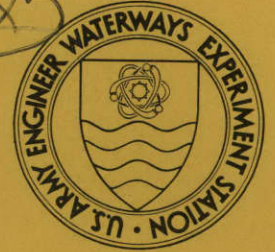


John D. B.

DREDGED MATERIAL RESEARCH PROGRAM



TECHNICAL REPORT D-77-24

AQUATIC DISPOSAL FIELD INVESTIGATIONS DUWAMISH WATERWAY DISPOSAL SITE PUGET SOUND, WASHINGTON

APPENDIX E: RELEASE AND DISTRIBUTION OF POLYCHLORINATED BIPHENYLS INDUCED BY OPEN-WATER DREDGE DISPOSAL ACTIVITIES

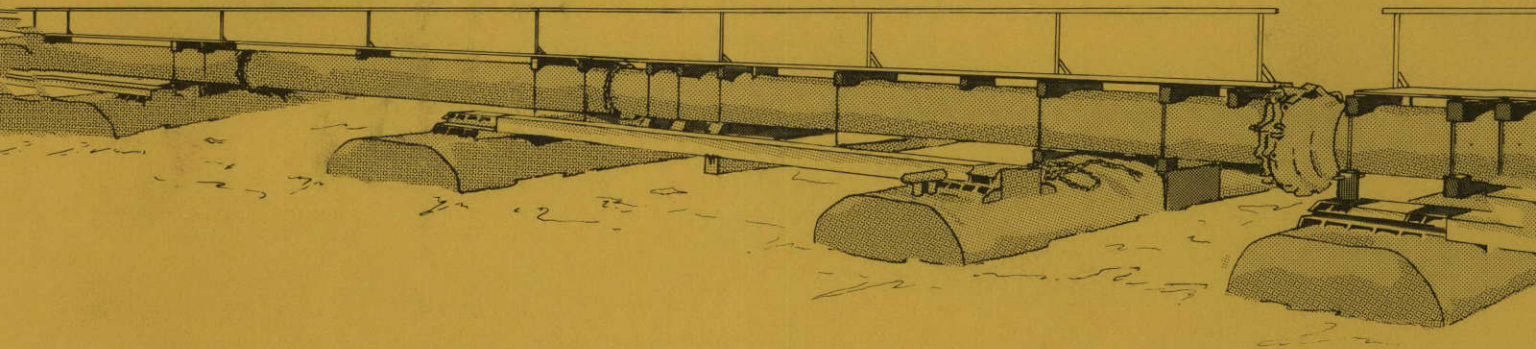
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January 1978
Final Report

Approved For Public Release; Distribution Unlimited



Prepared for Office, Chief of Engineers, U. S. Army
Washington, D. C. 20314

Under Contract No. DACW39-76-C-0167
(DMRP Work Unit No. 1A10D)

Monitored by Environmental Effects Laboratory
U. S. Army Engineer Waterways Experiment Station
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AQUATIC DISPOSAL FIELD INVESTIGATIONS
DUWAMISH WATERWAY DISPOSAL SITE
PUGET SOUND, WASHINGTON

- Appendix A: Effects of Dredged Material Disposal on Demersal Fish and Shellfish in Elliott Bay, Seattle, Washington
- Appendix B: Role of Disposal of PCB-Contaminated Sediment in the Accumulation of PCB's by Marine Animals
- Appendix C: Effects of Dredged Material Disposal on the Concentration of Mercury and Chromium in Several Species of Marine Animals
- Appendix D: Chemical and Physical Analyses of Water and Sediment in Relation to Disposal of Dredged Material in Elliott Bay
- Appendix E: Release and Distribution of Polychlorinated Biphenyls Induced by Open-Water Dredge Disposal Activities
- Appendix F: Recolonization of Benthic Macrofauna over a Deep-Water Disposal Site
- Appendix G: Benthic Community Structural Changes Resulting from Dredged Material Disposal, Elliott Bay Disposal Site

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IN REPLY REFER TO: WESYV

15 March 1978

SUBJECT: Transmittal of Technical Report D-77-24 (Appendix E)

TO: All Report Recipients

1. The technical report transmitted herewith represents the results of one of several research efforts (Work Units) undertaken as part of Task 1A, Aquatic Disposal Field Investigations (ADFI), of the Corps of Engineers' Dredged Material Research Program (DMRP). Task 1A is a part of the Environmental Impacts and Criteria Development Project (EICDP), which has as a general objective determination of the magnitude and extent of effects of disposal sites on organisms and the quality of surrounding water, and the rate, diversity, and extent such sites are recolonized by benthic flora and fauna. The study reported on herein was an integral part of a series of research contracts jointly developed to achieve the EICDP general objective at the Duwamish Waterway Disposal Site, one of five sites located in several geographical regions of the United States. Consequently, this report presents results and interpretations of but one of several closely interrelated efforts and should be used only in conjunction with and consideration of the other related reports for this site.

2. This report, Appendix E: Release and Distribution of Polychlorinated Biphenyls Induced by Open-Water Dredge Disposal Activities, is one of seven appendices published relative to Waterways Experiment Station Technical Report D-77-24 entitled: Aquatic Disposal Field Investigations, Duwamish Waterway Disposal Site, Puget Sound, Washington. The titles of all appendices of this series are listed on the inside front cover of this report. The main report will provide additional results, interpretations, and conclusions not found in the individual appendices and will provide a comprehensive summary and synthesis overview of the entire project.

3. The purpose of this study, conducted as Work Unit 1A10B, was to collect data pertaining to the release of polychlorinated biphenyls (PCB's) from contaminated sediment from the Duwamish River to the water column at the Elliott Bay disposal site. The authors also assessed the mobility of the dredged material at the disposal site and discuss the physical and chemical variables that could affect the release of

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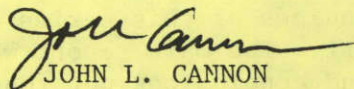
15 March 1978

SUBJECT: Transmittal of Technical Report D-77-24 (Appendix E)

PCB's from the dredged material to the water, suspended particulate matter, or other sediments. Environmental samples consisting of whole water, suspended particulate matter, and sediments were obtained prior to the dredging operation from the Duwamish River and the Elliott Bay disposal site. Similar samples were collected during and after the disposal operation. These samples were analyzed by electron capture gas chromatography methods described in detail in Appendix E of the main report. The data revealed that the sediment from the Duwamish River was contaminated with PCB's; however, the release of PCB's to the water column during disposal was shown to be a highly transient event associated with the temporary increase in suspended particulate matter due to the disposal operation.

4. Duwamish sediment contained PCB's at concentrations as high as 7 mg/kg (ppm). The levels of total (particulate and dissolved) PCB's in the water column during the disposal operation increased from approximately 3 ng/l (parts per trillion) to 3 µg/l (parts per billion) in some cases. These increases, however, were detected for only a few minutes after dumping. Sediments at the disposal site increased from about 0.5 to 3.0 mg/kg after the disposal operation. There was evidence from the data that the deposited material was spreading outward over the disposal site.

5. The results of this study are important in determining placement of dredged material for open-water disposal. Referenced studies, as well as the ones summarized in this report, will aid in determining the optimum disposal conditions and site selection for either the dispersion of the material from the dump site or for its retention within the confines of the site, whichever is preferred for maximum environmental protection at a given site.



JOHN L. CANNON

Colonel, Corps of Engineers
Commander and Director

20. ABSTRACT (Continued).

contaminated sediments from the Duwamish River.

- b. An evaluation of the spatial and temporal trends in PCB levels at the disposal site and its immediate vicinity.
- c. An examination of the dependence of PCB residues measured in water, suspended particulate matter (SPM), and sediments on physical and chemical variables (appropriate to each marine phase examined) which might affect the accumulation and release characteristics of these chemicals from the disposed material.
- d. An assessment of the change in the distribution characteristics of PCB's in the impact zone as compared to the prevailing ambient conditions in the area prior to disposal.

Appendices A'-E' to this volume present the raw data tables, descriptions of materials and techniques, along with the computer program used for PCB data reduction and a sample input and output. The appendices were reproduced in microfiche and are enclosed in an envelope attached inside the back cover of this report.

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SUMMARY

The potential for adverse impacts associated with open-water disposal of contaminated dredged material is well recognized. However, the physical and chemical behavior of toxic trace constituents in these sediments during disposal operations is poorly understood, thus making regulatory criteria development an extremely difficult process.

The objective of the study reported herein was to investigate the release and translocation of polychlorinated biphenyls (PCB) associated with the disposal of contaminated sediments from the Duwamish River in Elliott Bay, Puget Sound, Washington.

Based on a detailed analysis of the data obtained during the field program, the most significant findings of this study are outlined below:

- a. The material dredged from the Duwamish River contained PCB's as high as 7 mg/kg, a level substantially higher than anticipated for this area of the river. It is unknown whether these high levels represent historic loading which has gone undetected or is recent input.
- b. The primary release of PCB's in the water column during disposal was a highly transient event associated with the temporary increase in suspended particulate matter introduced by the dumping operation. PCB concentrations in the water column increased during the dumping events from about 3 ng/l to as high as 3 µg/l. These extreme values were observed only for a few minutes after dumping.
- c. A less dramatic increase in PCB levels, to about 10 ng/l, was observed one week after the cessation of dumping at the study site. Within one month, water column PCB levels returned to predisposal concentrations.
- d. Long-term elevations of PCB concentrations due to dumping were localized within the sediments of the disposal zone. The values for the surface sediments increased from approximately

0.5 mg/kg to about 3 mg/kg. No dispersal or mobilization of the PCB was observed during the monitoring period.

- e. A continuous slumping and spreading of the deposited material was indicated by tracing the changes of the PCB distribution over time. The increasing concentrations in the surface sediments over time and the apparent burial by the highly contaminated materials of the periphery of the disposal zone provided evidence of this occurrence.

It is anticipated that the results of this study, coupled with the physical and biological investigations conducted in the area over the same monitoring period, will provide a basis for a realistic evaluation of the environmental impacts of open-water dredged material disposal operations. These will assist in establishing environmentally sound management strategies for future dredged material discharge activities.

PREFACE

This report presents the results of an investigation to determine the release and distribution of polychlorinated biphenyls during the open-water disposal of contaminated sediments in Elliott Bay, Puget Sound, Washington.

The research was performed as a component of the Environmental Impacts and Criteria Development Project (EICDP) of the Dredged Material Research Program (DMRP), for the Office of the Chief of Engineers. It was supported by the U.S. Army Engineer Waterways Experiment Station (WES), Environmental Effects Laboratory (EEL), Vicksburg, Mississippi, under Contract No. DACW 39-76-C-0167 to the Department of Oceanography, University of Washington, Seattle, Washington. The sampling program for the project was conducted in conjunction with an ongoing project sponsored by the U.S. Environmental Protection Agency, Grant No. R-800362, Dr. S. P. Pavlou, Principal Investigator.

The work was accomplished by Dr. Pavlou and his research group consisting of Dr. R. N. Dexter, Messrs. W. Hom and A. J. Hafferty, and Ms. K. A. Kroglund.

The EEL Project Manager was Mr. J. H. Johnson, under the supervision of Dr. R. M. Engler, Manager of the EICDP.

The entire DMRP is administered by the EEL at WES under the general supervision of Dr. John Harrison, Chief, EEL. Director at WES during the study and preparation of this report was Col. J. L. Cannon, C.E. Technical Director was Mr. F. R. Brown.

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CONVERSION FACTORS, U.S. CUSTOMARY TO
METRIC (SI) UNITS OF MEASUREMENT

U.S. customary units of measurement used in this report can be converted to metric (SI) units as follows:

<u>Multiply</u>	<u>By</u>	<u>To Obtain</u>
inches	25.4	millimetres
miles (U.S. nautical)	1.852	kilometres
miles (U.S. statute)	1.609344	kilometres
cubic feet per second	0.02831685	cubic metres per second
cubic yards	0.7645549	cubic metres
gallons (U. S. liquid)	3.785412	cubic decimetres

AQUATIC DISPOSAL FIELD INVESTIGATIONS,
DUWAMISH WATERWAY DISPOSAL SITE, PUGET SOUND, WASHINGTON

APPENDIX E: RELEASE AND DISTRIBUTION OF
POLYCHLORINATED BIPHENYLS INDUCED BY
OPEN-WATER DREDGE DISPOSAL ACTIVITIES

PART I: INTRODUCTION

1. Compared to some other inland waters of the United States, Puget Sound is considered to be a relatively pristine system with respect to toxic substances. The area is largely undeveloped and does not receive excessive quantities of municipal and industrial effluents as is the case with other major estuaries in the country. In addition, riverine fresh water input coupled with tidal action results in rapid dilution and flushing of pollutants from the system. In April, 1972, a project was initiated to study the distribution of chlorinated hydrocarbons in the region under support from the Environmental Protection Agency, Grant No. R-800362. The first samples were collected from Elliott Bay and when analyzed they revealed the presence of significant quantities of polychlorinated biphenyls (PCB).

2. Since that time the presence of these chemicals has been documented in all areas of the Sound. In general, the PCB concentrations were found to correlate with sites of increased industrial and municipal activity with no apparent temporal trends. The highly industrialized Duwamish

Estuary contained the highest PCB concentrations observed in the Sound. Elliott Bay, which receives the Duwamish River discharge, also was found to contain elevated PCB levels showing a spatial distribution in surface sediments which decreased with distance from the mouth of the river. A more detailed discussion on these aspects have been presented elsewhere.^{1, 2, 3}

3. A thorough examination of the PCB levels in the sediments of Elliott Bay and the Duwamish River indicates that the history of PCB input into this area has been somewhat sporadic over a fairly long period of time. Sediment cores often show marked differences in both the PCB types and their total concentrations as a function of core depth (1 cm horizon).

4. Recently, the lower Duwamish River received a substantial input of PCB's when a transformer was cracked while being loaded onto a barge. Virtually the entire contents (250 gallons) of nearly pure PCB (Aroclor 1242) were spilled into the river. The majority of this material was recovered initially by small, diver-operated suction dredging, followed by a major hydraulic dredging effort which removed the sediments from the entire affected area to a diked upland disposal site. These operations were monitored to evaluate the release of PCB into the river from resuspended contaminated sediments. The mean concentrations of PCB's during the monitoring period were within the ranges normally observed in the river, suggesting that the dredging operations did not induce a significant PCB pulse of potential hazard to the estuary.⁴

5. During the course of these studies, part of the research effort has been directed to defining the important factors which affect the

transport of PCB within marine environments and the distribution of these compounds between the various components of the ecosystem (water, suspended particulate matter, plankton, and sediments). The results indicate that, in general, the PCB's are distributed by equilibrium partitioning between the water and the other components. Within the context of the present investigations, these observations have some important connotations with respect to the environmental impact associated with open-water disposal of dredged material. Sediments that have accumulated significant quantities of PCB's in a relatively contaminated area may subsequently re-equilibrate by releasing the bound PCB as a result of the relocation of the sediments into a less contaminated area, i.e., the trap may become the source. More specific considerations are as follows:

- a. During open-water disposal, the PCB's that are bound to the sediments have an increased exposure to the relatively uncontaminated water which may result in their dissolution, and in turn can impose an immediate hazard to some organisms by direct uptake from the water column.
- b. The resuspension and dispersion of fine material from the contaminated sediments may also present a hazard for some organisms such as filter feeders.
- c. The sediments deposited at the disposal site may constitute a long term source of contamination to the system, both via uptake by benthic organisms and via desorption and dissolution into the water column.

6. This report presents a detailed examination of the above aspects based on data obtained from the field program. The primary emphasis is placed on the evaluation of spatial and temporal trends of the PCB levels in the sediments and the water column within the disposal zone. It is

anticipated that the interpretations and conclusions drawn from this analysis will be incorporated into the overall considerations in assessing the environmental effects associated with open-water disposal of dredged materials and in establishing realistic management practices. Appendices A'-E' to this volume present the detail data matrix, descriptions of methods and materials, along with the computer program and sample of the input/output used for PCB data analysis. The appendices were reproduced in microfiche and are enclosed in an envelope attached inside the back cover of this volume.

PART II: DESCRIPTION OF STUDY AREA

Regional Characteristics

7. Elliott Bay is situated midway on the eastern shore of the central basin of Puget Sound (Figure 1). The surface area of the bay is approximately 14.4 km² and is defined by Magnolia Bluff as its northwest boundary and on the southwest by the Duwamish Head. The total volume of the bay comprises approximately 1.0% of the total volume in the Main Basin⁵ and 0.5% of the entire Puget Sound volume. Bottom topography is characterized by steep marginal shore slopes around an internal basin of about 130 m in depth. This basin slopes gently to the northwest until it merges with the central Puget Sound basin.

8. The southern portion of the bay is divided into two smaller basins by a bottom ridge which slopes northwesterly from the northern end of Harbor Island and extends to the center of the bay. This ridge may represent a delta built by the Duwamish River which discharges into the southern portion of the bay.

9. The current structure in Elliott Bay has received little study. It appears that tide fluctuations (3.2 m mean tide range) generate a weak, generally counterclockwise, flow in the upper layers (< 50 m) of the bay, with water from the main basin entering around Duwamish Head. While deep water exchange between the bay and the main basin has no topographic restrictions, circulation in the deep layers is probably limited except during periods of deep water renewal within the entire Puget Sound system.

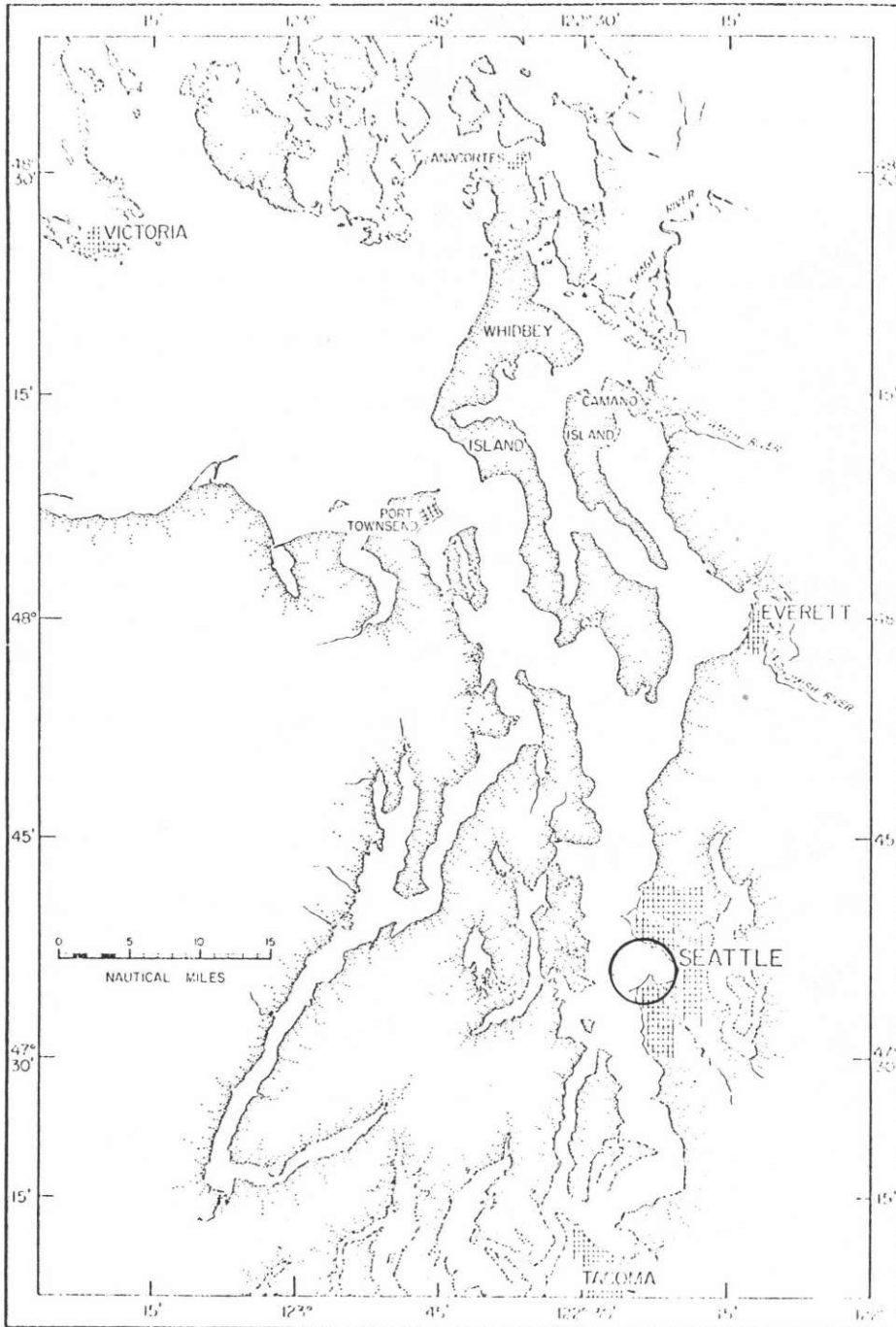


Figure 1. Geographical Location of Elliott Bay, Puget Sound, Washington (encircled area).

10. The Duwamish River provides freshwater input to Elliott Bay at an average annual rate of about 1,300 cfs.⁶ The flow is highly seasonal, reflecting the variations in precipitation and snow melt. The river discharge normally increases in late fall and again in late spring. The lower Duwamish forms a vertically stratified salt-wedge estuary with net outflow of fresh to brackish water at the surface and net inflow (upriver) of saline Elliott Bay water at depth. The highly variable flow of freshwater is nearly always seaward. However, the instantaneous movement in both layers may be either up or downstream. At its mouth, the river is split and discharges into Elliott Bay around both sides of Harbor Island. Dredging of the western channel and a shallow sill at the south end of the eastern channel result in the majority of the water exchange taking place via the West Waterway. The freshwater discharge forms a low salinity surface plume (1-15 m) in the southern portion of the bay. The behavior of this plume reflects a response to both tidal currents and wind stress. In the absence of strong southerly winds, the plume is "compressed" into the southern bay around the river mouth by flood tides. During ebb tides, the plume normally drifts northward, spreading along the northeastern waterfront and following the shoreline until its identity is lost by mixing with Puget Sound surface water. As a result, the primary influence of the river discharge is felt in the southern and southeastern portions of Elliott Bay and along the Seattle waterfront.

11. The lower Duwamish River is a navigable waterway, routinely dredged at three to four year intervals to maintain channel depths of 10 to

15 m. The lower river is highly industrialized and receives significant quantities of industrial wastes, as well as some municipal wastes discharged by the sewage treatment plant at Renton, Washington.

Description of Study Site

12. The total volume of dredge material disposed in Elliott Bay for the purpose of this study was approximately 114,000 m.³ The source of these sediments was a 1.88 km stretch of the upper Duwamish Estuary between river miles 3.90 and 5.07 (Figure 2). Previous studies in this area have established that the sediments of the entire Duwamish Estuary are contaminated with PCB.^{2, 4, 7} However, the area of the river dredged has a rapid sedimentation rate and is upstream of most industrialization. It was anticipated therefore that these sediments would not be grossly contaminated.

13. The disposal buoy was located over the 60 m depth isoline due north of the mouth of the West Waterway (47° 35' 41" N; 122° 21' 42" W) and the disposal site station grid (1-16) comprised an area of 0.98 km² with the disposal buoy as its center point. The two reference sites were also located over 60 m of water and positioned east and west of the disposal site as shown in Figure 2. The west reference site has received historically the least impact from the municipal, commercial and industrial activities of the Seattle area. Water flow over this location originates primarily from the main basin of Puget Sound rather than from the interior of Elliott Bay. On the other hand, the east reference site has received effluents from the Duwamish River, an unknown contribution from shipping

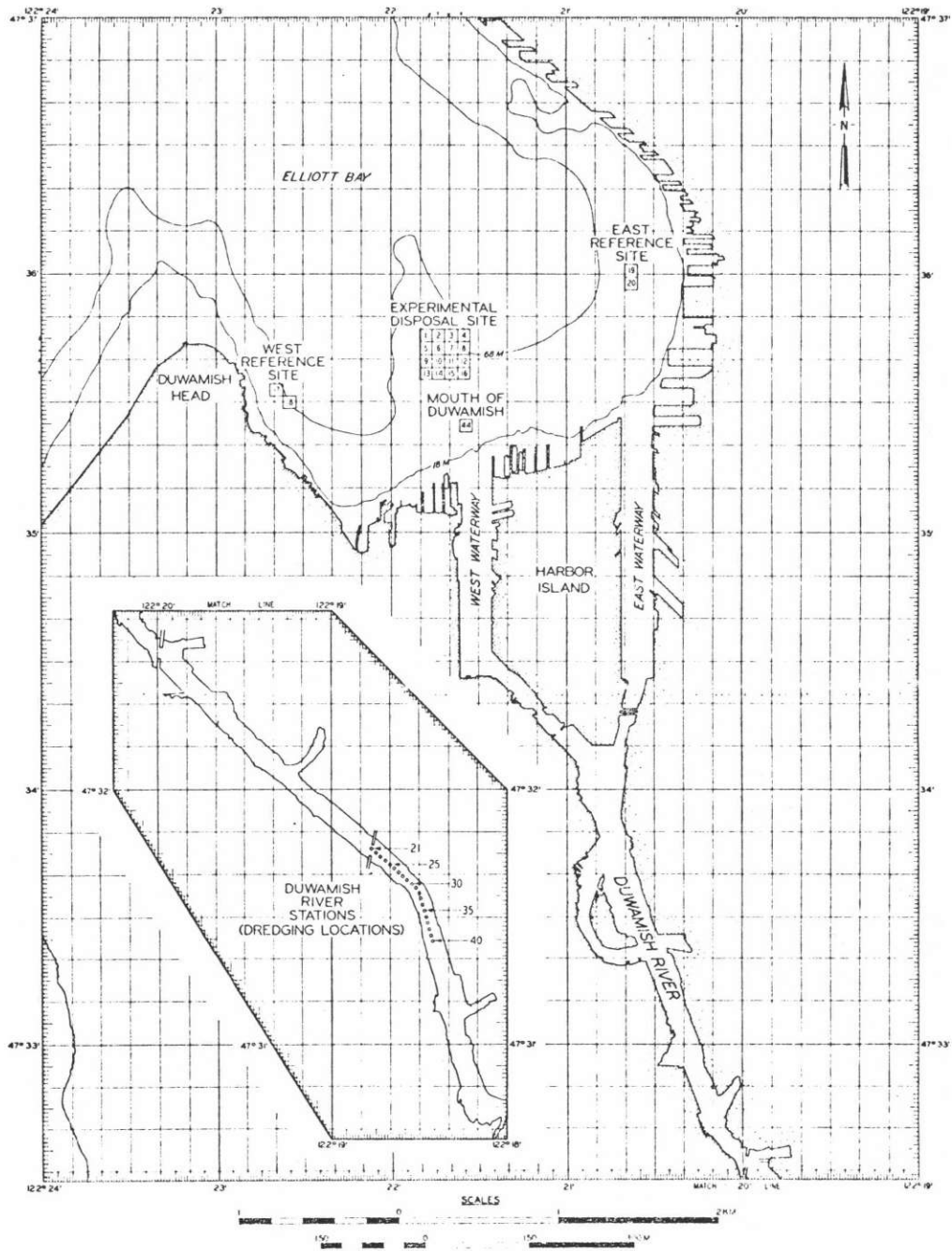


Figure 2. Location of the Dredge and Disposal Sites in Elliott Bay and the Duwamish River, Puget Sound, Washington.

and nearby shore-based activities, as well as from a number of contaminated materials originating from sewage overflow discharges along the Seattle waterfront.

Literature Review

Regional studies

14. No other study on the environmental impact of PCB's released during dredge disposal operations in Puget Sound has been conducted to date. Previous studies related to the environmental dynamics of PCB's in the region have been carried out primarily by our laboratory and are appropriately referred to throughout the main body of this report. The only investigation addressing some general aspects of sediment and water quality chemistry related to disposal of dredge spoils in this region has been conducted by Schell, et al.,⁸ under support from the Municipality of Metropolitan Seattle (METRO). This project was a minor component of METRO's overall Interim Studies Program designed to assess the dispersion of chemical constituents released from the disposal of 283,000 yd³ of Duwamish River material at Fourmile Rock, and the coupling of this perturbation to the water quality changes induced by the West Point effluent discharge. The parameters measured were limited to hydrography, nutrients, turbidity, suspended solids, pH (water column), and trace metals in water, suspended particulate matter (SPM), and a few sediment cores. Although the data were considered insufficient to warrant a reliable assessment of the

impact to the ambient chemistry within the disposal zone, it was indicated that the lateral spreading of the dredged material was localized to the immediate vicinity of the disposal site and dilution of the material by the tidal action reduced concentrations of the trace constituents to background levels. It was therefore concluded that no significant effects on the water quality parameters measured were observed.

Other studies

15. In view of the paucity of the data related to environmental effects of PCB's released by open-water disposal activities, a literature search was conducted through the computerized bibliographic services available at the University of Washington's libraries to assembly information obtained in any similar studies conducted elsewhere. The search was carried out using the POLLUTION data base on the SDC/ORBIT system and by coupling PCB with the following keywords: DREDGING, POLLUTANT DISPOSAL, SOLID WASTE DISPOSAL, OCEAN DUMPING, DISPOSAL IMPACT, SEDIMENT TRANSPORT corresponding to pertinent processes, SEDIMENTS, SUSPENDED SOLIDS, and DREDGE SPOIL for material; and BENTHOS, BAYS, BRACKISH WATER, COASTAL WATERS, COASTAL ZONES, DISPOSAL SITES, MARINE ENVIRONMENTS, ESTUARIES for identifiers of locations.

16. The search produced only one article of interest which summarizes the environmental impact associated with the dredging and disposal of contaminated materials in a stratified fjord of the west coast of Sweden.⁹ A brief summary of relevance to the Elliott Bay disposal project follows.

17. The disposal material ($2 \times 10^6 \text{ m}^3$) originated from pipeline dredging associated with the extension of the Uddevalla Shipyard and consisted of clay material highly contaminated with PCB (0.7-7 ppm) and mercury (1-6 ppm). The total amount of PCB in the spoil was 53 kg, contained mainly at the surface layer (3% of the total spoil volume) of the sediments. The material was disposed below the permanent pycnocline of Byfjorden (usually between 11 and 20 m depth) at the deepest part of the region (50 m), which is normally anoxic. Although the author stated that the polluted material was buried by subsequent disposal of unpolluted sediments, thus minimizing long term impact, no detailed justification for these conclusions was provided.

PART III: METHODS AND MATERIALS

General Considerations

18. This section provides a detailed discussion of the sampling, analytical, and data reduction methodology employed to complete the objectives of the project. The procedures described herein were designed to ensure the quality control required to establish a reliable data bank for assessing the impact of introducing PCB-contaminated dredged material in the water column and sediments of the disposal zone.

Sampling Scheme

19. The impact of the disposal operations on the water column was examined by monitoring concentrations of PCB in samples of whole water and suspended particulate matter (SPM) collected prior, during and following disposal. Basin hydrographic parameters (salinity, temperature, and dissolved oxygen) were also measured to describe the water mass movement within the study area. A similar scheme was established for the sediments. Samples were collected both in the river and disposal area prior to dredging, followed by extended monitoring during the disposal operations and after they were terminated.

20. The sampling schedule is presented in Table 1. Sediment samples were collected approximately 10 days prior to the initiation of dredging (cruises 35 and 37). Only water and SPM samples were collected during the disposal operation (cruises 55 and 57), and immediately after the cessation

TABLE 1

Sampling Schedule by Cruise Numbers for the
Elliott Bay Dredge Disposal Project

Sample Type	Date*									
	Pre-Disposal (Phase II)		Disposal (Phase III)		Post-Disposal (Phase IV)					
	35	37	55	57	67	76	99	168**	265**	342**
Water Column										
Whole Water (PCB)			X	X	X	X	X	X	X	X
SPM (PCB)			X	X	X	X	X	X	X	X
HYDRO (S, O, Temp.)						X	X	X	X	X
Sediments										
Whole Core										
PCB	X	X				X	X	X	X	X
Oil and Grease	X	X				X	X	X	X	X
TOC									X	X
Interstitial Water		X				X				
Elutriate	X									

* The numbers are the Julian dates.

** Water and SPM samples were collected on dates 170, 266, and 343.

of dumping (cruise 67). Water, SPM, and sediment samples were collected at intervals of ten days (cruise 76), one month (cruise 99), three months (cruises 168 and 170), six months (cruises 265 and 266), and nine months (cruises 342 and 343) after disposal ceased.

21. The station locations are shown in Figure 2. The center of the dump-site station grid (stations 1-16) was marked by an anchored buoy which served as the reference point for the disposal and the dump-site stations. Reference sites were established, one on the east side of the bay (stations 19 and 20) and one on the west side (stations 17 and 18). Station 44 was also occupied as a reference for monitoring the water column quality associated with the Duwamish River discharge.

Water column

22. Samples of whole water and SPM for PCB analyses were collected at three depths for each station: at the surface (0-1 m), intermediate depth (10 m from bottom), and deep (1 m from the bottom). Throughout Phase III (cruises 55 and 57), replicate water samples were collected at the reference sites (stations 17, 19, and 44) both before and after each daily series of disposals. During the actual disposal operation, a time series of water and SPM samples was collected at the center of the grid (station 6). A detailed sampling scheme for the Phase III cruises is presented in Table 2.

TABLE 2

Sampling Scheme for Disposal Monitoring Cruises
(Phase III, Cruises 55 and 57)

Station	Time	Number of Samples Collected	
		Whole Water	SPM
17, 19, 44	BD*	2(R)+	
6	-30-1++	1	1
	0-1	1	1
	30-1	1	1
	60-1	1	1
	90-1	1	1
	0-2	1	1
	30-2	1	1
	60-2	1	1
	90-2	1	1
	0-3	1	1
	30-3	1	1
	60-3	1	1
	90-3	1	1
17, 19, 44	AD**	2	

* Before disposal.

+ R denotes replicate sample.

++ The time is expressed in minutes relative to the disposal episodes monitored on each of the Phase IV Cruises. t = 0 refers to the "dump" time.

** After disposal.

23. During the first two Phase IV cruises (67 and 76), replicate water and SPM samples for PCB analysis were collected at the disposal site (stations 6 and 10). Replicate water samples were also collected at the reference sites (stations 17, 19, and 44). For the last four post-disposal cruises (99, 168, 265, 342), replicate water and SPM samples were taken at all stations (stations 6, 10, 17, 19, and 44).

Sediments

24. Sediment samples were collected during the pre-disposal monitoring (Phase II, cruises 35 and 37) and during Phase IV (cruises 76, 99, 168, 265, 342). For cruise 35, sediments were obtained from 19 stations (stations 21-39) located in the section of the Duwamish River that was subsequently dredged (Figure 2). Depending on the penetration of the core tube, single samples of variable length were taken. On cruise 37, replicates of the upper 10 cm of the cores were collected at all stations in Elliott Bay (stations 1-20, Figure 2). On the post-disposal cruises, replicate cores were taken at each station. These cores were sectioned and both an upper horizon (from the sediment/water interface to 10 cm deep in the core) and a lower horizon (sediments deeper than 20 cm in the core) were collected.

25. Hydrographic measurements were conducted by this laboratory only during the last five Phase IV cruises (76, 99, 170, 266, 343) at both the reference (17, 19, and 44) and grid stations (6 and 10). River water depths sampled at each station were: 1 m, 5 m, 10 m, 10 m above bottom, and 1 m above bottom.

Shipboard Procedures

Water column

26. Whole water and SPM samples were collected with 53-liter, stainless steel samplers,¹⁰ modified by the replacement of the drain valve with a one half inch stainless steel Swagelok^R quick disconnect. Approximately four liters of water were transferred from the sampler through a teflon-lined neoprene tube directly to solvent-rinsed glass jugs. Pesticide grade hexane was immediately added and the jugs sealed with teflon-lined screw caps.

27. The remaining volume of water (~49 liters) was drawn through a pre-combusted 8" by 10" glass fiber filter (Reeve Angle 934 AH) using a large volume filter system (LVF) designed specifically for the collection of particulate PCB samples. A detailed description of this system is included in Appendix B'. Upon completion of filtering, the filters were transferred to solvent-rinsed glass jars, sealed with aluminum foil-lined screw caps, and stored frozen until processing and analysis.

Sediments

28. Sediment samples were collected using either a single or double barrel gravity corer with two inch fiberglass core liners. Samples for PCB analysis were extruded on board ship directly into solvent-rinsed glass jars, sealed with aluminum foil-lined screw caps, and stored frozen until processing and analysis. In the laboratory the samples were homogenized and aliquots prepared to determine the following:

- a. PCB concentrations in the total core.

- b. PCB concentrations in the interstitial water (cruises 37 and 76).
- c. Potential PCB release as indicated by the modified elutriate test.
- d. Oil and grease concentrations in the total core.
- e. Total organic carbon content (cruises 265 and 342).

A detailed outline of the sediment sampling scheme is presented in Table 3.

TABLE 3
Detailed Sediment Sampling Scheme

Sampling Area	Horizon	35	37	76	Cruise 99	168	265	342
River (21-39)	upper	X						
Disposal Grid (1-16)	upper		X	X	X	X	X	X
	lower		X	X	X	X	X	X
West Reference (17, 18)	upper		X	X	X	X	X	X
	lower			X	X	X	X	X
East Reference (19, 20)	upper		X	X	X	X	X	X
	lower			X	X	X	X	X

Hydrography

29. Hydrographic samples were collected by standard oceanographic techniques using five liter PVC Scott-Richard bottles fitted with reversing thermometers. Samples were drawn for the determination of salinity and dissolved oxygen.

Chemical Analysis

30. The techniques developed in this laboratory for the analysis of chlorinated hydrocarbon (CH) residues in natural samples are based on established methods,^{11, 12, 13} appropriately modified to accommodate specific types of samples. All procedures consisted of the same four basic steps:

- a. Extraction of the residues from the sample matrix using organic solvents.
- b. Removal of co-extracted interfering organic material.
- c. Analysis of the sample extract by electron capture gas chromatography (EC/GC).
- d. Spectral analysis and final data reduction.

Steps c and d were identical for all sample types and are discussed separately.

Processing of samples for PCB analysis

31. Whole Water. The extraction and clean-up procedures for whole water samples are basically those of Thompson.¹¹ A teflon-coated magnetic stirring bar was added to the jug containing the water sample and the

hexane which was added during sample collection. The jug was placed on a magnetic stirrer and a strong vortex maintained for approximately 20 minutes to ensure sufficient dispersion of solvent and maximum sample-solvent contact. The phases were allowed to separate until both were clear (~20 minutes). The hexane phase was drawn off by vacuum through a teflon tube into a one liter separatory funnel. The stirring-extraction process was repeated two times with additional 100 ml aliquots of hexane. Any water brought over into the separatory funnel while collecting the hexane layers was drained into a graduated cylinder and combined with the remainder of the sample for an accurate volume determination. The sample was then discarded.

32. The combined hexane extracts were eluted through a drying column containing pre-combusted anhydrous Na_2SO_4 and transferred into a one liter Kuderna-Danish evaporative concentrator (KD) equipped with a three-ball Snyder column. The solvent volume was reduced to approximately 5 ml on a water bath. The reduced extract was then transferred quantitatively to a glass-stoppered graduated conical centrifuge tube. An equal volume of concentrated H_2SO_4 was added, the tube was stoppered and shaken vigorously for two minutes, and then the mixture was allowed to settle and react for a minimum of 12 hours. The solvent extract was then transferred, either quantitatively or as a measured aliquot, to a second graduated centrifuge tube and saponified by the method of Thompson.¹¹ After saponification, the sample extract was made up to volume (~1 ml) with trimethylpentane (TMP) and was ready for gas chromatographic (GC)

analysis. This procedure was used because the use of TMP reduces the solvent "tailing" during the GC analysis and also minimizes volume changes due to evaporation.

33. SPM The SPM filters were macerated while still frozen or thawing, transferred into a pre-extracted Soxhlet Thimble (Whatman single thickness cellulose), and then extracted for a minimum of 36 hours with pesticide free acetonitrile (Burdick and Jackson "Distilled in Glass," or Mallinkrodt "Nanograde"). The thimbles were pre-extracted with acetonitrile for at least 12 hours prior to use (a number of thimble lots were found to be contaminated with Aroclor 1242 which was effectively removed by pre-extraction). The thimbles were normally re-used for many extractions. The solvent was run through the entire analytical procedure to ensure against residual contamination prior to its first use and at intervals between samples.

34. The acetonitrile extraction was quantitatively transferred to a separatory funnel containing enough distilled water to produce at least a 3:1 dilution. The acetonitrile-water solution was then extracted four times by two-minute shakings with approximately 50 ml of 6% diethyl ether (Et_2O) in hexane. The aqueous layer was discarded and the combined hexane layers dried in a column of pre-combusted anhydrous Na_2SO_4 . The solvent volume was reduced to approximately 3 ml in a KD and the reduced extract was quantitatively transferred to a graduated glass-stoppered centrifuge tube. One milliliter of TMP was added and the volume again reduced carefully on the water bath to less than 1 ml. One ml

of concentrated H_2SO_4 was then added to the cooled centrifuge tube. The tube was then stoppered and shaken for one minute. The resulting mixture was allowed to react and the phases to separate for approximately 12 hours. For most of the samples, the acid treatment was usually sufficient to remove interferences and to allow reliable quantitation of the PCB's. For additional cleanup, the samples were saponified.

35. Sediments. The entire sample was thawed, usually in a cold room ($< 15^\circ C$), and carefully homogenized with a cleaned stainless steel spatula. An appropriate aliquot (4 to 50 g) was transferred to a clean, tared 100 ml Pyrex beaker, weighed, and the beaker covered with aluminum foil. The aliquot was refrozen, freeze-dried, and reweighed. The dried sample cake was then broken up with a spatula and enough hexane was added to just wet the sample but not create a slurry. A portion of precombusted, granular anhydrous Na_2SO_4 was added to the hexane-wet sample in the beaker, mixed carefully into the upper portion of the sample, and transferred to a pre-cleaned Soxhlet thimble. Na_2SO_4 was added repeatedly until all of the sample was transferred. The total volume of Na_2SO_4 used was about fifteen times the volume of dry sediment. The empty beaker was then reweighed to confirm the measurement of dry mass.

36. The sediment- Na_2SO_4 mixture was Soxhlet extracted with 2:1 hexane/acetone (v/v) for at least 12 hours. A small amount of bright copper filings were added to ensure complete sulfur removal. The volume of the eluant was reduced, using a KD, and quantitatively transferred to a graduated, glass-stoppered centrifuge tube. An appropriate volume of

TMP was added and the hexane removed by distillation on a water bath (the centrifuge tube was equipped with a micro Snyder column). An equal volume of concentrated H_2SO_4 was then added and the mixture allowed to react for about 12 hours. Finally, saponification was sometimes required for additional cleanup.

37. Interstitial water. An aliquot of approximately 250 g of the thawed, homogenized sediments was transferred to a clean 300 ml stainless steel centrifuge tube (Sorvall Model 55-3 centrifuge) and spun at 8000 RPM for 15 minutes. The separated interstitial water was carefully decanted and filtered through a pre-combusted glass fiber filter (Reeve Angel 934 AH, 2.5 cm) and collected into a tared 250 ml Erlenmeyer flask. The flask was reweighed to determine the mass of the sample. The flask and its contents were then extracted for PCB analysis by the whole water technique.

38. It should be noted here that many of the samples were unavoidably biased (to an unknown extent) by the inclusion of some of the overlying water with the sediment during collection.

39. Modified elutriate. An aliquot of the thawed homogenized sediment sample was transferred to a clean, graduated cylinder containing 100 ml of filtered seawater. Sufficient sediment was transferred to displace about 200 ml volume, the actual value being accurately determined. The entire content of the cylinder was transferred into a clean glass bottle and 700 ml of filtered seawater was added to the bottle, some of which was used for washing the contents from the graduated cylinder. The bottle was sealed with a teflon-lined screw cap and shaken vigorously

several times over a period of about one hour

40. After standing overnight to allow most of the sediments to settle, the water from the bottle was decanted and filtered through a precombusted glass fiber filter (Reeve Angel 934 AH, 4.5 cm) into a second clean and tared glass bottle. The bottle was reweighed, hexane added, and the sample extracted by the whole water technique.

41. The seawater used in this procedure was collected at 60 m at station 6 of the disposal grid and was analyzed for PCB residues prior to the initiation of the test. Flow schemes for handling and pre-analysis processing of the main sample types are shown in Figures 3, 4, and 5.

Processing of sediment samples for other chemical analyses

42. Oil and grease (OG). A modification of the established technique¹⁴ was used to determine the oil and grease levels in the sediment samples.

43. Approximately 50 g aliquot of the homogenized, freeze-dried sediment sample was transferred to a tared Soxhlet extraction thimble and reweighed. The sample was extracted for 24 hours with 300 ml of hexane. The hexane extract was quantitatively transferred to a Kuderna-Danish evaporator equipped with a tared receiver and a three-ball Snyder column. The extract was carefully reduced to dryness on a hot water bath. The receiver was subsequently vacuum desiccated for 24 hours and reweighed. The amount of hexane extractable was determined by weight difference.

44. Total organic carbon (TOC). Approximately 4 g aliquot of homogenized, freeze-dried sediment was transferred to a tared beaker and

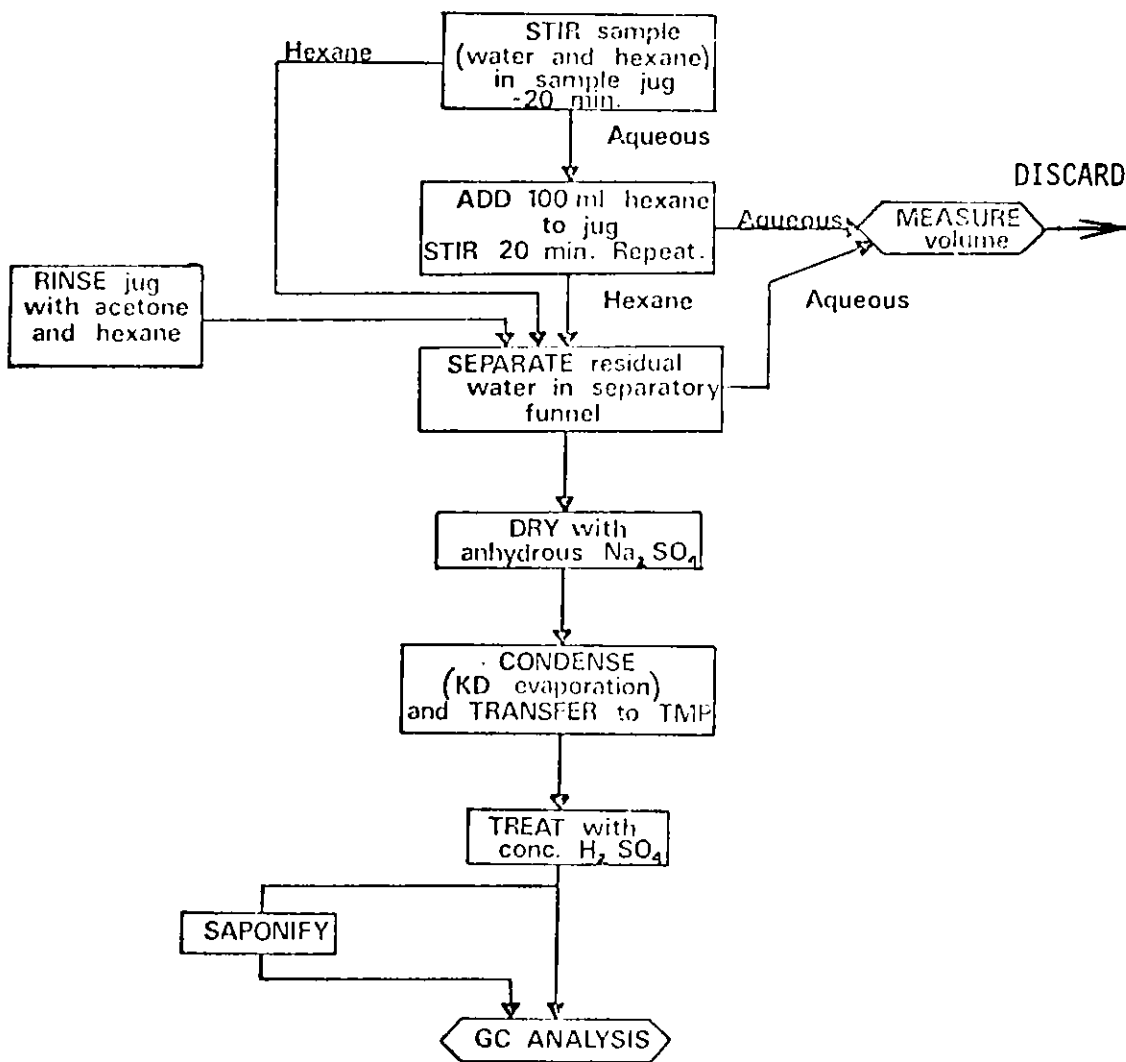


Figure 3. Flow Scheme of Procedures for Whole Water Extraction.

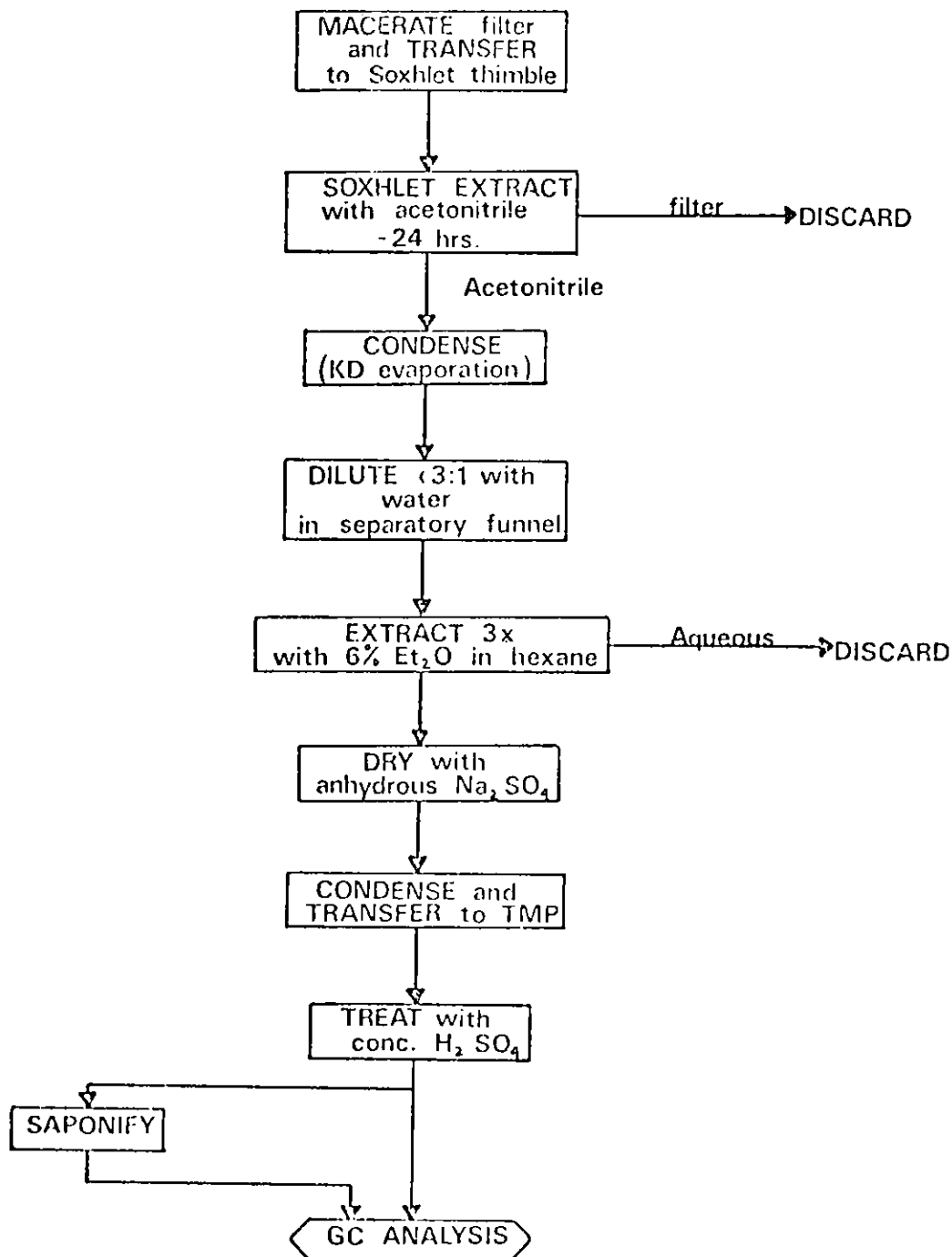


Figure 4. Flow Scheme of Procedures for SPM Extraction.

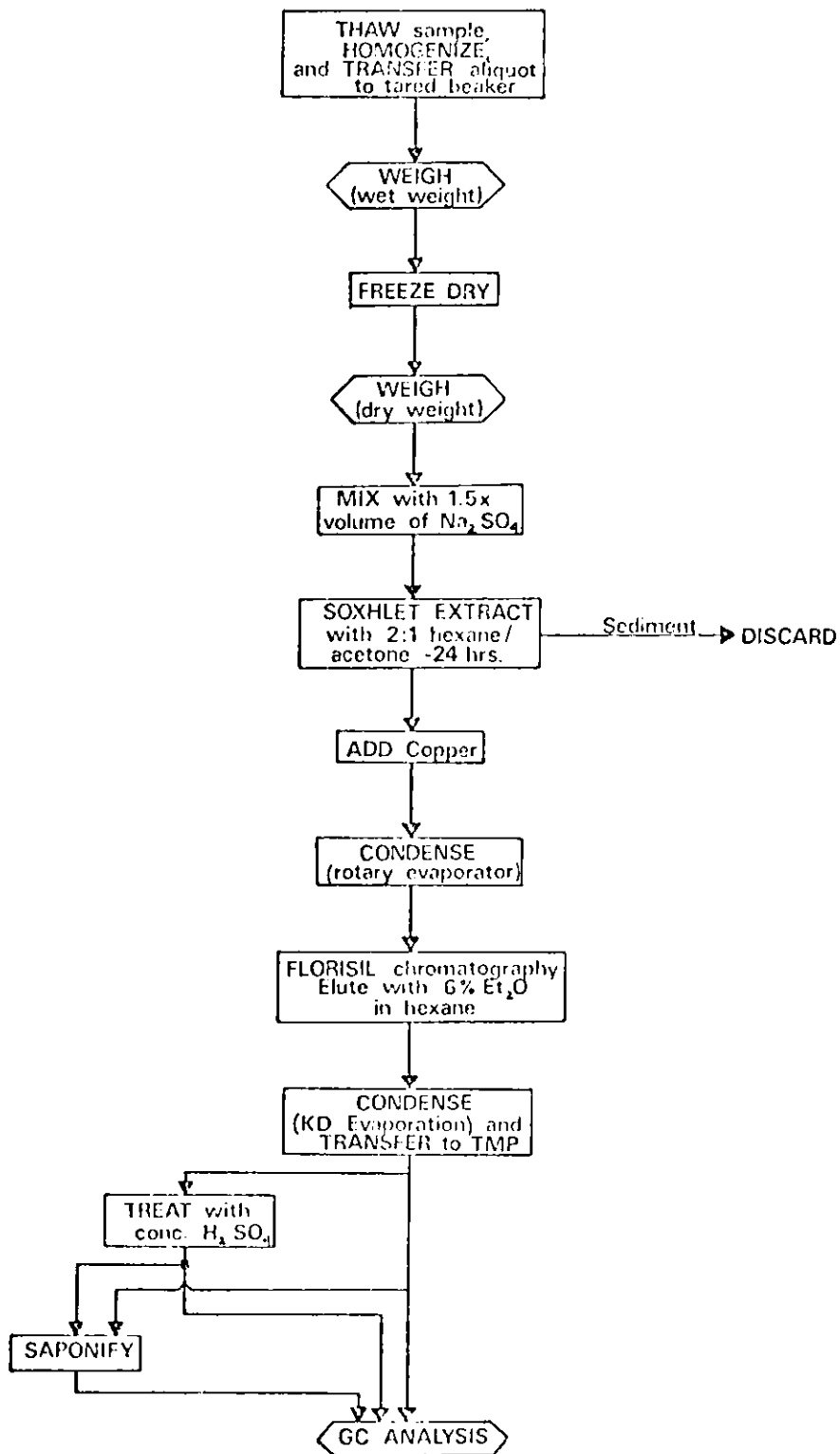


Figure 5. Flow Scheme of Procedures for Sediment Extraction.

reweighed. Five milliliters of reagent grade 30% hydrogen peroxide (H_2O_2) was slowly added as the sediment was stirred. The beaker was placed on a warm heating plate ($80^\circ C$) for several minutes to promote digestion. Frothing was controlled by careful stirring and immersion of the beaker in cold water.

45. After this initial digestion, the beaker was covered with aluminum foil and placed in a $70^\circ C$ oven for approximately one half hour. The beaker was removed, an additional 5 ml of H_2O_2 solution was carefully added with stirring, and then returned to the oven to complete digestion. The sample remained in the oven until dry. It was then transferred to a desiccator to cool and finally reweighed to determine the mass loss as a result of oxidation of the organic carbon.

46. Although pyrolytic methods, attaining better precision than the technique employed in this work, are often used to determine TOC, the type of sediments analyzed here required the use of H_2O_2 digestion. The Duwamish River Basin drains through rather extensive coal deposits which contribute significant quantities of fine coal fragments to the sediments in the study area. Similar to the inorganic carbonate-carbon, the carbon associated with the coal cannot be included in the "total organic" content of sediments. Most instrumental techniques which rely on high temperature oxidation are inappropriate for these sediments since the coal-carbon would bias the TOC measurement. Although the digestion method normally determines 95% of the actual TOC, it has the advantage of avoiding coal-carbon interference.

Hydrography

47. Hydrographic samples were analyzed by standard techniques. Salinities were determined by an induction salinometer,¹⁵ and dissolved oxygen by the modified Winkler method of Thompson and Robinson.¹⁶ Final data reduction, including the calculation of sigma-t and percent oxygen saturation, was performed on the IBM 1130 computer system at the Department of Oceanography, University of Washington.

Gas Chromatographic Methods of PCB Determination

48. After processing, the final TMP samples' extracts were analyzed by electron capture gas chromatography (EC/GC). All analyses were performed on a Tracor MT-220 gas chromatograph equipped with two ⁶³Ni high temperature electron capture detectors. The columns were 2 m by 2 mm Pyrex glass tubing packed with 1.5% OV-17/1.95% OV-210 on 100-120 mesh Chromosorb W-HP. The carrier gas was a mixture of 5% methane in argon. Spectra were recorded on a Westronics MT-22 strip chart recorder. Peak retention times and areas were determined by a Columbia Scientific Industries Model Supergrater-2 digital integrator. The PCB residues were characterized based on the following criteria:

- a. Only a limited number of organic compounds possess the specific chemical characteristics of PCB's; i.e., low polarity and resistance to both strong acid and alkali degradation required by the pre-analysis processing of samples.
- b. Their retention times must agree with the corresponding peaks in known standards on two different columns.

- c. Their relative spectral intensities (peak areas or heights) must resemble the pattern generated by known standards.
- d. DDT and DDD are converted to DDE and DDMU, respectively, by ethanolic-KOH dehydrochlorination.
- e. The residues from randomly selected samples have been subjected to mass spectrometric analysis (GC/MS) under similar GC conditions. Confirmation of chlorobiphenyl content in these samples was based on the observed mass-fragmentation patterns. Good agreement between GC/MS and EC/GC elution patterns for all sample types provided good evidence of their identity.

49. The components of the PCB mixtures were identified by retention time. For residue confirmation a second column, Silar 10C on 100-120 mesh Gas-Chrom Q, was recently added to the system. This alternative produces strongly different separations for the PCB and pesticides and is advantageous when the elution pattern is greatly altered compared to a standard, or in the presence of interferences not removed by the pre-analysis processing. However, the resolution with this column is not as great, and therefore the column has not been used for primary identification and/or quantitation.

PCB Data Reduction

50. The concentrations of the chlorobiphenyls (CB) were determined by comparing the response of individual peaks via the spectral analysis technique developed as part of our EPA study¹⁷ and are described in detail in Appendix C' to this report. With this technique the concentrations of the residues with the same degree of chlorination, N, could be determined, as well as the total residue content. This computational

scheme was programmed into the CDC 6400 computer system at the University of Washington for automatic data reduction. Detailed computational flow schemes and the program listing, including data inputs and outputs, are presented in Appendix D' of this report.

51. Prior to the final analysis, the raw data for all sample types were evaluated according to the procedures listed below:

- a. Confirmation of GC spectral patterns and initial quantitation.
- b. Internal consistency check of residue values.
- c. Preliminary synoptic assessment of temporal and spatial trends.

52. This procedure was adopted as a preliminary screening for flagging suspect data and detecting gross errors introduced by accidental mishandling of samples, incorrect spectral quantitation, inconsistencies in replication, and contamination during analysis. In this manner, unreasonably large disparities from normal trends over the sampling periods and deviations of the data from historical and predicted behavior in the area could be identified prior to the initiation of statistical treatment and correlation analysis.

Statistical analysis

53. The chemical data generated throughout this project were first examined by a modified split-plot design and analysis technique.¹⁸

54. Water parameters. For the PCB concentrations in whole water, the dominant variables were station, location, time, and the depth at which

the sample was collected. These variables were incorporated in the model as follows:

$$\underline{a.} \quad Y_{ijk} = \mu + S_i + (SD)_{ij} + T_k + (ST)_{ik} + (SDT)_{ijk} + \epsilon_{1(ijk)}$$

where Y is the sample value, μ refers to the true population mean, with variance due to station (S, with $i = 1, 2, 3, 4, 5$), depth (D, with $j = 1, 2, 3$), time (T, with $k = 1, 2, 3, 4, 5, 6$), and error (ϵ , with $l = 1, 2$, replication). SD, ST, and SDT refer to the station by depth interaction, the station by time interaction, and the station by depth by time interaction, respectively. Station locations are considered to be the dominant spatial factor in this design.

$$\underline{b.} \quad Y_{ijk} = \mu + D_j + (DS)_{ji} + T_k + (TD)_{jk} + (DST)_{jik} + \epsilon_{1(ijk)}$$

where Y is the sample value, μ refers to the true population mean, with variance due to station (S, with $i = 1, 2, 3, 4, 5$), depth as the dominant spatial factor.

55. Sediment Parameters. A similar design was used to examine the concentration of PCB and oil and grease in the sediments. In this case

$$Y_{ijk} = \mu + H_i + S_{j(i)} + T_k + (HT)_{ik} + (ST)_{jk(i)} + \epsilon_{1(ijk)}$$

where H_i refers to subgroups of stations, i.e., the habitats. The other notations are the same as presented above. The habitats were chosen based on initial inspection (visual) of the spatial trends exhibited by Y.

56. The results of these analyses of variance (ANOVA) calculations allowed an initial determination of significant differences in the residue levels either spatially or with time. For all statistical tests the significance level of $\alpha = 0.05$ (95%) was chosen.

57. When factorial analysis indicated that significant discontinuities were present, the means were compared pairwise, either between different habitats within the same cruise (spatial differences), or between cruises within the same habitat (temporal effects). For these analyses the Scheffe multiple comparison procedure was used.¹⁹ The equation is as follows:

$$\text{Test statistics} = \bar{X}_1 - \bar{X}_2 + \sqrt{(k-1)F_{(k-1, \nu)} \hat{\sigma}^2 \left(\frac{1}{n_1} + \frac{1}{n_2} \right)}$$

where \bar{X}_1 and \bar{X}_2 are the habitats' means being compared; k corresponds to total number of means being compared; F is the ratio of the mean squares at significance level $\alpha = 0.05$ for k-1 and ν degrees of freedom; $\hat{\sigma}^2$ is the appropriate variance (mean square) generated in the factorial analysis; and n_1 and n_2 refer to the number of samples constituting the means.

58. The difference between the means was considered significant when the range of the test statistic was greater or less than zero:

a. When $(\bar{X}_1 - \bar{X}_2) \pm \sqrt{\quad} > 0.$

b. Or when $(\bar{X}_1 - \bar{X}_2) \pm \sqrt{\quad} < 0.$

Quality assurance

59. The statistical analysis of the data as described previously includes a consideration of the random error associated with each data point. The procedures employed in this laboratory to ensure against systematic error or bias affecting results were as follows.

60. The principal source of bias is contamination. For all sample analyses, blanks (comprising approximately 10% of the total number of samples corresponding to a specific type) were run at regular intervals. These blanks were processed by carrying extraction solvents through the entire analytical procedure, but with no sample. At no time was any significant contamination observed in these blanks. The contribution was normally <2% of the lowest sample value.

61. In the PCB analyses, the quantitation was based on direct comparison with standard PCB solutions. Alteration of these standards, e.g., by solvent evaporation, could result in erroneous results. The response data for the standards were stored in computer memory for each chromatographic run. This provided a convenient data base for comparing any changes in the response of the standards with time. No such changes were noted.

62. To determine the errors associated with the make-up of the original standard solutions, or with the computation scheme, an inter-laboratory calibration check was performed. Table 4 shows the results of this intercalibration experiment between our laboratory (University of Washington) and Dr. Stout's facilities at the National Marine Fisheries Service (NMFS), Seattle, Washington. Each laboratory exchanged 15 sample extracts which were analyzed and quantified by the techniques used routinely by their respective staffs. The data show that while there were some relatively small differences for some samples, there was no apparent systematic error.

TABLE 4A

Summary of the Intercalibration Results
With The National Marine Fisheries Service
For PCB Analysis of Tissue Samples

Sample No.	PCB (ug/g tissue)		Fractional Deviation (Δ)
	UW	NMFS	
V1758	0.09974	0.164	-0.64
V1760	0.08248	0.107	-0.30
V1772	0.1696	0.168	0.01
V1776	0.1613	0.168	-0.04
V1786	0.7068 \pm 0.0018	0.680	0.04
V1795	0.2528	0.333	-0.32
V1797	0.1302	0.190	-0.46
V1798	0.9905	0.821	0.17
V1801	0.2321	0.291	-0.24
V1803	0.4056	0.524	-0.25
V1804	0.5660	0.593	-0.05
V1841	0.4273	0.265	0.38
V1857V	4.426	3.66	0.17
V1868F	2.095	1.66	0.21
V1908(1:10)	4.782	5.90	<u>-0.23</u>
			$\bar{\Delta} = -0.11$

Δ is the fractional deviation and is defined as $\Delta = \frac{UW - NMFS}{UW}$

TABLE 4B

Summary of the Intercalibration Results
With The National Marine Fisheries Service
For PCB Analysis as Sediment Samples

Sample No.	PCB (ug/g dry sediment)		Fractional Deviation (Δ)
	UW	NMFS	
AS 170	0.294	0.398	-0.35
412	0.497	0.341	0.31
413	1.629	0.873	0.46
416	0.476	0.538	0.13
417	0.243	0.347	-0.43
418	1.222	0.659	0.46
421	0.031	0.016	0.48
422	0.184	0.259	-0.41
424	0.029	0.018	0.38
426	0.031	0.019	0.39
427	0.009	<0.012	----
438	0.684	0.550	0.20
441	0.306	0.343	-0.12
442	0.305	0.350	-0.15
443	0.592	0.492	0.17
446	0.574	0.574	<u>0.00</u>
			$\bar{\Delta} = +0.08$

Δ is the fractional deviation and is defined as $\Delta = \frac{UW - NMFS}{UW}$

PART IV: RESULTS AND DISCUSSION

63. All chemical data collected in this subproject for all sample types are tabulated in Appendices A' and D' to this volume. For clarity, water column and sediment parameters are discussed separately below.

Water Column Parameters

Hydrography (salinity, temperature, and sigma-t)

64. The salinity, temperature and sigma-t data collected during the post-disposal cruises are tabulated in Appendix D'. Vertical profiles for each station are also included. These data show the common features exhibited by the water column in Elliott Bay; i.e., the relatively thin halocline and pycnocline at the surface, and an essentially uniform water mass in the lower portion of the bay.

65. Seasonal effects are apparent in the excursion of the surface temperatures from about 7.5°C in March of 1976 to about 12°C in June, followed by decreasing temperatures again in the early and late fall.

66. During this particular cruise series, river discharge was much lower than what is commonly observed in normal years, reflecting the unusually low precipitation conditions in the Pacific Northwest during 1976. As a result, the surface low salinity was not well developed and essentially disappeared with the onset of fall cooling and the accompanying surface mixing. By December (cruise 343) nearly all vertical density and salinity structure was lost, exhibiting vertical homogeneity in the

water column.

PCB characteristics

67. The chlorobiphenyls (PCB) concentrations measured in whole water and SPM samples are presented in detail in Appendix A'. The results are examined in two independent sections.

- a. In terms of the time series generated during the two cruises where the disposal operations were monitored on a continuous basis.
- b. In terms of the six cruise series conducted over a nine month period after disposal had ceased.

68. Time plots of the total chlorobiphenyl (TCB) concentrations at the buoy site during the two disposal monitoring cruises (55 and 57) are shown in Figures 6 and 7. In general the data from both days indicate rather rapid pulses of very high concentrations associated with each of the three large dumping events. The highest concentrations were observed at the bottom depths. These pulses are of very short duration and are within the same time frame of the dumping episodes. After each pulse the ambient concentrations rapidly return to pre-dump conditions. However, on both days there was a significant residual increase after each dump which resulted in an overall but slight increase in TCB levels by the end of each monitoring period. This can clearly be seen by comparing the values at the reference station measured before and after each disposal operation (Table 5). The TCB concentrations measured prior to disposal are of similar magnitude to those observed in earlier studies within the Elliott Bay area, approximately 3 ppt.^{2, 3}

69. The temporal and spatial trends were examined over the post-disposal cruise series. The discussion which follows relies primarily on the whole water measurements, since they provide a more complete data set. The TCB data for water and SPM are summarized in Tables 6 and 7. Plots of the average concentrations at each station versus time are shown in Figures 8 and 9. In general the TCB concentrations in the SPM correspond well with the trends in whole water.

70. Since the water column is normally stratified, at least in the surface layers within Elliott Bay, it was deemed appropriate to examine the vertical profile of PCB concentration in terms of the hydrographic characteristics of the sampling site and to determine whether residues originating from the disposal operation were maintained and distributed primarily at specific depth layers. The data indicated that within the depth strata sampled the highest TCB levels were observed at the surface. However, depth dependence was not statistically significant and was consistent with the vertical uniformity observed in the salinity, temperature, and density profiles. Nevertheless, this gradient suggests that the low salinity water discharged by the Duwamish River is a major source of contamination within the bay. These considerations agree with the trends observed in our earlier studies.^{2, 3}

71. The data from all depths at each station were treated statistically to determine the existence of spatial and temporal trends. Although it appears that there is a general trend toward lower PCB concentrations in the water within each station, only the difference between the

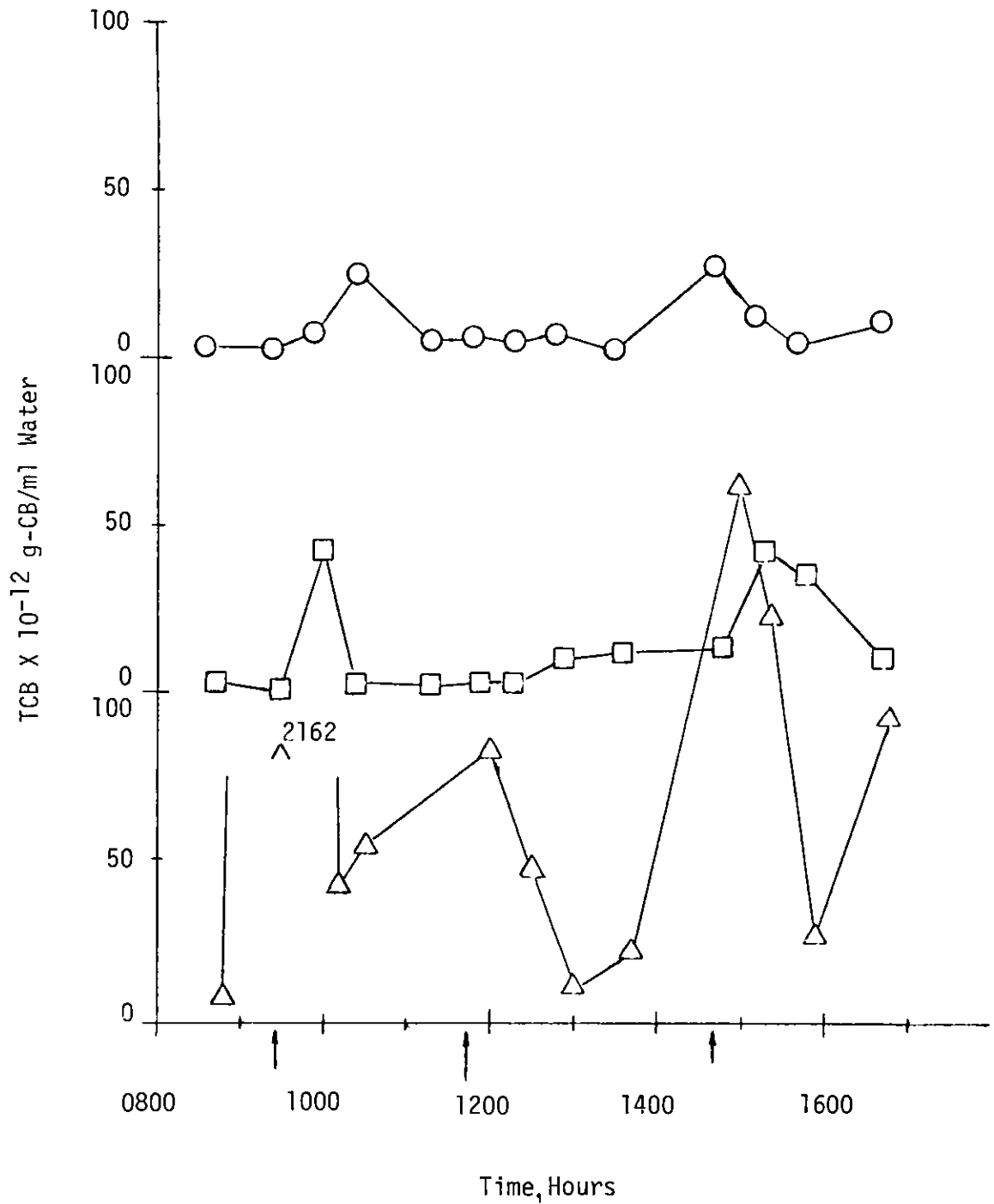


Figure 6A. Plots of Whole Water Total PCB (TCB) Concentrations at the Buoy Site (Station 6) Versus Local Time on Cruise 55; ○ - Surface, □ - Mid-Depth, △ - Bottom. Arrows indicate Approximate Times of Dump Episodes.

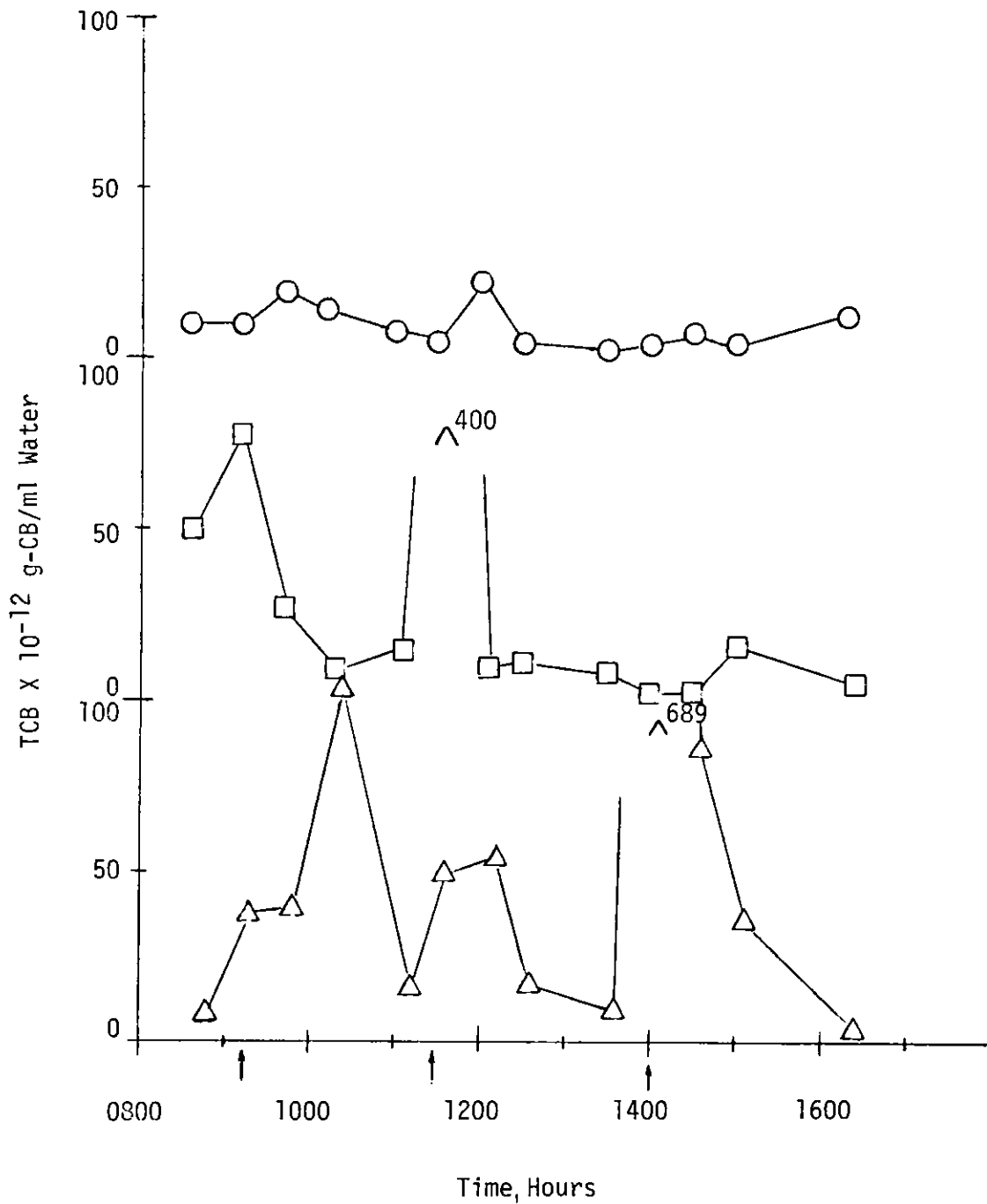


Figure 6B. Plots of the Whole Water Total PCB (TCB) Concentrations at the Buoy Site (Station 6) Versus Local Time on Cruise 57; ○ - Surface, □ - Mid-Depth, △ - Bottom. Arrows Indicate Approximate Times of Dump Episodes.

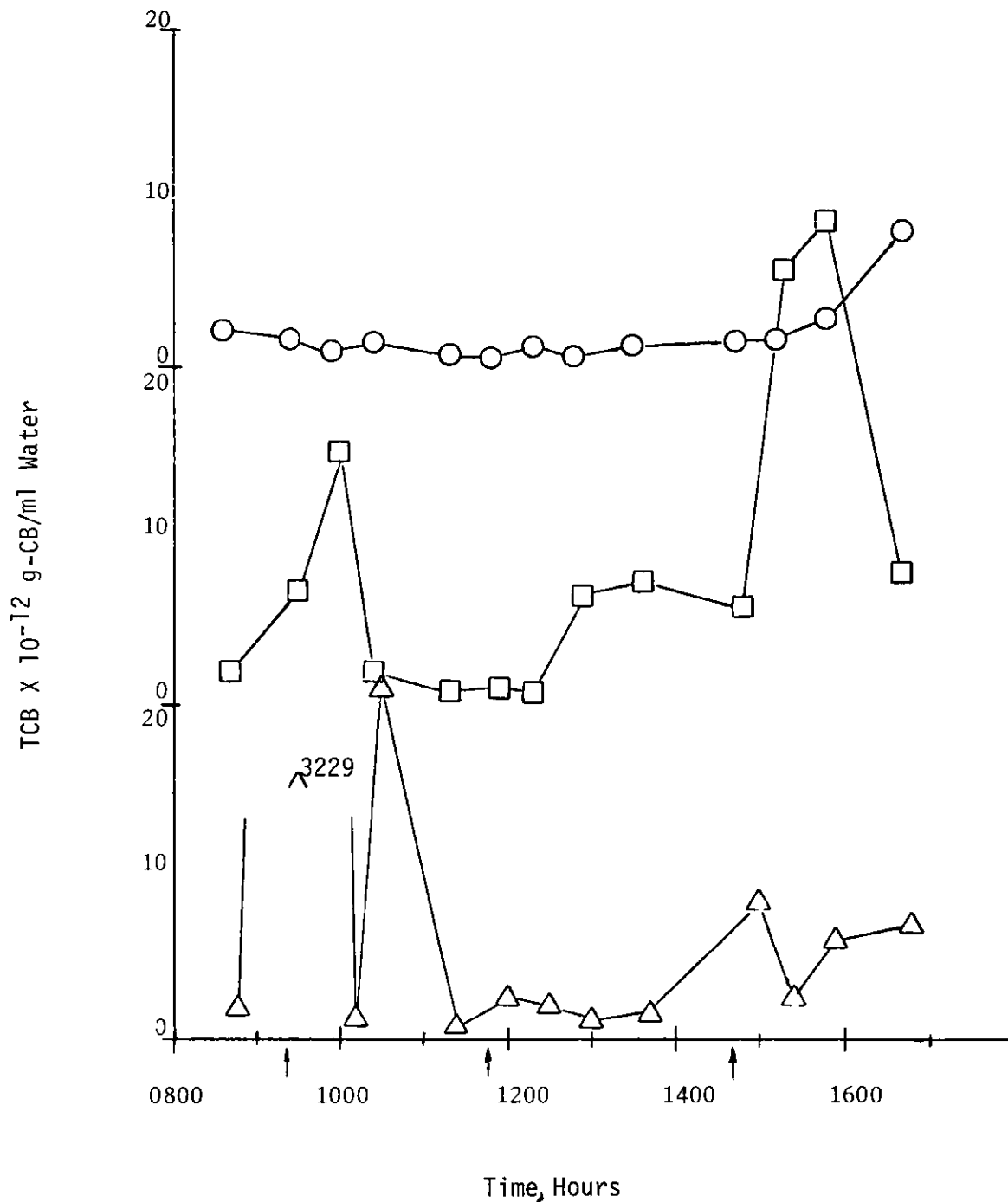


Figure 7A. Plots of the SPM Total PCB Concentrations (TCB) at the Buoy Site (Station 6) Versus Local Time on Cruise 55; ○ - Surface, □ - Mid-Depth, △ - Bottom. Arrows indicate Approximate Times of Dump Episodes.

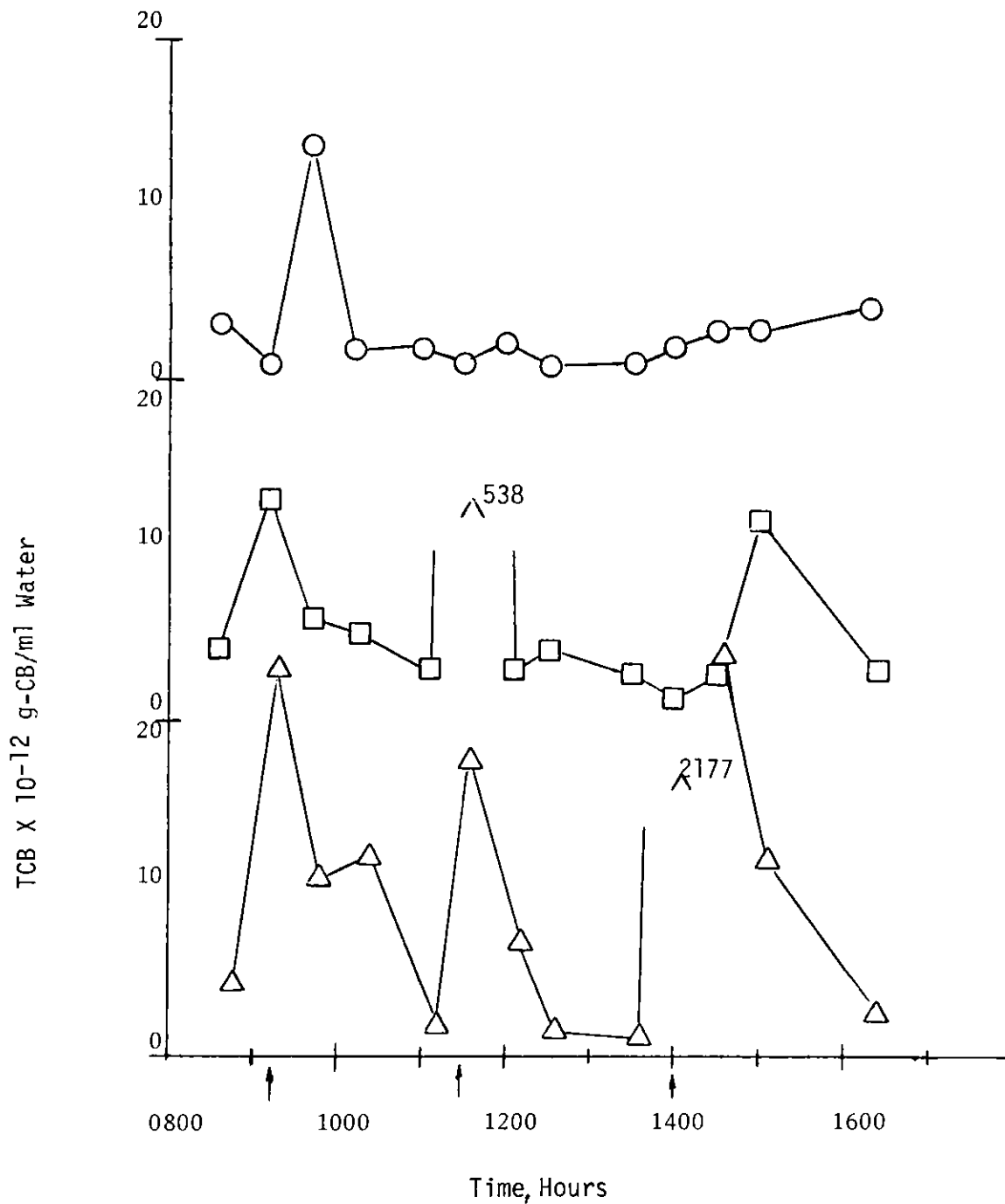


Figure 7B. Plots of the SPM Total PCB Concentrations (TCB) at the Buoy Site (Station 6) Versus Local Time on Cruise 57; ○ - Surface, □ - Mid-Depth, △ - Bottom. Arrows indicate Approximate Times of Dump Episodes.

TABLE 5

TCB Concentrations in Whole Water Samples
Collected Before and After the Disposal Operations*

<u>Cruise</u>	<u>Station 17</u>		<u>Station 19</u>		<u>Station 44</u>	
	<u>B</u>	<u>A</u>	<u>B</u>	<u>A</u>	<u>B</u>	<u>A</u>
55	2.28	7.45	3.23	10.69	3.98	9.30
57	3.46	10.96	6.52	13.35	6.09	14.03

*Values for TCB are in units of $\times 10^{-12}$ g/ml(ppt).

TABLE 6

Mean Total Chlorobiphenyl Concentrations in Whole Water
Samples at each station for the Post Disposal Cruises

HAB-STA NO. CRU	1	10	17	19	44
67	5.30*	4.06	4.44	12.25	6.05
76	1.62	3.31	2.11	3.31	4.86
99	3.43	3.13	2.19	3.21	7.75
170	2.93	7.93	1.95	1.41	1.65
266	2.32	2.29	1.47	2.25	1.40
343	.99	1.04	1.06	1.49	6.68

*TCB concentrations are in units of $\times 10^{-12}$ g .ICB/ml water.

TABLE 7

Mean Total Chlorobiphenyl Concentrations in SPMSamples at each station for the Post Disposal Cruises

<u>HAB-STA NO.</u>	<u>6</u>	<u>10</u>	<u>17</u>	<u>19</u>	<u>44</u>
<u>CRUISE</u>					
67	4.20*	2.58	-1.00	-1.00	-1.00
76	2.37	2.34	-1.00	-1.00	-1.00
99	1.86	1.64	1.62	1.75	3.75
170	1.45	1.14	1.00	1.49	1.35
266	.68	.49	.58	1.74	1.04
343	.98	1.12	1.06	3.11	3.06

*TCB concentrations are in units of $\times 10^{-12}$ g TCB/ml water.

▲ STA-6 Z STA-19
 X STA-10 X STA-44
 ♣ STA-17

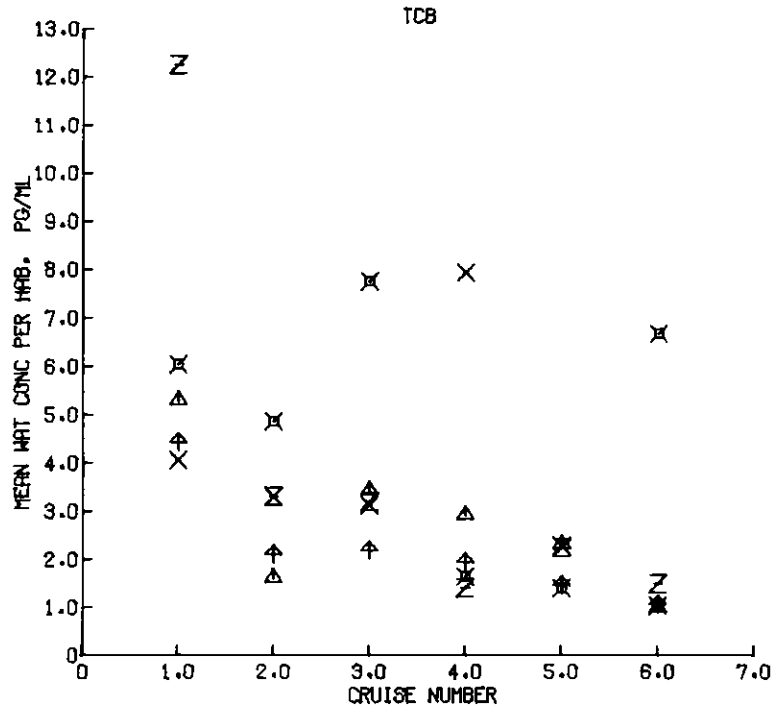


Figure 8. Plots of the Mean Habitat TCB Concentrations Versus Time for Whole Water (Post-Disposal Cruise Series).

△ STA-6
 X STA-10
 † STA-17
 Z STA-19
 ✕ STA-44

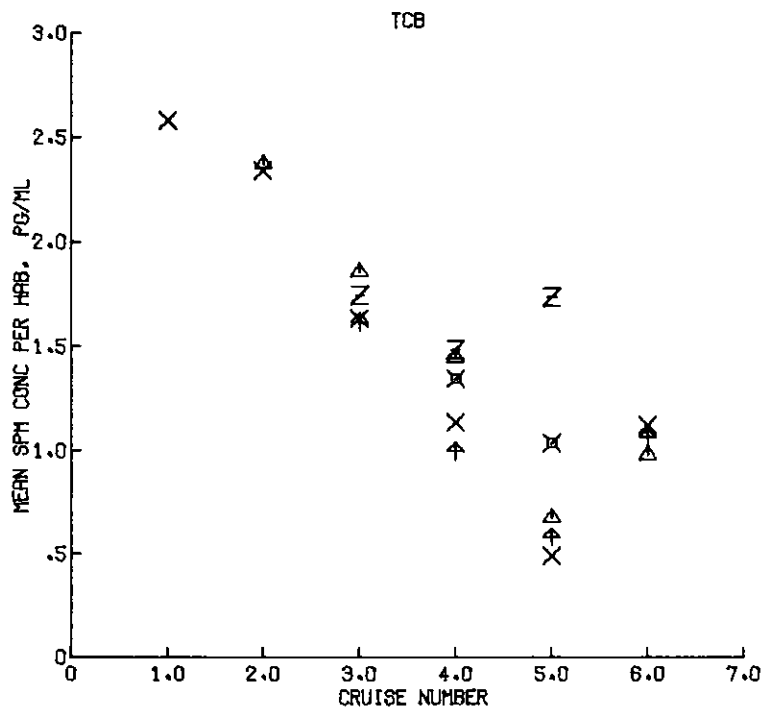


Figure 9. Plots of the Mean Habitat TCB Concentrations Versus Time for SPM (Post-Disposal Cruise Series).

first post-disposal cruise (67, two days after cessation of dumping) and all subsequent cruises was significant. The mean PCB value for all stations within the bay for cruise 67 was approximately 7 ppt and was higher than what has been observed in the past.

72. Comparisons between stations within each cruise did not yield any significant differences, although the levels at stations 19 and 44 were generally higher than the other three stations. This again probably reflects the input from the industrialized river and Seattle waterfront.

Sediment Parameters

PCB characteristics

73. River sediments. The concentrations of TCB observed in the river sediments (stations 21-39) which provided the source of material for the disposal project ranged between 0.01 and 6.98 ppm. A profile of these values over the stations sampled is presented in Figure 10. Considerable spatial variability was observed with high levels occurring in the northern section of the river. These high levels were associated with what appeared to be a rather narrow band of highly contaminated sediments centered around station 25. Both up and downstream the levels decrease fairly regularly. Upstream of station 13 there was a marked decrease in TCB concentrations to a constant level of about 0.2 ppm. The abnormally low values observed in stations 30 and 38 are due predominantly to the coarse grain of these sediments (sand) as compared to the other samples collected. The mean TCB concentration throughout the section of the river sampled was 2.05

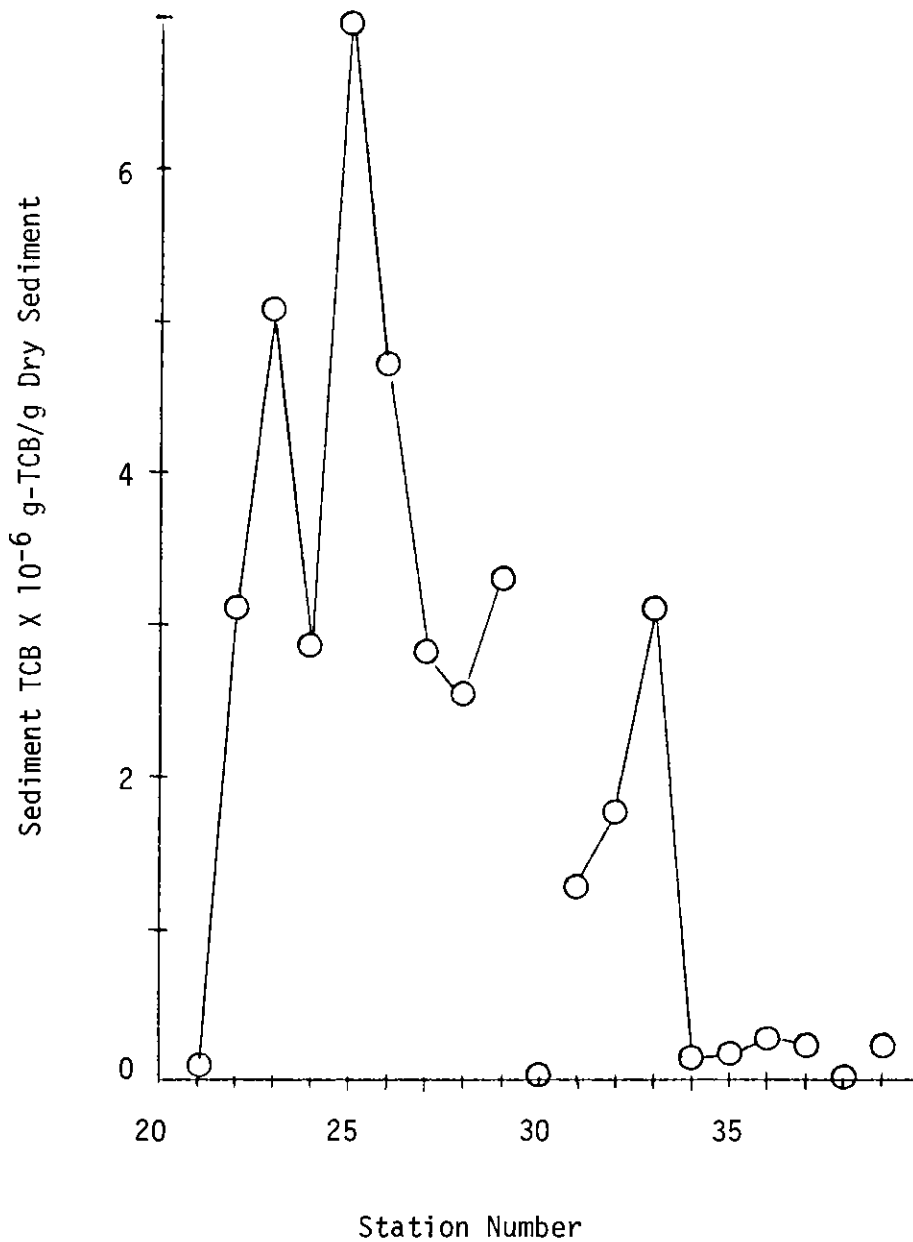


Figure 10. Plots of the Total PCB (TCB) Concentration in Sediments Versus Relative Distance (Station Number) Within the Duwamish River Site.

ppm. It should be noted that this value does not correspond to the mean value determined in the sediments at the disposal site because the spatial variability of PCB concentrations within the river sediments and the quantities of material dredged that contained a given concentration of PCB were not accounted for in the averaging process.

74. As has been discussed previously,⁴ characterizing environmental CB through measurements of the relative mass fractions, F_n , of the N-CB components constituting the PCB mixture provides useful data for assessing the dispersal of these chemicals and tracing their source. The characteristic F_n distribution, or "fingerprint", of the river sediments is shown in Figure 11 as a plot of F_n versus the chlorine number, N . The values were generated by determining the relative concentrations of corresponding N-CB, averaged over all the river stations. While the pentachlorobiphenyl (5-CB) residues predominated, significant quantities of lower chlorinated biphenyls were observed. In particular, the trichlorobiphenyls (3-CB) averaged about 20% of total. There was relatively little spatial variability in the F_n distributions of the river samples compared to the large fluctuations in the corresponding TCB concentrations. It is also worth noting that many of the CB values observed in the river were considerably higher than what had been anticipated. Previous studies have relied on relatively low intensity, synoptic samplings under the assumption that CB levels were reasonably continuous between sampling points. The CB concentrations in the upper reach of the dredged river site were comparable to these previous studies.^{2, 20} Unfortunately, the lower reach,

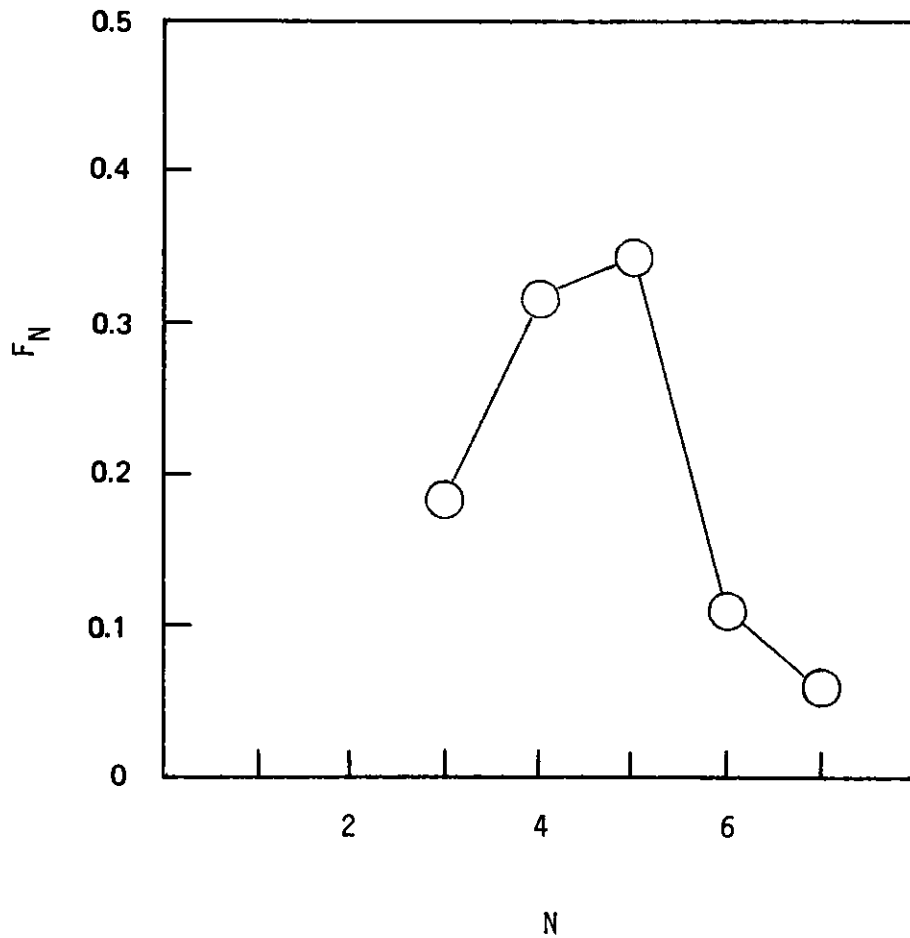


Figure 11. Plots of Averaged Relative Mass Fraction, F_N , Versus Chlorine Number, N , for the Sediments at the Duwamish River Dredged Site.

between stations 21 and 30, had not previously been sampled. As a result, it is not possible to determine the historical sequence of inputs leading to the elevated CB levels. These CB are most likely not related to the transformer spill in the lower Duwamish in September 1975. Although some upstream movement of the latter material was observed, the translocation was limited within a few hundred meters from the Slip 1 spill site.²¹

75. Background condition at the disposal site. TCB concentrations within the sediments of the disposal zone and reference areas prior to dumping (background conditions, cruise 37) are included for the upper horizon in Table 8 as mean values for each habitat. (The groups of stations constituting the habitats and the rationale for this breakdown are discussed in the next section.) A pronounced PCB gradient is shown which consists of significantly higher levels in the east (along the Seattle waterfront) and central portions of the bay, decreasing to the west. Although in general this is consistent with the deposition pattern of contaminated sediments discharged from the Duwamish River as observed in previous studies (see discussion in Part I), it should be pointed out here that the spatial nonhomogeneity within the grid is very pronounced. Even within as small an area as that defined by one station, PCB levels varied as much as eightfold. For example, although the average TCB concentration at the disposal site was 0.2 ppm, a single sample (station 13) had a measured value of 1.7 ppm. The field replicate of this sample was 0.15 ppm.

76. Spatial variability in the PCB type was also noted when the relative mass fractions were compared. For example, Figure 12 compares a plot of the Fn values averaged over all cruise 37 samples versus N with a similar plot for the high concentration sample from station 13 referred to above. While the 5-CB residues predominate in both, the station 13 sample was enriched in 6- and 7-CB and in fact had a component distribution nearly identical with that of Aroclor 1260 type PCB. Similar differences were noted in the relative N-CB concentrations at other stations. It seems improbable that such high variability in concentrations and PCB type could be generated by normal estuarine deposition. Rather the data indicate that the least part of the background CB levels resulted from direct inputs of CB containing materials, e.g., ship discharges, waste dumping, or spills. It is also important to compare the Fn relationships of river and disposal zone sediments. Even though there is some overlap in the concentration ranges observed in the two areas, all river samples were comparatively enriched in lower chlorinated biphenyls. This difference provides an effective means of accurately discriminating between the two sediments.

77. Post-disposal characteristics. To facilitate visualization of the general spatial and temporal trends of CB residues in the disposal and reference zones during the pre- and post-disposal cruises, three-dimensional histograms of TCB concentrations were constructed as shown for the upper horizon in Figures 13 and 14. Inspection of these histograms indicates that after disposal the highest concentrations were encountered

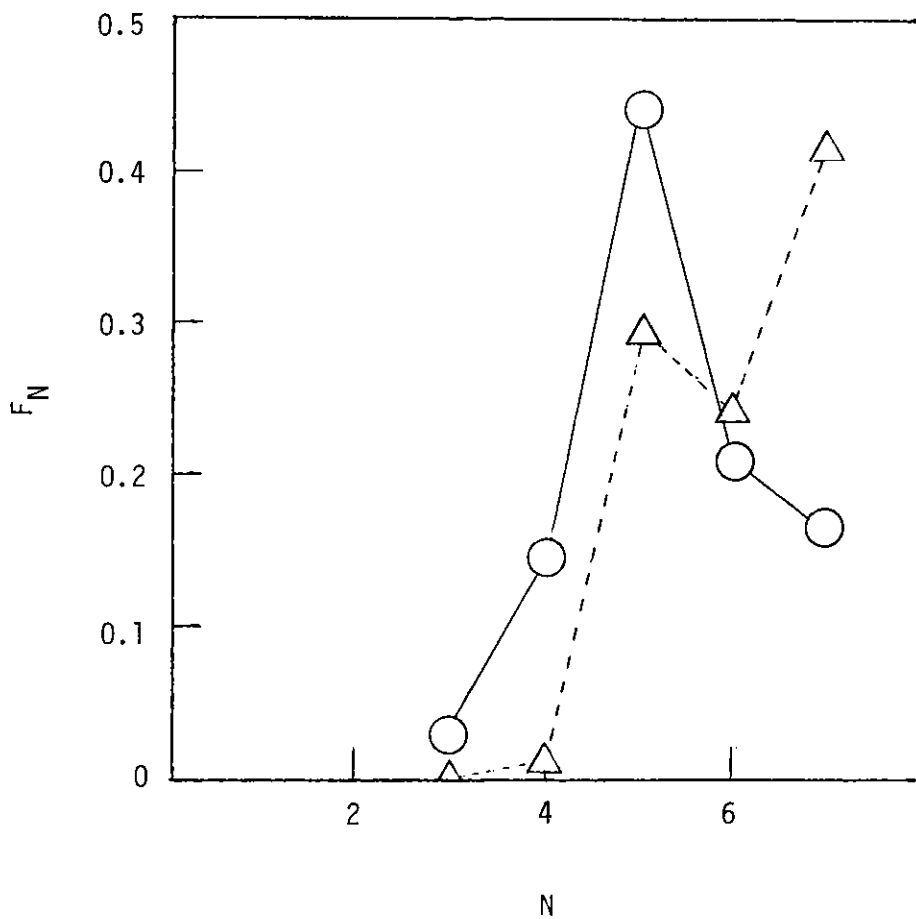
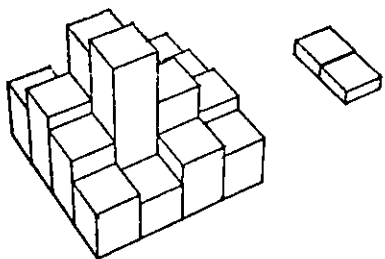


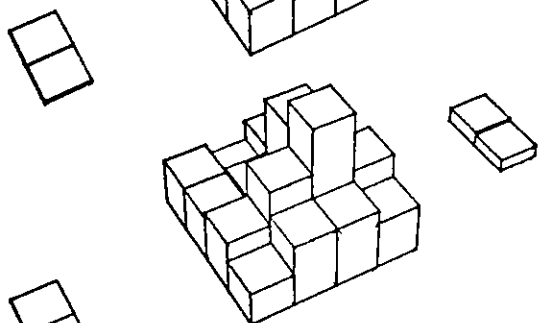
Figure 12. Plots of Relative Mass Fraction, F_N , Versus Chlorine Number, N , for Background Sediments at the Disposal Site: O , Averaged Values for All Stations; Δ , Values for Station 13.

Cruise
Number

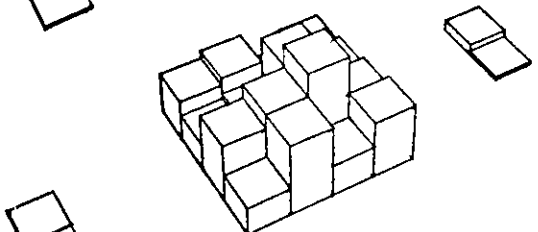
342



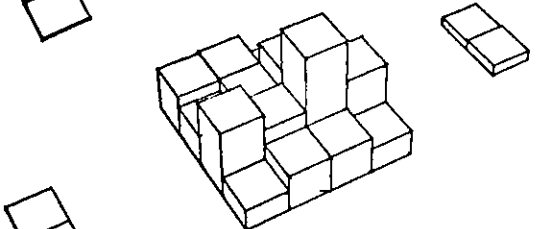
265



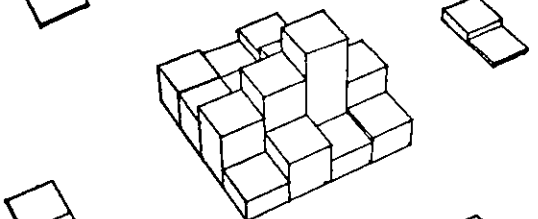
168



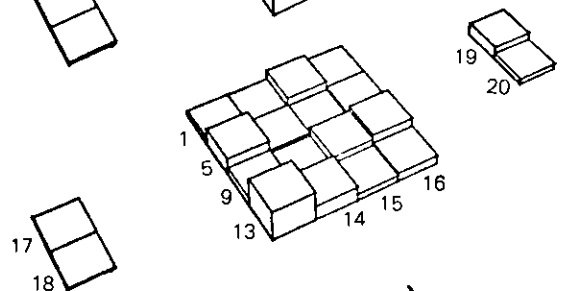
99



76



37



Scale
parts per million

10

5

1

Figure 13. Three Dimensional Histogram
of the Total PCB Concentra-
tions in Sediments for the
Upper Horizon (Northward
Direction).

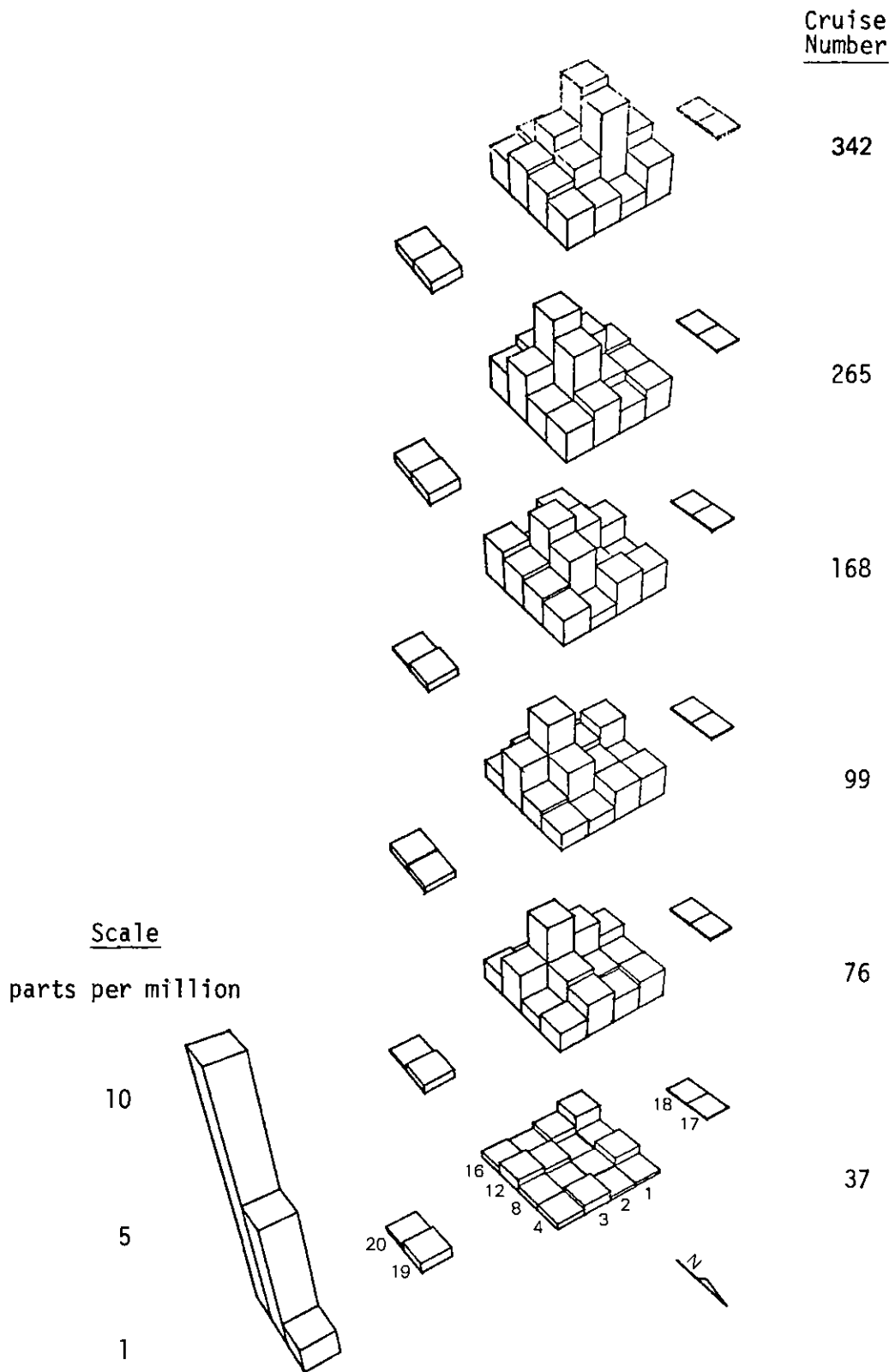


Figure 14. Three Dimensional Histograms of the Total PCB Concentrations in Sediments for the Upper Horizon (Southward Direction).

at the central section of the station grid with values diminishing roughly radially away from the center. Based on this feature, the grid stations were sorted into three habitats consisting of the corner (1, 4, 13, 16), side (2, 3, 5, 8, 9, 12, 14, 15), and central stations (6, 7, 10, 11). The residue levels within these habitats and the two reference habitats (17, 18 and 19, 20) are presented as habitat means in Tables 8 and 9. The mean values for each habitat are plotted as a function of time (sequential cruise number) in Figure 15.

78. By examining these data it is clear that there was a significant increase (at the 95% confidence level) in the PCB concentrations within the upper horizon at all grid habitats following disposal. At the same time, no significant change was noted during the cruise series at the reference stations. Although there is an apparent trend toward increasing concentrations at the grid site during the later cruises, (especially at the side and corner habitats) these increases were not significant.

79. Although the mean habitat CB concentrations decreased in the order central > side > corner during all post-disposal cruises, when the comparisons are based on the TCB concentrations, these differences are not statistically significant. However, the fact that these differences are real can be established by using the 3-CB levels for comparison, since this component provides a better discriminator between the disposal site background and the river sediments.

80. Based on the 3-CB concentrations, the central habitat had significantly higher CB levels than the corner habitat during the first two

TABLE 8
Mean Habitat TCB Concentrations in
the Upper Horizon Sediments for Each Cruise

HABITAT CRUISE	Corner	Central	Side	ERA	WRA
37	425.85*	246.47	369.83	310.92	59.45
76	912.38	2194.95	1256.56	243.10	86.61
99	894.78	2127.76	1320.05	309.59	85.94
168	1331.69	2187.23	1355.57	233.75	81.96
265	1339.10	2938.18	2257.83	451.00	86.33
342	1575.96	3441.79	1692.97	467.11	103.94

*TCB concentrations are in units of ng TCB/g dry sediment.

TABLE 9
Mean Habitat TCB Concentrations in
the Lower Horizon Sediments for Each Cruise

HABITAT CRUISE	Corner	Central	Side	ERA	WRA
37	425.85*	246.47	369.83	310.92	59.45
76	369.23	1758.32	366.51	26.59	14.81
99	185.11	1252.83	321.72	816.10	14.05
168	248.05	1259.05	631.39	78.70	17.24
265	439.37	1986.98	637.60	374.79	50.66
342	685.88	1635.24	980.38	251.16	17.17

*TCB concentrations are in units of ng TCB/g dry sediment.

▲ CORNER ZE-REF
 × MIDDLE W-REF
 † SIDES

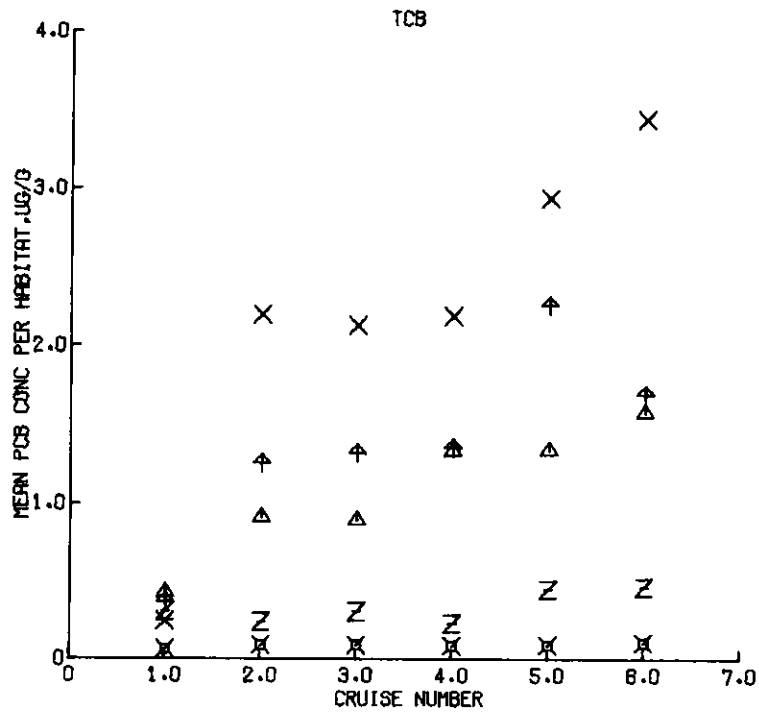


Figure 15. Plots of Mean Habitat TCB Concentrations Versus Time for Sediment in the Upper Horizon.

post-disposal cruises. Subsequently, as a result of the small increases in CB concentrations at the corner and side stations, these differences could no longer be distinguished.

81. PCB concentrations in the lower horizon of the grid during the post-disposal period showed the same general behavior. It must be remembered that the lower horizon consists of the section of the sediment corer greater than 10 cm in depth. As a result, they can be used to a certain extent to estimate the depth of the sediment deposit within that core.

82. The data obtained for the lower horizon sediments were organized and are presented in a manner similar to that provided for the upper horizon. Three-dimensional histograms of the averaged TCB concentrations at each station for each cruise are presented in Figures 16 and 17. Mean habitat TCB values are tabulated in Table 9 and plotted as a function of time (sequential cruise number) in Figure 18. In addition, the background sediment data (cruise 37) have been included for comparison since at many stations what was surface sediment prior to disposal became buried and a lower horizon constituent afterwards.

83. The statistical analyses of temporal and spatial trends was based on the trichlorobiphenyl (3-CB) concentrations to provide the most sensitive discrimination between the background sediments and those deposited during the disposal operation. The mean habitat concentration of 3-CB in the lower horizon are tabulated for each cruise in Table 10.

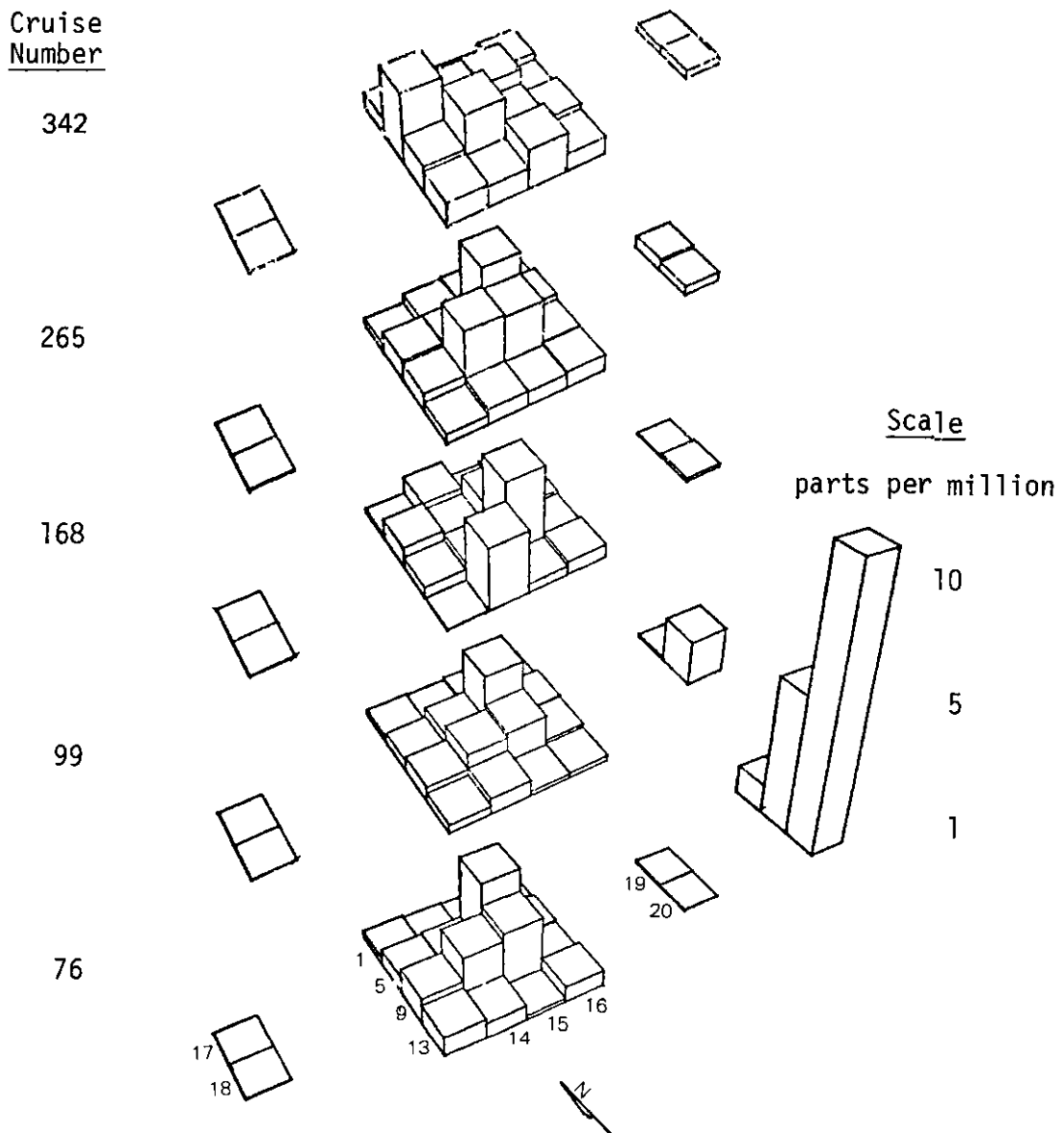


Figure 16. Three Dimensional Histograms of the Total PCB Concentrations for the Lower Horizon (Northward Direction).

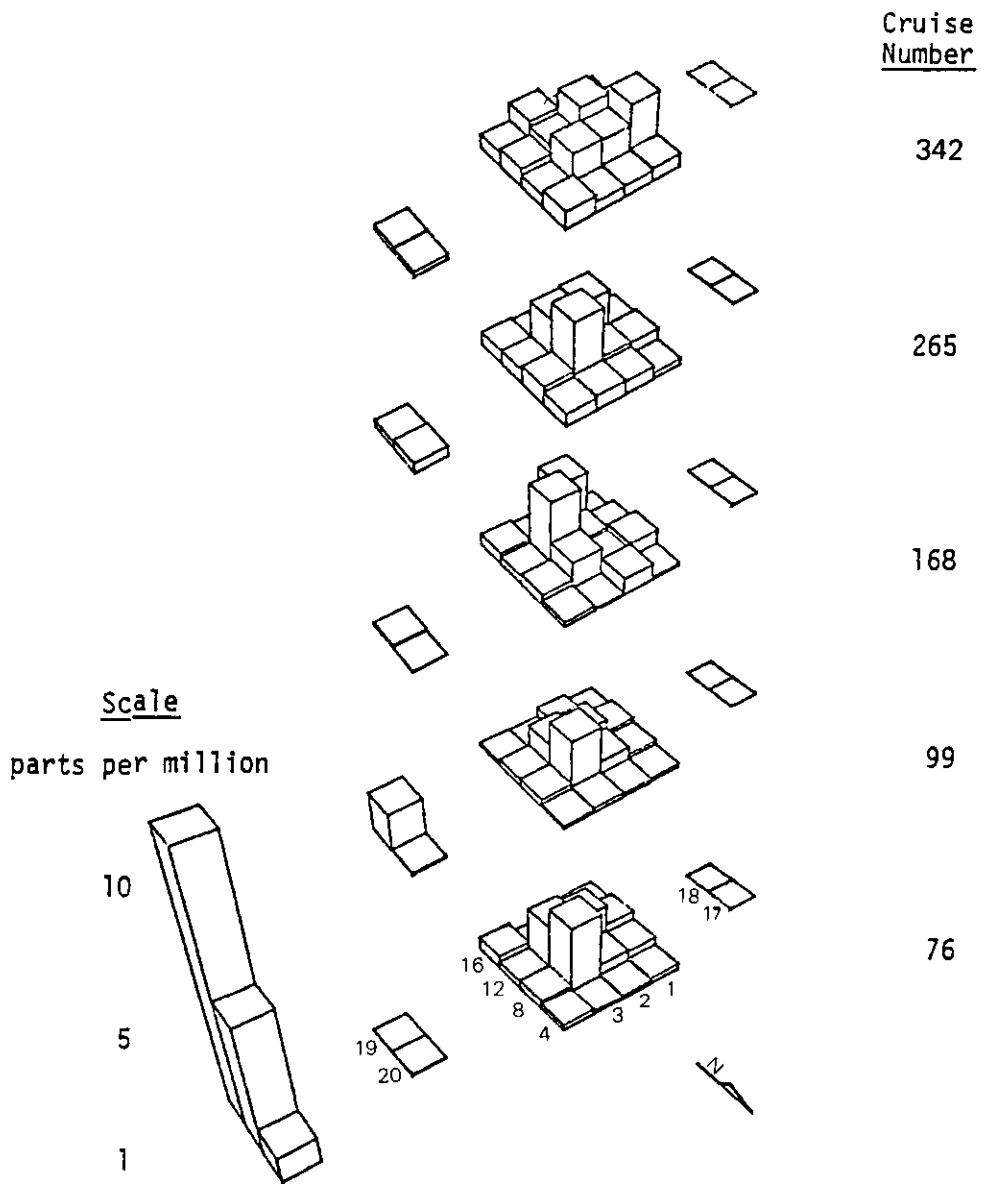


Figure 17. Three Dimensional Histograms of the Total PCB Concentrations for the Lower Horizon (Southward Direction).

▲ CORNER ZE-REF
 X MIDDLE XW-REF
 † SIDES

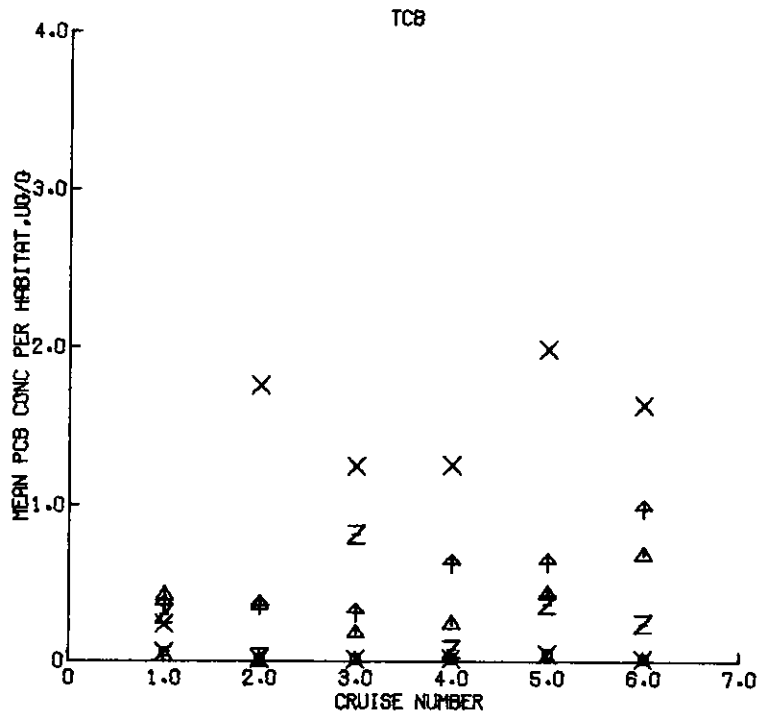


Figure 18. Plots of the Mean Habitat
PCB Concentrations Versus
Time for Sediments (Lower
Horizon).

TABLE 10
Mean Habitat 3-CB Concentrations in
the Lower Horizon Sediments for Each Cruise

HABITAT CRUISE	Corner	Central	Side	ERA	WRA
37	5.12*	3.02	13.45	9.98	1.39
76	12.64	292.82	32.55	1.22	.55
99	4.30	196.30	22.22	341.00	.80
168	9.91	220.34	45.91	2.31	.41
265	26.70	413.37	98.77	10.04	1.35
342	83.56	322.46	187.71	6.01	.07

*3-CB concentrations are in units of ng 3-CB/g dry sediment.

84. Comparisons of the 3-CB concentrations between the upper and lower horizons showed no significant differences within the central habitat during any post-disposal cruise, indicating that the depth of the deposited sediments was greater than the core tube penetration (as great as 30 cm). In contrast, both the side and corner habitats always showed significantly lower 3-CB concentrations in the lower horizon than was observed in the overlying sediment.

85. Similar to the residue levels in the upper horizon, the lower horizon of the central habitat showed a significant increase in CB concentrations immediately after disposal, with no changes noted in later cruises. On the other hand, neither the side nor corner habitats increased significantly immediately following disposal, indicating that the depth of the original dredged materials deposit was less than 10 centimeters thick around the periphery of the disposal zone. The data from later cruises, however, showed a trend toward increasing CB concentrations within the lower horizon sediments at the side and corner habitats. After six months (cruise 265), the lower horizon at the side habitat had reached CB concentrations significantly higher than those observed in the background surface sediments (cruise 37). Similar trends were seen at the corner habitat, but a significant increase in lower horizon CB concentrations did not occur until the ninth month (cruise 342).

86. Comparisons of the mean 3-CB concentrations for each habitat within cruises correlate with these temporal trends. For the first month after disposal (cruises 76 and 99), the lower horizon of the central

habitat had significantly higher residue levels than the corresponding horizon at either the side or corner habitats. By three months (cruise 168), however, the side and central habitats were no longer significantly different. At nine months, nine of the three habitats were significantly different from each other. These trends are apparent in the "leveling" of the histograms with succeeding cruises shown in Figures 16 and 17.

87. In view of the above considerations a number of factors should be emphasized:

- a. The overall spatial and temporal features of the CB concentrations suggest that the sediments deposited at the disposal site were not stabilized during the monitoring period; they were slumping from the center of the grid to the periphery. This phenomenon might have some important connotations to the impact on the benthic biota, specifically the process of recolonization of the disposal area. An unstable environment characterized by shifting, unconsolidated bottom material should provide a poor substrate in which benthic organisms can be established.
- b. The absence of significant reduction in CB levels in the grid site indicates that no major resuspension or bed-load transport of bottom material has occurred throughout the monitoring period. This is not unreasonable if one considers the rather weak and variable velocity field along the bottom of Elliott Bay, and the internal consistency of the PCB data with the other physical and chemical measurements conducted in the water column.
- c. Even though both the interstitial water measurements and modified elutriate test (described in the following sections) indicate that CB concentrations in water in equilibrium with these high CB concentrations in the sediments are greater than what were observed in the water column by an order of magnitude or more, there was no evidence of rapid desorption and mobilization of CB.

88. The total amount of PCB deposited in Elliott Bay as a result of the disposal operation was estimated as follows. An average value of 2.0×10^{-6} g TCB/g dry sediment was determined from the PCB data obtained in the river sediments prior to dredging. The total volume of the sediments dredged was about $1.1 \times 10^5 \text{ m}^3$. Assuming a wet density of 1.3 g/cm^3 and 50% water content by weight, a value of 1.4×10^5 g TCB was calculated to have been deposited in the sediments at the disposal site in Elliott Bay.

89. Based on the PCB levels observed in previous studies,^{2, 7, 20} an average background concentration of about 200×10^{-9} g TCB/g dry sediment was estimated for the entire bay. Although it must be recognized that the high spatial nonhomogeneity makes such an estimate suspect, the relatively low values ($50 - 100 \times 10^{-9}$ g TCB/g dry sediment) previously observed for most of the central, northern, and western portions of the bay,^{2, 20} suggest that this value is not unreasonable.

90. Assuming this value is uniform to a depth of 10 cm in the sediments, a surface area of 14.4 km^2 ⁵ and the sediments to be 50% solids, the amount of TCB contained in sediments of the bay prior to dredging was estimated to be 1.4×10^5 g.

91. Although these estimates are undeniably crude, they still indicate that the amount of PCB transferred to the sediments of Elliott Bay was not negligible, and may have doubled the previous quantities. However, with the present limited knowledge of the sediment dynamics of PCB, the

ecosystem importance and ultimate impact of this increase cannot be predicted.

Interstitial water

92. The concentrations of TCB measured in the interstitial water of the sediment samples from cruises 37 (background) and 76 (one week after disposal) are presented in Appendix A'. Unfortunately, the small volumes of water which could be recovered from the sediments (usually 40 ml or less) introduced a large error in quantitating the CB residues in these samples. Furthermore, a number of samples showed anomalously high CB levels, probably due to contamination of the filtrate by fine sediment particles.

93. Averaged values for the disposal grid and east and west reference areas are presented in Table 11. The values averaged near 100×10^{-12} g/ml in all areas and showed no obvious dependence on the PCB levels in the corresponding sediment matrix. Any significant trends or correlations were lost in the high variability associated with these measurements.

Modified elutriate test

94. Results of the modified elutriate test performed with river sediments are presented in Appendix A' and plotted as a function of river station in Figure 19. These values correspond very well with the concentrations of CB in the source sediment matrices as can be seen by comparing Figure 19 with Figure 10. As expected, a regression analysis performed on the data (Figure 20) showed a significant linear correlation ($R = 0.82$). Depending on the CB concentrations in the sediments, the water concentrations ranged from a high of 439.1×10^{-12} g/ml to a low of 12.7×10^{-12} g/ml.

TABLE 11

Averaged TCB Concentrations in the Interstitial Water*

<u>Cruise</u>	<u>Area</u>		
	<u>Disposal Grid</u>	<u>East Reference</u>	<u>West Reference</u>
37	122.8	160.5	42.68
76	154.9**	96.7	72.40
	128.7+	--	--

- * Concentrations are reported in units of 10^{-12} g CB/g H₂O (ppt).
 ** Upper horizon.
 + Lower horizon.

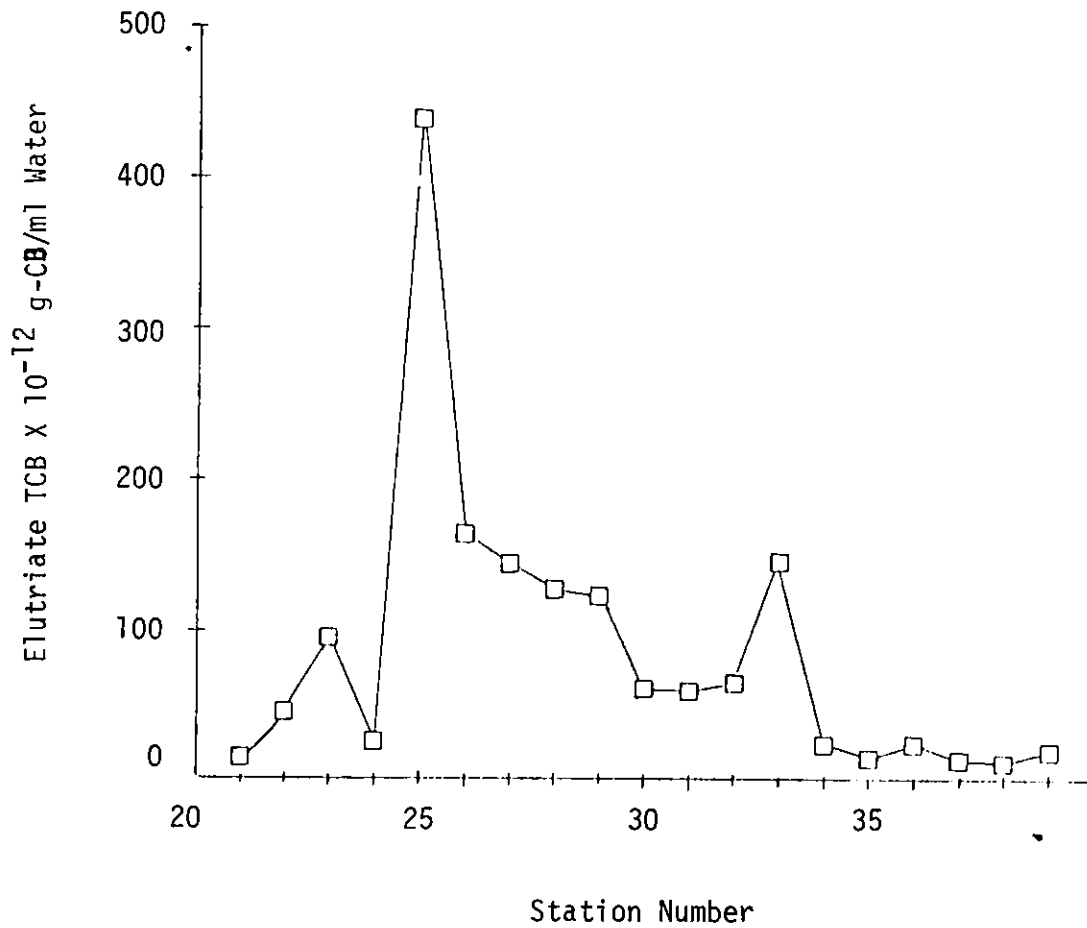


Figure 19. Plots of Modified Elutriate PCB Concentrations Versus Relative Distance (Station Number) Within the Duwamish River Site.

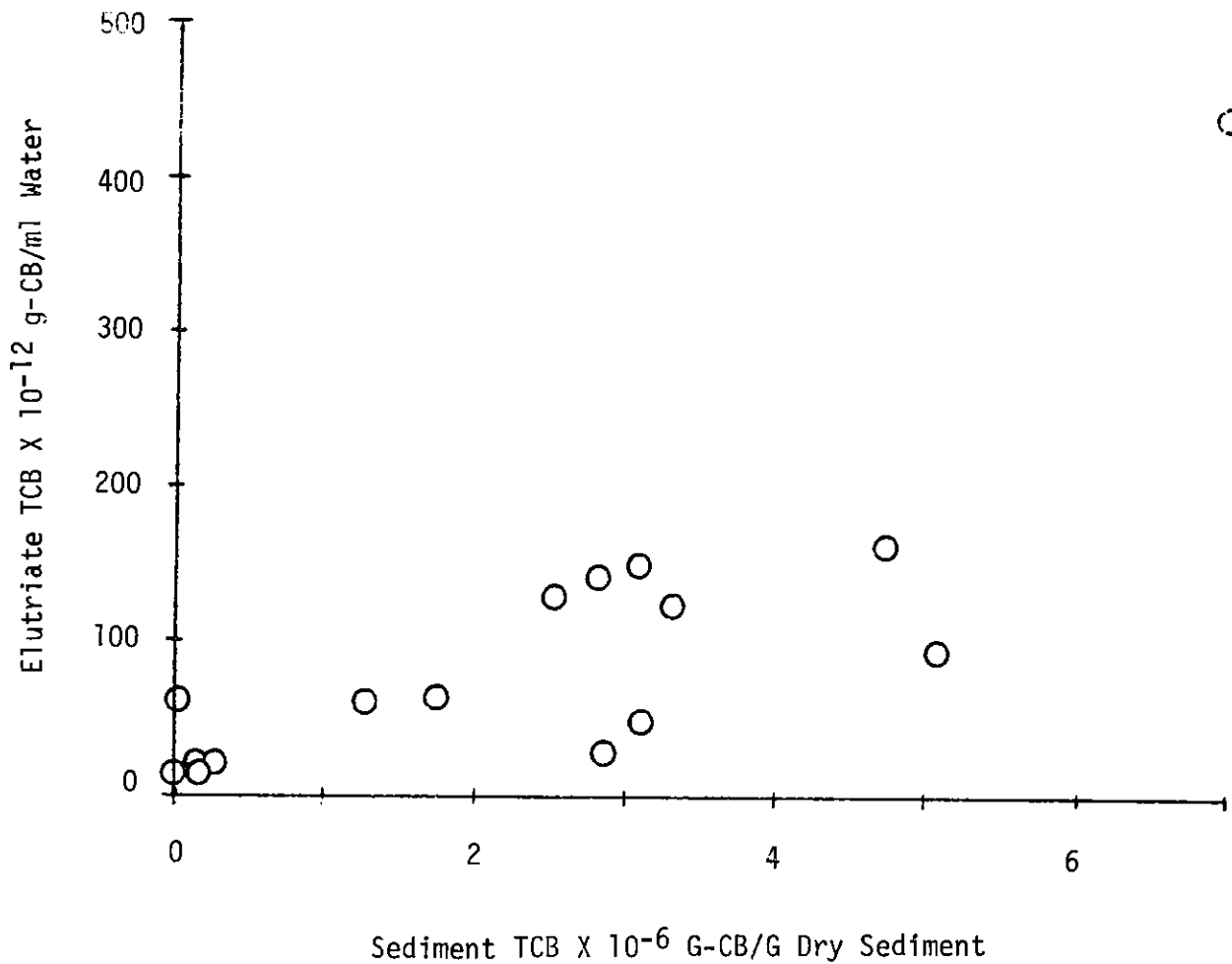


Figure 20. Plots of the TCB Concentrations in the Water From the Modified Elutriate Test Versus Their Concentration in the Corresponding Sediments for the Duwamish River Site.

Oil and grease

95. The concentrations of oil and grease (OG) observed in the sediments are presented in detail in Appendix A'. The mean values for each habitat are summarized in Table 12.

96. In general, the behavior at the dredging site, both spatially and temporally, of OG residues closely paralleled that of the PCB. A regression analysis on the OG and PCB data indicates a slight dependence of the PCB concentrations on OG ($\alpha = 0.05$) with a slope only slightly greater than zero. Due to the large scatter of the data ($R = 0.415$), no specific trends are apparent. Figure 21 shows the OG levels in the river as a function of river station. This distribution in the river agrees with the corresponding spatial trends of PCB data (Figure 10). However the averaged river value (0.92 mg OG/g dry sediment) must be interpreted with some caution as noted earlier for the PCB residues.

97. In the bay the spatial distribution of OG also decreased from east to west, although in this case the east reference area has significantly higher OG levels than the disposal grid or west reference habitats. The levels of OG at the east reference habitat were at least as high as the averaged river value.

98. After disposal the same spatial trends were exhibited. No temporal effects were noted at either reference habitat. Within the central grid habitat, a significant increase was noted immediately after disposal, but the concentrations remained essentially constant after that. Both the corner and side stations increased slightly, but not significantly,

TABLE 12-A
Mean Habitat Oil and Grease Concentrations in
Upper Horizon Sediments for Each Cruise

HABITAT CRUISE	Corner	Central	Side	ERA	WRA
37	.69*	.41	.66	1.07	.53
76	.75	1.26	.77	1.32	.33
99	1.00	1.48	.99	1.98	.42
168	1.42	1.54	1.09	1.54	.35
265	1.21	1.59	1.14	1.70	.37
342	1.31	1.59	1.30	1.99	.41

*Oil and grease concentrations are in units of mg OG/g dry sediments

TABLE 12-B
Mean Habitat Oil and Grease Concentrations in
Lower Horizon Sediments for Each Cruise

HABITAT CRUISE	Corner	Central	Side	ERA	WRA
37	-1.00*	-1.00	-1.00	-1.00	-1.00
76	.63**	1.15	.84	.85	.17
99	.92	1.05	.70	1.25	.31
168	.91	1.56	.95	1.07	.21
265	1.06	2.19	1.03	1.98	.42
342	1.05	1.96	1.20	2.34	.18

*-1.00 indicates that no data were collected.

**Oil and grease concentrations are in units of mg OG/g dry sediments

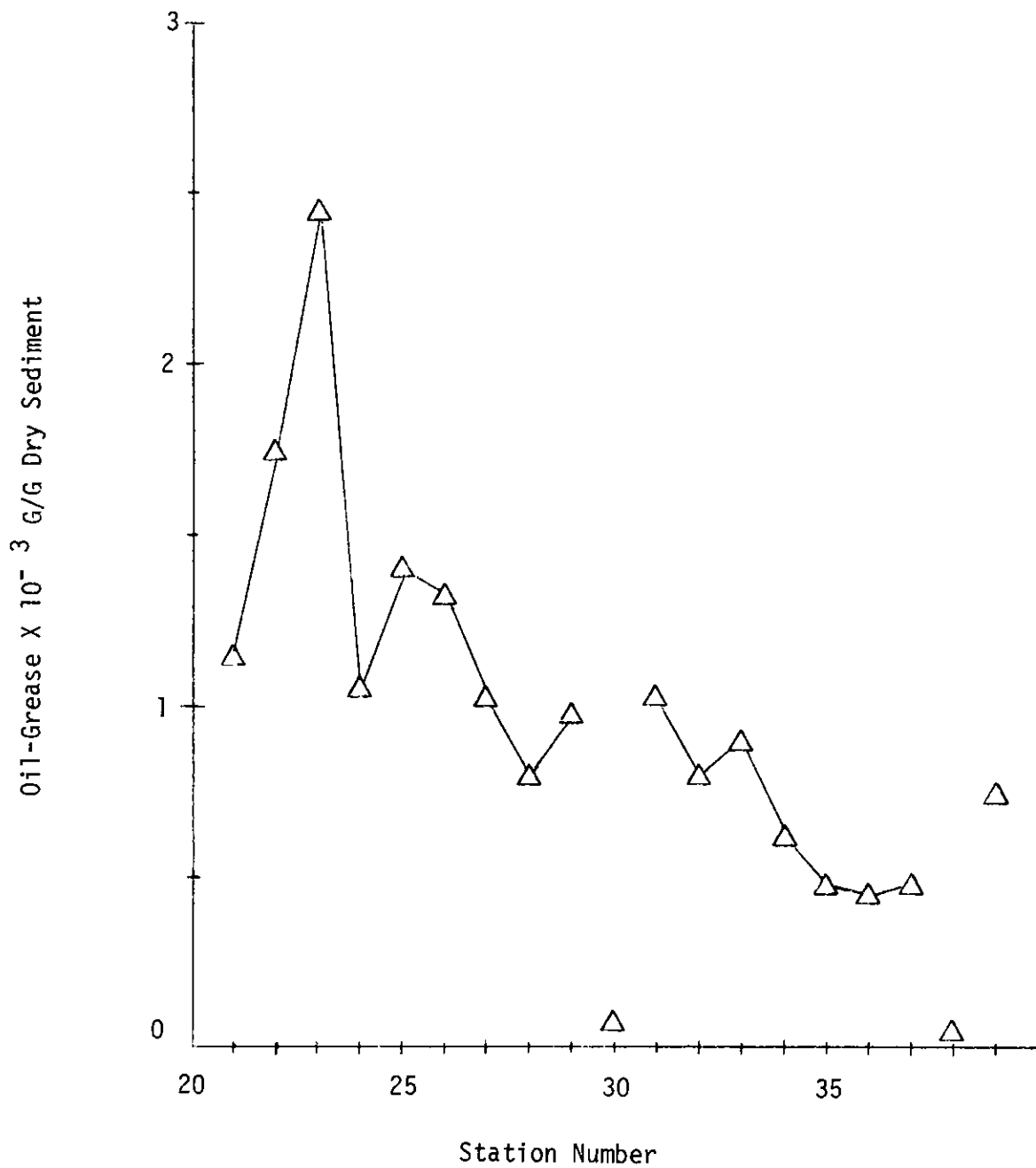


Figure 21. Plots of the OG Concentration Versus Relative Distance (Station Number) Within the Duwamish River Site.

immediately after disposal and continued an increasing trend through the remaining post-disposal cruise series. By the third month the values had increased to a level significantly greater than those observed prior to disposal. In comparing habitats, the OG concentrations prior to disposal were not significantly different at the grid habitats and the west reference station. All these areas were significantly lower than the east reference habitat. After disposal the concentrations at all grid habitats increased and were greater than the west reference habitat. Within the disposal grid, the mean OG level of the central habitat was higher than those of the corner and side habitats, but never significantly greater.

99. In general, it appears that sources for oil and grease are more uniformly distributed throughout the industrialized areas of the Seattle waterfront and lower Duwamish River as compared to the CB sources. This is indicated by the similar OG residue concentrations observed at the river stations and at the east reference area.

Total organic carbon (TOC)

100. The TOC values for the sediments collected during the last two cruises are presented in Appendix A'. The means are summarized in Table 13. Since a complete data set for the entire monitoring period was not generated by this laboratory, no ANOVA analyses were performed. However, by inspection of Table 13, the TOC/PCB and TOC/OG correspondence can be examined synoptically. TOC values are higher in the upper horizon, particularly within the central habitat. No temporal trends are apparent.

101. The relative TOC levels at the reference stations compare best with PCB residues. The per cent carbon at the east reference habitat was about the same as that at the lower horizon of the corner and side habitats, and higher than the west reference habitat. Correlations between TOC and TCB and OG were significant, although somewhat low ($R = 0.53$ for TOC/TCB; $R = 0.55$ for TOC/OG).

TABLE 13-A

Mean Habitat Percent Total Organic Carbon in
Upper Horizon Sediments for Each Cruise

<u>HABITAT</u> <u>CRUISE</u>	<u>Corner</u>	<u>Central</u>	<u>Side</u>	<u>ERA</u>	<u>WRA</u>
37	-2.00*	-2.00	-2.00	-2.00	-2.00
76	-2.00	-2.00	-2.00	-2.00	-2.00
99	-2.00	-2.00	-2.00	-2.00	-2.00
168	-2.00	-2.00	-2.00	-2.00	-2.00
265	2.93	3.45	2.82	2.06	1.39
342	3.02	3.22	2.71	2.30	1.13

*-2.00 indicates that no data were collected.

TABLE 13-B

Mean Habitat Per Cent Total Organic Carbon in
Lower Horizon Sediments for Each Cruise

HABITAT CRUISE	Corner	Central	Side	ERA	WRA
37	-1.00*	-1.00	-1.00	-1.00	-1.00
76	-2.00*	-2.00	-2.00	-2.00	-2.00
99	-2.00	-2.00	-2.00	-2.00	-2.00
168	-2.00	-2.00	-2.00	-2.00	-2.00
265	1.63	3.18	2.20	1.37	1.12
342	1.89	3.26	2.33	1.34	1.55

*-1.00 and -2.00 indicate that no data were collected.

PART V: SUMMARY AND CONCLUSIONS

102. The material dredged from the Duwamish River contained PCB at levels substantially higher than measured before in the area and enriched with lower chlorinated biphenyls. Historically, the sediments in that portion of the river were characterized predominantly by the higher chlorinated PCB (Aroclor 1254, 1260 types). Although this recent shift to lighter components might be related to the 1974 PCB spill in Slip 1, the apparent reduction of the residue levels at both the northern and southern boundaries of the dredging site suggest that the contamination was of local origin rather than a result of translocation of spill material.

103. The background PCB concentrations in the sediments of the Bay, as measured during the predisposal field sampling, are consistent with previous observations. The high sampling density within the grid area has provided a better representation of the spatial non-homogeneity of the PCB residues existing in the bay sediments. In the past we had considered deposition of suspended and bed-load sediments, originating from the Duwamish River, as the predominant source of contamination in the area. High PCB concentrations near the mouth of the East and West Waterways which decreased rapidly in a northwestward direction from the river mouth, and the higher PCB concentrations along the Seattle waterfront, were consistent with the general deposition patterns, the bulk transport of the river effluent within the bay, and the chronic PCB input from sewage overflows along the eastern side of the bay.

104. These features of circulation and sedimentation should be reflected by a relatively smooth PCB gradient within Elliott Bay. The anomalously high, discontinuous, and qualitatively variable nature of the PCB residues in the disposal zone do not fit this pattern and suggest an origin from direct and highly localized sources. These sources have not been identified.

105. The data obtained in this study provide indisputable evidence that there was an impact to the receiving area as shown by the increase in the PCB levels in the sediments of the disposal site. However, it should be recognized that Elliott Bay was not a pristine region prior to the disposal activities. Although most background PCB concentrations in the Bay sediments were nearly an order of magnitude lower than the values observed at the disposal site, following disposal, a number of locations, especially along the Seattle waterfront, were almost as contaminated prior to dredging. Even within the disposal site, the background levels from two samples collected during the pre-disposal monitoring exceeded 1 ppm. In terms of the effects on the water column, other than a highly transient elevation of the background PCB levels up to two orders of magnitude, the ambient conditions were not altered over the nine month monitoring period.

106. The total amount of PCB transferred to the sediments of Elliott Bay as a result of the disposal operation was estimated to have approximately doubled the quantities previously present. The ultimate impact of this increased load cannot be predicted at the present time.

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Aquatic disposal field investigations, Duwamish Waterway disposal site, Puget Sound, Washington; Appendix E: Release and distribution of polychlorinated biphenyls induced by open-water dredge disposal activities / by Spyros P.

Pavlou ... [et al.], Department of Oceanography, University of Washington, Seattle, Washington. Vicksburg, Miss. : U. S. Waterways Experiment Station ; Springfield, Va. : available from National Technical Information Service, 1978. 96, [449] p. : ill. ; 27 cm. (Technical report - U. S. Army Engineer Waterways Experiment Station ; D-77-24, Appendix E)

Prepared for Office, Chief of Engineers, U. S. Army, Washington, D. C., under Contract No. DACW39-76-C-0167 (DMRP Work Unit No. 1A10D)

Appendices A'-E' on microfiche in pocket.

References: p. 94-96.

(Continued on next card)

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TECHNICAL REPORT D-77-24, AQUATIC DISPOSAL FIELD INVESTIGATIONS
DUWAMISH WATERWAY DISPOSAL SITE, PUGET SOUND, WASHINGTON.

APPENDIX A': TABULATION OF CHEMICAL DATA

APPENDIX B': DESCRIPTION OF THE LARGE VOLUME FILTER

APPENDIX C': SPECTRAL ANALYSIS TECHNIQUE

APPENDIX D': DATA REDUCTION

APPENDIX E': HYDROGRAPHY DATA LIST AND DEPTH PROFILES

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