). To determine the relative toxicity of heavy metals, comparisons of short-term toxicity data are most meaningful if the data are obtained under comparable conditions. Although the majority of toxicity studies consider only a few metals, some studies are available that permit an overall comparison of relative toxicity of metals. Martin

et al. (1981) and Calabrese et al. (1973) determined the 48-hr and 96-hr LC50 values for all metals considered in this report. These authors used bivalve embryos and crab larvae, the most sensitive life forms of these organisms, as test animals. The results of these experiments are summarized in Table 11. The following ranking of metals toxicity emerged from these results:

Hg>Ag>Cu>Pb ≈ Zn ≈ Cd>Ni>As>Cr

Hollibaugh et al. (1980) considered the same group of metals with the exception of silver and observed the following order of metal toxicities to phytoplankton, using inhibition of plant growth as the toxic criterion:

Hg>Cu>Pb>Zn ≈ As>Cd>Ni ≈ Cr

These two orders of toxicities are generally in agreement. Mercury, silver, and copper stand out as the metals most toxic to marine organisms, followed by zinc, lead, and cadmium. Arsenic appears more toxic to phytoplankton than to marine invertebrates, while the reverse is true for nickel. Chromium exhibits low toxicity to marine biota.

Based on these toxicity data, numerical values from 1 to 5 were assigned to each metal, expressing its relative toxicity to marine invertebrates and phytoplankton (5 indicating the most toxic metals):

Silver, mercury	5
Copper	4
Zinc, lead, cadmium, arsenic	3
Nickel	2
Chromium	1

Bioaccumulation of sediment-bound metals. The bioaccumulation of sediment-associated metals by benthic organisms is difficult to predict. The relative availability of different heavy metals varies substantially and is influenced by the chemical and physical nature of the sediments. There also are substantial interspecies and intraspecies differences in the accumulation of heavy metals from sediments (Neff et al., 1978). Table 12 (Bryan, in press) presents a first estimate of the potential availability of sediment-bound metals.

By averaging the animal/sediment metal ratios (Table 12), five clusters of values emerged. Based on these groups, the following bioaccumulation ratings were assigned to the metals under consideration:

Silver	5
Cadmium, zinc	4
Arsenic, copper, mercury	3
Nickel, lead	2
Chromium	1

Table 11. Toxicity of metals to early life forms of marine invertebrates expressed in moles per liter $\times 10^{-9}$

Metal	<u>Crassostrea</u> <u>gigas</u> embryos ^a	<u>Mytilus</u> <u>edulis</u> embryos ^a	<u>Cancer</u> <u>magister</u> zoeae ^b	<u>Crassostrea</u> <u>virginica</u> embryos ^c
Mercury	33	29	41	28
Silver	204	130	510	54
Copper	83	91	771	1,620
Cadmium	5,440	10,700	2,200	33,800
Lead	3,660	2,300	2,780	11,800
Zinc	1,820	2,680	6,980	4,740
Arsenic	4,350	40,000	3,100	100,000
Nickel	5,940	15,200	74,300	20,100
Chromium	87,300	85,900	66,200	198,000

^a Martin et al. (1981); 48 hr EC₅₀ for abnormal development.

^b Martin et al. (1981); 96 hr LC₅₀.

^c Calabrese et al. (1973); 48 hr LC₅₀.

Table 12. Animal/sediment ratios for metals in three deposit feeders from two different areas ^a

Metal	Sediment concentration ppm dry weight		Animal/sediment metal ratio			Mean ratio
	Site A n=37-51	Site B n=32-35	<u>Scrobicularia</u> <u>plana</u>	<u>Macoma</u> <u>balthica</u>	<u>Nereis</u> <u>diversicolor</u>	
Silver	0.88	0.35	7.3	6.3	1.8	14.9
Cadmium	0.81	0.85	3.8	6.1	0.65	3.2
Zinc	446	223	3.6	3.1	0.45	2.5
Mercury	0.42	0.36	0.99	0.92	0.43	1.2
Copper	274	38.4	0.29	0.71	0.55	0.9
Arsenic	223	10.6	0.20	1.6	0.08	1.0
Lead	169	76.5	0.59	0.37	0.13	0.25
Nickel	28	30.9	0.23	0.16	0.14	0.16
Chromium	34.5	76.1	0.074	0.044	0.026	0.04

^a Bryan (in press).

Ambient metal concentrations. Concentrations of heavy metals in the Hudson-Raritan Estuary are best documented for lead and zinc. Cadmium, copper, and mercury concentrations have been recorded in the Raritan Bay, Newark Bay, Kill Van Kull, and Arthur Kill, while chromium and nickel are known only for the Raritan Bay. No reported values were found for silver and arsenic in the sediments of the HREP study area. The mean levels of metals in sediments of the Hudson-Raritan Estuary were compared with mean baseline metal levels measured in Rhode Island and Long Island Sounds, and off the coast of California (Table 13). These concentrations were very similar and were used as best available background levels of less impacted estuarine sediments.

A contamination factor representing the ratio of the average Hudson-Raritan Estuary concentration of a metal divided by the baseline concentration of the metal was calculated. Results are presented in Table 13. The contamination factor expresses the relative metal enrichment compared to less impacted estuarine sediments, rather than the relative increase in metals concentrations since preindustrial times. Metals were ranked on the basis of their contamination factors. A rating value of 5 indicates the highest level of metal enrichment in sediments, while a value of 1 suggests that the metal concentration in the Estuary approaches background levels. Pending the development of substantive data, a conservative value of 1 was given to silver and arsenic:

Lead	5
Cadmium, copper, mercury, zinc	4
Chromium, nickel	2
Silver, arsenic	1

A similar approach was followed for metal levels in the water columns of the Hudson-Raritan Estuary and for comparable but less impacted coastal waters. Metal concentrations from coastal waters were used rather than those from open-ocean waters to allow for a more realistic comparison. Table 14 lists ambient metal levels in the estuary and other coastal waters. Contamination factors similar to those described for sediments were calculated (Table 14). Metals were ranked on a scale of 1 to 5 according to the contamination factors:

Lead, copper	5
Mercury, zinc	4
Chromium	3
Silver, cadmium, nickel	2
Arsenic	1

Toxicity to Humans. Arsenic, chromium, copper, nickel, and zinc can be toxic to man when absorbed in excessive amounts; these metals also are essential to man, so deficiencies can cause disease (Mertz, 1981). The toxic effects of excessive absorption of the metals considered in this report have been extensively studied in relation to occupational exposures. Table 15 summarizes the effects of exposure to these metals. Although there is little likelihood of significant absorption of any of the metals under consideration by direct inhalation or ingestion of the saline waters of the Hudson-Raritan Estuary, ingestion of metals that

Table 13. Concentration of metals in sediments of the Hudson-Raritan Estuary and baseline coastal areas

	Metal concentrations										Baseline metal levels (ppm dry weight)			Contamination factor	
	Hudson-Raritan Estuary (ppm dry weight)					Rhode Island Sound d					California coast e		Long Island Sound f n=10		Mean baseline
	Raritan Bay a n=77	Newark Bay b n=21	Upper Bay c n=2	Kill Van Kull b n=3	Lower Hudson c n=g	Arthur Kill b n=4	Mean Hudson-Raritan Estuary	Rhode Island Sound d	California coast e n=44	Long Island Sound f n=10	Mean baseline				
Silver	-	-	-	-	-	-	-	0.2	0.20	<0.5	0.2	-			
Arsenic	-	-	-	-	-	-	-	-	-	-	-	-			
Cadmium	3	8	-	8	-	9	7	0.37	0.33	<1	0.35	20			
Chromium	63	-	-	-	-	-	63	9	22	23	18	4			
Copper	135	-	214	-	96	-	148	10	8	5	8	19			
Mercury	-	8	-	4	-	4	5	-	-	0.2	0.2	25			
Nickel	16	-	-	-	-	-	16	4	10	7	7	2			
Lead	101	267	171	368	192	1027	354	9	6	8	8	44			
Zinc	177	520	299	331	243	847	403	16	43	16	25	16			

NOTE: Dashes indicate no reported values.

a Greig and McGrath, 1977.

b Meyerson et al., 1981.

c Williams et al., 1978.

d Eisler et al., 1977.

e Hershelman et al., 1981. Median value, n=44.

f Greig et al., 1977. Mean value, n=10.

Table 14. Concentrations of metals in waters of the Hudson-Raritan Estuary and in comparable but unpolluted estuaries

Metal	Water column (ppb)		Contamination factor
	Hudson-Raritan Estuary	Coastal seawater	
Silver	1.0 a	0.04 d	25
Arsenic	2.0 a	0.45 e	4
Cadmium	0.5 b	0.022 f	23
Chromium	5.9 a	0.135 g	44
Copper	33 b	0.25 f	132
Mercury	0.3 c	0.0041 h	73
Nickel	8.0 b	0.35 f	23
Lead	15 c	0.11 i	136
Zinc	47 b	0.5 i	94

- a Interstate Sanitation Commission, 1979. Values represent the median total metal concentration measured in 12 stations of the Hudson-Raritan Estuary.
- b Mytelka et al. (in press) and Klinkhammer and Bender, 1981. Values represent the median total metal concentration of 13 observations measured in various Hudson-Raritan Estuary waters.
- c Mytelka et al. (in press). Mean of 9 observations of total metal concentration in various Hudson-Raritan Estuary waters.
- d Brewer, 1975.
- e Waslenchuk and Windom, 1978.
- f Bruland and Franks, 1983.
- g Cranston, 1978. Mean total chromium concentration in coastal northeast Pacific Ocean.
- h Mukherji and Kester, 1979. Total mercury concentration in northwest Atlantic Ocean.
- i Kester et al., 1981.

Table 15. Human toxicity and threshold limit values of heavy metals^a

Pollutant	Threshold limit values (mg/m ³) (atmospheric exposure)	Effects of inhalation or ingestion
Arsenic Arsine	0.5 0.2	Dermatitis, bronchitis, skin cancer, gastrointestinal disturbances (arsenic); inhalation of arsine produces hemolysis; combines with sulfhydryl enzymes and interferes with cellular metabolism; powerful poison by inhalation or injection
Cadmium (dust and soluble salts) Cadmium oxide	0.2 0.05	Inhalation produces pulmonary emphysema, hypertension, and kidney damage; ingestion produces gastrointestinal inflammation and liver and kidney damage; interferes with Zn and Cu metabolism; cadmium oxide - possible human carcinogen
Chromium (chromic acid, chromates)	0.1	Dermatitis and ulceration of the skin and nasal sinuses; toxic by inhalation or ingestion; carcinogenic (incidence of lung cancer increased up to 15 times normal in workers exposed to dusty chromite, chromic oxide, and sores)
Copper (fume dusts and mists)	0.2	Skin and mucous membrane irritant; inhalation causes lung and gastrointestinal disturbances
Lead (fumes and dusts)	0.15	Cumulative poison, produces behavioral disorders, brain damage, convulsions, death
Mercury and mercuric compounds	0.01-0.1	Nephritis, gastrointestinal tract disturbances, nerve damage, and death; depresses cellular enzymatic mechanisms by combining with (-SH) groups
Nickel (metal)	1	Dermatitis; probable nasal cavity and sinus carcinogen
Zinc oxide fume		Low toxicity; may cause dermatitis; respiratory tract irritant

^aTalmage (1977).

have accumulated in fish and shellfish inhabiting the Estuary could be a significant source of human exposure.

The toxicity of metals depends in part on the form in which they are administered and the route of exposure. Elemental mercury, for example, is poorly absorbed from the gut, but is readily absorbed through the lungs when inhaled as a vapor. It can also be absorbed through the skin. The kidney in particular is a target organ for effects of excessive intakes of cadmium, lead, mercury, and nickel (Buchet et al., 1981; Sunderman and Horak, 1981). Toxic syndromes of lead and mercury include neurological effects. Lead may interfere with learning processes and mercury with short-term memory rate of recall (Langolf et al., 1981). Some forms of arsenic, cadmium, chromium, lead, and nickel have been reported to cause cancer in experimental animals and/or humans by some routes of dosing (Hamilton and Hardy, 1974; National Academy of Sciences, 1974, 1977).

The rating system, although subjective, considers the human health concerns associated with each of the metals considered by the subpanel. Metals that are considered potential human carcinogens were given a rating value of 7 or higher. Further differentiation is based upon the likelihood of dietary uptake (cadmium, mercury, and lead) and human toxicity considerations (mercury and lead). On the lower end, silver was given a higher rating than copper and zinc because, based upon its high toxicity to invertebrates, it may be a threat to man as well. A rating of 1 to 10 (10 denoting most toxic) was used to emphasize the relative importance of the human toxicity factor in the overall matrix used for the final metal classification:

Lead, mercury	10
Cadmium	8
Arsenic, chromium, nickel	7
Silver	3
Copper, zinc	1

Metal Classification. The implications of individual heavy metal pollutants to the Hudson-Raritan ecosystem were evaluated using the rankings of toxicity to marine biota (TR), bioaccumulation (BR), concentration in the water column (WR), and concentration in sediments (SR) described above. The factors were combined into the following index:

$$\text{Ecosystem Index} = [2WR + (SR \times BR)] \text{ TR.}$$

In this index the sediment concentration rating of a metal is multiplied by its bioavailability ranking to provide an indication of the degree that sediment-bound metals might be available for uptake by benthic invertebrates. The potential threat of metals in the water column is determined primarily by their concentration and toxicity. An arbitrary factor of 2 was inserted to balance the water concentration rating (WR) relative to the sediment concentration rating (SR), since SR was subsequently multiplied by the bioaccumulation rating (BR).

The results of this classification system are summarized in Table 16. Based on the ecosystem index values for the metals under consideration, the following order emerged:

$$\text{Hg} > \text{Cu} > \text{Zn} > \text{Cd} = \text{Pb} > \text{Ag} > \text{Ni} = \text{As} > \text{Cr}$$

Based on these index values, mercury stands out as the metal of primary concern as an ecosystem threat, closely followed by copper. These metals are both considered potential Class A contaminants. Silver, cadmium, lead, and zinc are placed in Class B, while arsenic, chromium, and nickel are considered Class C metals.

The classification of metals according to human health concerns involved an analog index to that for ecosystem well-being:

$$\text{Health Index} = \left[2\text{WR} + (\text{SR} \times \text{BR}) \right] \text{HR},$$

in which HR represents the rankings of metal toxicity to humans described earlier.

The results of applying the health index are provided in Table 16. Once again, three clusters of index values emerged. Cadmium, lead, and mercury are proposed as Class A metals; chromium and nickel are grouped under Class B; and silver, arsenic, copper, and zinc belong in Class C based on this method of classification.

3.3 Conclusions

On the whole, the "minimum tolerance approach" and the "matrix approach" yielded similar results (Table 17). With respect to human health concerns, a discrepancy was found only for arsenic, which was considered a Class B metal in the final analysis. Regarding ecosystem concerns, whenever differences existed, the metal was placed in the class indicating the higher level of threat, which minimized the risk of underestimating detrimental effects. Thus, mercury was arrayed under Class A, although it was agreed that copper poses a larger threat than mercury to marine biota. Lead and cadmium were placed in Class B. The following composite classifications were adopted for metals in the Hudson-Raritan Estuary:

For ecosystem concerns:	<u>Class</u>
Cu, Hg	A
Ag, Cd, Pb, Zn	B
As, Cr, Ni, Se	C

For human health concerns:	<u>Class</u>
Cd, Hg, Pb	A
As, Cr, Ni	B
Ag, Cu, Zn, Se	C

Table 16. Threat ratings, indices and proposed classification of metals based upon the "matrix approach"

Rating categories	Ag	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Water concentration (WR)	2	1	2	3	5	4	2	5	4
Sediment concentration (SR)	1	1	4	2	4	4	2	5	4
Bioaccumulation (BR)	5	3	4	1	3	3	2	2	4
Toxicity to biota (TR)	5	3	3	1	4	5	2	3	3
Toxicity to humans (HR)	3	7	8	7	1	10	7	10	1
<u>Index</u>									
Ecosystem	45	15	60	8	88	100	16	60	72
Humans	27	35	160	56	22	200	56	200	24
<u>Classification</u>									
Ecosystem	B	C	B	C	A	A	C	B	B
Humans	C	C	A	B	C	A	B	A	C

Table 17. Comparison of metal classification using the "minimum tolerance approach" and the "matrix approach"

Metals considered	Minimum tolerance approach		Matrix approach	
	Ecosystem concern	Human health concern	Ecosystem concern	Human health concern
Copper	A	C	A	C
Mercury	B	A	A	A
Lead	C	A	B	A
Silver	B	C	B	C
Cadmium	C	A	B	A
Zinc	B	C	B	C
Arsenic	C	B	C	C
Chromium	C	B	C	C
Nickel	C	B	C	B

4. PETROLEUM HYDROCARBONS SUBPANEL REPORT

J. M. Neff

4.1 Introduction

The annual influx of petroleum to the oceans from natural and anthropogenic sources has been estimated variously at 6.2 million metric tons per annum (mta) (National Academy of Sciences, 1975), at 4-10 mta (Grossling, 1976), and at 1.9-11.1 mta (Connell and Miller, 1980,1981). Much of this influx is into estuarine and coastal waters. The most important anthropogenic sources of petroleum entering the marine environment are those associated with marine transportation (2.2 mta) and surface runoff from land (1.6 mta)(National Academy of Sciences, 1975). Inputs from marine transportation include losses during normal ship operations, oil spills resulting from accidents, and spills occurring during oil terminal operations.

Although more than 130 mta of petroleum products and 29 mta of crude petroleum are shipped through the Port of New York each year (Ray et al., 1980), the major source of petroleum hydrocarbons in estuarine waters of the Hudson-Raritan Estuary appears to be domestic/industrial wastewater effluents and runoff from land (Mueller et al., 1976; 1982; Searl et al., 1977; Tanacredi, 1977; Boehm, 1983; Connell, 1982). Tanacredi (1977) attributes much of the petroleum hydrocarbons in Jamaica Bay to disposal of waste automotive petroleum products (mainly crankcase oil).

Assessment of the environmental impact of the influx of petroleum to the Hudson-Raritan Estuary is complicated by the fact that crude oils and most refined petroleum products are complex mixtures of thousands of organic compounds. Hydrocarbons are most abundant, usually representing more than 75 percent of the oil, with the remainder being made up primarily of various sulfur-, oxygen-, and nitrogen-containing organic compounds (Speers and Whitehead, 1969; Kallio, 1976). The problem arises because individual petroleum hydrocarbons vary substantially in environmental behavior and toxicity to aquatic organisms, and because no single analytical technique specifically measures all petroleum hydrocarbons. In addition, petroleum is not the sole source of hydrocarbons present in marine waters, sediments, and organisms. Koons and Monaghan (1976) estimated the input of hydrocarbons from biosynthesis in the oceans to be 6 mta, a figure similar to the estimated total input of hydrocarbons from all petroleum sources. Alkenes, n-alkanes, and branched alkanes, in that order, are the predominant classes of biogenic hydrocarbons. In coastal waters and sediments, an important source of aromatic hydrocarbons, including polycyclic aromatics, is combustion or pyrolysis of organic materials including fossil fuels (Neff, 1979; Boehm, 1983). Pyrosynthesized aromatic hydrocarbons reach the aquatic environment in industrial and domestic wastewaters, in runoff from land (particularly road surfaces), and through

fallout or rainout of airborne particulate polycyclic aromatic hydrocarbons (Neff, 1979).

The dominant classes of hydrocarbons in petroleum in order of decreasing abundance are cycloalkanes, branched alkanes, n-alkanes, and aromatic hydrocarbons (Kallio, 1976). In the discussion that follows, three classes of hydrocarbon contamination will be evaluated: total hydrocarbons (oil and grease or carbon tetrachloride-extractable oily material), alkanes, and aromatic hydrocarbons.

4.1.1 Toxicity, Abundance, and Threat Ratings

Each of the three classes of petroleum hydrocarbons was rated according to toxicity to marine animals and man and according to abundance in the Hudson-Raritan system. Compounds that are toxic at concentrations of 10 µg/l (ppb) or less (usually measured as 96-hr median lethal concentration) were given a rating of 5. Those that are toxic at about 1 mg/l (ppm) were given a rating of 3, and compounds toxic at concentrations greater than 100 mg/l were given a rating of 1.

Concentration estimates were based on concentrations in the water, sediments, and biota, where such data were available. Environmental concentrations of 100 ppm or greater were rated 5. Compounds present at a concentration of about 1 ppm were rated 3; concentrations of 0.1 ppm were rated 2, and undetectable levels or concentrations of less than 0.1 ppm were rated 1.

The threat rating for each material was computed by multiplying the toxicity rating and the abundance rating. If the product was greater than 10, the compound was perceived as a Class A material--a major threat to the estuary. If the product ranged between 5 and 10, the compound was considered a Class B substance--a potential threat, and if the product was less than 5, the compound was categorized as Class C--no immediate threat.

4.2 Total Hydrocarbons

Total hydrocarbons, or oil and grease, in water and sediments are usually measured by simple, fairly nonselective techniques. Hydrocarbons are extracted from the sample with a nonpolar solvent such as carbon tetrachloride or trichloro-trifluoroethane (fluorocarbon-113). The extract is then either taken to dryness and the residue weighed (gravimetric method No. 413.1; U.S. Environmental Protection Agency, 1979) or analyzed by infrared spectrophotometry (infrared spectrophotometric method No. 413.2; U.S. Environmental Protection Agency, 1979). The techniques are not specific for petroleum hydrocarbons, but also measure vegetable oils, animal fats, waxes, soaps, greases, and related matter. If the extract is cleaned up by column chromatography and analyzed at three infrared wavelengths, interference is decreased and accuracy is improved (Rotteri, 1982). Volatile petroleum hydrocarbons are usually lost, especially in the gravimetric technique. More than 50 percent loss of the light refined oils (gasoline through No. 2 fuel oil) can be expected.

Mueller et al. (1982) and Connell (1982) have estimated the rate of influx of oil and grease or total petroleum, respectively, to the Hudson-Raritan Estuary system. Because oil and grease estimates include substances other than petroleum, estimates of Mueller et al. (1982) are about four times those of Connell (1982) (Table 18). The major sources of oil and grease or petroleum are the same: wastewater discharges and runoff from land. Atmospheric deposition and accidental spills, by comparison, are minor sources of these contaminants in the Hudson-Raritan Estuary. According to Connell (1982), the major processes by which petroleum leaves the waters of the Hudson-Raritan Estuary are, in decreasing order of quantitative importance, decomposition in water and sediments, permanent deposition in sediments, advection, dredging, evaporation, and bed sedimentary transport.

Searl et al. (1977) report values of 92-491 $\mu\text{g/l}$ (ppb) total carbon tetrachloride-extractable organics in water samples from a large number of stations in the Hudson-Raritan Estuary. Subsequent cleanup of the extracts by silica gel chromatography revealed that only 10-40 percent of the extracted organics were petroleum hydrocarbons. In nearby Jamaica Bay, water samples contained 0.5-5.1 mg/l total extractable hydrocarbons (Tanacredi, 1977). Recent investigations of total oil and grease in the waters of the Hudson-Raritan Estuary revealed typical concentrations of 0.5-1.0 mg/l at a depth of 1.5 m. Exceptional values reached 3-4 mg/l (A.I. Mytelka, personal communication). This oil and grease is primarily in particulate form and is dominated by saturated hydrocarbons (P.D. Boehm, personal communication).

Total petroleum hydrocarbon concentrations in bottom sediments are typically three to four orders of magnitude higher than concentrations in the overlying water column (McAuliffe, 1976). Concentrations of total hydrocarbons in sediments from Raritan Bay and Lower Bay range from 1 $\mu\text{g/g}$ to nearly 1,300 $\mu\text{g/g}$ dry weight (ppm) (Stainken, 1979; Stainken et al., 1983). Hydrocarbon concentrations tend to increase with increasing silt-clay content of the sediments and vary seasonally, with lowest values in the fall-winter (mean 160 $\mu\text{g/g}$) and highest values in the spring-summer (mean 327 $\mu\text{g/g}$). Selected sites near sewage outfalls or other point sources may contain 2,000-3,000 $\mu\text{g/g}$ of C_{15+} hydrocarbons (Koons and Thomas, 1979). Sediment hydrocarbon concentrations tend to decrease with distance from shore in the New York Bight, with the exception of the 12-mile and 106-mile dump sites. Koons and Thomas (1979) report concentrations of total C_{15+} hydrocarbons in sediments of the 12-mile dump site in the range of 102-6,530 $\mu\text{g/g}$ and in those of the 106-mile dump site in the range of 24-74 $\mu\text{g/g}$. Typical values for unpolluted portions of the continental shelf and rise in the New York Bight region are 80 $\mu\text{g/g}$ and 40 $\mu\text{g/g}$, respectively. Farrington and Tripp (1977) report total hydrocarbon concentrations of 35-2,900 $\mu\text{g/g}$ in sediments from the New York Bight. There is a gradient of decreasing concentration with distance from New York Harbor and the 12-mile ocean dump site.

Little information is available on total hydrocarbon levels in organisms from the Hudson-Raritan Estuary. Information on body burdens of polycyclic aromatic hydrocarbons in organisms from the Hudson-Raritan Estuary is discussed in Section 4.4. However, Westman and Hoff, in an

unpublished study, show that brook trout and flounder developed an oily taste indistinguishable from that of wild fish caught in Raritan Bay when they were exposed for a short period of time to kerosene plus clay (kaolin) in water. Esser (1982) reviews reports dating back to 1887 of instances of fish from the Hudson-Raritan Estuary having a gasoline or kerosene-like taste.

The toxicity of whole petroleum or of oil and grease is dependent on the chemical composition of the mixture, which, as discussed above, is highly variable. One-, two-, and three-ring aromatics and related heterocyclics are the most toxic and water-soluble components of petroleum. The toxicity of petroleum usually is directly proportional to the relative concentration of these compounds (Moore and Dwyer, 1974; Neff and Anderson, 1981). Generalizations about the toxicity of oil and grease are more difficult to make. Biological oils, fats, greases, and waxes usually have a low order of acute toxicity unless they are oxidized. They also are more readily biodegraded than petroleum hydrocarbons. However, many industrial and agricultural nonpolar organic chemicals are also measured as oil and grease, and many of these are highly toxic and persistent in the aquatic environment. Data for toxicity of whole petroleum are used here, while it is recognized that the petroleum contributions to reported environmental concentrations of total hydrocarbons or oil and grease are highly variable. The data on acute toxicity of crude and refined petroleum to marine organisms have been reviewed extensively (Hyland and Schneider, 1976; Craddock, 1977; Rice et al., 1977; Neff and Anderson, 1981). The acutely toxic concentration of oil to adult marine organisms usually is in the range of 1-100 mg/l (ppm). Acute toxicity to larval and other sensitive life stages of the most sensitive species is observed at oil concentrations of about 0.1 ppm. Chronic and sublethal responses also are sometimes observed at about 0.1 ppm total petroleum hydrocarbons in the water column.

Little information is available on acute toxicity of petroleum to humans and other terrestrial mammals. The limited data on effects of dermal or oral exposure of mammals to light refined oils (generally considered the most toxic) are summarized in Tables 19 and 20 (U.S. Environmental Protection Agency, 1981). As with aquatic animals, effects in mammals are related to concentration of aromatic hydrocarbons in the oils. The middle distillate fuels (high in aromatics) produced a variety of responses following prolonged dermal application. White oils (essentially free of aromatics) were without serious effects. Similar results were obtained when exposure was by oral ingestion. The oils evaluated had a relatively low order of acute toxicity to the species tested. The potential carcinogenicity and mutagenicity of petroleum to mammals will be discussed in the section on polycyclic aromatic hydrocarbons, since these effects are attributed to the polycyclic aromatics in the oil (Epler et al., 1978; Hermann et al., 1980).

Based on concentrations of total hydrocarbons measured in water and inferred in sediments of the Hudson-Raritan Estuary, the abundance of total hydrocarbons is given a rating of 4. In consideration of the extreme heterogeneity and variability in composition of what is defined as total hydrocarbons, this pollutant type is given a toxicity rating

Table 18. Estimated inputs of oil and grease ^a and petroleum ^b to the Hudson-Raritan Estuary (metric tons/day)

Source	Oil and grease	Petroleum
Waste water	168	53.3
Tributaries	42	-
Run-off from land	119	37
Atmospheric deposition	-	0.002
Oil spills	<u>21</u>	<u>1.5</u>
Total	<u>350</u>	<u>91.802</u>

^a Mueller et al. (1982).

^b Connell (1982).

Table 19. Terrestrial mammal toxicity resulting from dermal exposure to oil ^a

Animal	Experimental data	Results
<u>Middle Distillates (Kerosene and Light Fuel Oils)</u>		
Wistar rats	Undiluted diesel fuel applied to tail skin 6 hr/day for 10 days	Dermatitis; hair loss; decreased hemoglobin; erythrocytopenia; reticulocytosis; leukocytosis; neutrophilia; lymphocytopenia
5 albino guinea pigs	Diesel fuel applied to intrascapular skin 5 times/wk for 19 days	Erythema; desquamation; hair loss; ulceration; and crusting
Albino guinea pigs	Various petroleum fuel distillates applied to skin every other day; 4 applications total	Hyperplasia; hyperkeratosis; hair loss; aromatic fuels more toxic than paraffinic fuels
20 guinea pigs	Landsteiner and Jacobs skin sensitization method with diesel fuel	No skin sensitization
10 white Belgian rabbits	Draize method with diesel fuel	No skin sensitization
79 mice	0.10-0.15 g/animal of C ₈ -C ₁₂ aromatic distillate applied to skin 3 times/wk; 159 applications total	Dry, thick, scaly skin; hyperkeratosis; epidermal atrophy; dermatitis; ulceration
100 mice	Intrascapular skin; daily application of light grade diesel fuels	Dermatitis
<u>Lubricating Oils</u>		
Albino guinea pigs	0.6 ml/animal of yellow lubricating oil	Desquamation and hyperkeratosis
<u>White oils</u>		
2 Holstein Friesian calves	0.13 ml/kg of body weight/day of white lubricating oil for 8 weeks applied to skin	No gross skin pathology
Albino guinea pigs	0.6 ml/animal of white lubricating oil applied to skin every other day for 4 days	Slight erythema and desquamation

^aU.S. Environmental Protection Agency (1981).

Table 20. Terrestrial mammal toxicity resulting from oral administration of oils ^a

Animal	Experimental data	Results
<u>Middle distillates (kerosene and light fuel oils)</u>		
Wistar rats	20-25 ml/kg of body weight/day diesel oil by gastric intubation for 14 days	Hemoglobinemia; reticulocytosis; neutrophilia; lymphocytopenia; thrombocytopenia; elevated serum malate dehydrogenase, aspartate and alanine aminotransferase
138 Wistar rats	16.0 ml/kg of body weight diesel oil by gastric intubation	Acute oral LD ₅₀
5 Wistar rats	6.9 ml/kg of body weight/day diesel oil by gastric intubation for approx. 3 weeks	Subacute LD ₅₀
10 rabbits	1.0 ml/kg of body weight of fuel oil orally	23% drop in blood sugar in 5-7 hr; return to normal levels by 12 hr.
Cow	Approx. 7 liters of diesel fuel ingested accidentally	Low grade fever; diarrhea; constipation; lowered milk production; stiff uncertain gait; swelling of hind fetlocks; recovery in 8 days
Ewe	Ingestion of diesel fuel-soaked grass	Weakness; weight loss; nodular lesions on inner rumen wall; complete loss of fleece; neutro philia
<u>Lubricating oils</u>		
Mice	Chronic ingestion of spindle oil for 20-90 weeks (dose not specified)	Fatty infiltration and degeneration of liver, spleen, ovary, and adrenals
<u>White oils</u>		
Mice	20 ml/kg of body weight/day of white mineral oil ingested with diet	Rough, dry skin; piloerection; restlessness; weight loss in 5 days; all died by 7 days; fatty degeneration of liver; proliferation of reticuloendothelial cells of spleen; epidermal hyperkeratosis; renal tubular degeneration
Rats	5 ml/kg of body weight/day of white mineral oil ingested with diet	Same as above in mice
1 monkey	2.2 ml/kg of body weight/day of white mineral oil in diet; total consumption 96 ml	Weight loss; diarrhea; death in 3 weeks; hepatic and renal congestion; ulceration and inflammation of colon, heart, lung, and spleen
1 monkey	1.1 ml/kg of body weight/day of white mineral oil in diet; total consumption 36 ml	Diarrhea; weight loss; death in 11 days; same pathological findings as above
1 monkey	1.1 ml/kg of body weight/day of white mineral oil in diet; total consumption 195 ml in 3 months	No adverse effects; slight hepatic and renal congestion

^a U.S. Environmental Protection Agency (1981).

of 2-3 for aquatic organisms. The corresponding value for human exposure is 1-2. Thus, the threat ratings for total hydrocarbons in the Hudson-Raritan Estuary are 8-12 or Class A, a major perceived threat, for aquatic biota and 4-8 or Class B, a potential significant threat, for humans.

4.3 Alkanes

Three types of alkanes are common in petroleum: n-alkanes (normal paraffins), branched alkanes, and cycloalkanes (naphthenes). Partially unsaturated aliphatic hydrocarbons (alkenes or olefins) are rare in crude oils, but may be present in small amounts in some refined products as a result of catalytic cracking.

Alkanes have much lower solubilities than aromatics of similar molecular weight. Solubility of n-alkanes drops from 9.5 mg/l for hexane to 2.3 µg/l for tetradecane. Cycloalkanes are slightly more soluble (i.e., cyclopentane, 156 mg/l; cyclooctane, 7.9 mg/l) (Hutchinson et al., 1980). Because of their low solubilities, alkanes usually are present in aquatic environments in particulate or adsorbed form. Acute toxicity to aquatic organisms tends to increase with molecular weight of alkanes. However, acutely toxic concentrations for all but the lowest molecular weight alkanes are higher than aqueous solubility concentrations, so toxic concentrations do not occur naturally in aquatic environments (Hutchinson et al., 1980). Alkanes also have an anesthetic effect on aquatic animals, which increases with alkane molecular weight (Crisp et al., 1967). These sublethal responses also are seen in most cases at concentrations approaching or exceeding the aqueous solubility of the alkanes. Paraffin oils are considered relatively inert toxicologically to humans and are sometimes used as laxatives. Light alkanes (methane through octane) are an inhalation toxicology problem because of their high volatility. These light alkanes are lost rapidly from aquatic systems by evaporation. We can conclude that toxicity of alkanes to both aquatic organisms and humans is quite low.

Based on the above considerations, alkanes have been given an abundance rating of 2-3 and a toxicity rating of 1. The resulting threat rating is 2-3 or Class C, indicating no perceived threat on the basis of existing information.

4.4 Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAH) in the Hudson-Raritan Estuary originate from two sources: petroleum and incomplete combustion of organic materials. Petroleum PAH assemblages are dominated by 2- and 3-ring aromatics (naphthalenes, phenanthrenes, fluorenes). Alkylated forms are more abundant than the unsubstituted parent compound (Neff, 1979). PAH assemblages resulting from pyrolysis are dominated by 4- and 5-ring structures as well as larger molecules (i.e., chrysene, fluoranthene, pyrene, benzo(a)pyrene). The unalkylated parent compounds are more abundant than alkyl homologs. Monoaromatic hydrocarbons (e.g., benzene, toluene, xylenes) will not be considered here because they tend to be lost from the aqueous system rapidly by volatilization. Whipple et al. (1981) reviewed the environmental impacts of monocyclic aromatics in coastal environments.

PAH in estuaries come from spillage, industrial, domestic, and storm wastewater disposal, runoff from land, and fallout of airborne particulate PAH (Neff, 1979). PAH aqueous solubilities are low and decrease with increasing molecular weight from about 30 ppm for naphthalene to about 0.5-4.0 ppb for benzo(a)pyrene (Neff, 1979; May, 1980). Because of their low solubilities, most PAH entering the estuary quickly become adsorbed to particulates and are deposited in bottom sediments.

In the Hudson-Raritan Estuary, sewage outfalls have been identified as a major source of petroleum PAH (e.g., Newtown Creek) (Boehm, 1981; MacLeod et al., 1981; O'Connor et al., 1982). In eight sediment samples from the Hudson-Raritan Estuary analyzed by Boehm (1981), the ratio of petrogenic to pyrogenic PAH ranged from 0.4 to 2.2.

Concentrations of total particulate PAH in the water of the Hudson-Raritan Estuary range from 7 ng/l to 35 ng/l (parts per trillion) (Boehm, 1983). There is some evidence of outward transport of petroleum PAH derived from sewage from the estuary and of inward transport of pyrogenic PAH derived from resuspended sediments from the Bight Apex (Boehm, 1983).

PAH concentrations in sediments of the estuary are much higher than those in the water column. In five samples reported by O'Connor et al. (1982) and McLeod et al. (1981), total PAH concentration ranged from 2.0 $\mu\text{g/g}$ dry wt. (ppm), 15 km north of the Battery to 182 $\mu\text{g/g}$ in Newtown Creek. Values reported by Boehm (1981) for sediments from eight stations in the Hudson-Raritan Estuary range from 0.35-86 $\mu\text{g/g}$.

PAH concentrations in biota from the estuary and adjacent Bight are variable (MacLeod et al., 1981; O'Connor et al., 1982). Samples of zooplankton, including planktonic eggs of marine animals contained 20-200 ppb total PAH. Flounder and striped bass contained 3-40 ppb whole body residues, but flounder livers contained up to 1000 ppb PAH. Grass shrimp and lobsters contained up to 837 ppb PAH. However, hepatopancreas of lobsters from Raritan Bay contained up to 4,480 ppb total PAH, including 300 ppb of the carcinogen benzo(a)pyrene. Blue mussels contained 500-1,930 ppb total PAH. In most cases PAH assemblages in biota samples were dominated by the 4- and 5-ring PAH, probably of pyrogenic origin.

Acute toxicity of PAH to marine animals tends to increase with PAH molecular weight and degree of alkyl substitution (Table 21). The most toxic PAH of those tested to date are methylphenanthrene and fluoranthene. Higher molecular weight PAH are not acutely toxic in saturated solution, probably because of their very low aqueous solubilities. However, several of the higher molecular weight PAH are potent mammalian carcinogens (Table 22).

PAH, because of their high concentrations in sediments and some commercially important benthic invertebrates of the Hudson-Raritan Estuary, were given an abundance rating of 3-4. The toxicity rating of PAH for estuarine fauna was placed at 3, based on acute toxicity of lower molecular weight PAH and lack of evidence of carcinogenicity to them of higher molecular weight PAH. The main threat to human health of PAH is their

well-known mammalian carcinogenicity. Because carcinogenic PAH occur at relatively high concentrations in the estuarine system, including the tissues of exploited fish and shellfish species, the human toxicity rating was placed at 4. Thus, the threat rating for PAH to estuarine biota is 9-12 and for man is 12-16. In both cases they represent Class A, or major perceived threats.

Table 21. Acute toxicity, measured as LC₅₀ (concentration causing 50 percent mortality in the time indicated), to selected species of marine animals^a

Compound	Species	Conc. (ppm)	Effect
Naphthalene	<u>Neanthes arenaceodentata</u> (marine polychaete)	3.8	96h LC ₅₀
	<u>Cancer magister</u> (Stage I zoeae, Dungeness crab)	2.0	96h LC ₅₀
	<u>Elasmopus pecteniscus</u> (marine amphipod)	2.7	96h LC ₅₀
	<u>Eurytemora affinis</u> (marine copepod)	3.8	24h LC ₅₀
	<u>Palaemonetes pugio</u> (grass shrimp)	2.4	96h LC ₅₀
	<u>Cyprinodon variegatus</u> (sheepshead minnow)	2.4	24h LC ₅₀
	<u>Oncorhynchus kisutch</u> (coho salmon fry)	3.2	96h LC ₅₀
	1-methylnaphthalene	<u>Cancer magister</u>	1.9
<u>Cyprinodon variegatus</u>			
2-methylnaphthalene	<u>Cancer magister</u>	1.3	96h LC ₅₀
	<u>Palaemonetes pugio</u>	1.1	96h LC ₅₀
	<u>Eurytemora affinis</u>	1.5	24h LC ₅₀
	<u>Cyprinodon variegatus</u>	2.0	24h LC ₅₀
2,6-dimethylnaphthalene	<u>Neanthes arenaceodentata</u>	2.6	96h LC ₅₀
	<u>Palaemonetes pugio</u>	0.7	96h LC ₅₀
	<u>Eurytemora affinis</u>	0.9	24h LC ₅₀
2,3,6-trimethylnaphthalene	<u>Neanthes arenaceodentata</u>	2.0	96h LC ₅₀
2,3,5-trimethylnaphthalene	<u>Eurytemora affinis</u>	0.3	24h LC ₅₀
Fluorene	<u>Neanthes arenaceodentata</u>	1.0	96h LC ₅₀
	<u>Palaemonetes pugio</u>	0.3	96h LC ₅₀
	<u>Cyprinodon variegatus</u>	1.7	96h LC ₅₀
Phenanthrene	<u>Neanthes arenaceodentata</u>	0.6	96h LC ₅₀
	<u>Palaemonetes pugio</u>	0.3	96h LC ₅₀
1-methylphenanthrene	<u>Neanthes arenaceodentata</u>	0.3	96h LC ₅₀
Fluoranthene	<u>Neanthes arenaceodentata</u>	0.5	96h LC ₅₀
Chrysene	<u>Neanthes arenaceodentata</u>	1.0	NAT ^b
Benzo(a)pyrene	<u>Neanthes arenaceodentata</u>	1.0	NAT
Dibenz(ah)anthracene	<u>Neanthes arenaceodentata</u>	1.0	NAT

^a Neff (1982).

^b NAT, not acutely toxic in 96 hours.

Table 22. Relative carcinogenicity of PAH to laboratory mammals ^a

Compound	Carcino- genicity ^b	Compound	Carcino- genicity
Anthracene	-	Aceanthrylene	-
Phenanthrene	-	Benzo(j)aceanthrylene	-
Anthracene	-	Acenanthrylene	-
Phenanthrene	-	Benzo(j)aceanthrylene	++
Benzo(a)anthracene	+	= cholanthrene	++++
7,12-dimethylbenzo(a)anthracene	++++	3-methylcholanthrene	-
Dibenz(a,j)anthracene	+	Naphthacene	-
Dibenz(ah)anthracene	+++	Pyrene	+++
Dibenz(ac)anthracene	+	Benzo(a)pyrene	-
Benzo(a)phenanthrene	+++	Benzo(e)pyrene	+
Fluorene	-	Dibenzo(ai)pyrene	+++
Benzo(a)fluorene	-	Dibenzo(ah)pyrene	+++
Benzo(b)fluorene	-	Dibenzo(ai)pyrene	-
Benzo(c)fluorene	-	Dibenzo(cd,jk)pyrene	+
Dibenzo(ag)fluorene	+	Indeno(1,2,3-cd)pyrene	+
Dibenzo(ah)fluorene	+	Chrysene	+
Dibenzo(ac)fluorene	-	Dibenzo(b,def)chrysene	++
Fluoranthene	-	Dibenzo(def,p)chrysene	+
Benzo(b)fluoranthene	++	Dibenzo(def,mno)chrysene	-
Benzo(j)fluoranthene	++	= anthanthrene	-
Benzo(k)fluoranthene	-	Perylene	-
Benzo(mno)fluoranthene	-	Benzo(ghi)perylene	-
		Coronene	-

^a National Academy of Sciences (1972).

^b not carcinogenic; + uncertain or weakly carcinogenic; ++ carcinogenic; +++ highly carcinogenic; ++++ extremely carcinogenic.

5. HALOGENATED HYDROCARBONS SUBPANEL REPORT

V. Zitko and P.D. Boehm

5.1 Toxicity

Halogenated chemicals include compounds that are among the most acutely toxic of potential marine pollutants. While many of the compounds discussed in this report are highly toxic to marine organisms, the potential threat rating described below considers the environmental abundance as well as the toxicity of these compounds. As new data on environmental concentrations of these compounds become available, the potential threat rating, discussed below, may change. Indeed, as data become available on the levels of toxicants such as chlorinated dibenzodioxins ("dioxins") and chlorinated dibenzofurans in fish from the Hudson River, the perceived threat of these substances may increase.

Toxicity data suggest that the chlorinated pesticides aldrin, dieldrin, chlordane, DDT, endosulfan, endrin, heptachlor, lindane, and toxaphene all have 96-hr TLM aquatic toxicity values of less than 0.1 ppm. In addition, these compounds, together with kepone, have oral LD₅₀ (mammalian) values of about 100 mg/kg body weight or less. The chlorinated benzenes and chlorinated phenols also appear to be relatively toxic. In contrast, the low-molecular-weight chlorinated hydrocarbons (LMCH), such as chloroform, carbon tetrachloride, other chlorinated methanes, and the chlorinated ethanes, ethylenes, propanes, and propenes, generally have aquatic 96-hr TLM and rat and rabbit LD₅₀ values that are several orders of magnitude above those of the chlorinated pesticides.

Although acute toxicity values are useful for identifying compounds of potential concern, such information should not be used to exclude candidate toxicants from consideration. For example, toxicity data suggest that the PCBs are relatively nontoxic (Table 23). However, numerous investigations have demonstrated the chronic toxicity of these mixtures to a wide variety of terrestrial and aquatic organisms (Lincer and Peakall, 1970; Duke et al., 1970; Peakall et al., 1972; Vos, 1972; Nebeker, 1976; Hansen, 1976). One such study has shown that maintaining the rhesus monkey on a diet containing 2.5 ppm Aroclor 1248 for six months significantly decreased its rate of reproduction. Only five of eight pregnancies were carried to full term. All infants were abnormally small and within four months, three of the six nursing infants died of PCB intoxication (Allen and Norback, 1976). By comparison, PCB levels of 2.5 ppm in fishes from the Hudson-Raritan Estuary are not uncommon, and PCB levels in fishes from the upper Hudson River are an order of magnitude higher (Duttweiler, 1982).

Table 23. Summary of chronic toxic effects of PCB

Test	Effects
Chronic feeding	
Aquatic species	<p>Threshold effects in egg hatchability of vertebrates and invertebrates at levels of 2-5 µg/l</p> <p>Embryo toxicity evident at 50 µg/l</p>
Terrestrial species	<p>Mouse: some liver change with exposure to high chlorine containing products, 300-500 µg/g</p> <p>Rat: some liver changes, minimal reproductive effects 100-500 µg/g</p> <p>Monkey: Yusho symptoms, altered reproduction cycles, hyperplastic gastritis and ulceration, 2.5-5 µg/g</p> <p>Chicken: some morphologic deformity, reproduction decline, subcutaneous edema, 20-50 µg/g</p> <p>Mink: dose response relationship in growth and reproduction, 10 µg/g</p> <p>Pelican: some hepatocellular changes, 100 µg</p> <p>Dogs: reduced growth, some liver changes, 100 µg</p> <p>Dogs: reduced growth, some liver changes, 100 µg</p> <p>Wildfowl: some reproduction changes, varies with species, 50-200 µg/g</p>
Teratogenicity	Effects seen in avian species, 50-200 µg/g
Mutagenicity	<p>Chromosomal abnormalities: negative results</p> <p>Dominant lethal mutations: negative results</p> <p>Ames test: 1221, 4 chlorobiphenyl significantly mutagenic</p>
Oncogenicity	High chlorinated compounds produced tumors in rats and mice, relationship with PCB not always clear

5.2 Ranking Rationale

5.2.1 Compound Selection Rationale

A list of industrial halogenated compounds and a list of halogenated pesticides were compiled, based on analytical data for the study area and for other areas and on the anticipated persistence of some compounds in the environment. A number of pesticides containing halogens have not been placed on the pesticide list because they belong to other classes (e.g., phosphamidon--an organophosphate, Permethrin--a pyrethroid), because such pesticides are expected to be relatively biodegradable, or because the compounds are not likely to occur in the area according to their manufacture and usage patterns. Additional discussion of the pesticides not evaluated below as halogenated compounds is presented in Section 5.3.

5.2.2 Toxicity Rating

Acute and chronic toxicity as well as carcinogenicity were considered in rating the compounds. This approach has serious limitations, but appears useful for producing a general categorization of the materials. Toxicity to man and to aquatic fauna were considered separately. The most studied dioxin, 2,3,7,8-tetrachlorodibenzodioxin (TCDD), was used as benchmark with a toxicity rating of 5 (on a scale of 0-5). It is recognized that isomeric compounds differ widely in toxicity, but for the sake of simplicity, these differences were not considered. Thus, for example, all chlorinated dibenzodioxins and dibenzofurans were rated as TCDD. Similarly, chlorinated benzenes except hexachlorobenzene, brominated benzenes except hexabromobenzene, and chlorinated phenyls except pentachlorophenol, were rated as single compounds. Finer tuning may be required at a later date. Similarly, a more detailed classification of biphenyls may have to be used. Toxicity ratings for the compounds evaluated are presented in the first two columns of Table 24.

5.2.3 Abundance Rating

Concentration in sediments (MacLeod et al., 1981) was used as a measure of occurrence in the aquatic environment. Concentrations in the ppm range were rated 5, in the ppb range 3, and in the ppt range 1. Values of 2 and 4 were used to interpolate as necessary. Using concentrations in fish (MacLeod et al., 1981) as a measure of occurrence yielded the same rating, except for chlordane and trans-nonachlor. Concentrations in fish yielded higher ratings for these two compounds and the higher values were used. The concentration of compounds not detectable, not measured, or not reported was rated 1. Abundance ratings are presented in the third column of Table 24.

5.2.4 Threat Rating

Products of toxicity ratings and of concentration ratings were used to evaluate the threat of individual compounds to humans and marine biota. The following classification was used:

Table 24. Toxicity, abundance, and threat ratings of halogenated hydrocarbons

	Toxicity rating		Sediment Concentrations	Threat rating	
	Humans	Marine biota		Humans	Marine biota
Chlorinated benzenes	2	2	2	4	4
Hexachlorobenzene	3	2	3	9	6
Brominated benzenes	2	2	1	2	2
Hexabromobenzene	3	1	1	3	1
Pentabromotoluene	3	2	1	3	2
PCB-1016 (1242)	4	3	4	16	12
PCB-1254	4	4	5	20	20
PCB-1260	4	4	4	16	16
Polychlorinated terphenyls	4	4	1	4	4
Polychlorinated naphthalenes	4	4	1	4	4
Chlorinated paraffins	1	1	3	3	3
Polybrominated biphenyls	4	4	1	4	4
Chlorinated diphenyl ethers	3	3	1	3	3
Brominated diphenyl ethers	3	3	1	3	3
Dechloranes	2	2	1	2	2
Chlorinated dibenzofurans	5	5	1	5	5
Chlorinated dibenzodioxins	5	5	1	5	5
Chlorinated methanes	4	4	1	4	4
Chlorinated ethanes	4	4	1	4	4
Chlorinated ethylenes	4	4	1	4	4
Halogenated alkyl ethers	4	4	1	4	4
Hexachlorobutadiene	4	4	1	4	4
Hexachlorocyclopentadiene	4	4	1	4	4
Pentachlorophenol	4	4	1	4	4
Chlorinated phenols (other)	3	3	1	3	3
Chloronitrobenzenes	3	3	1	3	3

Table 24. Continued

	Toxicity rating		Sediment Concentrations	Threat rating	
	Humans	Marine biota		Humans	Marine biota
Dichlorobenzidine	4	4	1	4	4
Chlorinated anilines	2	2	1	2	2
Chlorinated styrenes	2	2	1	2	2
1,2 dibromo-3-chloropropane	4	3	1	4	3
Lindane	4	3	3	12	9
α-BHC	3	2	2	6	4
Heptachlor	4	3	2	8	6
Heptachlor epoxide	4	3	3	12	9
Aldrin	4	4	1	4	4
DDT and metabolites	3	4	4	12	16
Chlordane	3	4	4	12	16
Trans-nonachlor	3	4	4	12	16
Dieldrin	4	4	3	12	16
Endrin	4	5	2	8	10
Mirex	4	4	1	4	4
Kepone	4	4	1	4	4
Toxaphene	4	4	1	4	4
Endosulfan	4	4	1	4	4
Other Pesticides					
2,4-D	2	1	1	2	1
2,4,5-T	3	1	1	3	1

<u>Product</u>	<u>Threat rating</u>
5	Class A, major perceived threat
5-10	Class B, potentially significant threat
5	Class C, no threat based on existing information

The classification of halogenated hydrocarbons is given in Table 25. The ratings are flexible. For example, if a highly toxic compound (rating 4), which presently is not measured, is detected in the ppb range (rating 3), it becomes a major perceived threat ($3 \times 4 = 12$). As was pointed out at the start of this section, there are relatively few data points on the prevalence of many of the compounds considered in this section. Consequently, the classifications of individual compounds may change with time.

5.3 Other Pesticides and Organic Chemicals

The majority of insecticides used on a large scale belong to the classes of organophosphates and carbamates. As a rule, these insecticides are not accumulated by aquatic fauna to the extent encountered with organochlorine insecticides. Some of the organophosphates and carbamates are highly toxic to aquatic fauna, particularly to invertebrates. Intermittent presence of these insecticides, even in very low concentrations, is potentially detrimental to aquatic fauna (Zitko and Choi, 1971; Green, 1979; and Peakall, 1975).

A wide variety of organophosphate and carbamate insecticides may be present. Analytical techniques for trace levels of many of these compounds are not well developed. It is recommended that insecticides that act as acetylcholinesterase inhibitors be monitored, on a trial basis, in selected locations receiving agricultural runoff during spring and summer (see, for example, Coppage and Braidech, 1976).

Herbicides are generally less toxic to aquatic fauna than insecticides, and their nontarget effects on aquatic flora are not well documented. Atrazine is a herbicide detectable frequently in freshwater. It appears that relative to other chemicals considered up to this point, herbicides are of lower priority for further studies.

An overwhelming variety of industrial organic chemicals may reach the aquatic environment. Priority pollutants not covered in previous sections and detected frequently in industrial effluents include acrolein, acrylonitrile, isophorone, phthalates, nitrobenzene, dinitrotoluenes, phenols, and nitrophenols (Wise and Fahrenthold, 1981). The previous discussions were limited to considerations of halogenated hydrocarbons. Many other classes of synthetic organic compounds have been found in industrial effluents.

Other heterocyclic organic compounds containing nitrogen hetero atoms may be far more potent carcinogens than their hydrocarbon analogs. Data is not available on the abundance of these and other synthetic organic compounds in the marine environment; therefore, further study of these classes of compounds are needed before their threat ratings are postulated.

Table 25. Classification of halogenated hydrocarbons

Classification ^a	Halogenated hydrocarbon compounds	
	Humans	Aquatic invertebrates
Class A	PCB-1016 PCB-1254 PCB-1260 DDT and metabolites Chlordane Trans-nonachlor Dieldrin Lindane Heptachlor epoxide	PCB-1016 PCB-1254 PCB-1260 DDT and metabolites Chlordane Trans-nonachlor Dieldrin Endrin
Class B	Hexachlorobenzene Chlorinated dibenzofurans Chlorinated dibenzodioxins Heptachlor Endrin α -BHC	Hexachlorobenzene Chlorinated dibenzofurans Chlorinated dibenzodioxins Heptachlor Heptachlor epoxide Lindane
Class C	Chlorinated benzenes Brominated benzenes Hexabromobenzene Pentabromotoluene Polychlorinated terphenyls Polychlorinated naphthalenes Chlorinated paraffins Polybrominated biphenyls Chlorinated diphenyl ethers Brominated diphenyl ethers Dechloranes Chlorinated methanes Halogenated alkyl ethers Hexachlorobutadiene Hexachlorocyclopentadiene Pentachlorophenol Chlorinated phenols (other) Chloronitrobenzenes Dichlorobenzidine Chlorinated anilines Chlorinated styrenes 1,2 dibromo-3-chloropropane Aldrin Mirex Kepone Toxaphene Endosulfan 2,4-D 2,4,5-T	Chlorinated benzenes Brominated benzenes Hexabromobenzene Pentabromotoluene Polychlorinated terphenyls Polychlorinated naphthalenes Chlorinated paraffins Polybrominated biphenyls Chlorinated diphenyl ethers Brominated diphenyl ethers Dechloranes Chlorinated methanes Halogenated alkyl ethers Hexachlorobutadiene Hexachlorocyclopentadiene Pentachlorophenol Chlorinated phenols (other) Chloronitrobenzenes Dichlorobenzidine Chlorinated anilines Chlorinated styrenes 1,2 dibromo-3-chloropropane Aldrin Mirex Kepone Toxaphene Endosulfan 2,4-D 2,4,5-T α -BHC

^aProducts of toxicity ratings and concentration ratings.

6. PUBLIC HEALTH CONSEQUENCES OF CHEMICAL CONTAMINANTS IN THE HUDSON-RARITAN ESTUARY

M. S. Connor, C. E. Werme, and K.D. Rosenmann

Metropolitan New York has been affected by the chemical contamination in the Hudson-Raritan Estuary for over one hundred years. As early as 1880, the once-prized shad fisheries of Newark Bay had lost their reputation a result of coal oil tainting; at times, oysters from the area also were tainted (Goode, 1887). The effects on human health of exposure to chemical contaminants by the consumption of seafood have been difficult to identify. Acute impacts have not been observed, and chronic effects presently are not easy to decipher from other natural and environmental impacts on human health.

Human exposure to chemical contaminants in the Hudson-Raritan could come from:

- (1) Inhalation of contaminants that have evaporated or have aerosolized through wind or wave action;
- (2) Adsorption and ingestion of contaminants while swimming;
or
- (3) Ingestion of contaminated seafood.

Inhalation and adsorption of contaminants from the estuary are likely to be very minor pathways. Inhalation is likely to be more important than adsorption, particularly for hydrocarbons suspended in the water and sediments. Because a proportion of these hydrocarbons are almost constantly entering the atmosphere, neighboring communities and particularly workers in the vicinity of the water will be exposed. However, levels of emission will be small, and the excellent conditions for air mixing over the estuary will rapidly reduce concentrations by dilution.

A reevaluation of possible exposure levels may be appropriate in the future if research and the development of approved emission and concentration information suggest that the problem of contaminant exposure through inhalation has been underestimated.

Adsorption could occur from swimming or other bodily contact with the water and sediments. While swimming presently is restricted in some areas of the estuary, the restrictions have resulted from risk of infectious diseases rather than from danger of exposure to chemical contaminants. It is presumed that one would not swim in the areas of highest pollutant content (e.g., Arthur Kill region) or near industrial or sewage outfalls where concentrations of toxic compounds (including many volatile compounds) might pose a distinct health problem. In addition, normal prudence is expected in avoiding extended worker contact with water or sediments near outfalls.

Ingestion of contaminated seafoods is a major pathway for the transfer of contaminants from the Hudson-Raritan Estuary to humans. For some compounds, ingestion of seafood is probably the source of greatest total exposure to the populace at large. For instance, as much as 94 percent of human exposure to dieldrin results from ingestion of seafood (U.S. Environmental Protection Agency, 1980). Fishes are the major source of PCBs, mercury, and arsenic to individuals that are not occupationally exposed to these substances (U.S. Environmental Protection Agency, 1980). Increased PCB levels in the blood have been associated with fish consumption (Humphrey, 1976).

The U.S. Food and Drug Administration (FDA) is charged with protecting the consumer from foods that contain hazardous levels of contaminants. Fish offered for commercial sale must not contain concentrations of contaminants above set FDA Action Levels (Table 26).

For most heavy metals, levels measured in fishes and shellfish have been well under levels of concern (Jensen, 1977). However, mercury and cadmium have been of some concern. In 1970, mercury levels in fish from many New York waters, including the lower Hudson River, were near or exceeded the then-established FDA level of 0.5 ppm (Armstrong and Sloan, 1980). Since then, industrial mercury discharges have declined, and there is some evidence that body burdens of mercury have also declined. Also, in 1978, the FDA raised the action level for mercury to 1.0 ppm.

No FDA standard has been established for cadmium, but high levels of cadmium in blue crabs have forced the New York Department of Environmental Conservation to warn against eating more than one meal per week of hardshell blue crabs from the New York Harbor region (NYDEC, 1982). Consumers also were warned to not consume any softshell crabs or the broth in which crabs had been cooked.

FDA standards for petroleum hydrocarbons have not been established. Some PAH compounds are carcinogenic, and elevated levels of PAH have been found in selected food organisms (MacLeod et al., 1981).

Based on the FDA action level of 5 ppm for PCBs in fish flesh, the states of New Jersey and New York have closed the commercial fisheries for striped bass and American eel, and New York has also closed the common carp, goldfish, white catfish, and white perch fisheries intended for human consumption. While little has been done to regulate sportfishing, New York and New Jersey have issued fish consumption advisories. Pregnant women, nursing mothers, women of child-bearing age, and young children have been advised against eating finfish and blue crabs from the Hudson River. Others should not eat fish more than once a week.

For PAH and chlorinated hydrocarbons, carcinogenicity and/or mutagenicity may be the most important chronic human health hazards. FDA standards for these compounds are set by balancing margins of health safety with the ability of the fishing industry to meet the

Table 26. FDA action levels Class A human health for chemical contaminants in edible fish ^a

Compound	Level (ppm, wet weight)
Mercury	1.0 ^b
Cadmium	- ^c
Lead	-
PAH	-
PCB	5.0
DDT and metabolites	5.0
Chlordane	0.3
Dieldrin	0.3
Lindane	0.3 ^d
Endrin	0.3
Heptachlor and heptachlorepoide	0.3
Trans-nonachlor	-

^a Unless otherwise noted, information from U.S. Department of Health and Human Services (1982).

^b Information from Armstrong and Sloan (1980).

^c No level set.

^d Information from Federal Register, Dec. 6 (1974).

standards. Such a balancing is a difficult task. Pressing, immediate concerns of fishermen are well defined, whereas uncertain, statistical chances of late-appearing cancers are not. Studies of small groups of people who have eaten highly contaminated fish have not demonstrated any specific illnesses correlated with levels of DDT or PCBs (Humphrey, 1976; Kreiss et al., 1981). Because the immediate concerns of fishermen could overwhelm the uncertain chance of late-appearing cancer, the U.S. Environmental Protection Agency has developed a method to evaluate these compounds. The agency calculates "carcinogenic potency factors" from the slope of dose-response curves in animal-feeding studies. A potency factor ($\text{mg}^{-1}\text{kg day}$) can be multiplied by a dose ($\text{mg kg}^{-1}\text{day}^{-1}$) to calculate a lifetime cancer risk from a particular compound. EPA calculations assume the exposure of a 70-kg male person and an average daily per capita consumption of 6.5 g of freshwater and estuarine fish and shellfish products. On the basis of these and other assumptions, EPA has calculated the contaminant dose that would result in an increased lifetime risk of cancer of 10^{-5} , 10^{-6} , and 10^{-7} (1 additional case in 100,000 to 1 in 10,000,000) (44 Federal Register 15926, March 15, 1979). Since EPA assumes a linear dose-response relationship, other consumption rates will increase or decrease risk proportionately.

There are many assumptions made in extrapolating from high-dose animal-feeding studies to low-dose human exposure. Wilson and Crouch (1982), however, have compared animal-feeding studies to human epidemiology studies for the few compounds where both exist and found a general one-to-one correspondence between animal and human cancer susceptibility. They estimate an uncertainty factor of ten. Laboratory animal data generally are agreed to be the most reliable indicators of carcinogenic or mutagenic hazards for humans (Epstein, 1970, 1974; Saffiotti et al., 1971). However, there may be an error in extrapolating linearly from high-dose to low-dose exposures. Other extrapolation models have been proposed, but the experiments have not been developed to test them.

EPA's assumptions regarding body weight and seafood consumption may also be a problem, as they do not emphasize the risks to subsets of the population. While many individuals never eat fish or shellfish, sports fishermen and subsistence fish-eaters easily exceed the assumed 6.5 g per capita per day consumption. Assumed levels of consumption also do not account for atypical eating habits that substantially increase exposure, such as eating the hepatopancreas of lobster and crab. The assumptions may underestimate exposure effects to persons weighing less than 70 kg, especially breast-fed infants. Breast milk is thought to be a major source of PCB exposure to infants. For example, a Michigan woman with a PCB blood level of 0.053 ppm (through industrial exposure) had 4 ppm PCB in her milk (Humphrey, 1976). Human PCB blood levels in that study were as high as 0.366 ppm, suggesting that levels in the breast milk could greatly exceed 10 ppm. PCBs and other chlorinated hydrocarbon residues have also been found to be quite high in human milk of Hawaiian residents (Takahashi et al., 1981).

Notwithstanding the limitations of the EPA carcinogenic potency factors, the method has been used to estimate the potential risk of cancer from consuming Hudson-Raritan fish and shellfish (Tables 27 and 28). Table 27 summarizes the carcinogenic factors from EPA Water Quality Criteria Documents and wet weight concentration of organic contaminants in muscle of fishes and shellfish from the Hudson-Raritan Estuary (from MacLeod et al., 1981). PCB concentrations in the striped bass samples exceed the FDA tolerance levels, but for all other compounds for which levels have been set, the levels are well below the FDA limits.

Because of the many contaminants in individual fish from the estuary, the probabilities associated with individual organic contaminants were summed to determine a total risk. This summation assumes that, on the average, the compounds are acting neither synergistically nor antagonistically. Combined risks of all carcinogens in foods have not been studied sufficiently to allow predictions, and summation is only one possible method of dealing with multiple contaminants.

Despite the FDA standards for PAH, our calculations indicate that the range of lifetime risk from consuming average quantities of seafood such as flounder, lobster, and mussels from Raritan Bay is from 5×10^{-5} to 10×10^{-5} . The lifetime risk (Table 28) of consuming only 5 lbs. of striped bass from the Hudson River every year is from 1.7×10^{-3} to 6×10^{-3} additional lifetime cancers.

FDA has, in fact, acted to regulate the Hudson River striped bass fishery as a result of the high levels of PCB. However, FDA does little to consider the risks presented by the total suite of contaminants in estuarine fishes. In the past, there has been regulation of involuntary risks that exceed 10^{-5} to 10^{-6} annually (Wilson and Crouch, 1982). Recent evidence suggests that EPA intends to regulate carcinogens to ensure risks are less than 10^{-4} lifetime (equivalent to 1.5×10^{-6} annual risk; Marshall, 1982). While PCBs account for most of the carcinogenic risk of consuming Hudson-Raritan fishes (60-90 percent), chlordane, dieldrin, and DDT and its metabolites each show risk probabilities above 10^{-5} in some fish. In addition, the total estimated risk for every fish in this sample from the Hudson-Raritan Estuary is above 10^{-5} .

Additional research is required to establish more precisely the health risks of chemical contamination in the Hudson-Raritan Estuary. It is clear, however, that contamination of seafood from the Hudson-Raritan Estuary poses some definite risks, even for typical seafood consumers. Those risks could be substantial for those who consume large quantities of fish or shellfish from the estuary.

Table 27. Carcinogenic potency factor and wet weight concentrations of contaminants in individual fish or shellfish from the Hudson-Raritan Estuary ^a

Compound	Carcinogenic potency factor	Wet weight concentrations (ppb) from muscle							
		Raritan Bay winter flounder	Raritan Bay windowpane flounder	Hudson River striped bass	Raritan Bay lobster	Raritan Bay mussels			
Chlordane	1.61	8.0	6.0	144	4.8	1.7	2.3	1.1	10.4
DDT and metabolites	8.42	16.0	22.0	792	11.2	10.2	29.9	20.2	66.3
Dieldrin	30.40	0	0	0	6.4	5.1	0	2.2	0
Hexachlorobenzene	1.69	0	0	0	0.3	0.3	1.1	1.1	0
Heptachlor	3.37	0	0	0	0.8	0.7	0	0.2	0
Lindane	0.78	0	0	0	0	0	0	0	0
Nonachlor	0 ^b	4.0	4.0	192	3.2	3.4	4.6	2.2	6.5
PAH C	0	6.0	12.0	10	12.8	25.5	77.7	6.6	250.9
PCB	4.34	100	160	12960	96	357	230	220	156

^a Data from MacLeod et al. (1981).

^b No experimental evidence of carcinogenicity.

^c PAH included naphthalene, 1-methylnaphthalene, biphenyl, phenanthrene, fluoranthrene, pyrene, chrysene, and benz(a)anthracene. No experimental evidence has linked any of these compounds to cancer.

Table 28. Lifetime increased risk of cancer ($\times 10^{-6}$) from consuming 6.5 grams of Hudson-Raritan fish or shellfish per day

Compound	Wet weight concentrations (ppb) from muscle												
	Raritan Bay winter flounder		Raritan Bay windowpane flounder		Hudson River striped bass		Raritan Bay lobster		Raritan Bay mussels				
Chlordane	1.2	1.2	0.9	0.6	0.9	22	22	0.72	0.25	0.34	0.16	0.17	1.6
DDT and metabolites	13	7.8	17	10	15	620	1100	8.8	8.0	23.39	16	16	52
Dieldrin	0	11	0	11	12	0	0	18	14	0	6.2	6.5	0
Hexachlorobenzene	0	0	0	0.1	0.1	0	0	0.05	0.05	0.18	0.17	0.14	0
Heptachlor	0	0	0	0	0	0	0	0.25	0.21	0	0.07	0.04	0
Lindane	0	0.14	0	0	0.1	0	0	0	0	0	0	0.02	0
Nonachlor	0	0	0	0	0	0	0	0	0	0	0	.00	0
PAH	0	0	0	0	0	0	0	0	0	0	0	.00	0
PCB	40	32	64	31	51	5200	3600	39	140	93	89	84	63
Additive risk	54	53	83	52	78	5900	4700	67	170	120	110	110	120

7. ACKNOWLEDGEMENTS

We would like to thank Granville H. Sewell, G. Malcolm Meaburn, and Harry L. Seagran for their advice and critical comments regarding the public health section of this report.

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