

NOAA LISD SEATTLE

FY 80-82 FINAL REPORT



# ESTUARINE AND COASTAL POLLUTANT TRANSPORT AND TRANSFORMATION THE ROLE OF PARTICULATES

A PROJECT UNDER THE NOAA/OMPA SECTION 202 RESEARCH PROGRAM

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U.S. DEPARTMENT OF COMMERCE  
NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION  
ENVIRONMENTAL RESEARCH LABORATORIES

FY80-82 SUMMARY REPORT

and

FY82

NOAA LISD SEATTLE

ANNUAL REPORT

ESTUARINE AND COASTAL POLLUTANT TRANSPORT AND TRANSFORMATION

THE ROLE OF PARTICULATES

A PROJECT UNDER THE NOAA/OMPA SECTION 202 RESEARCH PROGRAM

Herbert C. Curl, Jr., Editor

PACIFIC MARINE ENVIRONMENTAL LABORATORY

SEATTLE, WASHINGTON 98115

SEPTEMBER 1982

U.S. DEPARTMENT OF COMMERCE

NOAA/ERL



**U.S. DEPARTMENT OF COMMERCE**  
**National Oceanic and Atmospheric Administration**  
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23 September 1982

Dr. Robert Burns  
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Dear Bob:

We're very pleased to transmit this copy of PMEL's FY82 Annual Report and third-year Summary Report of our research conducted under the Sec. 202, Long-Range Effects Research Program.

The Project is more interdisciplinary and addresses more processes than when first conceived; we believe it also has become more focussed, especially on relevant management issues. We owe this in no small part to the guidance developed in your office over the past two years.

Although the importance of the processes we are studying has been known for some time, we believe this is the first truly integrated project that examines the behavior of pollutants bound to particulates on a large scale, from their historical introduction, transport and transformation, to their final disposition and, moreover, attempts to develop predictions of the ability of an estuary to process increasing loadings of pollutants. We eagerly anticipate the future stages of this effort as concomittant effects research is coupled with our fate research to bring about a realistic test of the concept of assimilative capacity of marine estuaries.

Sincerely yours,

Herbert Curl, Jr.  
Project Coordinator



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## 1. EXECUTIVE SUMMARY

### 1.1 INTRODUCTION

#### 1.1.1 General Nature and Scope of Study

This report describes research conducted in two time frames; during the years FY80-82 research that was undertaken to better understand general processes that affect the transport of pollutants in estuaries, and research in FY82 that addressed the processes that lead to a better understanding of the assimilative capacity of marine estuaries; specifically watershed input functions, transport to ultimate sinks, loss terms, and potential buildup of pollutants in sensitive areas. The goal of the FY82 work and the out years is to provide a prediction of the rates of buildup of toxicants in estuarine sediments and waters on the basis of projections of future population, industrial activity and waste management procedures. These predictions, together with associated effect studies conducted by other laboratories, are directed at connection between the Consequences of Activities, and Decisions (Burns, 1981). The Project addresses Sec. 202 of P.L. 95-273 and the OMPA Sec. 202 Program Strategy (Burns, 1981). The General Goal and Objectives of the study are described in the FY82 Project Development Plan: Estuarine and Coastal Pollutant Transport and Transformation: The Role of Particulates (Curl, 1981).

#### 1.1.2. The Study Area

##### Duwamish River-Elliott Bay region

The physical characteristics of the Duwamish River-Elliott Bay region have been described by several authors (Dawson and Tilley, 1972; Santos and Stoner, 1972; Gardner and Smith, 1978; Hamilton and Cline, 1981; Baker, 1982; Massoth et al., 1982). The combined Green-Duwamish River system extends from the western slopes of the Cascade Mountains to Elliott Bay in Puget Sound. The Green River flows westward through forests, pastureland, and farmland until it reaches river kilometer 19 where it is joined by the Black River, forming the Duwamish River. This river continues to meander to the northwest through the industrialized regions of Renton, Tukwila, and Seattle, Washington (Fig. 1.1). The annual discharge curve for the Duwamish River (Fig. 1.2a) indicates a period of relatively high mean discharge during the months of November through June (mean range:  $40-80 \text{ m}^3 \text{ s}^{-1}$ ) and low discharge during the period July through October (mean range:  $10-20 \text{ m}^3 \text{ s}^{-1}$ ). Sediment discharge follows the same pattern, i.e., maximum discharge occurring in the November through June period (mean range:  $40-80 \text{ m}^3 \text{ s}^{-1}$ ) and low discharge during the period July through October (mean range:  $0.1-1.0 \times 10^3 \text{ metric tons d}^{-1}$ ) (Fig. 1.2b). The Municipality of Metropolitan Seattle (METRO) operates the Renton Sewage Treatment Plant which discharges approximately  $136 \times 10^3 \text{ m}^3 \text{ d}^{-1}$  of secondary-treated sewage at river kilometer 20.5. Industrial and storm water waste of significantly lesser amounts are also intermittently discharged at several locations

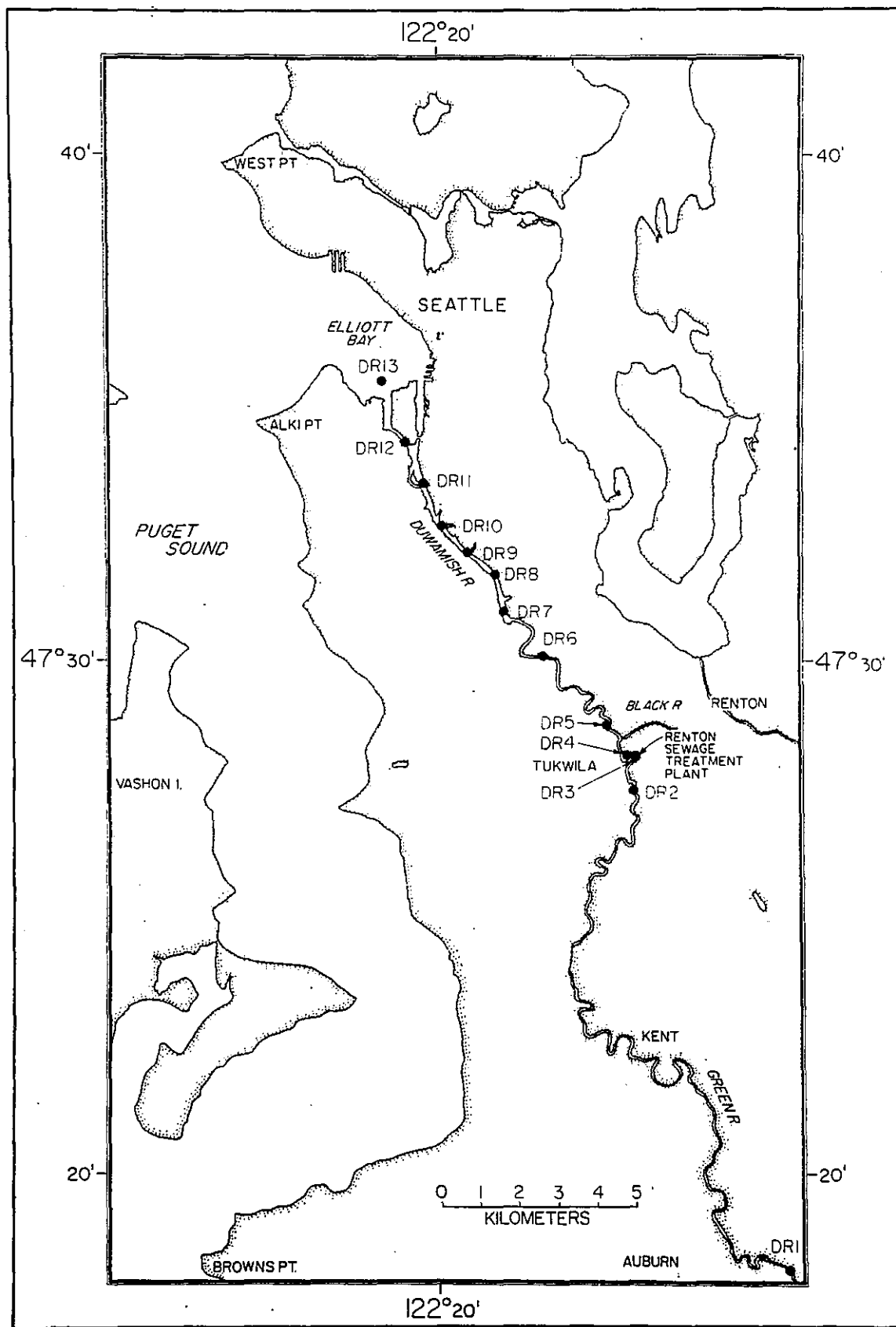


Figure 1.1. Locations of sampling stations in the Duwamish River.

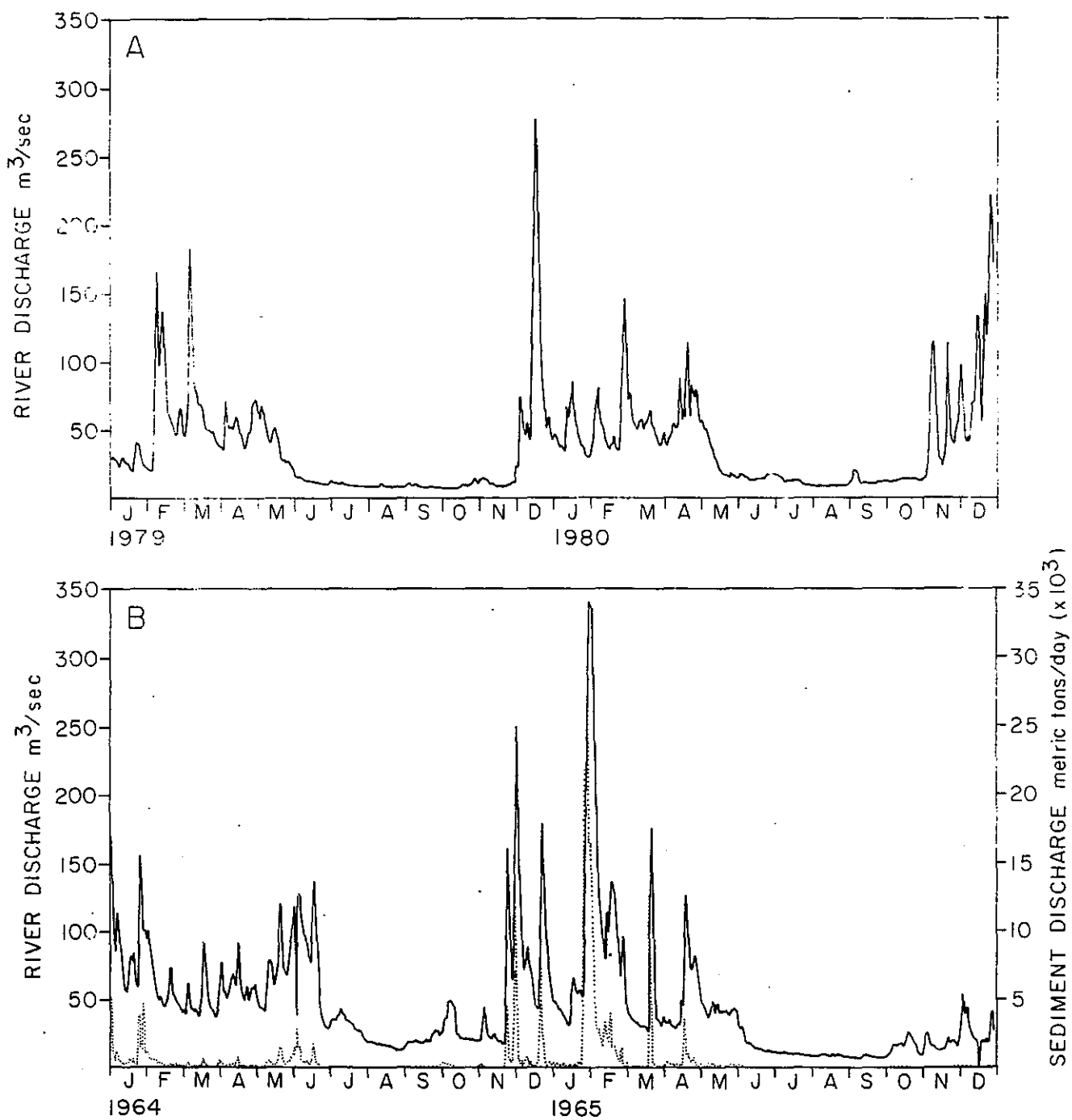


Figure 1.2a. Water discharge data for the Duwamish River at Tukwila (period of record: 1979-1980). B. water (-----) and sediment (.....) discharge data for the Duwamish River at Tukwila (period of record: 1964-1965). Data obtained from U.S. Geological Survey, Water Resources Division.



along the lower river. The lower ten kilometers of the Duwamish River have been dredged and straightened by the U.S. Army Corps of Engineers. This region forms a two-layered estuary (Type 2B of the Hansen Rattray convention). The upper layer consists of mixed salt and freshwater, and the lower layer is mostly unmixed salt water. The seaward end has a maximum of approximately four meters.

The Duwamish River discharges into Elliott Bay at its southeast end through the West and East waterways (Fig. 1.3). Elliott Bay forms a relatively small embayment on the east side of Puget Sound surrounded by the industrial sections of the city of Seattle. The bay has a surface area of approximately 20 km<sup>2</sup> and a total volume of approximately 2.1 km<sup>3</sup>.

### Puget Sound

The Puget Sound main basin (Fig. 1.4) is a tidally dominated estuary approximately 115 km long and 6 km wide. It is separated from the Strait of Juan de Fuca by Admiralty Inlet and from southern Puget Sound by the Narrows (Tacoma). The respective sill depths are 64 m and 50 m (Barnes and Ebbesmeyer, 1978). Because of numerous small rivers entering the eastern side of the basin, a halocline and a zone of minimal horizontal flow occur at approximately 40 m.

The surface layer north of Seattle moves to the north in response to normal estuarine flow. However, south of Seattle, mean flow apparently is toward the south at all depths, although complete seasonal current-meter data are not available for absolute field confirmation. Flow of new water toward the south is balanced by a strong northerly return flow through Colvos Passage. Significant deep water replacement usually occurs during flood tides exceeding 3.5 m (range) at Seattle, although small amounts may be introduced in each tidal cycle. Major replacement may occur seasonally as well.

Water which flows along the bottom toward the south is slowly entrained by the surface flow. Any residual water not lost through entrainment must exit at the southern end of the main basin and be reflexed south through the Narrows or north through Colvos Passage. Vertical transport at the southern end of the basin is believed to be accelerated by tidal pumping through the Narrows.

Tidal mixing over the sill entrances to the main basin is intense, although it is suspected that mean flow trajectories will show a two-layered flow. This results in a partial recycling of "old" water within the main basin proper. The recycling of water and dissolved constituents is characteristic of fjords and usually results in an accumulation of nutrients at the river end of the estuary. Because of these flushing characteristics, the region near Tacoma is particularly susceptible to the retention of dissolved components in the water column.

In the central portions of the main basin, exchange of salt and other dissolved and suspended materials occurs by horizontal advection and vertical diffusion.

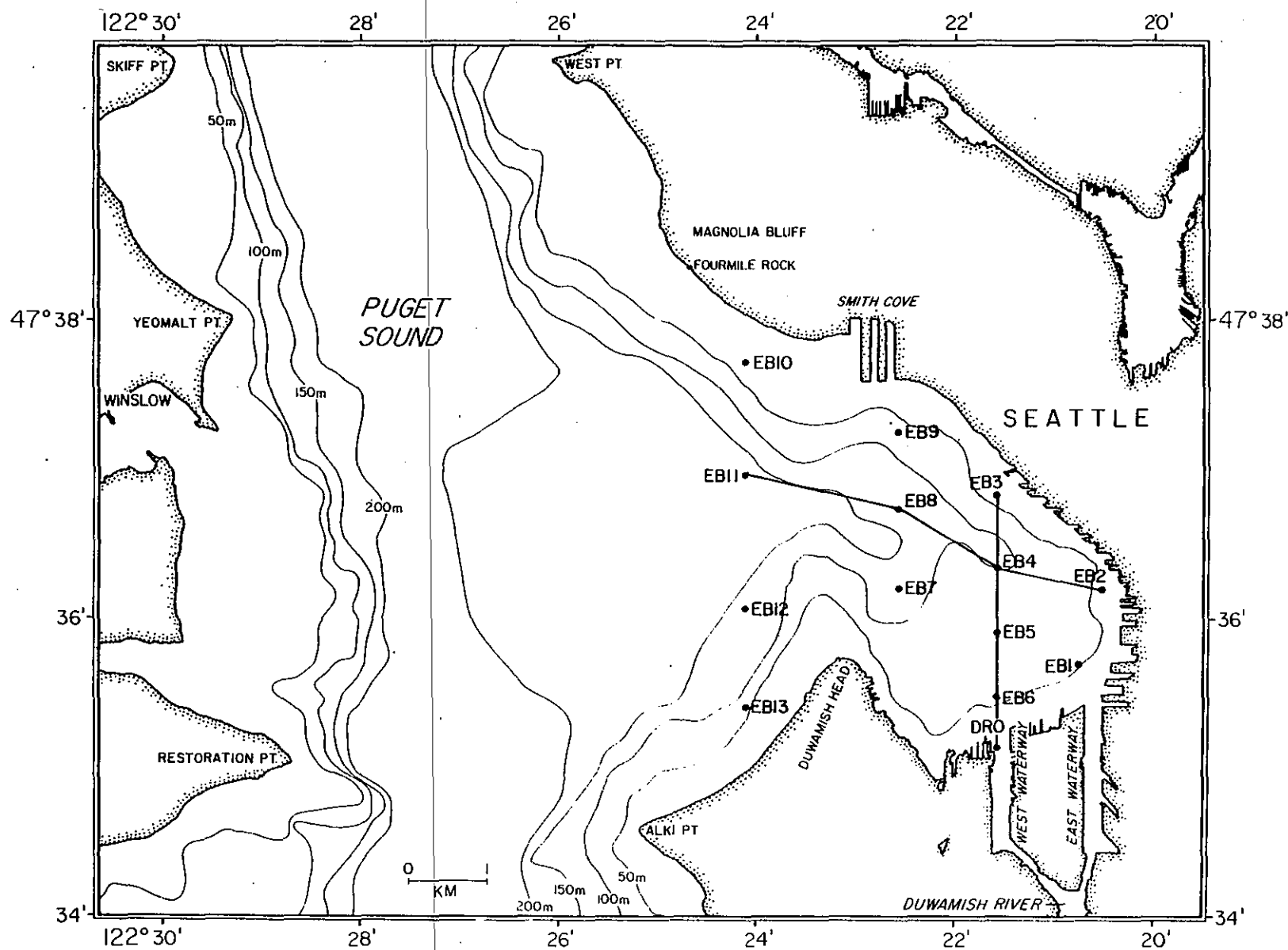


Figure 1.3. Locations of sampling stations in Elliott Bay. The solid lines show the locations of the east-west and north-south cross sections.

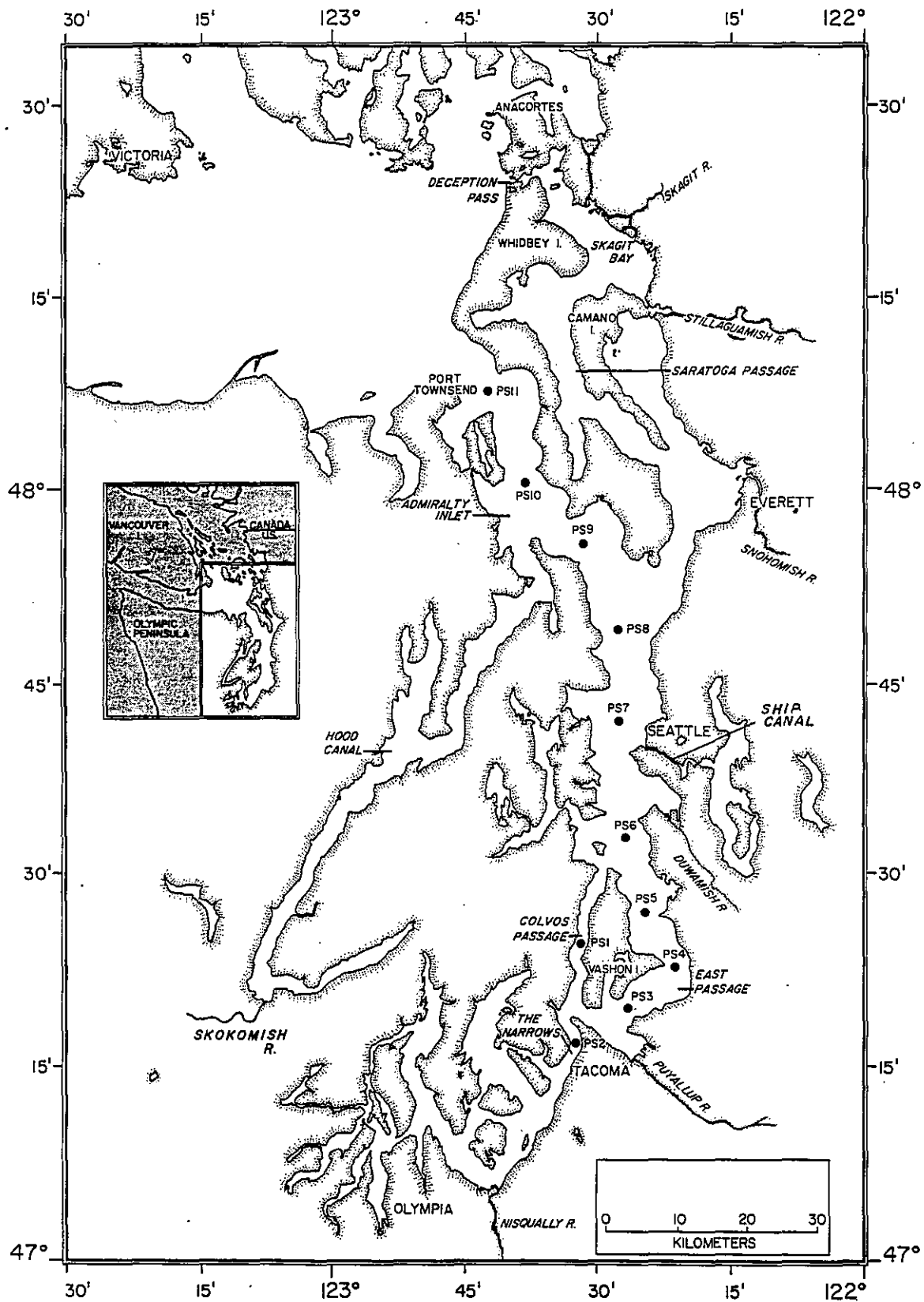


Figure 1.4. Locations of sampling stations in the main basin of Puget Sound.

It may be helpful to place the hydro-sedimentary dynamics of the main basin in context. An average of 1 m per year falls on a drainage area of  $28.5 \times 10^3 \text{ km}^2$  per year. Assuming no evaporation or transpiration,  $28.5 \times 10^9 \text{ m}^3$  of water should reach Puget Sound annually. The five major gauged rivers entering the main basin contribute  $3.1 \times 10^9 \text{ m}^3$  per year. This large discrepancy can be accounted for in part by a significant ground water drainage. For example, the Kitsap Peninsula (Great Peninsula) consists of unconsolidated, glacially derived sediments with a high water table and no major rivers.

Approximately a total of  $2.48 \times 10^6 \text{ mt}$  of sediment (suspended and bed load; mostly suspended) are discharged into the main basin annually. Thus the average load is  $1 \text{ mg L}^{-1}$ . It is worth noting that the two most contaminated rivers contribute only a total of 9% of the total sediment discharge to the main basin. Thus, once the contaminated sediments are carried into the main basin, they are probably diluted ten-fold unless, of course, the contaminated sediments have unique properties that facilitate winnowing and concentration.

#### 1.1.3. Objectives

Specific Objectives for each process study (Subproject) are given in the individual Research Reports that follow. The Overall Objectives of the Project are:

- To determine the historical urban and industrial pollutant sources to Puget Sound and to compare history with the record of pollutant deposition in the sediments.
- To determine the budgets, residence times, and ultimate fates of selected pollutant compounds associated with particulates in large estuaries, and to correlate these processes with physical forcing and chemical transformation.
- To predict the future concentrations of selected pollutant compounds in sediments based on projections of urban and industrial growth and alternative waste management scenarios.
- To provide information and data derived from the foregoing Goals to assist in formulations of assimilative capacity of estuaries.

#### 1.1.4. Relevance to Problems of Marine Pollution

Estuaries are critical marine ecosystems because they are productive biologically, receive pollutants from upstream water courses, or are the sites of pollutant generation from urban and industrial development, and possess circulation patterns that tend to retain pollutants. The assimilative capacity of an estuary for a pollutant or for a suite of pollutants principally is a function of the perceived environmental effects which, in addition to socio-economic concerns, are a function of the pollutant's physiological effects, residence time in the environment, biological availability and uptake, and physical and chemical transformations.

Table 1.1. Dates and locations of sampling expeditions for rivers discharging into Puget Sound.

SAMPLING EXPEDITION	INCLUSIVE DATES	SAMPLING REGION (River)
Duwamish River Estuary Cruises		
DEC-1	11 Aug - 12 Aug 1979	Duwamish, Elliott Bay
DEC-2	19 Feb - 20 Feb 1980	Duwamish
DEC-3	11 Sept - 12 Sept 1980	Duwamish
DEC-4	1 Mar - 2 Mar 1982	Duwamish
Trace Metal Inventories - Rivers Discharging into Puget Sound		
TIPS-1	23 June 1980	Skagit, Stillaguamish, Snohomish, Duwamish, Puyallup, Nisqually
TIPS-2	23 Sept and 2 Oct 1980	Skagit, Stillaguamish, Snohomish, Duwamish, Puyallup, Nisqually, Ship Canal
TIPS-3	2 Jan and 7 Jan 1981	Skagit, Stillaguamish, Snohomish, Puyallup, Nisqually, Ship Canal, Skokomish
TIPS-4a	25 Mar 1981	Puyallup
TIPS-4	28 May and 3 June 1981	Skagit, Stillaguamish, Snohomish, Duwamish, Puyallup, Nisqually, Ship Canal, Skokomish
TIPS-5	7 Oct - 9 Oct and 13 Oct 1981	Skagit, Stillaguamish, Snohomish, Duwamish, Puyallup, Nisqually, Ship Canal
TIPS-6	26 Jan 1982	Duwamish

Table 1.2. Dates and locations of Puget Sound cruises and sediment trap deployments and recoveries.

SAMPLING EXPEDITION	INCLUSIVE DATES	SAMPLING REGION
Long-Range Effects Cruises		
L-RERP 80	19 May - 3 June 1980	Main Basin of Puget Sound
L-RERP 81-1	5 Feb - 6 Feb 1981	Main Basin of Puget Sound
L-RERP 81-2	30 Apr - 1 May 1981	Main Basin of Puget Sound
L-RERP 81-3	16 Jul -17 July 1981	Main Basin of Puget Sound
L-RERP 81-4	25 Aug - 2 Sept 1981	Main Basin of Puget Sound
L-RERP 81-5	3 Nov - 4 Nov 1981	Main Basin of Puget Sound
L-RERP 82-1	22 Feb - 24 Feb 1982	Main Basin of Puget Sound
Sediment Trap Deployments and Recoveries		
STE-1	5 Dec - 3 Feb 1981	47°41.9' 122°27.2'
STE-2	8 Feb -15 Apr 1981	47°41.9' 122°27.2'
STE-3	26 Apr - 5 July 1981	47°41.5' 122°27.5'
STE-4	24 July-29 Sept 1981	47°41.7' 122°27.2'
STE-5	15 Oct - 19 Dec 1981	47°41.7' 122°27.3'

Data on bioavailability and uptake, and physiological behavior are best undertaken under controlled laboratory conditions, whereas the remaining processes are affected by the unique configuration and hydrographic and chemical characteristics of the estuary and must be studied in the field.

The pollutants of concern are toxic organic compounds: polycyclic aromatic hydrocarbons (PAH's) and chlorinated compounds, and trace metals: lead, copper, chromium, zinc, nickel, iron, and manganese. Polycyclic aromatic hydrocarbons have both natural sources, such as forest fires, and anthropogenic sources. They are toxic, carcinogenic, and persistent. With the exception of a relatively few low molecular weight compounds (e.g.  $\text{CH}_3\text{Cl}$ ), the chlorinated species are entirely formed by human activities for a variety of purposes (e.g., pesticides, solvents, transformer fluids, etc.). Because of their toxicity and persistence, these compounds present a long-range threat to marine organisms, particularly in estuaries where nutrients and toxic materials are constantly recycled. The metals lead, copper, chromium, zinc, and nickel are toxic, whereas iron and manganese form chemical precipitates of the toxic compounds. The selection of elements is on the basis of their toxicity, abundance and chemical/biochemical mobility in estuarine systems.

Management decisions are being made in all North American estuaries on a continuing basis. In Puget Sound alone overt decisions have been made or are being made on whether to: dredge and re-dispose of contaminated sediment, relocate sewage effluent outfalls, defer the switch to secondary treatment of effluents, build ship-loading facilities, deepen ports and build or expand waterfront manufacturing plants. Many other decisions are covert, inadvertent, by omission or indirectly affect the quality of estuaries: land-use decisions, zoning, individual decisions to relocate, formation of sanitary districts are a few. Many of these decisions are not based on a consideration of the ecological consequences of an activity (Fig. 1.5) although most people believe they should be. Moreover, we cannot judge the ecological consequences of activities without a knowledge of how a system works.

This research is expected to provide information on long-term cause-effect relationships that must be known and quantified before well-directed policy and be defined or overt management decisions made.

In Puget Sound there are two distinct classes of pollution problems: problems associated with localized, perhaps short-term, industrial activity and long-term growth-related problems. The former have created the most concern: the industrial refuse in the Hylebos Waterway in Tacoma, and around Harbor Island in the mouth of the Duwamish River, and the PCB spill in the Duwamish River for example. The growth-related problems are largely those of the disposal of municipal wastes; the level of treatment and location of disposal sites. These two classes of pollution problems tend to be confused, but they have different origins and different control or remedial strategies. In assessing the transport and transformation of particulate-bound pollutants we will make our results applicable to both classes of problems and their control.

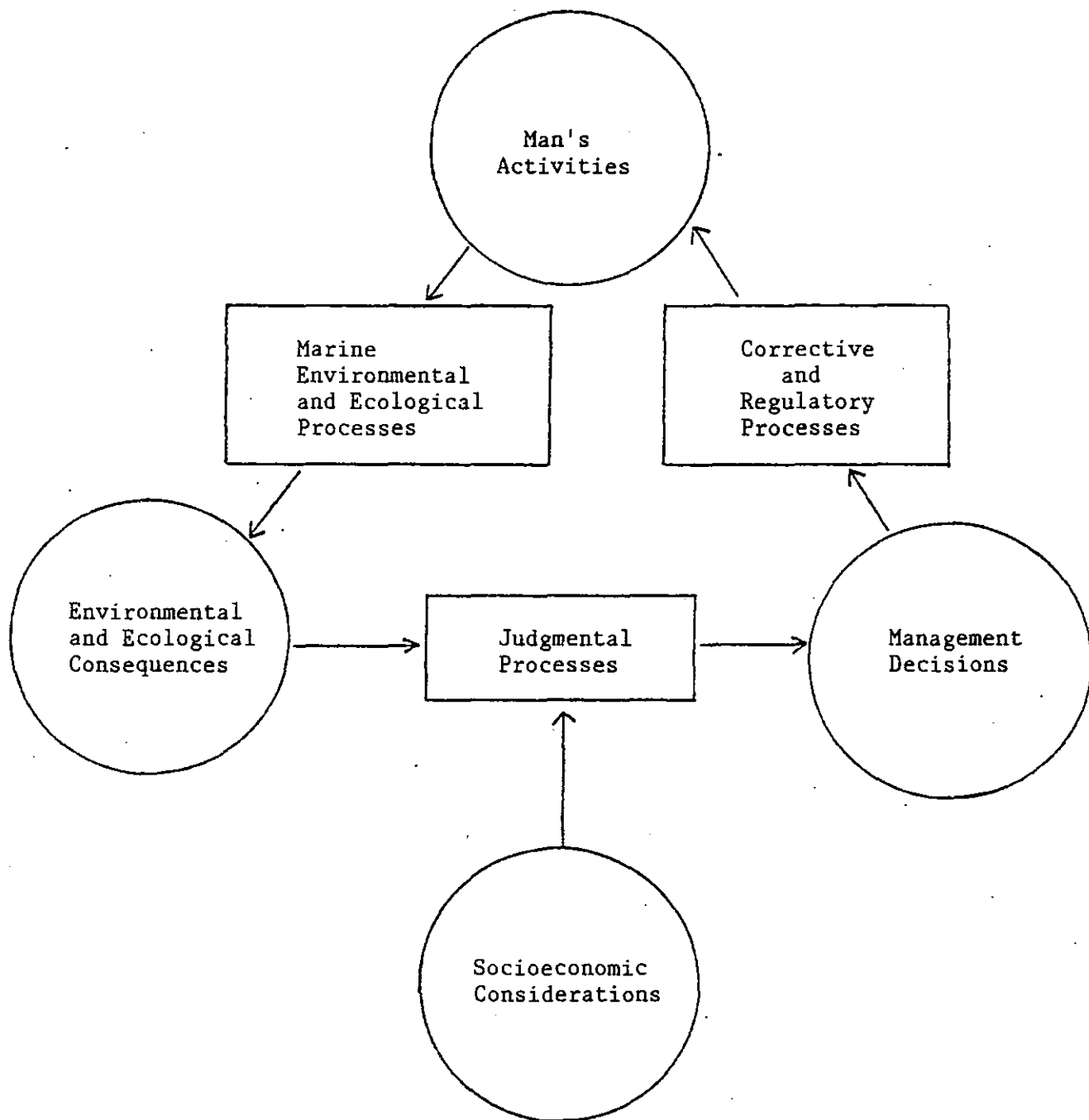


Figure 1.5. The 202 Program Ocean-Use Management Model.



## 1.2. CURRENT STATE OF KNOWLEDGE

This Project encompasses such a breadth and depth of subject matter nothing less than a literature review of some of the following topics is called for: estuarine circulation, behavior of particle-bound pollutants (see Kimrey, 1982, for a statement of current status and immediate research needs), current and future management decisions affected by pollutant buildup in estuaries, the evolving concept of assimilative capacity and its variants. We are willing to explore the preparation of one or more such reviews as one of the products of the out years of the Project.

Each Research Report summarizes the current state of knowledge for the processes involved. This summary will briefly review the kind of information now available in comparison to what we think we need to know.

At this point, apart from the work we have initiated and describe here, there has been no concerted effort by any agency to itemize the pollutant sources to Puget Sound on a watershed basis. The data for gasoline use, various manufacturing activities, forest fires, and petroleum and coal use and mining are available but have never been collected or analyzed. We are currently developing a hierarchical model and assembling the data base.

No models of river plumes in Puget Sound have been run until now. This activity will continue at a low level in FY83 and will be continued for Commencement Bay if sufficient data exist. Our modeling approach permits a determination of the rate of sedimentation from the plume as it traverses the salt water estuary, suggesting what the distribution of contaminated sediments on the bottom should be.

A considerable body of data has been accumulated over the past ten years by PMEL on the general circulation of Puget Sound which has led to the formulation of a number of testable hypotheses. This data set was fundamental in construction of a two-dimensional box model of water transport. We are now at the stage of measuring net flux through discrete cross sections of the Sound to provide additional data for the box model.

Two tidal models are currently available for Puget Sound, a physical hydraulic model and an empirical model based on extrapolation between currents observed at instrumented sites. Neither model is adequate for predicting the vertically averaged tidal currents in the main basin which are required for use in driving the bottom boundary layer model.

Although Puget Sound has a data base relating to hydrographic properties that goes back 50 years, there has been no work on the processes controlling the distribution of suspended matter or the distributions themselves. The processes are poorly understood in general, surprisingly, particularly in regard to settling in turbulent media, aggregation, and resuspension. The research described herein is totally new for Puget Sound and is contributing to an improved understanding of estuarine particulate transport in general.

Our research on benthic sedimentation processes is among the first to integrate the role of the bottom boundary layer current with the phenomena of erosion and deposition and complements the efforts being undertaken by the HEBBLE program. Our laboratory observations of erosion and deposition and their relationship to field observations.

Only in the last few years have a few analyses been made of trace metal concentrations in surficial sediments of the central basin. Even fewer have been made on suspended matter or in dissolved form. Analyses are presently being made on cores taken by us and for METRO, and a continuing series in polluted embayments are being taken by the Northwest and Alaskan Fisheries Center (sediments and organisms) under the MESA program. This activity is documenting the extent of contamination but not the processes involved.

In the past ten years considerable attention has been given to documenting the distribution of aliphatic hydrocarbons in organisms and sediments by investigators concerned with the potential effects of crude oil spills in Puget Sound and the Strait of Juan de Fuca. More recently, the Puget Sound MESA Program has supported investigations into the distribution of aromatic compounds in estuaries, bays, and inlets of Puget Sound. One study of the vertical flux of PAH compounds has been made in Dabob Bay, and a study was recently completed of the contribution of aliphatic and PAH compounds by the West Point (Seattle) sewage treatment plant.

### 1.3. SUMMARY OF WORK ACCOMPLISHED DURING FY80-FY82

The results described in this report cover work conducted through September 1982, including both field and laboratory research. The research conducted specifically under this Project since 1980 began much earlier as part of the other programs and without the present programmatic justification under the L-RERP Program. Some efforts began as early as 1970 (circulation studies) and others as late as 1982 (the several modelling activities). Even during the reporting period some of the efforts contributing to the results reported here were part of other programs (MESA, PMEL in-house). No attempt will be made in this summary or in the following reports to provide attribution, but we would not be at our present stage without the support provided by other programs.

A summary of field activities is provided in Tables 1.1 and 1.2. Our efforts in FY79 and FY80 were directed primarily at the processes occurring in rivers with salt wedges, principally the Duwamish and in two major embayments, Commencement Bay and Elliott Bay. In the Duwamish we studied the behavior of trace metals and organics from the Renton Sewage Treatment Plant as they flocculated in the salt wedge and were transported into the estuary mouth. In the two embayments we examined the transport of suspended particulate matter in surface river plumes and bottom nepheloid layers. Studies of circulation in the main basin and near the sills suggested that most of the material entering the Sound from rivers or directly had the sediments of the main basin as their ultimate sink. The question then arose as to the rate of transport into deeper water (or, conversely, how stable were materials in the shallow embayments) and their final fate.

In FY81 measurements began at station PS7 off West Point and in Commencement Bay to assess the rates of sedimentation of particulate-bound pollutants in the main basin. Sediment traps, current meters and transmissometers were deployed at both locations and samples for chemical analysis were taken from both sediment trap samples and cores. A conceptual model was developed for all the processes affecting the transport and transformation of pollutants and some box models were constructed in an attempt to derive budgets of selected pollutants, principally PAH's. These models helped to point out the areas where data were absent or inadequate.

The work in FY82 could be characterized as the end of the beginning. Up to that point we had concentrated on specific processes that affected the transport and transformation of water-borne pollutants, but did not address the overall impact of pollutant inputs. The previous two years' research had convinced us that a unified approach was possible and necessary. Therefore, we developed a project plan that included conceptual modeling of pollutant inputs on a watershed basis, modeling of transport processes, observations of the horizontal and vertical movement of water and suspended material and observations of movement of materials in the bottom boundary layer, observations of the vertical depositions, burial and decomposition of polyaromatic hydrocarbons. In addition we contracted for analysis of sediment cores for age-dating and vertical distribution of trace metals and for measurements of fluxes of materials across the sediment-water interface. The overall goal of these separate efforts has been to characterize the behavior of particulate-bound pollutants in marine estuaries and to estimate the long-term rates of accumulation of pollutants in sediments. These studies constitute a rather full menu and will take several years of effort to produce a coherent pattern.

#### 1.4 ACCOMPLISHMENTS AND RELEVANCE

##### 1.4.1. Econo-Demographic Model (3 months 1982)

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We have begun to establish historical data bases on a regional basis for population, watershed area and changing land use, auto registration, fuel use, forest fire, manufacturing, etc. The primary data are being entered and statistical tests are being performed to allow correlation amongst the variables and conversion from one data base to another. Interactive data bases of this kind are essential to understanding the pollution history of a receiving basin and analyzing and extrapolating trends.

##### 1.4.2. Fate of Riverine Discharge (6 months, 1982)

A physical and analytical model has been developed to determine where particles fall out as a buoyant river plume traverses a marine embayment. The unrefined model was run for two different discharge rates and high and low wind stress and gave reasonable results for the shape and velocity of a plume from the Duwamish River in Elliott Bay. When the model is complete it will be possible to hindcast deposition

sites for river plumes in the past using river discharge and tidal height data during flushing episodes. In turn, the prediction of deposition sites will improve our ability to improve sampling strategies and the use of techniques such as stratified random sampling.

#### 1.4.3. Eulerian Transport (1 year, 1982)

It has been well documented that Puget Sound bottom water is renewed fortnightly when spring flood tides exceed 3.5 m or during neap floods when vertical mixing allows undiluted salty water to enter from outside Admiralty Inlet over the sill. These incursions produce density currents that, together with the tidally generated bottom currents, resuspend and transport bottom sediment southward. In addition, approximately half the seaward flowing surface water with its burden of suspended matter may be refluxed downward at the sill and transported southward, as well. Bottom water is upwelled at the southern (Tacoma Narrows) sill. Current meter measurements have also demonstrated a "ratcheting" effect around Vashon Island, ebb tides tending to propel water at all depths northward through Colvos Passage on the west side of the island and flood tides moving water southward on the east side. The sum of these patterns is to retain water and entrained material within the estuary. We have targeted Poverty Bay as the region most likely to be the ultimate sink for particulate-bound pollutants and have designed an experiment for FY83 to test this hypothesis.

#### 1.4.4. Tidal Model (3 months, 1982)

A new grid mesh is being generated for Puget Sound. The technique being used is being adapted since most tidal models have been applied to wide shallow embayments with smooth coastlines. Bottom depths for the entire Sound are being digitized.

#### 1.4.5. Particle Flux in the Water Column (3 years, 1980-1982)

The combined use of transmissometers, current meters, and sediment traps has revealed some of the significant features of particulate-bound pollutants in Puget Sound. Most river-borne surface particles are deposited from plumes flowing along the shoreline except during maximum flow when the plumes expand horizontally. In the main basin surface particulates are removed as fecal pellets settling of downward refluxing at Admiralty Inlet. It is becoming obvious that mechanisms exist for the retention of particles in Puget Sound which exceed those of other estuaries with exception of fjords with very shallow sills. The "self-cleansing" machinery in Puget Sound appears limited at best.

#### 1.4.5. Bottom Boundary Layer Transport ( 1 year, 1982)

The accomplishments of this subproject, while significant, differ from what we had originally anticipated. In 1981 a joint experiment in Puget Sound was discussed with staff at AOML in Miami. This experiment

would have used bottom-mounted tripods instrumented with current meters, transmissometers, sediment traps, and a "Sea-Flume" (designed to measure erosion rate under controlled velocities). Availability of the tripods and loss of personnel at AOML precluded conduct of the experiment. Instead, instruments were placed on a tripod constructed at PMEL (minus the Sea-Flume) and data were obtained for an 11-day period. Data were also available from a regular current meter mooring located 1 km south of the tripod.

Strong tidal currents at the bottom with a net southerly signature transport significant quantities of sediments. Fine sediment concentrations increase six-fold about background when current speeds reach 30-40 cm/sec. The settling velocity distribution appears to be bimodal, i.e., particles less than  $0.1 \mu$  stay in suspension and constitute a background of 1 mg/l; larger particles are deposited and resuspended. Two types of models were developed and applied to data from the moorings in Puget Sound and data from the literature from Chesapeake Bay, the North Sea and laboratory flume experiments. Several results are worth mentioning here: in situ erosion rates for fine sediment have been calculated for the first time, chronically resuspended materials appear not to have erosion threshold velocities (the material to a depth of 0.25 cm is in an almost constant state of flux), and a generalized form of the bottom-stress dependence on eddy viscosity has been developed (leading to a more accurate numerical calculation of flow). The findings on the drag coefficients measured very close to the bottom will be used in the tidal model. These results are already influencing our thinking on the mode and rates of movement of contaminated particles, particularly as pollutants may be bound to different size-classes with differential rates of movement.

#### 1.4.6. Transport and Transformation of Trace Metals

Trace metals discharged from the Renton Sewage Treatment Plant and industrial discharges along the river (principally at Harbor Island) are flocculated and transported as suspended particulate matter into Elliott Bay where high surface levels of metals exist at the mouth of the Duwamish and high bottom levels in main basin water or in Elliott Bay. A similar distribution occurs in the main basin. The gradients of trace metals are clearly related to scavenging and co-precipitation with manganese. The competition between manganese and organic flocculants for trace metals directly determines the availability of the metals to organisms. One result of these studies will be an examination of the potential location of waste-water outfalls with respect to areas of rapid formation of manganese-iron oxides in the water column.

The results from the main basin are from a single station. Next year's sampling at multiple stations will provide much improved resolution of settling rates.

#### 1.4.7. Transport and Transformation of Polycyclic Aromatics

##### Polycyclic Aromatics

Polycyclic aromatics (PAH's) originate from "natural" and anthropogenic sources; principally as combustion products, natural plant products, industrial processes and sewage treatment. We have documented the occurrence of plant waxes and combustion PAH's in the Duwamish River and the Puget Sound Main Basin. Combustion PAH's increase below the Renton treatment plant and are particularly enriched around Harbor Island at the river's mouth. Although the treatment plant is an important source the concentrations around Harbor Island appear to be of local, industrial origin and combined sewer overflows.

In the main basin the accumulation rate of PAH's was measured as  $8.5 \mu\text{g m}^{-2} \text{d}^{-1}$  at PS7 off West Point. This rate was somewhat larger than the seasonally adjusted flux rate of  $6.7 \mu\text{g m}^{-2} \text{d}^{-1}$ . One explanation is that PAH are being transported from somewhere else in the bottom nepheloid layer.

PAH input into the bottom layer was fifty percent lower in summer than in winter probably reflecting decreased use of home heating oil. Age dating of sediments shows a PAH maximum in the years 1940-1955 corresponding to the period of maximum use of coal for home heating. Compounds comprising the unresolved complex mixture and n-alkanes increased sharply in the 60's reflecting a change from raw sewage discharge to primary treatment at West Point. It is clearly possible to follow trends in the sedimentary record, an effort to which we will be giving increased attention during the next three years.

#### 1.5. FUTURE PLANS

Our Objectives for the next three years remain the same (see Sec. 1.1.3). To accomplish these objectives we have proposed the following strategy beginning in FY83.

##### 1.5.1.

We have collected 20 long (2 m) sediment cores from the main basin of Puget Sound for age dating. These cores will be analyzed for trace metal and organic pollutants and will provide a history of pollutant inputs to these as a function of distance from putative sources of contamination. This data set will provide information on geographic variability of sedimentation rates, pollutant accumulation and transformation.

##### 1.5.2.

A picketline of moorings with current meters, sediment traps, and transmissometers, will be placed across Puget Sound, north and south of East Passage and Poverty Bay, the likely ultimate resting place for

pollutants introduced with Puget Sound. The deployment will take place in late spring during the period of highest river runoff and spring tides. We will measure bulk transport of water and dissolved and particulate compounds using current meters and transmissometers and will measure vertical transport using sediment traps. The sediment trap material will be analyzed for trace metals and PAH's. This experiment is a test of our working hypothesis that East Passage and Poverty Bay are the final resting place of pollutants introduced either in diffuse form or as translocated deposits (e.g., dredge spoils). We anticipate seeing a net difference between incoming and outgoing material. The sampling density should be sufficient to account for eddies, temporary current reversals, etc. in three dimensions.

1.5.2.

The pollutant input model will be refined, data bases expanded, and updated. The model itself will be documented and made available to other users. We are considering offering it on a fee basis to agencies such as the US Army Corps of Engineers and the Puget Sound Council of Governments.

1.5.3.

The tidal model will be completed in FY83 and used to refine the benthic bottom layer model and to produce a library to tidal trajectories and velocities for specific times and locations in Puget Sound. Since the model should solve some of the problems associated with predicting tidal transport in an irregular, narrow, deep estuary it will be documented and made available to other potential users.

1.5.4.

The refined benthic boundary layer model will be tested as part of the field experiment and will be applied to preexisting data from the literature. It will be used to predict the rate of movement of the benthic bed load as a function of tidal current velocities.

1.5.5.

Processes affecting the mobility of buried trace metals and toxic organics in sediments will receive major emphasis to determine remobilization, stabilization, and bioavailability, particularly to benthic infauna.

## 2. RESEARCH REPORTS

### 2.1. INPUT FUNCTIONS

#### 2.1.1. River Basin Land Use Model

### I. INTRODUCTION

#### A. General Nature and Scope of Study

A pollutant source model for the Puget Sound Region is under development. When completed in FY83 it will facilitate the study of pollutant accumulations by making available a host of time series of demographic, economic and environmental data. This information then will be regressed with data on the measured accumulation of pollutants in sediments and the regressions will be used to identify the principal pollutant sources, transport mechanisms and sinks. These studies lay the ground work for the forecast of future accumulation rates.

#### B. Specific Objectives

The purpose of this year's work was to gain some familiarity with the data with a special focus on the Duwamish-Green River watershed. The principal activities were to:

- o Acquire a representative sample of the readily available data;
- o Examine this data and identify the critical gaps and potential problems;
- o Develop computer software for archiving and displaying the data.

#### C. Relevance to Problems of Marine Pollution

There is considerable uncertainty surrounding the ultimate fate of pollutants in estuaries. Are they flushed from the system by the outflowing surface layer? Do they accumulate in a few locales characterized by high sediment deposition rates? Are they incorporated into the food chain and dispersed throughout the system or even transported from the estuary? Or are they uniformly distributed by sediment transport throughout the region? The answers to these questions must rely on some estimate of the pollutant budget within the estuary. The total amount of pollutant introduced to Puget Sound forms the input side of a pollutant budget. The output side of the budget is the subject of a variety of related field studies. The degree of certainty we have regarding the program's identification of the transport, deposition and dispersion mechanisms will ultimately rely on the degree to which the budget is in balance. Thus the pollutant source model is an integral part of the study of the region's assimilative capacity.



## II. CURRENT STATE OF KNOWLEDGE

To our knowledge, this is the first attempt to compile an extensive history of this type for the Puget Sound region. Rather surprisingly, we are finding that many municipal agencies retain records for only a few years, and there is no ready source for much of the information we seek. We are filling a real void in the documented history of the region.

## III. STUDY AREA

The Puget Sound region is a diverse area, characterized by a large urban center located around Seattle with outlying regions that remain relatively undeveloped. Although many regard Puget Sound as a pristine fjord, by 1975 there were over 300 entities that held permits for the discharge of municipal or industrial waste into Puget Sound (Stevens, Thompson and Rungan, 1976). In the same period, the Puget Sound region provided employment for approximately 850,000, and total population was at 2,250,000, with 1,824,000 living in the greater Seattle-Tacoma metropolitan region. The population of King County was 1,150,000 and that of the City of Seattle was about 550,000. The average flow of all industrial and municipal waste water discharges in this region was approximately 22 m<sup>3</sup>/s. (By comparison, the ten largest rivers in the region range from the Skagit at 461 m<sup>3</sup>/s annual average to the Cedar at 20 m<sup>3</sup>/s.) The total biochemical oxygen demand of all discharges was 2.5 million pounds per day. The principal dischargers were METRO of Seattle (5.4 m<sup>3</sup>/s at West Point, 1.3 m<sup>3</sup>/s at Renton, and .6 m<sup>3</sup>/s at Alki Point); the Scott Paper pulp and paper mill in Everett (3.0 m<sup>3</sup>/s); the Weyerhaeuser bleached Kraft pulp mill in Everett (1.5 m<sup>3</sup>/s); the St. Regis pulp and paper mill in Tacoma (1.4 m<sup>3</sup>/s); and the Tacoma Sewage treatment plants (1.3 m<sup>3</sup>/s). The largest source of BOD was the Scott paper and pulp mill in Everett (506,800 lbs/day). The METRO effluents were the largest permitted sources of all the other commonly measured water quality parameters (64,600 lbs. total suspended solids/day, 40,800 lbs nitrogen/day, 7,000 lbs phosphorus/day, and 98,100 lbs/BOD day).

Contributing also to pollutant levels in Puget Sound were a variety of non-point sources, such as highway runoff and atmospheric fallout. The pollutant quantities contributed by these sources are associated with a variety of economic and recreational activities, such as the operation of motor vehicles and trucks. In King County, for example, over 690,000 passenger vehicles were registered in 1975, or better than one vehicle for every two people. All of these vehicles burned leaded gasoline, until recently, and they may have contributed to pollutant levels in Puget Sound both through highway runoff and through the fallout of lead particles from the air.

There is also a substantial forest industry and it is presently believed that runoff from clear cut and slash-burned hills may contribute to the level of some of the polyaromatic hydrocarbons that are found in Puget Sound sediments. In the Duwamish-Green River watershed, as much as 7% of the total acreage (21,940 acres out of 310,000 acres) may have been in this clear-cut state in 1979.

#### IV. SOURCES, METHODS AND RATIONALE OF DATA COLLECTION

A variety of methods have been utilized to acquire the data for this study. A substantial part of the data is available in the University of Washington Library system, and several person weeks have been spent going over the Library's census holdings. In addition to readily available library publications, the U.W.'s Urban Data Center provides (at some cost) an automated data retrieval service based on the census tapes. We are presently considering making use of this service in the near future. We have also interviewed a number of experts on the history of Seattle, foremost being Dr. James R. Warren, Director of the Museum of History and Industry. He directed us to several references that have proven of value, and he arranged for us to have access to some of the Museum's special holdings on Chamber of Commerce publications and the like. We have also contacted a number of state, local and federal agencies that have records of interest to us. The State Department of Licensing has provided us with vehicle registration data dating from 1901. The State Department of Ecology has briefed us on their holdings and we have visited their offices in Olympia. The U.S. Forest Service has been contacted regarding fire records, and they directed us to a variety of data sources on this topic. We acquired Water Supply Bulletin 43, "Reconnaissance Data on Lakes in Washington," vols. 1 through 7, from the Department of Ecology. A summary of the moorage industry was obtained from Prof. Stokes of the University of Washington's Institute for Marine Studies (Goodwin and Stokes, 1980). Precipitation records and patterns have been obtained from the National Weather Service. We obtained a variety of studies and data products from METRO, and we obtained some effluent data from the Tacoma sewage treatment plants. We also acquired a variety of environmental impact statements for the region, and these are being examined to cull any special information they might contain.

The Army Corps of Engineers publishes a summary of water-borne commerce annually, and we are in the process of extracting the applicable data from this source. Other federal agencies that may have records of value to us include the EPA and the Department of Transportation. We have already obtained some EPA data, but we expect this source to be utilized more heavily in the coming year.

#### V. RESULTS

This year, our effort was focused on obtaining the more readily available data, and on preparing the computer software required to manipulate and present it. The readily available data turned out to be the various census products (population, households, etc.), land use information from governmental agencies and from the analysis of satellite imagery, and a variety of vehicle registration data. We also located, but did not acquire, data pertaining to forest fires, to the consumption of motor vehicle fuel, to the import and export of various hydrocarbons, and to the level of business and industrial activity in the Seattle and Tacoma regions.

The Duwamish-Green River watershed was selected as a test case for the development of our procedures. One product we would like to develop

is the population in the watershed dating back to 1890. From the Puget Sound Council of Governments, we obtained a METRO study that used census tract records to establish the population in 1970. This study also forecast the population for 1976, 1980, 1990, and 2000. Other readily available products include yearly and/or decadal populations of Seattle, Kent, Auburn, Tukwila and Renton. In principal, these should allow us to make some estimate of the watershed's population. For example, in 1970, the population in the Duwamish-Green River watershed was placed by METRO at 187,300. Of this total, 68,995 lived in the Duwamish Estuary portion of the watershed. This is about 12% of Seattle's population. If we assume this fraction is fixed through time, then we could estimate the watershed's population as 48,000 in 1930, for example. However, this is a very indirect way of estimating this value. It would be far better to obtain the census tract data for the preceding decades and calculate the number directly. Or if this proves to be unfeasible, it would be preferable to make the extrapolation using a more complete set of data so that the reasonableness of the 12% fraction could be assessed.

We also acquired a variety of land use data. The USGS publishes a very detailed set of land use maps, but these are extremely difficult to reduce to tabular form. Each map consists of thousands of numerically coded regions, the individual entries being as small as a neighborhood play field. The Puget Sound Council of Government also produced a land use study for the Duwamish-Green River watershed, and their data is in tabular form. The other source of land use data that we investigated was via computer processing of Landsat imagery. The University of Washington's Remote Sensing Applications Laboratory was contacted, and Mr. James Eby performed an analysis of a July 20, 1979 Landsat scene (Eby, 1982). The primary purpose of the study was to develop tabular data of land usage for all the Puget Sound watersheds. Examples for the Duwamish-Green and Puyallup watersheds are shown in Table 2.1. Also produced by Mr. Eby were several color slides depicting land usage. Figure 2.1 is a print of one of these slides for the Puyallup watershed. Mt. Rainier is in the lower right, and Tacoma is in the upper left. The red color depicts residential and commercial areas; yellow is grassland, cropland or alpine meadow; blue is clear cut; and olive is forest.

## VI. DISCUSSION

This report is to be viewed as a progress report, written at about the 33% completion point. In the course of our investigation to date we have identified some major data problems, and they include:

- o Difficulties in breaking out census data on a watershed specific basis.
- o Lack of historical records on discharge from municipal sewage treatment plants.
- o Sparsity of other records, such as the forest fire records, over fairly extended periods of time.

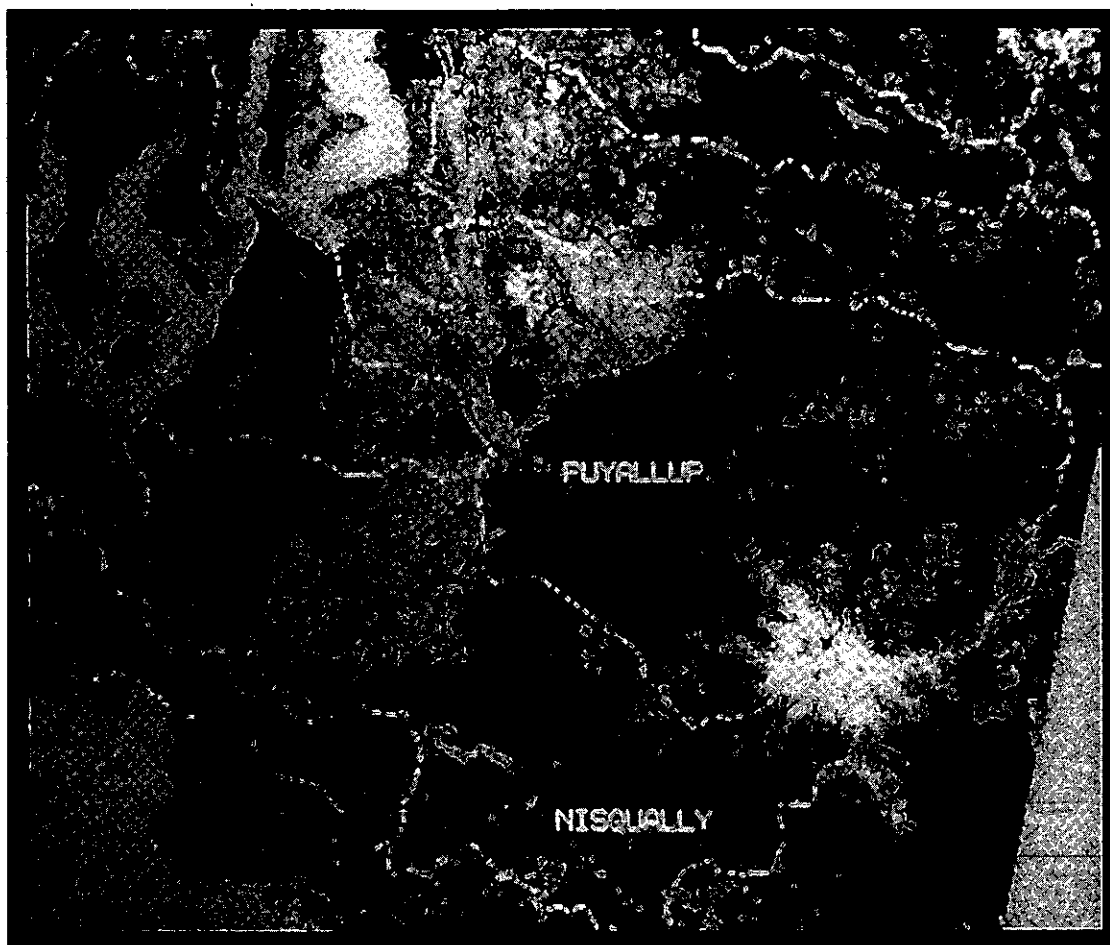


Figure 2.1. Land use in the Puyallup watershed, 1979.

Table 2.1

## Watershed Land Usage from 20 July 1979 Landsat Imagery

Category	Duwamish-Green		Puyallup	
	Acres	%	Acres	%
Inland Water	2038	.66	3281	.52
Forest	176621	57.15	414433	65.77
Grassland	24390	7.89	31724	5.03
Cropland	5345	1.73	5717	.91
Brush	29388	9.51	32020	5.08
Residential	21334	6.90	13122	2.08
Commercial	10262	3.32	3688	.59
Bare ground	10266	3.32	23748	3.77
Tideland	263	.09	347	.06
Clear Cut	21940	7.10	38770	6.15
Alpine Vegetation	372	.12	12801	2.03
Bare Rock	530	.17	18865	2.99
Snow	0	0	14156	2.25
Cloud	0	0	0	0
No Data	6308	2.04	17408	2.76

In some cases, those data exist, but we will have to go to the primary data sources to retrieve the data. In other cases, the data are lost and cannot be recovered, although it may be possible to reconstruct the lost information from related records. The focus of an important portion of our work in the coming year will be the development of statistically meaningful extrapolation and interpolation formulas so that we can create valid estimates of the missing sequences.

## VII. CONCLUSIONS

Progress to date has been good, and the information will be a valuable contribution to our understanding of pollutant assimilation in Puget Sound once it is assembled. No insurmountable problems have been discovered.

## VIII. NEEDS FOR FURTHER STUDY

The ultimate goal of this work is to document the historic, demographically related, pollutant inputs to the southern main basin of Puget Sound. The work performed this year was a start on this, but much needs to be done. It now appears necessary to dig into the census data on a tract-by-tract basis for at least two of the decadal counts. We have the 1970 values, and these could be usefully extended with watershed specific analyses of the 1910 and 1940 census results. We also need to obtain the state and federal forest fire files. These records cover only the last thirty years, more or less, but they can be supplemented with the 1902 USGS Timber Survey. We also need to establish and document the discharge histories of the principal present day discharges. Numerous other data sources need to be examined.

At the same time, we need to perform a variety of analyses on the primary data to establish useful regressions that will allow us to interpolate and extrapolate our somewhat sporadic time series. These studies will form the factual basis for some of the time series, and so they form an important link in the whole process.

## IX. REFERENCES CITED

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## 2.1.2. FATE OF RIVERINE DISCHARGE

### I. INTRODUCTION

#### A. General Nature and Scope of Study

Substantial quantities of pollutants are routinely discharged into rivers by municipalities and industries all across the nation. Water quality standards are, of course, applied to these discharges to protect downstream users, but little thought has been given to the fate of the pollutants once the river discharges into coastal or estuarine waters. It is now evident that organic and mineral particulates scavenge and concentrate the pollutants at the interface between the fresh effluent and the saline receiving waters (Feely, Massoth, and Lamb, 1981). This suggests that dilution properties determined for upstream locations may not be representative of conditions obtaining in the salt wedge and delta regions of the river. The general purpose of this study is to better characterize the accumulation, resuspension, advection and diffusion characteristics of a typical estuary so that we can improve our ability to responsibly manage the use of rivers as conduits for hinterland pollutants.

The prototypical estuary we have selected for this study is the Duwamish River which discharges into Elliott Bay in Seattle, Washington. Extensive work has been performed by PMEL investigators on the interaction of pollutants with suspended particulates in this estuarine system, and there is a substantial body of literature describing its physical characteristics. Hazardous levels of organic pollutants have been found in fish in the lower reaches of the estuary (Malins, Brown, Sparks, and Hodgins, 1980).

Over much of the year, the Duwamish discharge is in the range of 10 to 30 m<sup>3</sup>/sec, and in these circumstances, the toe of the salt wedge can be found as far upstream as 10 to 12 km from the mouth of the river in Elliott Bay (in very low flow and high tides, it can reach as far as 16 km upstream). The sediments in the vicinity of the toe in low and average flows have been shown to be fine-grained and much enriched with trace elements and organic pollutants (Feely, personal communication, 1982). Under conditions of high discharge, say 100 m<sup>3</sup>/sec to (rarely) 300 m<sup>3</sup>/sec, the salt wedge is swept downstream 3 to 5 km and the fine-grained material is resuspended and carried off. These particulates may have scavenged a substantial portion of the pollutants discharged into the river during low and average flow conditions, and so the high runoff freshets may account for the bulk of the net transport of the pollutants in the upstream portion of the salt wedge region of the river. As the resuspended particulates are swept to the sea, a portion will settle out of the surface layer. Once in the underlying salt wedge, the material will be redeposited, and these deposits will be fairly stable. It has been estimated that 70% to 90% of the river's total suspended load is deposited in the 7 to 10 km reach of the river, but no estimates are available for the fraction of the previously deposited pollutant load that is resuspended and redeposited in the downstream reaches of the

river. In high flow conditions it is likely the bulk of the resuspended material is advected to the river mouth.

When the river discharges into a confined embayment like Elliott Bay, the buoyancy-induced gravity current flow of the fresh but muddy surface waters will enhance the advection of the effluent. The higher the river discharge, the greater this effect will be. Thus, in conditions of high runoff, we may get the complementary benefits of increased resuspension and enhanced advection.

Tending to reduce these beneficial aspects of the Duwamish River's natural discharge and flushing characteristics are dredging of the upper reaches of the river for navigational purposes, and the control of the flow of water by the Howard Hanson Dam. These forms of intervention in the natural processes are typical of many other rivers discharging into an urbanized or industrial embayment.

Dredging has two consequences that must be considered. First, by deepening the channel, dredging stabilizes the location of the salt wedge. Simply put, the stress applied by the surface runoff to the salt wedge remains about the same irrespective of dredging, but the inertia of the underlying salt water increases in proportion to the depth, and the total force required to move the salt wedge increases with depth squared. These reduce the magnitude of the response of the salt wedge to variations in runoff, and so protect the sediment from resuspension. Secondly, the dispersion of dredge spoils is probably much less than that achieved by the buoyancy-induced spread of the muddy freshet.

Reducing the variability of the outflow at the Howard Hanson Dam has obvious advantages for the control of flooding in the winter and the conservation of water during the dry summer, but this reduced variability also serves to protect bottom sediments from resuspension and subsequent flushing. Thus, there are some rather important issues that need to be settled if these multiple and conflicting activities are to be managed rationally.

The PMEL project is a three year study to develop theoretical and empirical techniques that will allow us to predict the accumulation, resuspension, advection and diffusion properties of the Duwamish River estuary as it discharges into Elliott Bay.

## B. Specific Objectives

The principal objectives of this study are to:

1. Develop theoretical and/or empirical models for predicting the transport of resuspended sediments by high discharge river plumes.
2. Estimate the deposition and resuspension sites for low, average and high discharge conditions.
3. Develop a generalized approach for characterizing the dispersive properties of river discharges.



### C. Relevance to Problems of Marine Pollution

The present practices of dredging and river flow control may adversely affect the natural flushing properties of a river as it discharges into coastal or estuarine waters. It is also now apparent that a problem exists in the accumulation of undesired trace elements and organics in the immediate vicinity of the river mouth. The dredging and flow control practices are therefore not without environmental costs. From a management standpoint, this would suggest that an optimal policy could be found somewhere between the following extremes:

- o With existing dredging and flow control practices, impose stricter effluent standards on upstream pollutant sources.
- o Modify dredging and flow control practices to achieve the requisite dispersion with no changes to existing upstream pollutant source standards.

The development of a quantitative model will allow examination and comparison of alternative strategies.

## II. CURRENT STATE OF KNOWLEDGE

The Duwamish River and Elliott Bay have been the subject of a variety of studies that are germane to the present issues. Foremost amongst these are the related OMPA- and MESA-funded studies by PMEL and NMFS scientists on the fate and behavior of organic and trace element pollutants associated with suspended material in the Duwamish. Malins et al. (1980) have documented the unusually high incidence of pollutant-related diseases in bottom-dwelling fish in the East Waterway of the Duwamish. Associated with these findings are collaborative data showing high concentrations of a variety of toxic organics in the flesh of the fish sampled in this region. Massoth, Feely and Lamb (1982) have reported significant enrichment of trace elements, including lead, on suspended particulates in the Duwamish River and Elliott Bay. Hamilton, Bates and Cline (1982) have prepared a preliminary hydrocarbon budget for the river in the vicinity of the Renton Sewage Treatment Plant, and they have identified the principal sources of hydrocarbons, which include aquatic production, plant-waxes, highway runoff, sewage effluent, and the erosion of coal-bearing river sediments. Feely, Massoth and Lamb (1981) have shown that a portion of the dissolved trace-metal burden of the Duwamish River is transformed from the dissolved state to an organic-rich flocculant as the fresh river water mixes with the underlying saline water. Considerable attention has also been given to the accumulation and redistribution of polychlorinated biphenyls in the lower portions of the estuary (Hafferty, Pavlou and Hom, 1977, and Pavlou and Dexter, 1979).

The physical characteristics of Elliott Bay have also been studied. Baker (1981) reported the distribution and characteristics of suspended particulate matter in Elliott Bay during August of 1979 and February 1980. He found evidence of the transport of large diameter particles (order 50  $\mu\text{m}$ ) in the surface layer throughout the bay during February,

but not in August. He attributed this to the increased winter runoff. Roberts (1974) has compiled and charted the available information on marine sediments, showing that clay (.25 to 4  $\mu\text{m}$ ) and silt (4-62  $\mu\text{m}$ ) comprise the bulk of the sediments in the deeper portion of the inner and outer harbor. In the inner harbor, east of Duwamish Head, sand and silt are the principal constituents of the shallower sediments. In the outer harbor, off Alki Beach and Magnolia Bluff, the nearshore sediments are mostly sand (80% to 90%). Sillcox, Geyer and Cannon (1981) reported that currents in the region lying midway between Smith Cove and Duwamish Head were weak, and that they exhibited considerable variation in their vertical structure. Near the bottom, there was some indication of a steady, weak inflow along the southern shore of the embayment, but records from other locations and depths were highly oscillatory with no particular pattern. No long-term current measurements have been obtained in recent years from the inner harbor on account of the shipping traffic.

There is also a fairly well known numerical model of the Duwamish River that has been used to study a variety of water quality problems, most importantly the oxygen budget of the salt wedge. This model is based on the empirical relations developed by Stoner (1972), and the model itself is well described in Prych, Haushild and Stoner (1976) and Prych (1975). Unfortunately, we have found this model to be completely devoid of any dynamical formulation of the equations of motion for a stratified fluid, and so the model has almost no applicability to our problem. The hydrodynamics behind the model may be summarized as follows:

- o The depth of the fresh surface layer as it emerges into Elliott Bay is determined from a linear relationship employing the river's discharge and the daily tidal range(s).
- o The slope of the 25 ppt. isohaline, which is used to delimit the salt wedge, is an independent variable provided by the user (a typical value used by the modellers is .00006).
- o The vertical entrainment velocity is determined via a linear equation based on tidal range and river discharge.
- o The location of the toe of the salt wedge is determined from a second order polynomial in the tidal height in Elliott Bay, where the polynomial's coefficients are dependent on the river's discharge.

Using just the requirement that we conserve mass these relationships can be manipulated to yield an equation for the discharge velocity of the surface layer. The velocity so found will oscillate as the salt wedge moves back and forth in response to the tide, but it will never reverse itself and flow upstream, and for most practical purposes, it could just as well be held constant. These represent substantial failings in the model from our standpoint, but they are apparently acceptable when studying biological and chemical processes.

### III. STUDY AREA

The general nature of the study area is described in the Executive Summary.

The cross-sectional area of the Duwamish River is reasonably well described for the first 20 km with a decaying exponential of the form:

$$A = 7400 * \exp \left( - \frac{x}{3400} \right)$$

where A is the cross-sectional area in  $m^2$ , and x is the distance upstream from Elliott Bay, measured in meters (Stoner, 1972). The depth of the Main Channel is maintained at 16 m in the Waterways (relative to mean lower low water), 12 m for the next 4 km, and from there the depth decreases to 6 m in the area of the Sixteenth Avenue South Bridge (Km 7.5), to a final depth of about 3 m at the 12 km point which marks the normal upstream extent of the salt wedge (this is in the vicinity of the East Marginal Way Bridge).

Suspended sediment loads have been calculated for various flow conditions in the river, and a reasonably good fit to the data is obtained with the equation:

$$SS = 5.341 * 10^{-5} * Q^{2.09}$$

where SS is the suspended solids loading in tons/day and Q is the Duwamish discharge at Tukwila in cfs (Harper-Owes, 1981). Flows in excess of 4200 cfs occur less than 5% of the time, but due to the quadratic-like dependence on flow rate they account for about 52% of the total suspended solids load. The upper one-percentile discharges (8000 cfs and above) account for 21% of the total influx of suspended solids to the estuary. The total influx of sediments is estimated to lie in the range of 158,000 to 203,000  $m^3/yr$ . Dredging records have been analyzed by Harper-Owes (1981) to provide the following estimates of sediment loads by reach. From the mouth of the river to the First Avenue South Bridge (5.5 km), a total of 16,000  $m^3/yr$  is removed to maintain the channel; from the First Avenue South Bridge to the Sixteenth Avenue South Bridge (7.7 km) 17,000  $m^3/yr$  is removed; and upstream of the Sixteenth Avenue South Bridge to the Head of Navigation (10.0 km), about 154,000  $m^3/yr$  must be removed. Thus the lower reaches accumulate about 2% of the sediment load per kilometer, the midreaches accumulate about 5% per kilometer, and in the upper reaches, the sediment load is about 40% per kilometer.

The chemical characteristics of the sediments have also been studied. The sediment oxygen demand during August 1973 was shown to be an increasing linear function with distance upstream from the mouth (Matsuda, as quoted in Harper-Owes, 1981). At the 2 km point the demand was about .5 gm  $O_2/m^2d$ . This increased to about 2.1 gm  $O_2/m^2d$  at 9.3 km. Rather interestingly, the demand then fell rapidly to about .8 gm  $O_2/m^2d$  at 9.6 km. This could be explained by the tidally induced motions of the salt wedge that would serve to expose the sediments to the weak August river discharge, thus flushing the sediments. It would be interesting

to compare this result with analogous measurements immediately following a period of high discharge, but such measurements apparently are not available.

Various other chemical properties have been measured. In the midreach area, lead was found in slightly higher concentration than in the upper-reach area (23 ppm vs. 18 ppm), but COD decreased downstream (57 cm/kg in the midreach, vs. 76 gm/kg in the upper reach).

The stratification of the river is well documented in Stoner (1972) and more recently in Partch (1981). In periods of low flow, the upper layer is of high salinity with a linear stratification, but it is still easily recognized. In very high flows, the upper layer is diluted by a factor that ranges from less than 1 to as high as 3, and it forms a very well mixed lens of brackish water about 3-m depth. The flow in this upper layer does reverse itself, but only briefly during the typical tidal cycle. Typical summertime salinities of this plume as it emerges into Elliott Bay are 25 to 28 ppt. In the winter, when runoff is high, the salinity of the plume is typically in the range of 20 to 25 ppt, although lower values in conditions of extremely high runoff are possible.

#### IV. SOURCES, METHODS AND RATIONALE OF DATA COLLECTION

Since this project seeks to provide guidance to decision makers on an issue that probably has a range of "right" answers, and since there is no obvious decision criteria that is related to directly measurable parameters, the focus of our initial work has been to create models of the system based on theoretical considerations and empirical observations. Such models will allow us to examine a range of decision possibilities.

This focus on modelling has led to the examination and rejection of the existing Duwamish River model (Prych, 1975), to the development of a crude model of plume dynamics for application to Elliott Bay, and to the decision to develop a new analytical technique that will allow us to draw a variety of important inferences from readily collected field data. These inferences will support the development of a new empirical model for the estuary.

We mentioned the shortcomings of the Duwamish River model above. We are presently reviewing other models for application to the estuary, but we have so far found none that addresses our needs explicitly. What we seek are methods for predicting the movement of the salt wedge in response to varying runoff and tide, and a means of estimating the resuspension and exchange of sediments in the region that is uncovered as the salt wedge is swept downstream. In lieu of the implementation of an existing model for these purposes, we are now considering ways of achieving the same result via the collection, analysis and organization and extrapolation of field data; that is, using the estuary itself as a "model."

The practicality of the idea of using field data to create an empirical model of the river's resuspension and transport of pollutant-bearing particulates rests primarily on the observations that both the

exposure of the sediments in the upper reach and the bulk of the sediment input occur during the relatively rare periods of high discharge. As noted above, over half of the total input of sediment occurs in just 5% of the time. Further, the periods of low discharge are rather protracted, and we can expect the pollutant-bearing deposits that are formed during these periods to be swept away and redeposited elsewhere in the first strong runoff. Thus, we are not faced with the problem of measuring everything, everywhere, and at all times. Instead we can focus on the 5 or 10 days of very high runoff in November through February plus the first couple of fall rainstorms. Further, the data we require consists mainly of representations of the thickness of the upper layer and the evolution of the concentration of suspended material in the upper layer. It appears now that this information is obtainable from transmissometer, Coulter counter, and conductivity data provided these data are suitably analyzed.

The parameter most directly of interest to us is the mass flux of suspended materials across the interface between the low-salinity upper layer and the salt wedge. This is the material that will accumulate in the estuary or, if we extend the model to the Elliott Bay plume, it is the material that will settle in Elliott Bay. The mass flux is not directly measureable, but it can be inferred from changes in the concentration of material in the upper layer, although these changes are liable to be very subtle. In order to unscramble the subtleties, the inferential procedure for determining mass flux requires an explicit analytical model of the upper layer. Such a model would be based on the idea of a well mixed (high diffusivity) upper layer of variable depth (the response to the ebb and flood of the tides) containing a mixture of particles with varying size and density, resting on a relatively quiescent lower layer of higher density. Entrainment at the interface must also be included.

Quite obviously, developing inferential procedures from such a model is a relatively large undertaking involving considerable uncertainty. We have attempted this year to lay some of the necessary ground work to establish the theoretical and computational feasibility of the method. Utilizing an analytical model of particle settling beneath a free surface in a homogeneous fluid, we have developed procedures for determining the distribution of particle densities based on Coulter counter data. These density distributions have then been used to infer the settling time of a Coulter counter sample given initial and final counts (Stewart and Moehring, 1982). The mathematics behind this procedure is a straightforward application of Bayes Theorem, but the algebra and numerical requirements are somewhat cumbersome. Less awkward is the equation for the analytical model that predicts the evolution of the concentration of the number of particles of a given size range at depth  $z$ . For constant diffusivity and spherical particles, this equation is:

$$C(z,t) = C_0 \left\{ \frac{1}{2} \operatorname{erfc} \left( \frac{z + vt}{2\sqrt{Dt}} \right) - v \left( \frac{t}{\pi D} \right)^{\frac{1}{2}} \exp \left( - \frac{(z-vt)^2}{4Dt} \right) \right\}$$

$$+ \frac{1}{2} \left( 1 - z \frac{v}{D} + \frac{v^2 t}{D} \right) \exp \left( \frac{vz}{D} \right) \operatorname{erfc} \left( \frac{-z + v t}{2\sqrt{Dt}} \right) \}$$

where

$v$  = settling velocity of a particle of radius  $r$  and density  $\rho'$ , cm/sec,  
(a negative number in our coordinate system);

$D$  = coefficient of diffusion,  $\text{cm}^2/\text{sec}$ ;

$t$  = time, sec;

$z$  = vertical coordinate, positive upwards, free surface corresponds to  
 $z = 0$ ;

$C_0$  = initial concentration,  $\#/\text{cm}^3$ ;

and

$$v = \frac{2}{9} g \frac{(\rho' - \rho)}{\mu} r^2 ,$$

with

$\rho$  = density of water  $\text{gm}/\text{cm}^3$ , and

$\mu$  = viscosity of water,  $\text{gm}/\text{cm sec}$ .

The purpose of this year's work was to gain familiarity with the problems that arise in manipulating this equation so as to yield estimates of the distribution of the functional parameters (e.g.,  $\rho'$  or  $t$ ) given experimental observations of the particle concentrations.

The purpose of the plume model is to allow us to form some preliminary appreciation of the potential contribution of the plume to pollutant transport in Elliott Bay. The key elements of this model are our representation and simulation of the effects of wind stress and a constraining boundary (shoreline). The purpose of this model is to give us some feeling for the time and space scales associated with the plume's evolution. The model is intended to balance gross forces and accelerations, but it does not distribute forces and accelerations within the plume in a dynamically consistent fashion. Thus, our results can only be relied upon to suggest approximate orders of magnitudes.

We have idealized the problem in the following ways:

- o All runoff from the river over a twelve-hour period is assumed to have collected in the eastern corner of Elliott Bay.
- o This lens of buoyant water is characterized by an exogenously specified salinity and depth. From the depth value and the discharge rate, we calculate the areal coverage of the lens.

- o The lens is initially square.
- o The geometry of Elliott Bay is assumed to be that of a simple right-angled corner. We ignore the northwest projection of the West Seattle peninsula which culminates at the Duwamish Head.
- o The wind will be assumed to blow uniformly from the southwest. No consideration will be given to the effects of the component of wind stress that lies parallel to the main Seattle waterfront.
- o All motions to the northwest (along the waterfront and towards West Point) are attributed to gravity current dynamics.
- o All motions normal to the waterfront are attributed to the dynamical balance of wind stress, buoyancy-induced pressure forces, and frictional effects on the bottom of the lens.
- o Mass within the lens is conserved. That is, we will not consider the upward (or downward) entrainment of water.

Treating the problem as an initial value problem, we use the above conditions to determine the evolution of the length, width and depth of the plume. Letting  $L$  be the length of the lens along the waterfront,  $W$  be the width of the lens measured perpendicular to the waterfront, and  $D$  be the depth of the lens, the equations of motion are derived from the three equations below:

$$L * W * D = \text{Constant} \quad (\text{conservation of mass}) \quad (1)$$

$$\frac{dL}{dt} = 1.19\sqrt{g'D} \quad (\text{gravity current kinematics}) \quad (2)$$

$$\rho' (DLW) \frac{1}{2} \left( \frac{d^2 W}{dt^2} - \frac{(W')^2}{W} \right) = g\rho' \Delta \frac{D^2}{2} L - WL\tau - \frac{1}{2} \rho' C_D WL \frac{(\text{ABS}(W'))(W')}{3} \quad (3)$$

(dynamical balance in width direction)

where

$\rho'$  = density of the lens.

$\rho$  = density of underlying ambient water.

$\Delta = \frac{\rho - \rho'}{\rho}$  ; nondimensional buoyancy factor.

$g$  = acceleration of gravity.

$g' = g\Delta$  ; buoyancy corrected acceleration of gravity.

$\tau$  = wind stress.

$C_D$  = drag coefficient for lens motions in the 'W' direction.

$W' = \frac{dW}{dt}$  , etc., and

$ABS(W') \equiv \frac{dW}{dt}$

Equation (2) is a deceptively simple specification of gravity current velocity. In fact, the problem of gravity current behavior has intrigued fluid dynamicists for years, and it is still an area of active research. However, Huppert and Simpson (1980) recently demonstrated that much could be accomplished in reconciling observation and theory using simple ideas like (2), and so we adopt the approach here. Equation (3) simply says the mass times the acceleration in the 'W' direction equals the sum of the forces. The first term on the right is the buoyancy-induced spreading force, and it relies on the assumption of hydrostatic pressure in the lens. The second term is simply the wind stress times the area of the lens; and the third term is the frictional drag exerted on the lens by the underlying ambient water, which is assumed stationary. The velocity is assumed to be linearly distributed in both the W and L directions, and this results in some terms in (3) that would not be present if the lens was treated as a solid body. The factor of three in the denominator of the frictional drag term results from averaging stress over the width of the lens (as opposed to velocity which results in a factor of four). And the second term in the bracket on the left-hand side results from the requirement that the fluid within the lens accelerates in such a fashion that the velocity remains linearly distributed over the time-varying width.

## V. RESULTS

We examined the behavior of the plume model under a variety of assumptions for wind stress, discharge rate, initial depth, and the salinity of the buoyant plume. For low wind stress (.1 dyne/cm<sup>2</sup>), moderate discharge rates (30 m<sup>3</sup>/s), and most salinity values, the model predicts a fairly monotonic thinning of the lens, with corresponding steady advance of the front up the Seattle waterfront toward West Point. The model predicts that the plume should be found as a lens of fairly thin water (~ 30 cm) lying along the Seattle waterfront in a strip that is 600-700 m wide, and which extends as far as Smith Cove within four hours of its release in Elliott Bay. We found this behavior to be rather typical for a variety of assumptions regarding the initial salinity and depths of the plume.

If we consider higher wind stresses (.3 and 1.0 dyne/cm<sup>2</sup>), then the plume is much more effectively constrained against the Seattle waterfront. This maintains the plume's depth, which enhances the velocity of propagation of the plume's frontal region toward West Point. For a nominal discharge rate of 30 m<sup>3</sup>/sec coupled with a high, 1.0 dyne/cm<sup>2</sup>, wind



stress (corresponding to a 20-25 knot wind) the lens oscillates about a mean depth of 100 cm; it is constrained to a width of 400-500 m after one hour; and it advances to the Smith Cove region within 3 hours of its release.

Analogous behavior is found for discharge rates up to 100 m<sup>3</sup>/sec. However, at extreme discharge rates of 300 m<sup>3</sup>/sec and low plume salinities (4 ppt), we find that the spreading tendency of the lens is so strong as to overwhelm the wind induced compression. In such extreme discharges we would predict a rapid spread of the plume throughout Elliott Bay with little initial preference for either shore. Only if we couple this discharge with a 1 dyne/cm<sup>2</sup>, onshore wind stress is the plume constrained to the Seattle waterfront. In this case, we predict a width of about 2 km, a depth of about 100 cm, and the lens advances to the Magnolia Bluff region in about two hours.

The feasibility of the proposed Bayesian inference method on particle settling was demonstrated by a series of tests, each of which was similar to the following. A randomized and idealized Coulter counter data set was created numerically assuming a range of particle sizes from 11 to 21  $\mu$ m. The particle density was fixed at 1.2 gm/cc, water density at 1.0 gm/cc, the coefficient of diffusion was fixed at  $1 \times 10^{-5}$  cm<sup>2</sup>/sec, and the final sample was taken at a simulated time of 1080 sec. The data was then divided into two groups of 10 particle size classes. Treating time as a known parameter (i.e., 1080 sec), the first group of ten was used to infer the density of the particles. Then using this distribution on particle density, the data from the remaining group were used to infer the time that passed between the initial and final samples. The data is shown in Table 2.2, below, and the distributions on particle density and time are shown in Figures 2.2 and 2.3.

The reason for determining sample age in this test was that we envisage making use of an analogous method to age date (in hours) various portions of the Duwamish Plume as it is observed in Elliott Bay. As noted above, the transport times to West Point should be on the order of hours for high discharge plumes released into Elliott Bay following a strong flood in the Duwamish. The mass fluxes associated with this plume are enormous (hundreds of times greater than the corresponding river mass flux) and so this plume may be a very important mechanism for dispersing pollutants into the central Puget Sound Basin. The age dating for the plume in Elliott Bay will proceed along a path similar to the one outlined above, although we will require additional experimental protocols to determine effective diffusivities and particle densities.

## VI. DISCUSSION

A fundamental premise of the plume model is the assumption that the river's discharge into Elliott Bay could be treated as an instantaneous release of a full twelve hour's discharge. This idealization was prompted by consideration of the tidal currents in the Duwamish, which should serve to counterbalance the discharge current during the flood phase of the tide, thus effectively damming the river discharge for some part of the tidal cycle. However, the validity of this assumption rests on the comparison between the time required by the buoyant lens to spread along

Table 2.2. Simulated Coulter-Counter Data

Density Inference			Time Inference		
Group 1			Group 2		
Rad ( $\mu\text{m}$ )	$N_0$	$N_1$	Rad ( $\mu\text{m}$ )	$N_0$	$N_1$
11.42	102	94	11.78	94	106
12.15	93	100	12.52	91	72
12.91	97	69	13.32	98	64
13.73	77	90	14.16	73	53
14.60	73	38	15.06	70	0
15.53	43	0	16.01	63	0
16.51	31	0	17.03	34	0
17.56	33	0	18.10	37	0
18.67	35	0	19.25	10	0
19.85	6	0	20.47	11	0

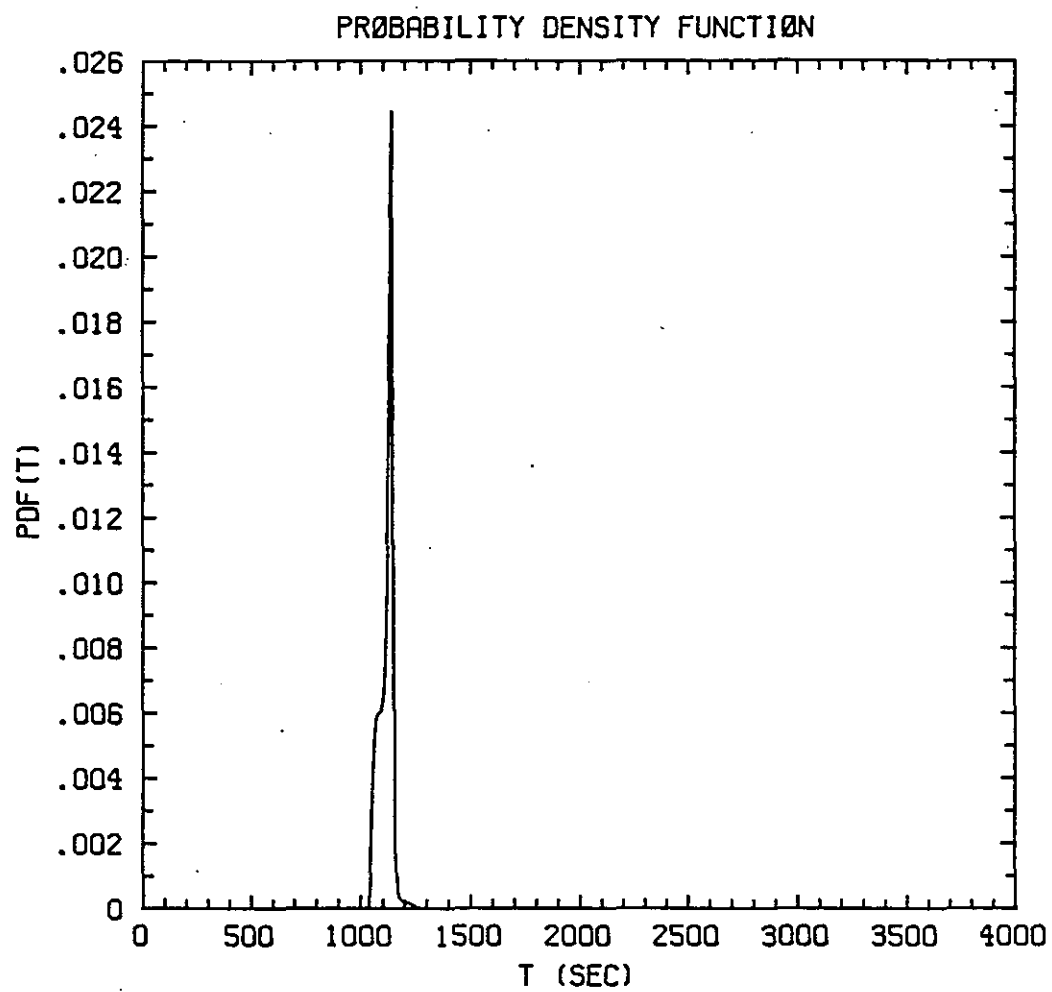


Figure 2.2. Posterior probability density function for  $R_{Ho}$ , the density of the suspended material (Gm/cc). Based on the data in Table 2.2.

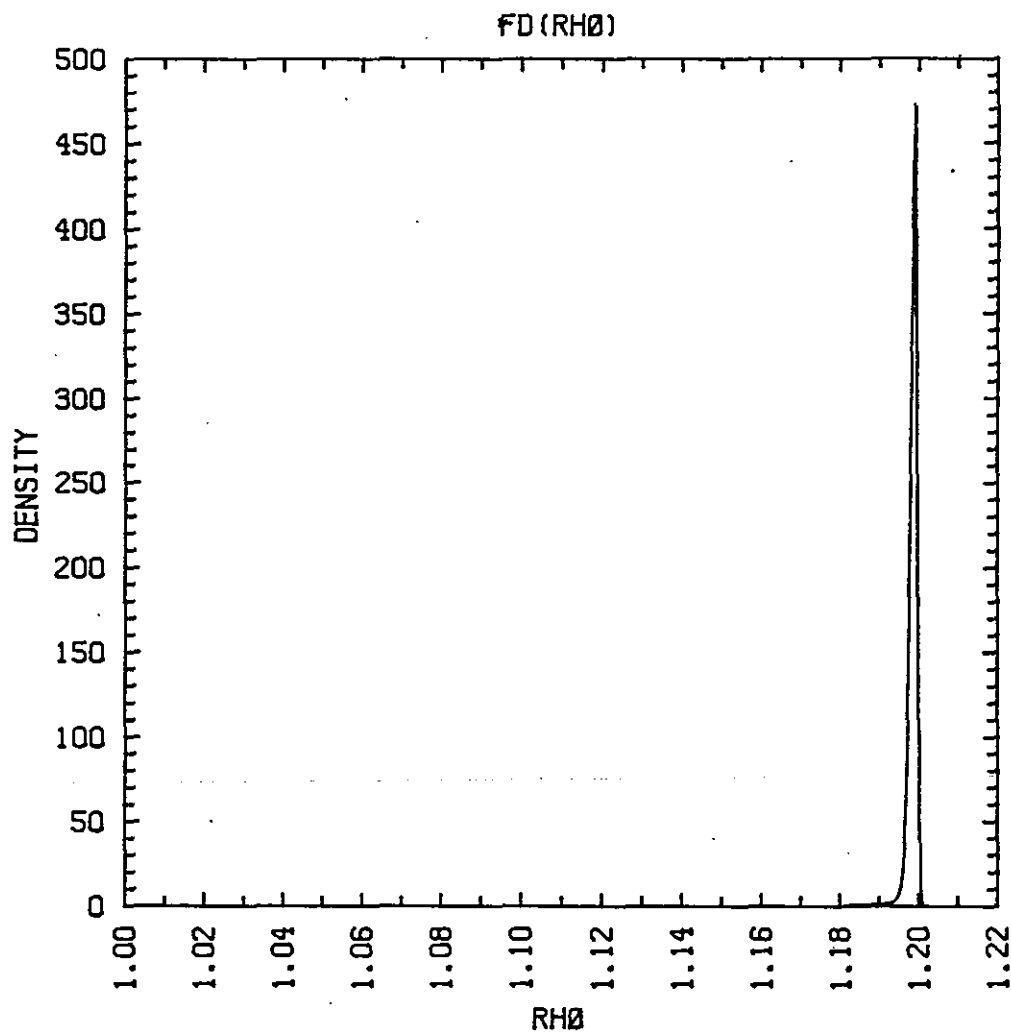


Figure 2.3. Posterior probability density function for the age of the Coulter counter sample based on data of Table 2.2 and the posterior density distribution of Figure 2.2.

the Seattle waterfront, and the duration and strength of the tidally modified river discharge. The spreading time scale is readily discerned in the model to be on the order of a few hours. From Figure 3.7 of Partch (1981), we can see that the depth-averaged, upper-layer velocity of the Duwamish is very much like a rectified saw tooth, with upstream motions encountered only rarely. Thus the river is not effectively "dammed" by the tide, except briefly during the tidal cycle. This being the case, we might characterize the time period for the introduction of the buoyant lens as being on the order of six to ten hours, and the discharge rate would be only about twice the average discharge rate. On the other hand, the spreading time for the buoyant lens is on the order of a few hours. Further, the model predicts volume fluxes along the Seattle waterfront that are 100 to 200 times the average river discharge rate. Consequently, the rates and fluxes of the model's transport processes in Elliott Bay are considerably faster and larger than their counterparts in the Duwamish River. This suggests that our instantaneous release model is not entirely appropriate, and implies that some of our length scales are probably considerably overestimated, particularly the lens' width and depth. In particular, for the low discharge case, we should not expect any substantial persistence of the lens along the waterfront. The predicted depth is already small (30 cm), and the processes of spreading and vertical entrainment may dispense these lenses very rapidly as they emerge from the Duwamish into Elliott Bay. Nevertheless, this preliminary examination of the buoyant lens' dynamics implies a very large mass transport and short time scales. This suggests that we focus our initial efforts on processes that may take only a few hours to occur.

## VII. CONCLUSIONS

The results of this year's work suggest that the high discharge plume in Elliott Bay may be a very important transport mechanism for pollutants that accumulate in the sediments of the upper reaches of the Duwamish. The magnitude of this transport process in any specific instance will be modified by tidal heights and discharge rates obtaining at the time, and because of this we can expect considerable variability from year to year. In some years, we may get very good dispersion into the central basin, while in others, the pollutants might well rain out and collect in the stable sediments of the middle and lower reaches of the Duwamish. The focus of our work is to develop quantitative models that will allow us to estimate where these deposition sites are (for given discharge rates and tidal ranges). This will require additional field experiments and data, but good progress has been made toward completing development of the analytical procedures whereby these data will be made to yield the required information. Once this model is complete, then it will be possible to hindcast the deposition sites for the last decade or two using daily river discharge rates and the corresponding tidal height data. This will allow a much improved understanding of the role that the Duwamish River plays in dispersing the pollutants that accumulate during periods of low flow in the upper reaches of the estuary.

## VIII. NEEDS FOR FURTHER STUDY

The principal theoretical deficiency hindering our modelling effort is the poorly understood dynamics of the region in which the fresh effluent first encounters the toe of the salt wedge. Other than the empirical model of the toe's motion used in the Prych model and theoretical models that average over a tidal cycle, there is virtually no guidance on this matter in the literature. This is an important problem, and it may provide the key to the ready adaptation of our results to other estuaries.

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## 2.2. CIRCULATION PROCESSES

### 2.2.1. Eulerian Transport

#### I. Introduction

In Puget Sound, we are attempting to quantify flushing processes which determine residence times for water and the relationship to transport of particulates in the main basin. This effort is an integral part of PMEL's interdisciplinary study of pollutant transport by particulates including physical, geochemical, and modeling efforts jointly funded by LRERP and PMEL.

#### II. Current State of Knowledge

Early studies have led to a conceptual model of Puget Sound which implied that considerable seaward flowing surface water was mixed with new water entering the deep basin at the southern end of Admiralty Inlet, and this mixture was refluxed back into the Sound in the deep water below sill depth. Observations from Admiralty Inlet were used for a first approximation of the average flux through Admiralty Inlet which supported the conceptual model. Only about half as much water was entering as the average observed going southward about midway along the Main Basin (Pt. Monroe - Meadow Pt. section). However, the sets of observations were from different seasons and different years (Admiralty Inlet from September-November 1977; main basin from January-February 1973), and it was unclear whether the speculations might be unreal because of as yet unknown seasonal changes in the transport.

During the past year, this study has proceeded along several directions:

- 1) ~~Year-long observations to describe the annual cycle of both water and sediment flux were completed at a site in the Main Basin.~~
- 2) Winter-spring observations were made to determine: a) the flux of both water and sediment simultaneously through sections in the Main Basin and on the Admiralty Inlet entrance sill, and b) the downward entrainment or reflux of water in the entrance region where no prior measurements existed.
- 3) Various detailed synthesis papers were completed describing our present state-of-the-art understanding of the circulation variations described briefly above (Cannon, 1983), of tides and tidal currents (Mofjeld and Larsen, 1983), and of some of the sill effects on flushing (Geyer and Cannon, 1982).
- 4) Two collaborative efforts were initiated with outside NOAA scientists to attempt to determine annual changes in Puget Sound transport using: a) a simplified two-dimensional box model, and b) a re-examination of historical data.



### III.-IV. Study Area and Data Collection

During early 1982, we completed an interdisciplinary year-long monitoring of water and suspended particulate matter (SPM) transport at a site near the major METRO outfall at West Point. Later in FY82, a series of moorings were deployed from this location northward onto the Admiralty Inlet sill. Moorings across the section at the year-long site were used to determine flux of water and SPM through the cross-section to put the year-long observations at a single site in proper perspective. Because it is unknown how much outflowing surface water is entrained into inflowing deeper water at the sill, a series of moorings and ship-board observations (5-10 days) were used to document the processes involved. A summary of the year-long observations is given in Table 2.3 and a status of the 1982 winter-spring experiment is given in Table 2.4.

Synthesis of existing data was a second major focus during FY82. Documentation of all current meter records collected in Puget Sound from 1908-1980 was completed jointly by Ebbesmeyer (industry), Barnes (UW), and Cannon (PMEL). The MESA Puget Sound Project supported the non-NOAA participants.

### V.-VII. Results, Discussion, and Conclusions

The major results from this year's effort are in the three papers indicated above. Two will be in a book to be published on Puget Sound and a third will be in the *Journal of Geophysical Research*. A synopsis of each is given below, and preprints can be made available.

#### 1. Variability of currents and water properties in Puget Sound, Cannon, 1983.

Prior to 1970 direct observations of circulation in Puget Sound and along its connection to the ocean were rarely made for more than a few days. Tidal current observations by the U.S. Coast and Geodetic Survey to develop predictive tables were perhaps the only exception. Their observations, however, were not made in conjunction with water property observations and were of limited use in describing other flow characteristics. The estuarine characteristics of net seaward flow near the surface and net landward flow at depth were observed at several locations in Puget Sound for one to a few days and also in a section midway along the Strait of Juan de Fuca for about a day at each of three stations. Other observations, primarily of the distribution of water properties, contributed to the initial descriptions of flow characteristics. However, relatively little was known about variations in the circulation and, hence any resulting consequences. The only known observations and descriptions of variations in mean flow were from electromagnetic flow measurements in Deception Pass. Those results suggested that prolonged high winds as well as the cessation of strong winds had a marked effect on net transport.

Because future decisions on questions regarding new and alternate uses of these waters require information on transport processes, an

Table 2.3. Sediment-Trap Experiment December 1980 to December 1981.

Mooring ID	Meter @depth(m)	Station depth(m)	Station Lat.	Location Long.	Deployment dates	Record length(days)	Variance (cm/sec) <sup>2</sup>	Net Flow Speed cm/sec	Dir. °T
STE-1	1815@27	217	44.70N	122.45W	12/4/80-1/30/81	17	62.8	4.3	35.0
STE-1	2163@57	"	"	"	"	"	"	"	"
STE-1	2492@107	"	"	"	"	68	66.0	5.3	239.2
STE-1	2510@167	"	"	"	"	57	"	"	"
STE-1	2496@206	"	"	"	"	12	"	"	"
STE-2	3296@12	202	44.70N	122.45W	2/5/81-4/16/81	"	"	"	"
STE-2	1811@42	"	"	"	"	70	52.8	5.2	32.7
STE-2	3286@92	"	"	"	"	"	"	"	"
STE-2	2496@152	"	"	"	"	8	93.6	10.7	236.6
STE-2	2510@196	"	"	"	"	70	71.9	7.0	224.4
STE-3	2248@20	210	44.70N	122.46W	4/23/81-7/10/81	"	"	"	"
STE-3	1686@51	"	"	"	"	78	49.5	3.2	26.8
STE-3	1490@101	"	"	"	"	78	39.6	2.9	239.7
STE-3	2496@161	"	"	"	"	42	86.6	8.6	250.4
STE-3	2510@205	"	"	"	"	77	108.7	11.5	222.7
STE-4	2501@20	210	44.70N	122.45W	7/22/81-9/29/81	"	"	"	"
STE-4	1827@53	"	"	"	"	21	54.9	3.7	236.6
STE-4	2157@103	"	"	"	"	69	51.6	4.3	238.8
STE-4	2502@163	"	"	"	"	69	140.0	12.6	223.4
STE-4	1825@206	"	"	"	"	69	140.0	12.6	223.0
STE-5	1823@20	211	44.70N	122.46W	10/13/81-12/21/81	69	110.7	9.2	16.2
STE-5	1452@53	"	"	"	"	69	51.2	3.3	39.1
STE-5	1686@103	"	"	"	"	"	"	"	"
STE-5	1825@163	"	"	"	"	69	79.9	4.9	246.7
STE-5	3291@206	"	"	"	"	69	77.6	6.3	225.5

Sediment-Trap Experiment, cont.

Concurrent CTD sections along Puget Sound:

<u>Cruise dates</u>	<u>Start point</u>	<u>End point</u>	<u># stations</u>	<u>Cruise name</u>
5-6 Feb. 81	Tacoma	Port Townsend	10	LRERP 81-1
30 Apr. - 1 May 81	Tacoma	Port Townsend	11	LRERP 81-2
16-17 July 81	Tacoma	Port Townsend	12	LRERP 81-3
27 Aug. - 2 Sept. 81	Tacoma	Port Townsend	54	LRERP 81-4
3-5 Nov. 81	Tacoma	Port Townsend	10	LRERP 81-5

1st full-day averages

<u>Mooring ID</u>	<u>Meter@depth(m)</u>	<u>Temperature(°C)</u>	<u>Salinity(‰)</u>	<u>Pressure(db)-for entire record</u>	<u>Transmissometer?</u>
46 STE-1	1815@27	11.06	29.82	25.14	No
STE-1	2492@107	9.53	30.61	110.35	No
STE-1	2510@167	10.28	30.94	n/a	Yes
STE-1	2496@206	9.87	30.60	n/a	Yes
STE-2	1811@42	9.26	29.37	44.59	No
STE-2	2496@152	9.13	30.07	n/a	Yes
STE-2	2510@196	8.99	30.18	n/a	Yes
STE-3	1686@51	9.31	29.37	50.05	No
STE-3	1490@101	9.07	29.69	102.41	No
STE-3	2496@161	9.23	29.76	n/a	Yes
STE-3	2510@205	9.22	30.31	n/a	Yes
STE-4	1827@53	11.06	29.82	61.46	No
STE-4	2157@103	10.88	30.04	112.79	No
STE-4	2502@163	10.78	30.21	n/a	Yes
STE-4	1825@206	10.75	30.16	n/a	Yes
STE-5	1823@20	11.90	30.14	22.22	No
STE-5	1452@53	11.83	30.29	56.64	No
STE-5	1825@163	11.28	30.79	n/a	Yes
STE-5	3291@206	11.14	30.94	n/a	Yes

Table 2.4. Puget Sound 1982 Mooring Summary

CODES	Data condition		Processing		Notes		
	4 - Excellent		6 - Completed		MR - missing records		
	3 - Good		5 - R2D2		SR - short record		
	2 - Fair		4 - C2C edit		NS - no speeds		
	1 - Poor		3 - CME edit		SP - special programming		
	0 - No date		2 - CMI initial				
			1 - Translated				

MOORING NAME	INSTRUMENT	DEPTH METERS	LOCATION	DURATION		CONDITION		
				START- YEAR	END DAY	DC	PR	NOTES
PS8201		108	47° 57.4N 122° 34.4W	041.0-118.0				
	1981	15		041.0-118.0		3	4.8	MR, P?
	1978	30		041.0-118.0		3	4.8	
	2157	50		041.0-118.0		3	4.6	MR
	1807	75		041.0-118.0		3	4.8	MR, P?
	2496	100		041.0-118.0		2	4.2	Overflows
PS8202		92	47° 58.2N 122° 34.0W	041.0-056.8				
	2501	30		041.0-047.9		2	4.5	many MR
	2500	75		041.0-049.0		2	4.2	many MR
PS8203		110	47° 57.5N 122° 35.3W	041.1-048.7				
	3210	28		041.1-048.7		2	4.8	MR
	2505	73		NO DATA		0	6	failed @ water
PS8204		132	47° 57.3N 122° 30.7W	076.8-117.9				
	603	17		076.8-117.9		2	4.5	speeds 9 days
	3185	37		076.8-117.9		3	4.0	
	3442	62		076.8-117.9		3	4.0	MR
	3138	77		NO DATA		0	6	Failed @ water
	3129	127		NO DATA		0	6	" " "
PS8205		200	47° 54.0N 122° 28.8W	040.8-117.9				
	1452	15		040.8-117.9		1	3.0	MR data
	1490	40		040.8-045.4		3	4.0	SR
	1686	90		040.8-117.9		1	2.0	SP selector
	1687	125		040.8-117.9		1	4.0	T,S,P?
	1803	175		040.8-068.2		2	4.0	SR P?
	1825	195		040.8-117.9		2	4.0	Overflows

Table 2.4, Cont.

PS8212	83	47° 41.9N 122° 25.0W	042.7-049.0			
3185	15		042.7-049.0	3	4.8	P?
1833	35		042.7-049.0	2	4.8	P?
3286	60		042.7-049.0	1	4.0	data?
PS8213	184	47° 29.4N 122° 23.8W	057.1-119.8			
2477	20		057.1-119.8	4	4.8	
2356	45		057.1-061.3	1	4.5	SR
2492	90		057.1-119.8	4	4.5	
2500	150		057.1-096.6	2	4.0	SR T&S?
2501	180		057.1-100.5	2	4.3	SR
PS8214	175	47° 21.6N 122° 23.0W	057.0-119.8			
1833	20		057.0-119.8	2	4.0	SP, data?
3286	45		057.0-119.8	3	4.5	
2494	90		057.0-119.8	3	4.0	
2505	150		057.0-119.8	4	4.5	
3210	170		057.0-074.8	3	4.0	MR S?
PS8215	194	47° 42.6N 122° 23.2W	057.7-074.8			
2501	189		057.7-074.8	3	5.5	
2510	191		057.7-074.8	3	5.5	
3291	193		NO DATA	0	6	Leaked
PS8216	198	47° 53.5N 122° 29.0W	076.9-117.8			
2158	125				2.0	
TC155	135-180		076.9-117.8	3	3.0	SP
PS8217	189	47° 46.9N 122° 26.8W	077.9-119.7			
3177	83				2.0	
TC149	88-188			3	3.0	SP
PS8218	-7	48° 46.9N 122° 36.3W	034.7-133.7			
DL322	-7		034.7-133.7	4	5.5	Bush Pt.
PS8219	-2	47° 39.5N 122° 26.0W	048.8-127.8			
DL337	-7		048.8-127.8	4	5.5	West Pt.
PS8220	-2	47° 23.4N 122° 22.3W	028.8-127.7			
DL288	-7		-28.8-127.7	4	5.5	Pt. Robinson

Table 2.4, Cont.

PS8206	192	47° 59.4N 122° 27.7W	077.8-117.8			
1971	17		077.8-117.8	4	4.0	
2163	42		077.8-117.8	4	4.0	MR
1453	92		077.8-117.8	3	4.2	P?
1828	127		077.8-117.8	2	2.0	SP
2168	187		077.8-117.8	3	4.2	
PS8207	190	47° 46.9N 122° 26.5W	041.7-119.7			
3135	15		041.7-119.7	3	4.5	
2249	35		041.7-043.0	3	3.0	SR
1813	60		041.7-119.7	4	4.5	
1815	90		041.7-119.7	4	4.5	
1823	125		041.7-047.9	2	3.0	SR
598	175		041.7-045.2	3	4.0	SR
PS8208	180	47° 47.1N 122° 24.7W	041.8-048.9			
2494	15		041.8-048.9	4	4.8	
3177	40		041.8-048.9	3	4.0	
1828	90		041.8-048.9	3	4.0	P?
2158	125		041.8-048.9	3	3.8	
PS8209	106	47° 46.8N 122° 27.8W	041.9-048.9			
2163	14		041.9-048.9	2	3.0	MR
3128	39		NO DATA	0	6	Failed @ water
3129	89		NO DATA	0	6	" " "
PS8210	203	47° 41.6N 122° 27.4W	042.9-107.5			
3293	1.5		LOST	0	6	
3446	17		042.9-107.5	3	4.5	
3132	37		042.9-104.4	2	4.0	MR T&P ?
1827	61		042.9-049.8	3	4.0	SR
3133	92		NO DATA	0	6	Capstan
1988	127		042.9-075.7	1	4.0	NS,SR
3444	177		LOST	0	6	
3134	197		042.9-106.5	3	4.7	MR
TG189	202		-----		1.0	
PS8211	172	47° 42.4N 122° 28.3W	043.0-049.0			
3442	15		043.0-045.6	3	4.8	SR
2477	40		043.0-049.0	4	4.8	
2356	90		043.0-049.0	1	3.0	data
2492	125		043.0-045.2	3	4.5	SR

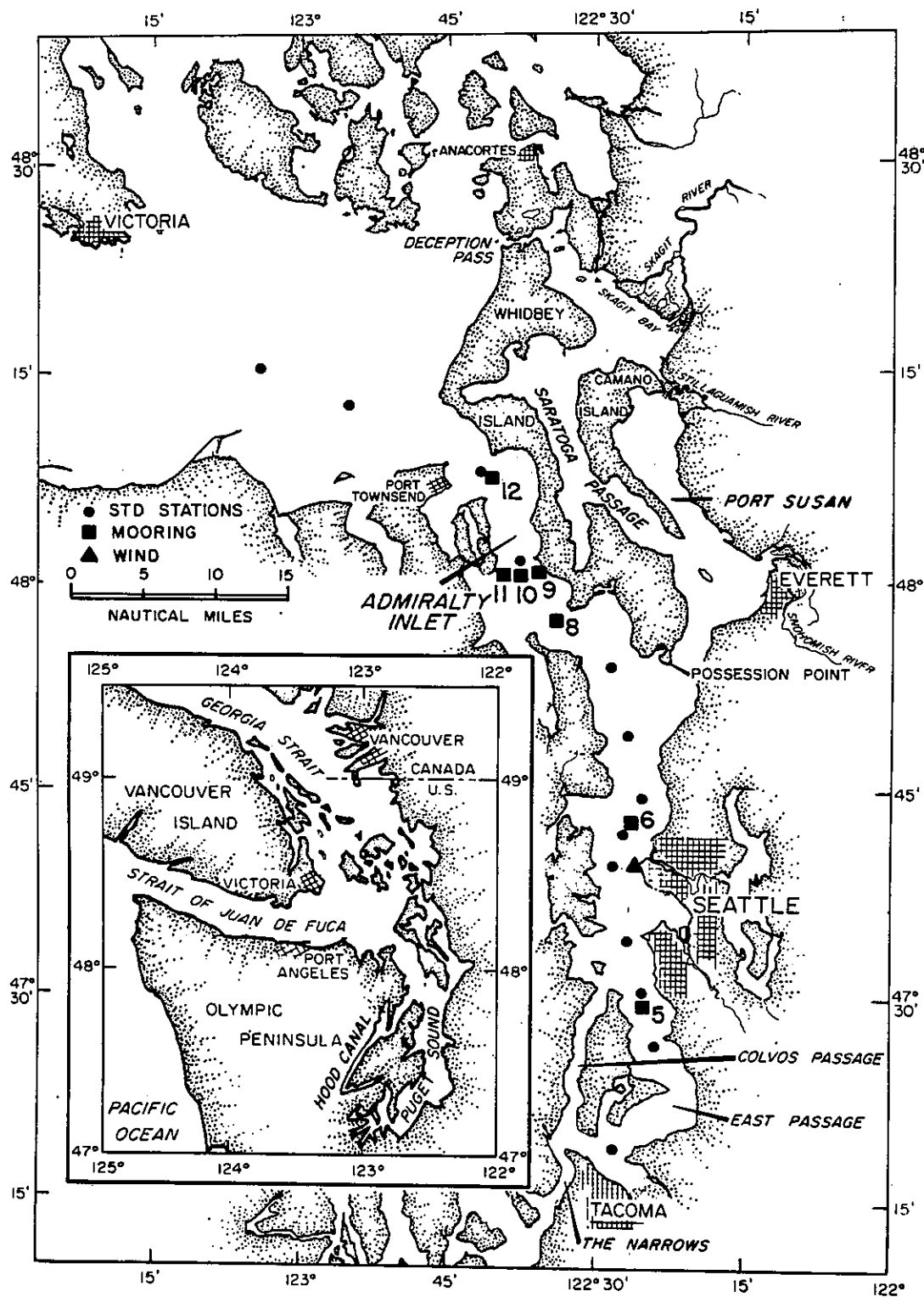


Figure 2.5. Puget Sound region showing mooring locations.

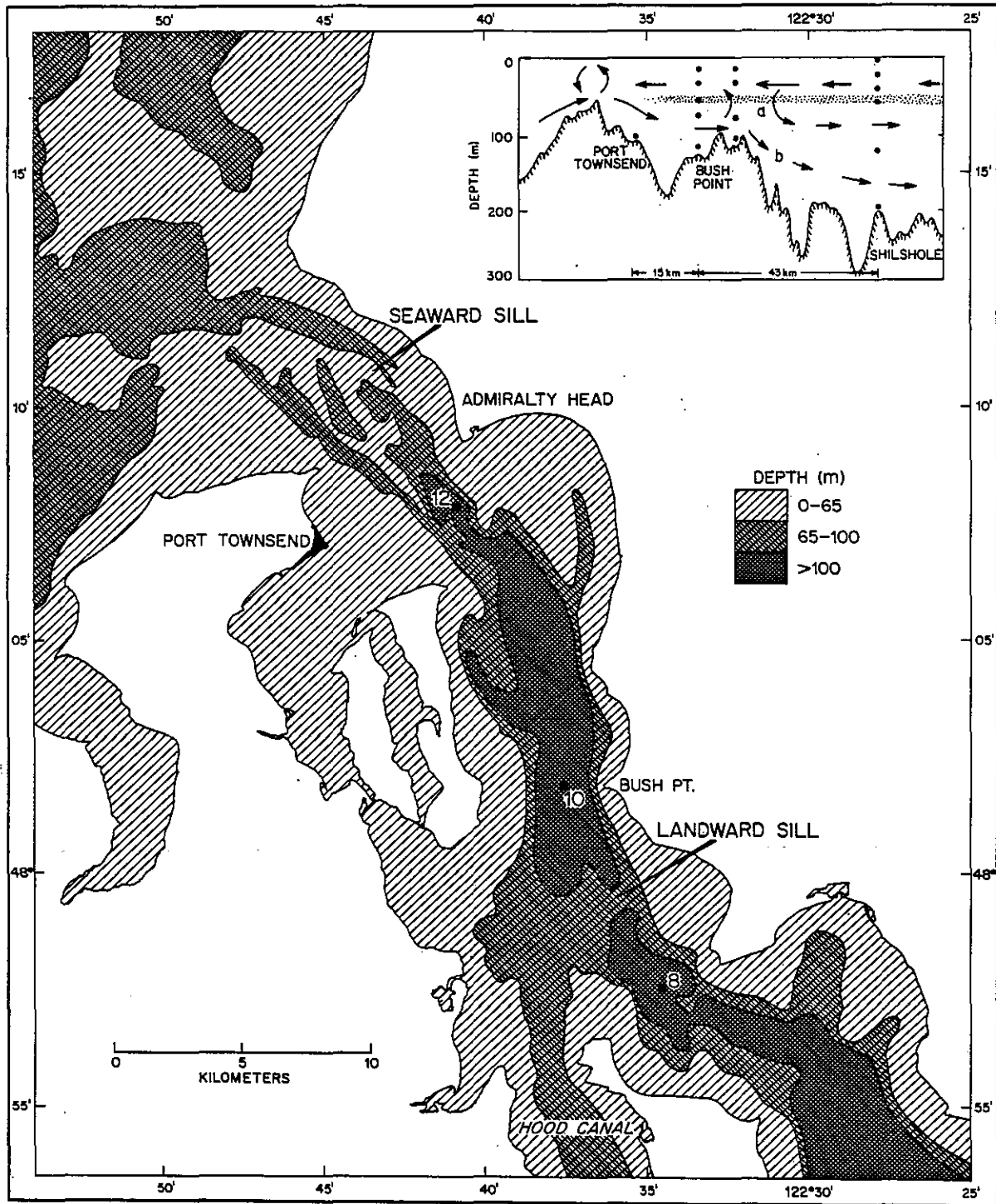
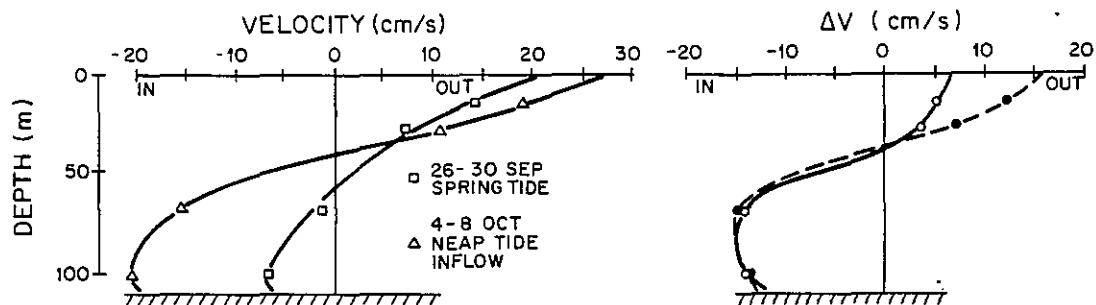


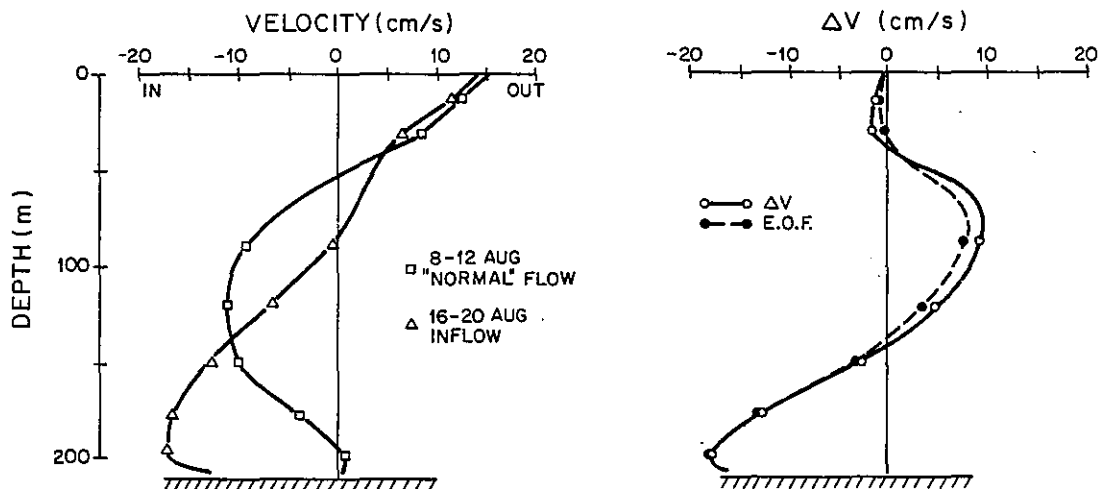
Figure 2.6. Bathymetry of the Admiralty Inlet sill region. Inset shows schematic non-tidal circulation (adapted from Cannon and Ebbesmeyer, 1978).



ALONG CHANNEL VELOCITY  
ADMIRALTY INLET, FALL 1977



SHILSHOLE MOORING, SUMMER 1979



VASHON MOORING, SUMMER 1979

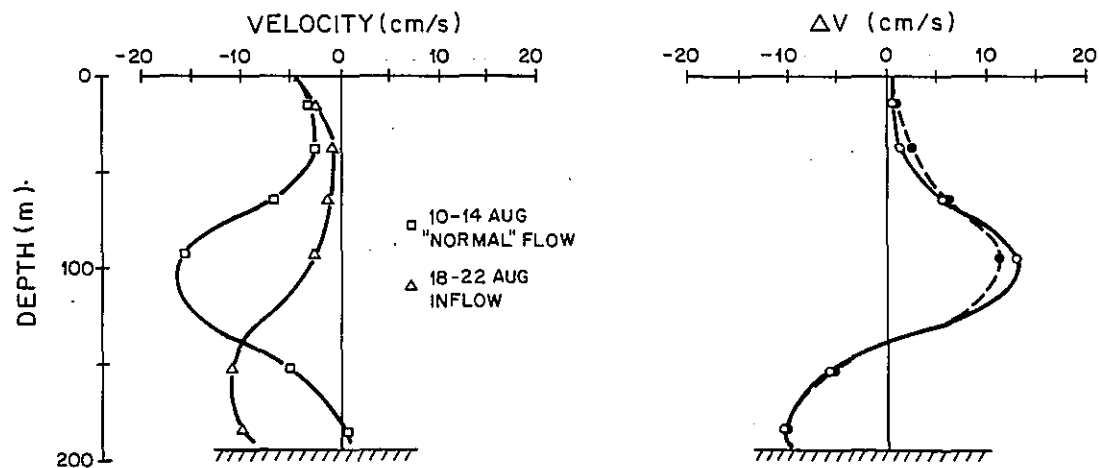


Figure 2.7. Vertical profiles of tidally averaged velocities during periods with (  $\square$  ) and without (  $\Delta$  ) inflow; profiles of velocity differences due to inflow (  $\circ$  ), and 1st eigenvector of 35-hour velocity variance (  $\circ$  ).

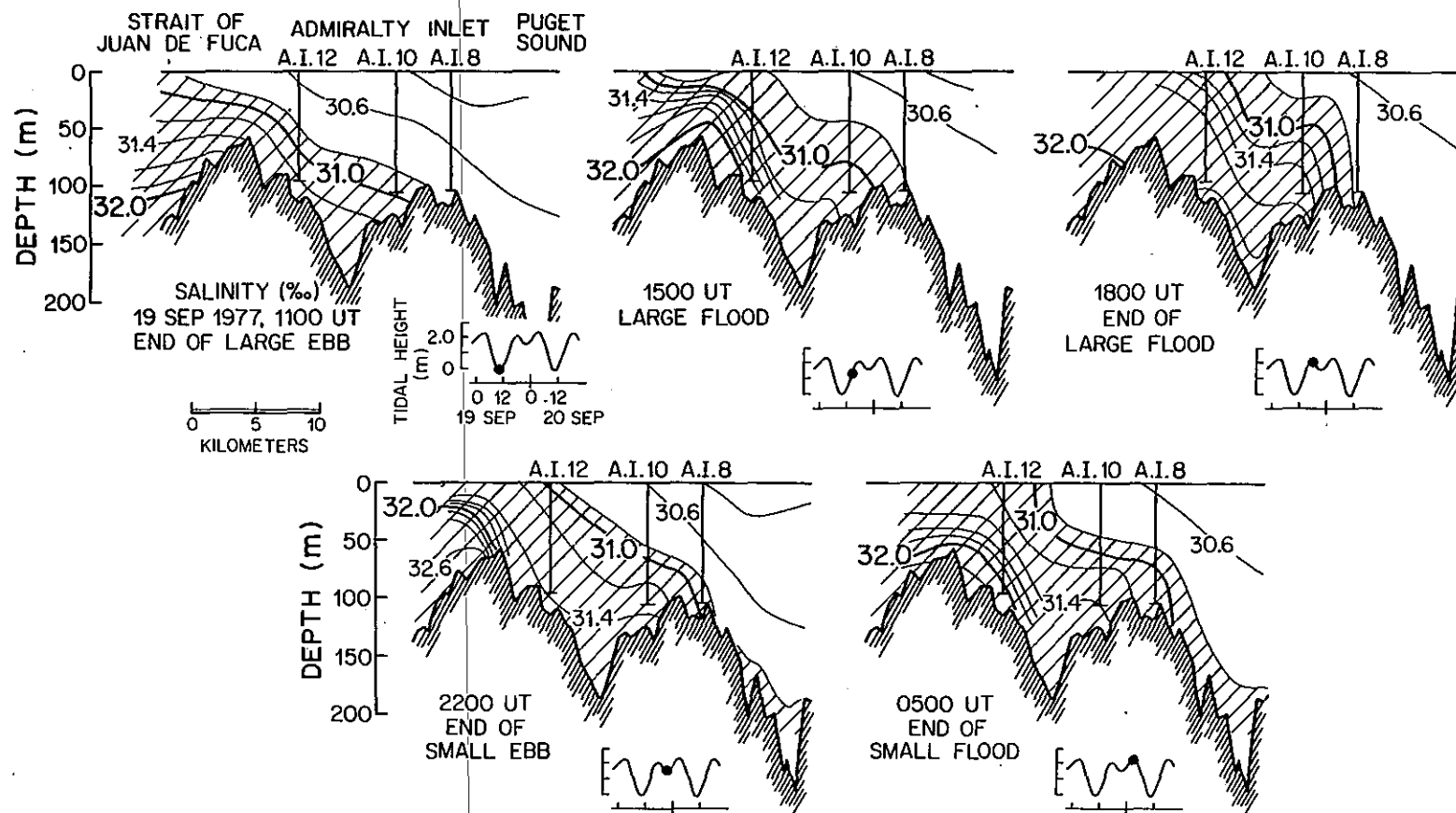


Figure 2.8. Salinity sections at various phases of the tide during the neap part of the cycle. The tidal height at Seattle is shown for each section in the inset. The shaded region indicates water more saline than the ambient Puget Sound water.

experimental program utilizing unattended current-meter moorings was initiated in 1970 by the author to characterize the temporal and spatial variability in the circulation and the large-scale dynamics of this estuarine system. Subsequently, many continuous observations in the main basin of Puget Sound have exceeded a month in duration, and in one case a mooring was maintained for an entire year. A tabulation of known current observations through 1980 has been made by Cox et al. (1981).

A summary of observations of tidally-averaged flow and its variations that are important to understanding the overall circulation of Puget Sound and the Strait of Juan de Fuca include three main aspects: deep water replacement, mean current profiles, and coastal interactions.

An overall rate of replacement of intermediate and deep water south of the Seattle long-term mooring (from a line between Meadow Point and Point Monroe) has been approximated using daily-averaged currents assumed to be uniform across channel. The average replacement time was less than two weeks when new bottom water was entering, and observation of water properties along the Sound showed the same transit time. New deep water has been observed to enter the Sound at about fortnightly intervals usually associated with the largest flood tides through Admiralty Inlet, but also associated with the smallest flood tides. Incoming bottom water can transit Admiralty Inlet in one flood cycle and is least mixed when the flood-tide range (higher high water minus lower low water) exceeds about 3.5 m. Incoming bottom water transits most of Admiralty Inlet on the larger flood cycle. Replacement occurs during the lowest flood tide ranges during the equinoxes in late winter and late summer. However, the subsequent small ebb is almost nonexistent at the bottom, and the following small flood is capable of completing the transit of the sill with minimal mixing. At intermediate tide ranges, floods and ebbs are more nearly equal causing maximum mixing of water in Admiralty Inlet. However, water more dense than is in the bottom of the Sound is always available at sill depth in the Strait and the intrusions do not occur every fortnight. The effects of tides and of winds in Admiralty Inlet on deep water replacement are only now receiving attention (Mofjeld and Larsen, 1983; Geyer and Cannon, 1982).

A recent conceptual model of the Sound's circulation implies that considerable seaward-flowing surface water is entrained or mixed downward and becomes part of new deep water entering the Sound at the south end of the Admiralty Inlet entrance sill (Ebbesmeyer and Barnes, 1980). Flux calculations using month-long-average currents midway along Admiralty Inlet, which show about half the inward volume transport as observed midway along the Main Basin, support this concept. Studies in 1982 were designed to attempt to determine how much "new" water actually enters during any given intrusion.

In addition, the constriction of the Narrows, the landward sill zone, appears to upwell deep water from the southern end of the main basin (Barnes and Ebbesmeyer, 1978). Thus, a combination of factors results in the main basin of the Sound being unusual as it is capable of renewing its deeper water at a much more rapid rate than classical fjords (Gade and Edwards, 1980).

Longer term average current profiles show characteristics of the Main Basin somewhat between those of classical fjords and partially mixed estuaries. However, significant variations in these profile have been observed when averaging over intervals of about a day. The concept of a mean current is obviously a function of time. Apparently, there is a delicate balance of forces along the basin due to the relatively small horizontal gradients. Thus, the wind contribution to the total horizontal pressure gradient results in major changes in flow throughout the water column.

## 2. Tides and tidal currents in Puget Sound and the Strait of Juan de Fuca-Strait of Georgia System, Mofjeld and Larsen, 1983.

Tidal mixing and advection are important processes determining the circulation in Puget Sound. It is the tidal mixing which maintains the density contrast (Ebbesmeyer and Barnes, 1980) across Admiralty Inlet, and it is tidal advection which brings new water into Puget Sound. The same processes create the efficient mixing of deep and shallow water at the Narrows which drives the circulation in the main basin of Puget Sound. The mixing may in turn have a significant effect on the tides and tidal currents because these same sill (also the sill in Haro Strait) dissipate tidal energy much more intensely than would occur with simple bottom drag. We may speculate therefore that the mixing of waters differing in density creates a substantial drag on the tides and tidal currents over the sills.

The relative magnitudes and phases of the diurnal and semidiurnal tidal currents may be important in determining when new water enters Puget Sound through Admiralty Inlet. The diurnal currents advect water with less mixing than the semidiurnal currents because they have longer periods. Hence, new water may be advected into Puget Sound when diurnal currents are strong while semidiurnal currents are weak. This occurs around the equinoxes. According to Geyer and Cannon (1982) it may be that new water enters simply when tidal mixing on the sill is small, allowing the baroclinic pressure contrast between the Strait of Juan de Fuca and the main basin to drive the new water through Admiralty Inlet. The minima in diurnal and semidiurnal currents, and hence mixing, coincide around the solstices. Since the observations (Cannon, 1983) indicate considerable inflow during the March-April period (around the vernal equinox), diurnal advection and the lack of semidiurnal mixing are probably important during this period. There are also smaller inflow events around the solstices which presumably occur during periods of small tidal mixing.

## VIII. Needs for further study

During FY83 the major analysis effort will be to synthesis the results from the 1980-81 year-long observations and the 1982 winter-spring observations to develop an understanding of the flux of particulates in the main basin as indicated in the introduction.

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## 2.2.2. Tidal Model

### I. INTRODUCTION

In estuaries toxic substances are associated with particles which are themselves suspended and transported by tidal currents. The objective of this work is to produce a numerical model of tidal currents in an estuary to ultimately be used in conjunction with models of particulate flux and pollutant equilibria to predict the fate of particulate-borne pollutants. Work is behind schedule due, in part, to a three-month delay in the receipt of funds. We point out some unique properties of the tides having to do with observed mean currents and the potential importance of horizontal eddies in our study area (Puget Sound), and we outline efforts to produce a numerical element mesh.

#### A. General Nature and Scope of Study

In estuarine waters most toxic substances are associated with particles, and the circulation of water plays a major role in determining the movement of particulate-borne pollutants. Strong currents suspend particles, mean currents transport them bodily, and weak currents allow for their deposition. In many semi-enclosed basins connected to the sea tidal currents dominate. Apart from their oscillatory components tides can set up long-term mean flows which can have associated sediment and pollutant patterns. Hence a quantitative measure of the currents is essential in order to delineate the pathway and history of particulate matter movement from source to ultimate site of deposition.

#### B. Specific Objectives

The specific objective of this one-year program as presented in the PMEL FY82 Project Development Plan is to

- o develop a computational model of tidal currents in Puget Sound and Elliott Bay.

#### C. Relevance to Problems of Marine Pollution

A number of PMEL projects have focused on Puget Sound as a case study of an estuary where pollutants are associated with suspended particulate matter. Nearly the entire thrust of this work has been observational and process-oriented. What is also needed is a model framework within which to interpret and make observations, sharpen our understanding and make predictions. The tidal model is a logical first step toward modelling the circulation of the region.

### II. CURRENT STATE OF KNOWLEDGE

The tides are shallow water waves caused by the mutual attraction of the ocean waters with the sun and the moon. In a confined basin such

as a bay or estuary the direct attraction is small, and tides there co-oscillate with the adjoining ocean, that is, the tides are forced by a flux of water through the basin's entrance. Up until the last few years tides in confined basins have been modelled by site-specific hydraulic models fashioned of plaster and plexiglass and filled with water. Such models are now being replaced by computational models which offer advantages in speed and flexibility. The models are based on numerical solutions to the shallow water equations. They can be adapted to various regions of study as the need arises although model set-up and calibration must be performed with each new adaptation. The models can be run at various grid resolutions to provide an overall picture of the tides or to focus in on a specific area. Numerical tidal modelling is still a very fertile area of research on three levels--mathematical, numerical and estuarine, and as yet few, if any, standardized, "best" techniques have been agreed upon. Much of the work has been done by research institutions in northern Europe and is related to North Sea tides and storm surge. Unfortunately most of the models are proprietary and not available to us.

A very comprehensive review of tides and tidal currents based on field observations in Puget Sound has recently been completed by Mofjeld and Larsen (1982). For the purposes of the present study the most useful information they provide are their diagrams of lunar semi-diurnal ( $M_2$ ) and solar diurnal ( $K_1$ ) tidal amplitudes and phases in the region.

There are two existing tidal models that cover the entire Puget Sound basin--the University of Washington Department of Oceanography's hydraulic model (Rattray and Lincoln, 1955) and Pease's (1980) empirical model. The hydraulic model is a scaled-down plaster model of the estuary in which the water level is forced up and down by a plunger to mimic the rise and fall of the tides. It is scaled to represent the propagation of the tidal wave in the absence of friction. Unfortunately the turbulent flow of Puget Sound is not well represented by the laminar flow of the model in which molecular friction plays too large a role. Although the hydraulic model reproduces well the gross features of Puget Sound tides, it is difficult to obtain quantitative results on a fine scale or to couple the model results with other models of, say, particulate transport.

The purpose of the empirical model of Pease (1980) is to approximate the tidal current at any site within Puget Sound as a weighted average of the reference currents at the three nearest NOS measurement sites. The reference currents are synthesized from previously measured currents. The weights between reference and predicted currents are assigned subjectively. It is restricted to only  $M_2$  tidal currents; the important  $K_1$  and mean residual tidal currents are neglected. The model has several shortcomings, not the least of which is the subjective nature of the weightings. It has no dynamical basis, hence mass conservation is most likely violated.

### III. STUDY AREA

Puget Sound has been chosen as the study area. It is a fjord-type estuary in which tidal currents are always important and often dominate.

Its waters are generally unpolluted although degrading slightly. It receives most of its pollutant load from two major urban areas, Seattle and Tacoma, via outfalls, runoff and river flow. It is near to PMEL and there exists a sizeable, but scant data set of water properties, tidal elevations and currents dating back at least 30 years.

Currents in the region are due in part to internal waves, winds, estuarine flow and tides. Currents induced by internal waves are usually weak, but can dominate in localized regions due to geographical effects. Strong surface currents are associated with strong winds, hence they are not always present. They have an unknown cumulative effect on the Sound's circulation. The estuarine circulation is driven by freshwater runoff into the basin which is balanced by a landward-moving, subsurface, salt water flow necessary to maintain a steady salinity. Tidal currents are responsible for the maximum, instantaneous currents throughout most of Puget Sound. It is these maximum currents which can suspend particles, carrying them into the water column where they adsorb pollutants as they are transported and settle out again at slack water.

The tidal wave enters the north end of Puget Sound at Admiralty Inlet and travels southward reflecting partially at the Narrows and partially at the end of the southern basin. One version of the model will operate on this scale to mimic the general, overall properties of the tides and currents. The main channel between Seattle and Tacoma is split by Vashon Island into two channels, East Passage on the east and Colvos Passage on the west. It has been observed (Larsen, Shi and Dworski, 1977) that a mean net northwards current of approximately 30 cm/sec exists in Colvos Passage which implies a net clockwise mean circulation around Vashon Island. This may have important implications for the particulate-borne pollutant budget in the region since the two major polluters, Seattle and Tacoma, border the north and south ends of this loop and an area of suspected net deposition, Poverty Bay, lies between them. The tidal model will contain a finer grid submodel to study this region in detail. This 30 cm/sec mean current is likely a net tidal residual flow due to the interaction of the tidal wave with the island. If so it represents a large residual velocity exceeded by only one other reported value, a 76 cm/sec current observed in Minas Basin (Tee, 1976) at the head of the Bay of Fundy. Typical tidal residuals for the oft-studied North Sea are only a few cm/sec.

#### IV. METHOD

The propagation of the tides is represented mathematically by the shallow water equations

$$\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} - fv = -g \frac{\partial h}{\partial x} - \frac{C(u^2+v^2)^{\frac{1}{2}}u}{\rho(H+h)}$$

$$\frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} + fu = -g \frac{\partial h}{\partial y} - \frac{C(u^2+v^2)^{\frac{1}{2}}v}{\rho(H+h)}$$



$$\frac{\partial h}{\partial t} + \frac{\partial}{\partial x} u(H+h) + \frac{\partial}{\partial y} v(H+h) = 0$$

where  $\rho$  is the fluid density,  $u(x,y,t)$  and  $v(x,y,t)$  are the vertically-averaged horizontal velocity components,  $f$  is the Coriolis parameter,  $g$  is the acceleration of gravity,  $h(x,y,t)$  is the water elevation above a reference level,  $H(x,y)$  is the water depth and  $C$  is the drag coefficient. The time is  $t$ , and  $x$  and  $y$  are horizontal Cartesian coordinates. We are using the spectral technique of Pearson and Winter (1977) in which the time variation of  $u$ ,  $v$  and  $h$  is approximated by a few terms of a Fourier series in time with fundamental frequency  $\omega$ , i.e.,  $u$ ,  $v$  and  $h$  are proportional to  $e^{i\omega t}$ . It makes sense to use this periodic representation rather than to timestep the equations of motion since the tides are very nearly periodic. It results in a considerable saving in computer time. The spatial part of the problem is solved by formulating the differential equations in terms of a variational problem and using a finite element technique. The nonlinear terms are solved for iteratively. The geographical region is subdivided into triangular finite elements, and flow velocities and tidal heights are solved for in each small triangle.

The laying-out of a triangular grid on an irregular geographic region can be time consuming. We are adapting the numerical algorithms of Thacker, Gonzalez and Putland (1980) first developed for use in storm surge modelling (Thacker, 1979). They produce a triangular mesh which fits the shoreline smoothly without great triangle distortion. Depths at arbitrary locations are linearly interpolated to each triangle.

## V. RESULTS

Work on the Puget Sound tidal model is behind schedule for two reasons: (1) there was a three-month delay in the receipt of funds, and (2) the job has proven more difficult than first thought. Three months work has been devoted to the project to date, and three more months work will carry over into FY83. Work is planned for completion in April 1983 resulting in a total of nine months effort as opposed to the six months effort originally proposed. This report will serve as a progress report rather than a final report. During the past fiscal year work has focused on two areas--reading the relevant literature and producing the triangular mesh.

A search through the scientific literature on tidal modelling has revealed two aspects of Puget Sound tides which are unique. The large mean residual circulation around Vashon Island has already been mentioned. The second aspect relates to the fact that Puget Sound is narrow (2-5 km) and deep (100-200 m) by estuarine standards. Much tidal modelling has been conducted in the North Sea which is wide (600 km) and shallow (50 m). The bottom friction provides the main retarding force; the horizontal transfer of momentum via eddies is small in comparison. In Puget Sound, however, a scaling analysis due to Robinson (1981) indicates that the horizontal momentum transfer may be as or more important than bottom friction. If true, this means that horizontal eddies might be an important component of Puget Sound's circulation. This has a bearing on

pollutant fluxes and residence times since such eddies may deflect the paths of particulates as they traverse the estuary. A current observed at a single site may not be part of a large-scale flow, but may instead be part of a local eddy circulation.

When a numerical tidal model is transferred from one region to another a new mesh based on the boundary points and depths must be generated. We are using an automatic grid-generating routine (Thacker, Gonzalez and Putland, 1980) so that the model can be quickly adapted to other regions or can be refined on a subset of the overall region. We have received a copy of the computer code from the Institute of Ocean Sciences, Patricia Bay, British Columbia, where some improvement to the work of Thacker et al. (1980) was made. We are in the process of adapting that code to transfer from a Univac to a CDC computer. It has been found recently that the automatic grid generation technique does not work as well for the angular shorelines characteristic of the Pacific Northwest as it did for smooth Gulf Coast shorelines.

Digitized depth data for Puget Sound is available on magnetic tape from the National Ocean Survey. A copy has been secured, but it is not useful to us since not all of the Sound is covered and that which is covered is done so on a very fine scale. We shall obtain depths from bathymetric charts in the usual way.

#### VI. NEEDS FOR FURTHER STUDY

Clearly the computational tidal model needs to be completed. This will provide a way to compute tidal currents which can be coupled with the work of Lavelle and Mofjeld (1982, reported elsewhere in this report) in two ways. Their work affects the tidal model in that they show a way to calculate the form of the time-dependent bottom drag for oscillatory flows. The bottom drag affects the magnitude and phase of the tidal currents. Conversely, the tidal model will give vertically-averaged horizontal velocities needed to drive their bottom boundary layer model to provide estimates of sediment erosion and deposition. These model predictions need to be compared with field observations of tidal currents and suspended particulate matter fluxes. All of these components are being proposed to OMPA by PMEL for a three-year FY83-85 study.

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## 2.3. PARTICULATE TRANSPORT

### 2.3.1. PARTICLE FLUX IN THE WATER COLUMN

#### 1. INTRODUCTION

##### A. General Nature and Scope of Study

Suspended particulate matter has extensive influence on the quality of estuarine waters. This influence arises from the role of particles both as transport agent for various natural and man-made substances and as mobile and ubiquitous sites for a diverse suite of physical/chemical/biological reactions which can create, alter, or eliminate these substances. The physical processes which control the distribution and transport of particles, particularly in semi-enclosed embayments where urbanization is concentrated, are important. Pollutants associated with particles undergo various fates after introduction into an estuarine system. They may accumulate near the point of introduction if they remain insoluble and if dispersal currents are weak or the supply rate high. They may be widely dispersed and removed entirely from the system if they pass through a soluble phase or if the current system is vigorous, or they may be transported to some other part of the system by a series of erosion and redeposition cycles. Since the distribution of particulate pollutants is so sensitive to the transport characteristics of a given environment, knowledge of these characteristics is critical, enabling subsequent monitoring efforts to be made in the right place at the right time for the greatest return on observational investment.

In response to these needs, PMEL is engaged in a long-term study of particle transport in Puget Sound, Washington. Seasonal cycles of distribution and composition of particle concentrations in the main basin of Puget Sound are being determined by periodic occupation of a standard 11 station grid (Fig. 1.4 ). Vertical profiles of salinity, temperature, and light attenuation (an optical measure of particle mass concentration) are collected at each station in order to compare temporal and spatial variations in particle concentrations with those of the hydrographic properties. Direct measurements of particle transport are being made with long-term (up to a year) deployments of current meter/transmissometer instrument packages to continuously record the horizontal flux of particles past key sampling locations, and with sediment traps to collect samples of the vertical flux of particles at these same locations. Integration of these measurements should allow us to describe the particle mass loading typical of various regions and depth horizons of the Sound, the transport processes which control the exchange of particles from one region or depth zone to another, and the dependence of the particle distribution and transport on the circulation pattern.

##### B. Specific objectives

The principal objectives of this four-year program were presented in the PMEL/LRERP FY82 Project Development Plan and are restated here:

1. Quantify the distribution of particles in a fjord estuary and relate the distribution to the hydrographic and circulation characteristics of the estuary.
2. Quantify the vertical flux and aggregation characteristics of the particulate matter at representative depth horizons and locations.
3. Quantify horizontal transport rates of particles at representative depth horizons and locations and relate the transport variability to circulation variability.
4. Determine the role of resuspension in recycling bottom sediments.
5. Estimate particle residence times--the mean length of time for a particle to be removed from the water column by flushing to the ocean, burial below the level of sediment resuspension, or destruction. Residence times may be expected to vary as a function of particle type and place of entrance into the estuarine system.

#### C. Relevance to the Problems of Marine Pollution

In estuarine waters, most toxic substances are associated with particles. Thus decisions regarding the management of toxic substances in a particular environment will be successful only to the extent that they are based on a sound understanding of the distribution and fate of particles and the effect of these particles and their chemical loading on the chemistry and biology of the entire system.

The research described in this report seeks to develop a predictive capability for particle transport in coastal and estuarine waters. Estuaries are oceanographically complex, and the fate of particles introduced into them depends to a large extent on when, where, and how the introduction occurs. This research is closely aligned with other OMPA-sponsored research which is specifically interested in the fate and transformation of the toxic substances associated with particles.

## II. CURRENT STATE OF KNOWLEDGE

Extensive reviews of particles in estuaries and coastal waters have been presented by Meade (1972), Drake (1976), and Schubel (in press) among others. Concentrations of particles in these environments vary over several orders of magnitude. Puget Sound, although it has a historical base of almost 50 years for hydrographic properties (Collias, 1970), has had no organized research into its particle load until very recently and is not mentioned in any of these summary articles. Although particle concentration levels for many estuaries are available, little systematic, long-term research has been directed at the processes which create these particle distributions. For example, Gibbs (1977) and Kirby and Parker (1977) state that the transport of particles in an estuary cannot be assumed to simply follow the transport of water;

settling, aggregation, resuspension, and other processes which control the distribution of particles result in a residual transport quite different from that for water. Schubel (in press) concludes in his review that high priority estuarine research areas include studies to determine the routes and rates of particle transport, studies to determine the effectiveness of estuaries in trapping river-borne particle discharges, and studies to quantify fluvial discharge of particles into estuaries. The present research is addressed to these areas.

### III. STUDY AREA

The Puget Sound main basin is a tidally dominated fjord-like estuary approximately 66 km long and 6 km wide (Fig. 1.4). The general area is described in the Executive Summary. Thus far studies of particulate transport have emphasized Elliott Bay and a station off of West Point (PS-7). Measurements of particulate concentrations have been made throughout the Sound.

### IV. SOURCES, METHODS, AND RATIONALE OF DATA COLLECTION

The primary data source for this project is light attenuation data from 0.25 m path length transmissometers and sediment traps. Continuous profiles of light attenuation are collected along with hydrographic information from a transmissometer interfaced to a CTD system. Long-term particle flux data are recorded by transmissometers interfaced to Aanderaa current meters. Discrete water samples are periodically collected and filtered through 0.4 mm membrane filters in order to calibrate the transmissometer readings in terms of the mass concentration of particles. This procedure and the results have been described by Baker (1982a). The correlation coefficient between the two measurements is normally  $\sim 0.85$  with a least-squares regression equation of  $\alpha = 0.6C + 0.4$  where  $\alpha$  = attenuation ( $m^{-1}$ ) and  $C$  is the particle concentration in  $g\ m^{-3}$ . Attenuation values are used almost exclusively in this report; they are roughly equal to particle concentrations in  $g\ m^{-3}$ .

Particle size distributions are measured for selected samples using a Coulter Electronics ZBI<sup>®</sup> particle size analyzer and C1000<sup>®</sup> Channelizer. Particle size distributions are used to identify different particle populations at different locations in the study area.

The vertical flux of particles in the water column is dominated by the large, rare, fast settling particles not easily sampled by water bottles or optical devices. These particles constitute an important pathway for the transfer of particles from the surface to the deep water layers. Their flux and composition is measured on samples collected by newly designed Sequentially Sampling Sediment Traps whose development was funded by OMPA (Baker, 1982b; Baker and Milburn, in press). Each trap collects 10 separate samples per deployment in order to measure short time variations important in estuarine environments. Samples in Puget Sound have been collected at approximately seven-day intervals.

In addition to the main basin work, limited investigations have also been carried out in two major urbanized embayments.

All cruises and mooring deployments undertaken to date in this project are summarized in Table 2.5.

## V. RESULTS AND DISCUSSION

### 1. Particle Distributions

Four characteristic features of the particle distribution in the Puget Sound main basin are always present to a greater or lesser extent: 1) a thin surface layer of high turbidity, 2) a mid-depth zone of low turbidity, 3) a bottom nepheloid layer (BNL) of variable thickness and turbidity, and 4) vertical particle fronts at the bordering sills. A representative particle distribution illustrating these features is given in Figure 2.3.1.

Attenuation values in the upper 10 m of the main basin are generally  $>0.8 \text{ m}^{-1}$ , reflecting quasi-seasonal particle sources such as freshwater runoff and phytoplankton production. Strong river sources such as the Skagit, Snohomish, and Stillaguamish entering via Possession Sound (approximately the position of station PS8) and the Puyallup in Tacoma (PS3) are often responsible for very high attenuation levels ( $>1.0 \text{ m}^{-1}$ ) near their discharge points. This layer can be expected to have high temporal variability on both weekly and seasonal time scales.

The surface layer is reduced or absent in both the landward and seaward sill zones. Mixing in the shallow Narrows (PS2) results in an almost uniform vertical particle distribution with only a weak surface turbidity zone. The situation is the same over the shallowest section of Admiralty Inlet where attenuation is normally uniform from top to bottom.

Below about 30 m there is a thick zone where attenuation values are almost invariably less than  $0.8 \text{ m}^{-1}$  and often less than  $0.6 \text{ m}^{-1}$ . Vertical and horizontal gradients in particle concentrations are low and generally uniform. The clearest water is found between 30 and 65m, bracketing the zone of no-net-motion which separates the seaward flowing surface water from the landward flowing deep water (Barnes and Ebbesmeyer, 1978; Cannon et al., 1979). The southern half of the main basin normally contains the best-developed minimum zone. The lateral extent of this feature is typically from PS3 to about PS6 or PS7; that is, within the East Passage separating Vashon Island from the eastern shore of the main basin. (Fig. 1.4 ).

The BNL exhibits strong particle gradients both horizontally and vertically. Concentration contours below  $\sim 150 \text{ m}$  are dominantly horizontal, increasing from  $\sim 1.0 \text{ m}^{-1}$  along the 150 m horizon to values  $>4 \text{ m}^{-1}$  at depths  $>200 \text{ m}$ . Near-bottom values vary markedly along the basin floor.

# PUGET SOUND MAIN BASIN

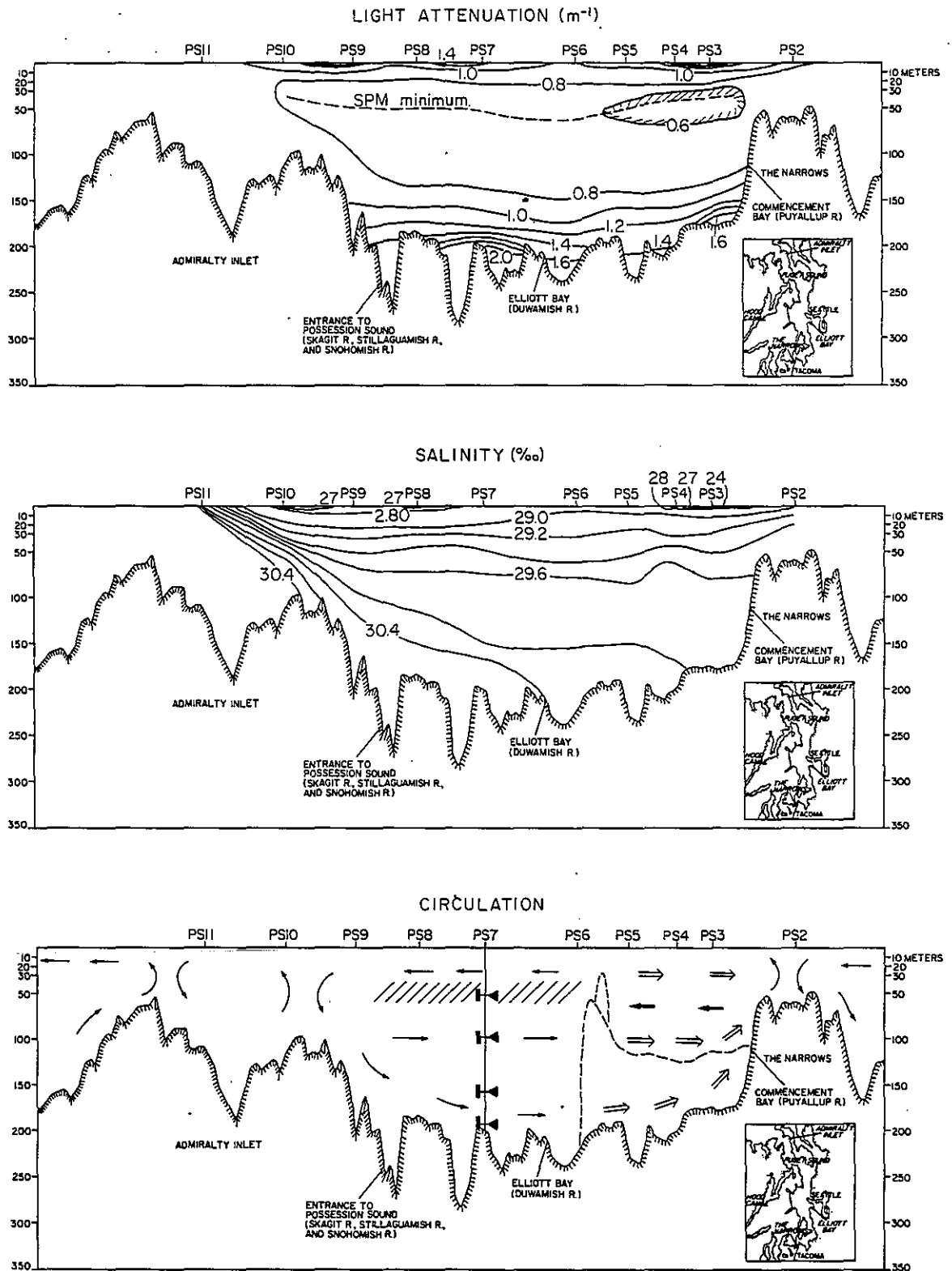


Figure 2.3.1. Idealized cross sections of light attenuation, salinity, and circulation in Puget Sound. The dashed bathymetry in the bottom box represents Colvos Passage, and the thick solid arrows the net circulation northward there. Zone of no-net-motion shown by slashes.



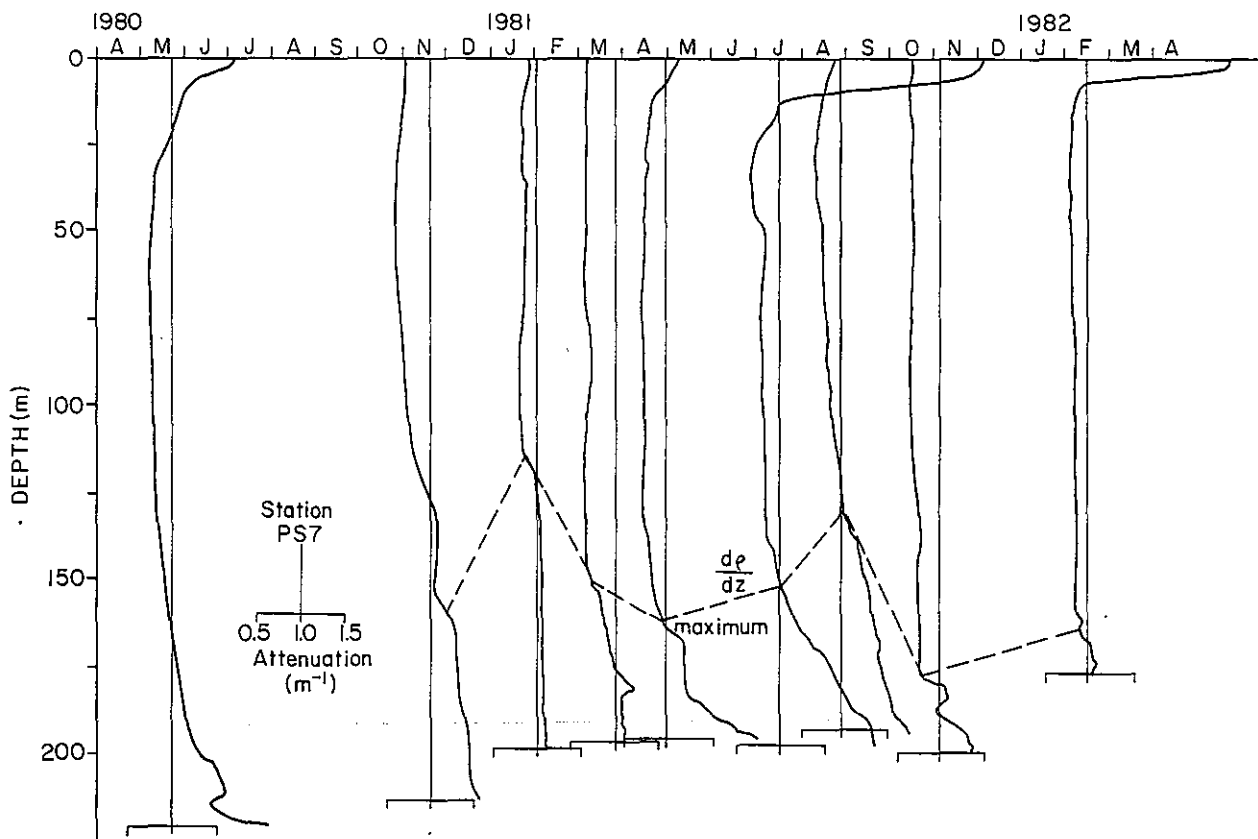


Figure 2.3.2. Time series of attenuation profiles at Station PS7. Straight vertical line marks the sampling time and the attenuation value of  $1.0 \text{ m}^{-1}$  on each profile. The deep layer stability (Brunt-Väisälä frequency) maximum generally occurs at the top of the BNL.

The cell-like circulation described above for the main basin (Fig. 2.3.1) creates vertical fronts in cross sections of salinity and attenuation, fronts which are noticeably distinct from the very low horizontal gradients within the mid-depth zone of main basin itself. The increase in particle concentrations within the Narrows appears to be the result of two factors: vertical mixing of the turbid surface plume of the Puyallup River, and upwelling of relatively turbid deep water from the main basin and waters south of the Narrows. Similarly, the particle front at Admiralty Inlet is at least partly the result of downwelling surface water made turbid from the plumes of several rivers within Possession Sound.

Particle distributions in Elliott Bay (Baker, 1982a) and Commencement Bay (Baker and Walker, in press) follow the three-layer distribution described above. Particle concentrations in the surface layer of each embayment are dependent on particle transport in the Duwamish and Puyallup Rivers and thus show a high degree of correlation with surface salinity.

## 2. Influence of Hydrography and Circulation on the Particle Distribution

The vertical distribution of particles in the main basin is intimately related to the vertical stratification of the water column. A time series plot of attenuation profiles recorded at station PS7 over 18 months indicates that the top of the BNL occurs at the depth of the maximum stability (Brunt-Väisälä frequency) in the deep water (Fig. 2.3.2). This stability maximum is caused by a weak halocline resulting from periodic inflows of new marine water over Admiralty Inlet and into the bottom layer of the main basin. The density gradient at the halocline creates a zone of minimum turbulence which inhibits diffusion of suspended particles upward and out of the BNL.

The principal source of excess particles in the BNL is resuspension from the bottom sediments. Strongly fluctuating tidal currents result in rapid and large increases in BNL turbidity. Data collected from a current meter/transmissometer 5 m above bottom during the STE-3 deployment at PS7 (Table 2.5) suggest that the erosion threshold at that time was  $\sim 30$  cm sec<sup>-1</sup>. Data from seven accelerating flood tides where the maximum speed exceeded 40 cm sec<sup>-1</sup> were combined and plotted as mean values of attenuation for successive 2.5 cm sec<sup>-1</sup> speed intervals (Fig. 2.3.3). Sharp increases in turbidity occurred between 32.5 and 40 cm sec<sup>-1</sup>. The attenuation decrease above 40 cm sec<sup>-1</sup> may be caused by a decrease in the erosion rate (perhaps because the most easily erodable surface "fluff" layer is removed at speeds below 40 cm sec<sup>-1</sup>), and/or by a mixing of the already suspended particles higher in the water column and thereby lessening the near-bottom concentration.

Changes in turbidity caused by local erosion are difficult to resolve from those caused by advection using only the single point measurements described above. Because of this confoundment more sophisticated measurements, using several near-bottom instruments arrayed vertically and horizontally, were carried out in the spring of 1982 and will be repeated during 1983. Preliminary analyses of these data are discussed in separate reports to OMPA. Nevertheless it seems clear

# ACCELERATING FLOOD TIDES 5m ABOVE BOTTOM

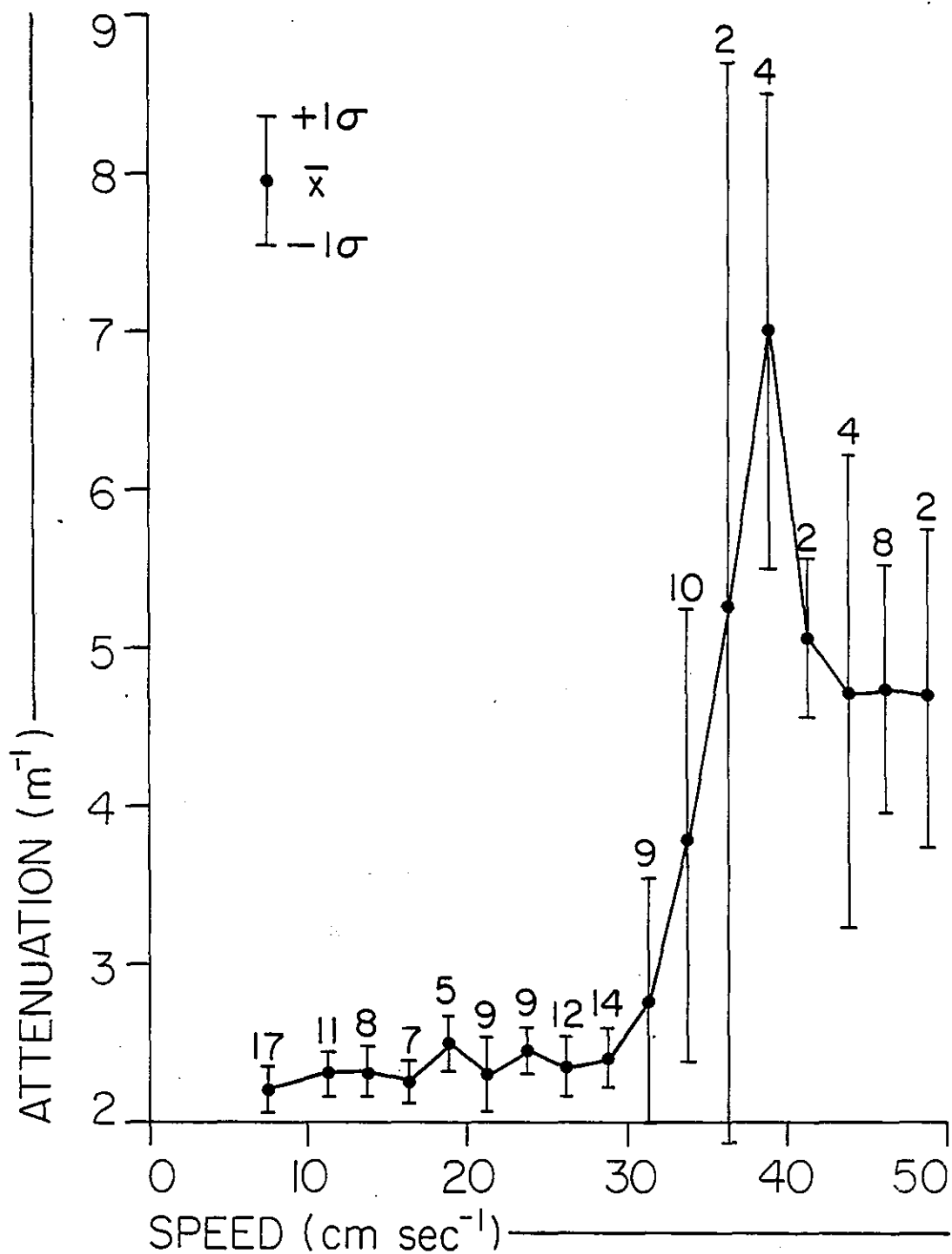


Figure 2.3.3. Plot of light attenuation vs. current speed compiled from seven tidal cycles.

from several lines of evidence that BNL turbidity at a particular site is predominantly the result of local, or at least nearby, erosion. Most basically, fjord-like basins provide little opportunity for advective sources of particles to the bottom water. Although salinity cross sections clearly show replenishment of the bottom water by inflows of marine water over Admiralty Inlet, this water is always of low turbidity relative to the bottom water in the main basin (Fig. 2.3.1). Furthermore, the BNL turbidity at a particular station waxes and wanes in proportion to the tidal cycle. Further discussion on resuspension and advection in the BNL will be presented in the following sections treating particle transport.

The influence of circulation on particle concentrations is summarized in Fig. 2.3.4, where the mean particle concentration and mean salinity in the surface and deep layers is plotted against station location. Concentration and salinity averages are based on all available data collected to date and include cruises from throughout the year (e.g., Table 2.5). The salinity plot identifies the important sources of fresh and salt water and describes their mixing. High salinity water from outside the main basin enters over Admiralty Inlet and is rapidly diluted before spreading into the deep layer where salinity is very homogeneous. Additional mixing with surface water at the Narrows further dilutes the bottom water salinity. Freshwater sources identified here are Puget Sound south of the Narrows, the Puyallup River (at PS3), and the rivers entering via Saratoga Passage (at PS8). Colvos Passage (station PS1) water is a mixture of surface and bottom water derived from the Narrows.

The particle concentration plot follows a similar pattern although many important details differ. Attenuation values in the surface water steadily increase from PS5 to PS11 because of continual addition of particles from fluvial and other sources as the surface water flows north from the surface divergence between PS6 and PS5. Lowest surface values consistently occur in the East Passage area as a result of the divergence. Vigorous tidal pumping over Admiralty Inlet causes the surface introduced particles to be mixed throughout the water column after which a portion is injected into the deep layer along with new bottom water. Bottom water on the seaward side of Admiralty Inlet typically has attenuation values on the order of  $0.9 \text{ m}^{-1}$  or less and is not a significant particle source.

Concentration values in the deep water are much more regionally variable than salinity. The persistent maximums between PS5 and PS7 may be explained by along-basin differences in tidal currents. Mofjeld and Larsen (in press) found that the deep tidal currents computed by harmonic analysis of near-surface current observations were higher between stations PS6 and PS7 than anywhere else between the sills. The fact that mean concentration values continually decrease from PS7 to PS2 makes clear that a substantial amount of those particles added to the deep layer by resuspension in the central main basin are lost to sedimentation as the bottom water flows southward. Finally, the intermediate concentrations characteristic of Colvos Passage emphasize its role as a northward conduit of East Passage surface and bottom water partially mixed in the Narrows sill zone.

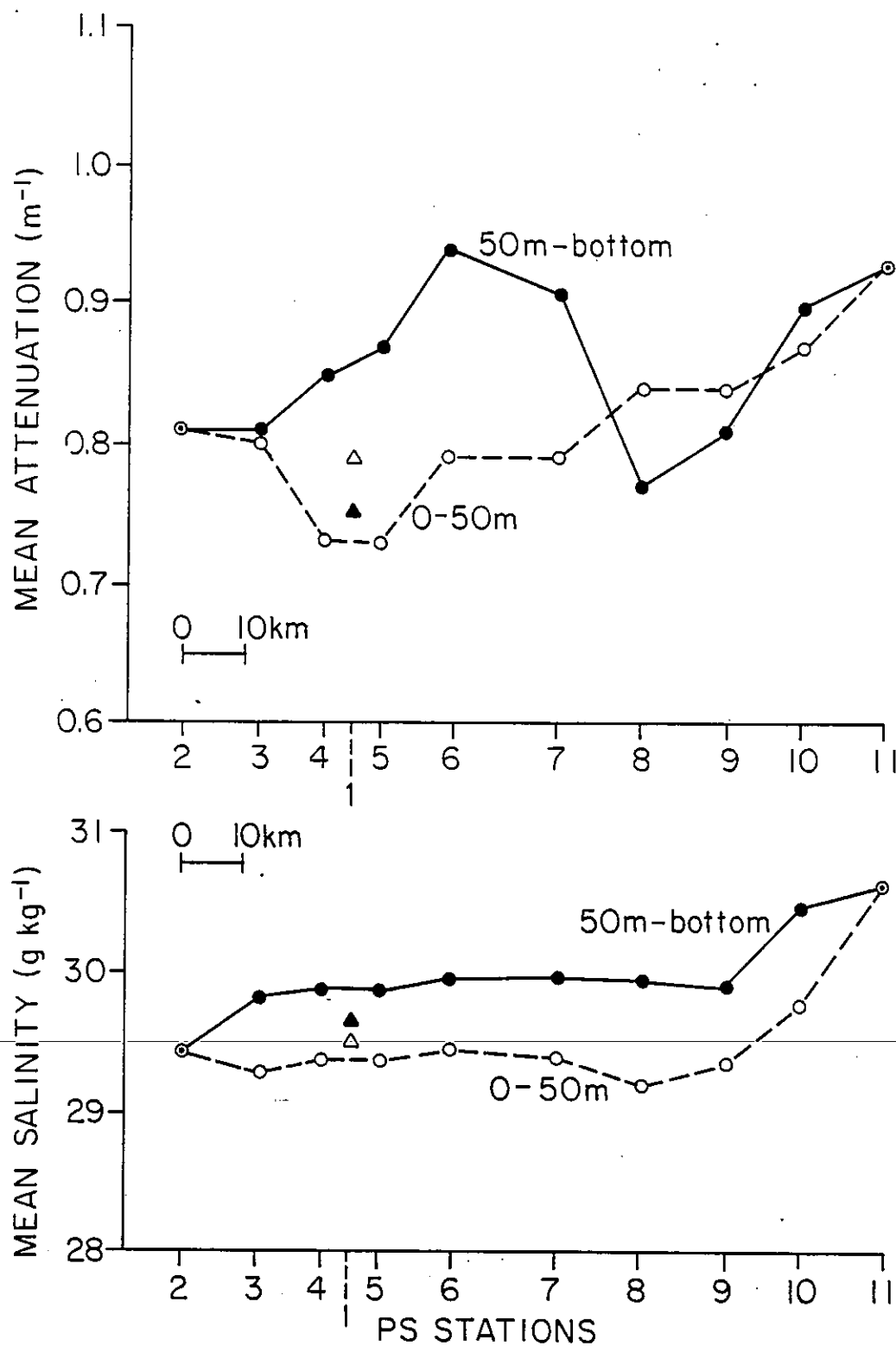


Figure 2.3.4. Scatter plots of average particle concentration and salinity from the surface and deep layers of PS1 and PS3-10. Only a single value (surface to bottom) was calculated for the sill stations, PS2 and 11. Note that Colvos Passage (PS1) is distinct from the East Passage stations.

### 3. Vertical Particle Transport

The particle distribution dynamics described above results in distinct particle populations in the surface, mid-depth, and bottom layers of the water column, as shown by the two-dimensional array of particle size distributions collected in the main basin during July, 1981 (Fig. 2.3.5). This distribution, however, does not imply that the surface and bottom particle populations are isolated from each other. Transfer of particles between these layers occurs by two principal methods. As described above, tidal pumping over the sill zones results in a homogeneous particle mixture--note the vertical uniformity of the particle size distributions at PS10 in Fig. 2.3.6. Of greater importance in transferring particles from the surface layer to the deep layer--where the probability of permanent retention in the estuary greatly increases--is the rapid vertical settling of relatively dense particles or agglomerates.

Figure 2.3.6 summarizes a year-long data set measuring the vertical flux of particles at five depths at station PS7. Each data point represents a week-long average of the flux. The principal feature is the continual increase in flux from surface to bottom, an average increase of ~65x for the gross sedimentation rate (GSR) between 50 and 200 m. Most of this increase occurred between the 160- and 200-m horizons and represents continued recycling of BNL particles by repeated erosion/deposition cycles. Flux at 50 and 100 m (above the resuspension zone) averaged  $\sim 2.4 \text{ g m}^{-2} \text{ day}^{-1}$  for the year, or  $\sim 1.7 \text{ mm yr}^{-1}$  based on a dry density of  $2.5 \text{ g cm}^{-3}$  and a water content of 80%. (This rate agrees favorably with an observed average rate of  $\sim 3.1 \text{ mm yr}^{-1}$  in the traps themselves. A mass flux of  $2.4 \text{ g m}^{-2} \text{ day}^{-1}$  would yield a  $3.1 \text{ mm yr}^{-1}$  sedimentation rate if the wet density was  $0.29 \text{ g cm}^{-3}$ .) Measured main basin accumulation rates based on  $^{210}\text{Pb}$  profiles in gravity cores from depths  $>160 \text{ m}$  are on the order of  $5\text{-}10 \text{ mm yr}^{-1}$  (Schell et al., 1977), although this data is uncorrected for bioturbation effects and thus may be in error (Turekian et al., 1980). If this imbalance is approximately correct, however, it implies that the fine-grained sediments along the central axis of the main basin are receiving sediment from sources not adequately measured by the sediment traps, such as downslope movement of fine-grained sediments along the sides of the main basin. The fact that fine-grained sediments preferentially accumulate at depths  $>\sim 160 \text{ m}$  supports this hypothesis.

Seasonal trends in the GSR were slight. Surface values were generally lowest in summer when river runoff was lowest. The greatest seasonal change was seen in the 160-m traps, where average values were high in the fall and winter and low in the summer. This trend may reflect seasonal changes in the thickness of the BNL; at times when the near-bottom halocline is near or below the 160-m level, sedimentation in the 160-m trap is reduced because resuspended sediments are largely trapped below the halocline.

Unlike the GSR, the flux of phytoplankton pigments (chlorophyll a plus phaeophorbide) showed a strong seasonal signal at all depths (Fig. 2.3.7). Maximum flux occurred not during May, the time of historically greatest productivity (Ebbesmeyer and Helseth, 1976), but during late summer.

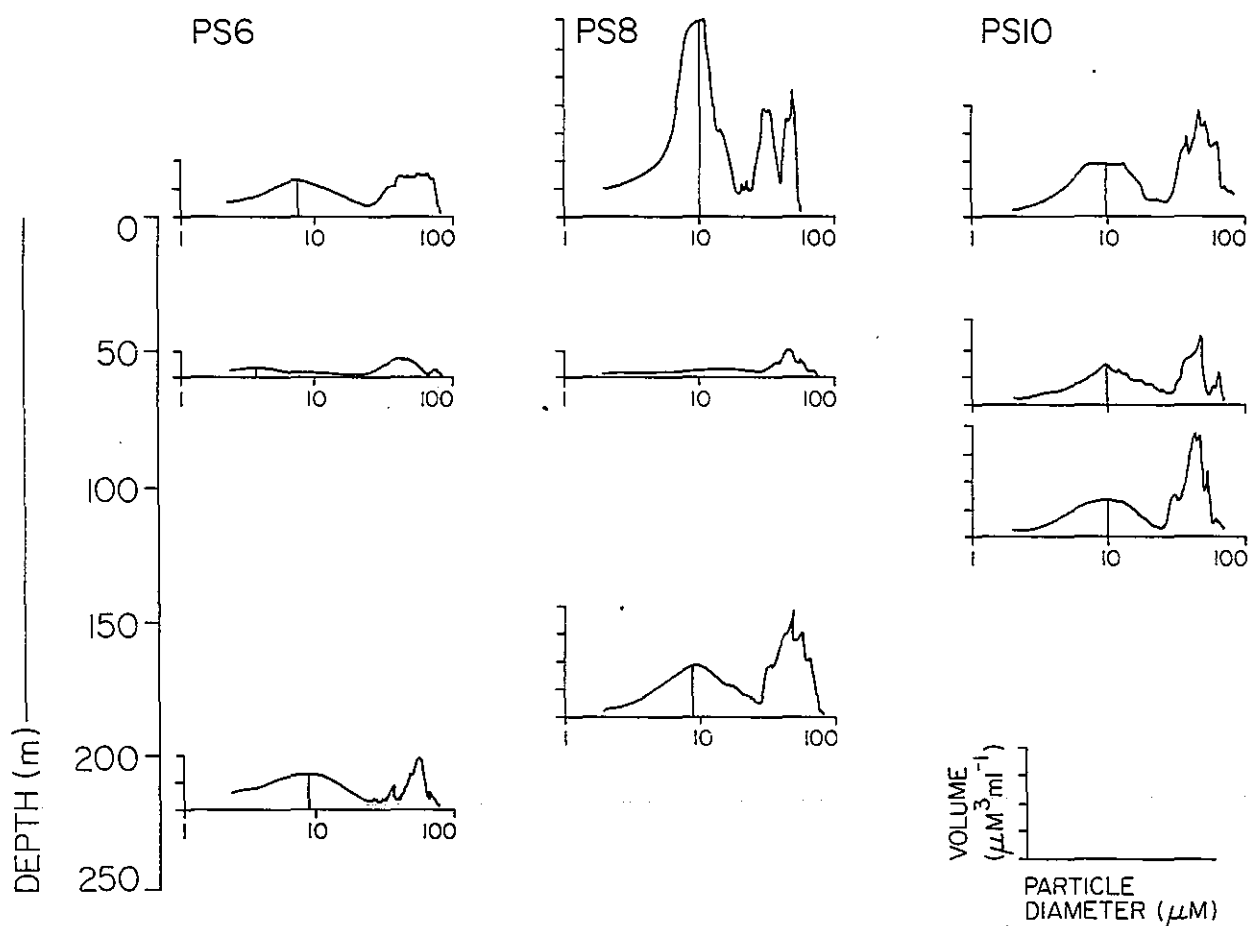


Figure 2.3.5. Particle size distribution plots illustrating the anomalous nature of the mid-depth water in the main basin (PS6 and 8) and the well-mixed water over the sill (PS10).

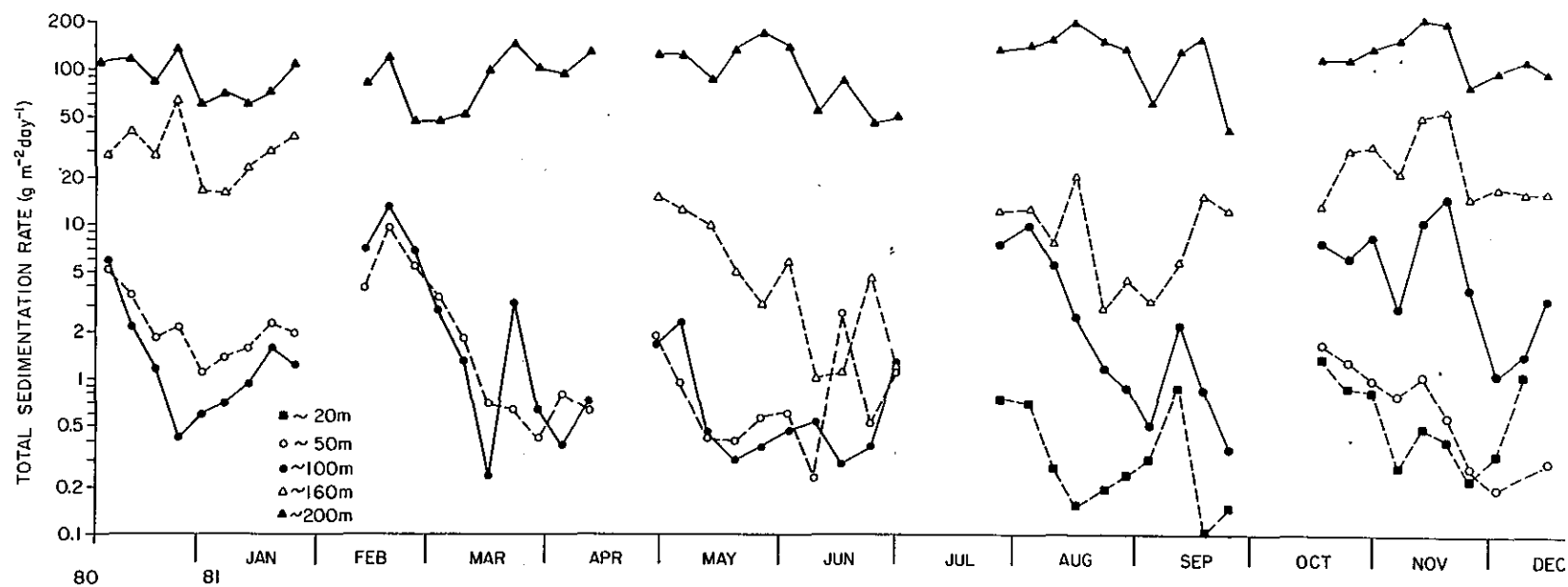


Figure 2.3.6. Sediment trap data from PS7. Each symbol represents an average sedimentation rate for about one week at a particular depth.



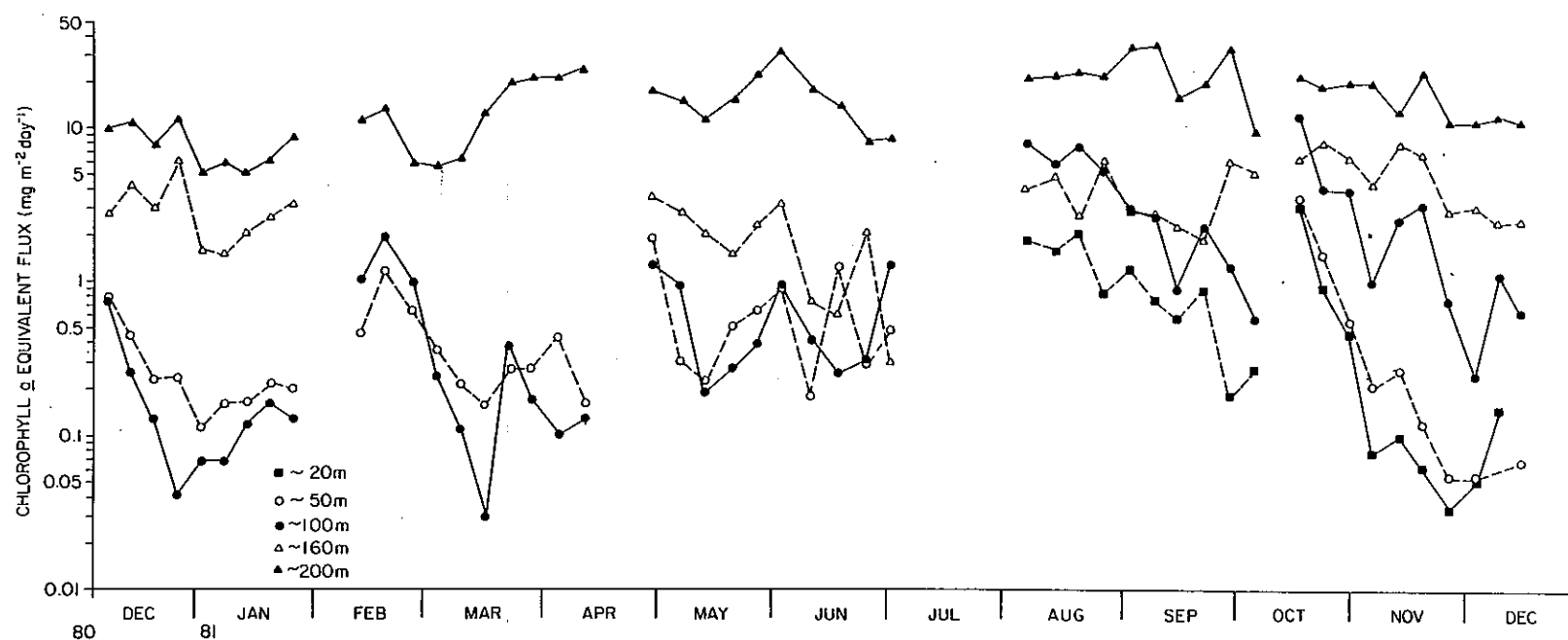


Figure 2.3.7. Concentration of phytoplankton pigments in the settled particles at various depths from the data in Fig. 7. 200-m samples are diluted by resuspended sediment.

Of particular interest to this study are the depth and temporal trends of the ratio of pigment sedimentation rate (PSR) to GSR (Fig. 2.3.8) because it can be used as a measure of particle mixing in the estuary. Because phytoplankton pigments originate essentially exclusively in the surface waters, the PSR/GSR ratio in rapidly settling particles is fixed at the surface and can be used to monitor vertical transport rates. During winter, the PSR/GSR ratio was low and uniform at all depths. In early spring the ratio rose sharply and became highly variable on a weekly scale. Large peaks were also observable in the near-bottom trap, even though the magnitude was reduced because of dilution by resuspension of relatively pigment-free bottom sediment (pigment concentration  $\approx 5 \times 10^{-5}$ ). Preliminary results from the 1982 field experiment during which sediment traps were deployed on five moorings from Admiralty Inlet to the south end of East Passage indicate that the PSR/GSR ratio is relatively uniform throughout the main basin even though GSR and PSR levels individually vary by as much as two orders of magnitude within a few weeks time. Sharp increases in the PSR/GSR ratio which marked the onset of the spring bloom (e.g., the March data on Fig. 2.3.8) occurred with a maximum offset of about two weeks between the northern and southern ends of the main basin.

The PSR/GSR ratio undergoes marked short-term variability as changes in light, nutrient concentration, and tidal mixing induce the growth and decline of phytoplankton blooms, and as the supply of non-biogenic material is effected by changes in fluvial input, shore erosion, and other sediment sources. The pronounced spatial and temporal uniformity of this ratio argues for an efficient particle mixing process in the main basin which results in vertical uniformity on a time scale of no more than a few days and horizontal uniformity on a scale of a week or two. Such rapid particle mixing implies that particles introduced into one part of the main basin will not long remain isolated from the rest of the estuary.

#### 4. Horizontal Particle Transport

Periodic inflows of new bottom water over Admiralty Inlet provide an important flushing mechanism to the entire Puget Sound system (Barnes and Ebbesmeyer, 1978; Cannon, 1975; Cannon and Ebbesmeyer, 1978). The effect of these inflows on particle transport in the deep layer, and the main basin as a whole, is significant (Figs. 2.3.9 and 2.3.10). Inflow events shown on Figs. 2.3.9 and 2.3.10 can be identified by approximately fortnightly increases in the daily peak speed 5 or 45 m above bottom. Inflow of new bottom water is believed to be enhanced during neap tides when dilution of marine water by mixing with estuarine water over Admiralty Inlet is at a minimum (Geyer and Cannon, in press). Inflows are accompanied by peaks in the 24-hour-average salinity, representing the actual arrival of the newly intruded bottom water. Inflows are also characterized by sharp changes in the turbidity of the bottom water. Turbidity changes are recorded both by attenuation (which deteriorates after several weeks because of progressive fouling of the transmissometer windows by biological growth) and the attenuation variance, which is less sensitive to absolute changes in light transmission. Note that turbidity changes are clearly observable at the 160-m level during the

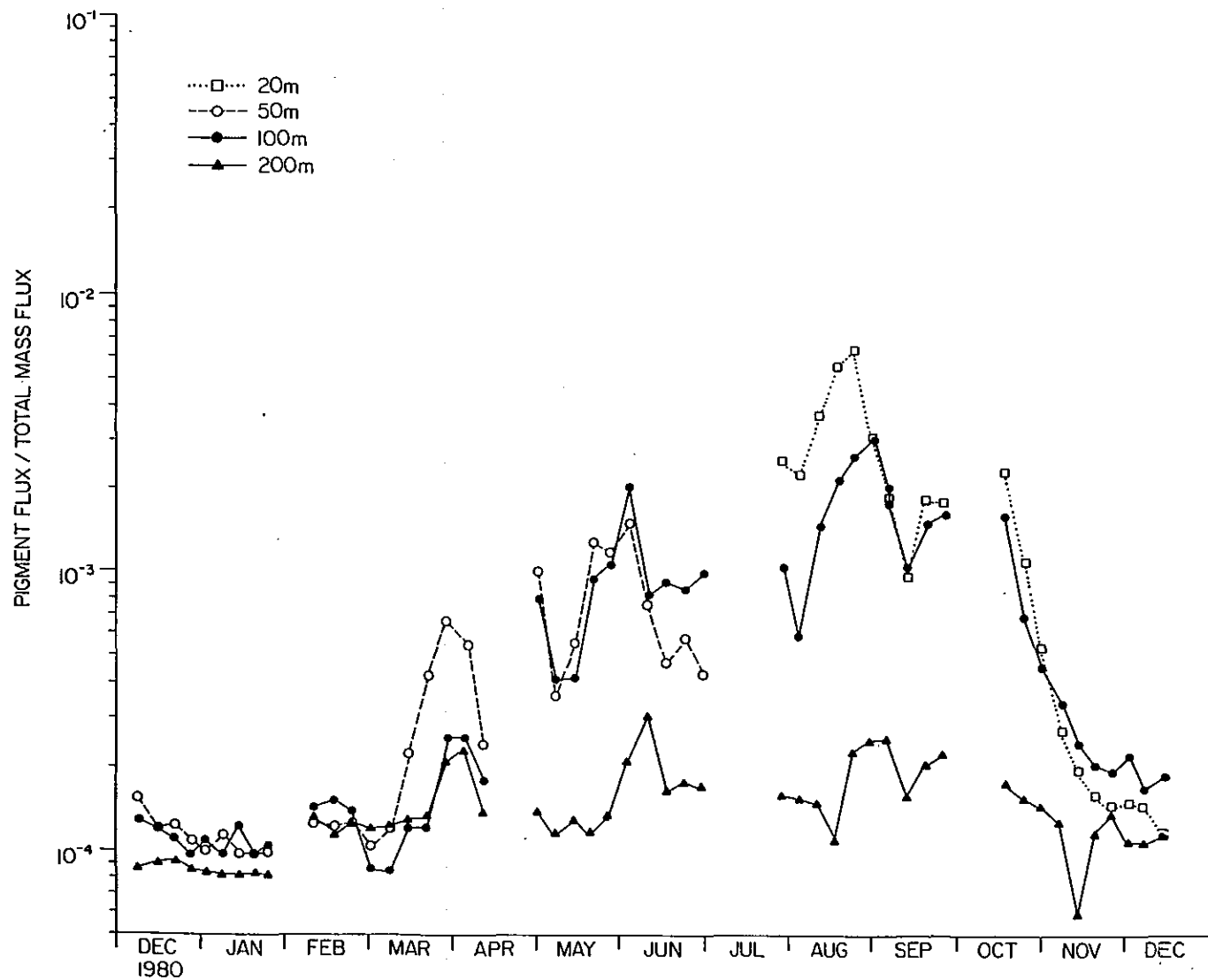


Figure 2.3.8. Seasonal trend of ratios of pigment sedimentation rate (PSR) to gross sedimentation rate (GSR) at three depths.

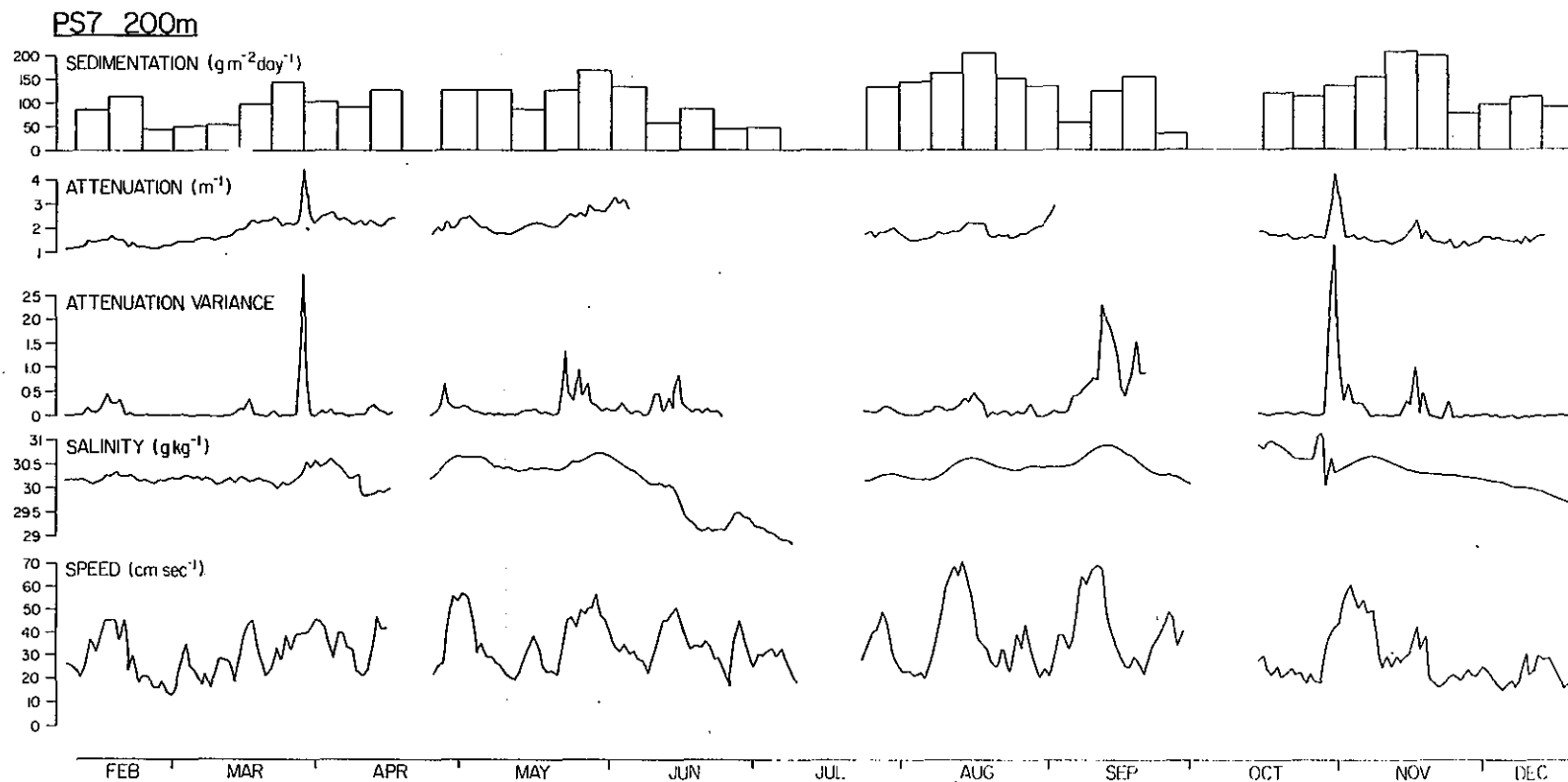


Figure 2.3.9. Sedimentation rate 24-hr mean and variance of attenuation, 24-hr mean salinity, and daily peak speeds from instruments moored 45 m above bottom at PS7.

PS7 160m

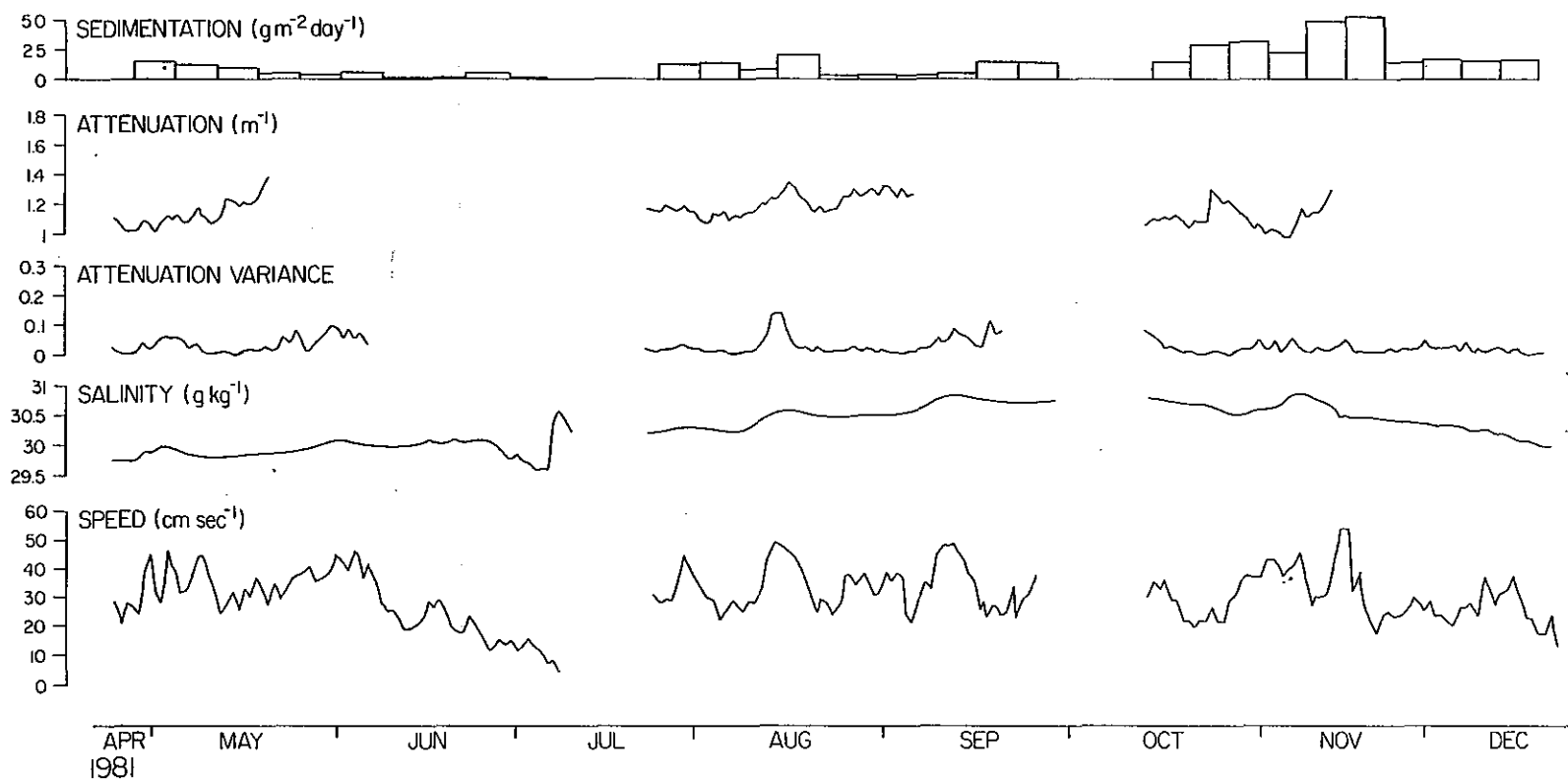


Figure 2.3.10. Sedimentation rate, 24-hr mean and variance of attenuation, 24-hr mean salinity, and daily peak speeds from instruments moored 45 m above bottom at PS7.

inflow events, although the magnitude is much reduced from the 200-m level. Peaks in the sedimentation record also correspond in a general way to the inflow events.

The horizontal particle flux can be calculated from the attenuation and current velocity time-series data by vector addition of the mean and variable portions of the flow along two component axes. Thus

$$\text{Flux} = [(\bar{u}\bar{c} + \frac{1}{n} \sum u'c')^2 + (\bar{v}\bar{c} + \frac{1}{n} \sum v'c')^2]^{\frac{1}{2}}$$

where  $\bar{c}$ ,  $\bar{u}$ , and  $\bar{v}$  are the series means of particle concentration and velocity, and  $c'$ ,  $u'$ , and  $v'$  are the deviation from the mean in each of  $n$  records. The direction of the flux relative to the component axes is given by

$$\theta = \tan^{-1} \left( \frac{\bar{u}\bar{c} + \frac{1}{n} \sum u'c'}{\bar{v}\bar{c} + \frac{1}{n} \sum v'c'} \right)$$

All records were terminated before fouling of the transmissometers was significant.

In order to estimate a landward particle transport in the deep layer at PS7, the flux measurements at 160 and 200 m were integrated over the water column below 50 m according to the following approximation: flux between 50 and 160 m is uniform and equal to the flux at 160 m, the approximate top of the BNL (Fig. 2.3.2); flux increases linearly from 160 m to 200 m; and flux below 200 m is uniform and equal to the 200 m flux. This approximation is based on a typical attenuation profile from station PS7 and the observations that flow at 160 m is a reasonably good (although conservative) indicator of flow between 50 and 160 m (Cannon et al., 1979). The results for moorings STE 2-5 (data recovery was poor during STE 1 and at 160 m during STE 2), expressed as the mass of material transported up estuary (225-260°T) through a unit cross section 150 m high, are shown in Fig. 2.3.11. Several implications are clear. Seasonal variations in the flux within each interval follow the historical summer increase in bottom water replacement--total net flux during STE 3 and 4 averaged 13.6 kg cm<sup>-1</sup> day<sup>-1</sup> compared to 7.5 kg cm<sup>-1</sup> day<sup>-1</sup> during STE 5. Although the transport per unit depth interval increases sharply as the seafloor is approached, the bulk of the total transport occurs in the region above the BNL.

Using these numbers to estimate a total landward transport across the channel is speculative because at present we have no transport measurements away from the channel axis. Large eddies along the sides of the channel may significantly reduce the net transport. Our present measurements are probably representative of at least the middle 2.5 km of the main basin where depths exceed 150 m. Total landward particle transport in this zone during the summer is thus  $\sim 3.4 \times 10^9$  g day<sup>-1</sup>; during the winter the transport may decrease to  $\sim 1.9 \times 10^9$  g day<sup>-1</sup> for a yearly total of  $\sim 9.5 \times 10^{11}$  g. This number is of the same order as the yearly sediment input from the Duwamish and Puyallup Rivers ( $\sim 6.5 \times 10^{11}$  g)

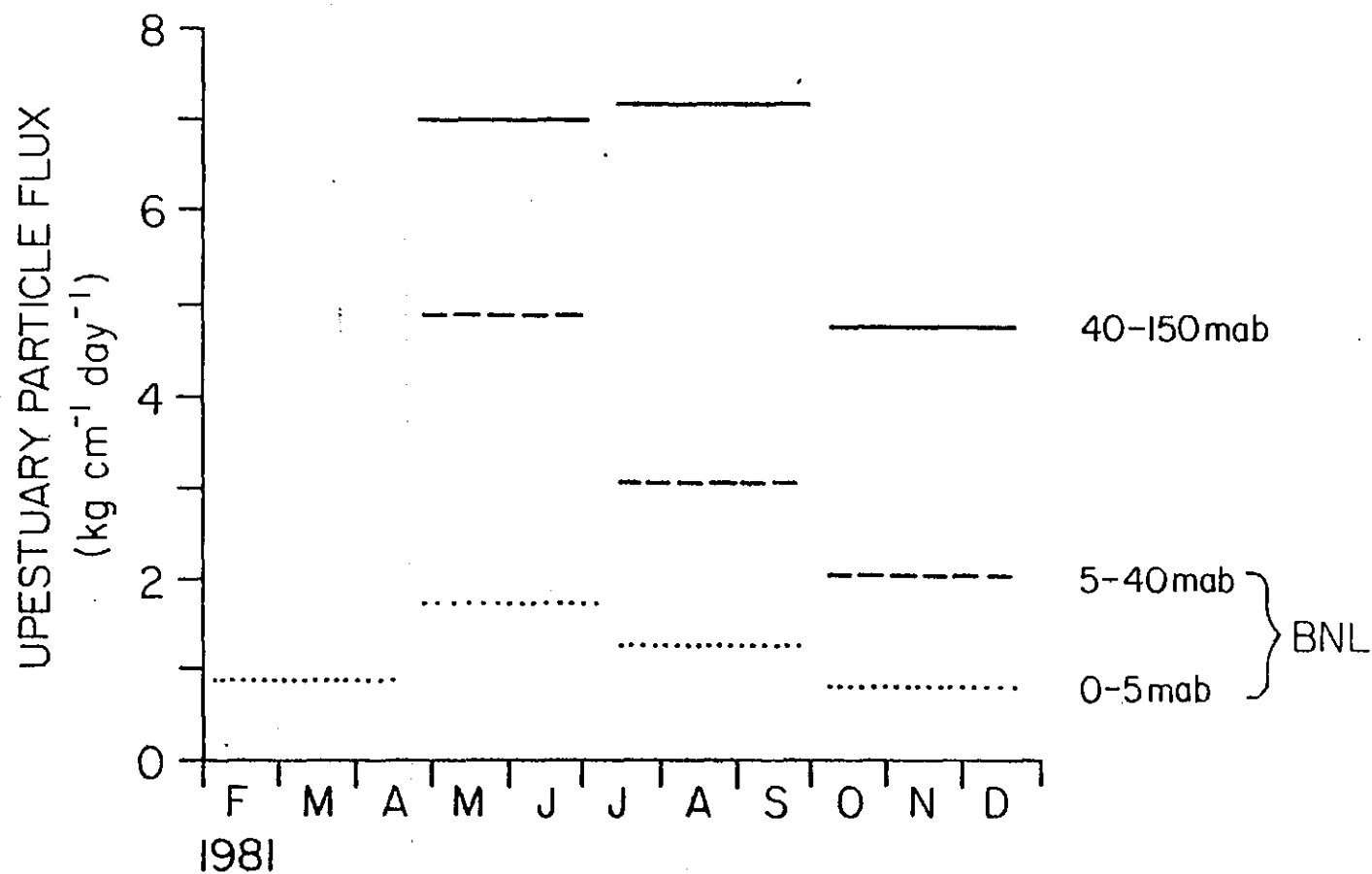


Figure 2.3.11. Horizontal flux estimates for three segments of the deep layer during deployments STE 2-5. Data recovery was very limited during STE 1 and incomplete during STE 2.

and the yearly mass of particles settling through the 50-m horizon ( $\sim 6 \times 10^{11}$  g), assuming station PS7 is typical of the entire main basin. The ultimate fate of this material must be ascertained in the course of making policy decisions about waste disposal resource utilization in Puget Sound or other deep estuaries.

Our studies in Elliott Bay suggest where a portion of this material may be deposited (Baker, 1982a; Baker and Cannon, submitted). In the bottom water of Elliott Bay light attenuation values are highly correlated with salinity but poorly and negatively correlated with current speed. Daily averages of salinity and attenuation from near-bottom moored instruments followed the fortnightly rise and fall of salinity recorded at a concurrent mooring near station PS7 in the main basin. These and other data imply that the nepheloid layer in Elliott Bay, unlike the BNL in the more energetic main basin, is not locally produced but is predominantly maintained by particles advected into the bay from the deep water of the main basin. A several-fold drop in mean current speed between the main basin and Elliott Bay results in increased particle fallout within the nepheloid layer, a high sedimentation rate, and thus the embayment functioning as a particle sink.

## VI. CONCLUSIONS

1. Patterns of particle distribution and concentration in an estuary form in response to hydrographic and circulation patterns, although the residual circulation of particles is generally different from that of the water itself. Average particle concentrations in the Puget Sound main basin surface layer (0-50 m) steadily increase from  $\sim 0.7 \text{ g m}^{-3}$  in the south to  $\sim 1.2 \text{ g m}^{-3}$  at the northern end of Admiralty Inlet. Particle concentrations in the deep layer ( $>50 \text{ m}$ ) are  $\sim 50\%$  higher than the surface layer in the central main basin where vertical mixing is weak and about the same as the surface layer over the sill zones where vertical mixing intensifies. Increased particle concentrations in the deep layer of the central main basin arise primarily from local resuspension and mixing below the deep halocline in contrast to the predominantly external supply of the bottom water itself. The pattern of low particle concentration in both the surface and deep layers of the East Passage suggests that this area is a significant depositional site for fine-grained particles.

2. The vertical flux of rapidly settling particles is a principal method of transferring material from the surface layer to the deep layer and bottom sediments in the main basin. The mass flux of material at the interface between these layers averaged  $\sim 2.4 \text{ g m}^{-2} \text{ day}^{-1}$  for a year-long deployment at a central main basin site, a loss rate of  $\sim 7\%$  of the fine-grained suspended material per day from the surface layer. The rapidity of this transfer is illustrated by the fact that large weekly changes in the phytoplankton pigment concentration of the surface flux were observed in the bottom waters with no more than a few days' lag. This active vertical transport refutes the impression that the surface



layer is a seaward-flowing conveyor belt for the removal particles and pollutants from the main basin. In addition to the downward mixing and landward return at the Admiralty Inlet sill zone, particles are rapidly and continually removed from the surface layer throughout the main basin at a rate of  $\sim 6 \times 10^{11}$  g yr<sup>-1</sup> (assuming PS7 is representative of the main basin away from the sill zones).

3. Horizontal transport of particles in the deep layer is strongly influenced by fortnightly and seasonal variations in the intensity of bottom water replacement. Turbidity levels in the BNL increase exponentially as the current at 5 m above bottom exceeds  $\sim 30$  cm sec<sup>-1</sup>. These elevated speeds usually result when the tidal flood current is augmented by a density current from a bottom water inflow event. Landward transport of particles in the deep layer thus consists of two phases: (1) particles derived primarily from resuspension are trapped in the BNL and occupy roughly the bottom 50 m of the water column, and (2) sediments derived primarily from refluxing of surface water at Admiralty Inlet occupy the region between the top of the BNL and the depth of no-net-motion ( $\sim 50$  m). Total landward transport estimated from data collected at a single central main basin site (PS7) is conservatively estimated at  $9.5 \times 10^{11}$  g yr<sup>-1</sup>. This material must either be deposited in the East Passage area, or refluxed to the surface water by tidal pumping at the Narrows. The regional distribution of average particle concentration suggests that within-basin deposition is the dominant loss term although transport measurements for the southern main basin do not yet exist.

## VII. FUTURE WORK

Particle flux investigations during the next several years will concentrate on expanding transport measurements from the current two-dimensional studies into three-dimensions, will examine in greater detail the aggregation characteristics of the vertical flux, will use the flux measurements to refine and extend our present particle mass balance calculations, and will use the acquired data to generalize on the residence times of particles in a deep estuarine environment such as Puget Sound.

Cross-channel variations in the transport are frequently neglected in estuarine research in order to make the field program simpler. All of our particle-flux data to date has been collected along the basin axis, for example. However, surveys of both bottom sediment type and vertical particle distributions indicate that cross-channel variations in these properties are significant. For instance, eddies created by bathymetric irregularities may significantly affect transport away from the channel axis. We plan to evaluate the importance of cross-channel variations during FY83 by means of two sets of "picketlines" of moorings across the Puget Sound main basin. In addition to information on cross-channel variability, these data will also result in an accurate measurement of the suspended material passing into, and out of, an important depositional site in the main basin.

The magnitude of vertical flux is governed largely by aggregation characteristics of the settling particles. We have made some initial examinations of the types of particles found in the traps by fractionating the settled material into fecal pellets, silt and clay (passed through a 38  $\mu\text{m}$  mesh), sand (density  $>1.5 \text{ g cm}^{-3}$  and retained on a 38  $\mu\text{m}$  mesh), and large biogenic detritus (density  $<1.5 \text{ g cm}^{-3}$  and retained on a 38  $\mu\text{m}$  mesh). These studies will be enlarged in the future.

Increasing detail in our transport measurements should allow us to construct a useful particle mass balance for Puget Sound. This balance will include losses to the ocean and bottom sediment, input from rivers and the ocean, and transport rates between various regions in the main basin and surrounding sill zones. Such budgets are critical for managerial decisions involving disposal of waste particles in estuarine environments.

Our ultimate goal is to calculate meaningful residence times for particles in estuarine environments. Such residence time calculations must take into consideration the episodic nature of particle movement, especially as regards erosion/deposition cycles. For example, a particle deposited during the winter when transport in the bottom layer is reduced may be reintroduced into the system during summer when erosion is at a maximum. Clearly, determining the residence times of particles is a necessary first step before the residence times of specific pollutants can be determined.

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## 2.3.2. Bottom Boundary Layer Transport

### I. INTRODUCTION

#### A. General Nature and Scope

The redistribution of fine, bottom, contaminated particulates in estuarine environments depends on a number of factors, the least understood of which is the ability of the near-bed currents to suspend or deposit particulates. Surprising though it may seem, little progress in a quantitative sense has been made on the issue since the landmark laboratory work on the erosion/deposition process by Krone (1962) and Parthenaides (1965). The work undertaken in the past year has sought to fill the gap by creating a theoretical framework for discussion of the erosion/deposition of chronically resuspended particulates and by taking field data which would calibrate those theoretical models. The work has focused on the bottom boundary layer as it is the region through and in which the fluid stresses the bed, generates turbulence, and causes erosion. This effort is meant to set the foundation for the longer range goal of describing the regional redistribution of contaminated particulates in estuaries.

#### B. Specific Objectives

- 1) Develop theoretical models of time-varying bottom boundary layer flow and models of time-varying particulate concentration levels near the bed encompassing erosion/redeposition.
- 2) Make boundary layer measurements of currents and concentration levels under tidal forcing in the main basin of Puget Sound.
- 3) Analyze that velocity data so that the spatial and temporal dependence of eddy viscosity (diffusivity) could be identified.
- 4) Test and/or calibrate the erosion/redeposition theory with the particulate measurements from Puget Sound or other estuaries where possible.
- 5) Evaluate *in-situ* erosion rates for fine-sediment and their dependence on bottom-stress (settling velocity might be a by-product).
- 6) Determine the depth of tidal reworking for Puget Sound main basin.
- 7) Examine flume data within the context of the erosion/redeposition models.

Only the last of these has not received the attention which we anticipated at the beginning of the year.

### C. Relevance to Problems of Marine Pollution

The work undertaken here is relevant to two of OMPA's highest priority concerns: marine waste disposal and the need to make quantitative statements about assimilative capacity; coastal land use where knowledge of long-term particulate transport processes will lead to better fate estimates and hence better informed economic and political decisions.

## II. CURRENT STATE OF KNOWLEDGE

The ability to make accurate estimates of short- or long-term transport of particulates in estuaries is very limited at present. Many of the problems confronting the soothsayers of sediment fate in estuaries are discussed in recent summary articles on the sediment transport problem (Bowden, 1977; Simpson et al., 1977; Kirby and Parker, 1977; Smith, 1977; Taylor and Dyer, 1977; Owen, 1977; Lick, 1982; Schubel, 1982). The capacity of a system to erode and transport fine sediment depends on the boundary layer currents and turbulence levels, on the physical and chemical characteristics of the bed material and on the biological processing at or below the bed surface. Some of these questions are being actively pursued within the HEBBLE program (McCave et al., 1978; Hollister et al., 1980). The theoretical work undertaken here is on the physical aspects of the resuspensions, and it complements the HEBBLE efforts.

This work differs from previous work on the transport of fine particulates in several crucial ways. First, this work integrates the boundary layer with what is occurring at the sediment-water interface, i.e., erosion and deposition. Earlier work in which boundary layers were considered have not explicitly dealt with erosion (Smith, 1977), or when erosion was given an explicit role (Ariathurai and Krone, 1976; Sheng and Lick, 1979), the boundary layer has not been included. Ignoring the special properties of the boundary layer can lead to quantitative error in describing erosion and redeposition.

Secondly, what is now known about erosion and deposition rates for fine sediment comes from laboratory measurements (e.g. Parthenaides, 1965; Sheng and Lick, 1979). Predictions based on that work are uncertain because, among other reasons, the analysis of those experiments did not consider the vertical profile of turbulence and the fine sediment artificially deposited and consolidated before the experiments is unlikely to represent the properties of *in situ* sediments. The ongoing work looks at *in situ* erosion by using near-bottom boundary layer flow and particle observations and theoretical models to make inferences about erosion rates. This is an alternate approach to the earlier work which avoids the two problems mentioned above.

## III. STUDY AREA

The theoretical work of the past year is not geographically specific, but rather process-oriented. The models can be used to interpret and

predict boundary layer flow and particulate resuspensions in tidally dominated estuaries in which fine sediment is chronically resuspended. This does not mean, however, that model parameters take universal values. At each site, bed roughness, the settling velocity distribution of the suspended material, and erosion rates will take site specific values. One use of the model is to infer these site characteristics from site specific data. In a following section, the theory and data from three geographically distinct resuspension environments will be compared. In the predictive mode, the models can be used to extrapolate the near-bed concentration responses to other flow conditions and eventually regional movements. A third distinct use of models is to understand the underlying competition of processes making up the whole. Results from model usage in this manner will also be reported on later.

Because Puget Sound is our prototype region for development of a regional fine sediment transport model of the predictive type, model parameters must be fixed by comparing theory and measurement in that region. In the past year, boundary layer flow and concentration time series have been taken in the main basin of Puget Sound off West Point at a site with a depth of 194 m. The area is underlain by fine sediment, is swept by diurnal and semi-diurnal tidal currents with combined maximum amplitude near 40 cm/s, and where transmissometer records show semi-diurnal peaks with concentration rising as much as 6-fold over the background concentration of approximately 1 mg/l. Flow at the site is primarily along the channel axis.

#### IV. SOURCES, METHODS, AND RATIONALE OF DATA COLLECTION

Data on current velocity and water turbidity were taken on a single mooring in 194 m of water in the main basin of Puget Sound during an 11-day period in February-March 1982 (47°43'N, 22°26'W). Three Aanderaa current meters with Oregon State transmissometers attached (Baker, 1981) were located 1, 3, and 5 m above the bottom and sampled at a 2-min interval. Upon recovery, it was found that the lowest instrument package was shorted by moisture, and consequently no data is available at 1 m.

Baker and Cannon took similar data at 5 m off the bottom and higher in the water column about 1 km south along the channel axis. Those instruments were deployed over a 4-month period, sampling at a 15-min. interval. Because they were only recently recovered, data are being processed and no comparisons with our measurements can yet be made. However, we expect the two sets of data at 5 m to be of use in examining down-stream correlations, and hence separating advective from erosive parts of the concentration signal.

Water samples, transmissometer profiles, and box cores in and around the boundary layer site were taken by Baker to complete the set of measurements. The water samples were analyzed for particle size distribution by Coulter counter. Those measurements are not reported on here.

## V. RESULTS

Over the past year theoretical models of two types have been developed:

- 1) boundary-layer flow models (Table 1) which confront the dual questions of bed-stress and its accurate estimation (on which the rate of particle erosion depends) and the strength and shape of the eddy viscosity or diffusivity (by which the suspended sediment diffuses upward from a boundary)
- 2) boundary layer particulate concentration models (Table 1) which depend on erosion and deposition through a boundary condition on the mass conservation equation.

In the first category, currents are driven by harmonic forcing. These models include height-variations of vertical viscosity which are self-consistent with bottom stress.

One model also includes the time-dependence of the viscosity; results from this model form the basis for a research paper entitled "The effect of time-varying viscosity on oscillatory turbulent channel flow" by Lavelle and Mofjeld (1982). This model shows that the bottom stress (which causes resuspension of sediment) is not sinusoidal in time and has a phase-offset relative to the current well above the bottom boundary layer. This explains the apparent paradox that observed concentration of suspended sediment can decrease even as the current is accelerating.

A second model has been developed to study the effects of the earth's rotation on tidal currents in channels. Using a time-independent viscosity, the model shows that the bottom stress never goes to zero. For conditions typical of Puget Sound, the minimum current speed is around 10% of the maximum speed; there is little change in the orientation of the current ellipses due to the earth's rotation. This model has been fit to tidal current observations in Admiralty Inlet with encouraging results.

A third model uses a second-order turbulent closure scheme to compute the viscosity; a comparison has been made with selected results of the other models to check important parameters scaling the viscosity.

In the second category, two models have been developed for suspended sediment subject to tidally driven bottom stress and time-independent viscosity. The first uses an eddy viscosity approach, with the strength and shape of the profile determined self-consistently with the flow. In the second, the diffusivity uses a Businger-Arya (1974) form that is self-consistent with the maximum bottom stress. Comparisons of these theories with data will be given below. These models are to be generalized to include time-dependent diffusivity which is appropriate to Puget Sound.

The boundary layer particulate concentration results are discussed first. Light attenuations and current speed time series taken in the

main basin of Puget Sound at 5 m from the bed over two 12-hr periods as shown in Fig. 1 (solid lines). The data are representative of measurements taken in the benthic boundary layer (BBL) experiments in February-March, 1982, though these data were actually taken in 1981 a few km south of the BBL site by Baker (1982). Maximum currents in this area are typically 30-40 m/s. Fourier analysis of the BBL records shows the presence of many higher harmonics in both the diurnal and semidiurnal frequencies which can account for the unusual shape of the velocity series.

Attenuation records typically show a very rapid rise from background concentration levels to maximum and slower declines thereafter. The concentration in these records increases nearly 6 times within a  $\frac{1}{2}$ -hr period. The return to ambient levels within a 5-hr period is the result of the relatively large settling velocity of the resuspended material ( $\sim .1$  cm/s).

The theoretical simulation of the same erosion event is given in Fig. 2.3.12 (dashed line). The currents were approximated and the bed-stress and interval mean eddy viscosity (diffusivity) profile was calculated using results from the boundary layer flow model to be discussed later. The suspended sediment series was then predicted up to an overall normalization, the erosion coefficient  $\alpha$  (Table 1).

The simulation of Fig. 2.3.12 is based on a single settling species having a velocity of .1 cm/s. A larger settling velocity narrows the width of the response peak in the attenuating time series and sharpens the contrast between background and maximum attenuation; a smaller settling velocity has opposite effects. It is therefore possible to improve the correspondence of theory and data by using two settling species--one to provide background and the other to provide the rapidly rising and falling part of the attenuation series. Using Coulter analysis, Schubel et al. (1978) also found two components to the resuspended materials in Chesapeake Bay.

Using the coarsest of the components, a comparison of theoretical prediction with Schubel's measurements leads to other valuable conclusions. Fig. 2.3.13a shows near-bed concentrations and currents measured over 28 hrs in Chesapeake Bay in  $9\frac{1}{2}$  m of water, with concentrations showing 20-fold increases at maximum currents; simulations based on the measured currents are also shown (Fig. 2.3.13b). One notes that the four concentration maxima in the simulation are dissimilar in magnitude while the data show more uniform maximum values. The model variations stem from the erosion rate dependence on the fourth power of velocity (stress squared) and the relative magnitudes of the current maxima: 72, 48, 60, 75 cm/s. Thus, the erosion rate at 72 cm/s is five times that at 48 cm/s.

The boundary layer flow theory which had been part of this year's work has identified some of the circumstances in which stress is linear in the free-stream velocity rather than quadratic, which would make the erosion rate differences vary by a factor of 2 rather than 5 as discussed above. One such circumstance would be the superposition of surface waves on tidal currents. These Chesapeake Bay data, therefore, point to the need to consider the full erosional environment (depth of water, wind and wave conditions, etc.) before assigning a bed-stress and free-



# PUGET SOUND NEAR-BOTTOM FLOW AND PARTICULATE CONCENTRATIONS

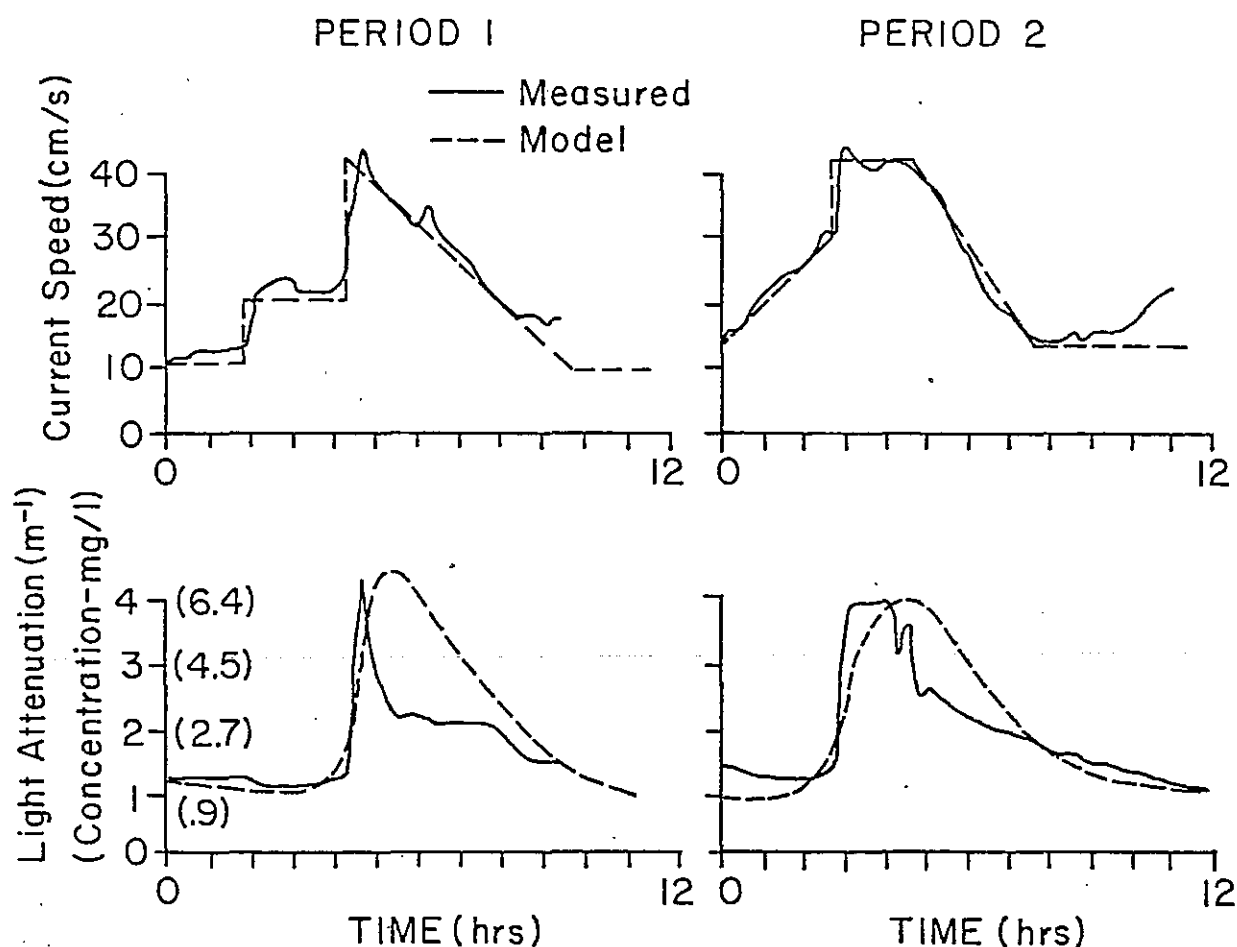


Fig. 2.3.12 Near-bottom current speeds and attenuation records (solid line), taken 5 m from the bottom in the main basin of Puget Sound and model simulations (dashed lines) of same events. Attenuation values have been converted to mass concentration using Elliott Bay Transmissometer calibrations (Baker, 1981). In the simulation, settling velocity is .1 cm/s and roughness length is .05 cm. Maximum eddy diffusivity occurs 2 m from the bed and has a value of 75 cm<sup>2</sup>/s.

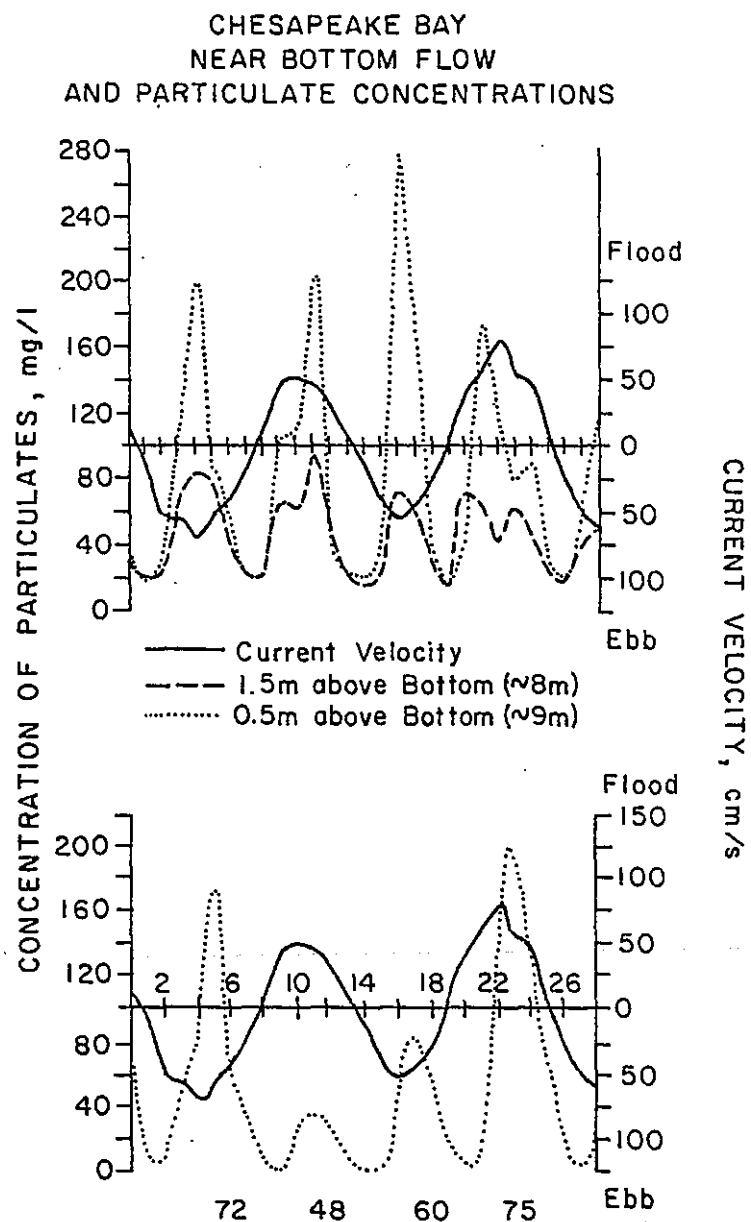


Fig. 2.3.13 a) Measurements of current speed and suspended sediment concentration over a 28-hr period in 9.5 m of water in Chesapeake Bay (Schubel et al., 1978). b) Model suspended sediment concentrations using measured currents to calculate bed-stress and the eddy diffusivity profile and using an erosion rate which is quadratic in bed-stress.

stream velocity relationship. A second result of this comparison is that two settling species are required to describe the data, as Schubel concluded from other evidence.

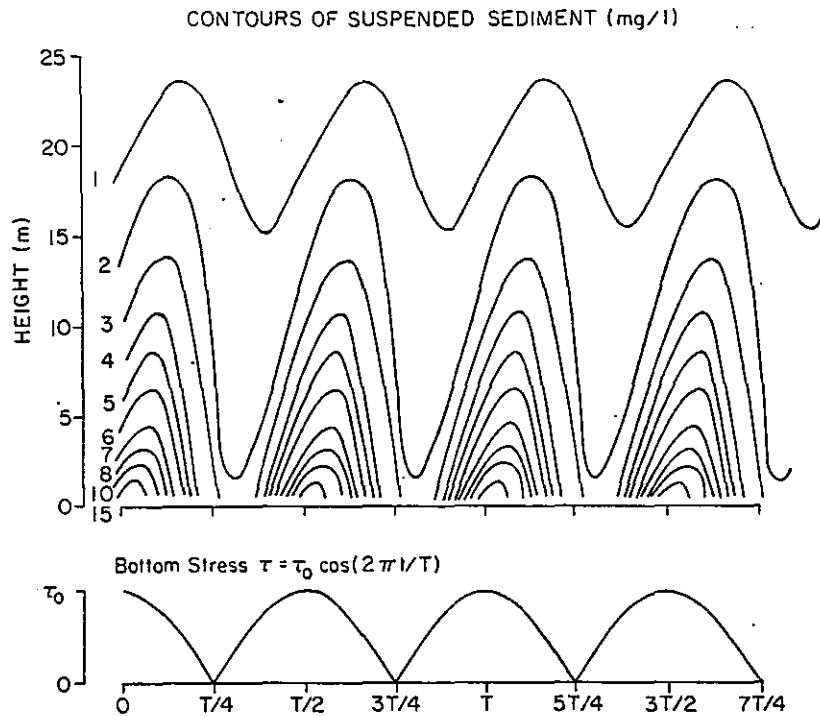
A third comparison of model and data has been made in the case of silts resuspended by tidal currents in the North Sea (Joseph, 1955). Rectilinear tidal currents with maxima of near 60 cm/s result in pronounced variations in particulate concentrations as high as 20 m off the bed (Fig. 2.3.14a). The simulation (Fig. 2.3.14b), which uses a Businger-Arya form for the diffusivity, well reproduces the data patterns, both in time-dependence and magnitude. Note the phase shift of the concentration maxima with height, a result of the time required for diffusion of material away from the sea bed.

Using the vertical profile of suspended sediment from the calibrated models, it is possible to calculate the loading in a vertical column at each part of the tidal cycle. The difference between high and low values is the amount of material which is reworked by the tidal currents from the bed. For the Puget Sound data (Fig. 1), this amounts to about 300 mg/cm<sup>2</sup>. Using a wet density of 1.2 gm/cm<sup>3</sup> for sediment with high porosity expected of material at the erosional surface, the depth of reworking amounts to 0.25 cm. Further refinement of these calculations is underway.

Flume measurements have provided the first indication of erosion rate magnitudes and the dependence in bottom stress (Fig. 2.3.15). Laboratory experiments by others have been conducted on San Francisco Bay and Great Lakes muds which had been reconsolidated in the flumes. Two features of the laboratory data are to be noted. First, there is no apparent threshold down to 1 dyne/cm<sup>2</sup>. Secondly, the relationship of erosion rate to bedstress is a power law with a power in the neighborhood of two, though Lick (1982) has suggested an exponential rate with the exponent depending on the water content of the sediment. The laboratory rates in Fig. 2.3.15 differ by approximately 3 orders of magnitude which may reflect differences in fresh and salt water sediments, or differences in bed preparation prior to the experiments.

In the previous simulations, the stress dependence of erosion has been quadratic based on this laboratory evidence. Having fixed the power, the constant  $\alpha$  (Table 1) is used to bring the absolute concentration values for the theoretical results and the data into agreement. The constant  $\alpha$  is the erosion rate coefficient, and the comparisons of theory and data is therefore on inference of an *in situ* erosion rate. Inferred erosion rates are on the order of  $1-3 \times 10^{-6}$  for Puget Sound data and  $5.8 \times 10^{-6}$  for the North Sea data in units of (cm/cm<sup>2</sup>/sec)/(dynes/cm<sup>2</sup>)<sup>2</sup>. We report no rate values for the Chesapeake Bay data until further analyses can be made. Both results reported here should also be regarded as tentative until checks on the effects of two species settling, roughness, and the possibility of advective sediment transport can be made.

It has been somewhat of a surprise to find that *in situ* rates more resemble the freshwater than the salt water laboratory rates. Several explanations are available, and we have now no preference of one over



### CONCENTRATION VARIATION IN A TIDAL REGIME

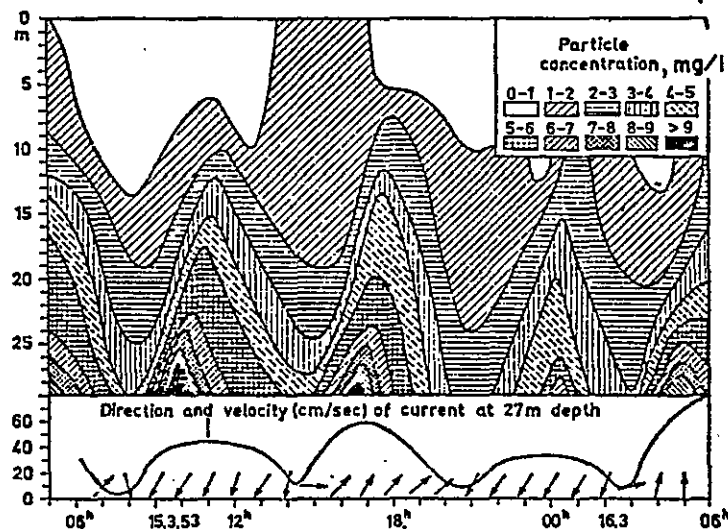


Figure 2.3.14 a) Concentration contours taken in a tidally dominated region of the North Sea (Joseph, 1955). Bed sediment is composed of silt ( $10\text{-}40\text{ }\mu\text{m}$ ). b) Theoretical simulation of suspended sediment for time-independent diffusivity and an erosion rate proportional to the square of the bottom-stress. Maximum stress is  $2.6\text{ dynes/cm}^2$ , roughness length  $.10\text{ cm}$ , settling velocity  $.2\text{ cm/s}$ ; erosion rate coefficient,  $\alpha$ , is  $5.8 \times 10^{-6}\text{ (g/cm}^2\text{/s)/ (dynes/cm}^2\text{)}^2$ . Eddy viscosity has a maximum value of  $270\text{ cm}^2\text{/s}$  at about  $10\text{ m}$  off the bed.

# RATES OF EROSION vs BED STRESS

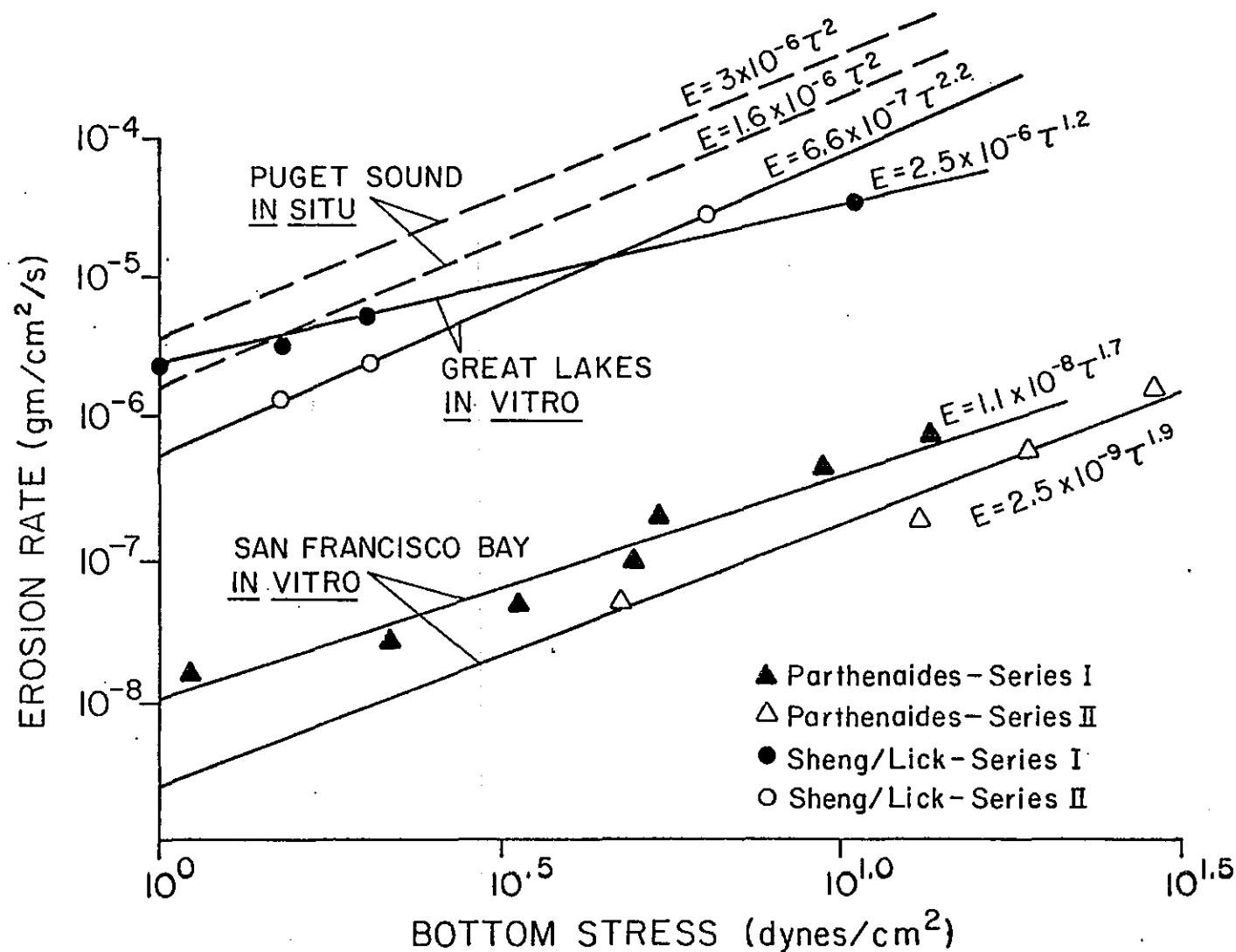


Figure 2.3.15. Rates of erosion of fine-sediment vs. bottom-stress. Great Lakes and San Francisco Bay sediment measurements were made in the laboratory. The Puget Sound rates were inferred from time-series of near-bed current speed and concentration data (Fig. 2.3.12), and represent *in situ* rates.

the other. One possibility is that large, laterally inhomogeneous roughness elements, which might occur in the natural setting cause more erosion than would take place over a smooth laboratory bed. Another has to do with the condition of the bed at the time of erosion. The *in situ* data comes from regions which are resuspended on a semi-diurnal basis, and little consolidation or healing of the bed can take place in that period. In the laboratory experiments, sediment is dispersed in a flume and allowed to settle and consolidate over a period of days to weeks. Differences in salt- and freshwater erosion experiments might occur because of physico-chemical differences in the environments which change how the fine sediment settles and compacts. One might reasonably expect the freshwater sediments to take longer to reach the final settled state, and they might therefore behave more like the chronically resuspended *in situ* sediments.

For slowly settling particles, concentrations change slowly and the mass balance is between settling and diffusive fluxes. For turbulence created at the seafloor by the flow, one would expect diffusivity to rise linearly near the bed, reach a maximum, and decline above toward zero (Fig. 2.3.16aa, solid line). In some cases, other turbulence sources might lead to other profiles (Fig. 2.3.16a, dashed line). The resulting concentration distribution (Fig. 2.3.15b) shows the importance of the eddy diffusivity in the vertical distribution of sediment. In the first case, particulates have a nearly constant concentration to about 20 m and a rapid decline above. This results in a layer similar to the nepheloid layer observed in Puget Sound (Baker, 1982) and many other places. On the other hand, the concentration will decrease only slowly if there is sufficient turbulence to keep material diffusing upward (Fig. 2.3.16b, broken line). Concentration profiles are thus very sensitive to the shape and magnitude of the eddy diffusivity profile, while velocity profiles are not.

Adequate boundary layer flow characterization is essential to the sediment transport problem because the bottom-stress exerted by the fluid on the bottom determines the amount of sediment erosion, and because the turbulence generated in the fluid by the seafloor determines the magnitude and vertical structure of eddy viscosity (diffusivity). An important aspect of this problem is the effects time-dependent viscosity have on flow behavior. We have examined how time variable viscosity effects the flow profile and have found, among other things, that bottom-stress can be enhanced by nearly 60% when variable viscosity is included (Fig. 2.3.17).

Another result of our work on boundary layer flow of practical importance is the characterization of bottom friction provided by the model. In Fig. 2.3.18, values of bottom-stress,  $\tau_b$ , from the full model (points) are compared to a bulk representation of bottom-stress expressed as a power of the free-stream velocity,  $u_o$ . The theory suggests the circumstances under which one might want to use a linear friction expression, or when a quadratic expression might be appropriate. Since the forms of the friction expression can radically affect residual flow calculations in vertically integrated models, the correct dependence of  $\tau_b$  on  $u_o$  is important. Note also that the times of zeros of bottom-stress and velocity are phase shifted with respect to each other by the amount  $\theta$ .

# THEORETICAL TIME-AVERAGED CONCENTRATION PROFILES

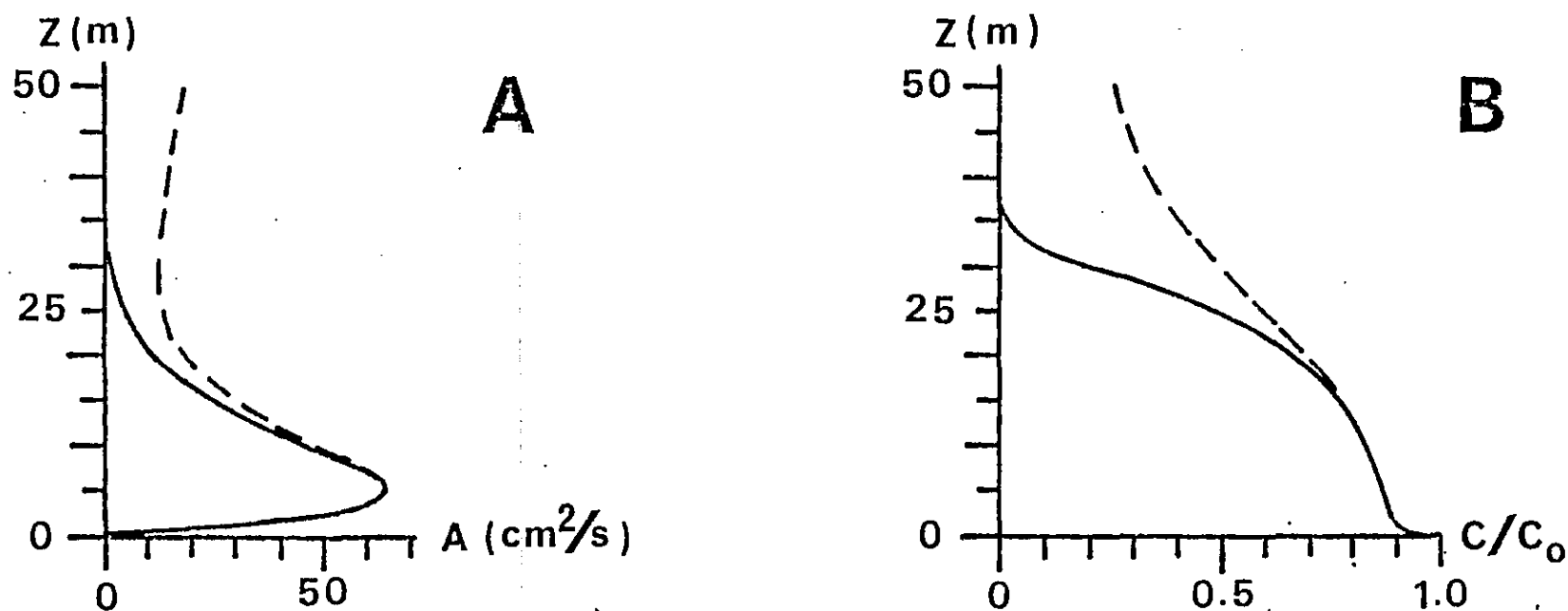


Figure 2.3.16. Theoretical steady-state profiles of a) diffusivity and b) suspended sediment concentration for a bottom nepheloid layer. The diffusivity (solid line) that becomes small with height produces a distinct top to the nepheloid layer while the other diffusivity (dashed line) that does not become small produces a gradual trend with height. The settling velocity is 0.005 cm/s.

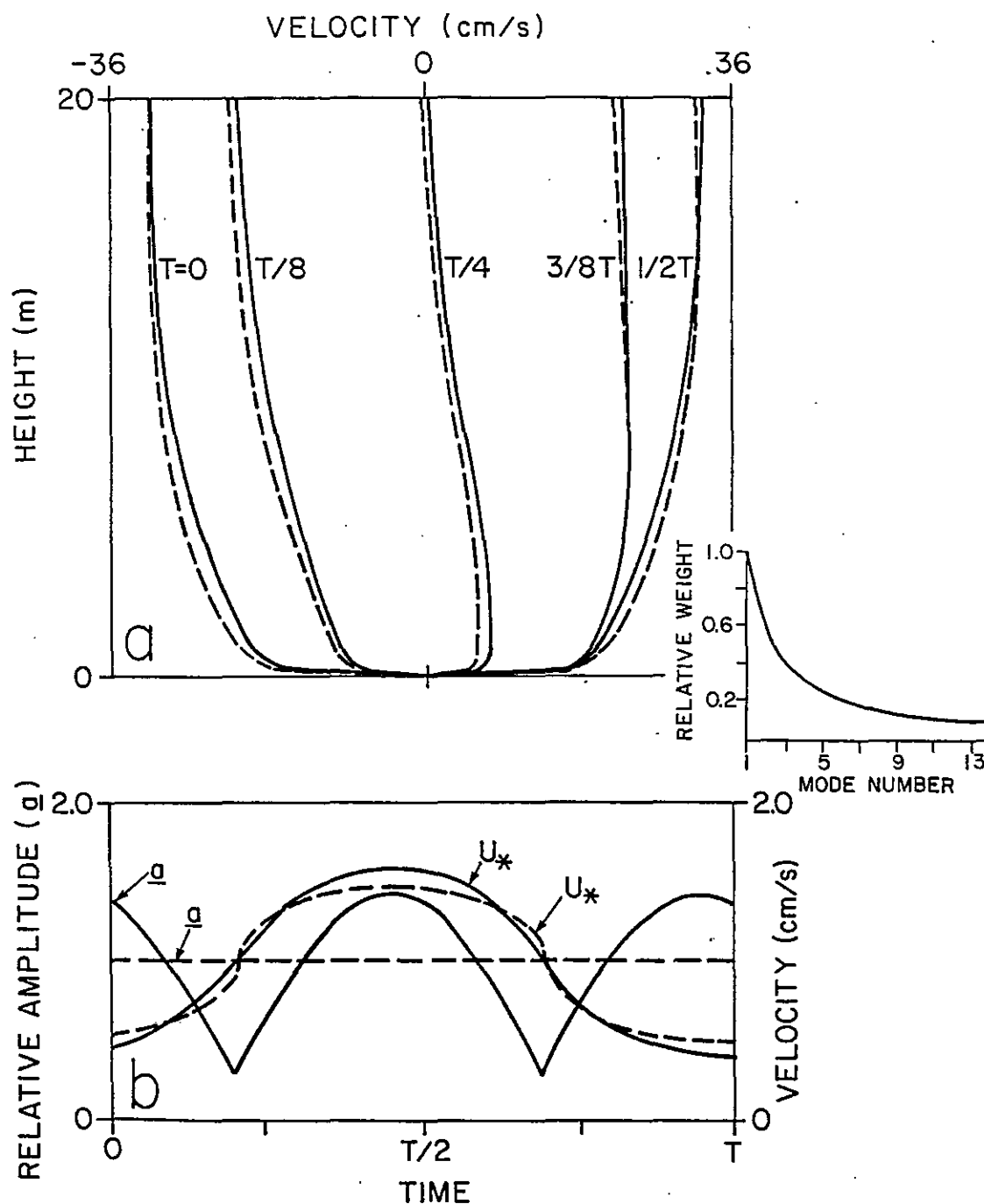


Figure 2.3.17. a) Semi-diurnal current profiles at various tidal stages for an eddy viscosity which is constant (dashed line) and variable (solid line) in time. Depth of water is 20 m. b) Time series of the friction velocity,  $u$ , and the eddy viscosity time modulation function,  $\bar{a}$ , for each of the two cases. Since bottom-stress on which erosion depends is equal to  $u^2$ , not considering the time variable nature of viscosity will lead to a 60% underestimate of bed-stress (Lavelle and Mofjeld, 1982).



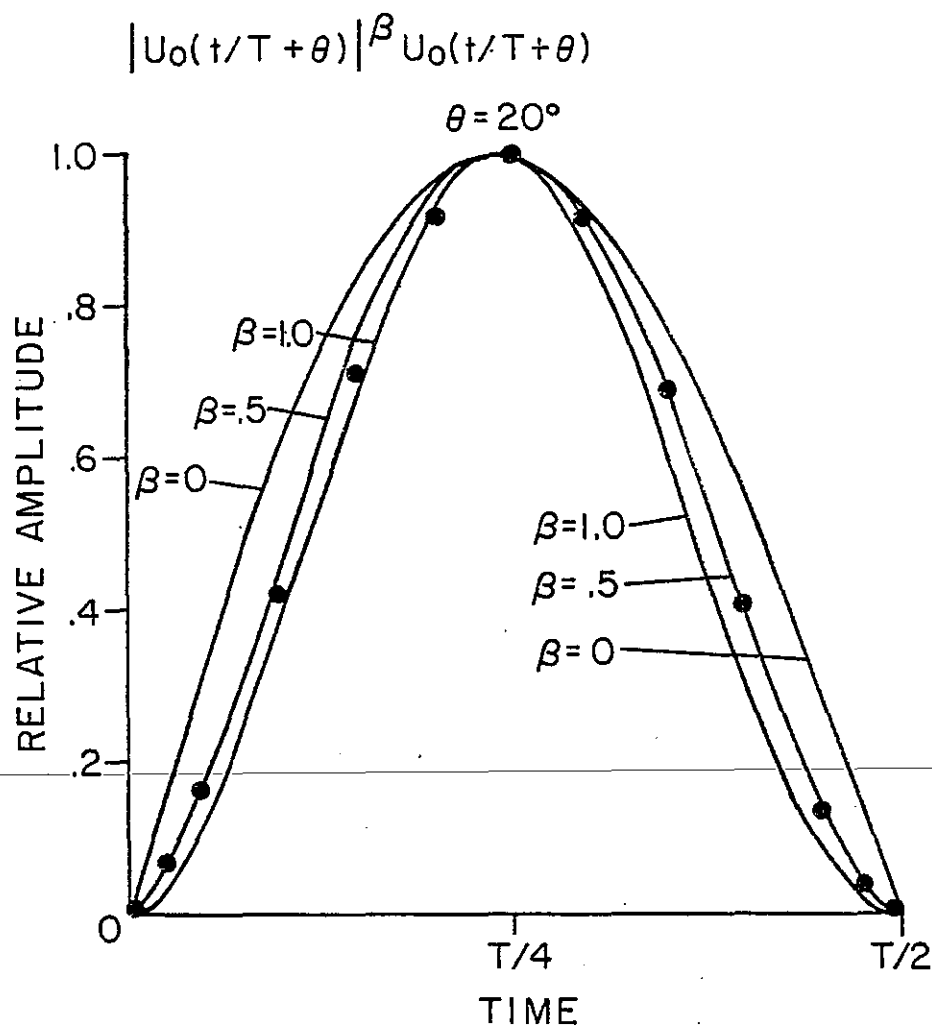


Figure 2.3.18. Bed-stress values given by a full-vertical model (solid points) compared to values of bed-stress based on the bulk expression  $|u_0(t/T + \theta)|^\beta u_0(t/T + \theta)$ , where  $u_0$  is the free-stream velocity,  $\theta$  the angular phase difference between zeros of  $u$  and  $u_0$ ,  $T$  is the period of the motion. A  $\beta$  value of .5 best reproduces actual bed-stress values.

# COMPARISON OF THEORY WITH OBSERVATIONS AT MESA 10 (ADMIRALTY INLET)

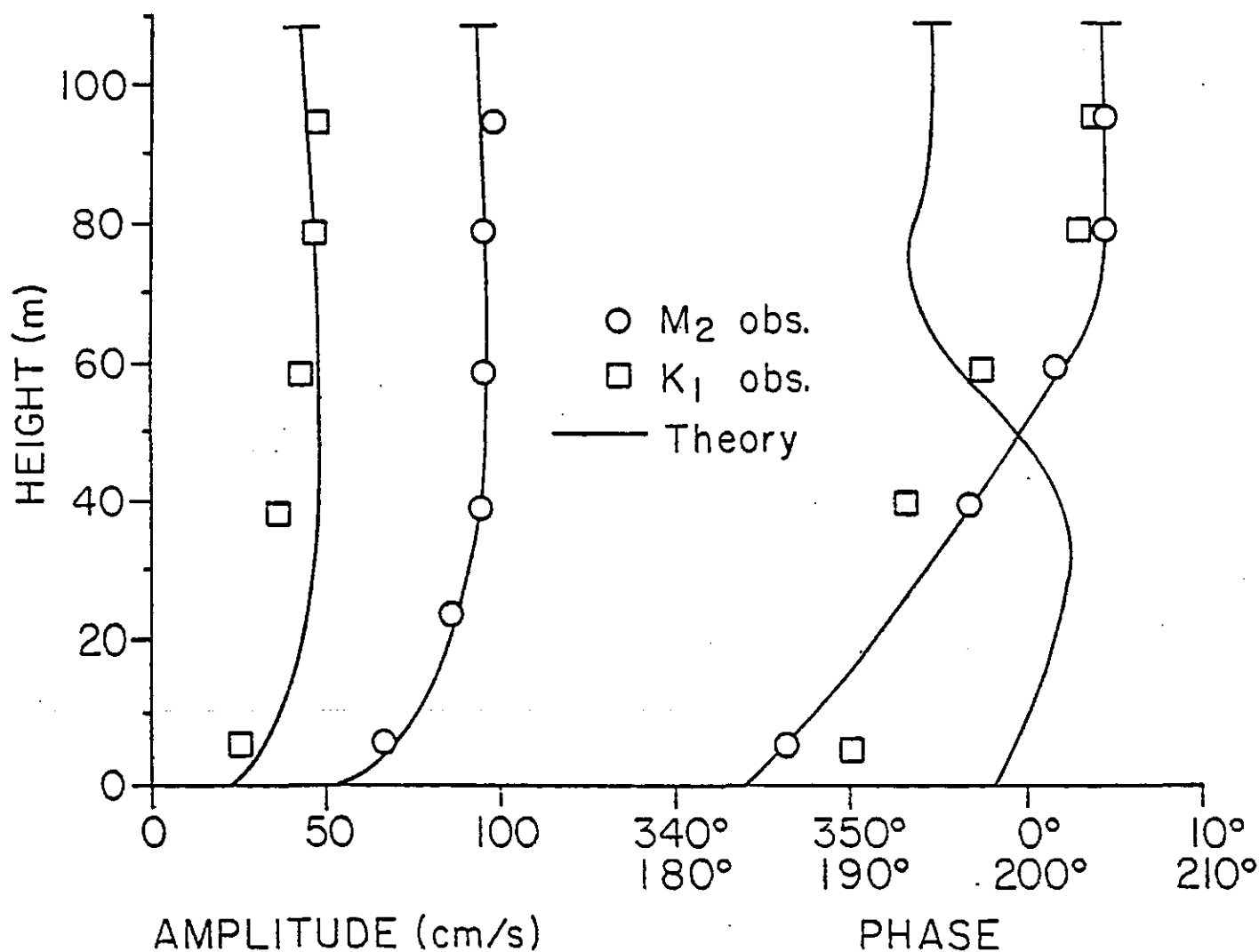


Figure 2.3.19. Comparison of boundary layer current theory with observations of  $M_2$  and  $K_1$  tidal currents at MESA 10 (Admiralty Inlet). Water depth is 108 m, roughness length .05 cm. Maximum bed-stress and eddy viscosity are estimated to be 4.7 dynes/cm<sup>2</sup> and 370 cm<sup>2</sup>/s (11.6 m from the bottom) respectively.

An application of one of the theoretical flow models has been made to tidal currents observed in Puget Sound's Admiralty Inlet (Fig. 2.3.19). The model requires only the strength of the free-stream flow and the bed roughness as given conditions, yet for the dominant  $M_2$  tidal current constituent shows excellent agreement in both amplitude and phase. For the smaller  $K_1$  constituent there is some discrepancy between the observed and theoretical profiles. This discrepancy may be due to non-linear interactions between the constituents that are not part of the current model. Such interactions have been observed in numerical experiments (P. Crean of Environment Canada, private communication) when strong tidal currents flow in channels that are rapidly changing in cross sections. This is the case for the channel near this station; it is probably less of a problem in the main basin of Puget Sound where its currents are much weaker than in Admiralty Inlet.

Similar analysis can be done in the vicinity of the BBL site after initial processing of the long-term mooring records. Analysis of the BBL data has shown that during the 11-day experiment both particulate and fluid transport were to the north, in contradiction to what is usually observed for currents near the site. Many higher harmonics of the fundamental tidal frequencies occur, indicating the time variability of the turbulence levels over the flow cycle. Records show little difference in concentration signals between the 3 and 5 m levels, both showing rapid semi-diurnal increases as in Fig. 2.3.12. Further analysis of the BBL data await processing of records taken down channel from which spatial features of the time series might be interpreted.

## VI. CONCLUSIONS

Computationally efficient theoretical models of time-varying bottom boundary layer flow and models of time-varying concentration levels which are coupled to the flow through the erosion function have been constructed, as evidenced by the results given here. These models have been compared to flow profiles taken in Puget Sound, and to concentration data taken in Puget Sound and other estuaries. From the exploration of the model and its application to the data, we find:

- 1) Consideration of the time-dependence of viscosity is important in determining bottom stress, which in turn influences the amount of erosion.
- 2) Accelerations and time-dependent viscosity add extra terms to the conventional  $\log(z)$  profile near the bottom. Boundary layer measurements taken in unsteady boundary layers and analyzed without the more complete theory developed in our work are likely to lead to erroneous bottom and roughness length estimates.
- 3) When eddy-viscosity is time-independent, bottom stress is linear in the overlying velocity for oscillatory flow. When eddy-viscosity is time-dependent, bottom stress is more nearly quadratic. We have found a new, generalized form of the bottom-stress dependence which incorporates these two limits, and the phase difference between bottom stress and the

overlying flow. This discovery should lead to more accurate numerical calculations of flow in a wide variety of situations.

- 4) Given bottom stress and eddy diffusivity from the flow models, the data allow inferences of erosion rates to be made. These are *in situ* rate estimates; *in situ* erosion rates for fine sediment have never been previously reported.
- 5) Chronically resuspended materials are unlikely to have erosion threshold velocities.
- 6) The depth of reworking at the BBL site in Puget Sound is about .25 cm/tidal cycle. The mean settling velocity of the resuspended material is about .1 cm/s. The resuspension occurs against a background of much more slowly settling particles.
- 7) Concentration profiles and time series are sensitive to settling velocity, so boundary layer time series data should be able to resolve not only erosion rate, but provide some quantitative characterizations of the settling velocity operation.
- 8) Concentration profiles are sensitive to the strength and shape of the eddy diffusivity profile, though flow profiles are less so.

## VII. NEEDS FOR FURTHER STUDY

Further development of the models discussed above need to take place along several lines. Models should be extended to include the mixed type (semi-diurnal plus diurnal) of tidal currents. Calculations should be made with a near current superimposed and with the eddy viscosity varying in time. Earth rotational effects on the currents should also be added. That would allow better estimates of bottom stress and diffusivity during periods of low current speed. These generalized model(s) would provide a more realistic description of near-bottom flow and turbulent processes over a wide range of real estuaries.

Time-dependent diffusivity should be incorporated into the sediment resuspension model. The models should be expanded to include settling velocity spectra, and should be used to examine the power dependence of erosion on bottom stress. The resuspension models should be tested on the widest variety of available data, including that taken in areas of fine sand.

Sediment models which incorporate erosion/deposition and horizontal transport/diffusion as functions of bottom type and currents measured above the bottom boundary layer need to be created. This can be done using models of the bottom boundary layer to obtain bottom stress, the suspended load of sediment, and the tidal Reynolds transport as functions of the currents above the bottom boundary layer. These models could lead to accumulation zone identifications and accumulation rate estimates, given source volumes.

Finally, two-species (contaminated and uncontaminated) sediment models need to be constructed and the consequences explored. These would address the questions of contaminated sediment dilution and burial. Sub-models which incorporate the chemical reactivity/description process should be considered a necessary element of this effort.

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# BASIC EQUATIONS

## FLUID

$$\frac{\partial \vec{u}}{\partial t} + \vec{f} \cdot \vec{u} = -g \nabla \eta + \frac{\partial}{\partial z} \left( A \frac{\partial \vec{u}}{\partial z} \right)$$

$$A = A(z, t)$$

$$A \frac{\partial \vec{u}}{\partial z} = \vec{0} \quad \text{at } z = H \quad (\text{surface})$$

$$\vec{u} = \vec{0} \quad \text{at } z = z_0 \quad (\text{bottom})$$

$$\frac{\partial N}{\partial t} + \int_{z_0}^H \nabla \cdot \vec{u} \, dz = 0$$

## SUSPENDED SEDIMENT

$$\frac{\partial C}{\partial t} - w_s \frac{\partial C}{\partial z} - \frac{\partial}{\partial z} \left( A \frac{\partial C}{\partial z} \right) = 0$$

$$A = A(z, t)$$

$$-w_s C - A \frac{\partial C}{\partial z} = 0 \quad \text{at } z = H \quad (\text{surface})$$

$$-w_s C - A \frac{\partial C}{\partial z} = E - V_d C \quad \text{at } z = z_0 \quad (\text{bottom})$$

$$E = \alpha \tau^2$$

$$\tau = A \frac{\partial y}{\partial z} \quad \text{at } z = z_0$$

$$E = \alpha A^2 \left( \frac{\partial y}{\partial z} \right)^2$$

Table 1.

## 2.4. TRANSPORT AND TRANSFORMATION OF TRACE METALS

### 1. INTRODUCTION

#### A. General nature and scope of the study

The next decade will see increased pressure on the quality of our nation's estuarine and coastal marine environments due to their use as dumping grounds for highly toxic municipal and industrial waste materials. Natural or anthropogenic particles introduced into the marine environment can have a controlling or moderating influence on the fates of these toxic substances and, most importantly, the extent to which they impact our valuable living resources. In particular, many trace elements which are known to be toxic to marine organisms have an affinity for particulate materials (cf., Fowler, 1982) and, in most cases, their bioavailability to marine organisms is directly affected by interactions and associations with them (Luoma and Jenne, 1977; Luoma and Bryan, 1978; 1982). Understanding the complex interactions between trace elements and particles in the water column and at the seawater-sediment interface is fundamental to rational management of waste-water disposal in coastal marine waters.

A major fraction of trace elements in waste-water effluents reacts with estuarine particulate matter. Upon entering the estuary, the particulate matter undergoes a number of physico-chemical interactions, resulting in remobilization of some associated trace elements and flocculation of others (Rohatgi and Chen, 1975; Sholkovitz, 1978; Feely et al., in press). Further remobilization of trace elements can occur when the particles reach the seafloor and become part of the sediment column (Elderfield and Hepworth, 1975). In coastal environments where circulation is restricted by topography and/or incomplete flushing, these processes can have a significant effect on the distributions of trace elements.

Krauskopf (1956) conducted an experimental evaluation of several processes controlling the concentrations of a number of trace elements in seawater and concluded that hydrous manganese and ferric oxides, organic detritus and certain clay minerals are all effective in removing metals from seawater. Using estuarine mixing simulation experiments, Sholkovitz (1978) observed the flocculation of several trace elements when filtered river water and seawater were mixed. However, laboratory investigations by other researchers have indicated that suspended solids, which are typical of riverine materials, release trace elements after exposure to seawater (Kharkar, et al., 1968; Murray and Murray, 1973). Similar results for trace elements associated with particles from wastewater effluents were demonstrated by the laboratory studies of Rohatgi and Chen (1975). Evans and Cutshall (1973) also observed that the radioactive isotopes  $^{54}\text{Mn}$  and  $^{65}\text{Zn}$ , associated with suspended solids from the Columbia River, were released at the freshwater-seawater interface. Fukai et al. (1975) similarly reported that Zn was desorbed from particles discharging into the Var River estuary. However, Grieve and Fletcher (1977) observed that Zn was both desorbed and adsorbed in



different regions of the Fraser River estuary. These results indicate that several competing reactions occur simultaneously which affect trace element concentrations in estuarine and coastal waters.

Recent studies by several investigators have indicated that sinking biogenic particles, including fecal pellets and fecal aggregates, are an important means of stripping trace elements from surface seawater and transporting them to deeper depths or to the seawater-sediment interface (Krishnaswami et al., 1976; Boyle et al., 1977; Bishop et al., 1977; Spencer et al., 1978; Bruland, 1980; Feely et al., 1982). Investigations of trace element distributions in the open ocean by Boyle et al. (1977) and Bruland (1980) have indicated that the vertical distributions of Cd, Ni, Zn, and Cu are strongly correlated with nutrient profiles, suggesting that the distributions of these metals are primarily controlled by biogeochemical processes involving biogenic matter. Using sediment traps deployed in the deep waters of the Sargasso Sea, Spencer et al. (1978) determined that a major fraction of the flux of organic C and Cu was delivered by green fecal pellets consisting of fresh biogenic matter. Similarly, Feely et al. (1982) observed a strong covariance between the flux of organically bound Cu and Mn in settling particulate matter and the flux of fecal pellets in Cook Inlet, a large subarctic estuary in south central Alaska. In both cases biogenic matter appeared to be the major carrier of the trace elements involved.

In coastal regions trace elements can also be removed from solution by interactions with hydrous Mn and Fe oxide coatings on suspended and resuspended particles. For example, Cossa and Poulet (1978) found enrichments of total particulate Zn, Pb and Cd in the deep waters of Saquenev Fjord which were correlated with an increase in total particulate Mn. In the suspended matter from Norton Sound, Feely et al. (1981) found enrichments of weak-acid-soluble Zn associated with weak-acid-soluble Mn. The major source of the Mn was found to be the underlying sediments which released Mn into the overlying water column and the Mn rapidly precipitated onto suspended material forming a fresh surface coating suitable for adsorption of Zn. Similarly, Carpenter et al. (1981) found that  $^{210}\text{Pb}$  in the sediments of the Washington continental shelf and slope was primarily associated with hydrous Mn oxides. Presumably, the adsorbed trace metals remain associated with the hydrous Mn phase until they are ingested and assimilated by marine organisms or buried and regenerated as the hydrous Mn oxides redissolves in anoxic marine sediments.

The above brief discussion illustrates some of the complexity involving reactions of trace elements with particulate materials in coastal waters. Since the bioavailability of a particular trace metal to a marine organism is directly dependent upon the form of the metal in association with a given particle type (Luoma and Jenne, 1977), then an understanding of the mechanisms and rates of trace element removal by specific particle phases is a necessary requirement for predicting the fates of these toxic substances in coastal waters.

The purpose of the present study is to describe the major removal mechanisms for trace elements in estuarine and coastal waters. We have chosen the Duwamish River-Elliott Bay region as the setting for our

estuarine studies because it represents a well-stratified two-layer estuary with a large pollution source in the freshwater endmember. The main basin of Puget Sound was chosen as the setting for our coastal studies because it receives pollution inputs from a variety of specific and non-specific sources and because it is apparently a major sink for sediments and associated contaminants.

## B. Specific objectives and relevance

The principal focus of the L-RERP Trace Element Program during fiscal years 1980 through 1982 has been the determination of the concentrations, sources and fates of dissolved and particulate trace elements in the Duwamish River-Elliott Bay region, and the distributions, vertical fluxes and particle associations of trace elements in the main basin of Puget Sound. Specific objectives of this program include: 1) the determination of the concentrations and principal sources of trace elements in the Duwamish River; 2) the determination of the nature and extent of trace element flocculation in the estuarine zone of the Duwamish River; 3) the determinants of the transport and sedimentation of temporal variability of dissolved trace elements in the central basin of Puget Sound; and 4) the determination of the mechanisms controlling vertical fluxes of particulate trace elements at station PS7 in the central basin.

These objectives have been designed to identify the major mechanisms by which trace elements are scavenged by particulate phases in the water column, particularly associations with phases formed *in-situ* (i.e., biogenic material and hydrous Mn and Fe oxides). Of particular importance are the fundamental relationships between the physical, biological and geochemical processes occurring in the water column and at the sediment-seawater interface and the resulting removal rates for trace elements in specific particle phases. As these relationships are established the information may be applied to other coastal regimes where similar removal processes are occurring. This information can then be used to provide specific recommendations as to how municipal and industrial waste materials can be discharged in coastal environments with the least amount of impact of the ecology of the indigenous biota.

## II. CURRENT STATE OF KNOWLEDGE

Historical data on trace elements in Puget Sound is limited to a few analyses of water samples in the region of the West Point outfall and near Admiralty Inlet (Schell and Nevissi, 1977), some analyses of metals in surficial sediments of the central basin of Puget Sound and several of its embayments (Crecelius et al., 1975; Schell et al., 1977; Malins et al., 1980; Riley et al., 1980), and a few analyses of suspended material from selected Puget Sound embayments (Riley et al., 1980). The concentrations of total dissolved Ni, Cu, Zn, Pb and Co are several times higher (range: 5-100x) in Puget Sound waters than in open-ocean waters (Schell and Nevissi, 1977; Feely and Curl, 1979). Similarly, trace element concentrations in the underlying sediments were also significantly elevated. Schell et al. (1977) computed the ratio of

average concentrations of metals in sediments deposited between 1955 and 1975 with sediments deposited between 1900 and 1920 and found enrichments ranging from 1.0-3.6 in the main basin of Puget Sound. Malins et al. (1980) found enrichment factors ranging from 1-12 for the same elements in the smaller embayments, particularly Elliott and Commencement Bays.

A comparison of data on analyses for Cu, Zn, Pb, and Ni in the Duwamish River, Elliott Bay, and Puget Sound, from a variety of sources (Feely et al., unpublished; Riley et al., 1980; Schell and Nevissi, 1977; Stukas and Wong, 1981), shows a significant gradient in dissolved metals proceeding from river to sound, a significant increase in trace metals in the suspended particulate phase in Elliott Bay and the highest concentrations in the sediments of the Duwamish River.

Tissue samples of edible forms of bottom-dwelling fishes, crabs, shrimps and clams were found to have trace metal concentrations which were correlated with several indices of population (Malins et al., 1980).

#### IV. SOURCES, METHODS AND RATIONALE OF DATA COLLECTION

In order to obtain information about the trace element removal mechanisms in the Duwamish River-Elliott Bay region, we have conducted three cruises to the area (11 August, 1979, 19-20 February 1980, and 12 September 1980) to provide data for low and high runoff periods. In addition, samples from August 1979 sampling period were used for dissolved and particulate samples were also collected on a quarterly basis from the other major rivers discharging into Puget Sound to provide additional information on trace metal inputs. Table 1.1 lists the locations and times for each of the river sampling expeditions.

The sediment program consisted of a series of gravity and box cores collected at stations along the axis of the main basin and in Elliott Bay (Fig. 2.4.1). The cores were used to obtain <sup>210</sup>Pb data for the purpose of obtaining the sedimentation history, trace element profiles to obtain the history of metal pollution, and porewater trace elements and nutrients to obtain information on trace element recycling processes. In addition, in cooperation with Dr. James W. Murray of the University of Washington, a Lander was deployed at 200 m depth near Shilshole Bay (Fig. 2.4.2). The Lander was employed to determine fluxes of nutrients and trace elements from the sediments. A complete description of the methods employed for these studies is given below.

##### A. Sampling Methods

##### 1. Particulate matter

Water samples were collected from preselected depths in General Oceanics 10-L PVC GoFlo Niskin<sup>®</sup> bottles. Nominally these depths included: 0-2 m, 10 m, 20 m, 50 m, 100 m, 150 m, 175 m and 5 meters above the bottom. Aliquots were drawn within 10-15 minutes after collection from

Table 1.1. Dates and locations of sampling expeditions for rivers discharging into Puget Sound.

SAMPLING EXPEDITION	INCLUSIVE DATES	SAMPLING REGION (River)
Duwamish River Estuary Cruises		
DEC-1	11 Aug - 12 Aug 1979	Duwamish, Elliott Bay
DEC-2	19 Feb - 20 Feb 1980	Duwamish
DEC-3	11 Sept - 12 Sept 1980	Duwamish
DEC-4	1 Mar - 2 Mar 1982	Duwamish
Trace Metal Inventories - Rivers Discharging into Puget Sound		
TIPS-1	23 June 1980	Skagit, Stillaguamish, Snohomish, Duwamish, Puyallup, Nisqually
TIPS-2	23 Sept and 2 Oct 1980	Skagit, Stillaguamish, Snohomish, Duwamish, Puyallup, Nisqually, Lake Washington Ship Canal
TIPS-3	2 Jan and 7 Jan 1981	Skagit, Stillaguamish, Snohomish, Puyallup, Nisqually, Lake Washington Ship Canal, Skokomish
TIPS-4a	25 Mar 1981	Puyallup
TIPS-4	28 May and 3 June 1981	Skagit, Stillaguamish, Snohomish, Duwamish, Puyallup, Nisqually, Lake Washington Ship Canal, Skokomish
TIPS-5	7 Oct - 9 Oct and 13 Oct 1981	Skagit, Stillaguamish, Snohomish, Duwamish, Puyallup, Nisqually, Lake Washington Ship Canal
TIPS-6	26 Jan 1982	Duwamish

Table 1.2. Dates and locations of Puget Sound cruises and sediment trap deployments and recoveries.

SAMPLING EXPEDITION	INCLUSIVE DATES	SAMPLING REGION	
Long-Range Effects Cruises			
L-RERP 80	19 May - 3 June 1980	Main Basin of Puget Sound	
L-RERP 81-1	5 Feb - 6 Feb 1981	Main Basin of Puget Sound	
L-RERP 81-2	30 Apr - 1 May 1981	Main Basin of Puget Sound	
L-RERP 81-3	16 Jul -17 July 1981	Main Basin of Puget Sound	
L-RERP 81-4	25 Aug - 2 Sept 1981	Main Basin of Puget Sound	
L-RERP 81-5	3 Nov - 4 Nov 1981	Main Basin of Puget Sound	
L-RERP 82-1	22 Feb - 24 Feb 1982	Main Basin of Puget Sound	
Sediment Trap Deployments and Recoveries			
STE-1	5 Dec 1980 - 3 Feb 1981	47°41.9'	122°27.2'
STE-2	8 Feb -15 Apr 1981	47°41.9'	122°27.2'
STE-3	26 Apr - 5 July 1981	47°41.5'	122°27.5'
STE-4	24 July-29 Sept 1981	47°41.7'	122°27.2'
STE-5	15 Oct - 19 Dec 1981	47°41.7'	122°27.3'

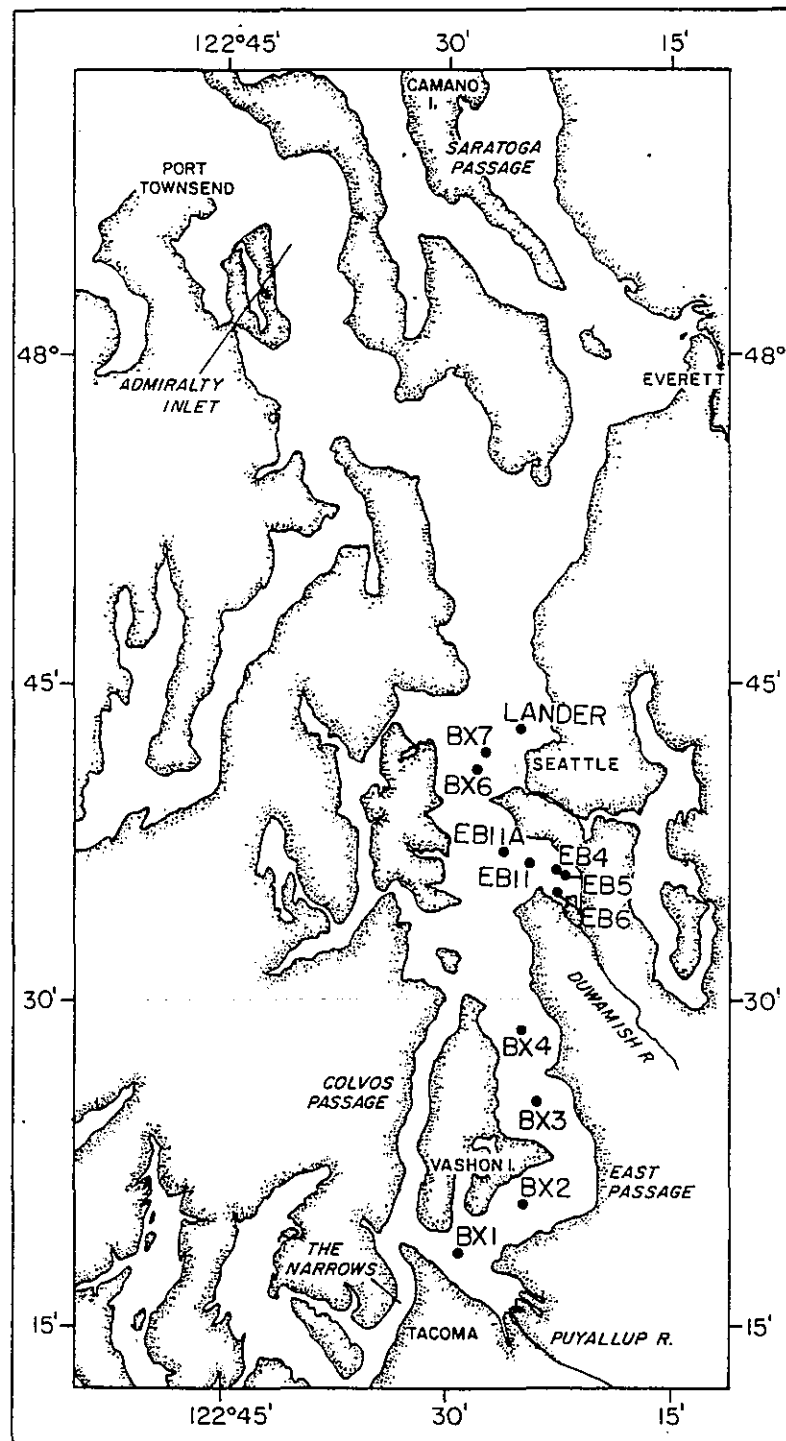


Fig.7.4.1.. Locations of core sampling stations in Elliott Bay and main basin of Puget Sound.

each sample and vacuum filtered through preweighed 0.4  $\mu$ m pore diameter Nuclepore polycarbonate filters. 47 mm filters were used for total suspended matter concentration determinations, and 25 mm and 37 mm filters for multielement particulate composition analyses. Samples were also filtered through 25 mm, 0.45  $\mu$ m pore diameter Sela<sup>s</sup> silver filters for particulate C and N analyses. All samples were rinsed with three 10 mL aliquots of pH adjusted deionized and membrane-filtered water, placed in individual petri dishes with lids slightly ajar and dessicated over NaOH for 24 hours.

## 2. Conductivity (salinity), temperature, and depth

Standard hydrographic data were acquired with a Plessey Model 9040<sup>®</sup> Environmental Profiling System (CTD probe) and a Model 8400<sup>®</sup> digital data logger using 7-track, 200 B.P.I. magnetic tape. Temperature and salinity calibration data were provided by ship personnel from discrete water samples utilizing reversing thermometers and a bench salinometer, respectively.

## 3. Interstitial porewater and Lander studies

Four types of samples were collected; interstitial water from in-situ sampler, interstitial water from 600 cm<sup>2</sup> box cores, water samples from flux chambers, and interstitial water from 400 cm<sup>2</sup> Lander box cores. A summary of the dates and samples is listed below.

- 7 May 1982. 1) Two Lander cores
- 2) Three subcores from one box core
- 3) One in situ profile
- 9 June 1982 1) Two Lander cores
- 2) One Lander chamber

The bottom Lander operates as follows: it is lowered by polypropylene line to the seafloor, and upon contact, two 20 cm<sup>2</sup> box cores are inserted into the sediments. The lid containing a timer, stirrer and sample loops then slides into place and seals the top of the box cores. The first sample is not collected until after one hour to allow any disturbed sediments to settle out. Samples are then collected every three hours until a total of eight samples have been collected from each chamber. When a sample is collected, ambient bottom water is allowed to replace the sample volume. The Lander samples are collected in polypropylene syringes whose existing dead volume is filled with distilled-deionized water before deployment.

Interstitial water was collected in situ using the gas tight sampler described in Murray and Grundmanis (1980). The sampler is fitted with a large diameter wooden wheel or "frisbee" to support the sampler at the sediment-water interface. Box cores were subcored with 2" and 4" liners immediately following retrieval, kept upright, and stored less than 6 hours before processing. In the laboratory, under a nitrogen atmosphere, the subcores were sectioned into  $\frac{1}{2}$ , 1, and 2 cm intervals, loaded into 50 ml polystyrene centrifuge tubes and capped. Interstitial water was

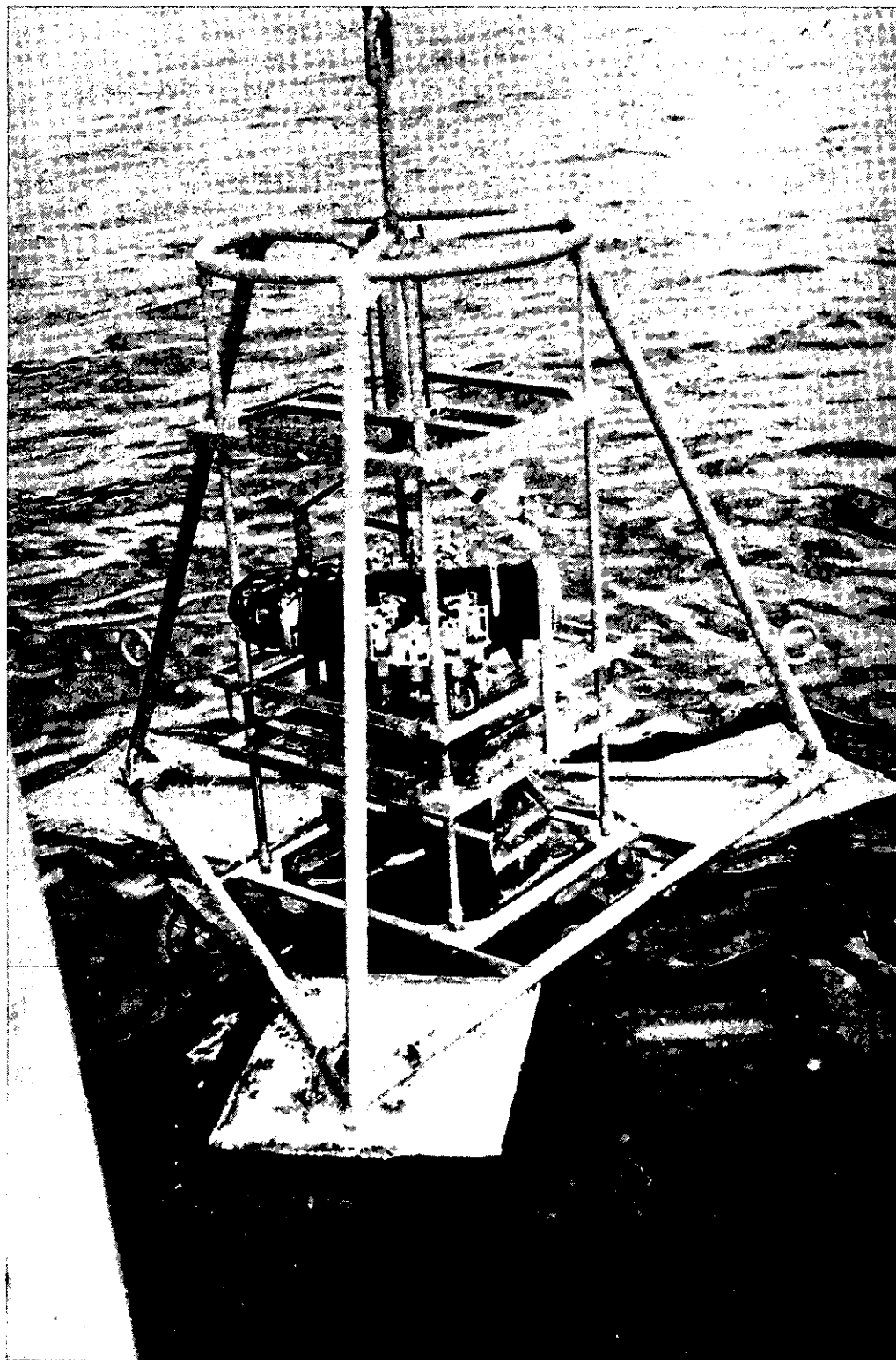


Fig. 2.4.2 The Lander used to measure the flux of solutes between the sediments and the overlying water.



separated by centrifugation at 13,000 RPM for 15 minutes. Aqueous samples were drawn into polypropylene syringes and expressed through 0.45  $\mu\text{m}$  Millipore filters into polystyrene test tubes. Unfiltered samples were collected for total  $\text{CO}_2$  ( $\Sigma\text{CO}_2$ ),  $\text{CH}_4$ , and stable C isotopes ( $\delta^{13}\text{C}$ ).

Samples for dissolved gases were obtained from all *in-situ* and flux chamber aqueous samples and stored in nylon tubing sample loops.  $\text{O}_2 + \text{Ar}$ ,  $\text{N}_2$  and  $\text{CH}_4$  were separated on a molecular sieve 5A column (100-200 mesh, 1/4" x 6') at 60°C with a helium carrier flow of 100 cc/min. The thermistor detector was operated at 25°C $\pm$ 0.1° for maximum sensitivity.

Samples for  $\Sigma\text{CO}_2$  were drawn into 3 ml polypropylene syringes, capped, and stored at 4°C for up to 12 hours before analysis. A 1 mL calibrated nylon loop was used to inject the sample into the stripping system. The sample was acidified with  $\text{H}_2\text{SO}_4$  and  $\text{CO}_2(\text{g})$  stripped with a helium flow of 75 cc/min. The  $\text{CO}_2$  was separated from the other gases on a Porapak Q column (100-120 mesh, 1/4"x4') at 40°C. The precision was  $\pm 1\%$  on duplicate samples.

Aliquots were drawn from all aqueous samples (interstitial waters and flux chambers) for pH, alkalinity, nutrients,  $\text{SO}_4$ , Ca, Mg, Fe, Mn and frequently for dissolved organic C (DOC) and  $\delta^{13}\text{C}$ . Alkalinity and pH were analyzed immediately. The pH was determined at 25°C using a Corning combination electrode and an Orion digital pH meter. The electrode had been soaked in sea water prior to use. Standard N.B.S. buffers were used to calibrate the pH measurements. Alkalinity was determined on a 1,000 ml sample using a microtitration with 0.0100 ml sample using a microtitration with 0.0100 N HCl to 0.53 N NaCl. A Gran plot (Bradshaw et al., 1981) was used to determine the endpoint with an average precision of  $\pm 0.5\%$ .

## B. Analytical methods

### 1. Gravimetry

Total suspended matter concentrations were determined gravimetrically. Volumetric total suspended matter samples were collected on 47 mm, 0.4  $\mu\text{m}$  pore diameter Nuclepore<sup>®</sup> filters which were weighed on a Cahn Model 4700<sup>®</sup> Electrobalance before and after filtration. The suspended matter loadings were then determined by difference. The weighing precision ( $2\sigma = \pm .011$  mg) and volume reading error ( $\pm 10$  mL) yield a combined coefficient of variation in suspended matter concentration (mg/L) of approximately 1% at mean sample loading and volume (2.057 mg and 2 L, respectively). However, preliminary investigations of sampling precision (coef. of var.: 25%) suggest that the actual variability in the particulate matter concentrations of these waters is much greater than the analytical precision mentioned above.

## 2. $^{210}\text{Pb}$ activity

The  $^{210}\text{Pb}$  activities of the sediment samples were determined using a modification of the procedure described by Gaggler et al. (1976). Dried and homogenized sediment samples of about 100 g were placed into plastic petridishes and counted with an anticoincidence-shielded Ge(Li) gamma-ray spectrometer. The counting efficiency for the 46.5 Kev gamma ray was found to be 2.0%.

## 3. Gas chromatography

Analysis of total particulate C and N in suspended matter was performed with a Hewlett Packard Model 185B<sup>®</sup> C-H-N analyzer. In this procedure, particulate C and N compounds are combusted to  $\text{CO}_2$  and  $\text{N}_2$  (micro Pregl-Dumas method), chromatographed on silica gel, and detected sequentially with a thermal conductivity detector. NBS acetanilide is used for standardization. Analyses of replicate surface samples yield coefficients of variation ranging from 1% to 4% for C and 2% to 6% for N.

## 4. X-ray secondary emission spectrometry

The chemistry of both major elements (Mg, Al, Si, K, Ca, Ti, and Fe) and trace elements (Cr, Mn, Ni, Cu, Zn, and Pb) of the suspended particulate matter and sediment trap samples were determined by x-ray secondary-emission (fluorescence) spectrometry utilizing a Kevex x-ray energy spectrometer and the thin-film technique (Feely et al., 1981).

A Kevex Model 7077-0700 x-ray energy spectrometer with a rhodium x-ray tube was used in the direct and secondary-emission (Ge and Zr targets) modes to obtain maximum efficiency for excitation of individual elements in the sample. Standards were prepared from suspensions of finely ground, U.S.G.S. standard rocks (W-1, AGV-1, GSP-1; 90 percent by volume less than 15  $\mu\text{m}$  in diameter) collected on Nuclepore filters identical to those used for sample acquisition. At a filter loading of 290  $\mu\text{g cm}^{-2}$  the determination limits (three times the minimum detection limits) were less than 0.02% and 10 ppm for the major and trace elements, respectively. Total dissolved Mn and Fe in the pore fluids was determined by x-ray secondary-emission spectrometry using a Cu secondary target and a 3-mL aliquot of the sample contained in a spectro cup. Determination limits of 12  $\mu\text{M}$  and 13.6  $\mu\text{M}$  Fe were obtained with this procedure.

## 5. Atomic absorption spectrophotometry

The sediment trap and sediment samples from station PS7 were analyzed for Fe, Mn, Cr, Cu, Ni, Zn, Cd and Pb by means of several extraction procedures. The first extraction procedure involves the use of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) to release organically bound trace metals. The second treatment utilizes hydroxylamine hydrochloride in 25% acetic acid to dissolve amorphous Mn and Fe oxides. The details of these procedures are outlined below.

a.  $H_2O_2$  treatment

Crecelius et al. (1974) have demonstrated that 30%  $H_2O_2$  efficiently oxidizes particulate organic matter and thus removes certain trace metals from sediments. Landing and Feely (1981) had shown that the modification of this procedure efficiently removes organic C and N from suspended matter. The release of trace metals from suspended matter during this procedure is attributed to the dissolution of organically bound trace metals.

Separate 100 mg aliquots of sediment trap material were heated in 10% Ultrex  $H_2O_2$  at 65°C for 18 hrs and then sonicated with continued heating for another 24 hrs. The samples were decanted and filtered through an acid-cleaned 0.2  $\mu$ m Nuclepore filter. The samples were rinsed with two portions of quartz-distilled water, acidified with 0.5 mL Ultrex HCl and transferred to acid-cleaned CPE bottles and diluted with quartz distilled water to 20 g. The trace elements in these solutions were analyzed by flameless atomic absorption methods described elsewhere (Feely et al., 1981).

b. Hydroxylamine hydrochloride in 25% acetic acid

The trace elements associated with the poorly structured hydrous oxide phases of the sediment trap samples were determined by the method of Chester and Hughes (1967) with slight modifications. Desiccated samples were leached with 5 mL of a mixed reagent containing 0.04 N hydroxylamine hydrochloride in 25% Ultrex acetic acid at room temperature for 2 hrs. The resulting supernate was filtered through an acid-cleaned polypropylene-glass apparatus containing a 0.2- $\mu$ m Nuclepore filter. The residue was rinsed with quartz-distilled water, then filtered; the supernate was then combined with the original supernate, acidified with 0.5 mL of concentrated Ultrex HCl diluted to 20 g total weight, and stored in an acid-cleaned polyethylene bottle. The trace metals in this solution were analyzed by flameless atomic absorption procedures. The remaining solid suspended matter was dissolved in an Ultrex HCl- $HNO_3$ -HF matrix according to Eggiman and Betzer (1976) and analyzed for trace elements in a similar manner.

c. Dissolved Trace Metals

The determination of Fe, Mn and Zn in river water samples was conducted by direct injection methods whereas Cu, Cd, Ni and Pb analyses were performed by preconcentrating 200 ml samples onto 3.5 g of Chelex-100 ion exchange resin following the procedures outlined in Curl et al. (1981). Extraction efficiencies of 95%  $\pm$  4%, 89%  $\pm$  15% and 102%  $\pm$  11% were obtained for Cu, Cd, Pb and Ni respectively, using standard addition methods. For the dissolved trace elements in Puget Sound and Strait of Juan de Fuca, 400 ml samples were preconcentrated onto 5 g of Chelex-100. The columns were rinsed with 1 N  $NH_4Ac$  to remove excess salts and eluted with 2 N  $HNO_3$ . The extraction efficiencies for the marine samples were 106%  $\pm$  7%, 97%  $\pm$  9%, 97%  $\pm$  6% and 101%  $\pm$  4% for Mn, Cu, Cd and Ni, respectively.

## 6. Nutrients and major elements

$\text{NH}_4$ ,  $\text{NO}_3$ ,  $\text{NO}_2$ ,  $\text{PO}_4$ , and silica were analyzed by standard autoanalyzer techniques.  $\text{SO}_4$  samples were acidified and stored at room temperature prior to 1000-fold dilution with distilled, deionized water and analysis by ion chromatography. Precision of replicate analyses is better than 6%.

Ca and Mg were analyzed by flame atomic absorption spectrophotometry. The Fe and Mn samples were acidified and stored for later analysis by x-ray fluorescence. Dissolved organic C (DOC) was determined by a UV-persulfate oxidation method using a Dohrmann Model DC-80 analyzer. Precision of replicate samples is better than 3% and the detection limit is 0.1 mg/L.

## V. RESULTS AND INTERPRETATIONS

### A. Riverine inputs

Previous reports on trace metals in Puget Sound have shown that rivers are major contributors of metals to the Sound; however, these models have large uncertainties because the data are scarce (Schell et al., 1977; Dexter et al., 1981). This program attempted to evaluate the river contribution in a systematic manner. Major rivers were seasonally sampled for both dissolved and particulate trace metals during 1980 and 1981. The preliminary results of this investigation are listed in Table 5.1. In conjunction with flow and suspended matter discharge data from other sources, these results were used to calculate the trace metal flux of each river (Table 5.2). With the knowledge that the RSTP significantly affected the trace metal burden of the Duwamish (Paulson et al., in preparation), we extended the study of the Duwamish into 1982 in an effort to separately account for the river and RSTP flux. In general the mass flux of trace metals to the Puget Sound is primarily a function of annual water discharge with the Skagit River being the largest contributor and the Lake Washington Ship Canal being the smallest. However, there are several striking features concerning the partitioning of metals between dissolved and particulate phases.

In the rivers, less than 3% of the Fe and Pb are in the dissolved form while up to 17%, 18% and 22% of the Cu, Ni and Zn, respectively, are in this form. In contrast to the rivers, a much larger fraction of the flux of the Lake Washington Ship Canal and the RSTP is in the dissolved form. Although the RSTP annual contribution is only 6%, 8%, 10% and 21% of the Pb, Zn, Cu and Ni combined flux, respectively, the predominance of the dissolved form could result in a two-fold increase in the amount of dissolved trace metal delivered to the estuary.

Table 5.1. Preliminary results on the dissolved and particulate trace metal concentrations in freshwater sources entering the main and Whidbey Basins of Puget Sound.

a) Average dissolved metal concentration in $\mu\text{g/L}^a$							
Source	Fe	Mn	Cu	Ni	Pb	Zn	Cd
Skagit R.	36 $\pm 9$ (8)	3.0 $\pm 1.5$ (8)	0.58 $\pm 0.06$ (8)	0.78 $\pm 0.30$ (3)	0.07	1.3	0.03
Stillaquamish R.	76 $\pm 25$ (5)	11 $\pm 4$ (5)	0.72 $\pm 0.18$ (4)	1.5 1.1 (3)	0.07	1.0	0.04
Snohomish R.	84 $\pm 24$ (5)	11 $\pm 3$ (5)	0.69 $\pm 0.10$ (4)	1.0 $\pm 1.0$ (3)	0.10	1.3	0.02
Lake Washington Ship Canal	27 $\pm 17$ (4)	3.7 $\pm 2.8$ (4)	1.48 $\pm 0.62$ (4)	1.1 $\pm 0.1$ (2)	0.27	3.3	0.03
Duwamish R.	75 $\pm 43$ (6)	33 $\pm 18$ (6)	0.66 $\pm 0.29$ (5)	0.5 $\pm 0.4$ (5)	0.04 $\pm 0.04$ (2)	1.1 $\pm 0.7$ (3)	0.05 $\pm 0.04$ (3)
Puyallup R.	66 $\pm 27$ (5)	22 $\pm 11$ (5)	0.68 $\pm 0.21$ (3)	0.3 $\pm 0.2$ (3)	0.04	2.8	0.02
b) Average Particulate Concentration in $\mu\text{g/g}^b$							
Source	Fe	Mn	Cu	Ni	Pb	Zn	Cd
Skagit	48,200 $\pm 6,700$	873	54 $\pm 2$	88 $\pm 14$	48 $\pm 9$	158 $\pm 11$	--
Stillaquamish R.	62,000 $\pm 1,000$	1150 $\pm 12$	70 $\pm 4$	200 $\pm 18$	91 $\pm 25$	231 $\pm 42$	--
Snohomish R.	48,100 $\pm 3,500$	1014 $\pm 105$	62 $\pm 4$	83 $\pm 13$	92 $\pm 11$	140 $\pm 25$	--
Lake Washington Ship Canal	14,700 $\pm 3,800$	1089 $\pm 304$	79 $\pm 15$	52 $\pm 19$	230 $\pm 80$	635 $\pm 483$	--
Duwamish R.	33,800	1071	32	32	75	169	--
Puyallup R.	29,000 $\pm 1,800$	488 $\pm 12$	51 $\pm 1$	27 $\pm 3$	20 $\pm 7$	65 $\pm 3$	--

a) Average of all samples which were greater than twice the blank during five seasonal field trips. The Skagit was sampled at the North and/or South Forks. The number in parentheses is the number of samples meeting the quality control criteria.

b) Average of duplicate analyses of samples collected during spring.

Table 5.2. Annual discharge of water, sediment and trace metals from freshwater sources entering the Main and Whidbey basins of Puget Sound.

Source	Water Discharge ( $\times 10^9 \text{ m}^3$ )	Total Sediment Discharge ( $\times 10^{12} \text{ g}$ )	Fe ( $\times 10^9 \text{ g}$ )	Mn ( $\times 10^6 \text{ g}$ )	Cu ( $\times 10^6 \text{ g}$ )	Ni ( $\times 10^6 \text{ g}$ )	Pb ( $\times 10^6 \text{ g}$ )	Zn ( $\times 10^6 \text{ g}$ )
Skagit River	15.1 <sup>a</sup>	1.1 <sup>d</sup>	54(1%) <sup>f</sup>	1005(5%) <sup>f</sup>	68(13%) <sup>f</sup>	109(11%) <sup>f</sup>	55(2%) <sup>f</sup>	193(10%) <sup>f</sup>
Stillaguamish River	5.2 <sup>a</sup>	0.40 <sup>d</sup>	25(1%)	517(11%)	32(12%)	88(9%)	37(1%)	98(5%)
Snohomish River	8.4 <sup>a</sup>	0.46 <sup>d</sup>	23(3%)	558(16%)	34(17%)	46(18%)	43(2%)	73(13%)
Lake Washington Ship Canal	1.2 <sup>b</sup>	0.002 <sup>e</sup>	0.6(52%)	7(66%)	2(90%)	1(92%)	2(74%)	5(76%)
Duwamish River	1.42 <sup>a</sup>	0.17 <sup>d</sup>	5.9(1%)	228(20%)	6.1(10%)	6.2(12%)	13.3(1%)	30(5%)
RK 21.0 Renton STP	0.06 <sup>c</sup>	0.0005 <sup>c</sup>	0.02(38%)	4(63%)	0.8(90%) <sup>g</sup>	1.7(88%) <sup>g</sup>	0.8(47%) <sup>g</sup>	2.5(86%) <sup>g</sup>
Combined	1.48	0.17	5.9(1%)	232(21%)	6.9(21%)	7.9(28%)	14.1(3%)	33(9%)
Puyallup River	30.0 <sup>a</sup>	0.46 <sup>d</sup>	13.3(1%)	290(23%)	25(18%)	13(7%)	9(2%)	38(22%)
TOTAL	34.4	2.59	122	2609	168	265	160	440

a) USGS (1981)

b) Schell et al. (1977)

c) monthly reports (METRO)

d) Dexter et al. (1981)

e) Flow  $\times$  2.1 mg/L total suspended matter

f) Percent dissolved in parentheses

g) monthly reports (METRO) augmented with our data in cases where the effluent values were below their detection limit.

## B. Estuarine interactions

### 1. Flocculation processes in the Duwamish River estuary

The flocculation studies were conducted with samples collected from the Duwamish River Estuary (Fig. 3.1). This estuary was chosen because: (1) it has a well-defined and extensively studied salt wedge; (2) it is reasonably accessible; and (3) the discharge from the RSTP makes up a significant amount on the total river discharge (up to 25%). Freshwater samples were collected on August 11, 1979 from 4 stations in the Duwamish River above the salt wedge. Stations 1 and 2 were located above METRO's RSTP (Station 3) and stations 4 and 5 were located in the river immediately below the sewage treatment facility. Stations 6 through 12 were located in the estuary and station 13 was located in Elliott Bay. The results of the product mode experiments are graphically represented in Figures 2.4.3 and 2.4.4. Figure 2.4.3 shows the results for total flocculated material and major elements. The concentrations have been corrected for the zero salinity in the amount of flocculated material per liter of river water. The data for total flocculated material indicate a general increase in concentration with increasing salinity. At the highest salinities, samples from stations 1 and 2 produced 2-3 mg of newly flocculated material per liter of riverwater, whereas the samples from stations 4 and 5 produced 2-3 times more flocculated material. These data suggest that the effluent from the RSTP significantly increases the total amount of flocculated material that is produced in the experiments. Similarly, the data for P, K, and Ca show 2- to 4-fold enrichments in the downstream samples relative to the upstream samples. In contrast, Al and Ti do not show a consistent pattern of enrichment. Figure 2.4.3 shows the data for the trace elements. 2- to 5-fold enrichments in the downstream samples were found for Cr, Fe, Ni, Cu, and Zn, whereas Mn showed no significant enrichment in the downstream samples relative to the upstream samples. In fact, the data for Mn were anomalous in that no flocculation was observed below a salinity of 17.5‰. This effect may be due to the relatively slow kinetics of Mn precipitation.

To verify these results, a product mode experiment was conducted using the effluents from the sewage treatment plant in place of the riverwater end-member. The results of these studies are shown in Figure 5.3. The data indicate that for most of the elements in the effluent, flocculation occurs over the entire range of salinities, with individual elemental concentrations generally increasing with increasing salinity. P shows the greatest amount of flocculation. This element is followed by Ca and Fe. These elements are primary constituents of organic materials and, therefore, a flocculation mechanism involving organic materials from sewage effluent may be indicated.

In order to evaluate this possibility we computed the concentrations of the elements in the newly flocculated material from stations 2 and 5 for three salinities: 2.5, 12.5 and 22.5 ‰. The data, which are presented in Table 5.3 are representative of what was found for all the experiments. The results indicate that organic material is probably the major particulate phase in the flocculated matter. C, N, P and Ca,

DUWAMISH RIVER PRODUCT MODE STUDY  
(AUGUST 1979)

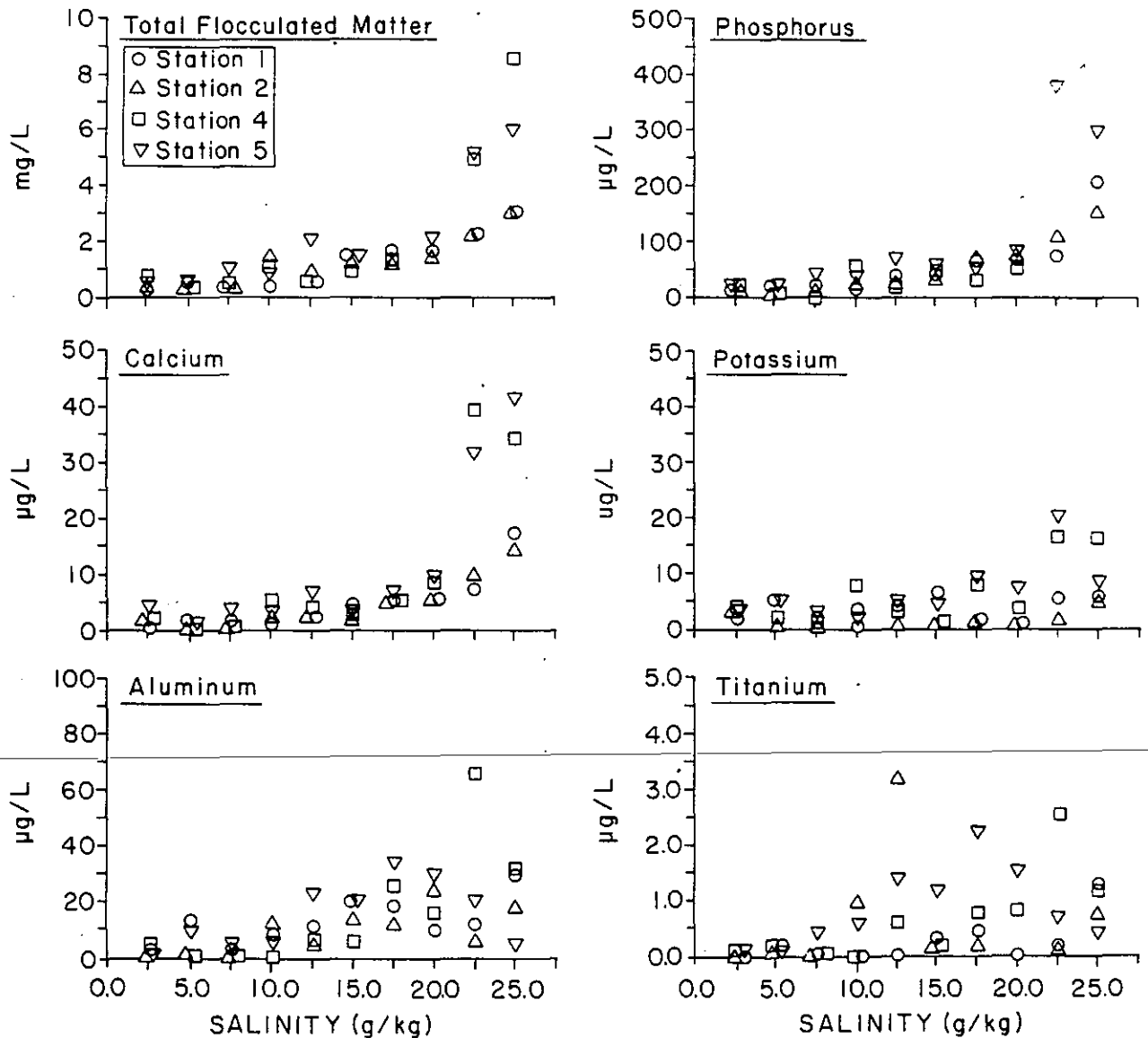


Fig. 2.4.3 Results of mixing riverwater from the Duwamish River with seawater from Elliott Bay. Concentrations are given in mg or µg per liter of riverwater mixed. Stations 1 and 2 were located above the Renton Sewage Treatment Plant outfall and stations 4 and 5 were located immediately below it. Samples were collected on August 11, 1979 during ebb tide.



DUWAMISH RIVER PRODUCT MODE STUDY  
(AUGUST 1979)

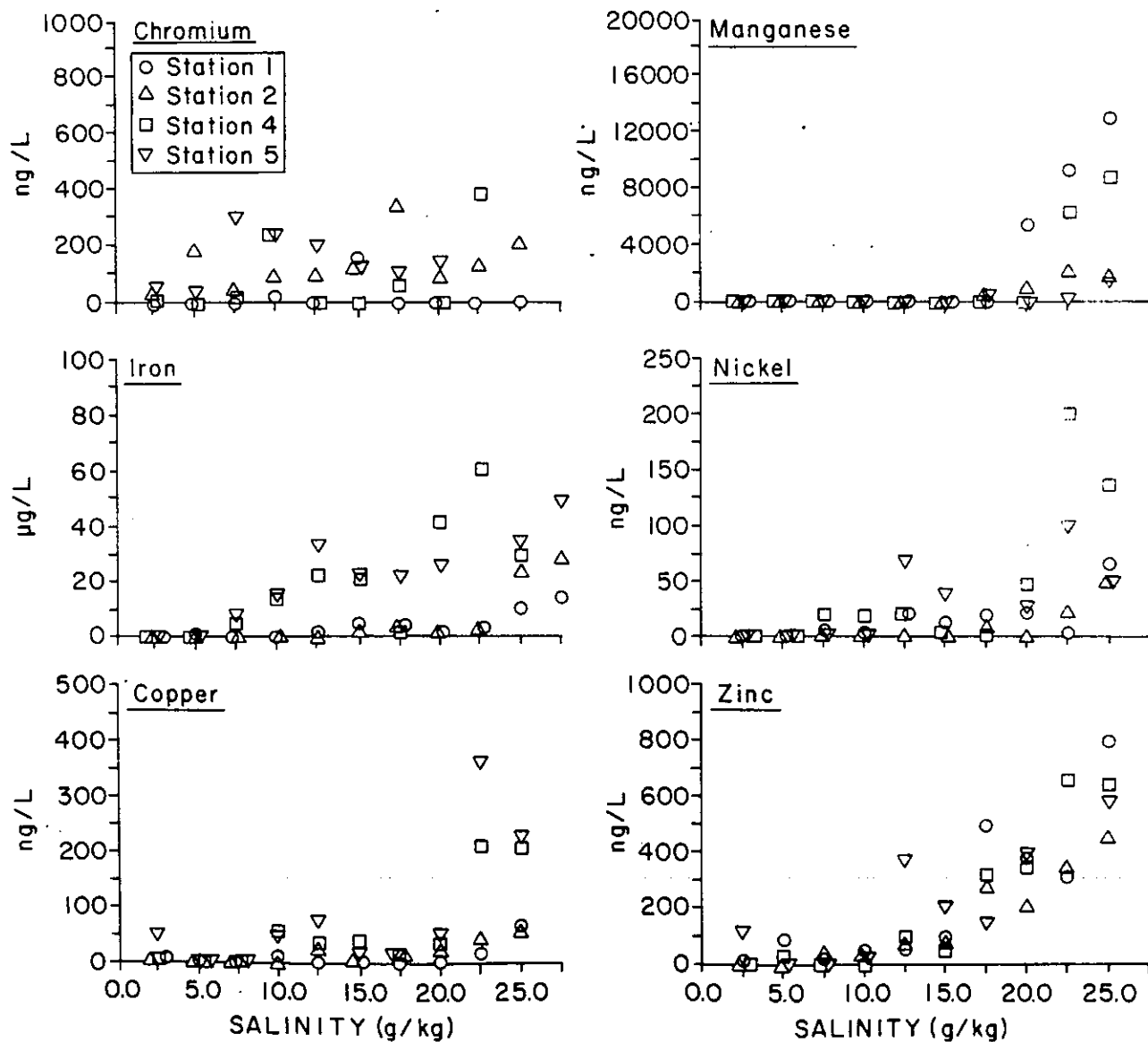


Fig. 2.4.4

Results of mixing river water from the Duwamish River with seawater from Elliott Bay. Concentrations are given in ng or µg per liter or riverwater mixed. Stations 1 and 2 were located above the Renton Sewage Treatment Plant outfall and stations 4 and 5 were located immediately below it. Samples were collected on August 11, 1979 during ebb tide.

which are the major elemental constituents of organic matter, are also the most abundant elements in the flocculated matter. Si, Al, and Ti, which are usually associated with inorganic materials, comprise only about 5-15% of the flocculated material.

With respect to the major elements one other trend is worth noting. With increasing salinity, P concentrations increase while the concentrations of Al and Ti decrease. Moreover, this trend is more dramatic for station 5 than for station 2. These data suggest that as salinity increases flocculation of organic materials predominates over flocculation of inorganic materials, especially when sewage materials are present. These trends are consistent with Sholkovitz's (1976) general conclusion that, in the case of the Scottish estuaries he studied, flocculation processes are dominated by interactions involving organic matter.

The trace metals also show a general increase in concentration with increasing salinity and, again, the station 5 values are greater than the values from station 2. These data are interpreted as evidence for concentration of the trace metals in the flocculated material with increasing salinity, with the concentration effect being enhanced by the sewage effluents.

The flocculation of trace metals in the Duwamish River estuary is a major factor affecting the geochemistry and, very probably, the ecology of the surrounding local marine environment. As stated earlier, the product-mode experiments indicate that from 18% to 62% of the dissolved trace-metal burden of the Duwamish River is transformed from a dissolved state to an organic-rich flocculant during estuarine mixing. For some elements (i.e., Fe and Mn) this estimate may indeed be minimum since the catalytic effect of the riverine particulate matter is removed in the laboratory experiments. For example, the Fe data of Murray and Gill (1978) indicate up to 90% removal by flocculation in the Duwamish River. A large fraction of the flocculated material settles to the seafloor of the lower estuary and Elliott Bay and significantly increases the trace-metal burden of these sediments as indicated by the enrichments of the concentrations of Fe, Zn, and Pb in the weak-acid soluble phases of the sediments (Fig. 5.4a). Malins et al. (1980) and Riley et al. (1980) reported enrichments of trace metals in the sediments from the Duwamish River and Elliott Bay ranging from about 100 to 900 percent compared with previously reported concentrations of near-shore sediments from Puget Sound and other coastal areas. These enrichments were significantly higher than corresponding enrichments for the central basin of Puget Sound (Schell et al., 1977), indicating rapid removal of the flocculated material by sedimentation processes. Thus, the net effect of the flocculation reactions is to decrease the concentrations of the dissolved trace metals in the estuary and to concentrate the metals in the suspended matter and ultimately in the local estuarine and near-shore sediments.

## 2. Trace element scavenging in Elliott Bay

In February, 1980, we conducted a survey of the trace element composition of suspended materials in Elliott Bay in order to determine

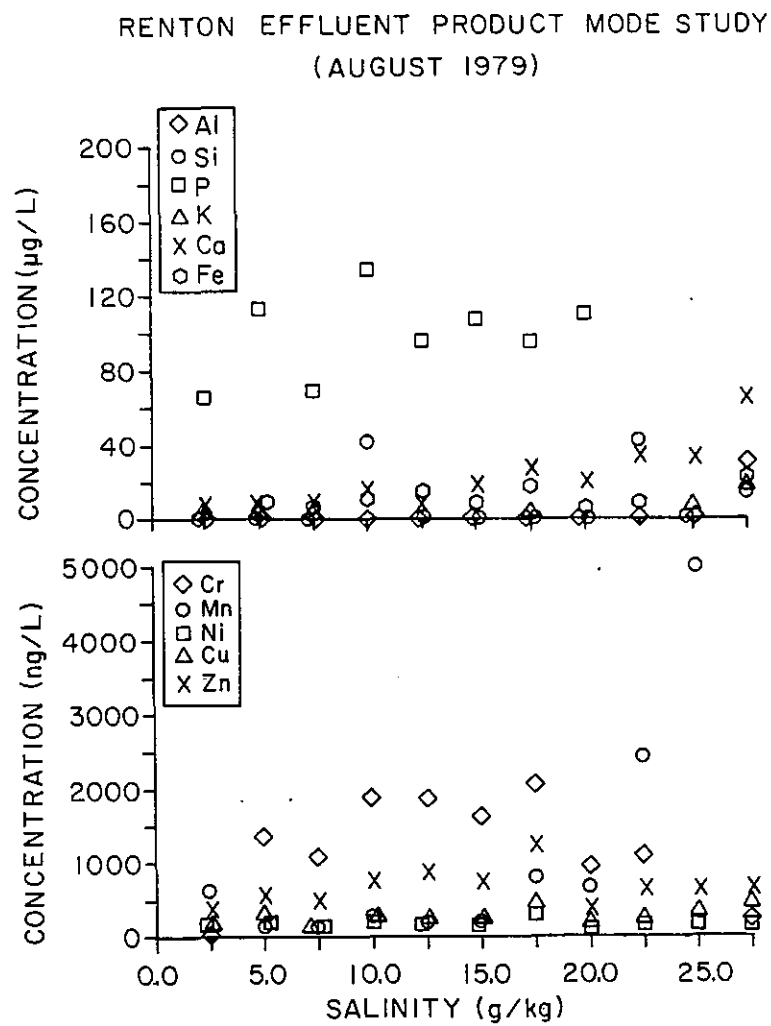


Fig. 2.4.5 Results of mixing filtered effluent from the Renton Sewage Treatment Plant with filtered seawater from Elliott Bay. (Concentrations are given in µg of ng per liter of effluent mixed. A composite sample was collected on August 11, 1979).

Table 5.3. Chemical composition of flocculated material from stations 2 and 5 at salinity ranges of 2.5-10.0‰, 12.5-20.0‰ and 22.5-27.5‰.

ELEMENT	2.5-10.0‰		12.5-20.0‰		22.5-27.5‰	
	Sta. 2	Sta. 5	Sta. 2	Sta. 5	Sta. 2	Sta. 5
N† (Wt. %)	8.8 ±2.0	8.9 ±4.1	8.8 ±1.5	3.4 ±0.8	7.7 ±0.4	7.2 ±1.2
C† (Wt. %)	ND	ND	62.0	77.0	67.0 ±15.9	74.5 ±21.1
P (Wt. %)	1.77 ±0.70	2.85 ±1.50	3.90 ±0.27	3.47 ±0.27	4.78 ±0.07	6.18 ±1.76
Al (Wt. %)	1.19 ±1.02	2.25 ±0.57	1.42 ±0.25	2.09 ±0.45	0.64 ±0.33	0.49 ±0.17
Si (Wt. %)	6.66 ±6.28	7.47 ±4.53	7.98 ±7.09	9.50 ±1.49	2.64 ±1.54	3.15 ±3.19
K (Wt. %)	0.23 ±0.27	0.39 ±0.24	0.08 ±0.03	0.33 ±0.11	0.11 ±0.07	0.26 ±0.14
Ca (Wt. %)	2.45 ±0.96	2.11 ±0.58	1.41 ±0.17	1.25 ±0.20	0.93 ±0.16	0.88 ±0.10
Ti (Wt. %)	0.15 ± 0.10	0.11 ±0.05	0.13 ±0.16	0.13 ±0.03	0.04 ±0.02	0.03 ±0.01
Cr (ppm)	104 ± 74	332 ± 61	152 ± 82	439 ±562	80 ± 5	244 ±199
Mn (ppm)	ND	ND	507 ±595	ND	987 ±197	538 ±109
Fe (Wt. %)	2.08 ±1.23	2.80 ±0.93	1.35 ±0.11	2.56 ±0.37	1.06 ±0.29	2.13 ±1.67
Ni (ppm)	ND	57 ± 25	ND	60 ± 50	13 ± 4	15 ± 6
Cu (ppm)	ND	38 ± 30	25 ± 9	91 ±118	31 ± 12	53 ± 16
Zn (ppm)	136 ±128	179 ±127	195 ± 62	182 ± 47	162 ± 38	278 ±234

ND = Not detected above blank values.

† = Weight percentages of N and C were determined using samples collected with Nuclepore filters. The uncertainty of the blanks in the filters were ±2.8 µg N and ±100 µg C.

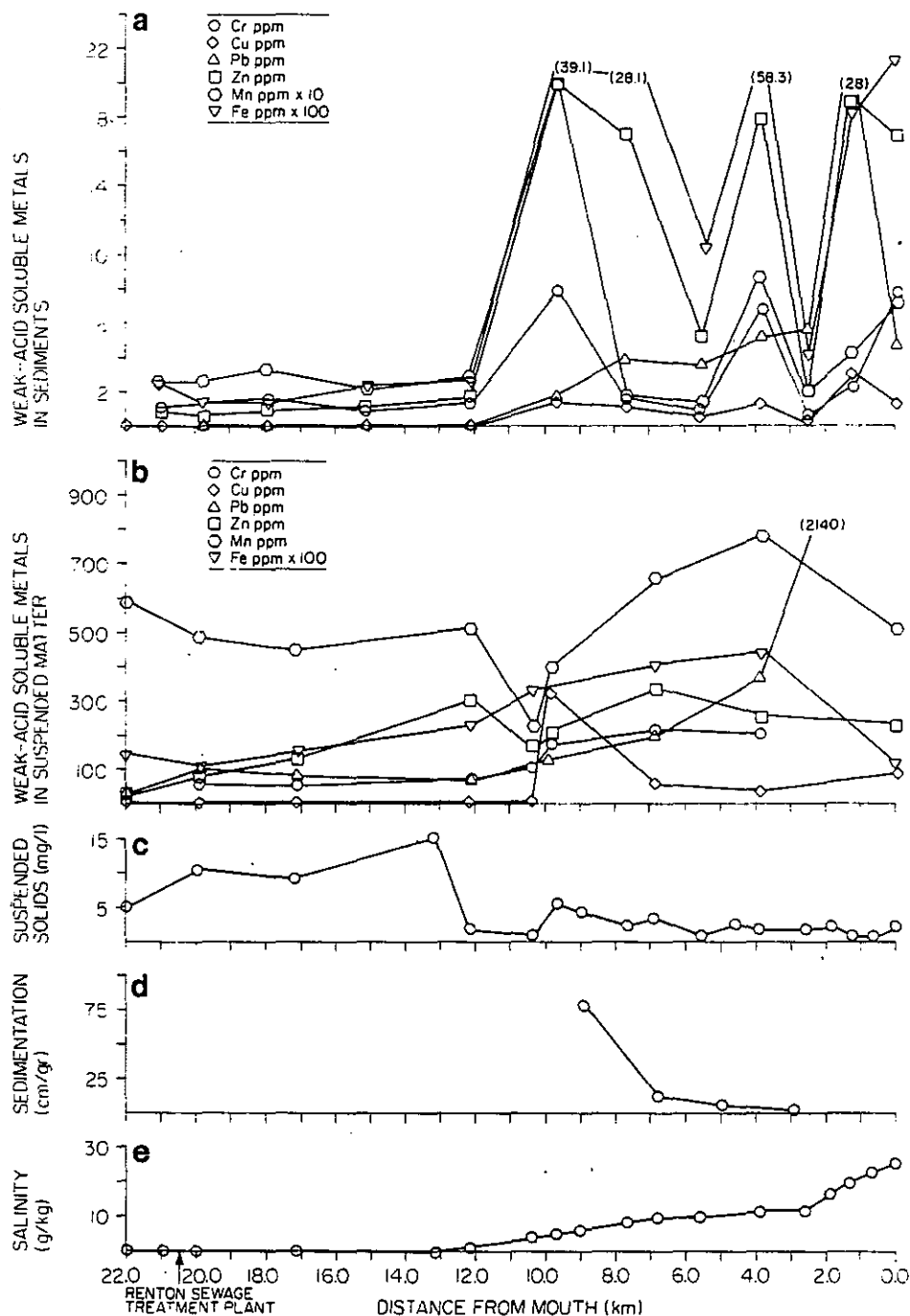


Fig. 2.4.6

Transects of: (a) weak-acid-soluble trace elements in sediments; (b) weak-acid-soluble trace elements in near-surface (<2m) suspended matter; (c) sedimentation velocity; (d) near surface total suspended matter; and (e) near surface salinity along the Duwamish River from river kilometer 22.1 to river kilometer 0.0.

their sources and transport pathways. Our objective was to establish the pathways for transport of particulate trace elements from the Duwamish River to the main basin of Puget Sound. We also wanted to identify specific scavenging processes as the particles were transported through the Bay. The results of the chemical analyses of major and trace elements in the suspended matter from Elliott Bay are summarized in Table 5.2 and the data are also graphically presented in Figs. 5.5 through 5.11. The near-surface data clearly illustrate that the Duwamish River is the major source of particulate trace elements in the surface waters of Elliott Bay. Near the mouth of the Duwamish River particulate trace element concentrations were about the same (e.g., Cr, Ni, Cu and Zn) or slightly higher (for Mn and Pb) than near-surface particulate matter of the Duwamish River Estuary. Also, the surface distributions of particulate Cr, Fe, Ni, Cu, Zn and Pb show concentration gradients that decreased by as much as a factor of five away from the mouth of the river. The trace-element-enriched particulate matter formed a plume that flowed north across the Bay and to the northwest towards West Point where it dispersed into the central basin. These data are generally consistent with the corresponding suspended matter distributions reported by Baker (1982). However, the concentration gradients of the particulate trace elements decreased more rapidly than the gradient of total suspended matter. This observation suggests that the near-surface particulate matter is diluted, to some extent, by trace-element deficient particulate matter from another source. Only particulate Mn data show increasing concentration in offshore waters. This appears to be the result of further scavenging of dissolved Mn by the suspended matter as indicated by the maxima in particulate Mn at 20 m at stations EB 4 and EB 11 (Fig. 5.6). This interesting result implies that dissolved Mn continues to be scavenged by suspended matter in the subsurface (>15 m) waters of Elliott Bay. Indeed, Mn concentrations in some samples exceed 10,000 ppm by weight in the particulate matter which is more than a factor of ten higher than Mn concentrations in suspended matter from the Duwamish River (Table 5.4). Along with the enrichment of Mn in the subsurface particulate matter are corresponding enrichments of particulate Cr, Cu, Ni, and Pb (Table 5.4). For example, the highest concentrations of Cr, Cu, Ni, Zn and Pb in subsurface particulate matter are in samples where Mn concentrations approach or exceed 10,000 ppm. Plots of the relationships between total particulate trace elements and total particulate Mn in the subsurface suspended matter are presented in Fig. 5.12. The correlation coefficients for Cr, Ni, Cu, and Zn vs. Mn are all significant at the  $p < 0.01$  level and the correlation coefficient for Pb vs. Mn is significant at the  $p < .05$  level. These results suggest that in the subsurface waters of the Bay the trace element samples were collected along with sediment trap, sediment, and pore water concentration increases in the suspended matter are primarily controlled by scavenging processes involving hydrous Mn oxide coatings.

In order to further illustrate the nature of the relationships between the trace elements and hydrous Mn oxides in the suspended matter, selected samples were treated with 25 percent (v/v) acetic acid to separate those metals associated with amorphous acid-soluble metal oxides (Bolger et al., 1978). The results of these experiments are given in Table 5.5. The data show higher amounts of weak-acid-soluble Ni, Cu, Zn, and Pb as well as Mn in the Elliott Bay samples relative to

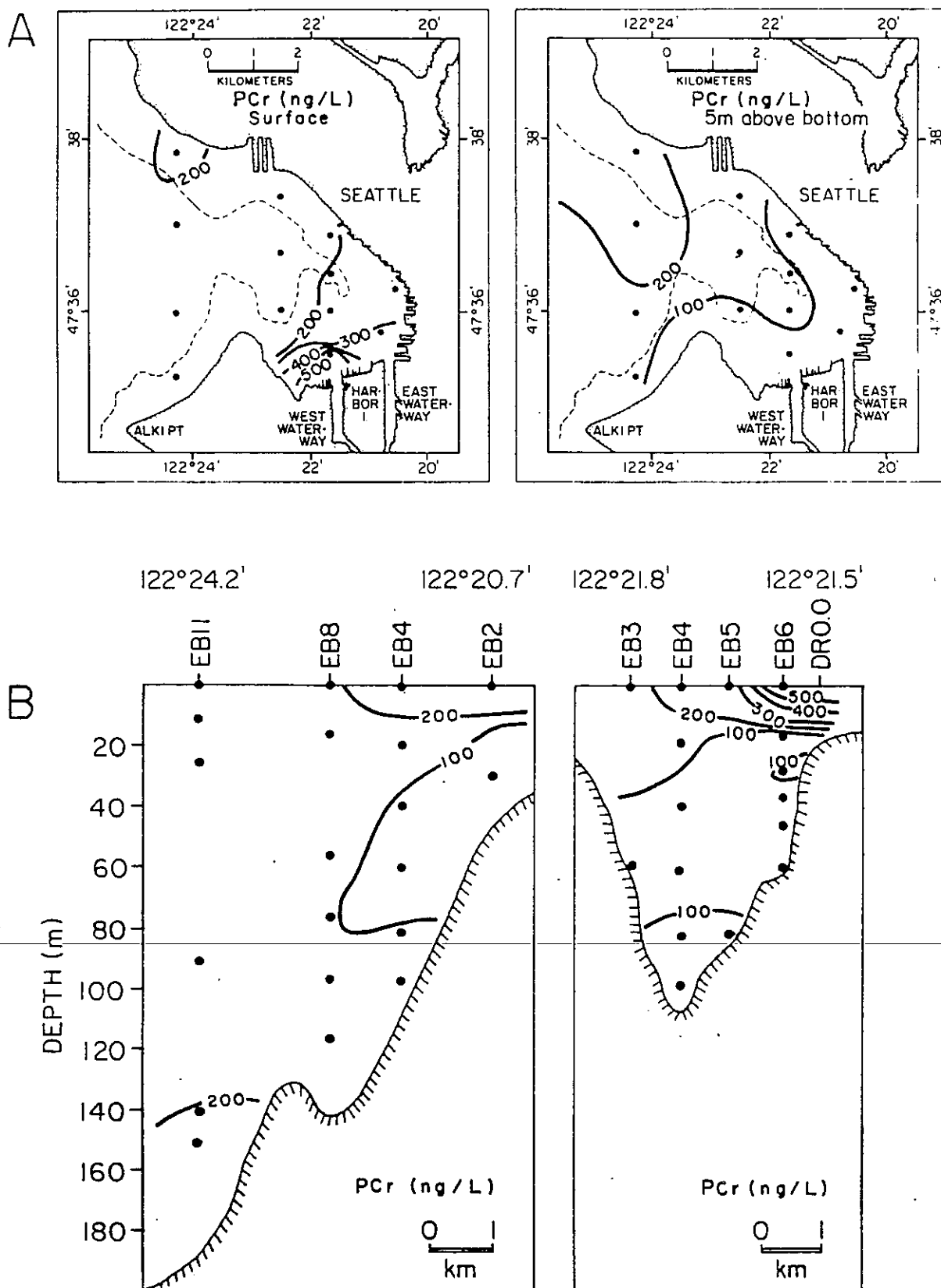


Fig. 2.4.7 A. Areal distributions of total particulate Cr at the surface and 5 m above the bottom. B. East-West and North-South cross sections of particulate Cr in Elliott Bay.

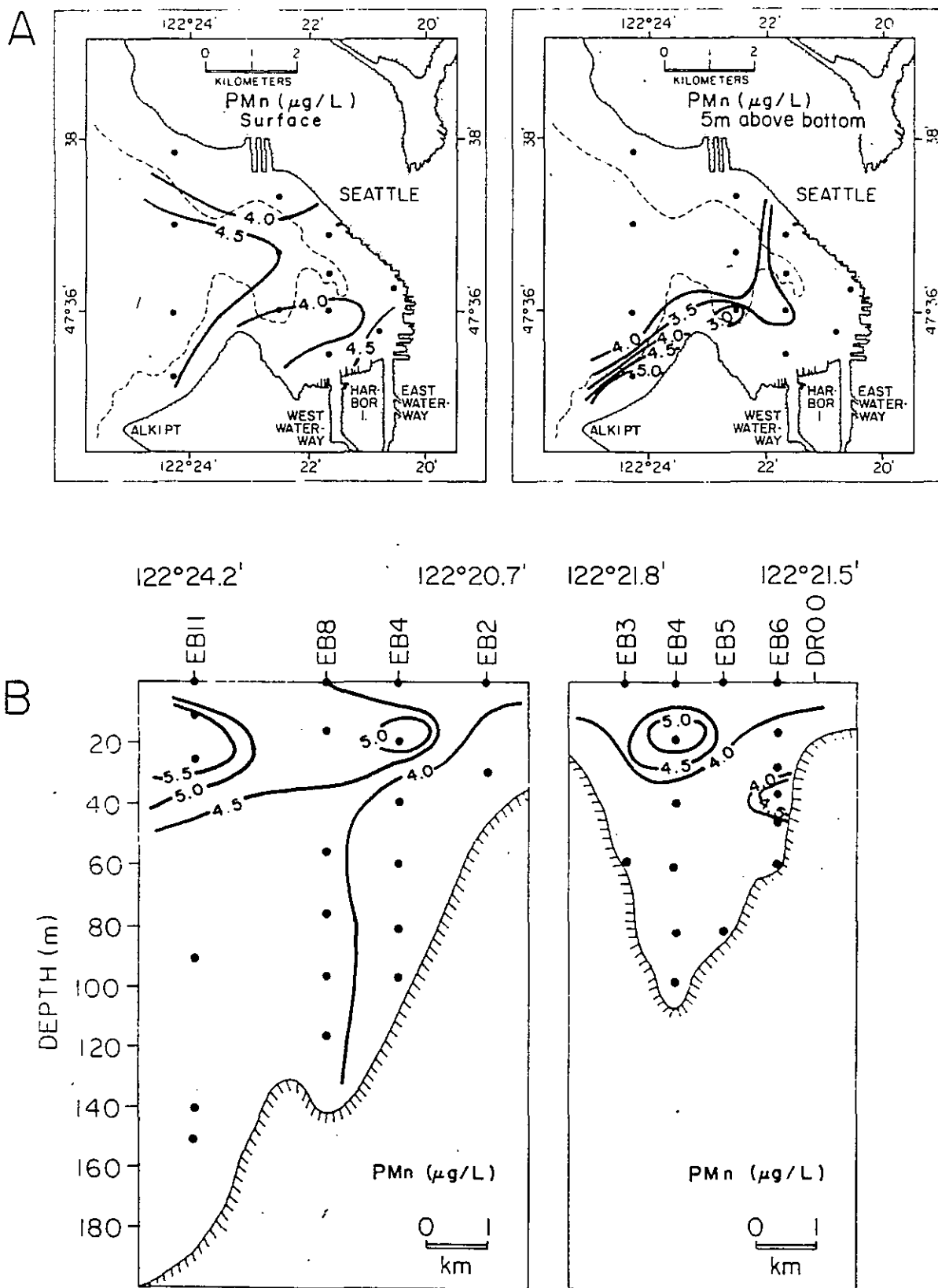


Fig. 2.4.8 A. Areal distributions of total particulate Mn at the surface and 5 m above the bottom. B. East-West and North-South cross sections of particulate Mn in Elliott Bay.



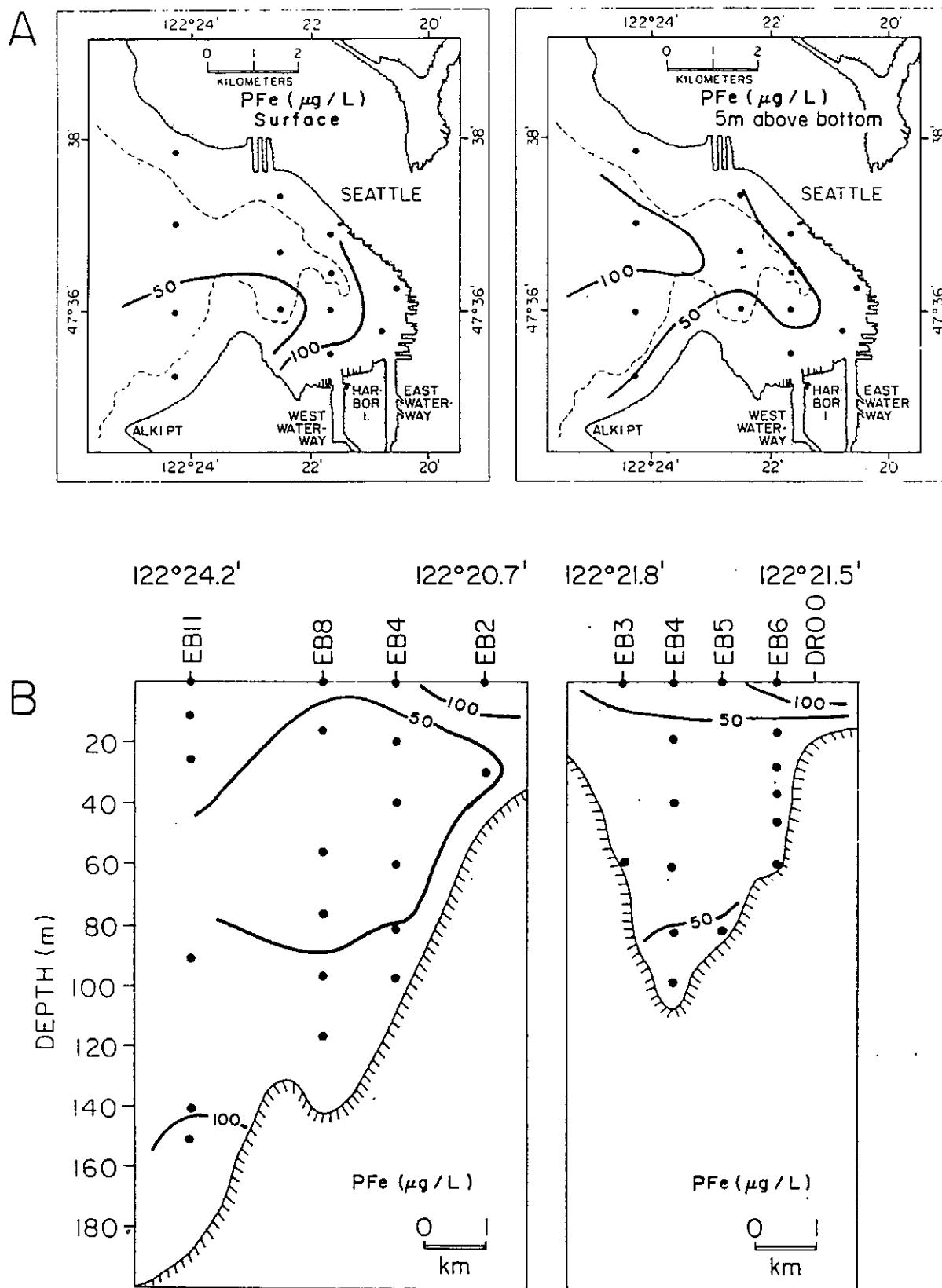


Fig. 2.4.9 A. Areal distributions of total particulate Fe at the surface and 5 m above the bottom. B. East-West and North-South cross sections of particulate Fe in Elliott Bay.

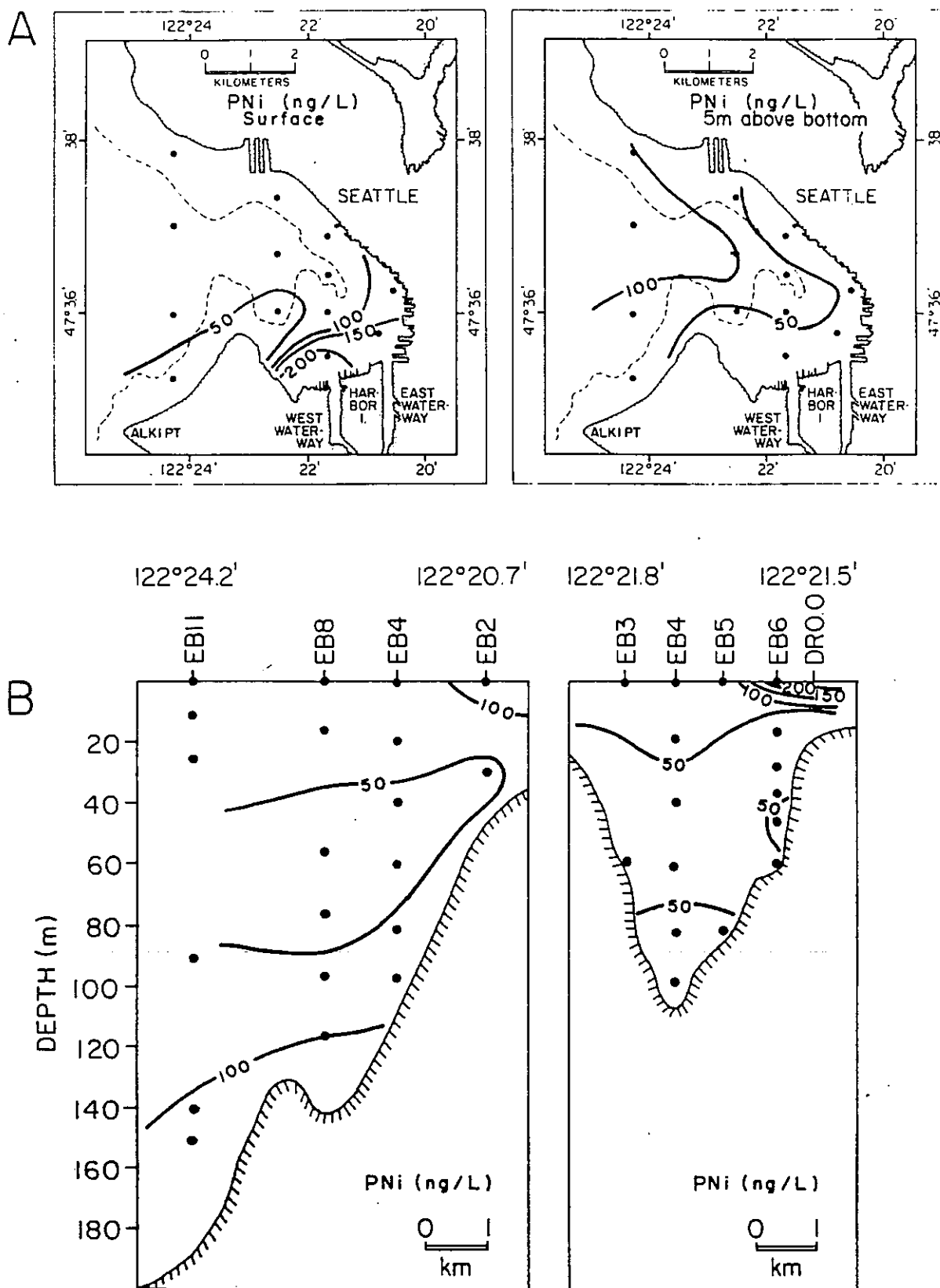


Fig. 2.4.10 A. Areal distributions of total particulate Ni at the surface and 5 m above the bottom. B. East-West and North-South cross sections of particulate Ni in Elliott Bay.

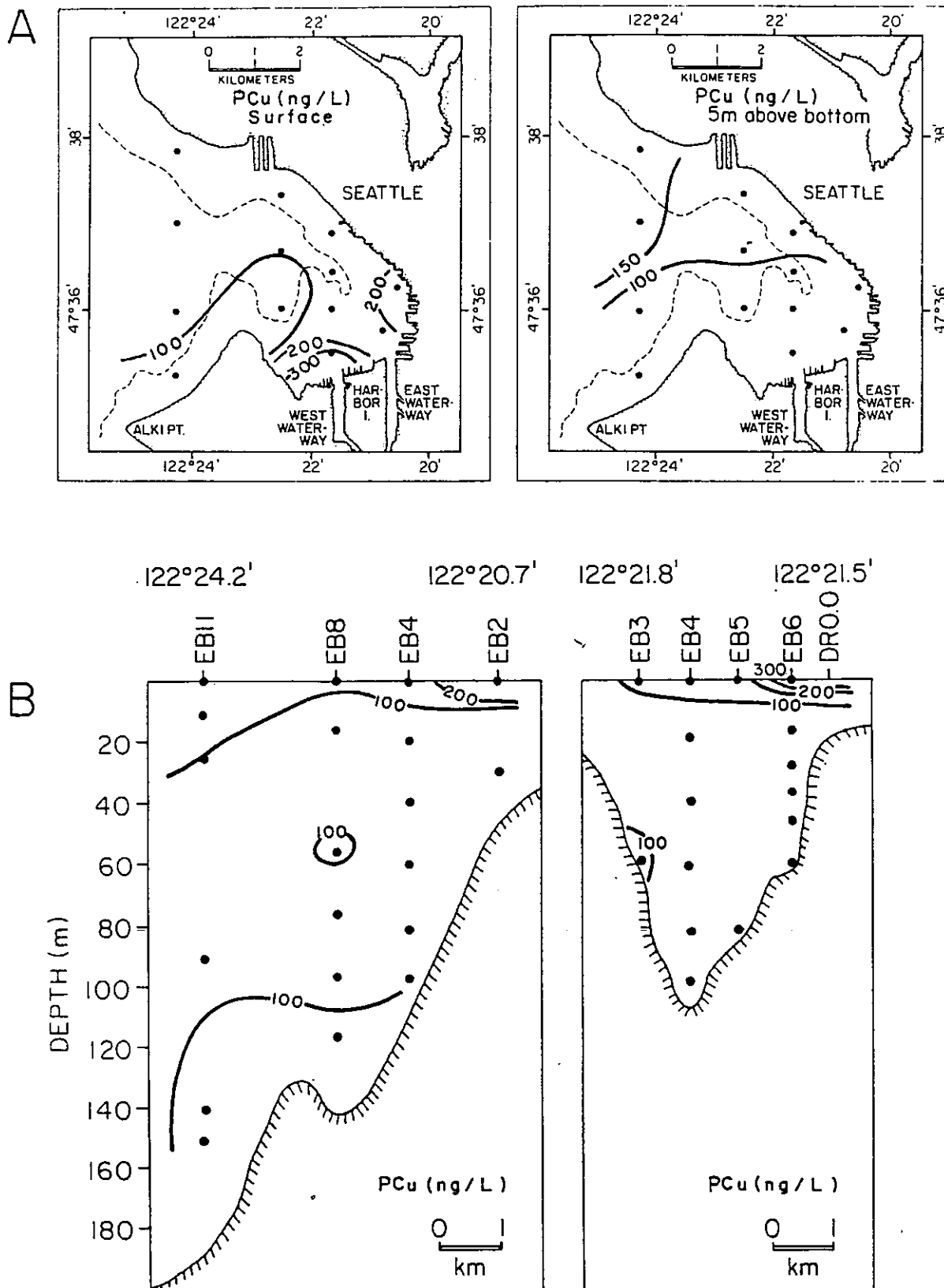


Fig. 2.4.11 A. Areal distributions of total particulate Cu at the surface and 5 m above the bottom. B. East-West and North-South cross sections of particulate Cu in Elliott Bay.

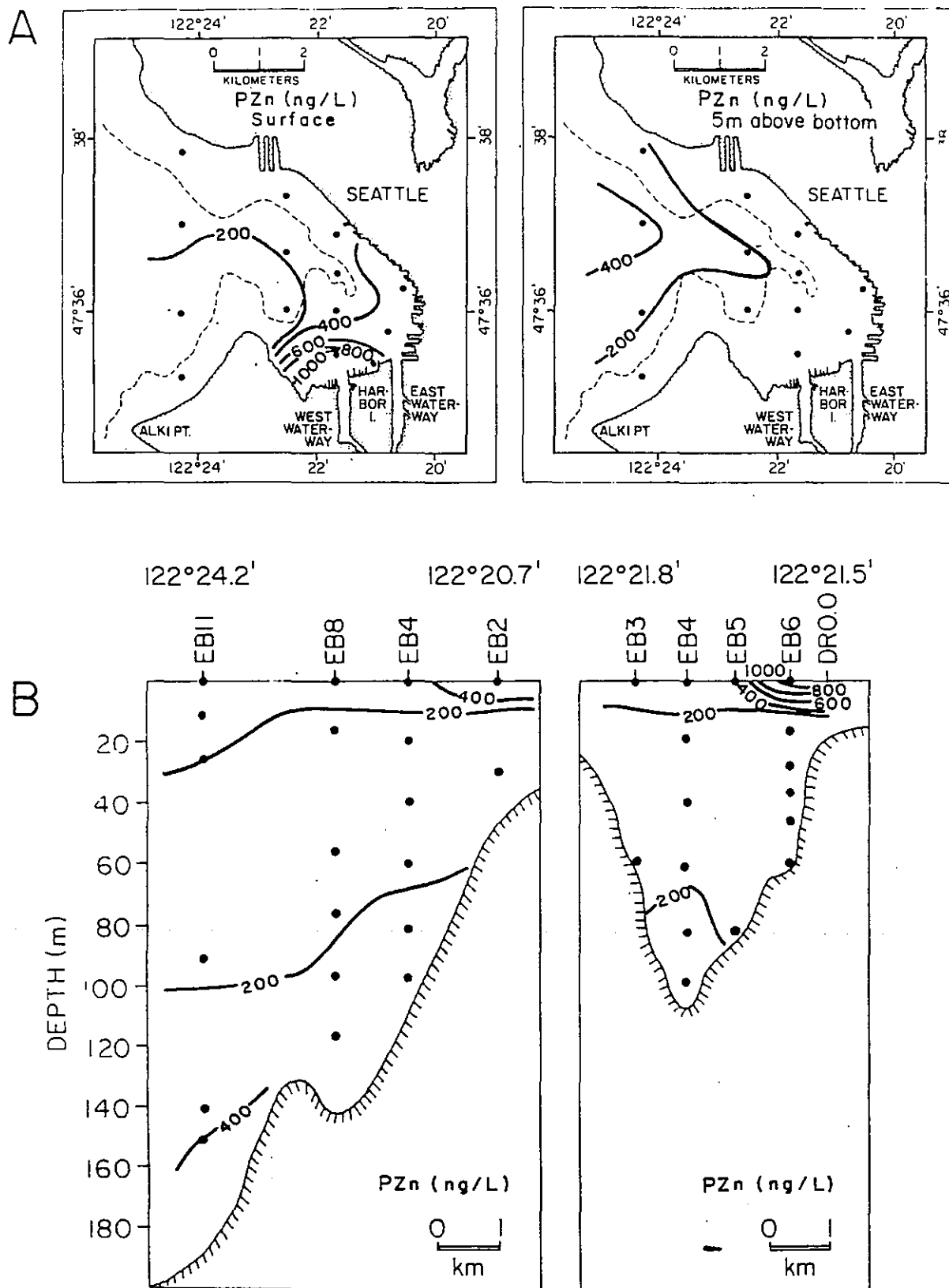


Fig. 2.4.12 A. Areal distributions of total particulate Zn at the surface and 5 m above the bottom. B. East-West and North-South cross sections of particulate Zn in Elliott Bay.

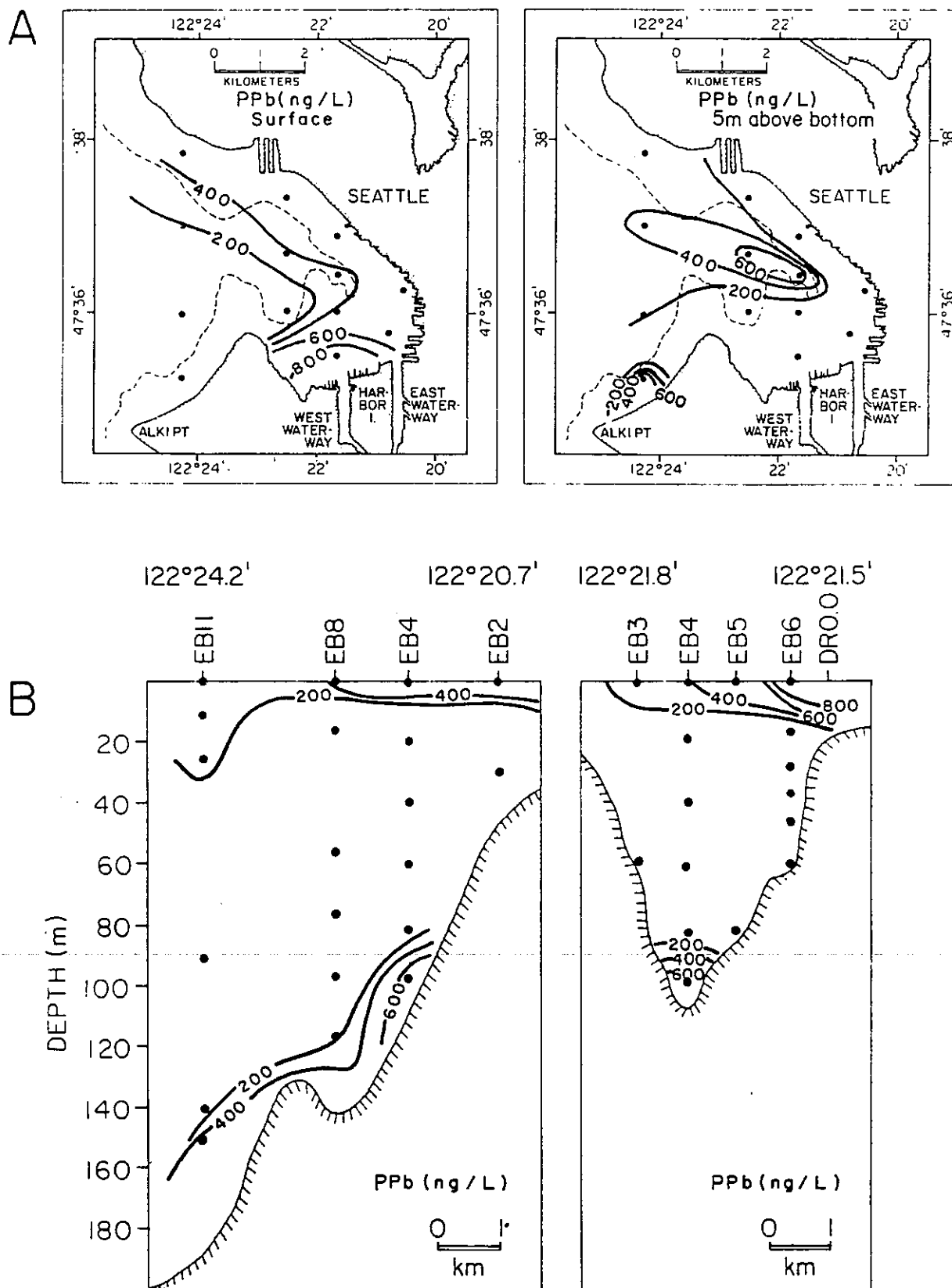


Fig. 2.4.13

A. Areal distributions of total particulate Pb at the surface and 5 m above the bottom. B. East-West and North-South cross sections of particulate Pb in Elliott Bay.

Table 5.4. Comparison of the mean elemental composition of near-surface (<2m) and subsurface (>15m) suspended matter from Elliott Bay with the elemental composition of the underlying sediments and suspended matter and sediments from the Duwamish River. Elliott Bay suspended matter collected February 20, 1980. Standard deviations are given at the 1σ level.

Sample Description	No. of Samples	C (Wt.%)	Al (Wt.%)	Ti (Wt.%)	Cr (ppm)	Mn (ppm)	Fe (Wt.%)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Pb (ppm)
<u>Elliott Bay surface suspended matter</u>											
(<2 m)	18	13.6 ±3.9	---	0.38 ±0.04	190 ±50	4094 ±1675	6.91 ±2.00	83 ±16	127 ±24	301 ±85	370 ±182
<u>Elliott Bay subsurface suspended matter</u>											
Manganese Maximum: (15-40 m)	5	12.5 ±4.9	---	0.42 ±0.05	242 ±49	9451 ±2937	6.05 ±0.96	105 ±19	136 ±30	292 ±73	246 ±18
Near-bottom: (>40 m)	24	8.6 ±3.2	---	0.38 ±0.01	148 ±40	5012 ±2006	5.29 ±1.09	67 ±14	96 ±79	197 ±81	151 ±54
<u>Elliott Bay sediments*</u>	5	---	---	0.11 ±0.01	53 ±1	405 ±71	3.20 ±0.22	52 ±5	83 ±31	110 ±17	82 ±16
<u>Duwamish River suspended matter</u>											
(<1 m)	21	8.4 ±2.0	9.85 ±1.28	0.42 ±0.03	109 ±26	1175 ±164	7.28 ±1.38	69 ±17	55 ±19	213 ±63	86 ±29
<u>Duwamish River estuary suspended matter</u>											
(0-10‰)	10	8.28 ±2.45	---	0.44 ±0.02	154 ±17	1087 ±195	9.88 ±0.44	84 ±16	91 ±13	298 ±30	211 ±61
<u>Duwamish River sediments**</u>			8.01	0.50	94	590	5.30	31	124	227	316
Average shale***		0.05	8.00	0.50	100	500	4.70	95	54	80	20

\* Data from Malins et al. (1980).

\*\* Sample collected from West Waterway (after Riley et al., 1980).

\*\*\* After Krauskopf (1967).

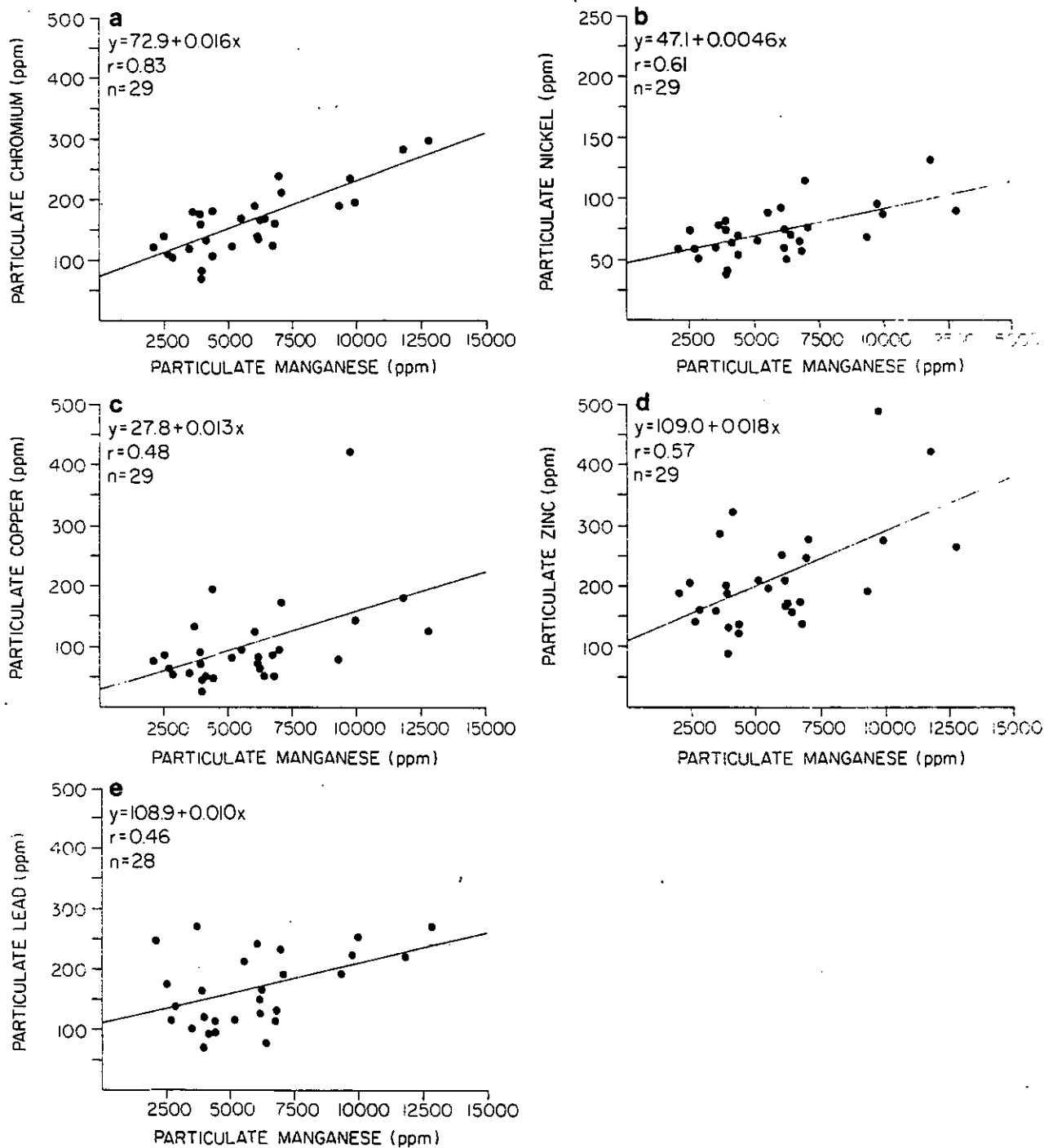


Fig. 2.4.14 Scatter diagrams of the relationships between Cr, Ni, Cu, Zn and Pb with Mn (a-e) in subsurface particulate matter from Elliott Bay.

Table 5.5. Concentrations of weak-acid-soluble (WAS) Mn, Fe, Ni, Cu, Zn, and Pb in suspended matter from the Duwamish River and Elliott Bay, Washington. Number of samples are given in parenthesis.

Region	WAS Mn (ppm $\pm$ 1 $\sigma$ )	WAS Fe (Wt% $\pm$ 1 $\sigma$ )	WAS Ni (ppm $\pm$ 1 $\sigma$ )	WAS Cu (ppm $\pm$ 1 $\sigma$ )	WAS Zn (ppm $\pm$ 1 $\sigma$ )	WAS Pb (ppm $\pm$ 1 $\sigma$ )
Duwamish River	510 $\pm$ 59(4)	1.59 $\pm$ 0.51(4)	8.1 $\pm$ 8(4)	7.4 $\pm$ 4(4)	83 $\pm$ 48(3)	70 $\pm$ 29(4)
Elliott Bay	3480 $\pm$ 3114(10)	1.61 $\pm$ 0.82(10)	26.5 $\pm$ 24(10)	27.2 $\pm$ 14(10)	211 $\pm$ 133(10)	453 $\pm$ 375(10)
Probability that means are significantly different	>95%	<50%	>90%	>99%	>90%	>95%



the Duwamish River samples, with the enrichments being significant at the  $p < 0.10$  level or better for the trace elements. For Ni and Cu, an average of approximately 37 and 24 percent of the total metal content, respectively, exists in the weak-acid-soluble fraction, whereas more than 80 percent of the Zn and 90 percent of the Pb are associated with this phase in the Elliott Bay samples. These results indicate that in the suspended matter from Elliott Bay these trace elements are being concentrated in a weak-acid-soluble phase which appears to be primarily composed of newly formed, poorly structured hydrous Mn oxides.

### 5.3 Main basin of Puget Sound

#### 5.3.1. Trace Metal Distributions

Vertical distributions of the concentrations of dissolved and particulate trace elements have been determined for the main axis of the main basin of Puget Sound and in Elliott and Commencement Bays (Cruise L-RERP 80; May 1980). In addition time series studies were conducted at stations PS7 in the central basin (Cruises L-RERP 81-1 through L-RERP 81-5). Water column samples to provide data necessary for the determination of vertical fluxes of trace elements in the water column and across the sediment-seawater interface.

The distributions of dissolved Mn, Cu, Ni and Cd along the axis of the main basin of Puget Sound are shown in Fig. 5.13. High concentrations of these trace metals are found in the surface waters near Commencement Bay, Elliott Bay and Possession Sound where exchange of low-salinity, metal-enriched embayment water with high-salinity, metal-poor main basin water elevates the metal concentrations in the surface waters of the main basin relative to middepth waters of the Strait of Juan de Fuca (Table 5.6). For example, the data in Table 5.6 indicate that the central basin surface waters are elevated in Mn, Cu and Ni by factors of 24, 4 and 2, respectively, over the inflowing water from the Strait. Plots of the concentrations of Mn and Cu versus salinity are roughly linear (Fig. 5.14) for stations located in the region around Elliott Bay and PSB-16 which suggests that mixing is a major factor influencing dissolved trace metal distributions in the surface waters of the main basin. Apparently, the combined input of trace elements from natural and anthropogenic sources to the embayment is sufficiently high to influence trace metal concentrations in the main basin as well. Below the surface, the dissolved trace metal concentrations decrease to a minimum at 100 m. These waters are more saline and relatively depleted in trace metals such that the concentration decreases are due, in part, to an admixture of the outflowing surface water with the inflowing deep water from the Strait (Cannon and Ebbesmeyer, 1978). However, some of the trace metal depletions are also due to scavenging reactions involving the particulate matter in the water column (see below).

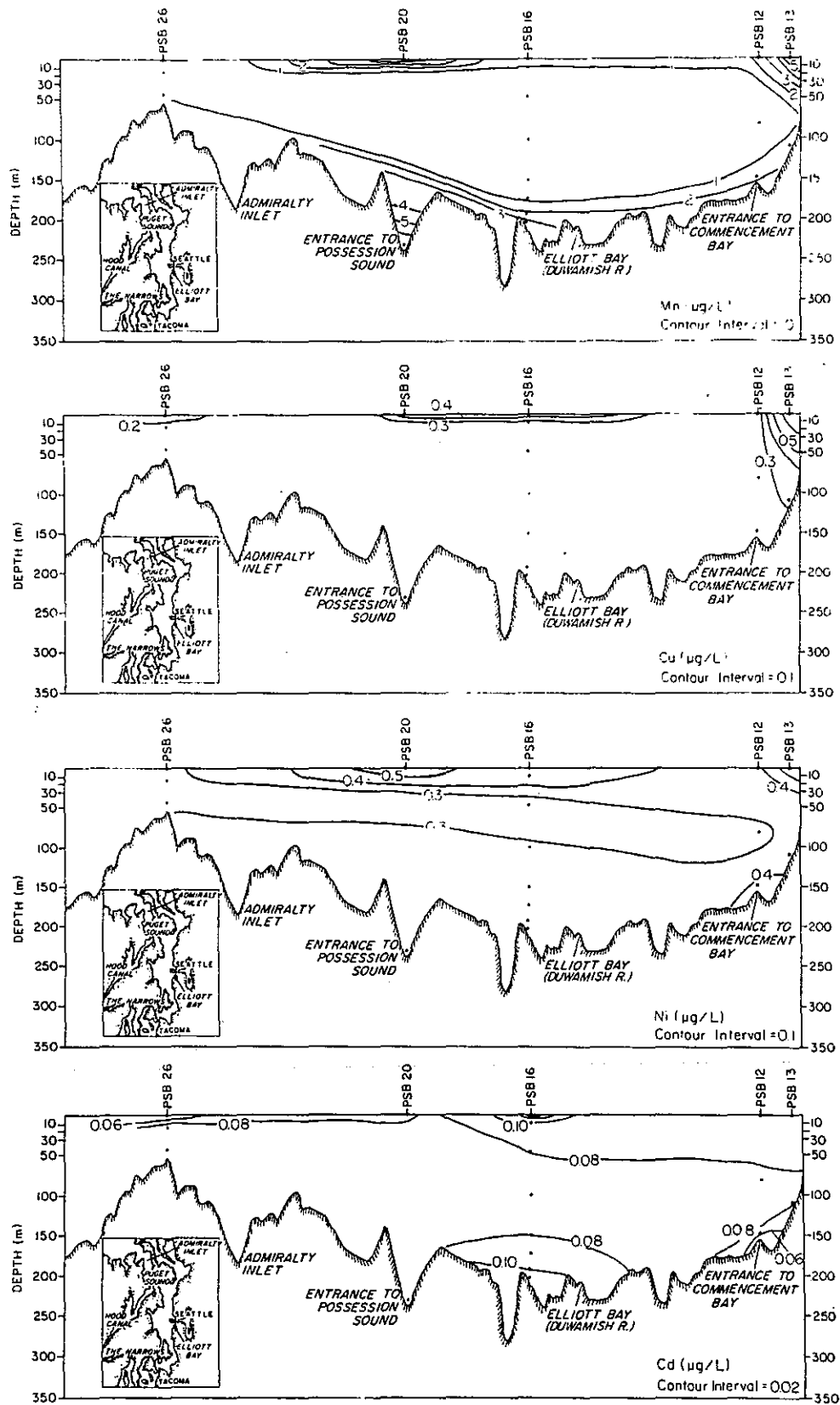


Fig. 2.4.15 Cross sections of total dissolved Mn, Cu, Ni, and Cd in Puget Sound (May, 1980).

Table 5.6. Concentrations of trace elements in selected regions of Puget Sound and the Strait of Juan de Fuca

Region and Depth	No. of Samples	Mn (µg/L)	Cu (µg/L)	Ni (µg/L)	Cd (µg/L)
Inner Commencement Bay surface	1	5.4	0.68	0.57	0.08
Elliott Bay surface	3	3.8±0.8	0.76±0.14	0.48±0.02	0.08±0.01
Possession Sound surface	1	4.5	0.48	0.51	0.08
Central Puget Sound surface	2	2.4±1.7	0.36±0.14	0.43±0.08	0.10±0.04
mid-depth	2	0.27±0.02	0.28±0.02	0.30±0.06	0.08±0.01
Strait of Juan de Fuca mid-depth	2	0.10±0.01	0.09±0.04	0.24*	0.09±0.01

\* Number of samples = 1.

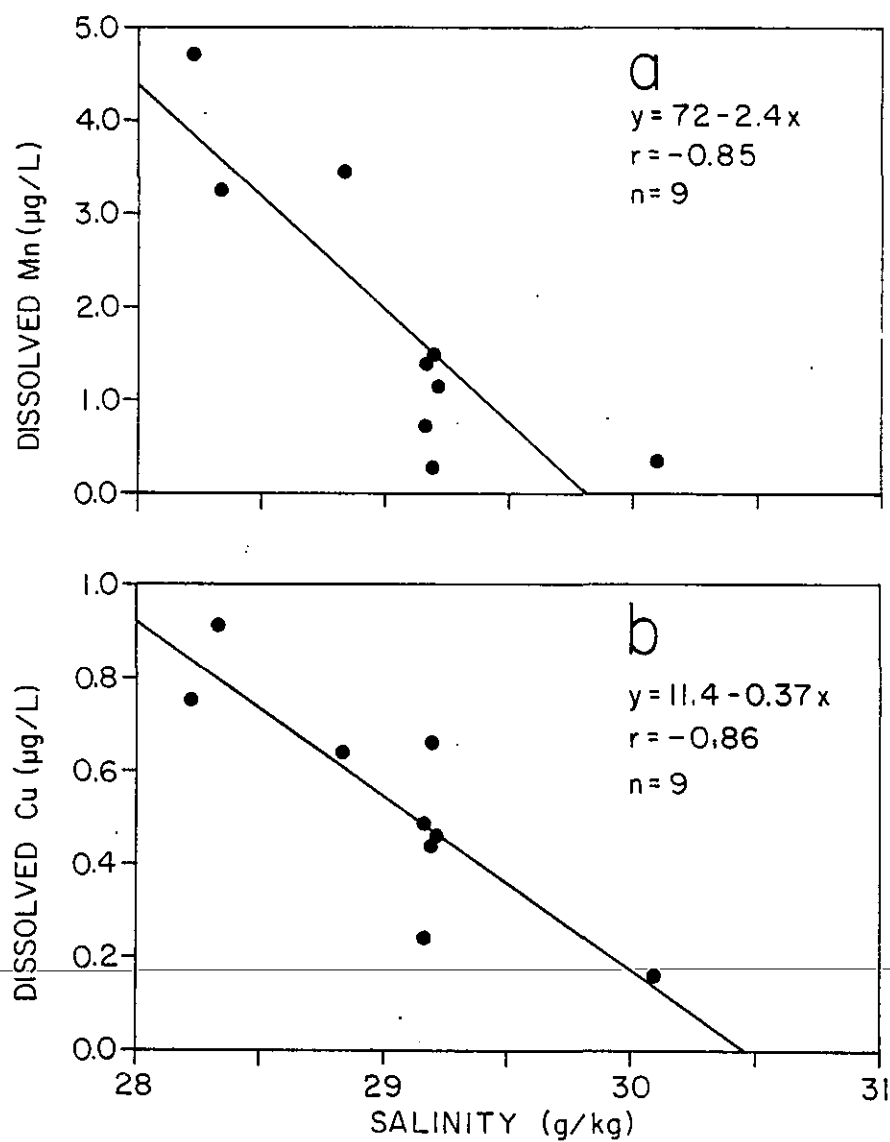


Fig. 2.4.16 Scatter diagrams of total dissolved Mn(a) and Cu(b) versus salinity in Elliott Bay and the central basin of Puget Sound.

In near-bottom waters, the concentrations of the dissolved trace metals vary with time. For example, the time-series studies at station PS7 (Fig. 5.15) indicate significant enrichments of Mn, Cd, and Cu in the near-bottom waters relative to midwater concentrations in July (i.e., 7.5, 2.8 and 1.4 times midwater values, respectively). Similar enrichments of these elements were observed in August and November of the same year. In February of the following year near-bottom Mn and Cd concentrations were only slightly enriched and Cu concentrations remained constant throughout the bottom 100 m. These differences in the relative enrichments may be due to a variable rate of release of trace elements in the water column or at the sediment-seawater interface, a variable rate of flushing of bottom waters in the Sound, or some combination of both processes. For example, the highest concentrations of Mn in the bottom waters occurred in August during a period of relative quiescence in circulation (Fig. 5.15). Apparently, there was sufficient time between flushing events for the Mn, Cd and Cu concentrations to build up on the near-bottom waters. These data clearly indicate that sufficiently large amounts of trace elements are being remobilized into the bottom waters of the main basin. This is particularly important for Puget Sound because bottom waters are being returned to the surface in the vicinity of the Narrows (Barnes and Ebbesmeyer, 1978). This means that some trace elements may be recycled through the euphotic zone several times before they are ultimately buried within the sediments or dispersed into the Strait of Juan de Fuca.

### 3. Sediment Trap Studies

The results of the trace element analyses of the sediment trap and sediment samples from station PS7 are summarized in Figs. 5.16 through 5.19 and Table 5.7.

The sediment traps were deployed for roughly 10 week intervals from 5 December 1980 through 19 December 1981. Composite samples from each trap were filtered onto preweighed 142 mm 0.4  $\mu\text{m}$  pore-sized Nuclepore filters in a vertical laminar flow hood. The samples were dried and weighed, ground in a boron carbide mortar and transferred to acid-cleaned polyethylene bottles for storage. Total metal concentrations were determined by the x-ray fluorescence and total dissolution procedures described in section 4.2 of this report. Metals associated with hydrous oxide phases and organic phases were determined using the selective dissolution procedures described in sections 4.2.5.3 and 4.2.5.4. The data are presented as fluxes ( $\text{mg m}^{-2}\text{d}^{-1}$  or  $\mu\text{g m}^{-2}\text{d}^{-1}$ ) associated with hydrous Mn and Fe oxides (OX), organic (ORG), and residual (RES) lattice phases so that the modes of transport of the metals associated with specific particle phases can be compared.

Figures 5.16 and 5.17 show that for Fe, Mn, Co, Zn and Pb residual (presumed to be primarily lattice) and oxide phases controlled the vertical flux; whereas residual and organic phases controlled the flux of Cu and Cr. The Cd flux was predominantly controlled by oxide and organic phases. For several trace metals, notably Mn, Co, Cr, Ni and Zn, the flux in the organic phase was higher in summer than in winter. The elemental flux data for winter show a slight decrease from

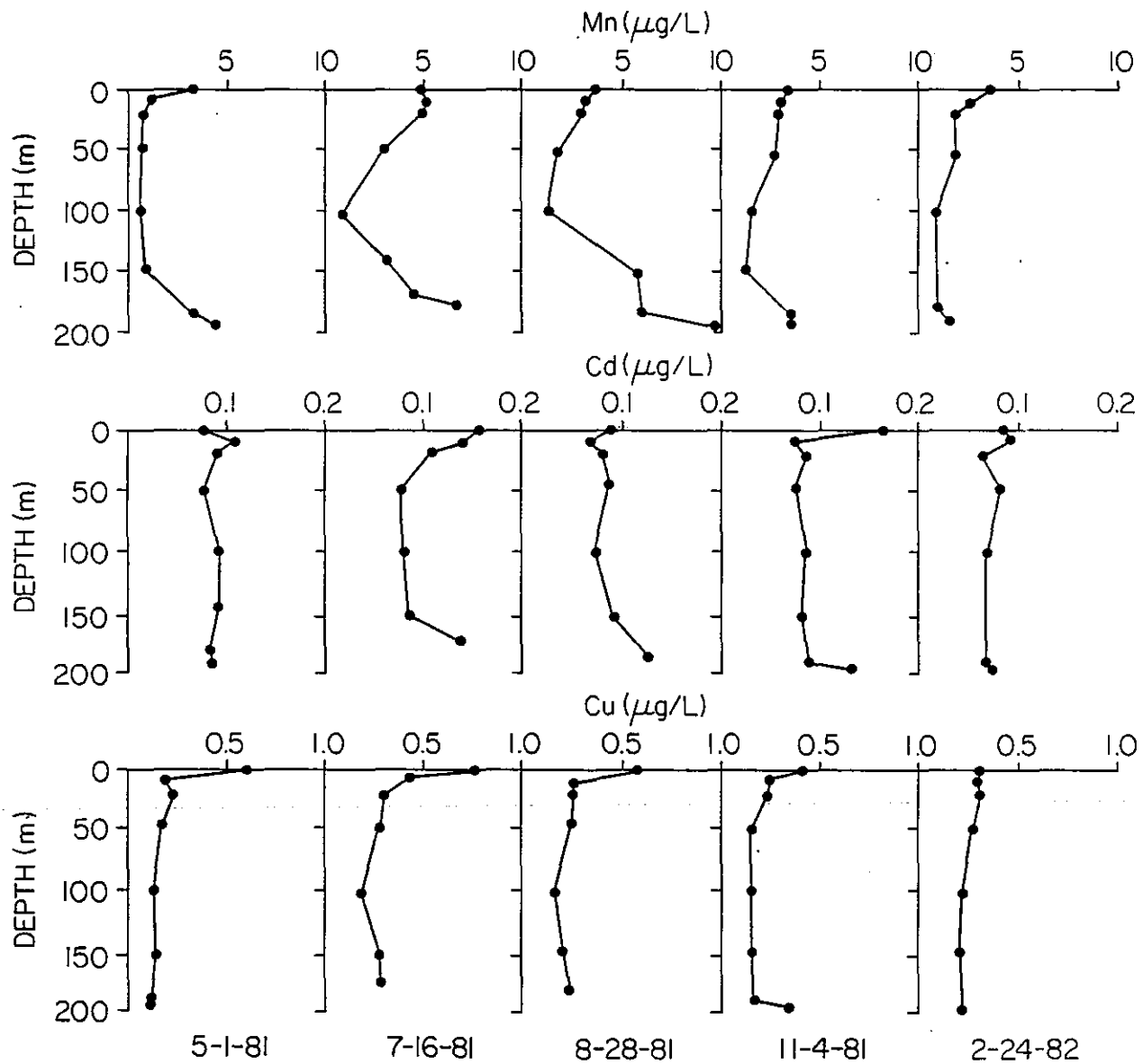


Fig. 2.4.17 Temporal variations of labile Mn, Cd and Cu at PS7 in the main basin of Puget Sound.

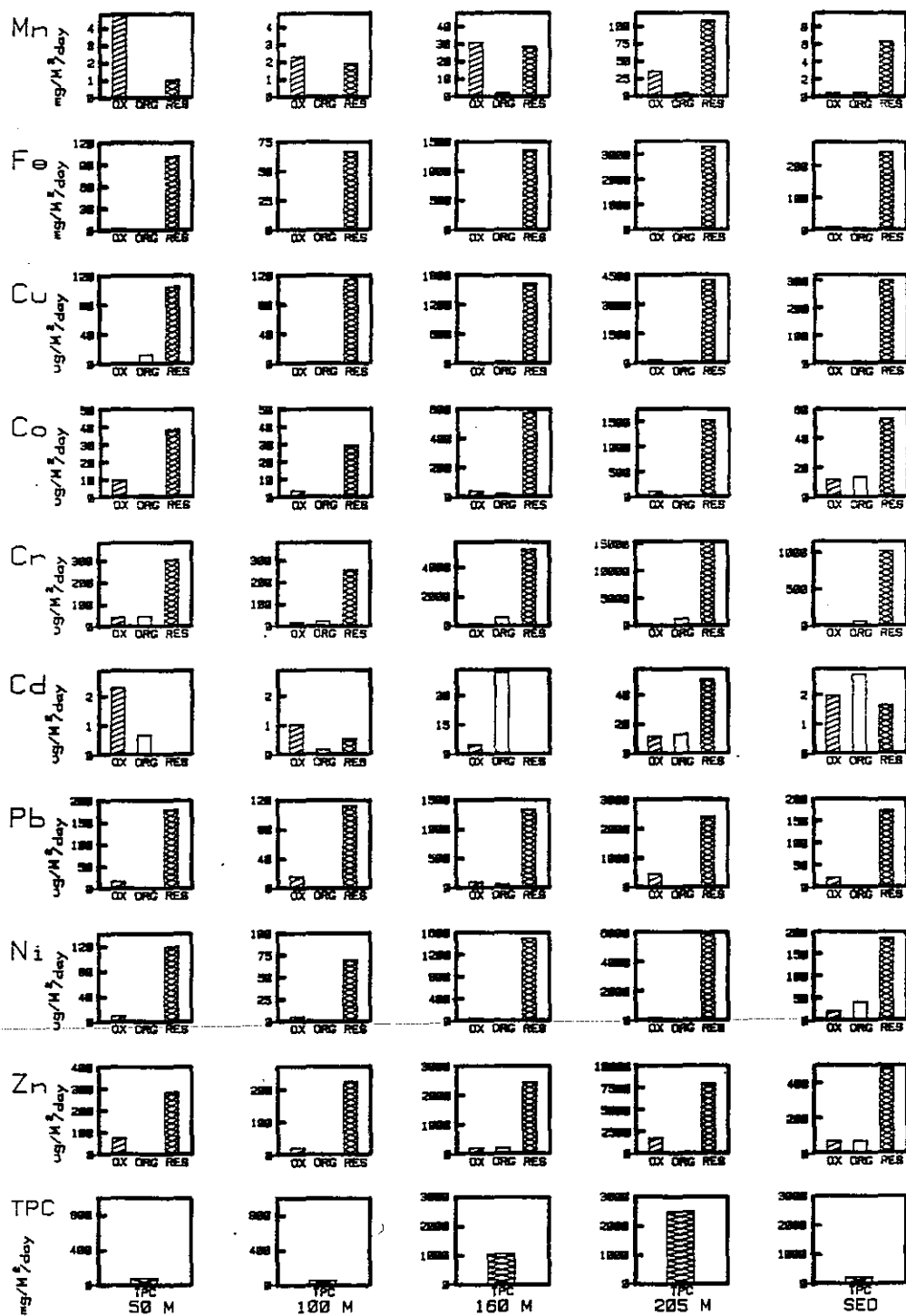


Fig. 2.4.18 Fluxes of Mn, Fe, Cu, Co, Cr, Cd, Pb, Ni, and Zn in oxide, organic and residual phases, and total particulate C in sediment trap material collected at PS7 in winter (5 Dec 1980 - 3 Feb 1981).

# SUMMER

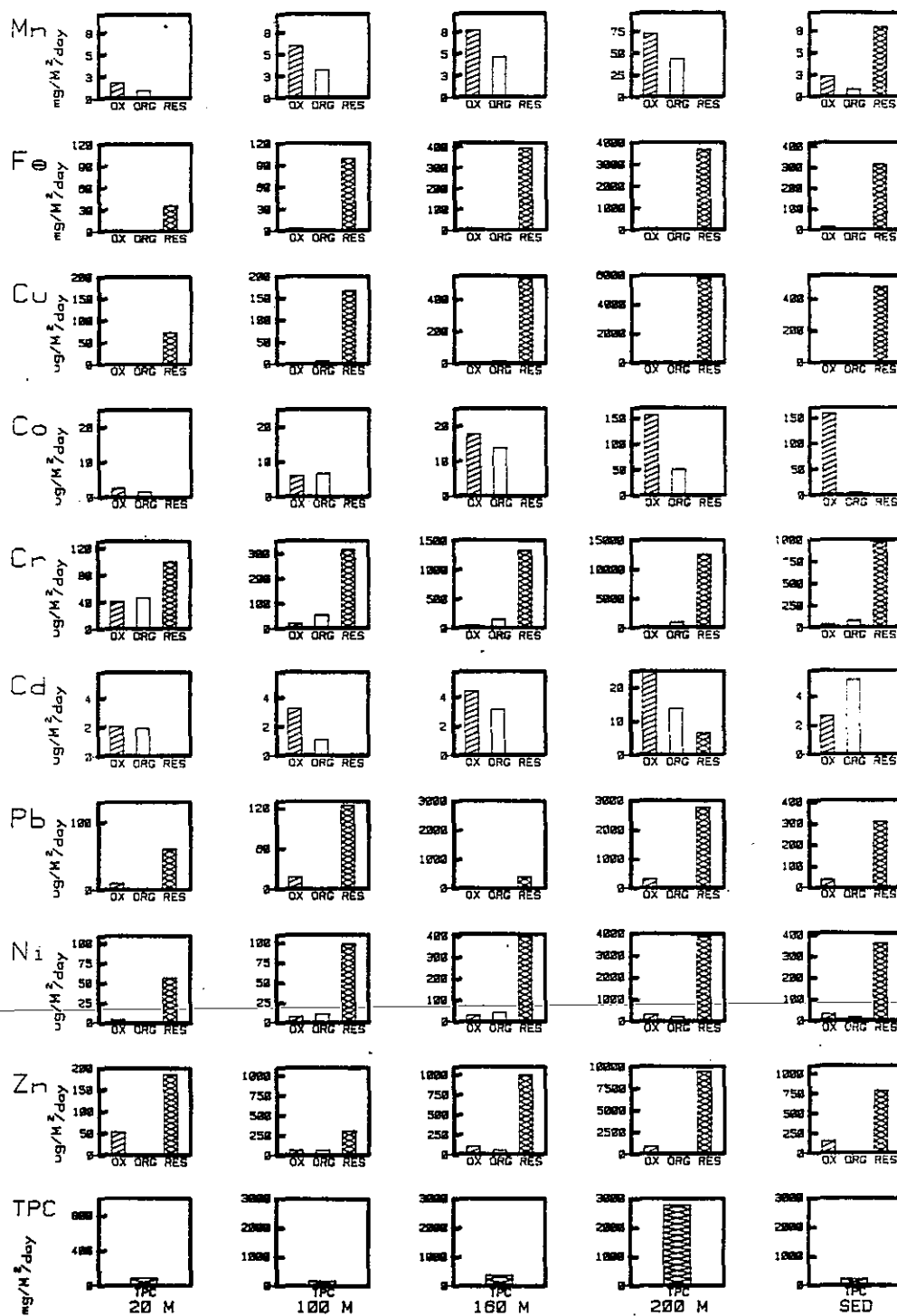


Fig. 2.4.19 Fluxes of Mn, Fe, Cu, Co, Cr, Cd, Pb, Ni, and Zn in oxide, organic and residual phases, and total particulate C of sediment trap material collected at PS7 in summer (24 July - 29 Sept 1981).



# WINTER

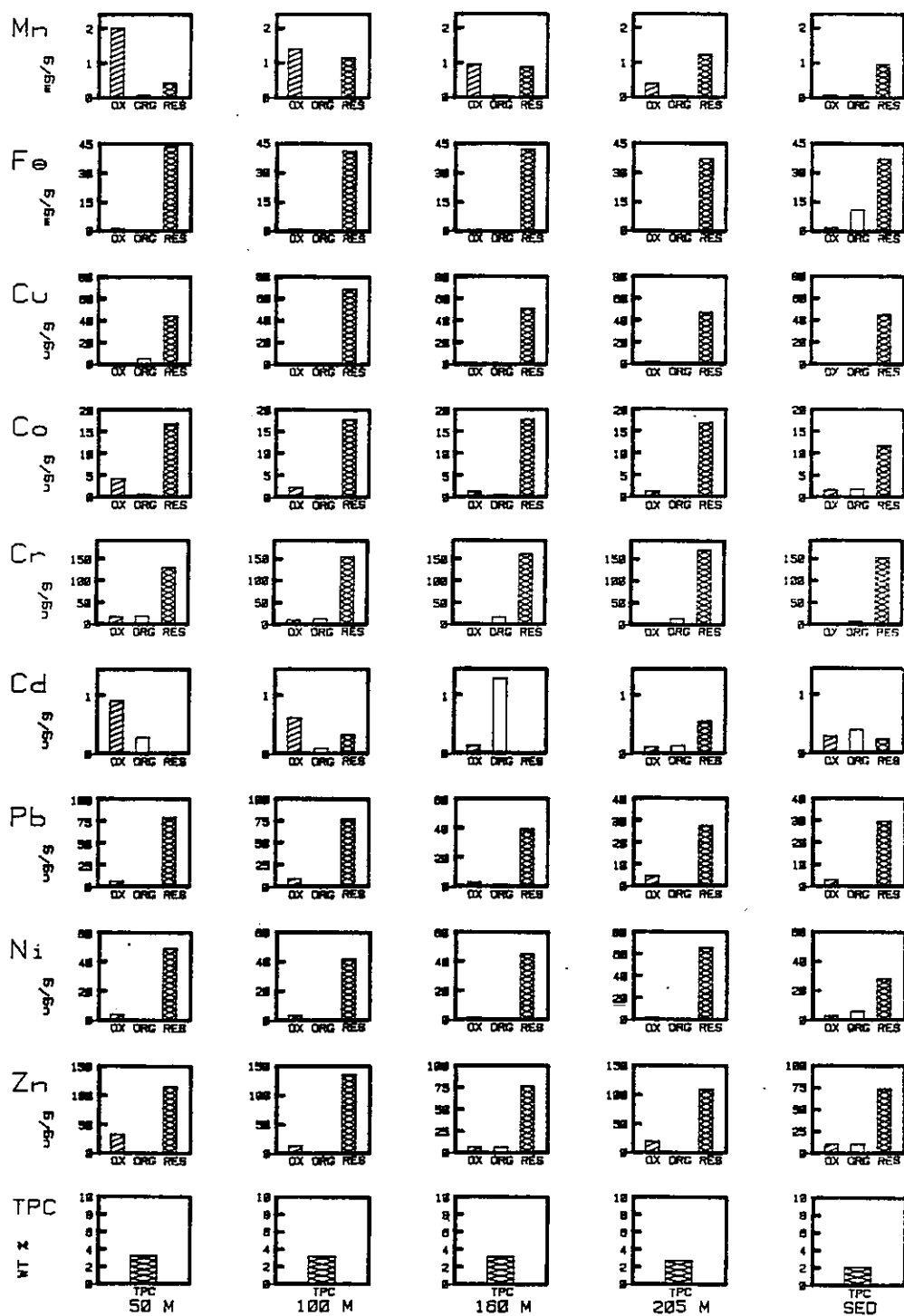


Fig. 2.4.20

Concentrations of Mn, Fe, Cu, Co, Cr, Cd, Pb, Ni, and Zn in oxide, organic and residual phases, and total particulate C of sediment trap material collected at PS7 in winter (5 Dec 1980 - 3 Feb 1981).

# SUMMER

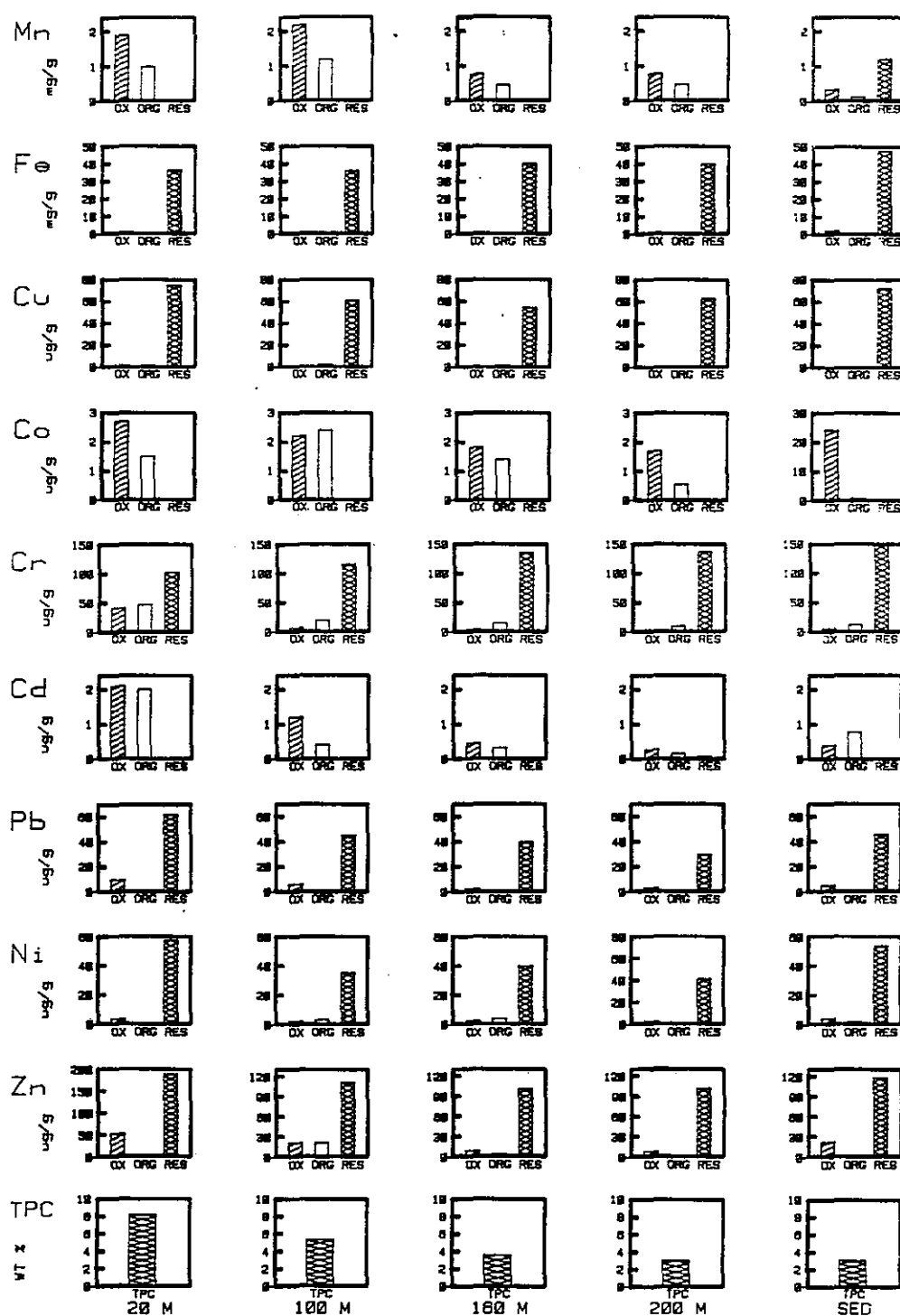


Fig. 2.4.21 Concentrations of Mn, Fe, Cu, Co, Cr, Cd, Pb, Ni, and Zn in oxide, organic and residual phases, and total particulate C of sediment trap material collected at PS7 in summer (24 July - 29 Sept 1981).

Table 5.7. Elemental composition of suspended matter in sediment traps from STE-1 and STE-4.

		ppm Mn	% Fe	ppm Cu	ppm Cr	ppm Cd	ppm Pb	ppm Ni	ppm Zn
<u>STE-1</u>									
50 m	$\bar{x}$	2500	4.5	50	169	1.2	88	54	160
	*S.D.	$\pm 58$	$\pm 0.6$	$\pm 2$	$\pm 5$	$\pm 3$	$\pm 4$	$\pm 6$	$\pm 10$
100 m	$\bar{x}$	2600	4.2	71	181	1.08	80	46	150
	S.D.	$\pm 58$	$\pm 1$	$\pm 3$	$\pm 8$	$\pm 3$	$\pm 13$	$\pm 5$	$\pm 6$
160 m	$\bar{x}$	1900	4.3	53	184	1.45	45	48	90
	S.D.	$\pm 58$	$\pm 2$	$\pm 2$	$\pm 1$	$\pm 3$	$\pm 2$	$\pm 21$	$\pm 3$
205 m	$\bar{x}$	1700	3.8	51	189	.85	33	69	130
	S.D.	$\pm 58$	$\pm 2$	$\pm 2$	$\pm 8$	$\pm 3$	$\pm 2$	$\pm 7$	$\pm 40$
Sediment	$\bar{x}$	1100	4.0	48	167	.96	34	38	96
	S.D.	$\pm 120$	$\pm 1$	$\pm 11$	$\pm 8$	$\pm 3$	$\pm 2$	$\pm 4$	$\pm 16$
<u>STE-4</u>									
20 m	$\bar{x}$	2900	3.9	78	193	4.1	73	63	245
	S.D.	$\pm 170$	$\pm 2$	$\pm 5$	$\pm 14$	$\pm 1$	$\pm 8$	$\pm 4$	$\pm 10$
100 m	$\bar{x}$	3400	3.8	64	143	1.6	52	42	156
	S.D.	$\pm 200$	$\pm 1$	$\pm 2$	$\pm 6$	$\pm 5$	$\pm 3$	$\pm 2$	$\pm 6$
160 m	$\bar{x}$	1200	4.2	56	155	.77	42	47	117
	S.D.	$\pm 20$	$\pm 0.5$	$\pm 1$	$\pm 11$	$\pm 2$	$\pm 2$	$\pm 4$	$\pm 2$
200 m	$\bar{x}$	1300	4.1	55	150	.42	34	47	113
	S.D.	$\pm 100$	$\pm 2$	$\pm 3$	$\pm 5$	$\pm 1$	$\pm 1$	$\pm 5$	$\pm 8$
Sediment	$\bar{x}$	1800	5.0	73	167	1.2	52	61	143
	S.D.	$\pm 100$	$\pm 1$	$\pm 4$	$\pm 8$	$\pm 3$	$\pm 2$	$\pm 5$	$\pm 5$

\*Standard deviation is at the 1 $\sigma$  level.

the 50 m to the 100 m sediment trap followed by a striking increase in the near-bottom sediment traps located at 160 m and 205 m. For example, Fe, Mn, Cu, Co, Pb, Ni and Zn in winter show increases in flux ranging from 3500 to 8100% between the 100 m and 205 m traps. These increases are due to resuspension and advection of bottom sediments (see chapter by Baker). The elemental concentration data give some indication of the most probable sources of these materials (Table 5.7). The sediment trap samples at 50 m and 100 m are elevated in Mn, Cu, Pb and Zn, indicating a surface injection from the more polluted waters of Elliott Bay (Figs. 5.18 and 5.19). In contrast, the near-bottom samples have elemental concentrations which are significantly lower than corresponding samples from 50 m and 100 m. Furthermore, these samples are compositionally the same as the underlying sediments with respect to trace elements. Therefore, it is probable that the near-bottom suspended matter is diluted with materials that are relatively depleted in trace metals, such as suspended material from the Puyallup River.

Another interesting feature of the trace metal flux data is that the percentage of the total flux of trace metals associated with the oxide phases generally decrease with depth. For example, Mn in the oxide phase decreases from 81% of the total flux at 50 m to 24% of the total flux at 205 m in the winter data. Similar decreases are also observed for most of the other trace metals in the oxide phase. Since the percentage of Mn and other trace metals in the oxide phase of the sediments are relatively lower than corresponding values for the upper sediment trap samples, the net effect of resuspension and advection of bottom sediments appears to be dilution of the sediment trap material with particles containing metals predominantly in the residual phases. These data suggest that much of the oxide phases that control the Mn flux in the upper sediment traps originates in the water column rather than the sediments. Indeed, the particulate Mn cross section (Fig. 5.20) shows a concentration maximum between 20 and 125 m, supporting this interpretation of the data. Apparently, the Mn and Fe that are reduced to dissolved forms in the sediments and consequently released back into the overlying water rapidly precipitate onto suspended matter. According to Yeats et al. (1979) Mn precipitating in the water column will tend to be preferentially enriched in small-sized resuspended particles and, hence, will form particulate Mn maximum immediately above a bottom nepheloid layer where the grain size distribution of the particle population is at a minimum. In Puget Sound the grain size minimum in the particle population occurs at about 50 m (see chapter by Baker). Thus, it appears that hydrous Mn and Fe oxides are forming in the water column primarily in the region between 20 m and 125 m depth and the new oxide phases that are formed appear to be the major phase contributing to the Mn flux in the near surface sediment traps. Similarly, several other trace metals including Fe, Zn, Co, Cd and Pb are enriched in the oxide phases of the near-surface sediment traps. These data may be interpreted as indicating evidence for scavenging of these trace elements by the newly formed oxide phases. Table 5.8 shows an interelement correlation coefficient matrix for the hydroxylamine hydrochloride-acetic acid soluble phases of the sediment trap samples. Significant correlations exist for Co and Ni with Fe ( $p < 0.07$ ) and for Cd, Cr, Zn, and Pb with Mn ( $p < 0.10$ ) these results indicate that in the subsurface waters of Puget Sound several trace metals are being scavenged by hydrous Mn and Fe oxide coatings on the surface of particles in the water column.

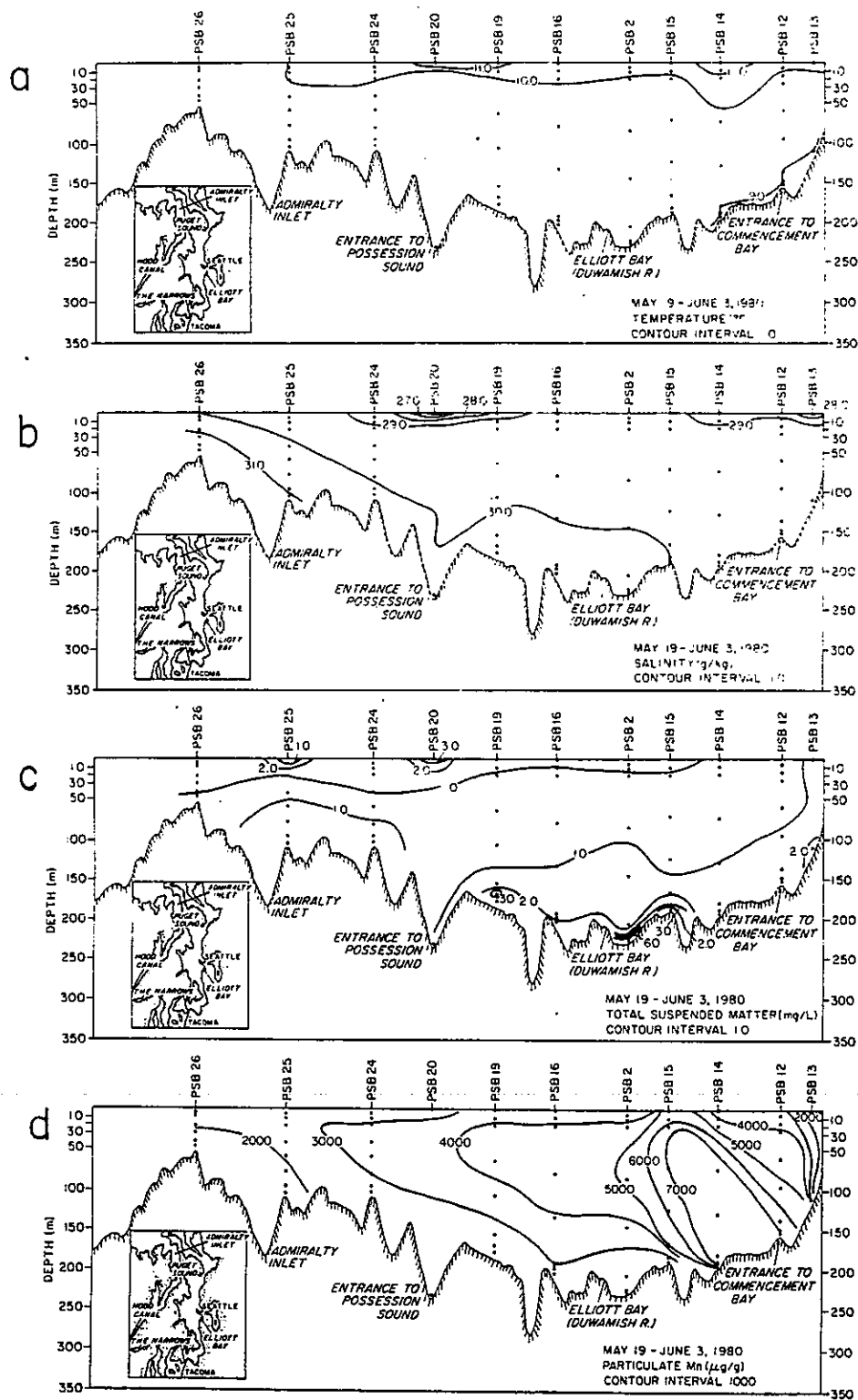


Fig. 2.4.22 Distributions of: a) temperature; b) salinity; c) total suspended matter; and d) particulate Mn in the suspended matter along the axis of the main basin of Puget Sound.

The one element that does not appear to be highly correlated with either Mn or Fe in the oxide phases of the sediment trap samples is Cu (Figs. 5.18 and 5.19). In fact, Cu appears to be more enriched in the organic phases of the summer and winter trap samples. Enrichments of Cu in the organic phase are highest in the near-surface traps (i.e., up to 11% of the total). In the near-bottom sediment trap at 205 m, organically bound Cu is about the same as in the underlying sediments (e.g. 2.6% of the total).

#### 4. Sediments

##### a. Solid phase chemistry

Several investigators have combined  $^{210}\text{Pb}$  geochronological studies with the distributions of heavy metals in sediment cores to show the recent history of metal pollution in a number of estuarine and coastal environments (Bruland et al., 1974; Goldberg et al., 1977; 1978; Presley et al., 1980). These studies have demonstrated that anthropogenic metal inputs are often recorded as metal enrichments in sediment profiles which can be traced to specific changes in human activities. Presley et al. (1980) further demonstrated that the extent of metal enrichment in cores is dependent not only upon the magnitude of the individual metal inputs, but also on the dilution effect of the sediment load from the local rivers. With these concepts in mind, we have been determining excess  $^{210}\text{Pb}$  and metal concentrations in box and gravity cores collected along the axis of the main basin of Puget Sound and in Elliott and Commencement Bays. This work is an ongoing part of our research project and, therefore, only preliminary results and interpretations are given below.

Fig. 5.21 gives vertical profiles of Mn, Cu, Zn, Ag, Cd and Pb in sediments cores collected from Elliott Bay (core EB-5) and the main basin of Puget Sound (cores BX-7; BX-4 and BX-2; see Fig. 4.1 for the sample locations). These profiles are representative of what was found in other cores we have studied and preliminary sedimentation rates have been assigned to the cores based on the  $^{210}\text{Pb}$  data. These sedimentation rates are still provisional because they have not been corrected for the effects of bioturbation (Benninger et al., 1979; Turekian et al., 1982) and because there exists a possibility that some of the core tops could have been lost due to "bow-wave effect" of the gravity coring device (Baxter et al., 1981). We are presently studying the relative importance of these two effects by making measurements of  $^{210}\text{Pb}$ ,  $^{239-240}\text{Pu}$ , and Th isotopes in box cores and Kasten cores collected from the same locations as the gravity cores.

The preliminary sediment data exhibit significant concentration variations with depth for several trace metals. The cores collected in this study provide a record back to about the middle of the last century. Since the metal concentrations at depth in the cores are about the same as metal concentrations found in soils from the Puget Sound region (Table 5.9), the increases of Cu, Zn, Ag, Cd and Pb towards the sediment surface are attributed to recent anthropogenic inputs. For Ag and Pb,

Table 5.8. Interelement correlation coefficient matrix for the hydroxylamine hydrochloride-acetic acid soluble phase of suspended matter from the sediment traps collected at PS7.

	Mn	Fe	Cd	Pb	Cu	Cr	Co	Ni	Zn
Mn		-0.336	0.779*	0.652*	0.019	0.642*	-0.263	0.206	0.584
Fe			-0.036	-0.057	-0.299	-0.100	0.783*	0.636*	0.096
Cd				0.711*	0.250	0.912*	-0.080	0.413	0.872*
Pb					0.367	0.731*	0.043	0.503	0.697*
Cu						0.321	-0.107	-0.166	0.473
Cr							-0.064	0.486	0.907*
Co								0.572	0.148
Ni									0.545
Zn									

<sup>1</sup>Ten samples were used in this analysis. At the 95 percent confidence level a correlation coefficient of 0.602 or higher is significant.

\*Significant at the 95 percent confidence level.

Table 5.9. Comparison of the elemental composition of Puget Sound regional soils with Puget Sound "background" sediments.<sup>1</sup>

Element	Puget Sound Regional Soils <sup>2</sup>	Puget Sound "Background" Sediments
Al	7%	6.4% <sup>3</sup>
Fe	3%	3.6% <sup>3</sup>
Mn	700 ppm	496 ppm <sup>4</sup>
Cr	80 ppm	101 ppm <sup>4</sup>
Ni	80 ppm	42 ppm <sup>5,6</sup>
Cu	20 ppm	35 ppm <sup>5,6</sup>
Zn	80 ppm	87 ppm <sup>5,6</sup>
Co	10 ppm	12 ppm <sup>6</sup>
Pb	15 ppm	21 ppm <sup>5,6</sup>
Cd	<7 ppm	3 ppm <sup>6,7</sup>
Ag	<0.7 ppm	1.9 ppm <sup>6</sup>
Hg	---	0.06 ppm <sup>3,6</sup>

<sup>1</sup> Data compiled by Dexter et al. (1980).

<sup>2</sup> Pevear, D., Geology Department, Western Washington University, (unpublished data).

<sup>3</sup> Crecelius et al. (1975).

<sup>4</sup> Riley et al. (1980).

<sup>5</sup> Schell et al. (1977).

<sup>6</sup> Malins et al. (1980).

<sup>7</sup> Cummins et al. (1976).



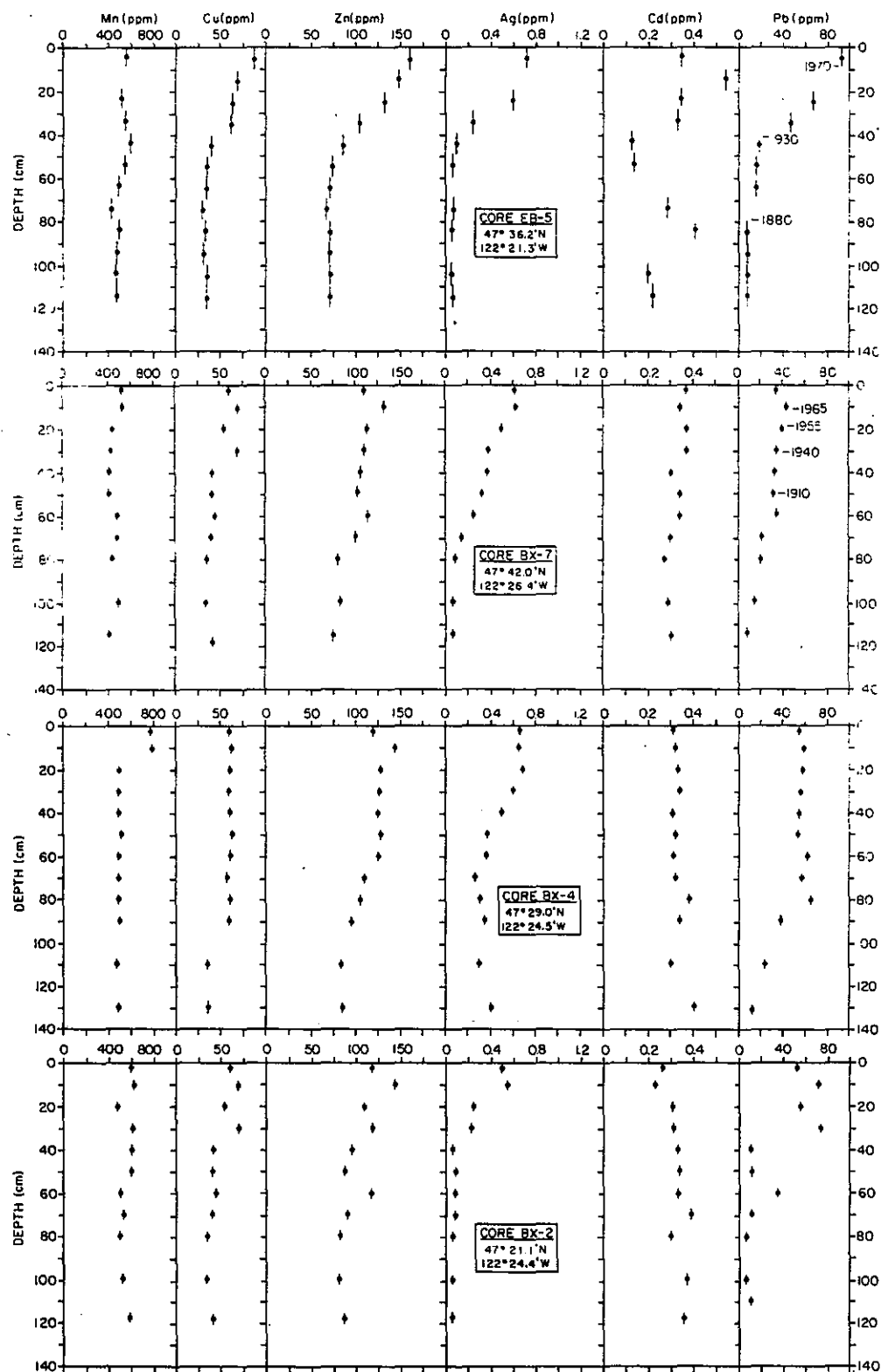


Fig. 2.4.23 Vertical profiles of Mn, Cu, Zn, Ag, Cd and Pb in selected cores from Elliott Bay and main basin of Puget Sound. Note that the  $^{210}\text{Pb}$  dates are provisional (see text).

the increases are as high as 2800% and 1000% respectively in the Elliott Bay core and 1000% and 700%, respectively, in the main basin cores. Cu and Zn show increases in the range between 75% and 200%. Cd shows very little increase in the main basin cores but there is a significant increase of about 150% in the core from Elliott Bay.

The highest metal increases are observed in the cores collected from Elliott Bay and in the southern part of the main basin of Puget Sound (core BX-2). The metal increases in the sediments from Elliott Bay appear to be the result of local wastewater inputs from the Duwamish River and stormwater discharges along the Seattle waterfront; whereas, the metal increases in the sediments of the southern main basin appear to result from inputs from a variety of sources including wastewater discharges into Elliott Bay, Commencement Bay, Sinclair Inlet and direct wastewater discharges into the main basin, such as the West Point outfall. These data support our belief that the sediments of Elliott Bay and the southern main basin are major sinks for anthropogenic trace metals in Puget Sound.

Figure 5.21 also shows the  $^{210}\text{Pb}$  dates for various depth horizons within the cores at EB-5 and BX-7. The  $^{210}\text{Pb}$  dates from these regions have been verified by studies carried out by other investigators (Schell et al., 1976, Barrick, 1982) which lead us to make a preliminary interpretation that in these cases the sedimentation rates are probably good to within a factor of about 2 or 3 or better. (The results should be considered to be provisional until we have completed the other isotope studies). The data show that the major increase of Cu, Zn, Ag, Cd and Pb in Elliott Bay and Puget Sound sediments have occurred since about 1910, a period of increased industrial activity and increased usage of gasoline containing tetraethylene lead. At BX-7 the maximum trace metal concentrations were found in sediments deposited in 1960-1970. This is the period when Seattle's METRO West Point wastewater treatment plant began operations. Prior to this time, most of Seattle's wastewater and sludge materials were discharged untreated into Puget Sound. The small decrease in metal concentrations near the surface might be interpreted as indicating that METRO's wastewater treatment procedures have been somewhat effective in reducing metal inputs to the sediments. However, we believe the data are still too sketchy at this point to make any definitive statements about this. In FY83, we will be making detailed studies of metal concentrations and radioisotopes in several 2 m and 3 m Kasten cores collected along the main axis of the main basin of Puget Sound.

#### b. Porewater and Lander studies

##### 1) Porewater concentrations

The *in situ* sampler was used in order to obtain a set of representative data free of temperature and pressure artifacts which can result for cored samples. The sampler also provides a way to collect gas samples to complement the analyses for nutrients and metals. The results are given in Table 5.10. Samples are collected from 1 cm to 53 cm

Table 5.10. Nutrient, pH, alkalinity, DOC, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, ΣCO<sub>2</sub>, and elemental concentrations in an *in-situ* sampler at the Lander station in the main basin of Puget Sound. Samples were collected May 6-7, 1982.

<i>In-situ</i> sampler		6-7 May 1982													
Depth	PO <sub>4</sub>	Si	NO <sub>3</sub>	NO <sub>2</sub>	NH <sub>4</sub>	pH	Alk	Ca	Mg	SO <sub>4</sub>	DOC	O <sub>2</sub>	N <sub>2</sub>	CH <sub>4</sub>	ΣCO <sub>2</sub>
(cm)			(μM)				(meq/L)		(mM)		(mg/L)		(mM)		
Bottom															
Water	1.43	37.73	18.37	0.33	10.45	7.88	2.104	0.53	0	24.2	4.45	0.272	1.621	--	--
1	99.36	646.24	1.44	0.64	106.56	7.21	3.316	9.19	47.3	25.3	5.95	0.029	0.622	--	4.127
4	18.88	573.44	5.76	0.80	129.12	7.01	3.329	8.67	44.9	14.2	10.55	0.052	0.877	--	4.618
7	127.52	645.76	2.56	1.28	197.92	7.11	4.649	9.07	45.5	25.0	--	--	--	--	--
10	151.68	687.36	2.88	1.28	290.72	7.10	5.157	9.01	45.3	23.8	7.63	0.028	0.731	--	5.377
13	130.08	753.92	1.76	1.44	355.04	7.07	5.673	9.24	47.8	24.4	9.38	0.029	0.731	--	6.670
16	185.76	777.12	1.44	0.64	380.96	7.26	6.209	9.15	47.6	24.2	10.24	0.034	0.691	--	7.324
19	264.64	904.80	1.76	0.48	500.64	7.23	7.126	9.22	47.8	23.3	10.18	0.033	0.665	--	7.702
22	244.32	877.28	1.44	0.48	447.52	7.23	5.952	9.31	47.6	23.4					
25	166.40	810.24	1.92	0.64	447.52	7.23	5.952	9.38	47.6	24.0	--	0.044	0.710	--	6.657
28	103.52	672.80	4.96	0.80	379.68	7.24	4.832	9.38	47.3	24.2	20.62	0.055	0.764	--	5.828
33	117.44	782.72	2.56	0.48	436.80	7.24	5.276	9.07	47.8	23.8	11.81	0.045	0.691	0.004	5.736
38	142.08	799.52	3.20	0.64	450.72	7.27	5.247	9.07	47.3	21.8	11.32	0.031	0.650	0.004	5.915
43	112.16	801.60	4.80	0.64	475.84	7.22	5.287	9.31	47.1	21.6	--	0.040	0.718	--	5.673
48	137.44	831.36	1.28	0.48	501.60	7.29	6.137	9.27	47.8	21.6	12.95	0.032	0.594	0.012	6.477
53	132.64	823.36	1.92	0.48	501.76	7.32	6.114	0.15	47.8	21.6	12.50	0.045	0.673	0.006	6.400

Table 5.11. Nutrient, pH, alkalinity,  $\Sigma\text{CO}_2$  and elemental concentrations in the Lander box cores at the Lander Station in the main basin of Puget Sound. Samples were collected May 6-7, 1982.

Lander

Depth	PO <sub>4</sub>	Si	NO <sub>3</sub> ( $\mu\text{M}$ )	NO <sub>2</sub>	NH <sub>4</sub>	Alk (meq/L)	Ca	Mg	Fe ( $\mu\text{M}$ )	Mn	$\Sigma\text{CO}_2$ (mM)
Core A											
0-0.5	5.88	472.5	0.84	0.21	43.7	2.616	--	--	9	141	2.77
0.5-1.0	8.64	478.2	0.64	0.16	49.0	2.792	8.74	47.0	10	183	--
1.0-1.5	7.36	519.0	0.32	0.16	61.8	2.889	8.67	44.7	11	209	--
1.5-2.0	16.5	603.0	0.96	0.32	73.4	2.927	8.48	44.3	52	168	--
2.0-3.0	25.8	696.2	0.96	0.48	97.9	3.163	8.67	44.7	82	152	3.41
3.0-4.0	35.7	751.0	2.56	0.48	127.5	3.544	8.61	45.0	95	160	--
4.0-5.0	27.7	769.1	1.76	0.48	156.0	3.958	8.74	45.2	55	171	--
6.0-7.0	117.9	841.4	0.64	0.48	195.0	4.518	8.61	45.7	124	137	--
7.0-8.0	126.2	841.3	0.80	0.48	216.0	4.705	8.80	45.7	119	144	--
8.0-9.0	147.5	853.8	0.80	0.32	236.3	4.971	8.86	46.1	70	120	--
9.5-10.5	178.4	866.4	0.48	0.32	271.0	5.188	--	--	116	106	4.95
12.0-13.0	158.2	919.7	0.48	0.48	319.0	5.842	8.93	47.2	20	118	--
14.5-15.5	206.7	933.4	1.12	1.44	350.1	6.020	--	--	51	114	5.91
Core B											
0-0.5	5.44	441.1	0.00	0.32	31.2	2.523	8.67	47.7	6	97	--
0.5-1.0	4.64	542.9	1.12	0.32	45.8	2.567	8.80	46.6	24	122	--
1.0-1.5	7.68	588.8	1.44	0.32	53.3	2.692	8.80	46.8	54	113	--
1.5-2.0	9.12	607.8	1.12	0.48	71.8	2.946	8.61	45.9	77	147	--
2.0-3.0	15.2	639.2	2.56	0.64	116.2	3.426	8.67	45.7	113	216	--
3.0-4.0	33.4	699.2	2.56	0.64	161.8	4.104	8.80	45.7	118	282	--
4.0-5.0	45.3	743.1	1.12	0.64	181.8	4.192	8.67	45.9	99	263	--
6.0-7.0	92.6	733.9	0.96	0.64	205.9	4.720	8.80	45.9	139	284	--
7.0-8.0	117.3	765.6	1.12	0.64	217.6	4.834	8.93	46.3	137	248	--
8.0-9.0	124.5	815.7	0.80	0.64	219.2	4.878	8.80	45.9	125	229	--
9.5-10.5	137.1	879.0	0.96	0.48	251.0	4.973	8.74	45.7	81	195	--
12.0-13.0	148.0	900.3	0.96	0.64	276.6	4.823	8.74	44.7	99	159	--

Table 5.12. Nutrient, pH, alkalinity, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, ΣCO<sub>2</sub> and elemental concentrations in Lander box cores at the Lander Station in main basin Puget Sound. Samples were collected June 8-9, 1982.

Depth	PO <sub>4</sub>	Si (μM)	NH <sub>4</sub>	pH	Alk (meq/L)	Ca	Mg	SO <sub>4</sub>	Fe (μM)	Mn	O <sub>2</sub>	N <sub>2</sub> (μM)	CH <sub>4</sub>	ΣCO <sub>2</sub> (mM)
LA-1	1.56	29.0	4.80	7.62	1.781	7.50	37.8	21.4	--	.76	187	506	--	1.757
LA-2	2.07	46.5	6.95	7.60	1.815	7.56	40.6	--	--	2.75	200	551	--	1.746
LA-3	2.24	58.0	6.76	7.59	1.743	7.09	35.8	20.6	--	4.13	211	583	--	1.697
LA-4	2.75	71.7	7.54	7.51	1.832	7.37	37.1	--	--	6.93	172	641	--	1.817
LA-5	3.32	92.0	12.42	7.47	1.970	7.78	39.1	22.4	--	10.08	176	708	--	1.896
LA-6	3.72	102.7	10.08	7.41	2.013	7.83	39.3	--	--	12.60	146	683	--	1.706
LA-8	3.83	128.7	10.86	7.39	1.958	7.49	38.2	21.5	--	15.78	129	811	--	1.925
LB-1	1.50	29.3	5.29	7.65	--	--	--	--	--	--	198	518	--	1.755
LB-2	1.84	42.8	5.29	7.64	--	--	--	--	--	--	242	645	--	1.767
LB-3	1.73	34.3	5.09	7.63	--	--	--	--	--	--	184	428	--	2.002
LB-4	1.84	33.7	5.29	7.64	--	--	--	--	--	--	228	534	--	1.990
LB-5	2.86	77.3	7.15	7.70	--	--	--	--	--	--	272	990	--	1.839
LB-6	2.47	74.0	6.07	7.62	--	--	--	--	--	--	271	895	--	1.040
LB-8	1.61	36.0	5.29	--	--	--	--	--	--	--	230	533	--	2.021
Bottom water	1.78	34.6	4.02	--	--	9.16	45.7	--	--	--	240	530	--	2.050

Table 5.12 cont.

Depth	PO <sub>4</sub>	Si (μM)	NH <sub>4</sub>	pH	Alk (meq/L)	Ca	Mg	SO <sub>4</sub>	Fe (μM)	Mn	O <sub>2</sub>	N <sub>2</sub> (μM)	CH <sub>4</sub>	ΣCO <sub>2</sub> (mM)
Core A														
0-0.5	14.82	653	65.5	7.27	2.950	8.98	46.7	26.8	--	224	--	--	--	2.862
0.5-1.0	28.12	771	86.1	7.06	2.946	9.07	45.8	26.8	21.3	239	--	--	--	3.141
1.0-1.5	37.10	821	84.1	6.92	3.140	9.21	45.1	27.5	40.3	205	--	--	--	3.241
1.5-2.0	57.10	868	125.2	7.00	3.325	9.03	--	25.8	49.7	213	--	--	--	3.453
2-3	293.6	879	133.0	6.90	4.013	9.05	45.8	21.9	56.7	253	--	--	--	4.157
3-4	100.4	899	209.3	6.88	4.562	9.05	45.3	26.2	54.1	296	--	--	--	4.969
6-7	152.5	904	206.3	6.93	5.953	8.93	44.2	23.9	63.4	336	--	--	--	6.351
9-10	98.5	892	146.8	7.00	5.794	9.05	56.0	25.5	42.2	328	--	--	--	6.123
Core B														
0-0.5	12.32	620	50.9	7.27	2.664	9.10	48.7	--	0.3	153	--	--	--	2.830
0.5-1.0	25.73	725	75.3	7.15	2.764	9.12	46.0	--	56.2	203	--	--	--	2.958
1.0-1.5	40.05	792	82.6	7.06	2.816	8.93	46.2	--	68.5	206	--	--	--	2.980
1.5-2.0	92.54	888	111.5	7.03	3.366	9.07	44.7	--	119	200	--	--	--	3.313
2-3	81.97	854	144.8	7.02	--	9.15	46.4	--	112	233	--	--	--	3.562
3-4	70.03	876	114.8	7.08	3.579	9.15	45.8	--	46.3	187	--	--	--	--
6-7	86.04	931	138.9	6.93	3.917	9.18	46.0	--	46.8	220	--	--	--	4.076
9-10	127.5	937	266.1	7.12	4.546	9.17	45.8	--	D.L.	154	--	--	--	5.074
Core A, Overlying water														
353					~2.44	9.22	46.4	--	--	--	--	--	--	--
Core B, Overlying water														
220	--	--	--	--	~2.27	9.00	46.4	--	--	--	--	--	--	--

within the sediments as well as a bottom water sample. Silica,  $\text{PO}_4$ ,  $\text{NH}_4$ ,  $\Sigma\text{CO}_2$  and alkalinity increase with depth to a maximum at about 20 cm. Below 30 cm the concentrations tend to remain constant.  $\text{O}_2$  decreases to almost detection limit at 1 cm; however, there is measurable  $\text{O}_2$  throughout the profile. Low levels of  $\text{CH}_4$  ( $<20 \mu\text{M}$ ) appear below 30 cm.

Evidence for irrigation can be seen in these data although it is much less obvious than in some of our earlier results at this same site. Note that when silica is high at 20 cm,  $\text{PO}_4$ ,  $\text{NH}_4$ ,  $\Sigma\text{CO}_2$ , and alkalinity are also high.  $\text{O}_2$ ,  $\text{NO}_3$ ,  $\text{NO}_2$ , and  $\text{SO}_4$  show a corresponding minimum. Silica decreases to a minimum at 28 cm, suggesting irrigation of the sediments by low silica bottom water.  $\text{PO}_4$ ,  $\text{NH}_4$ ,  $\Sigma\text{CO}_2$ , and alkalinity are also a minimum there while  $\text{O}_2$ ,  $\text{NO}_3$  and  $\text{NO}_2$  show a small maximum.

The Lander was deployed twice and on both occasions two box cores were collected and subsampled for interstitial water. These cores are spaced about 100 cm apart on the Lander frame so these results give us an opportunity to examine variability in the sediments over that scale. The results from May are given in Table 5.11 so that they can be compared with the harpoon which was collected on the same date. The results from June are shown in Table 5.12. The chamber over core A appeared to give reliable fluxes.

The Lander core results in May tend to agree well with the *in situ* sampler results. Silica is higher in the cores but this is probably due to the temperature effect. But the  $\text{PO}_4$ ,  $\text{NH}_4$ , Ca, Mg and  $\Sigma\text{CO}_2$  results agree almost perfectly. There is slightly more  $\text{NO}_3$  and  $\text{NO}_2$  in the *in situ* samples than in the cored samples.

The horizontal variation between the two cores in May is slight. A small difference in  $\text{PO}_4$ , Fe and Mn can be seen, especially below 5 cm.

The analyses from the June samples show much larger variations (Table 5.12). The two cores tend to agree down to about 5 cm and then diverge markedly at greater depths. Core A has higher values of  $\text{PO}_4$ ,  $\text{NH}_4$ , alkalinity,  $\Sigma\text{CO}_2$ , Fe and Mn below 4 cm. Ca, Mg and pH are linear for core A. Interestingly, silica shows little variation between the two cores.

## 2) Three Dimensional Box Core Study

The interstitial water from three sub-cores from a single box core was analyzed in May. The results are given in Table 5.13. The sub-cores were taken in a triangular arrangement with the center-to-center separation about 10 cm. Striking horizontal gradients were observed for many of the constituents.

Silica increases from bottom water ( $38 \mu\text{mole kg}^{-1}$ ) to about  $500 \mu\text{mole kg}^{-1}$  by 10 cm. Except for silica minima the silica concentrations are relatively constant below 10 cm. One example of silica minimum can be seen in core B around 10-15 cm. The horizontal gradients for silica can reach  $10 \mu\text{mole kg}^{-1} \text{ cm}^{-1}$ .

Table 5.13. Nutrient, pH, alkalinity,  $\Sigma\text{CO}_2$  and elemental concentrations in three subcores from a box core at the Lander Station in the main basin of Puget Sound. Samples were collected May 6-7, 1982.

Depth	$\text{PO}_4$	Si	$\text{NO}_3$ ( $\mu\text{M}$ )	$\text{NO}_2$	$\text{NH}_4$	Alk (meq/L)	Ca	Mg (mM)	$\text{SO}_4$	Fe ( $\mu\text{M}$ )	Mn	$\Sigma\text{CO}_2$ (mM)
Core A												
0-2	4.32	604.8	1.12	0.48	49.6	2.709	8.74	46.1	25.8	7	194	2.73
2-4	21.9	756.2	2.88	0.32	72.8	2.895	8.61	45.2	--	95	138	2.96
4-6	14.1	804.0	2.08	0.32	118.7	3.780	9.12	48.2	26.6	85	275	3.99
6-8	27.8	791.8	1.44	0.32	171.8	4.671	8.86	46.3	25.3	65	363	--
8-10	120.0	941.0	0.32	0.48	213.3	4.985	--	--	--	1137?	364	--
10-12	195.5	938.2	0.64	0.32	272.2	5.080	8.80	47.0	24.9	169	169	--
12-14	153.2	990.2	0.32	0.32	328.0	5.373	8.67	45.2	24.2	14	144	--
14-16	162.6	1011.4	1.12	0.32	361.3	5.786	8.74	46.8	--	34	153	5.58
16-18	159.8	1058.1	0.48	0.48	361.3	5.617	8.74	46.3	24.5	30	150	--
19-21	118.1	1023.5	0.16	1.92	344.5	5.168	8.99	47.9	--	27	104	5.03
24-26	104.8	938.2	0.48	0.48	306.2	4.789	8.86	46.6	24.8	36	57	--
29-31	64.8	907.7	2.24	0.64	293.4	4.759	9.38	49.8	--	15	42	4.54
32-34	105.6	941.0	1.28	0.64	293.4	4.718	8.86	46.3	25.3	17	42	--
Core B												
0-2	8.32	537.1	0.32	1.12	42.9	2.978	8.80	45.7	5	208		
2-4	15.0	645.8	0.16	0.96	42.6	2.764	--	--	25	151		
4-6	17.0	844.2	0.48	0.64	74.9	2.969	8.61	45.9	51	139		
6-8	30.1	888.6	0.32	0.96	86.7	3.026	8.67	45.2	125	147		
8-10	28.6	875.4	0.80	0.96	104.8	3.091	8.86	47.3	113	148		
10-12	39.7	844.2	0.32	0.96	126.9	3.477	8.93	46.1	90	119		
12-14	20.5	986.8	0.00	0.96	161.0	3.653	8.67	45.7	62	133		
16-18	97.8	966.7	0.00	0.80	287.0	3.528	9.32	48.4	53	98		
18-20	53.1	981.4	0.00	0.80	299.4	4.623	8.54	45.9	26	95		
24-26	61.1	949.6	0.00	0.80	344.0	4.833	8.48	45.7	9	52		
29-31	15.0	794.2	0.00	0.80	335.4	4.394	9.54	50.7	10	33		



Table 5.13., continued

Depth	PO <sub>4</sub>	Si	NO <sub>3</sub> (μM)	NO <sub>2</sub>	NH <sub>4</sub>	Alk (meq/L)	Ca (mM)	Mg (mM)	SO <sub>4</sub>	Fe (μM)	Mn	ΣCO <sub>2</sub> (mM)
Core C												
0-1	3.52	434.4	0.96	0.16	16.0	2.447	8.70	45.6	27.0	8		76
1-2	3.52	606.6	0.96	0.16	21.0	2.508	8.61	46.8	--	18		110
2-3	2.08	712.3	1.12	0.16	40.6	2.738	8.61	45.4	25.6	72		147
3-4	4.80	757.9	1.92	0.16	78.4	3.309	8.74	46.3	--	59		210
4-5	17.3	788.8	1.12	0.16	104.3	3.726	8.74	46.6	23.9	95		193
5-6	28.3	779.0	1.12	0.16	134.9	4.189	8.67	45.7	--	83		212
6-7	44.5	813.0	1.44	0.16	143.0	4.235	8.80	45.2	25.1	122		216
7-8	53.1	856.0	1.60	0.16	162.1	4.322	8.93	46.3	--	119		190
8-9	2.99	898.2	1.28	0.16	169.9	4.168	8.80	45.9	23.9	199		171
9-10	65.4	964.4	1.28	0.16	194.1	3.990	8.87	45.7	--	138		158
12-13	35.5	1009.9	1.12	0.80	235.5	3.801	9.15	46.6	25.5	341		157
14.5-15.3	17.9	936.6	0.48	2.24	196.6	2.435	8.99	45.9	--	507		129
17-18	42.1	905.9	0.96	0.64	202.2	3.238	8.67	45.4	--	213		101
19.5-20.5	38.7	950.6	1.44	0.16	253.6	3.499	8.67	45.9	--	106		87
24.5-25.5	69.4	991.2	1.92	0.16	307.4	4.138	8.61	45.9	25.1	59		65
27-28	149	1009.3	1.60	0.32	330.8	4.415	8.61	45.0	24.9	111		67
29.5-30.5	117.3	993.9	2.56	0.32	324.5	4.514	8.87	47.3	--	30		66
32-33	116.2	1009.0	0.32	0.16	333.9	4.554	8.87	47.3	25.5	29		60
34.5-35.5	139.4	1055.5	2.08	0.16	338.9	4.667	9.12	49.1	--	48		50
37-38	95.8	1008.6	0.32	0.16	330.9	4.799	8.74	46.1	24.2	9		44
39.5-40.5	101.0	1023.8	0.48	0.16	353.1	4.816	8.74	46.3	--	16		40
42-43	124.3	1039.4	0.48	0.16	356.8	4.809	8.57	44.5	25.0	18		38
43-44	101.1	1011.4	0.48	0.16	364.6	4.869	8.93	46.6	--	26		38

$\text{PO}_4$ ,  $\text{NH}_4$  and alkalinity also tend to increase with depth. In these cores the horizontal variability is much more dramatic. Core A tends to have the highest values indicating more extensive diagenesis or less irrigation. Core A has especially high values of phosphate centered around 10-15 cm. For more  $\text{PO}_4$  and  $\text{NH}_4$  the horizontal gradients approach  $15 \mu\text{M kg}^{-1} \text{cm}^{-1}$ .

Mn and Fe show maxima, especially well developed in core C for Mn and core A for Fe. The Mn maxima tend to be shallower than the Fe maxima.

$\text{NO}_3$  and  $\text{NO}_2$  tend to be low and variable. The absorbances are so low that it is justifiable to question whether the data are even reliable.

### 3) Lander results

In the May deployment neither chamber showed consistent results. The results for chambers A and B from the June deployment are given in Table 5.12. Only chamber A appeared to give consistent results. Silica,  $\text{PO}_4$  and  $\text{NH}_4$  increase systematically with time and extrapolate to bottom water values while  $\text{N}_2$  increases and  $\text{O}_2$  decreases with time. Alkalinity and total  $\text{CO}_2$  increase with time after a slight decrease during the first 7 hours. The gradients shown in Fig. 5.22 translate into the fluxes shown in Table 5.14.

We define the effects of biological activity in two ways. Bioturbation is the movement of sedimentary particles caused by biological activity. Irrigation is the result of the movement of the water through burrows, tubes and other biological structures. The interstitial water results presented here primarily reflect the results of irrigation. The effects of bioturbation can best be studied using short-lived isotopes attached to particles (e.g.,  $^{234}\text{Th}$ ,  $^{210}\text{Pb}$ ,  $^{230}\text{Th}$ ). These analyses are in progress and the results will be presented later. Qualitatively the effects of irrigation can be seen in the large degree of small-scale variability in the detailed structure of the individual pore water profiles and in the relationship between the diffusive fluxes calculated from Fick's law and the Lander chamber fluxes (to be discussed below).

Small-scale variability is extremely pronounced over all scales. The two Lander cores are centered about one meter apart and the June data show  $\Sigma\text{CO}_2$ , Fe and Mn. Core A systematically appears to be more reducing or less influenced by irrigation than core B. Interestingly, the May Lander core data do not show such variability, but this is more the exception than the rule. Even over the scale of a 20 cm by 30 cm box core the variability can be pronounced. As a general rule it appears that  $\text{PO}_4$ , Fe and Mn are the elements most likely to show pronounced variability. This probably reflects the sensitivity of Fe and Mn oxides to the redox environment.

The structure of the various profiles and correlations among the various elements also demonstrates the effects of irrigation. The data

from the *in situ* sampler is useful in this regard because it includes  $O_2$ . In this data set there is a silica minimum at 4 and 28 cm.  $PO_4$  and  $NH_4$  also show a minimum at these depths, while  $NO_3$  and  $N_2$  show small but significant maxima. All of these correlations are consistent with dilution or exchange of bottom water with pore water.

#### 4) Fluxes

The diagenesis of organic debris in the sediments of Puget Sound results in vertical gradients within the pore water of the sediments. Due to the effects of irrigation and possibly also non-homogeneous lateral deposition of organic debris there are horizontal gradients within the sedimentary pore waters. In Puget Sound the horizontal gradients are significant and the resulting horizontal fluxes are of the same magnitude as the vertical fluxes out of the sediments.

The vertical gradients were calculated between bottom water and the first pore water value. The gradient was calculated by dividing the

Table 5.14. Flux of  $N_2$ ,  $NH_4$ ,  $PO_4$ , Si and Mn into and  $O_2$  out of Lander chamber A, collected on 8-9 June 1982. Fluxes are given in  $\mu\text{ cm}^{-2}\text{ d}^{-1}$ .

Compound	Lander Flux	Lander Flux Diffusive Flux
$N_2$	1.43	--
$O_2$	-0.54	--
$NH_4$	0.028	2.9
$PO_4$	0.014	2.5
Si	0.47	16.2
Mn	0.070	4.7
$NH_4/PO_4$	2.00	1.2

PUGET SOUND 8-9 JUNE 1982  
LANDER A

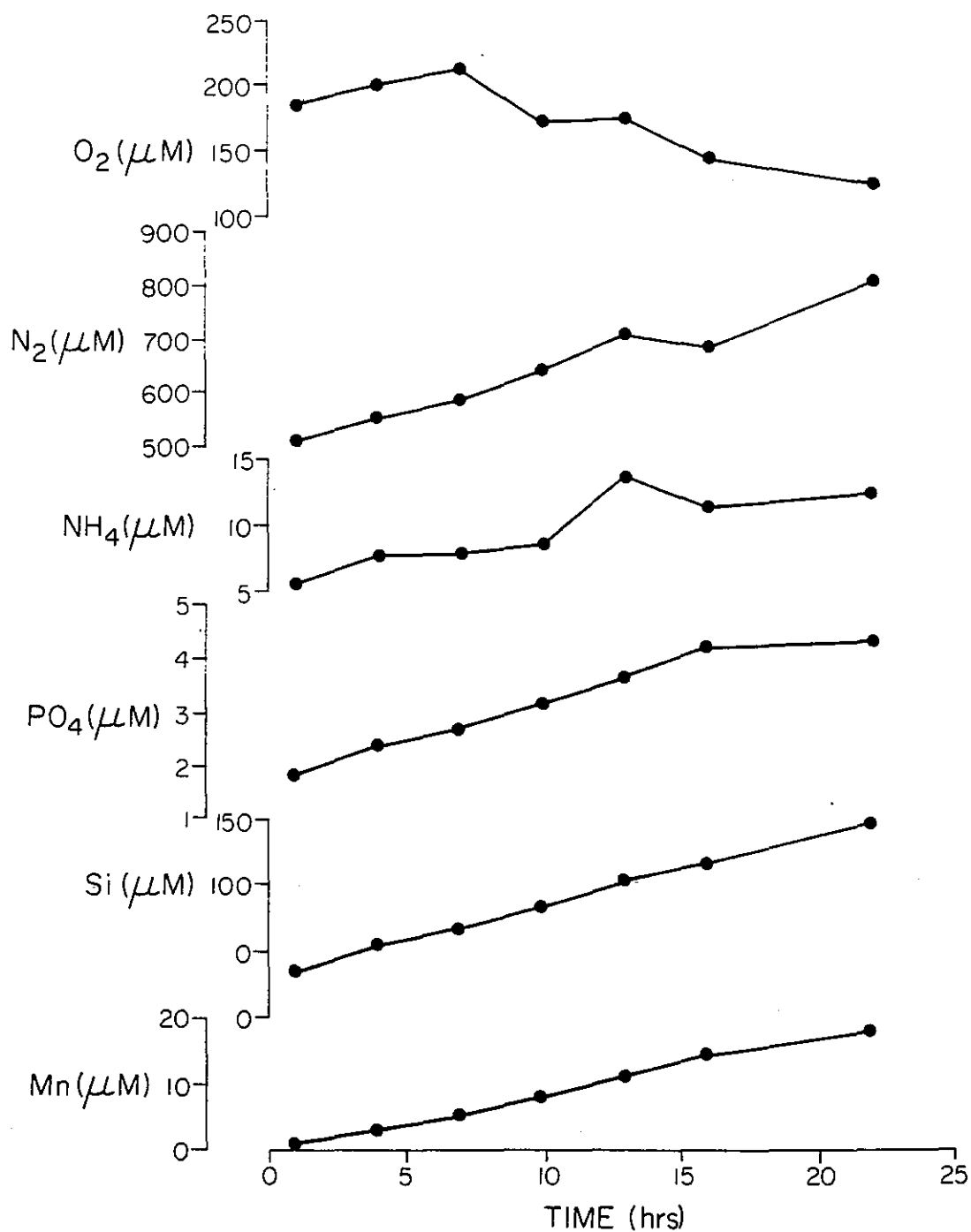


Fig. 2.4.24 Temporal variations of O<sub>2</sub>, N<sub>2</sub>, NH<sub>4</sub>, PO<sub>4</sub>, silica and Mn in Lander chamber A.

difference in composition by the depth interval. We are thus assuming that the gradients are linear. In reality the gradients are not always linear and our gradients thus probably represent minimum values. In most cases we sampled the core tops in 0.5 cm intervals in order to approximate the natural gradients as closely as possible. The mean vertical gradients for silica,  $\text{NH}_4$ ,  $\text{PO}_4$  and Mn from the four sets of samples are summarized in Table 5.15. The fluxes are calculated from these gradients using Fick's First Law (see Berner, 1980, p. 38).

$$J_s = -\phi D_s \frac{\partial c}{\partial x} \quad (1)$$

where  $J_s$  = diffusion flux in the sediments in terms of mass per area of total sediment per unit time;

$\phi$  = porosity of sediments;

$D_s$  = whole sediment diffusion coefficient in terms of area of sediment per unit time.

In these calculations we assume an average porosity of 80%. We use diffusion coefficients for 5°C taken from Krom and Berner (1980) and Elderfield et al. (1981). These are "in sediment" diffusion coefficients that include the effects of porosity, tortuosity and adsorption. The values used by us are given in Table 5.16. The calculated diffusive fluxes for the appropriate gradients are also shown in Table 5.15. The vertical gradients and fluxes calculated for the four data sets agree with each other reasonably well. The value given for the 3-D box core is the average for the three sub-cores. The values given for the Lander represent the average of the two Lander cores. The grand average vertical diffusive flux is  $1.05 \text{ nmole cm}^{-2} \text{ d}^{-1}$  for silica,  $4.0 \text{ nmole cm}^{-2} \text{ d}^{-1}$  for  $\text{NH}_4$ ,  $5.4 \text{ nmole cm}^{-2} \text{ d}^{-1}$  for  $\text{PO}_4$ , and  $12.7 \text{ nmole cm}^{-2} \text{ d}^{-1}$  for Mn.

The horizontal gradients and fluxes were calculated by dividing the concentration difference at a given depth by the distance (10 cm) between the centers of the cores. For the 3-D box cores the values in Table 5.14 represent the average of three calculations. For the pairs of Lander cores only one calculation is involved. The horizontal gradients and fluxes for silica are only about 1 to 2% of the vertical gradients across the sediment-water interface. For  $\text{NH}_4$ ,  $\text{PO}_4$  and Mn the horizontal fluxes are a significant fraction of the vertical fluxes. The average maximum horizontal fluxes are  $1.7 \text{ nmole cm}^{-2} \text{ d}^{-1}$  for silica,  $1.6 \text{ nmole cm}^{-2} \text{ d}^{-1}$  for  $\text{NH}_4$ ,  $2.0 \text{ nmole cm}^{-2} \text{ d}^{-1}$  for  $\text{PO}_4$  and  $2.4 \text{ nmole cm}^{-2} \text{ d}^{-1}$  for Mn.

The vertical and horizontal sedimentary diffusive fluxes can be compared with the Lander chamber fluxes measured in chamber A in June 1982. The chamber covered an area of  $400 \text{ cm}^2$  and was occupied by a volume of 1.6 liters. Seven samples were collected with time over a 24-hour period.  $\text{NH}_4$ ,  $\text{PO}_4$ , silica, Mn and  $\text{N}_2$  increased linearly with time.  $\text{O}_2$  decreased with time after the third sample. The fluxes were calculated from the linear gradients after correcting for the dilution that occurs because bottom water replaces the samples as they are drawn. The fluxes are summarized in Table 5.14.

In the last column of Table 5.14 the ratio of the Lander chamber flux to calculated pore water diffusive flux is given. The pore water

Table 5.15. Gradients ( $\mu\text{mole l}^{-1} \text{ cm}^{-1}$ ) and fluxes ( $\text{nmole cm}^{-2} \text{ d}^{-1}$ ) of silica,  $\text{NH}_4$ ,  $\text{PO}_4$ , and Mn in the sediments of Puget Sound.

	mean vertical gradient	mean vertical flux	mean horizontal gradient	mean horizontal flux	maximum horizontal gradient	maximum horizontal flux
<b>Silica</b>						
3-D Box Core	488	102	6.5	1.4	9.7	2.0
Lander Cores (May)	495	103	10.8	2.2	10.8	2.2
Lander Cores (June)	424	88	4.5	0.9	4.5	0.9
Harpoon	608	126	--	--	--	--
<b><math>\text{NH}_4</math></b>						
3-D Box Core	14	2.4	9.7	1.6	14.5	2.4
Lander Cores (May)	31	5.2	2.0	0.3	2.0	0.3
Lander Cores (June)	57	9.6	11.9	2.0	11.9	2.0
Harpoon	96	16.1	--	--	--	--
<b><math>\text{PO}_4</math></b>						
3-D Box Core	2.0	0.3	10.4	1.6	15.6	2.4
Lander Cores (May)	5.7	0.9	4.1	0.6	4.1	0.6
Lander Cores (June)	37	5.6	20.2	3.1	20.2	3.1
Harpoon	98	--	--	--	--	--
<b>Mn</b>						
3-D Box Core	85	12.2	14.4	2.1	21.6	3.1
Lander Cores (May)	78	11.2	10.7	1.5	10.7	1.5
Lander Cores (June)	103	14.8	17.4	2.5	17.4	2.5

Table 5.16. Whole sediment diffusion coefficients at 5°C applied to Puget Sound data. These values include the effects of adsorption, porosity, and tortuosity.

Compound	$D_s$ ( $\text{cm}^2 \text{sec}^{-1}$ )	$D_s$ ( $\text{cm}^2 \text{d}^{-1}$ )
$\text{NH}_4$	$2.4 \times 10^{-6}$	$2.1 \times 10^{-1}$
$\text{PO}_4$	$2.2 \times 10^{-6}$	$1.9 \times 10^{-1}$
Si	$3.0 \times 10^{-6}$	$2.6 \times 10^{-1}$
Mn	$2.1 \times 10^{-6}$	$1.8 \times 10^{-1}$

data used in this case were the data obtained for the June core which underlay the chamber. For this June deployment the Lander chamber flux was greater than the diffusive flux by a factor of 2.9 for  $\text{NH}_4$ , 2.5 for  $\text{PO}_4$ , 16.12 for silica and 4.7 for Mn. This comparison shows the net effect of biological activity on the flux across the sediment-seawater interface.

Since the near-bottom enrichments of trace elements in the main basin of Puget Sound indicated that reactions near the sediment-seawater interface are important, we initiated studies of trace metal distributions in interstitial pore fluids of sediments taken from station PS7. Box cores were collected and the pore waters extracted by centrifugation. Table 5.17 shows a representative sample of trace metal concentrations in a typical box core. The data show significant enrichments of Mn in the top few centimeters of the sediments at PS7 relative to the overlying water. Mn concentrations were observed ranging from 36 to 290  $\mu\text{M}$  which is approximately 200-800 times the dissolved Mn concentrations in the overlying water. Thus, a Mn flux across the sediment-seawater interface could be expected to support the enrichments of Mn in the bottom waters of Puget Sound. Fluxes of Mn and other trace elements from coastal and open-ocean sediments have been observed elsewhere (Elderfield and Hepworth, 1975; Bender and Klinkhammer, 1978; Elderfield et al., 1981) and the fluxes appear to be related to the reducing potential of the sediments. In Puget Sound the sediments are reducing (Grundmanis and Murray, 1978) and significant Mn excesses occur as a result of the reduction of Mn oxide phases in the sediments (Sundby et al., 1981). While the Mn data are too variable to go through a rigorous analytical model to determine diffusive fluxes from the sediments, we can apply a simple Fickian diffusion model to estimate the time scales for maintaining the excess Mn concentration in the water column. If we assume a uniformly mixed bottom layer approximately 20 m thick with an average concentration of Mn of 0.9  $\mu\text{M}$  (Fig. 5.15), then by applying equation (1) to the  $_{\text{PS7}}$  data the flux of Mn to the bottom water is about 0.025  $\mu\text{mole Mn cm}^{-2}\text{d}^{-1}$  based on an average pore water concentration of 160  $\mu\text{moles of Mn in the top centimeter of the sediments}$ . This estimate of the flux agrees within a factor of three of the measured flux of 0.07  $\mu\text{mole Mn cm}^{-2}\text{d}^{-1}$  obtained in the Lander experiment. Using a flux of 0.07  $\mu\text{mole Mn cm}^{-2}\text{d}^{-1}$ , the Mn content of the bottom waters can be doubled in approximately 25 days which is close to the time interval (about 2-3 weeks) between flushing events in the Sound (Cannon and Ebbesmeyer, 1978).

When the same analysis is applied to the data for Cd and Cu, doubling times of 2226 and 2968 days, respectively, are obtained (Table 5.18). Since these estimates for doubling times are many times greater than the time interval for bottom flushing in the Sound, the interstitial pore waters cannot be a major source for the enriched concentrations of these trace metals to the bottom waters of the sound. Another possible explanation for the enriched trace metals is that the metals are recycled from decaying suspended matter in the water column or at the seawater-sediment interface. These results are supported by the recent studies of Elderfield et al. (1981) in which they found that in the reducing sediments of Narragansett Bay Mn was significantly enriched in the pore waters while Cu and Cd were depleted. This was found to be due to formation of insoluble sulfides.



Table 5.17: Concentrations of several trace elements in pore waters collected with a box core at station PS7.

Depth (cm)	Mn ( $\mu\text{M}$ )	Fe ( $\mu\text{M}$ )	Cu ( $\mu\text{M}$ )	Cd ( $\mu\text{M}$ )
0-2	295	22.9	0.013	<0.0038
2-4	112	<13.4	0.015	<0.0036
4-6	65	<13.4	0.009	<0.0036
6-8	65	<13.4	0.009	<0.0036

Table 5.18. Benthic fluxes and doubling times for trace metals in Puget Sound.

Trace Metal	Benthic Flux ( $\mu\text{mole cm}^{-2}\text{d}^{-1}$ )	Doubling Time in Bottom 20 m (days)
Mn	0.078	25
Fe	0.018	--
Cu	$2.2 \times 10^{-6}$	>2963
Cd	$8.0 \times 10^{-7}$	>2226

## VI. DISCUSSION AND CONCLUSIONS

### A. Duwamish River and Elliott Bay

The distributions of particulate trace elements in Elliott Bay delineate the sources and mode of transport of anthropogenic contaminants. Trace elements which are discharged from the Renton Sewage Treatment Plant and other smaller discharges along the river are rapidly flocculated in the Duwamish River, significantly enriching the trace element burden of suspended matter in the Bay. This material traverses the Bay and is advected to the north and west along the northern coast. Some of the material settles to the bottom of the Bay and the remainder disperses into the main basin. The evidence for significant enrichments of particulate metals in the subsurface waters of Elliott Bay strongly indicates the scavenging reactions involving hydrous Mn oxides occur in the Bay. This result is highly significant because we have found that several trace elements are scavenged by newly formed Mn oxides in large estuaries as well as small ones (Feely et al., 1981; Massoth et al., 1982). Thus, the formation of hydrous Mn oxides on the particulate matter in Elliott Bay is providing a mechanism for trace-element removal within the Bay.

From an ecological point of view these results are important because trace elements associated with Mn oxides are not readily assimilated by particle-feeding organisms. For example, Luoma and Jenne (1977) conducted laboratory experiments with the detritus-feeding clam, *Macoma balthica*, to show that metals bound to detrital organic matter were more easily assimilated by the clams than metals bound to Mn and Fe oxides. Similarly, Luoma and Bryan (1978) found that the amount of Pb in the bivalve *Scarbicalaria plana* inversely varied with the amount of Fe in the underlying sediments of several European estuaries, indicating that sediment-bound Pb is not readily available to benthic organisms when the Pb is bound to Fe oxides. These findings provide a foundation for evaluating the ecological significance of the trace element scavenging processes that occur in the Duwamish River-Elliott Bay region which can reduce the potential for bioaccumulation of trace elements in the indigenous marine organisms. Since trace elements bound to Mn oxides appear to be less available to organisms than trace elements bound to organic materials (e.g., organic flocculants), it seems prudent to identify those regions where formation of organic flocculants and Mn oxides are maximized with the intent to provide possibly useful recommendations about where wastewater dischargers, particularly those containing elevated concentrations of trace elements, ought to be located. For example, our data indicate that organic flocculants are formed in the low-salinity regions of the Duwamish River estuary and that a portion of the flocculants settle out in the estuary and in nearshore regions of Elliott Bay. Although the formation of organic flocculants reduces the potential toxicity of trace elements to free-swimming organisms, they apparently increase the potential for bioaccumulation of trace elements to suspension- and detritus-feeding benthic organisms. In contrast, in the deeper waters of Elliott Bay the scavenging of trace elements by Mn-Fe oxides and the subsequent sedimentation of this material may reduce the potential for bioaccumulation of trace elements in both free-swimming and detritus-feeding organisms. Thus, in light of this simple analysis, locating waste-water dischargers

may be more advantageous in areas where Mn-Fe oxides are forming in the water column than in regions where organic flocculants are forming, such as the Duwamish River estuary.

## B. Main basin of Puget Sound

### 1. Trace metal removal processes

The distributions of dissolved and particulate trace elements in Puget Sound delineate the sources and mode of transport of trace metals. A significant fraction of metals released into surface waters from rivers and outfalls discharging into the major embayments are transported to the main basin in the outflowing brackish water, significantly enriching the trace metal burden of surface waters relative to intermediate waters. The evidence for significant enrichments of particulate trace metals in the hydrous oxide phases of the sediment trap material collected at intermediate depths strongly indicates that scavenging reactions involving hydrous Mn and Fe oxides occur in the Sound. This result is highly significant because we have found that several trace metals are scavenged by newly-formed Mn oxides in Elliott Bay. Thus, the formation of hydrous Mn and Fe oxides on the particulate matter in the main basin is providing an important mechanism for trace element removal in Puget Sound. The fact that both Mn and Fe are rapidly remobilized in the underlying sediments suggests that the process is cyclic, with the hydrous oxides being major agents for trace metal transport to the sediments. The metal enrichments observed in the underlying sediments may be due, in part, to the efficiency of this mechanism for stripping trace metals from the water column.

The evidence that Cd and Cu are not appreciably enriched in the porewaters of the underlying sediments suggests that when the hydrous oxide phases are redissolved under the reducing conditions present within the sediments these metals are quickly precipitated as in soluble sulfides (Elderfield et al., 1981). Thus, the reducing sediments in Puget Sound appear to be major one-way sinks for certain trace metals. Since several other trace metals (i.e., Pb, Zn, Ag, etc.) form insoluble sulfides in the presence of reduced sulfur species, the reducing sediments may represent one-way sinks for these metals as well.

From an ecological point of view these results are important because they suggest that in areas of high sedimentation and low resuspension activity certain potentially toxic trace metals will be rapidly scavenged from solution and buried within the sediments with little opportunity for remobilization. If metals bound to insoluble sulfides are in a form that is essentially unavailable to organisms, then the potential for serious contamination of bottom-feeding organisms may be reduced. It should be pointed out, however, that this simple analysis does not take into account the possible solubilization of metals through irrigation processes. These processes can be important in well-oxygenated environments such as Puget Sound. We believe a combination of porewater and Lander studies is the best method for investigating these important processes in coastal environments.

## 2. Preliminary budget for Pb in the main basin of Puget Sound

In order to assess the relative importance of the various sources and sinks for trace metals in Puget Sound, we have initiated the development of budgets for each of the metals. This work is still in its preliminary stages as some of the source and sink terms have not been fully evaluated. However, we believe an example is useful to show the progress we have made and also to illustrate the needs for future research. We have chosen Pb for our example because the Pb data are more complete and reliable than data for other metals. The inputs to the budget include river discharge, shoreline erosion, oceanic input, atmospheric deposition, municipal and industrial waste-water discharges, and stormwater runoff. Major exports include sedimentation and sill transport.

The riverine input is based on the water and sediment discharge data summarized in Dexter et al. (1981) and our data for Pb concentrations in the dissolved and particulate fractions of the local rivers (Tables 5.2 and 5.3). Because of our clean procedures the Pb concentration in the rivers have been revised downward when compared with previous reports (i.e., Dexter et al., 1981). Similarly our estimates of the oceanic inputs have also been revised downward in light of the new data of Stukas and Wong (1981) for dissolved Pb in the Strait of Juan de Fuca ( $\sim 0.02 \mu\text{g Pb/L}$ ) and our own data for particulate Pb in the Strait ( $\sim 0.05 \mu\text{g Pb/L}$ ). Shoreline erosion is taken from the data of Dexter et al. (1981). Atmospheric deposition is based on the work of Hardy and Crecelius (1981), assuming an average concentration of Pb in atmospheric dust of 5000 ppm. Anthropogenic inputs were obtained from a combination of METRO's West Point sewage effluent Pb concentrations and waste-water discharge data. Contributions from other municipalities were calculated on the basis of their volume discharge, assuming their Pb concentrations were similar to the West Point sewage effluent. Industrial inputs were based on data provided by the Washington State Department of Ecology. At present, we have no data on stormwater runoff, although we feel the inputs are relatively low.

The export of Pb across Admiralty Inlet is not well known. We have attempted to estimate it by assuming a water exchange of  $5.0 \times 10^{14} \text{ L yr}^{-1}$  and a mean Pb concentration of  $0.12 \times 10^{-6} \text{ g Pb/L}$ , the average Pb concentration in the surface waters of Puget Sound. At present, we have no data for Pb exchange across the Narrows. Sedimentation of Pb in the main basin has been estimated by assuming a sedimentation area of  $2.6 \times 10^8 \text{ m}^2$  (after Barrick, 1982), an average Pb concentration in the surface sediments of 38 ppm, and an average sedimentation rate of  $1.0 \text{ g cm}^{-2} \text{ yr}^{-1}$  (data from E. Crecelius). Of these three parameters, the average sedimentation rate is the least well known and errors as high as  $\pm 100\%$  or more are not impossible. We have also included the average annual flux of Pb based upon the 50 m and 100 m sediment traps at PS7 for comparison, although the data have not been used to compute total exports.

Table 6.1. Preliminary Pb budget for the main basin of Puget Sound.

IMPORT	
Source	Transport (mt/yr)
Riverine <sup>1</sup>	
Dissolved <sup>1</sup>	2.3
Particulate <sup>1</sup>	154
Bedload <sup>2</sup>	9
	<hr/>
Total riverine	165.2
Stormwater runoff	?
Shoreline erosion <sup>2</sup>	30
Oceanic input <sup>3</sup>	24
Atmospheric deposition <sup>4</sup>	25
Municipal and industrial wastes <sup>5</sup>	33
	<hr/>
GRAND TOTAL	283.3
EXPORT	
Sinks	
Admiralty Inlet	60
Narrows	?
Sedimentation	
Sediment <sup>6</sup>	91.2
Sediment traps <sup>7</sup>	(49)
	<hr/>
GRAND TOTAL	151.2

1 Water and sediment discharge from Dexter et al. (1981); trace metal data from Table 5.2.

2 Data from Dexter et al. (1981).

3 Water input from Dexter et al. (1981); trace metal data from Stukas and Wong (1981), and Feely and Massoth, unpublished data.

4 Data from Hardy and Crecelius (1981).

5 Data from METRO and Washington State Department of Ecology.

6 Assumes a mean sedimentation area of  $2.6 \times 10^8 \text{ m}^2$  (Barrick, 1982) and a mean sedimentation rate of  $1.0 \text{ g cm}^{-2} \text{ yr}^{-1}$ .

7 Assumes the annual mean vertical flux through the 50m and 100m horizons at station PS7 is representative of the main basin of Puget Sound.

The results of the computation reveal a number of interesting observations. First, the total amount of Pb (in units of metric tons per year) that is transported into Puget Sound greatly exceeds the amount that can be accounted for by advective transport through Admiralty Inlet and by sedimentation in the main basin. Assuming our estimates are correct, only about 53% of the Pb input can be accounted for by these two major sinks for Pb. One possible explanation for this discrepancy is that much of Pb is deposited in the sediments of Whidbey Basin. Since two of the major rivers discharging into the region, the Skagit and Snohomish Rivers, discharge directly into Whidbey Basin, this explanation does not seem unreasonable. Furthermore, some of the Skagit River discharge is transported directly into the eastern Strait of Juan de Fuca through Deception Pass. At this point we have no estimate of the amount of Pb that is exported out of region through the Pass, although it could be significant. If we assume that all of the Pb from Skagit and Snohomish Rivers is not transported into the main basin, then the Pb sinks in the main basin exceed the sources by about 29% (151.2 vs. 117.1 mt/yr). These results seem to suggest that some component of the Pb from Skagit and Snohomish Rivers enters the main basin. However, considering the uncertainties of the calculations we cannot be certain of this conclusion at the present time.

Another observation that can be made about the Pb budget is that since the advent of clean procedures for the determination of trace metals in the Puget Sound region, the fluxes of Pb associated with natural inputs have been revised downward; whereas, the anthropogenic inputs have increased. The net effect is that the anthropogenic inputs comprise a larger fraction (>20%) of the total Pb input into the main basin. This fraction could be higher if most of the sediments from the Skagit and Snohomish Rivers are indeed deposited in Whidbey Basin. This result may explain, in part, why the near-surface sediments of the main basin are significantly enriched in Pb relative to older sediments; the anthropogenic input of Pb has undoubtedly increased with time over the past century.

The vertical transport of Pb based on the sediment trap data is about 54% of the total Pb that is buried within the sediments of the main basin. This difference might be indicating that there are regional variations of particulate Pb of fluxes within the Sound or it might be due to the fact that deep water advection of particulate material plays an important role in the Pb budget. The sediment trap data were averaged from the 50 m and 100 m sediment traps at PS7 and, consequently, advection and eventual sedimentation of particulate material containing Pb along the bottom would not be included in the calculation. Since the Pb concentrations in the underlying sediments are about a factor 2.0 lower than the sediment trap material, an additional source for the sedimentary Pb seems likely. More information on regional variations of Pb fluxes in sediment traps and Pb accumulations in sediments is needed before a completely definitive comparison of this kind can be made.

## VII. NEEDS FOR FUTURE STUDIES

The trace element studies to date provide new insight into the mechanisms of transport and deposition of toxic trace metals in Puget Sound. However, the data are sparse and a number of important assumptions need to be verified. From a budgetary point of view the data on sedimentation processes are inadequate from several standpoints. The  $^{210}\text{Pb}$  sedimentation rates need to be corrected for the effects of bioturbation. Some of the gravity core data need to be verified with box core data. At present, there is very little information on the variability of cross-channel sedimentation processes. Also, almost nothing is known about sedimentation processes in Whidbey Basin.

With regard to the other components of the metals budget, more information is required on stormwater runoff, hydraulic transport across the sills, and regional variability of metal fluxes in suspended material.

Lastly, more work is needed on irrigation processes and the metal distributions in the interstitial porewaters. We need to understand more about the relationships between biological and diagenetic processes in the sediments and metal fluxes across the sediment-seawater interface.

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## 2.5. TRANSPORT AND TRANSFORMATION OF POLYCYCLIC AROMATICS

### I. INTRODUCTION

#### A. General Nature and Scope of Study

The purpose of this study is to quantitatively assess the origin, transport and ultimate fate of organic pollutants introduced into an urbanized estuary. The classes of pollutant compounds common to estuaries include polycyclic aromatic hydrocarbons (PAH) (3 ring and larger), polychlorinated biphenyls (PCB), and chlorinated pesticides. These compounds are introduced into the marine environment from both point and diffuse sources, and ultimately are incorporated into sediments and tissues of marine organisms. Because many of these compounds or their oxidation products are mutagenic and/or carcinogenic, serious alterations to the health and structure of marine biological communities can occur (Coombs, et al., 1976; Harvey, 1982).

Our principal focus in the current research effort is on processes that lead to the accumulation of polycyclic aromatic hydrocarbons in marine sediments or in the food of marine organisms. Most of the compounds are lipid soluble and are commonly associated with organic-rich particles. Thus, urbanized estuaries with fine-grained sedimentary basins will tend to accumulate these compounds. Puget Sound is a fjord-like estuary with these characteristics and represents an ideal system in which to study the transport and fate of particulate pollutants.

#### B. Objectives

The major objectives addressed by this program are (PDP, 1982):

- Identify and quantify the major sources of toxic organic compounds to the waters of Puget Sound.
- Identify and quantify the significant transport processes leading to deposition or removal of these compounds from the system.
- Evaluate the physical/chemical sorption properties of suspended matter and its capacity to retain toxic organics.
- Provide estimates of the residence times of organic pollutants in the water and sediment reservoirs given time varying input rates.

The foregoing objectives address the transport and fate of a wide variety of toxic organic compounds. Currently we are studying the sources and transports of polycyclic aromatic hydrocarbons (PAH) in Puget Sound because of their toxicity, ubiquitousness, and chemical stability in the marine environment. Our intent is to expand our capabilities into the chlorinated organics (e.g. pesticides, PCB) in the near future as personnel and financial resources are made available.

Our program is ongoing and cooperative with current research activities in Puget Sound. The observational program is cognizant of and interfaced with other organic geochemical research programs in Puget Sound funded by OMPA, EPA, and METRO.

Our research started in the Duwamish River, a small river discharging into Elliott Bay. It was chosen for study because of its observational tractability. Almost all industrialization is limited to the tidally-dominated lower reaches, although a source of organic pollutants is located at Renton, Washington, in the form of a secondary wastewater discharge. This study was designed to seasonally characterize the particulate organic constituents along the river as well as the composition and quantity of organic constituents introduced by METRO at Renton, WA. From this investigation, the transports of both natural and anthropogenically-introduced organics were obtained.

During the past two years, emphasis was placed on specific transport processes in the main basin. The goal is to perform an inventory and transport budget of selected organic constituents in the main basin and balance this against known inputs. From a knowledge of input and removal rates, residence times and transformation rates can be estimated. These critical environmental parameters are required if meaningful impact scenarios are to be constructed.

#### C. Relevance to Marine Pollution

The goal of most environmental assessment programs is to identify impending environmental deterioration before it becomes a social or political issue. The casual or deliberate use of marine waters for the disposal of toxic wastes creates the potential for harm. Thus, the consequences of pollutant discharge must be examined in terms of sources, kinds of materials, input rates, redistribution of toxic components by physical transport, depositional processes, and chemical and biochemical transformations. As the contaminant levels increase in a given system, its ability to accomodate increased chemical stress becomes a function of these internal chemical, biological and physical transport processes.

The polycyclic aromatic hydrocarbons (PAH) are known to adversely affect the marine biological community. By analogy with other biological systems that have been studied, these compounds may be mutagenic and carcinogenic to economically important marine species or to their food supply (Harvey, 1982). PAH are pervasive in our environment and arise from a multiplicity of sources. Because these compounds are likely to increase significantly in the marine environment as the population increases, there is a need to understand their origin, modes of transport, chemical and biochemical degradation rates, and their net accumulation rate in the marine environment. Without these dynamic considerations, input rates of toxic materials cannot be related to environmental accumulation rates or to the deterioration of marine biological communities.

## II. CURRENT STATE OF KNOWLEDGE

Innumerable organic compounds are introduced daily into the atmosphere and natural waters from a myriad of natural and anthropogenic sources. Of these, only a few compound classes are considered environmentally significant, and as such, may cause significant harm to living organisms. Among the compound classes receiving the most attention currently are the polycyclic aromatic hydrocarbons (PAH).

The PAH are constituents of crude oil and refined products (Clark and Brown, 1977), and also are produced through the combustion of fossil fuels in automobiles, power plants, and by natural fires (Blumer and Youngblood, 1975; Baum, 1978; Hites et al., 1980). The most labile components are the two and three ring arenes, which are photochemically reactive (Baum, 1978) and biochemically metabolized (Malins et al., 1979; Sims and Grover, 1974; Varanasi and Malins, 1977). However, the 3-, 4-, and 5-ring arenes are more stable and tend to persist in soil and marine sediments (Giger and Blumer, 1974; Blumer and Youngblood, 1975; Hites, et al., 1980). In remote areas, the principal mode of transport of PAH appears to be airborne particulates (Baum, 1978; Hites et al., 1980; Gschwend and Hites, 1981), but in highly urbanized areas PAH are also introduced in surface runoff and wastewater discharge (Lake et al., 1979; Hites et al., 1980; Barrick, 1982).

The multi-ring aromatics (3-ring and greater) are less soluble than the 1-, and 2-ring aromatics, and tend to be associated with lipid-rich organics (Baum, 1978). For example, the solubility of naphthalene in seawater is approximately 20mg/L, whereas phenanthrene and fluoranthene are 0.6 mg/L and 0.1 mg/L respectively (Neff, 1979). In general, the greater the number of rings, the lower the solubility.

During the past ten years, organic geochemical studies in Puget Sound have concentrated primarily on the abundance of aliphatic hydrocarbons in marine organisms and bottom sediments. The early work on the distributions of petroleum hydrocarbons can be found in the reports by Clark and his co-workers (Clark et al, 1973; Clark and Finley, 1973; Clark and Finley, 1974; Clark et al., 1975). This work emphasized the distributions of aliphatic hydrocarbons with little or no quantitative assessment of the aromatic fraction.

In recent years, however, Puget Sound MESA has completed extensive baseline studies on the distributions of organic compounds, including PAH in sediments (Malins et al., 1980; Riley et al., 1980). The dominant multi-ring aromatic compounds found in surficial marine sediments and in suspended matter were phenanthrene, fluoranthene, pyrene, perylene, benz(b)fluoranthene, and benz(k)fluoranthene. The highest concentrations were observed in Elliott Bay and Commencement Bay, ports for the cities of Seattle and Tacoma. In Elliott Bay, for example, concentrations of phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(e)pyrene, and benzo(a)pyrene ranged from 2-11 µg/g in the most contaminated sediments to a low of 3-20 ng/g in coarser grained sediments. Similar results were obtained in Commencement Bay (Malins, et al., 1980). Concentrations of the same compounds in fish livers were generally below the threshold level of



50-100 ng/g of dry weight tissue, however, some benthic feeding organisms did show enrichments in body tissues. Clams taken from the Duwamish Waterway showed elevated concentration of fluoranthene, (1.3 ppm), pyrene (1.0 ppm), benz(a)anthracene (1.0 ppm) and chrysene (0.6 ppm) (Malins et al., 1980). In more pristine areas such as Port Madison and Case Inlet, the levels of PAH were generally in the range 10-60 ng/g of dry weight tissue or a factor of 20-60 less. These compounds are oxidized by organisms at varying rates, hence the concentration levels in liver and tissue represent a balance between intake and metabolism.

Much of the work to date has emphasized distributions, with little emphasis on transport mechanisms and processes. However, a detailed study of the vertical flux of PAH compounds was conducted in Dabob Bay, an embayment of Hood Canal by Prah1 and Carpenter (1979). They observed that the PAH composition of the sediment trap material was the same as the composition of the receiving sediments. Examination of the sediment trap material revealed the source to be zooplankton fecal material. Apparently, the arenes are adsorbed to particles that are ingested by zooplankton and subsequently removed from the water column via fecal pellet transport.

In a study of the hydrocarbon composition of combined sewer/stormwater runoff effluent from METRO (Seattle), Barrick (1982) estimated sources of PAH as well as their per capita input rates. Based on his analysis, arenes of 3 or more rings are mostly derived from storm water runoff. The total contribution of 3- to 7-ring aromatics from the METRO Westpoint facility (primary treatment) was estimated to 1MT/yr. The 4- to 7-ring compounds are accumulating in the bottom sediments of the main basin of Puget Sound.

Other indicators of anthropogenic input include the unresolved complex mixture (UCM) and the sum of the aliphatic hydrocarbons ( $\Sigma$ ALK). Both complex mixtures are elevated in Puget Sound sediments near urban centers and show a chronology indicative of population growth during the past 60 years (Barrick et al., 1980).

### III. STUDY AREA

The study area encompasses the Green Duwamish River and the main basin of Puget Sound as described in the Executive Summary.

### IV. METHODS

#### A. Field sampling

Sediment traps were deployed at four depths (20 m, 50 m, 160 m, and 200 m) at Station PS7. Every 10 weeks the traps were recovered, the contents removed, and the traps redeployed, providing a continuous particle flux record from December 1980 through December 1981.

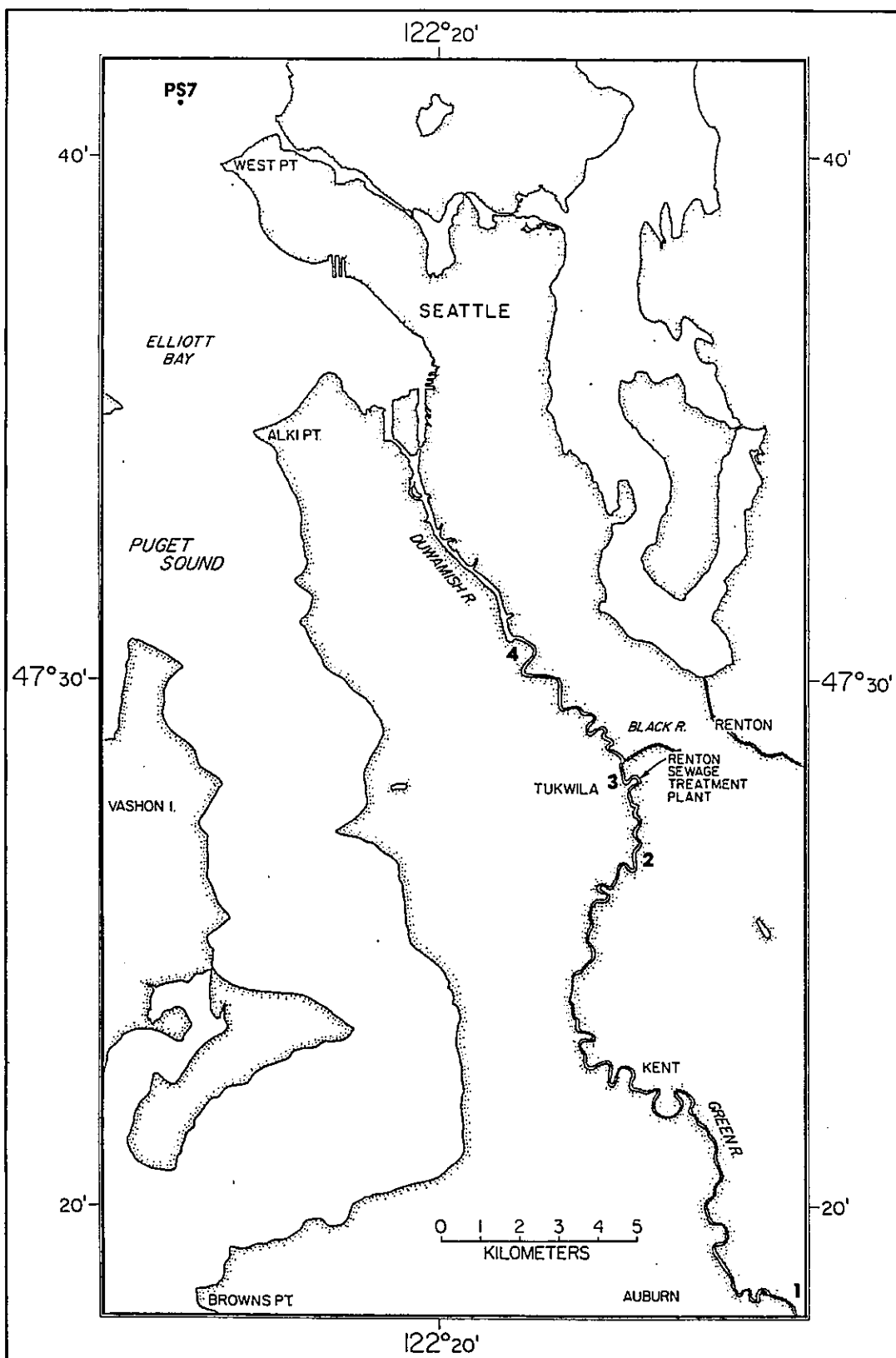


Figure 2.5.1. Station locations on the Green-Duwamish River and in Puget Sound.

The sediment traps were sequential sampling, which allowed material to be collected over weekly intervals (Baker and Milburn, 1983). The particles are concentrated at the bottom by a steep walled funnel which leads to one of 10 separate sampling tubes containing sodium azide to reduce microbial degradation. A self-contained sampling mechanism rotates a new tube into position under the funnel at preset intervals (seven days during this experiment). Upon retrieval the samples were split volumetrically for various analyses. The material from the ten tubes was combined to obtain sufficient suspended matter for hydrocarbon analyses. The surface sediment was collected with a box core with deeper samples being recovered with a gravity core.

River stations were occupied for 18 to 30 hours during which water was retrieved midchannel with a well-head pump and directed into a high-speed continuous-flow centrifuge operating at 21,000 gravitational units. The flow rate was regulated to 0.5L/min. Centrifuge efficiency, based on 0.4  $\mu$ m Nuclepore filtration, averaged 80% at Station 3 (Bates et al., 1983). Wastewater composites were obtained concurrently and filtered through glass fiber filters. Bottom sediments were retrieved with a Van Veen grab sampler.

#### B. Laboratory analyses

Samples were Soxhlet extracted for 48 hours in methanol/methylene chloride mixture. Approximately 97% of the extractable hydrocarbon were recovered in this period. Samples were washed with distilled water to remove the methanol and eluted through a clean-up silica gel column. Aliphatic and aromatic hydrocarbons were separated on a second silica gel column with petroleum ether/methylene chloride mixtures. The aromatic fraction was subsequently passed through a Sephadex column to remove methyl esters of fatty acids.

Microgravimetry, gas chromatography and GS-MS were performed to determine fraction and component concentrations. Samples were analyzed on Hewlett Packard model 5730A or 5880 gas chromatographs equipped with FID detectors and programmed from 70°C and 270°C at 4°/min. Compound separations and quantitations were accomplished with an SP-2100 glass capillary or an OV-1 fused silica column for the aliphatics and an SE-54 fused silica column for the aromatics. The latter column was used in a Hewlett Packard 5993 GC-MS for analyzing the more complicated fractions. The analytical precision of this method expressed as the percent standard deviation of the mean was 10%.

The total carbon and nitrogen contents of the sediments were determined by the micro-Dumas combustion procedure (Sharp, 1974), using a Hewlett-Packard C-H-N analyzer.

## V. RESULTS AND DISCUSSION

### A. Duwamish River Studies

The hydrocarbon composition of suspended matter and bottom sediments in the Green-Duwamish River indicated five distinguishable sources: planktonic and algal production, plant wax contribution, highway run-off, sewage effluent and erosion of river bed sediments.

Aquatic production was evident in the predominance of pentadecane, and heptadecane common to plankton (Wakeham, 1976) and several heptadecenes found in plankton and algae (Philp et al., 1977). Concentrations of these compounds decreased dramatically in the winter, verifying that the source was planktonic.

Table 1 summarizes the hydrocarbon compositional parameters and concentrations of the riverine suspended matter. The carbon preference index is a weighted ratio of odd-to even-carbon n-alkanes (Clark and Finley, 1974). For hydrocarbons C<sub>21</sub> through C<sub>32</sub>, this index is a relative indicator of plant wax sources. Values between 4 and 10 suggest vascular land plant production of alkanes (Clark and Blumer, 1967). This index was highest at the upper stations reflecting the forested source region. The ratio decreased down river corresponding to a smaller contribution from terrestrial plants.

The influence of runoff is reflected by changes in the carbon preference index for the low molecular weight hydrocarbon fraction, C<sub>13</sub> through C<sub>20</sub>. This index drops between Stations 1 and 2 reflecting the increase in concentrations of C<sub>14</sub> and C<sub>16</sub> relative to the algal and planktonic compounds, C<sub>15</sub> and C<sub>17</sub>. Surface and bridge runoff are indicated by high concentration of the lower molecular weight hydrocarbons and reflect index values of unity (Clark and Brown, 1977). The changes between Stations 1 and 2 are likely due to diffuse injections of surface runoff containing fossil fuel hydrocarbon. Increases in concentrations of combustion polycyclic aromatic hydrocarbons derived from fossil fuel sources also verify runoff contamination. A visual survey of the Green River located 49 pipes between 2 stations, 29 of which transport highway runoff.

The effect of sewage effluent is evident in most parameters, especially in the concentration of total saturates. Concentrations in the effluent are an order of magnitude greater than river values at station 3, 0.5 km downstream of the outfall. Concentrations at this station are greater than those reported for surface sediment in the Gulf of Mexico (Gearing et al., 1976), Narragansett Bay (Wade and Quinn, 1979), and Puget Sound (Barrick et al, 1980). The relative magnitude of the unresolved complex mixture also has been used to approximate anthropogenic contributions to hydrocarbon assemblages (Farrington and Quinn, 1973). This indicator shows variations similar to those in the total saturates profile in the river.

Bottom sediments at Stations 2 and 3 revealed a sedimentary source of hydrocarbons with terpenoids as major components. Diterpenoids are

Table 2.5.1. Concentrations and compositional parameters of hydrocarbons associated with suspended solids recovered from the Green-Duwamish River and Renton METRO sewage effluent.

	Total Saturates (µg/g)	UCM (µg/g)	CPI <sub>14_20</sub>	CPI <sub>20_32</sub>	Pr/C <sub>17</sub>	pr/Phy
<u>October 1978</u>						
Station 1	100	52	11	7.5	0.04	2.2
Station 2	300	120	2.6	8.0	0.17	2.9
Effluent	8,700	3,500	2.3	1.1	0.42	1.3
Station 3	2,000	600	3.1	2.6	0.28	1.5
<u>December 1978</u>						
Station 1	630	240	2.5	14	0.50	1.1
Station 2	410	120	1.6	10	0.60	1.5
Effluent	12,000	4,100	1.1	1.6	1.5	1.2
Station 3	740	3,200	1.0	5.0	0.68	1.8
<u>October 1980</u>						
Station 1	280	70	25	8.5	0.03	2.7
Station 2	480	200	10	6.1	0.06	2.3
Effluent	18,000	9,500	4.6	1.3	0.31	0.9
Station 3	4,200	2,900	8.0	1.5	0.19	1.1
Station 4	2,100	1,100	3.4	2.1	0.40	1.7

common isoprenoids in fossils and tree resins (Streibl and Herout, 1969). The Green-Duwamish River diterpenoids were present in total concentrations of 4.2 ug/g at Station 2 and 0.4 ng/g at Station 3. These hydrocarbons were detected in suspended-matter extracts only in February 1981, a period of high discharge. Terpenoids are present in coals (Streibl and Herout, 1969) and fossil resins (Grantham and Douglas, 1980). A possible but untested source of terpenoids in the coarse Green River sediments is coal fragments. The river drainage basin contains several coal outcrops from the Hammer Bluff formation (upper Miocene) and Puget Group (upper Eocene), both of which were mined intermittently for 100 years (Mullineaux, 1970). The mobilization of these compounds during periods of high runoff illustrates the importance of river discharge and particle size in the transport of organics down river. Consequently, the random measurement of suspended matter is not necessarily an accurate estimate of hydrocarbons reaching coastal waters via rivers.

The concentrations of quantifiable PAH in the suspended matter of the Duwamish River is shown in Table 2. These measurements were made in October 1980 and reflect low flow conditions. At Station 1 above Auburn, the dominant PAH were retene and perylene, all others were less than 70 ng/g dry weight. The influence of stormwater runoff is seen at Station 2 where the concentrations of the combustion PAH have increased by a factor of two or more. Presumably the source is numerous small pipes draining the local roads between Station 1 and 2. Concentrations of combustion PAH associated with suspended matter are much higher in the METRO effluent than at Station 2. Enrichment factors run from 1.9 for benz(e)pyrene to more than 21 for benz(a)anthracene. The concentrations of the 3-ring aromatics in the effluent are similar to those measured in the METRO Westpoint discharge (Barrick, 1982). As expected the naturally occurring PAH, retene and perylene, are low in the effluent, indicating they do not principally arise from petroleum or combustion products. The Green River contribution of combustion PAH used in subsequent budget calculations is based on measurements at Station 2.

Transport of suspended hydrocarbons was assessed quantitatively from a knowledge of hydrocarbon concentrations, the magnitude of the suspended load, and river discharge (Fig. 2). Imbalances between stations were examined for sources and sinks. Because major point sources of sediment and hydrocarbons between Stations 1 and 2 are unknown, transports at these two stations can be directly compared. The heavier hydrocarbons  $C_{21}$  through  $C_{32}$  exhibited conservative behavior; increases in suspended load and water discharge merely diluted the heavier hydrocarbons. The increase in the even-carbon low molecular weight hydrocarbons however, indicated a source of these compounds in the upper river. The transport of seven combustion PAH in suspended sediment also showed an increase in the upper river. Such a source, contributing both PAH and low molecular weight aliphatics would be highway runoff. Hydrocarbon transports at Stations 3 and 4 were also compared, and found to be in near agreement, indicating the dominance of a dilution effect.

Table 2.5.2. Concentrations of PAH associated with suspended matter in the Green River. Measurements were made in October 1980. The combustion PAH (Prah1, 1982) are indicated by an asterisk (\*).

Location	Sta 1	Sta 2	Metro	Sta 3
ng/g (dry weight)				
phenanthrene	110	160	730	170
anthracene	23	13	260	33
fluoranthene*	67	160	660	210
pyrene*	53	170	680	270
retene	160	330	---	350
benz(a)anthracene*	14	21	440	130
chrysene*	49	130	330	140
benzofluoranthenes*	71	150	420	140
benz(e)pyrene*	40	93	180	92
benz(a)pyrene*	26	35	180	66
perylene	160	450	60	85

## TRANSPORTS OF HYDROCARBONS IN THE LOWER GREEN RIVER

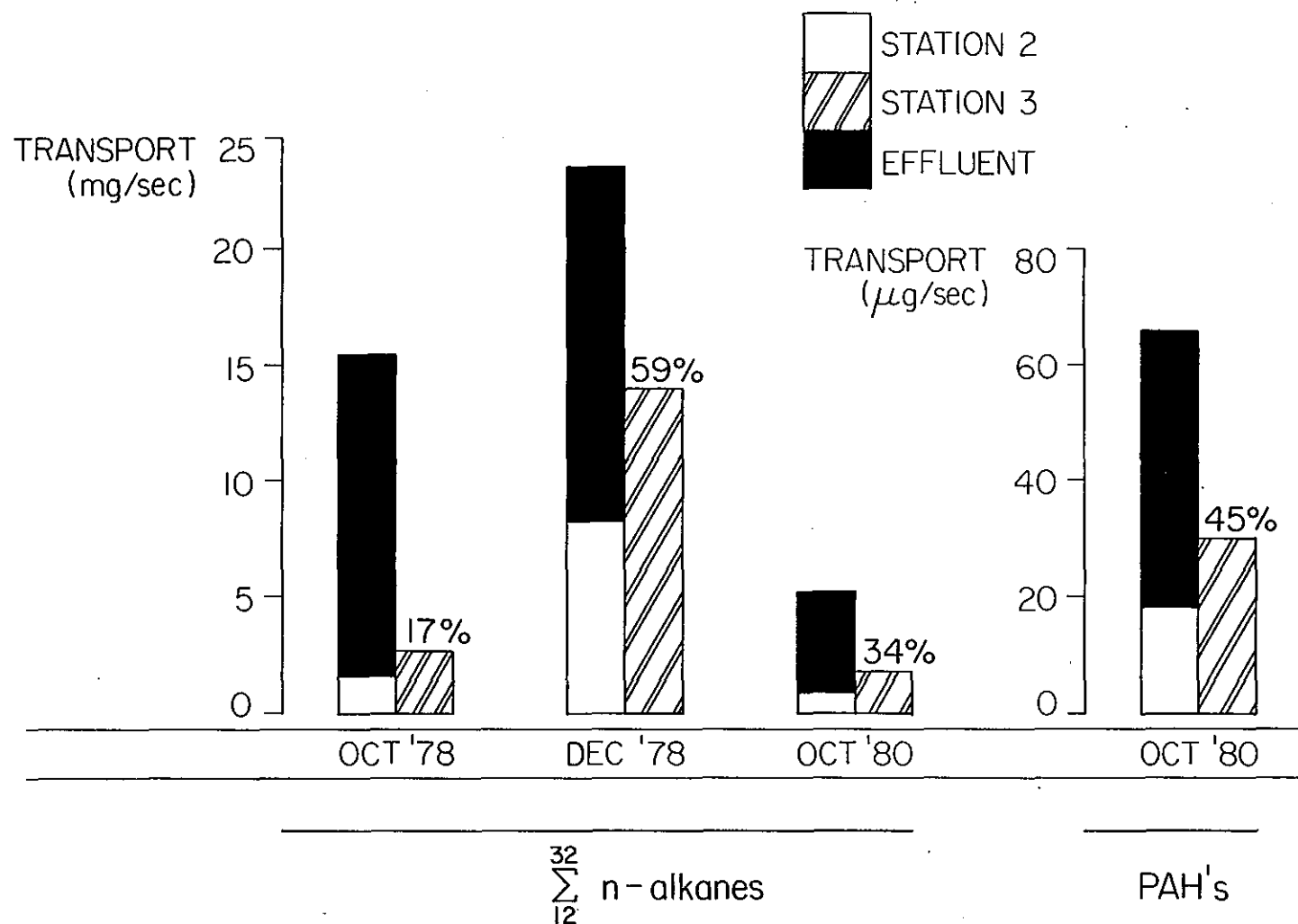


Figure 2.5.2. Transports of aliphatic and aromatic hydrocarbons at Stations 2, 3 and METRO in the lower Green River (see Fig.1 for station locations). Calculations were based on suspended solid concentrations and stream flow at the time of the measurements.



Between Stations 2 and 3, quantitative hydrocarbon data are available for one source, the sewage discharge at Renton. The hydrocarbon transport measured at Station 3 should equal the sum of the transports at station 2 and the outfall, assuming there were no intermediate sources or sinks. However, transports at Station 3 are only 17% to 59% of the sum of the transports at Station 2 and the outfall (Fig. 2). When the n-alkane data were divided into heavy and light fractions (Fig. 3), a greater loss of the heavy n-alkanes  $C_{21}$  to  $C_{32}$  (50-90%) than the lighter alkanes  $C_{13}$  to  $C_{20}$  (10-60%) is evident.

The inequality in the mass balance may be due to one or more processes. Wastewater is transported 0.5 km to the river before being injected through the diffuser. Station 3 is an additional 0.5 km downstream from the diffuser. Assuming a mean river velocity of 10 cm/s (conservative), the transport time to Station 3 is about 1.5 hrs. Significant biological modification within such a short time is highly improbable. The unresolved complex mixture (UCM), which has been shown to be quite refractory (Barrick, 1982), is also partially removed from the suspended load (Table 1).

Because the river was narrow at the point of sampling (about 15 m wide), there exists the possibility that horizontal suspended matter gradients were present. However, nutrient and suspended matter samples at three points across the river showed that the midpoint was a good average of the endpoints. It is apparent that the sampling protocol was representative.

The heavy hydrocarbon deficit between Stations 2 and 3 might have been due to an over-estimate of hydrocarbon concentration in the effluent because these samples were obtained by glass fiber filtration. Concentration of the n-alkanes in a filter sample of METRO effluent were found to be 1.4 times greater than the concentration in a centrifuge sample of the same effluent (Bates et al., 1983; in press). The transport deficits remain significant despite a correction for this bias.

The disparity is probably due to a flocculation and subsequent sedimentation of organic matter as the effluent mixes with the river water. Concurrent work at PMEL on trace metal removal in this section of the river also supports this contention (Curl et al., 1981). We would expect the less soluble, heavy hydrocarbons would be adsorbed to the particulate phase more readily from the volatile compounds accounting for greater deficits of the former (Neff, 1979).

Bottom sediments were sampled as well as suspended matter in October 1980. The highest concentrations of the UCM and total saturates were associated with the suspended matter at Station 3, while values at Station 4 were a factor of two lower. In contrast, bottom sediments at Station 4 exhibited concentrations in excess of those measured in bottom sediments at Station 3. This comparison, in conjunction with the budget deficit at Station 3, implies that suspended hydrocarbons injected by the outfall flocculate and settle to the sediment-water interface where they are transported as bedload during periods of high runoff.

## TRANSPORTS OF N-ALKANES IN THE LOWER GREEN RIVER

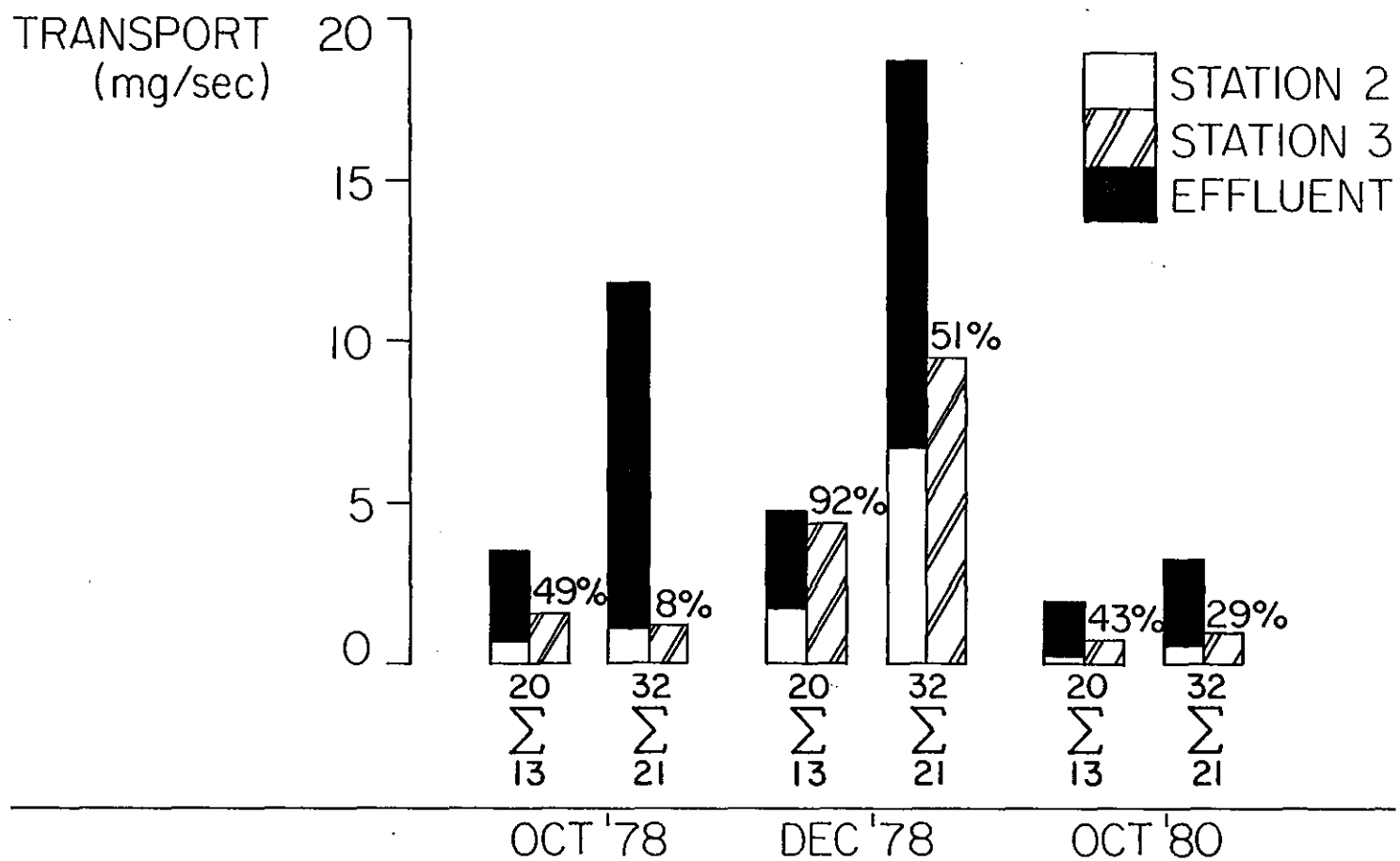


Figure 2.5.3. Transports of n-alkanes in the lower Green River at Stations 2, 3, and the METRO discharge. Calculations are based on the suspended solid concentrations and stream flow at the time of measurements.

The lower Duwamish river is a salt-wedge estuary (Tilley and Dawson, 1971). Material transported downriver in the bedload encounters the salt-wedge, where additional flocculation may occur. This region of the river exhibits relatively high sedimentation rates because of the water depth, small hydraulic head, and the counter flow of seawater along the bottom. All these factors combine to promote the flocculation and settling of particulate matter with its adsorbed organics and trace metals in the lower estuary.

The importance of the lower estuary as a collection basin for particulate-borne PAH is revealed in Table 3. Here we show a comparison of the concentrations of combustion PAH in the Duwamish River and Elliott Bay. The concentrations of PAH in the bottom sediments of the West Waterway (column 3) are 15x the level measured downstream of METRO and a factor of 7x the levels measured along the central axis of Elliott Bay. The suspended PAH were measured in the West Waterway and appear only slightly elevated above our measurements at Station 3. The agreement may be fortuitous because of sampling times and procedures. Our sample was taken in October 1980 with a high-speed centrifuge and represents a 24-hr composite. The sample taken by Riley and co-workers (1980) was taken in 2 m of water in July 4-7, 1979 with a large-volume-filtration apparatus fitted with glass fiber filters. The suspended matter concentration was 4.3 mg/L indicating a large riverine contribution of suspended particulates, but a salinity of 28 ‰ suggested significant dilution of the river component had occurred.

Nevertheless, the data clearly indicate that PAH are being enriched in the fine-grained sediments of the lower estuary. The sources of the PAH are not unequivocal, however. The report by Harper-Owes and Herrera Environmental (1981) indicate that 90% of the combined sewer overflow (CSO) is injected in the lower 5 km of the river (First South Bridge to the entrance), but that 90% of the fluvial deposition occurs between the First South Bridge and the terminus of the dredged channel (about 8.4 km). The concentration of combustion PAH at the First Avenue Street Bridge (River Km 5) was about 700 ppb(w) (Station 10019; Malins et al., 1981), or approximately equal to the 900 ppb(w) measured by us at Station 3 (Table 3). This comparison would argue that the enriched levels of PAH found in the lower river are not derived from the fluvial input unless selective flocculation and enrichment have occurred within the salt wedge portion of the estuary. This, of course, is a possibility.

Another useful observation was the relative contributions of CSO and PAH in the East Waterway. The report by Harper-Owes and Herrera Environmental (1981) indicates that between the years 1974 and 1977, the mean CSO discharge to the East Waterway was 3.5 x the discharge in the West Waterway, yet the concentration of combustion PAH in the East Waterway sediments was 3700 ppb(w), compared to the concentration in the West Waterway of 24,500 ppb(w), or a factor of 6 higher (Malins, et al., 1980) (Table 3 reflects an average between Station 10039 and 10038 in the East and West Waterways; Malins et al., 1980). A grain size analysis of the sediments from the two locations shows the East Waterway to have the highest mud ratio (W.W.  $\phi$  = 7.1; E.W.  $\phi$  = 8.5), although the organic carbon contents are about the same (1.8%).

Table 2.5.3. A comparison of the concentrations of combustion PAH at three locations along the Duwamish River and Elliott Bay.

Compound	Sta 3 <sup>1</sup>	Harbor Is <sup>2</sup>	Harbor Is <sup>3</sup>	Elliott Bay <sup>4</sup>
Fluoranthene	210	360	2700	390
Pyrene	270	580	2200	480
Benz(a)anthracene	130	70	1900	220
Chrysene	140	120	1700	200
Benzofluoranthenes	140	-	4900	420
Benz(e)pyrene	92	-	1100	190
Benz(a)pyrene	66	<10	1000	130
Totals	908	>1130	15,500	2,030

1/ Suspended matter collected at Station 3, October 1980 (PMEL).

2/ Suspended matter collected in West Waterway, July 4-7, 1979. (Riley et al., 1980).

3/ Bottom sediments from Stations 10031 and 10038, West Waterway (Malins et al., 1980).

4/ Bottom sediments from Stations 10038 and 10039, Elliott Bay (Malins et al., 1980).

These observations would suggest that the CSO's are not a major source of PAH on an annual basis or that flocculation and enrichment is a more important process in the West Waterway. That the West Waterway is dredged and provides a major conduit for seawater in the estuary also may be a contributing factor.

Depending on river discharge and tidal amplitude, the toe of the salt wedge ( $S = 25\text{‰}$ ) is found between 6-10 Km (Stoner et al., 1975; Fischer, 1975), whereas the highest concentrations of combustion PAH were observed near river Km 1 (we assume the sample was representative). The depth of water was 15-20 m (Malins et al., 1980).

The layer of no net estuarine flow in Elliott Bay is 40-70 m (Silcox et al., 1981), although this layer shoals near the Duwamish River. This region also shows a suspended particulate minimum, suggesting insufficient turbulence to keep particles suspended (Baker, 1982). Extrapolation of suspended matter concentration isopleth (Fig. 5; Baker, 1982) suggests that a region of minimum turbulence occurs at water depths of about 15-25 m in summer, which is coincident with the sampling depth by Malins and co-workers (1980).

The deposition of combustion PAH in a minimum turbulence zone implies that the associated particles are of low density and/or small size and tend to accumulate with fine-grained sediments. Gschwend and Hites (1981) state that the combustion PAH are primarily associated with soot, which is material of small particle size and low density. The soot particles may arise from surface runoff or atmospheric deposition. If the previous observations are correct, then we would expect to find PAH enrichments in areas of low sedimentation. PAH would not necessarily correlate with organic carbon, but would be found in association with fine-grained particles of low density.

At present, the sources of PAH in the lower Duwamish cannot be uniquely defined, although all the heretofore mentioned sources are undoubtedly important. The concentration of PAH in bottom sediments near and in the Duwamish River appears to be a function of the sources, flocculation characteristics of the salt wedge, and the near field depositional environment. The accumulation of PAH in the West Waterway and north of Harbor Island is an artifact at low sedimentation rates and the proximity of nearby sources.

#### B. Vertical flux of hydrocarbons at Station PS7

In this section we describe the seasonal flux of PAH and other hydrocarbons at Station PS7 located near Seattle (Fig. 1). Sequential sampling sediment traps were placed at 20, 50, 100, 160 and 200 m; each tube collected material for approximately one week. Measurements extended from December 1980 to December 1981. Because a small amount of material was collected each week in the upper traps, a ten week composite was analyzed for aliphatic and aromatic hydrocarbons.

Aliphatic and aromatic hydrocarbon fractions of the various sediment trap samples from PS7 were compositionally similar to each other and to

SUSPENDED MATTER 160m PS7  
APRIL 23-JULY 10, 1980

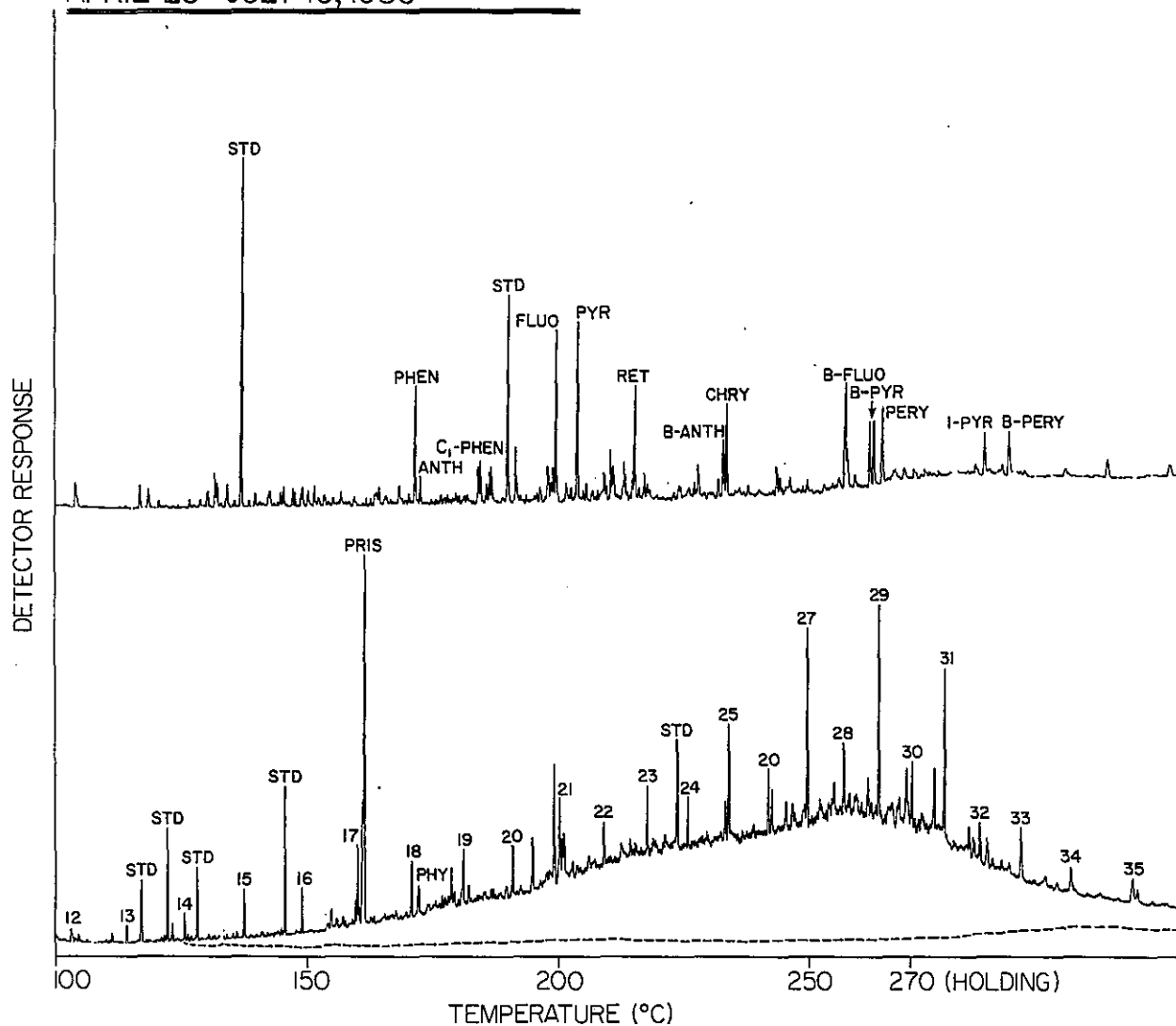


Figure 2.5.4. Chromatograms of hydrocarbons associated with suspended matter taken from 160 m at Station PS7. Polycyclic aromatic hydrocarbons are shown in the upper panel (a), while aliphatics are shown in the lower panel (b). The unresolved complex mixture (UCM) is represented by the difference between the baseline (dashed line) and the baseline of the chromatogram.

the surficial bottom sediments (Fig. 4). Hydrocarbon assemblages were typical of those found in other urban sedimentary environments (Barrick et al., 1980, Gschwend and Hites, 1981, and references therein).

The aliphatic hydrocarbon fraction is dominated by pristane (PRIS), the n-alkanes (summed C<sub>12</sub>-C<sub>35</sub>), and an unresolved complex mixture (UCM). Pristane is produced by marine zooplankton (Blumer et al., 1963). The low-molecular-weight, C<sub>14</sub>-C<sub>20</sub> n-alkanes, with a carbon preference index (CPI) of  $1.59 \pm 20\%$  (one standard deviation expressed as a percentage of the mean), result from a mixed contribution of marine plankton, terrestrial plants, and petroleum. The higher molecular weight C<sub>21</sub>-C<sub>35</sub> n-alkanes (CPI =  $2.20 \pm 18\%$ ) are indicative of terrestrial plant waxes and petroleum (Clark and Blumer, 1967). The UCM (computed after Barrick et al., 1980) is indicative of an anthropogenic petroleum input (Farrington and Quinn, 1973).

The PAH fraction (Fig. 4a) contains compounds from both natural (retene (RET) and perylene (PERY)) and anthropogenic sources. The sum of nine PAH (fluoranthene (FLUO), pyrene (PYR), benz(a)anthracene (B-ANTH), chrysene (CHRY), benzofluoranthenes (B-FLUO), benzo(e)- and benzo(a)pyrene (B-PYR), indeno(cd) pyrene (I-PYR), and benzoperylene (B-PERY)) and is referred to as total combustion PAH (Prahl, 1982).

Particulate hydrocarbon and total carbon concentrations decrease with depth in the water column. The concentrations given in Table 4 are averages of the 5- to 10-week deployments. The stated errors represent one standard deviation expressed as a percentage of the mean. The large deviations in carbon, the n-alkanes and pristane reflect the seasonal variability of biological production. The individual carbon concentrations for each sediment trap sample are shown in Fig. 5. The percent carbon in the near surface suspended matter samples was highest during the April-June deployment, whereas the samples from 200 m and the surface bottom sediments showed little seasonal variability. This observation is due to the effects of resuspension in the bottom boundary layer (see Baker, this report), which remobilizes carbon deficient sediments and carbon utilization in the water column. The linear correlations of the various hydrocarbon fractions (table 5) indicate a similar seasonal trend for pristane and the C<sub>14-20</sub> n-alkanes. The PAH concentrations showed no significant seasonal variability.

The vertical distribution of PAH, UCM, and n-alkane concentrations in the underlying sediments at PS7 show distinctly different profiles (Fig. 6). Provisional dates have been assigned from the Pb-210 data (.75 cm/yr) of Barrick (1982) and E. Crecelius (personal communication). PAH concentrations increase above background around 1900 and reach a maximum at about 1950. Similar PAH profiles were observed in Dabob Bay (Prahl and Carpenter, 1979), Lake Constance (Grimmer, et al., 1977), and in both remote and urban sites in the northeastern United States (Gschwend and Hites, 1982). UCM and n-alkane concentrations increase above background around 1900 and peak about 1965. Organic carbon in this core decreased from 2% in the surface sediments to 1.6% at depth.

Table 2.5.4. Hydrocarbon ( $\mu\text{g/g}$ ) and total carbon ( $\text{mg/g}$ ) concentrations for sediment trap suspended matter and bottom sediments (0-2 cm). Concentrations are averages of five deployments  $\pm$  one standard deviation expressed as a percentage of the mean.

Depth (m)	PAH	ALK 14-20 ( $\mu\text{g/g}$ )	ALK 21-35 ( $\mu\text{g/g}$ )	Pristane	UCM	Carbon ( $\text{mg/g}$ )
50	3.1 $\pm$ 5%	8.6 $\pm$ 45%	16 $\pm$ 24%	15 $\pm$ 100%	690 $\pm$ 13%	49 $\pm$ 44%
100	2.4 $\pm$ 23%	4.3 $\pm$ 37%	12 $\pm$ 21%	6.0 $\pm$ 90%	500 $\pm$ 27%	34 $\pm$ 25%
160	1.5 $\pm$ 9%	1.4 $\pm$ 25%	6.0 $\pm$ 35%	1.5 $\pm$ 60%	240 $\pm$ 19%	29 $\pm$ 6%
200	1.2 $\pm$ 21%	.92 $\pm$ 41%	4.7 $\pm$ 14%	.60 $\pm$ 50%	190 $\pm$ 25%	26 $\pm$ 3%
0-2cm	1.0 $\pm$ 24%	.45 $\pm$ 16%	3.7 $\pm$ 2%	.20 $\pm$ 30%	140 $\pm$ 10%	20 $\pm$ 5%

Table 2.5.5. Linear correlations of total carbon and hydrocarbon concentrations in sediment trap suspended matter (n=22).

$r^2$	ALK 14-20	ALK 21-35	Pristane	UCM	PAH
Carbon	.85	.61	.81	.56	.35
ALK 14-20		.79	.75	.71	.35
ALK 21-35			.66	.70	.44
Pristane				.64	.29
UCM					.30



Hydrocarbon and total carbon fluxes are the product of the concentration and the sedimentation rate in each trap. Flux measurements in the lower traps (160 and 200 m) are largely influenced by bottom resuspension (E. Baker, this report). The fluxes for sediment trap suspended matter shown in Table 6 are averages of the 50 and 100 meter traps averaged over the 5 deployments. As mentioned above, the surface sediment flux was calculated from the Pb-210 sedimentation rate (.75 cm/yr) and the surface sediment hydrocarbon concentration. The individual PAH fluxes to the surface sediments are equivalent to those given by Gschwend and Hites (1982) for their average urban environment.

The sedimentary hydrocarbon record at PS7 (Fig. 6) shows increased concentrations paralleling the urbanization of the Seattle area. The maximum PAH concentrations were found in sediments deposited in 1940-1950. Gschwend and Hites (1982) have suggested this maxima corresponds to the transition from home heating using coal to that using oil and gas. The dwelling units using coal or wood in the Seattle area decreased from 35,856 in 1950 to 14,453 in 1956 (Seattle Times Consumer analysis, 1950 and 1956), which supports this hypothesis. The ubiquity of this PAH maximum in sediment cores from Europe and both anoxic and oxic environment in the U.S. has lead Gschwend and Hites (1981) to suggest that this profile may serve as a sedimentary time marker. The PAH concentrations in the sediments deposited during the last 15 years are consistently 10 times that of background.

The sedimentary history of UCM and n-alkane concentrations show a similar increase with increased industrialization of the Seattle area. The maximum concentrations are found at ~1965. This is when Seattle's waste treatment plant came on line (METRO-Westpoint). Prior to this time, much of Seattle's waste sewage was dumped untreated into Puget Sound. The proximity of the Westpoint discharge to station PS7 lends support to this conclusion. It should be noted, however, that the maximum in UCM and n-alkanes is subtle and rests upon two or three data points. Similar profiles of particulate trace metals were made at PS7 and only arsenic, silver, and lead show discernable decreases with depth (Feely, this report). With the possible exception of Pb, none show a maximum in concentration at about 10cm or 1965. This would imply that the sources of some trace metals are different than organics or that their input rates have not varied significantly during the past 200 years. This of course does not seem to be the case for the aforementioned metals. Given the lack of corroboration by the trace metal data, our explanation for the maximum in UCM and n-alkanes remains provisional.

The UCM, composed of branched and cyclic alkanes, and the straight chain aliphatics are rather uniform over the last 8 years (Fig. 6). Because the n-alkanes and the UCM are biodegradable, at least over the long term, the uniform distributions suggest a balance between input and degradation, possibly modulated by bioturbation. The other factor is the source strength. Whereas improvements have been made in the quality of waste discharge to the Puget Sound basin, it is also true that the discharge volume has increased. Apparently we are at a juncture in which current input levels are approximately balanced by natural removal processes.

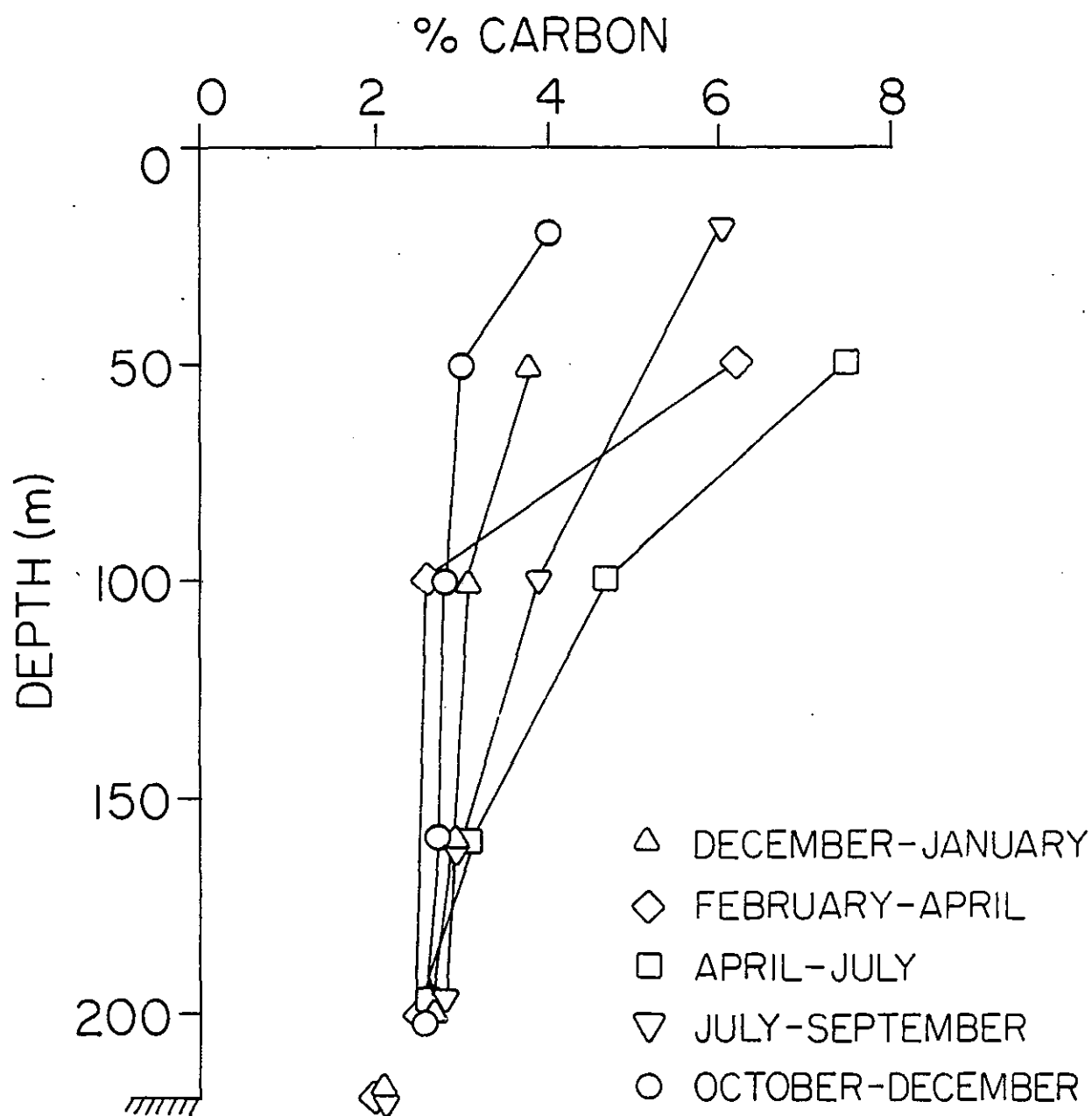


Figure 2.5.5. Seasonal variability of total particulate carbon (mostly TOC) at Station PS7 (see Fig. 1). Analysis was made on material collected in sediment traps from the nominal depths of 20, 50, 100, 160, and 200 m (see Baker, this report).

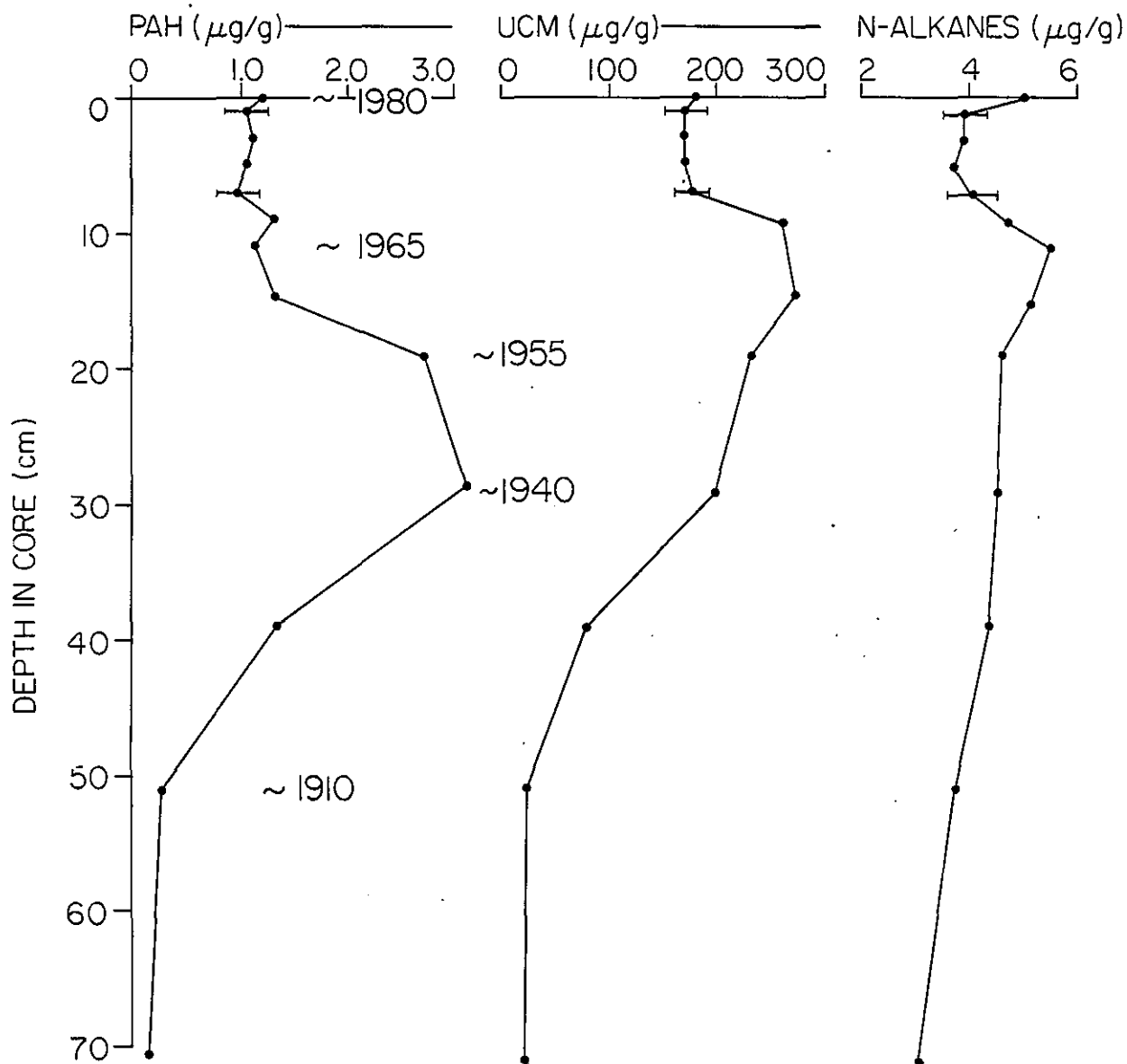


Figure 2.5.6. The vertical distributions of PAH ( $\mu\text{g/g}$ ), UCM ( $\mu\text{g/g}$ ), and n-alkanes ( $\mu\text{g/g}$ ) in the underlying sediments at Station PS7. Both box and gravity cores were used to obtain the profile. Provisional dates were assigned from a mean sedimentation rate of 0.75 cm/yr based on uncorrected Pb-210 profiles.

Table 2.5.6. Seasonally averaged fluxes of hydrocarbons ( $\mu\text{g}/\text{m}^2/\text{d}$ ), total carbon ( $\text{mg}/\text{m}^2/\text{d}$ ), and total particulate matter ( $\text{g}/\text{m}^2/\text{d}$ ) through the 50-100 m horizon. Accumulation rates in surface sediments (0-2 cm) are based on Pb-210 rates of 0.75 cm/yr. The combustion PAH are indicated by an asterisk (\*).

	Suspended matter	Surface sediment
Combustion PAH	6.7	8.5
PHEN	0.80	1.0
ANTH	0.20	0.22
C <sub>1</sub> -PHEN	0.89	1.3
FLUO*	1.2	1.5
PYR*	1.3	1.6
RET	.70	0.75
B(a)ANTH*	0.45	0.55
CHRY*	0.65	0.80
B-FLUO*	1.2	1.5
B(e)PYR*	0.55	0.65
B(a)PYR*	0.50	.60
PERY	.50	.75
I-PYR*	0.45	0.60
B-PERY*	0.53	0.70
ALK 14-20	13	3.4
ALK 21-35	32	28
Pristane	23	1.5
UCM	1500	1000
Carbon	72	150
Particulate Matter	2.5	7.5

The vertical flux of combustion PAH at PS7 are comparable to measured sedimentation fluxes (Table 6). This was not true for the LMW n-alkanes, in which the vertical flux through 50 m was several times larger than the sedimentary accumulation rate. Microbial degradation of the alkanes, particularly the LMW compounds, is presumably responsible for their low relative abundance in sediments. The similarity of the PAH fluxes suggests that these compounds are more refractory and may remain compositionally unaltered for very long periods of time. As noted by Gschwend and Hites (1981), the combustion PAH serve as a useful time marker in both lacustrine and marine sediments.

The atmospheric flux of total combustion PAH in the Seattle area is about 1  $\mu\text{g}/\text{m}^2\text{-day}$  (Prahl, 1982). This is only 15% of the observed PAH flux at PS7, the remainder is presumably derived from wastewater discharge, stormwater runoff and riverine inputs. Seasonal variations in the flux of PAH at PS7 show an apparent maximum in winter and a minimum in summer (Table 7). Because rainfall is higher in winter, the increased flux may be due to soil erosion (riverine transport), storm sewer runoff, and increased consumption of fuel oil.

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Table 2.5.7. Seasonal variations in the mean flux of PAH through the 100 m horizon at station PS7.

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Time Months	Flux $\mu\text{g}/\text{m}^2\text{-day}$
Dec.-Jan.	6.5
Feb.-Apr.	7.3
Apr.-July	4.4
July-Sept.	7.1
Oct.-Dec.	8.2

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The mean annual flow of the other rivers is about 20× the stream flow of the Duwamish River (Dexter et al., 1981). If the rivers have similar relationships between suspended matter and PAH, then the total riverine transport is 280 kg/yr (20×14kg/yr). Implicit in this calculation are the assumptions that the PAH are only associated with the fine-grained particulates (e.g., silt-clay size range) and that the final residence of these particles is the main basin of Puget Sound. Two of the major rivers discharging into the region are the Skagit and Snohomish Rivers. How much of their annual suspended load is retained in Whidbey Basin and what portion actually finds its way into the main basin is conjective at this point. The situation for the Skagit is even more obscure because some of the Skagit discharge exits directly through Deception Pass into the eastern Strait of Juan de Fuca.

Contributions of PAH from the municipal discharges are based on our measurements in the Duwamish River (METRO, Renton) and those made by Barrick (1982) in the Westpoint discharge. Whereas METRO Westpoint discharges about 60% of the total to the main basin (Barrick, 1982), contributions from other municipalities were calculated on the basis of their volume discharge.

Atmospheric deposition was computed from a mean PAH depositional flux of  $1\mu\text{g m}^{-2}\text{d}^{-1}$  (Prahl, 1982) and a total surface area of  $7.2 \times 10^8 \text{ m}^2$  (McLellan, 1954). This flux is quite similar to other urban areas (Gwchwend and Hites, 1981).

Contributions from stormwater runoff are believed to be large (Neff, 1979; Barrick, 1982), but are not quantifiable at this time. That part of stormwater runoff that is processed through primary or secondary treatment is pooled with other sewage and industrial sources, but contributions from separate stormwater discharges, either directly or indirectly (e.g. Lake Washington Ship Canal) into the main basin are not known at this time.

The transport of PAH across Admiralty Inlet is potentially large, but is also unknown. Two sets of measurements have been taken, but the samples have not been fully analyzed. The first observations were made over a 48-hr period near Admiralty Head in about 30 m of water. The mean difference in PAH concentration between ebb and flood was only 0.04  $\mu\text{g/g}$  suspended matter (dry weight). The mean PAH concentration was 0.45  $\mu\text{g/g}$ . Suspended loads on ebb and flood (averaged) were 3.8 mg/L and 4.8 mg/L respectively. The high concentrations of suspended matter suggest that resuspension was an important factor and these concentrations may not be representative of concentrations at midchannel. The second set of measurements were synoptic and should provide a better estimate of the transports through Admiralty Inlet.

The accumulation rate of PAH in the main basin sediments is based on our measurements at PS7. The measured sedimentation rate at PS7 was 0.75 cm/yr ( $^{210}\text{Pb}$ ), however for the purpose of the calculation, a lower mean rate of 0.54 cm/yr was used (Dexter et al., 1981). Assuming that PS7 is representative, we compute a sediment accumulation rate of 610 kg/yr. Because not all the sediments are fine-grained, a depositional

Table 9. An estimate of the combustion PAH budget for the main basin, Puget Sound.

IMPORT	
<u>Source</u>	<u>Transport (kg/yr)</u>
Duwamish River (above METRO)	14
Other Rivers (est) <sup>1</sup>	280
<u>Total Riverine Input</u>	<u>294</u>
METRO (Renton) <sup>2</sup>	1
METRO (Westpoint) <sup>3</sup>	100
Other Municipal Discharges (est) <sup>4</sup>	85
<u>Total Sewage Discharge</u>	<u>186</u>
Atmospheric Deposition (est) <sup>5</sup>	300
Storm Sewer Runoff	?
EXPORT	
<u>Sinks</u>	<u>Transport (kg/yr)</u>
Admiralty Inlet	?
Narrows (Tacoma)	?
Sedimentation	
Sediment Traps <sup>6</sup>	1760
Bottom Sediment <sup>7</sup>	610
Biodegradation	?
<ol style="list-style-type: none"> <li>1) The combined mean annual flows of the Skagit, Stillaguamish, Snohomish, and Puyallup Rivers is 20 times the mean annual flow of the Duwamish (Dexter et al., 1981).</li> <li>2) Hamilton et al., 1982 (submitted).</li> <li>3) Barrick, 1982.</li> <li>4) METRO Westpoint contributes about 60% of the total combined wastewater and storm sewer runoff to the main basin (Barrick, 1982).</li> <li>5) Assumes <math>\Sigma</math>PAH flux of <math>1\mu\text{g}/\text{m}^2/\text{d}</math> (Prahl, 1982).</li> <li>6) Assumes the annual mean vertical flux through the 50 m horizon at station PS7 is representative of the main basin. Area of the Main Basin below the 50 m depth is <math>4.5 \times 10^8 \text{m}^2</math> (McLellan, 1954).</li> <li>7) Assumes a mean sedimentation rate of 0.54 cm/yr (Dexter et al., 1981) and a sedimentation area of <math>2.6 \times 10^8 \text{m}^2</math> (Barrick, 1982).</li> </ol>	

area of  $2.6 \times 10^8 \text{ m}^2$  was used (Barrick, 1982). However, if the PAH flux through 50 m is used and again assuming that PS7 is representative, we calculate a vertical transport (basin average) of 1760 kg/yr, a value three times the sedimentation rate. Here, we used an area of  $4.5 \times 10^8 \text{ m}^2$ , or the area of the main basin below 50 m (McLellan, 1954).

The disparity between the vertical flux and the sediment accumulation rate is due to several problems. First, the sedimentation area used by Barrick (1982) may be too small, although the error could not be a factor of 3. Secondly, PS7 may not represent the depositional environment for the main basin, namely the accumulation rate of PAH is higher in the southern main basin. And lastly, we do not know the net transports across the embracing sills at Admiralty Inlet and the Narrows. It would appear that PS7 is not a typical depositional environment given the low accumulation rate relative to the vertical flux rate. If the vertical flux measurements at PS7 are typical, then PAH are preferentially deposited elsewhere, biodegraded, or lost from the system by sill transport.

The major sink for these PAH appear to be the fine-grained sediments prevalent along the axis of the main basin. Municipal discharge appears to contribute no more than 24% of the total, assuming all other discharges are similar to METRO Westpoint. Contributions from rivers, sewage discharge, and atmospheric deposition are all about equal in magnitude.

## VI. CONCLUSIONS

### A. Duwamish-Green River Transport Studies

The sources of hydrocarbons in the Green-Duwamish River are aquatic production, plant waxes, surface runoff, and secondary sewage effluent.

The plant waxes dominate the hydrocarbon in the upper river, but diminish in relative abundance downstream. Dilution by relict sediments from shore erosion in the lower river and biodegradation are presumable the principal causes.

Low molecular weight alkanes (even carbon number) increase in concentration downstream reflecting increases in surface runoff. This is confirmed by a systematic increase in the combustion PAH, which are known to be elevated in highway runoff.

A hydrocarbon budget constructed for the lower Green River in the vicinity of the METRO outfall did not balance. It appears that the wastewater discharge enhanced flocculation of the heavier hydrocarbons, selectively removing them from true suspension. Only about 40% of the total particulate hydrocarbons in the river at the discharge site were found 0.5 km downstream. Apparently, flocculation and precipitation occurred as the wastewater mixed with the river water and the particulates were transported along the bottom during periods of high runoff. The receiving area for these hydrocarbon-enriched particles would be the tidal portion of the estuary, which is routinely dredged for navigational



purposes. A comparison of the concentrations of PAH above the navigational channel with similar measurements made in the lower river (near Harbor Island) show that considerable enrichment has occurred. The high concentrations of PAH (and trace metals) in the lower 1-2 km of the river are due to a low sedimentation rate and sources in the industrialized lower river.

The METRO wastewater discharge, located on the Green River, is characterized by high concentrations of PAH relative to the river. On the average, the concentration levels in the effluent are about a factor of 4 above the river values near the METRO discharge. However, because the mean discharge of the METRO outfall is only 4% of the mean riverine discharge ( $5.0 \times 10^{10} \text{ L/S} \div 1.3 \times 10^{12} \text{ L/S}$ ), the normal river transport of PAH are more significant. Our calculations show that METRO at Renton contributes no more than 6% of the particulate PAH found in the Duwamish-Green River. These transports are calculated for the river near the discharge site at Renton, and do not include the combined sewer overflows along the lower river.

#### B. Vertical Fluxes at Station PS7

The short-term PAH flux at station PS7 near Seattle are typical of other urban environments with maximums during the winter months. The flux of PAH through the 50 m horizon ranged from  $4.4 \mu\text{g m}^{-2} \text{d}^{-1}$  in Spring to  $8.2 \mu\text{g m}^{-2} \text{d}^{-1}$  in winter. Based on the sedimentation rate as determined by  $^{210}\text{Pb}$ , the accumulation rate of PAH was about  $8.5 \mu\text{g m}^{-2} \text{d}^{-1}$  as compared to a seasonally adjusted flux of  $6.7 \mu\text{g m}^{-2} \text{d}^{-1}$ . Thus it appears that a near balance is achieved at PS7 between the vertical flux and sediment accumulation rate. That the accumulation rate is about 27% larger than the measured flux, could be explained by an excessive sedimentation rate of 0.75 cm/yr.

Concentrations of PAH in surface waters are greater than concentrations in the underlying bottom sediments. Selective transport and dilution, are probable causes for the deficit. If the PAH are associated with fine-grained organic-rich particles, they may be winnowed to more quiescent sedimentary regimes (e.g. East Passage). They may also be diluted by clean sediments being transported in the bottom boundary layer.

Whereas the concentrations of combustion PAH are little degraded in the water column, this is not true for the aliphatic hydrocarbons. By normalizing to the more refractory PAH, only 4% of the pristane, 16% of the C14-20 alkanes, 64% of the UCM and 71% of the C21-35 alkanes present in surface waters are being deposited in the sediments.

The distribution of PAH, UCM, and n-alkanes in bottom sediments shows a concentration increase paralleling the industrialization of Seattle. PAH concentrations were a maximum in the 1940-1950's, corresponding to maximum usage of coal for home heating. Compounds that comprise the UCM and n-alkanes concentrations were at a maximum in the middle 1960's, reflecting the change from raw sewage discharge to primary treatment.

A preliminary budget of PAH has been constructed for the main basin using the extant data. Although a number of assumptions were made, it appears that riverine input and municipal discharges are about equal at 200 kg/yr. Atmospheric deposition is estimated to be 300 kg/yr and stormsewer runoff is unknown, but probably large. If our estimates are correct, municipal discharges account for less than 24% of the PAH burden in the main basin, assuming no contribution from storm sewer runoff.

The seasonally adjusted vertical flux of combustion PAH at PS7 is about  $6.7 \mu\text{g m}^{-2} \text{d}^{-1}$ . If this flux is typical for the main basin, then we would calculate a vertical transport of 1800 kg/yr through the 50 m horizon. The area of the main basin below the 50 m isobath is about  $4.5 \times 10^8 \text{ m}^2$ . Assuming that the accumulation rate at PS7 is typical for the main basin, we estimate the current sediment accumulation rate to be about 600 kg/yr for the basin. The depositional area was  $2.6 \times 10^8 \text{ m}^2$ ; the mean sedimentation rate adopted was 0.54 cm/yr. It is not possible to further refine the budget until more data are available on storm sewer discharge, sill transports, and vertical fluxes in the southern reaches of the main basin.

## VII. Needs for Future Studies

The quantitation of the transport and fate of PAH in an urbanized estuary centers on mass balance closure. The research to date reveals several important data gaps, among them are seasonal flux measurements on a regional basis, sediment accumulation rates, hydraulic transport across the sills, and source strengths within the basin. Source strengths that need to be quantified are stormwater runoff, rivers, and wet and dry atmospheric deposition. Some measurements do exist, but the data base is inadequate.

Sedimentary processes also are in need of sharper definition. Specifically sedimentation rates as determined by  $^{210}\text{Pb}$  must be corrected for bioturbation in order that the recent accumulation history may be elucidated. Biodegradation is also an important factor that controls the persistence of these compounds and must be quantified.

Lastly, more work needs to be done on the primary sources of PAH to the marine environment, not only the transport mechanisms. The sources are thought to be combustion, but what combustion processes? Compositional parameters and isotopic characterization may be useful in documenting the sources of these compounds found in air and waters.

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### 3. ACCOMPLISHMENT OF OBJECTIVES

#### 3.1. PUBLICATIONS AND REPORTS (1979-1982)

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### 3.2. STATUS OF ACCOMPLISHMENT OF OBJECTIVES

The objectives, formal hypotheses and information products formulated in 1979 for this Project are shown in Table 3.1. A symbol under the status column shows our progress in the accomplishment of the objectives as of October 1982 (A = accomplished, U = underway and NS = not yet started).

A review of the entire set of objectives and proposed products is currently underway and a milestone chart will be established for the next three years.

Table 3.1. Summary of objectives, hypotheses, information products and status.

A = Accomplished, U = Underway, NS = Not yet started

TRANSPORT

<u>Objective</u>	<u>Hypothesis</u>	<u>Products</u>	<u>Status</u>
1. Quantify horizontal transport rates for water and particles in appropriate subregions of the estuary.	1. The flux of water through the Puget Sound main basin is a quasi-continuous process occurring at variable rates with a seasonal signature reflected in a correlated change in concentration and flux of SPM and removal of pollutants from the main basin.	1A. Seasonally averaged suspended matter distributions. 1B. Mean trajectories and transports of water and particles within the surface layer, subsurface layer and BNL. 1C. Correlation of temporal and spatial particulate matter variability with hydrographic variability. 1D. Seasonally averaged residence times for water and particles.	A P A U
2. Quantify the vertical flux and aggregation characteristics of particulate matter at key depths and locations in Puget Sound.	2. Loss of particulate matter from the upper water mixed layer is accelerated by incorporation into fecal pellets and other large aggregates and subsequent removal via sinking.	2A. Calculation of biweekly sedimentation rates at mooring sites. 2B. Comparison of aggregate and non-aggregate vertical flux. 2C. Temporal variability of aggregate flux. 2D. Resuspension parameters and vertical settling rates for sediment on transport models.	U U U U
3. Examine the relationship between fluid circulation and SPM concentrations in the main basin and in Elliott Bay.	3. Tidally-forced convection at the sills is a principal agent for the vertical transport of fine-grained SPM between the surface and deep circulation layers in Puget Sound.	3A. Quantification of the dependence of sediment resuspension on current velocity at specific mooring sites. 3B. Quantification of vertical exchange of particulate matter by tidal-forced convection. 3C. Identification of sediment and pollutant sink areas.	U U U

Table 3.1 Continued.

TRANSPORT

<u>Objective</u>	<u>Hypothesis</u>	<u>Products</u>	<u>Status</u>
4. Determine the role of resuspension in recycling bottom sediments.	4. In the deeper waters of the estuary, tidal currents are the principal factor contributing to the bottom nepheloid layer.	<p>4A. Temporal variability of sediment volume (i.e., mass) in the BNL.</p> <p>4B. Correlations between current velocities and resuspended sediment volumes in the BNL.</p> <p>4C. Textural and compositional parameters of the BNL and their comparison to bottom sediments and vertically settling material.</p> <p>4D. Recent sedimentation rates at selected core locations by lead-210 dating.</p>	<p>NS</p> <p>NS</p> <p>NA</p> <p>U</p>

## TRANSFORMATIONS AND FATE

Objective	Hypothesis	Products	Status
1. Identify and quantify, from all available data, the major sources of trace metals and organic compounds to Puget Sound.	1A. The major sources of most trace metals and organics to the estuary is surface runoff and wastewater discharge and to a lesser extent atmospheric deposition. 1B. Trace metals and lipid soluble PAH's, and chlorinated organics undergo accelerated flocculation in the presence of wastewater discharge,	1A. Determine seasonal particulate transport of organics and trace metals in the Duwamish, Puyallup and Skagit Rivers. 1B. Determine seasonal average trace metal and organic compositions for Renton Secondary Treatment Plant and West Point Outfall (primary). 1C. Compute atmospheric input rates from literature data and/or work currently underway in Puget Sound. 1D. Estimate from the literature and measurements, contributions of trace metals and organics from storm sewer runoff into Elliott Bay.	P  A  U U
2. Identify and quantify the major sink terms for particulate organics and trace metals.	2. Increasing the rate of input of organics and trace metals into Puget Sound will be followed by an increasing burden of these compounds in both particulate matter and bottom sediments.	2A. Seasonally averaged vertical fluxes of organics and trace metals to the sediments of Elliott Bay and the main basin. 2B. Residence and biological exposure times for trace metals and organics in the near surface layer of the sediments. 2C. Seasonally averaged net transport rates of particulate trace metals and organics across the sill at Admiralty Inlet. 2D. Description of the temporal variations of particulate trace metals and organics as related to changes in the geochemical and hydrographic regimes in Puget Sound.	U  NS U U

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Table 3.1 Continued.

## TRANSPORT AND TRANSFORMATION MODELING

<u>Objective</u>	<u>Hypothesis</u>	<u>Products</u>	<u>Status</u>
1. Develop a computation model of tidal currents in Puget Sound and Elliott Bay.	1. Horizontal variations in tidal currents determine the sites of contaminated-sediment deposition in Elliott Bay and the main basin of Puget Sound.	1A. A numerical model of horizontal tidal currents in Puget Sound and Elliott Bay. 1B. Periods and duration of maximum and minimum tidal flushing.	U U
2. Develop a 2-D, tidally driven model of sediment-borne/pollutant transport in Elliott Bay.	2. Horizontal variations in tidal currents determine the sites of contaminated-sediment distribution in Elliott Bay and the main basin of Puget Sound.	2A. Suspended particle transport in the BNL and residence times. 2B. Test of the model (distribution and transport) using the published PCB distribution observed in Elliott Bay. 2C. Test the model using other PAH, chlorinated organics and trace metals derived from the Duwamish River (§2.4).	U NS NS
3. Develop a model of the erosion and deposition of cohesive sediments to use in pollutant transport prediction.	3. The vertical flux of sediment to and from the seabed can be described as an advection-diffusion process with a local erosion/deposition source function.	3A. An algorithm of the erosion function's dependence on velocity. 3B. Erosion/depositional parameters to be used in the 2-D tidal model.	NS U