NOAA Technical Memorandum OMPA-17

ELEMENTAL COMPOSITION OF

SUSPENDED PARTICULATE MATTER

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AND ELLIOTT BAY, WASHINGTON

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ATMOSPHERIC ADMINISTRATION Pollution Assessment

Errata

The captions for Figures 3.1 and 3.2 are reversed.

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Pacific Marine Environmental Laboratory
National Oceanic and Atmospheric Administration
7600 Sand Point Way NE, Bldg. 32
Seattle, Washington   98115

Boulder, Colorado
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DISCLAIMER

Contents

Abstract

The distribution and trace element compositions of suspended-particulate matter in the Duwamish River and Elliott Bay were determined from samples collected in February 1980. The results show significant enrichments of Fe, Cr, Ni, Cu, Zn, and Pb in suspended matter from the Duwamish River estuary which is attributed to flocculation processes. In Elliott Bay the trace-element-enriched particles from the Duwamish River form a narrow plume that flows north across the inner Bay and westward along the northern coast where it eventually disperses into the outer Bay and central basin of Puget Sound.

In subsurface and near-bottom particulate matter from Elliott Bay significant correlations exist between a number of the trace elements and manganese. These data suggest that newly formed hydrous manganese oxide coatings in the subsurface particulate matter effectively scavenge several trace elements, including Cr, Ni, Cu, Zn, and Pb. The biological implications of these results are discussed.

1. INTRODUCTION AND OBJECTIVES

1.1 General Statement

The Office of Marine Pollution Assessment (OMPA), a part of the National Oceanic and Atmospheric Administration (NOAA), was established in 1980 to focus scientific research on environmental problems relating to human-induced impacts on estuarine and coastal environments in selected geographic areas of the United States. As part of this activity, the Pacific OMPA Office established the Marine Ecosystems Analysis (MESA) Puget Sound Project to develop an understanding of the environmental impacts of human actions upon the marine ecosystems of Puget Sound. The primary goals of the MESA Puget Sound Project are 1) to assess critical environmental problems in Puget Sound waters, 2) to determine the effects of critical environmental stress within the Puget Sound ecological systems, and 3) to identify and characterize the major marine components and processes of Puget Sound ecosystems involved in critical environmental problems. The basic design for the Project has been ecosystem research on a multidisciplinary level. The Project seeks to integrate physical, chemical, geological, and biological research efforts towards a better understanding of the nature and degree of environmental impacts, their sources and distributions, and their effects upon biological resources important to the region.

During the first two years of the Project, emphasis was placed on determining the nature and extent of human impacts in several Puget Sound embayments including Sinclair Inlet, Port Madison, Commencement Bay, Elliott Bay, Case Inlet, and Budd Inlet. Preliminary reports by Malins et al. (1980) and Riley et al. (1980) indicate that Elliott Bay and Commencement Bay appear to be the most severely affected by human activities. Significant enrichments of heavy metals and toxic organic compounds were found in sediment samples from these areas. In addition, suspended-matter samples from these embayments were also found to have elevated concentrations of Cr, Mn, Ni, Cu, Zn, and Pb (Riley et al.,

1980). Since only a few samples were collected from each region, further studies were needed before the sources or transport pathways for the toxic substances associated with the particulate materials could be identified.

1.2 Program Rationale and Objectives

Particles suspended in seawater play a major role in regulating the chemical forms, distributions, and deposition of trace metals. This is particularly true in coastal waters where flocculation reactions, exchange reactions, and biological uptake and settling processes act to alter the trace metal content of seawater and concentrate metals in marine suspended matter and sediments (cf. Sholkovitz, 1976, 1978; Sayles and Mangelsdorf, 1979; Trefry and Presley, 1976; and Sholkovitz and Price, 1980; Feely et al., 1981a). Particles are also a major food source for marine organisms and, hence, are an important vehicle for pollutant transfer through food webs (National Academy of Sciences, 1975; Feely et al., 1982). In Elliott Bay in Puget Sound, particulate materials are derived from a variety of sources and, as such, have varying concentrations of toxic metals associated with them. By studying the concentrations of the major and trace elements in the particulate materials, it is often possible to determine the source regions and transport pathways for these substances, as well as to provide some information about the nature of the scavenging reactions that occur as the particles are transported through or deposited in the estuarine embayment system.

In February of 1980, under the sponsorship of the MESA Puget Sound Project, the Pacific Marine Enviromental Laboratory (PMEL) conducted a study of the distribution and elemental composition of suspended matter in Elliott Bay in order to determine the sources and distribution patterns of suspended materials and particulate trace metals. This work was expanded to include a companion study of particulate trace elements in the Duwamish River Estuary with support from PMEL's Long-Range Effect Research Program. The results of the suspended-matter distribution studies are reported in

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Baker (1981). In this report we describe the results of the elemental analyses of the suspended matter. The data will be used to complete the following objectives: 1) to determine the concentrations of Cr, Mn, Fe, Ni, Cu, Zn, and Pb in the suspended matter and identify their major source regions; 2) to estimate the enrichments of metals associated with particulate materials from Elliott Bay; and 3) to relate the concentrations of particulate trace metals to major elemental constituents in order to determine the geochemical processes causing their enrichments.

1.3 The Study Region

The physical characteristics of the Duwamish River-Elliott Bay region have been described by several authors (Dawson and Tilley, 1972; Santos and Stoner, 1972; Gardner and Smith, 1978; Baker, 1981; Hamilton and Cline, 1981). The combined Green-Duwamish River system extends from the western slopes of the Cascade Mountains to Elliott Bay in Puget Sound. The Green River flows westward through forests, pastureland, and farmland until it reaches river kilometer 19 where it is joined by the Black River to form the Duwamish River. This river continues to meander to the northwest through the heavily industrialized regions of Renton, Tukwila, and Seattle, Washington (fig. 1.1). For the purpose of this report, the combined Green-Duwamish River will be referred to hereafter as the Duwamish River.

The annual discharge curve for the Duwamish River (fig. 1.2) indicates a period of relatively high mean discharge during the months of November through June (mean range: 40-80 m^3 s^{-1}) and low discharge during the period from July through October (mean range: 10-20 m^3 s^{-1}).

The Municipality of Metropolitan Seattle (METRO) operates the Renton Sewage Treatment Plant (RSTP), which discharges approximately 136,000 m^3 day^{-1} of secondary-treated sewage at river kilometer 20.5 (RK 20.5). Industrial and storm water wastes of significantly lesser amounts are also intermittently discharged at several locations along the lower river. The lower 10 kilometers of the Duwamish River have been dredged and straightened by the

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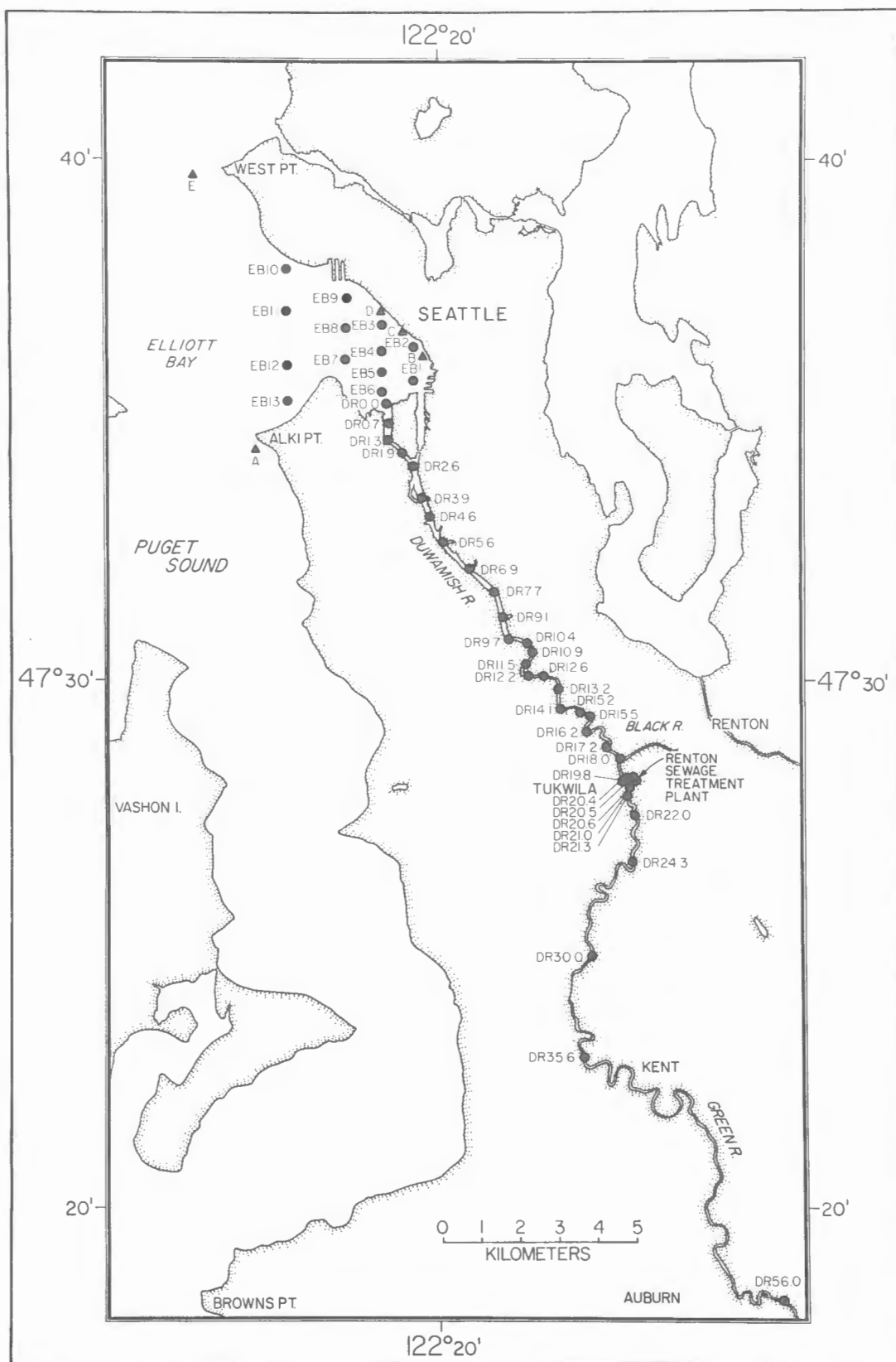
Figure 1.1.   Locations of sampling stations in the Duwamish
River and Elliott Bay.   Stations in the Duwamish
River are designated by river kilometer.

Duwamish River (Green River at Tukwila)

RIVER DISCHARGE m³/sec

200 —

150 —

100 —

50 —

☐ Monthly Range (1968-1978)
▨ Monthly Standard Deviation
• Monthly Mean

JAN FEB MAR APR MAY JUN JUL AUG SEP OCT NOV DEC

Figure 1.2. Monthly means, standard deviations, and ranges for the Duwamish River discharge. Data compiled from the U.S.G.S. stream flow records obtained at Tukwila for the period 1968-1978.

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U.S. Army Corps of Engineers. This region forms a two-layered estuary (type 2B of the Hansen-Rattray convention). The upper layer consists of mixed salt water and freshwater, and the lower layer is mostly unmixed salt water. The seaward end has a maximum tidal range of approximately four meters.

The Duwamish River discharges into Elliott Bay at the southeast end through the west and east waterways (fig. 1.3), a relatively small embayment on the east side of Puget Sound surrounded by the industrial secti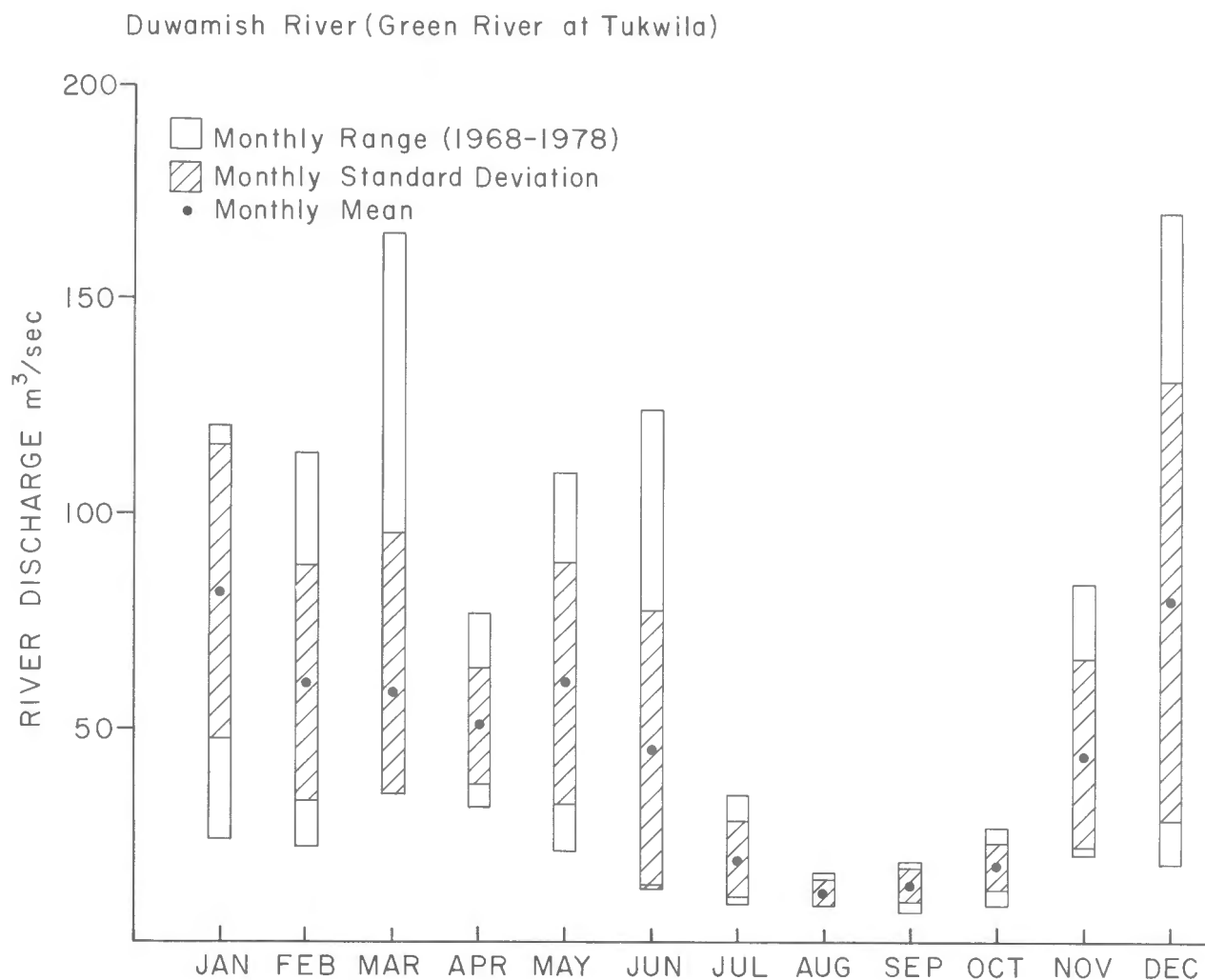ons of the city of Seattle. The bay has a surface area of approximately 20 km^2 and a total volume of approximately 2.05 x 10^{12} L. The bathymetry of Elliott Bay is dominated by a submarine canyon in the center of the bay which trends in a northwest-southeast direction and debouches onto the floor of the central basin of Puget Sound.

2. SAMPLING AND ANALYTICAL PROCEDURES

2.1 Sampling Methods

The sampling program consisted of an areal survey conducted February 19-20, 1980, aboard the *R/V Onar*. On February 19, stations were occupied in the Duwamish River during ebb tide. This was followed by the occupation of 18 stations in Elliott Bay on February 20. At each station in Elliott Bay, water samples were collected in 12-L, Teflon-lined, GoFlo Niskin bottles and immediately transferred to 1-L, acid-cleaned polyethylene bottles for transport and processing in the laboratory. Water samples were collected from the surface and 5 m above the bottom at all stations in the bay. In addition, water samples were collected to provide detailed vertical profiles at stations EB4, EB6, EB8, and EB11. A sediment core sample was also collected at EB4 using a Benthos Model 2171 gravity corer with a 6.7-cm I.D. plastic core liner. Pore water samples were obtained by centrifugation of 2-cm core sections under atmospheric conditions within 6 hours of core collection.
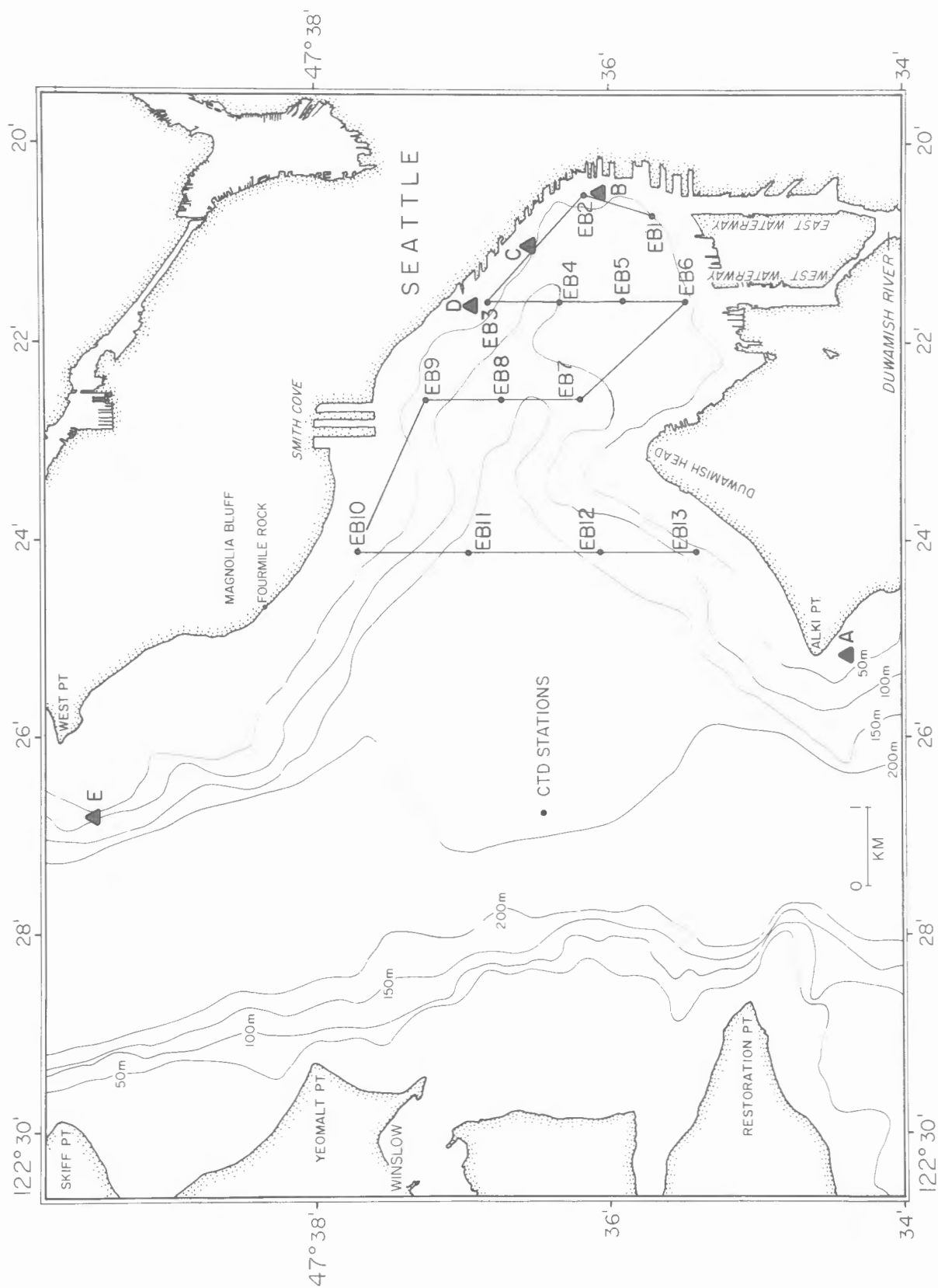
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Figure 1.3. Locations of suspended-matter stations in Elliott Bay. The solid line shows the cruise track starting with station EB1 and ending at station EB 13. Outfall stations are indicated as A through E.

2.2 Analytical Methods

In the laboratory the samples were vigorously hand shaken and vacuum filtered through 0.2-µm pore size Nuclepore polycarbonate filters (47 mm in diameter for determination of suspended-matter concentrations and 25 mm in diameter for elemental analyses other than C) and precombusted 0.2-µm pore size Selas silver filters (25 mm in diameter for C analyses). All samples were rinsed with three 10-ml aliquots of deionized membrane-filtered water (adjusted to pH 8.0), placed in individual polycarbonate petri dishes with lids slightly ajar for a 24-hour desiccation period over sodium hydroxide, and then sealed and stored for subsequent analysis.

Total concentrations of suspended matter were determined gravimetrically. The weighing precision (2σ = ±0.011 mg) and volume-reading error (±10 ml) yield a combined coefficient of variation in suspended-matter concentration of approximately 1 percent. This variability is overshadowed, however, by that associated with sampling precision which usually ranges between 5 and 25 percent in coastal waters (Feely et al., 1979).

The major (Al, Ti, and Fe) and trace (Cr, Mn, Ni, Cu, Zn, and Pb) elements in the suspended matter were determined by X-ray, primary- and secondary-emission (fluorescence) spectrometry and thin-film technique (Baker and Piper, 1976; and Feely et al., 1981a). A Kevex Model 7077-0700 X-ray energy spectrometer with a rhodium X-ray tube was used in the direct and secondary-emission mode to obtain maximum efficiency for excitation of individual elements in the sample. Standards were prepared from suspensions of finely ground U.S.G.S. standard rocks (W-1, AGV-1, and GSP-1; 90 percent by volume less than 15µm in diameter) collected on Nuclepore filters similar to those used for sample acquisition. At a filter loading of 290 µg cm^{-2} the determination limits (three times the minimum detection limits) were less than 0.02 percent and 10 ppm for the major and trace elements, respectively. Total dissolved Mn and Fe in the pore fluids were simultaneously determined by X-ray secondary-emmission spectrometry using a Cu secondary target and a 3-ml sample volume contained in a spectra

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cup.   Determination limits of 0.75 ppm were obtained for both metals with this procedure.

Analysis of total particulate C in the suspended matter was performed with a Perkin-Elmer Model 240B CHN analyzer.   In this procedure, particulate C compounds were combusted to CO_2 and detected sequentially with a series of thermal conductivity detectors.   NBS acetonilide was used for standardization.   Analytical uncertainties are typically less than 10 percent relative for the procedure described above and are often overshadowed by sampling variabilities (Feely et al., 1981a).

3.   RESULTS AND INTERPRETATIONS

3.1.   Suspended-Matter Distributions and Transport

3.1.1   Duwamish River Estuary

Figures 3.1 and 3.2 show the distributions of total suspended matter and salinity for the Duwamish River Estuary for February 19, 1980, during an ebbing tide.   The data indicate an inverse relationship between suspended matter and salinity, with the highest concentrations of suspended matter (> 14.0 mg/L) being found in the surface waters at the landward end of the estuary (salinity $\leq$ 4.0°/$_{oo}$).   In the near-surface layer (0-2 m) suspended-matter concentrations decrease in a seaward direction to values averaging about 3.8 mg/L near the mouth of the river (station DR 0.0).   Below the surface layer, suspended-matter concentrations decrease steadily with depth while salinity increases. This decrease is due to inflow of nonturbid saline Elliott Bay water along the bottom (Gardner and Smith, 1978).   The saline water mixes upward into the outflowing riverwater, dilutes it, and then effects the seaward decrease in suspended-matter concentrations.   Moreover, sedimentation of suspended matter in the estuary also occurs as indicated by the plot of the relationship between total suspended matter and salinity for near-surface samples (fig. 3.3).   In particular, the data show evidence for
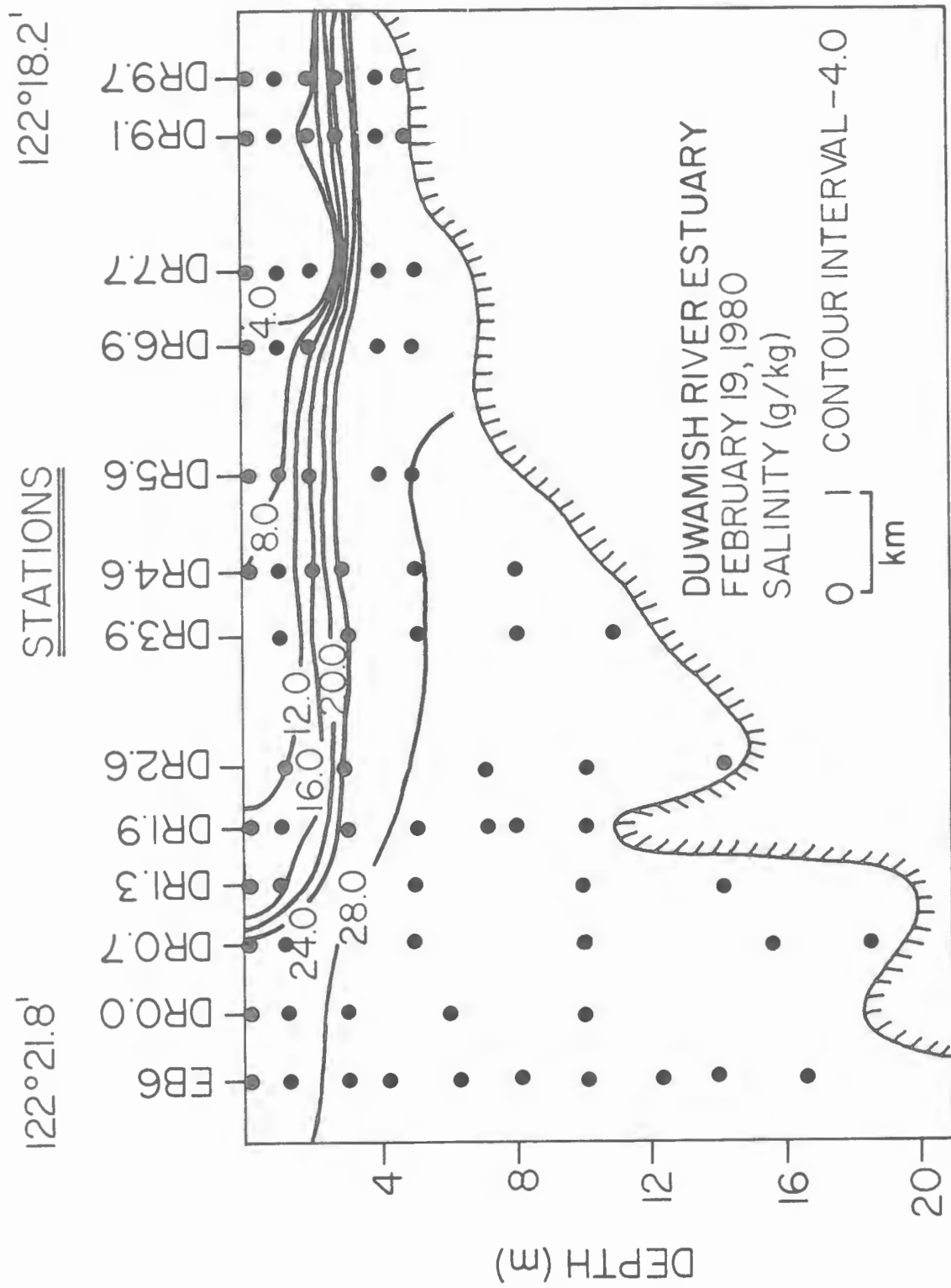
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Figure 3.1. Distribution of total suspended matter in the Duwamish River estuary.
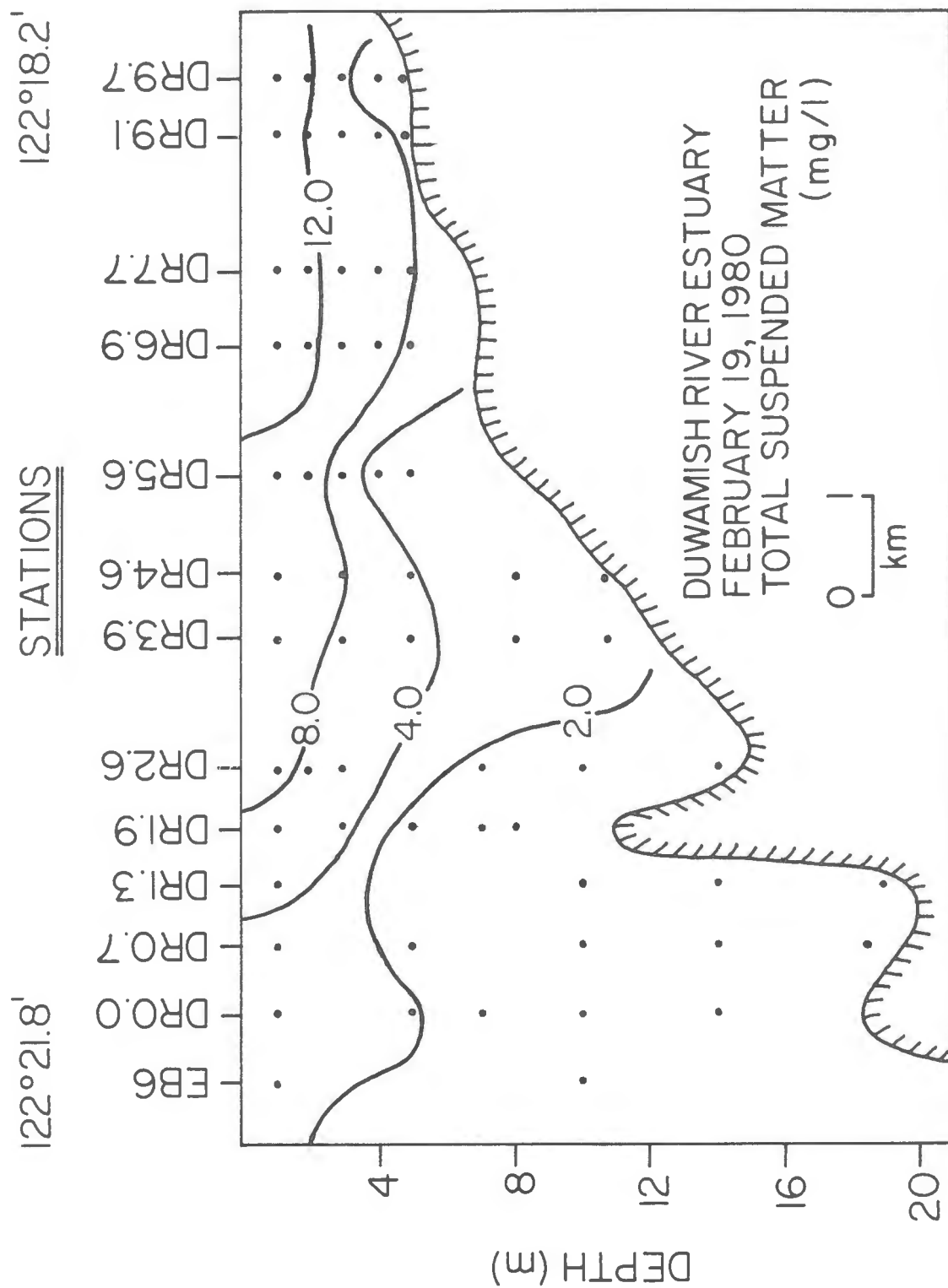
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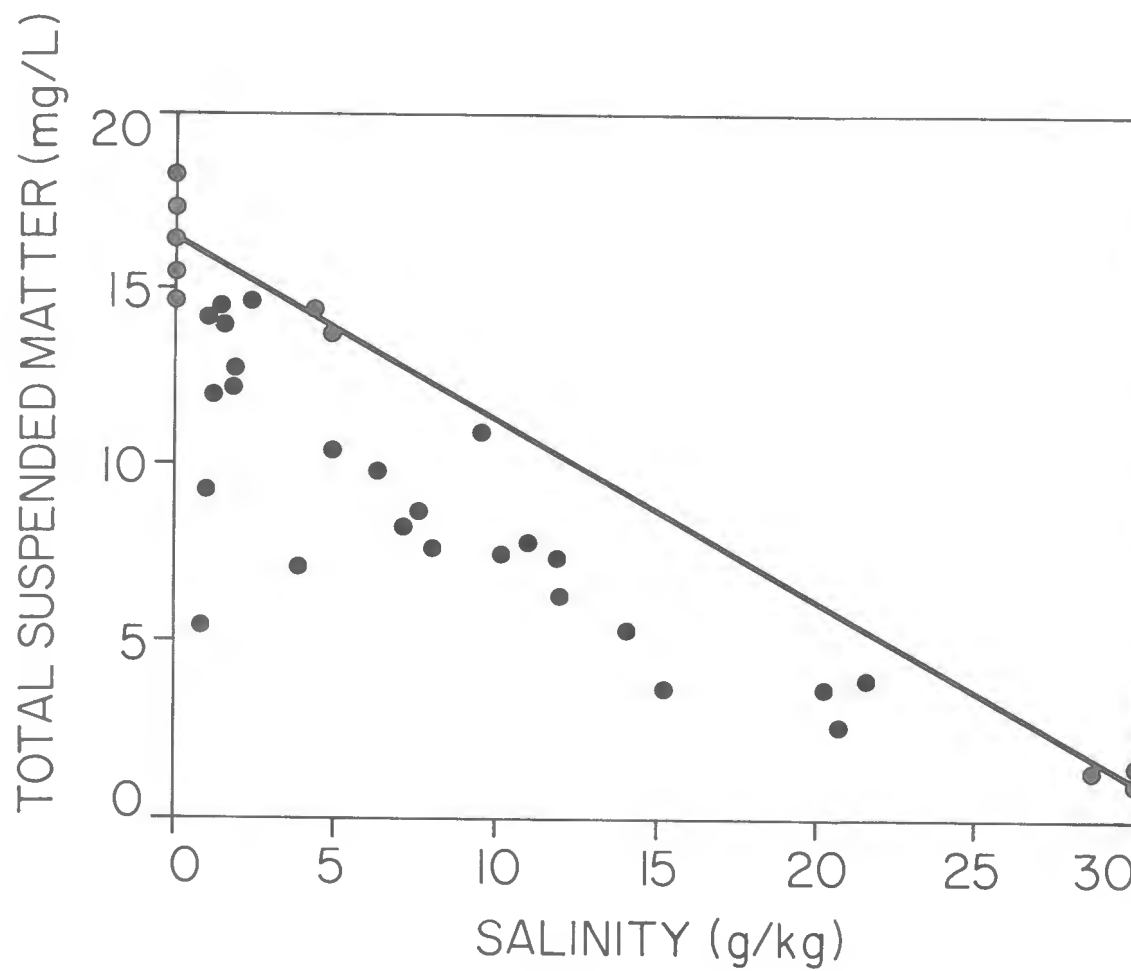Figure 3.2. Distribution of salinity in the Duwamish River estuary.

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Figure 3.3. Plot of the relationship between total suspended
matter and salinity in the Duwamish River
estuary. Data collected February 19, 1981. The
solid line denotes the theoretical dilution line
for conservative mixing.

sedimentation in the low-salinity region of the estuary. These data are supported by the sediment accumulation data (METRO, 1981), which indicate that more than 50 percent of the sediment accumulation occurs in the region between RK 7.5 and RK 9.7. Near the bottom, slight increases in suspended-matter concentrations were observed at stations DR1.9 and DR5.6 which may be due to local resuspension of bottom sediments.

3.1.2. Elliott Bay

Suspended-matter distributions for February and August 1980 have been thoroughly discussed by Baker (1981); consequently, only a brief discussion of the February 20 data will be presented here. Figure 3.4 shows the distributions of total suspended matter and salinity for samples collected from the surface and 5 m above the bottom in Elliott Bay. The surface concentration maps show the Duwamish River plume, with suspended-matter concentrations averaging about 1-2 mg/L, spreading to the north and west along the northern shore. Baker (1981) states that on February 20 the net wind direction was 190°T at 11.4 MPH. This caused the plume to flow in a northerly direction across the bay and to the northwest towards West Point. This interpretation of the data is supported by the salinity data which also shows a northerly transport of low-salinity water ($< 28.0^o/_{oo}$) from the mouth of the Duwamish River across the bay and up the northern shore. The near-bottom data show the highest concentrations of suspended matter in the deepest portions of the submarine canyon (fig. 3.4), where values in excess of 1.6 mg/L were observed on February 20. Associated with these enrichments in near-bottom suspended matter are corresponding increases in bottom water salinity. For example, the salinity data indicate evidence for upcanyon movement of high-salinity bottom water from the central basin (fig. 3.4). These data suggest that the near-bottom increases in suspended matter concentrations may be related to bottom water flow along the axis of the canyon (Baker, 1981).
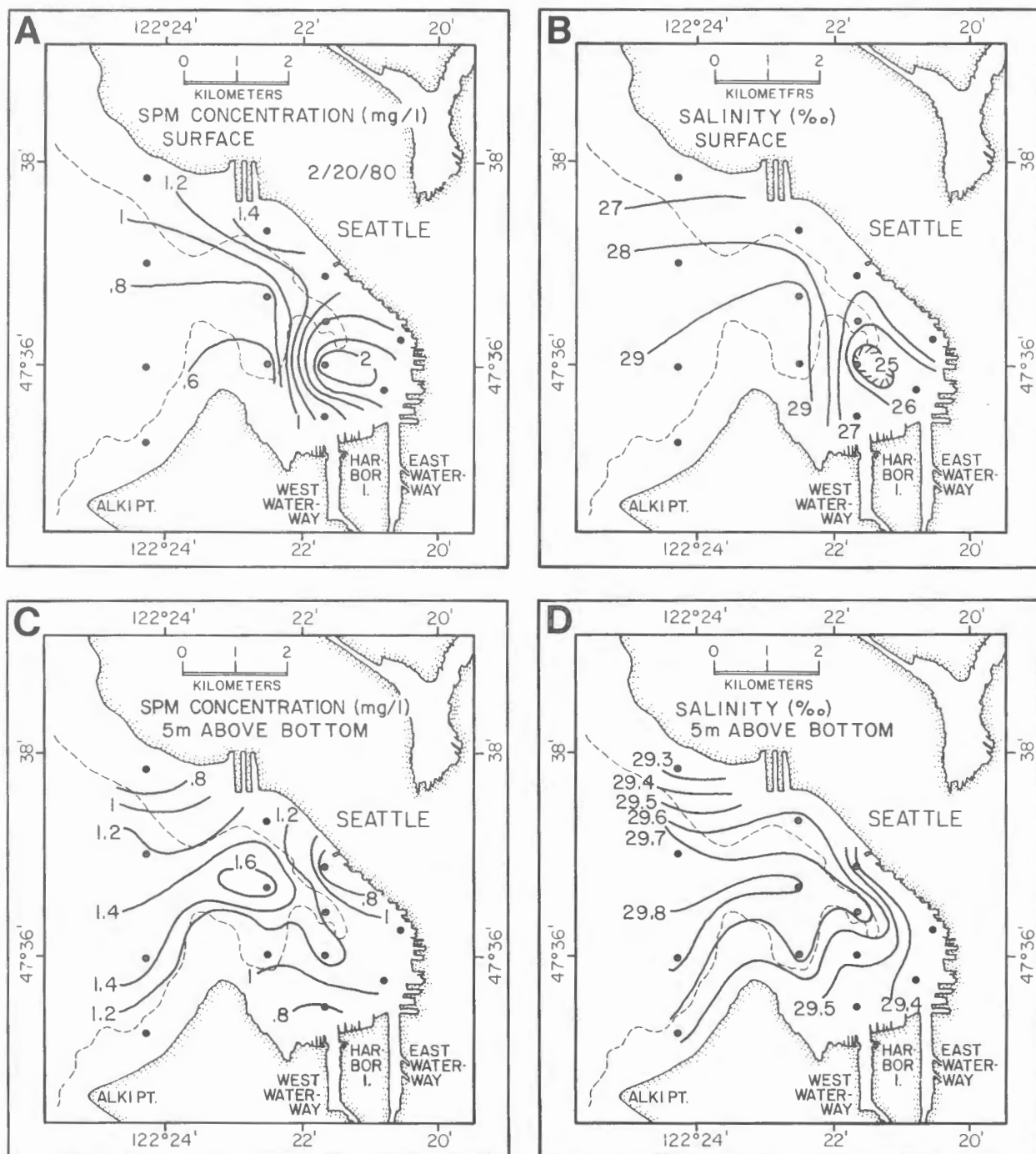
Figure 3.4. Distribution of: A. Total suspended matter B. Salinity at the surface; and C. Total suspended matter, and D. Salinity 5 m above the bottom in Elliott Bay. Data collected February 20, 1980 (after Baker, 1981).

3.2 Major and Trace Element Composition of the Particulate Matter

3.2.1 Duwamish River Estuary

Table 3.1 summarizes the elemental composition of suspended matter above and below the RSTP, suspended matter in the Duwamish River estuary, bottom sediments from the Duwamish River estuary, and average shales. With the exception of C, the major element composition of the suspended matter collected upstream of the RSTP is about the same (within 2-3 percent by weight) as average shales (Krauskopf, 1967), indicating that natural weathering of primary rock materials is the principal source of the suspended matter in the upper river. The fact that C is enriched in the suspended matter relative to average shales indicates that the suspended matter contains about 15 percent terrestrial organic matter as indicated by the data of Hamilton and Cline (1981). Below the RSTP the suspended matter becomes progressively enriched in Fe and all other trace elements with the exception of Mn. The trace element enrichments range from 14 percent for Cr to 70 percent for Zn. Curl et al. (1981) demonstrated that the RSTP is a major source for dissolved trace elements in the estuary and that a portion of the trace elements is adsorbed to particulate matter in the lower river. Apparently the trace element enrichments in the suspended matter of the lower river are a direct result of the adsorption phenomenon.

Table 3.1 also shows the elemental composition of near-surface suspended matter from the Duwamish River Estuary for various salinity ranges. The low-salinity samples (0-10$^o/_{oo}$) roughly correspond to stations located between river kilometer 9.7 (RK 9.7) and river kilometer 3.9 (RK 3.9). The data show significant enrichments of total particulate Fe, Cr, Ni, Cu, Zn, and Pb, ranging from 47 percent for Fe to 219 percent for Pb. These enrichments have been attributed to flocculation of organic matter in the estuary (Feely et al., in press). These authors stated that on the basis of laboratory experiments with samples collected from the Duwamish River anywhere from 18 percent to 68 percent of

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Table 3.1 Comparison of the elemental composition of suspended matter from the Duwamish River with the composition of suspended matter and sediments from the Duwamish River estuary (samples collected February 19, 1980). Percentage increases or decreases from upstream samples are given in parentheses.

Sample Description	No. of Samples		C wt% ±1σ	Al wt% ±1σ	Ti wt% ±σ	Fe wt% ±σ	Cr ppm ±1σ	Mn ppm ±1σ	Ni ppm ±1σ	Cu ppm ±1σ	Zn ppm ±1σ	Pb ppm ±1σ
Samples upstream of RSTP (RK 20.6–RK 56.0)	7	x̄	8.25	9.26	0.412	6.25	100	1218	53	46	145	66
		S.D.	±1.80	±1.51	±0.017	±2.06	±14	±221	±7	±7	±20	±14
Samples down-stream of RSTP (RK 20.5–RK 12.2)	14	x̄	8.46	10.14	0.430	7.80	114	1154	77	60	247	95
		S.D.	±2.12	±1.17	±.040	±1.04	±32	±135	±22	±26	±85	±37
		%	(+2.5)	(+9.5)	(+4.4)	(+25)	(+14)	(−5)	(+45)	(+30)	(+70)	(+44)
Duwamish River Estuary (0–10°/oo)	10	x̄	8.28	--	0.439	9.18	154	1087	84	91	298	211
		S.D.	±2.45	--	±.022	±0.44	±17	±195	±16	±13	±30	±61
		%	(+0.4)	--	(+6.5)	(+47)	(+54)	(−10.7)	(+56)	(+97)	(+105)	(+219)
Duwamish River sediment**				8.01	0.50	5.30	94	590	31	124	227	316
Average shale***			0.05	8.00	0.45	4.70	100	500	95	54	80	20

** Samples collected from the west channel of the Duwamish Waterway (after Riley et al., 1980).
*** (After Krauskopf, 1967).

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the dissolved-trace-element burden of the Duwamish River are transformed from a dissolved state to an organic-rich flocculant during estuarine mixing. For some elements (i.e., Fe and possibly Mn) this estimate may indeed be a minimum since the catalytic effect of the riverine particulate matter is removed in the laboratory experiments (Feely et al., in press).

3.2.2 Elliott Bay

The results of the chemical analyses of major and trace elements in suspended matter from Elliott Bay are given in table 3.2 and summarized in table 3.3. The data are also graphically presented in figs. 3.5 through 3.11. The near-surface data clearly illustrate that the Duwamish River is the major source of particulate trace elements in surface waters of Elliott Bay during the February sampling period. Trace element enrichments for near-surface particulate matter are about the same as (e.g., for Cr, Ni, Cu, and Zn) or slightly higher (for Mn and Pb) than the enrichments in the near-surface particulate matter of the Duwamish River estuary. Also the surface distributions of particulate Cr, Fe, Ni, Cu, Zn, and Pb show concentration gradients that decrease by as much as a factor of five away from the mouth of the river. The trace-element-enriched particulate matter formed a plume that flowed north across the bay and to the northwest towards West Point (e.g., figs. 3.5, 3.7, 3.8, 3.10, and 3.11) where it dispersed into the central basin. These data are generally consistent with the suspended-matter distributions in near-surface waters as indicated in fig. 3.4. However, the concentration gradients of the particulate trace elements decrease more rapidly than does the gradient of total suspended matter. This observation suggests that the near-surface particulate matter was probably diluted, to some extent, by trace-element-deficient particulate matter from another source (e.g., *in situ* production of organic matter). Only particulate Mn shows increasing concentrations in offshore waters. This appears to be the result of further scavenging of dissolved Mn by the suspended matter as indicated by the maxima in particulate Mn at 20 m at stations EB4

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Table 3.2. Concentrations of total suspended matter and some major and trace elements in suspended matter from Elliott Bay. Samples were collected on February 20, 1980.

Sta. No.	Depth (m)	TSM (µg/L)	C (wt%)	Al (wt%)	Ti (wt%)	Fe (wt%)	Cr (ppm)	Mn (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Pb (ppm)
EB 1	1	1535	12.1	----	0.385	8.16	216	3021	107	107	288	318
EB 1	50	912	17.1	10.3	0.307	4.73	125	6705	66	89	173	117
EB 2	1	1440	13.1	----	0.437	6.77	193	2954	94	165	390	398
EB 2	30	705	6.4	10.2	0.400	5.55	126	5125	67	85	209	118
EB 3	1	1060	12.8	----	0.393	8.17	183	4133	75	114	295	400
EB 3	60	345	13.6	10.9	0.385	5.18	236	9696	97	422	487	227
EB 4	1	1100	4.6	9.6	0.314	6.28	151	3050	60	118	245	274
EB 4	20	457	12.0	----	0.556	7.70	284	11764	133	181	422	223
EB 4	40	663	14.0	----	0.393	5.59	196	9818	89	146	275	256
EB 4	60	927	3.2	6.1	0.171	2.55	73	3921	39	29	91	74
EB 4	80	912	7.3	10.2	0.363	5.19	134	4122	66	55	322	97
EB 4	95	880	13.1	----	0.481	6.51	179	3881	83	74	189	--
EB 5	1	814	17.2	----	0.409	9.96	335	4370	110	165	435	591
EB 5	80	1115	4.8	9.2	0.398	5.38	120	3447	61	60	160	105
EB 6	1	2643	7.7	----	0.411	5.51	202	1690	84	146	420	364
EB 6	17	308	17.9	----	0.363	5.56	299	12737	92	129	264	271
EB 6	27	597	8.2	----	0.308	3.96	170	6198	52	66	171	168
EB 6	37	387	10.5	----	0.383	5.14	191	9261	70	81	192	194
EB 6	47	765	5.8	----	0.402	5.16	172	6382	71	54	159	81
EB 6	60	865	8.3	----	0.249	3.53	86	3935	42	49	132	124
EB 7	1	462	13.0	----	0.370	5.27	169	8639	67	89	190	128
EB 7	110	477	12.4	----	0.372	5.62	140	6105	61	84	210	131
EB 8	1	990	12.7	----	0.394	6.39	196	4642	77	112	262	413
EB 8	15	715	----	----	0.388	5.33	240	6924	116	98	247	235
EB 8	55	618	9.7	----	0.327	4.70	213	7024	78	175	278	194
EB 8	75	902	9.7	----	0.362	4.74	163	6760	59	54	141	136
EB 8	95	1092	6.6	----	0.454	6.30	183	4342	81	71	197	123
EB 8	115	1667	5.0	----	0.427	5.25	117	2777	63	69	148	124
EB 9	1	1300	9.6	----	0.359	7.63	149	2722	74	139	309	461
EB 9	75	1060	10.3	----	0.378	5.02	110	4343	56	50	137	100
EB 10	1	882	15.0	----	0.428	8.45	256	3445	92	142	307	409
EB 10	25	1263	9.6	----	0.358	6.14	181	3611	79	135	287	272
EB 11	1	1130	15.5	----	0.398	7.02	143	4076	71	128	291	837
EB 11	10	913	6.1	----	0.455	6.07	191	6010	94	127	252	244
EB 11	25	987	8.9	----	0.417	5.45	171	5468	90	98	198	214
EB 11	90	1140	7.2	----	0.489	6.39	162	3874	76	92	200	168
EB 11	140	1450	6.2	----	0.451	6.65	142	2466	75	89	207	178
EB 11	150	2140	6.1	----	0.455	6.05	124	2048	60	79	188	249
EB 12	1	844	10.4	----	0.352	4.54	181	5536	86	162	189	214
EB 12	140	1457	6.0	----	0.389	4.82	105	2801	53	57	162	141
EB 13	1	823	10.9	----	0.348	4.54	114	6531	57	104	160	100
EB 13	75	----	----	----	0.418	2.40	108	2237	68	49	118	66
Outfall A 1		788	12.1	----	0.331	4.45	163	5478	65	90	216	120
Outfall B 1		1960	11.2	----	0.427	9.17	178	2422	89	151	413	385
Outfall C 1		1631	19.4	----	0.370	9.67	217	3350	106	139	408	550
Outfall D 1		1240	13.2	----	0.325	7.42	155	2627	77	103	313	380
Outfall E 1		525	15.1	----	0.333	5.29	198	5621	98	118	268	347

Table 3.3. Comparison of the mean trace element composition of suspended matter near the surface and from depths >10 m below the surface in Elliott Bay with the trace element composition of the underlying sediments. Suspended matter collected February 20, 1980. Percentage increases or decreases from upstream Duwamish River samples are given in parentheses.

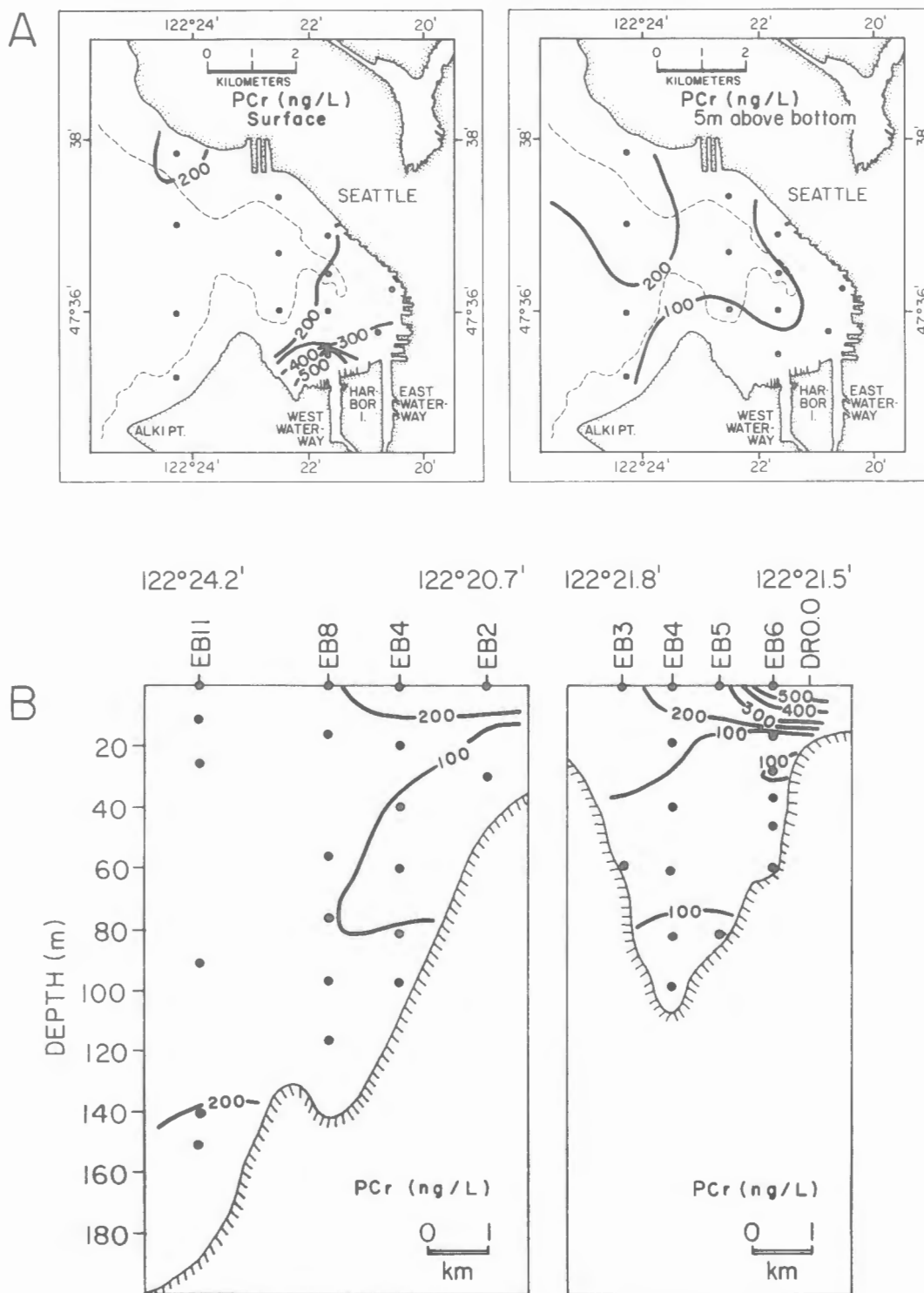| Sample Description	No. of Samples	C (wt%)	Cr (ppm)	Ti (wt%)	Mn (ppm)	Fe (wt%)	Ni (ppm)	Cu (ppm)	Zn (ppm)	Pb (ppm)
Surface (<3m)	18	13.6±3.9 (+65.3)	190±50 (+90)	0.38±0.04 (-7.8)	4094±1675 (+236)	6.91±2.0 (+10.4)	83±16 (+57)	127±24 (+176)	301±85 (+107)	370±182 (+460)
Subsurface (>10m)	29	9.0±3.7	162±55	0.38±0.07	5797±2859	5.38+1.14	71±20	106±78	215±91	168±62
Sediments*	5		53±1	0.11±0.01	405±71	3.20±0.22	52±5	83±31	110±17	82±16

* Data from Malins et al. (1980).

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Figure 3.5.   A. Areal distributions of total particulate Cr
at the surface and 5 m above the bottom.
B. East-west and north-south cross sections of
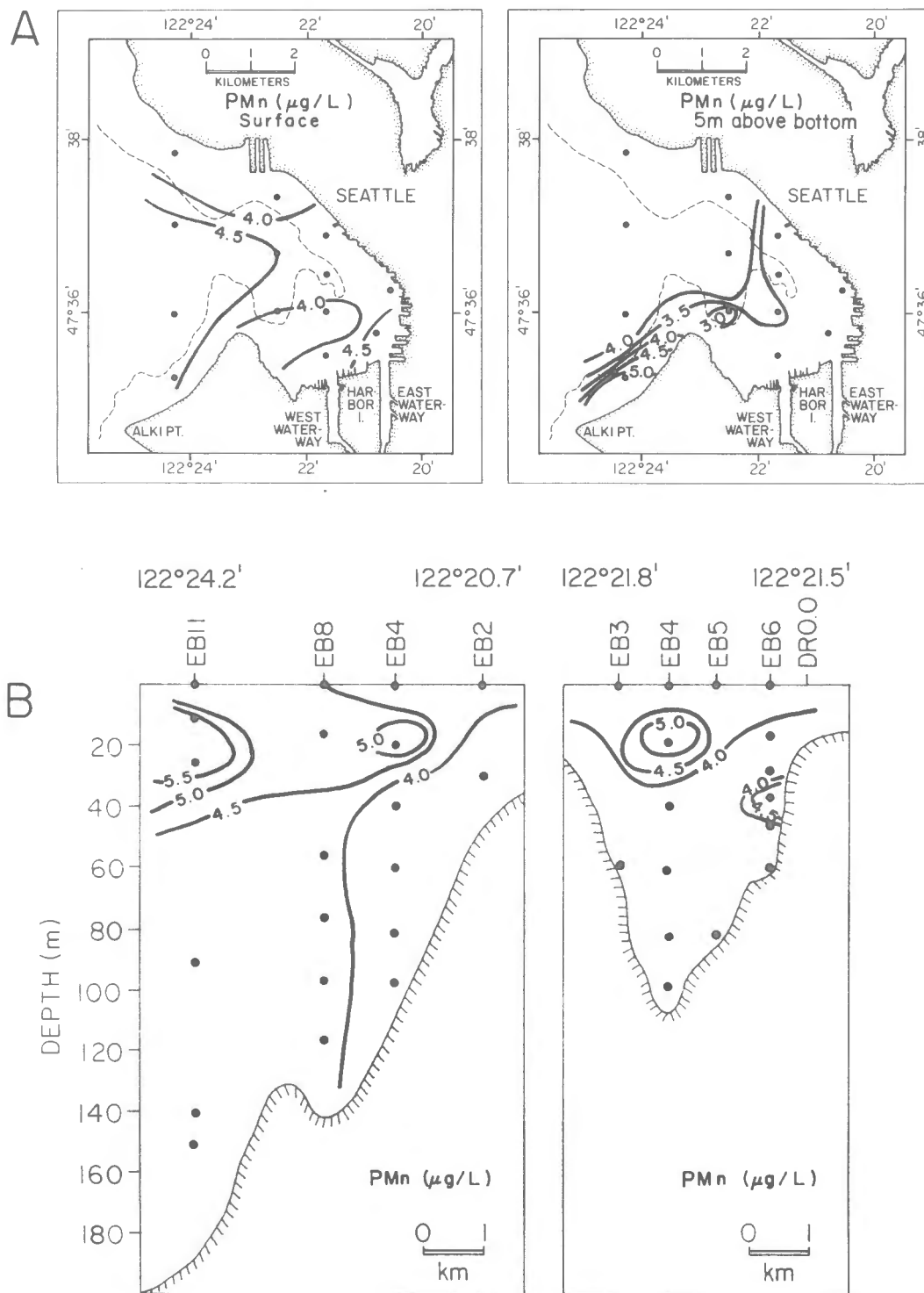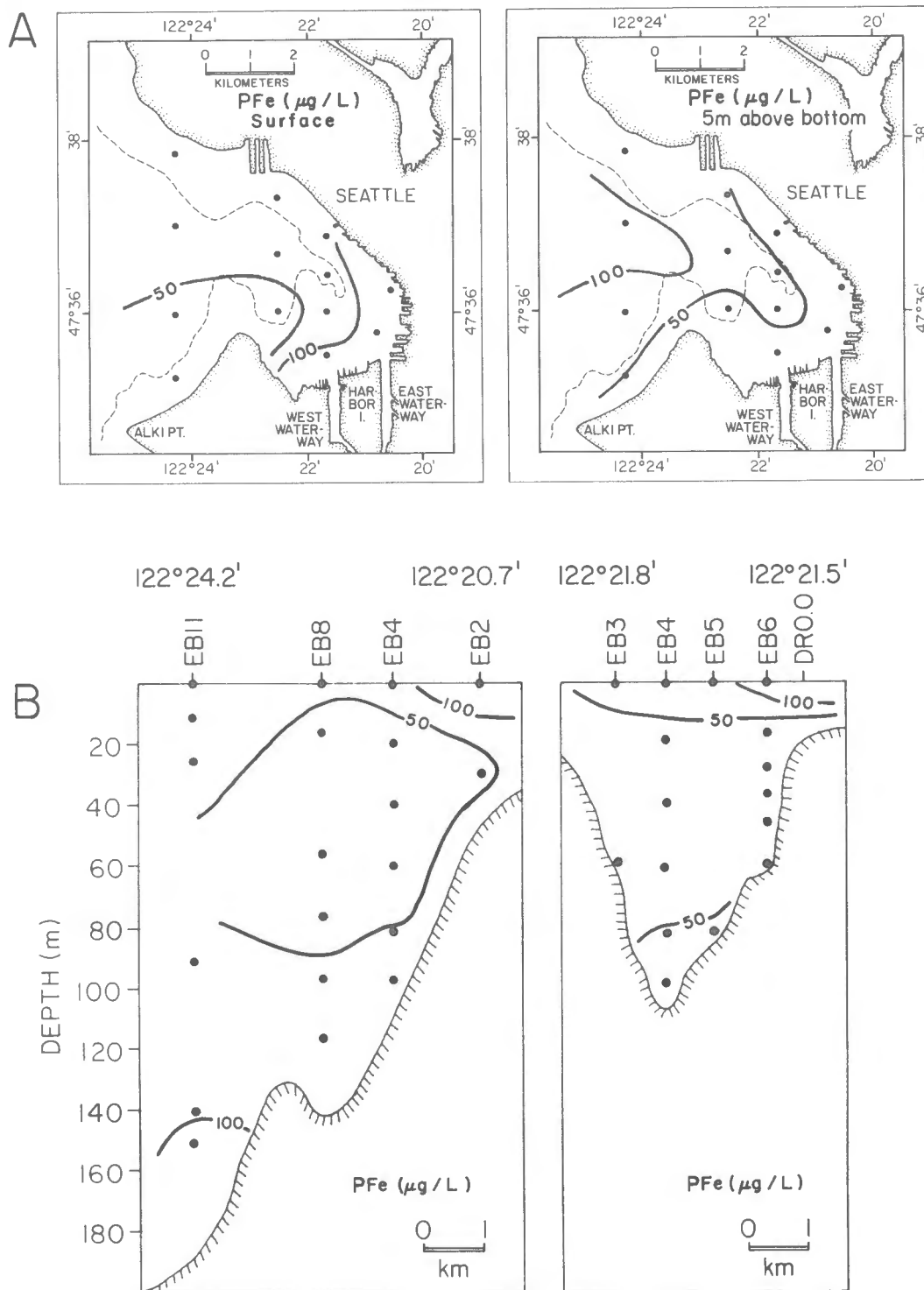particulate Cr in Elliott Bay.

Figure 3.6.   A. Areal distributions of total particulate Mn
              at the surface and 5 m above the bottom.
              B. East-west and north-south cross sections of
              particulate Mn in Elliott Bay.

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Figure 3.7. A. Areal distribution of total particulate Fe at the surface and 5 m above the bottom. B. East-west and north-south cross sections of particulate Fe in Elliott Bay.
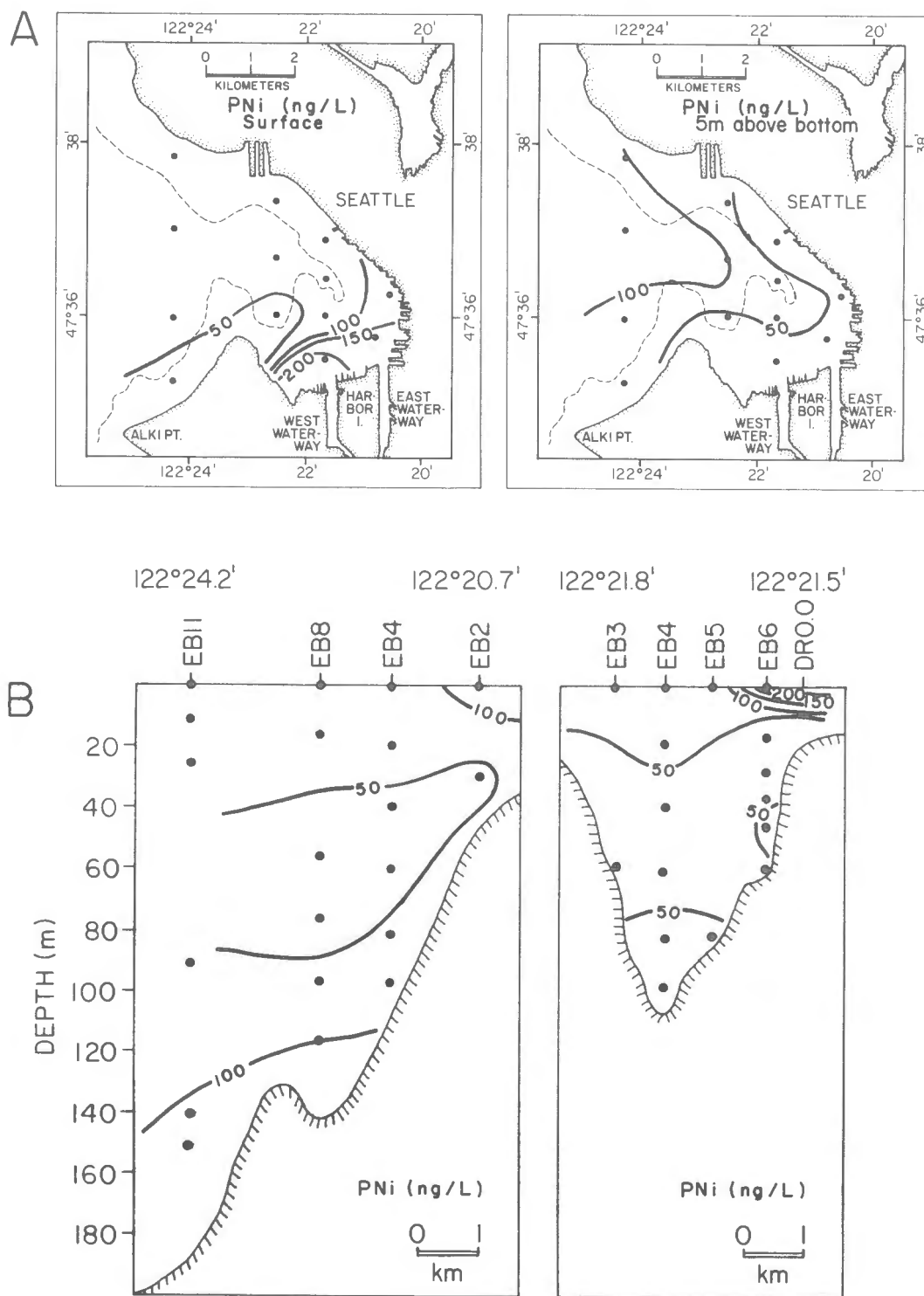
22

Figure 3.8. A. Areal distributions of total particulate Ni at the surface and 5 m above the bottom. B. East-west and north-south cross sections of particulate Ni in Elliott Bay.
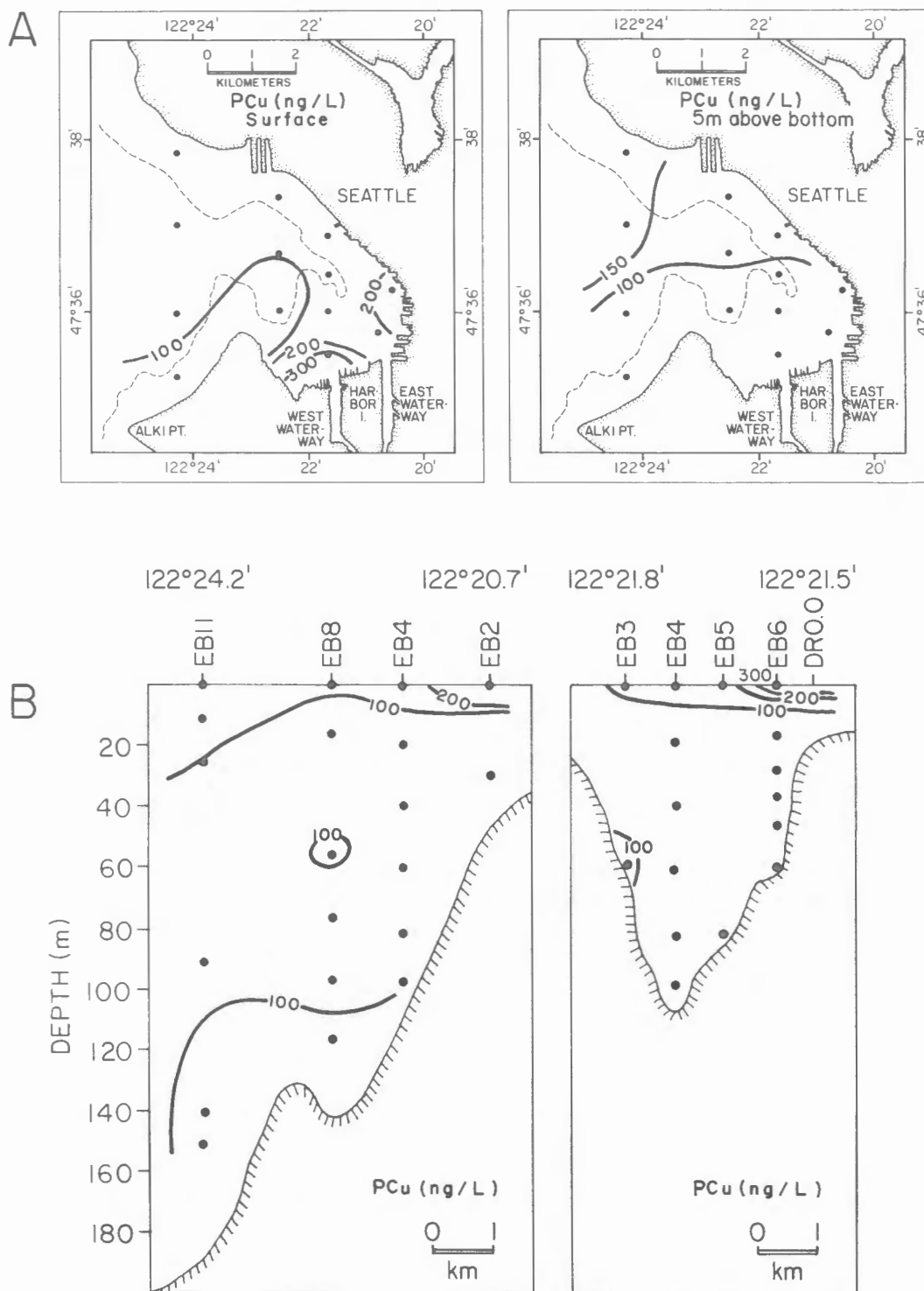
23

Figure 3.9. A. Areal distributions of total particulate Cu at the surface and 5 m above the bottom. B. East-west and north-south cross sections of particulate Cu in Elliott Bay.

Figure 3.10. A. Areal distributions of total particulate Zn at the surface and 5 m above the bottom. B. East-west and north-south cross sections of particulate Zn in Elliott Bay.
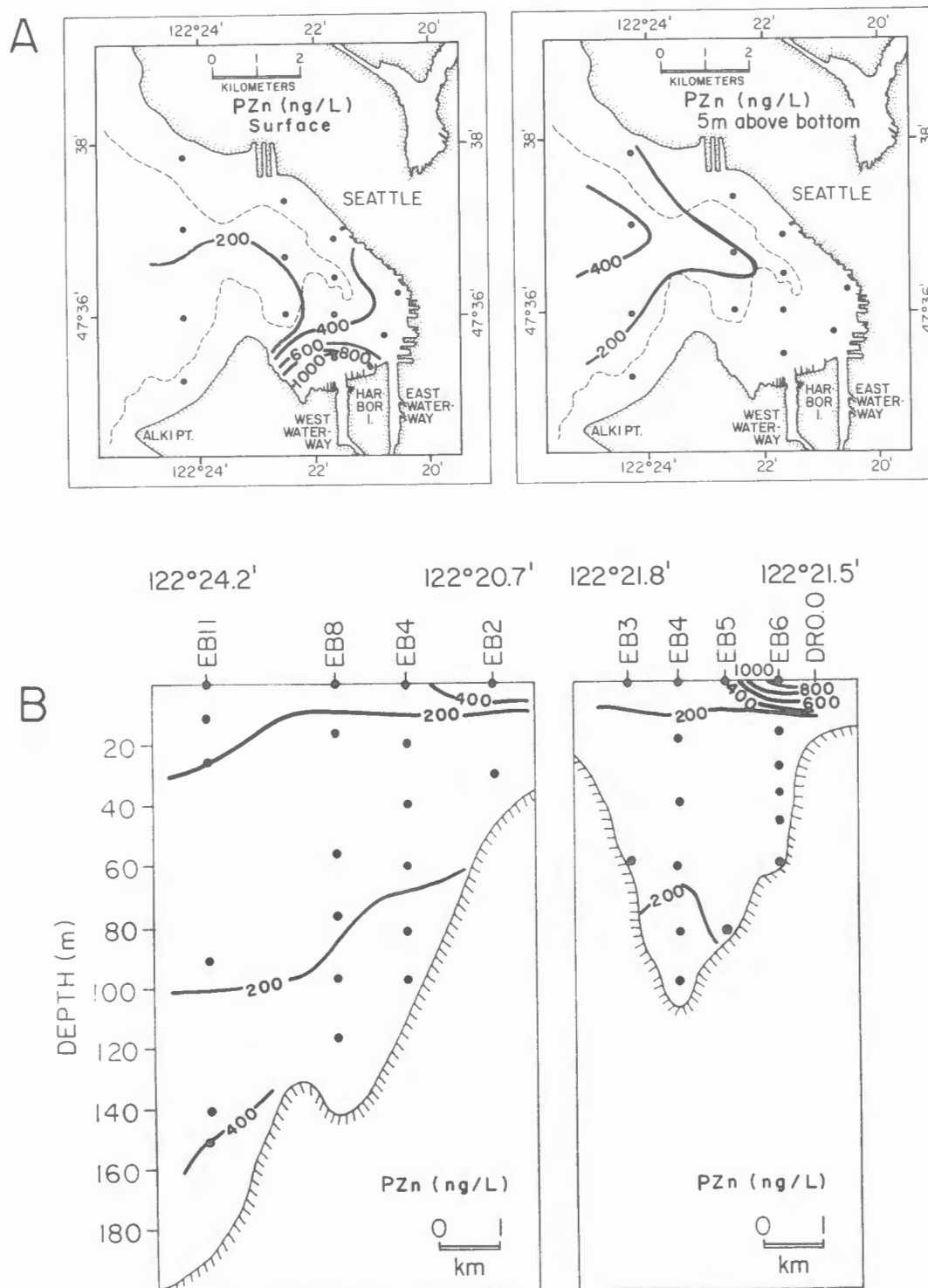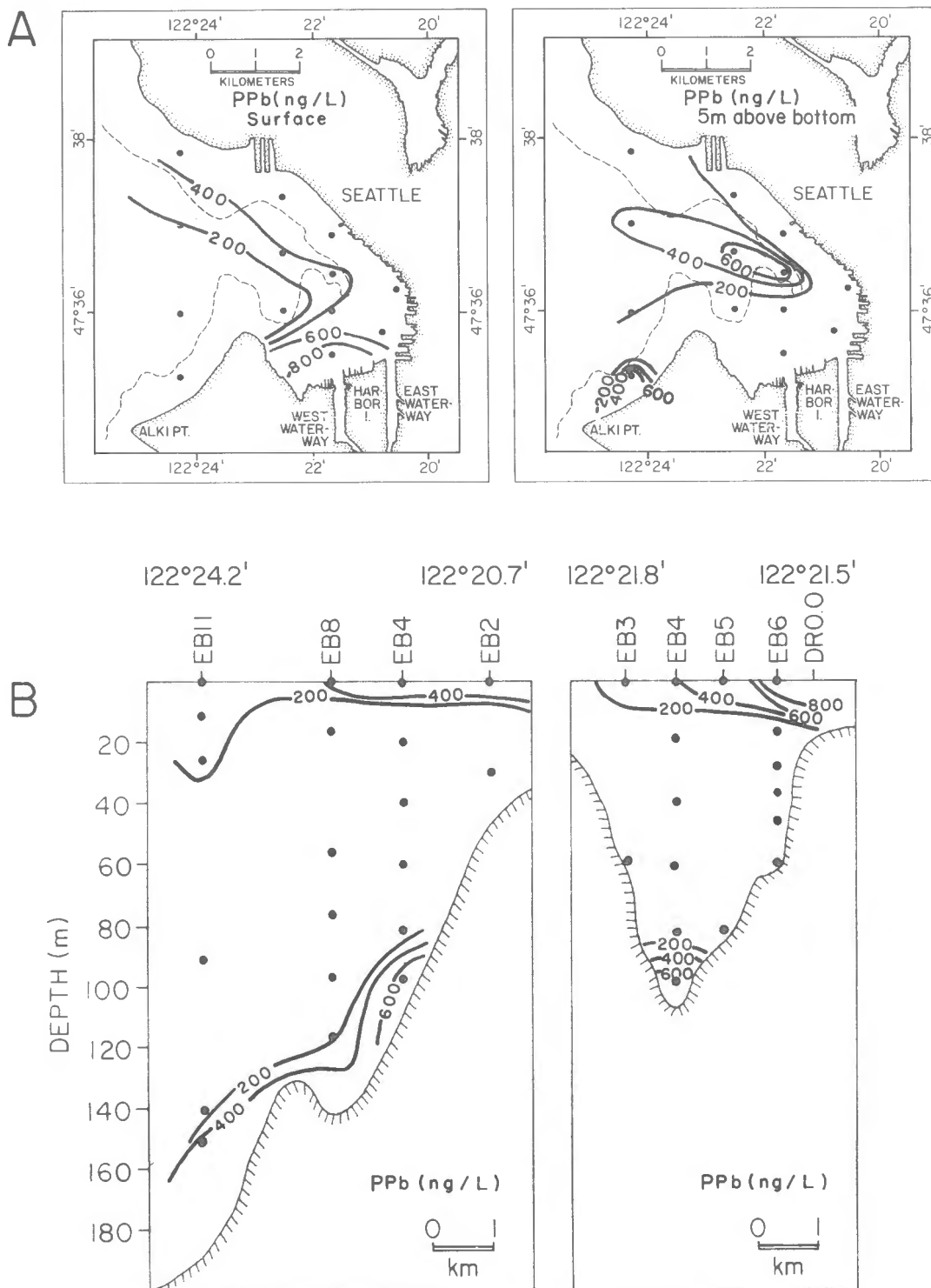
Figure 3.11. A. Areal distributions of total particulate Pb at the surface and 5 m above the bottom. B. East-west and north-south cross sections of particulate Pb in Elliott Bay.

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and EB11 (fig. 3.6B). Some of the Mn-enriched particulate matter at the 20 m level may have also been advected into Elliott Bay from the central basin of Puget Sound. This rather interesting result implies that dissolved Mn continues to be scavenged by suspended matter in subsurface waters (>10 m) of Elliott Bay and the central basin of Puget Sound. Indeed, Mn concentrations in some samples from EB-4 exceed 8,000 ppm by weight in the particulate matter which is more than a factor of two higher than Mn concentrations in suspended matter from the upper Duwamish River (tables 3.1 and 3.2). Along with this enrichment of Mn in the subsurface particulate matter are corresponding enrichments of total particulate Cr, Cu, Zn, and Pb (table 3.2). For example, the highest concentrations of particulate Cr, Cu, and Zn in subsurface particulate matter are in samples where the Mn concentrations approach or exceed 10,000 ppm by weight. These data suggest that several of the potentially toxic trace elements are scavenged along with the Mn in the subsurface particulate matter. Plots of the relationships between total particulate trace elements and total particulate Mn in the subsurface suspended matter are given in figure 3.12. The correlation coefficients for Cr vs. Mn, Ni vs. Mn, Cu vs. Mn, and Zn vs. Mn are all significant at the 99 percent confidence level or better, indicating evidence for a scavenging mechanism involving Mn.

In near-bottom waters, the particulate trace element concentrations (in units of ng/L) increase toward the sediments, with the highest concentrations observed in the submarine canyon (figs. 3.5 through 3.11). Here, suspended-matter concentrations in excess of 1.5 mg/L were observed. Associated with these enrichments in near-bottom suspended matter and particulate trace elements are corresponding increases in bottom water salinity (fig. 3.4). These data seem to indicate that the near-bottom increases in suspended-matter concentrations and particulate trace elements may be related to bottom water flow along the axis of the canyon. Both the trace elements in the near-bottom suspended matter and the bottom sediments have lower concentrations in the solid phase (except for Mn in the near-bottom suspended matter)
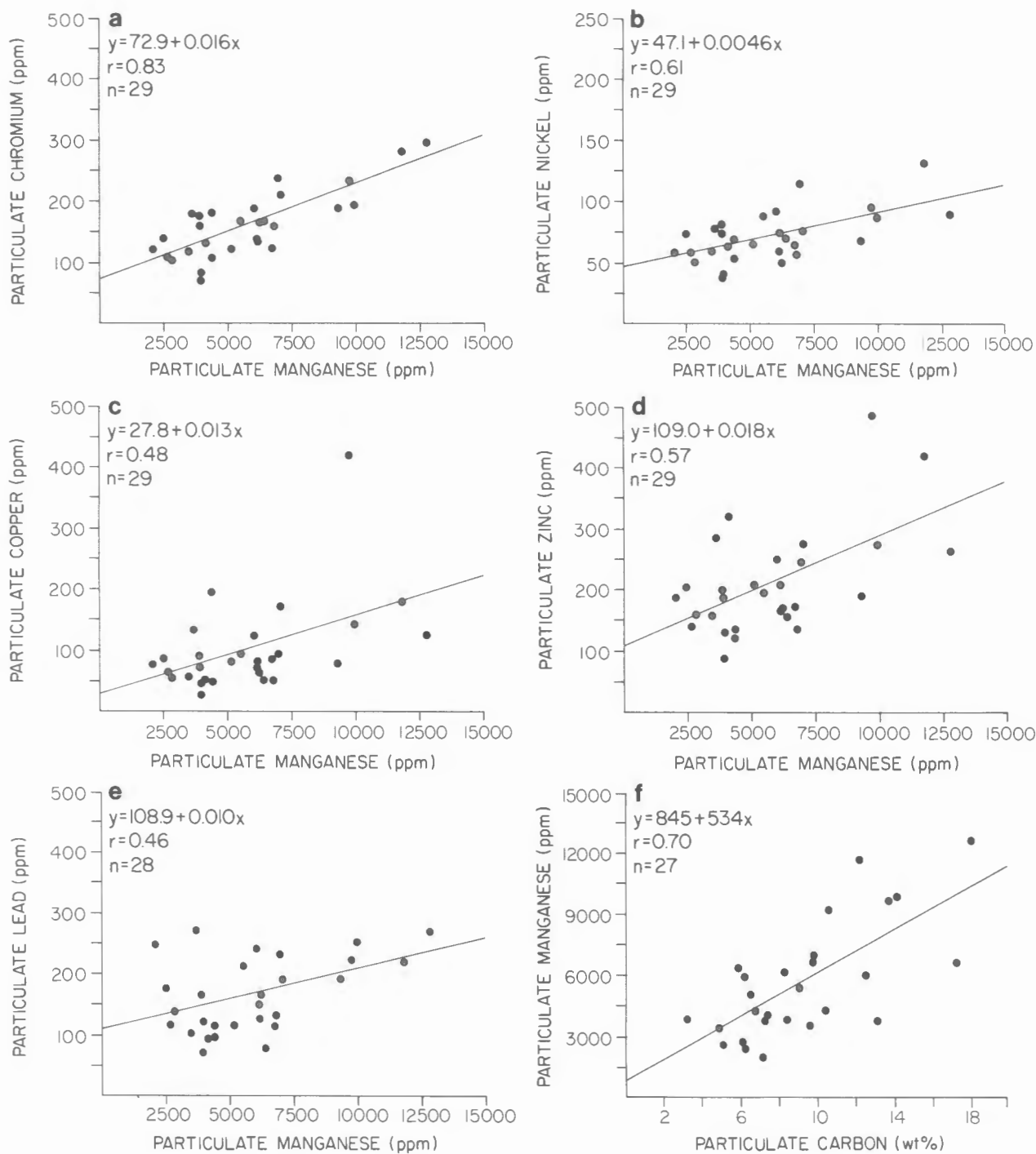
27

Figure 3.12. Scatter diagrams of the relationships between Cr, Ni, Cu, Zn, and Pb with Mn (a-e) and between Mn and C (f) in subsurface particulate matter from Elliott Bay.

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than the near-surface suspended matter (table 3.2). Thus, the near-bottom suspended matter and sediments are being diluted with particles from a source other than the surface plume. Since there is some evidence for movement of central basin water up the submarine canyon (Baker, 1981), and because the suspended material from the central basin is depleted in trace elements relative to suspended matter in the near-surface waters of Elliott Bay (Curl et al., 1981), the central basin appears to be the most probable source for near-bottom suspended material and sediments in the bay.

The near-bottom concentrations of particulate Mn exceed those in the near-surface suspended matter of Elliott Bay and the near-surface suspended matter of the upper Duwamish River (e.g., 4650 ppm Mn in the near-bottom suspended matter vs. 4000 ppm Mn in the near-surface suspended matter vs. 1600 ppm Mn in the Duwamish River suspended matter; cf., tables 3.1 and 3.2.). This unique behavior for particulate Mn in the near-bottom suspended matter is probably due, in part, to diffusive flux of dissolved Mn from the interstitial pore fluids of Elliott Bay sediments followed by precipitation of Mn onto the particulate matter. Mn enrichment in near-bottom suspended matter has been observed elsewhere in coastal regions where riverborne suspended matter is rapidly deposited in near-shore environments (Graham et al., 1976; Sundby, 1977; Massoth et al., 1979; Feely et al., 1981b) and in all cases has been attributed to a "benthic flux" from the sediments. We have measured Mn concentrations in pore fluids from Elliott Bay sediments and have found Mn concentrations ranging from 3-6 mg Mn/L (fig. 3.13). At these concentrations, a benthic flux of Mn from the sediments can support the near-bottom enrichments of Mn in the suspended matter if its oxidation rate in the water column is about the same as or faster than the residence time of the particles. Emerson et al. (1979) and Wollast et al. (1979) have found that Mn oxidation in coastal waters is essentially complete within 2 to 10 days and the process is mediated by several strains of marine bacteria indigenous to coastal environments. In Elliott Bay the average residence time of the
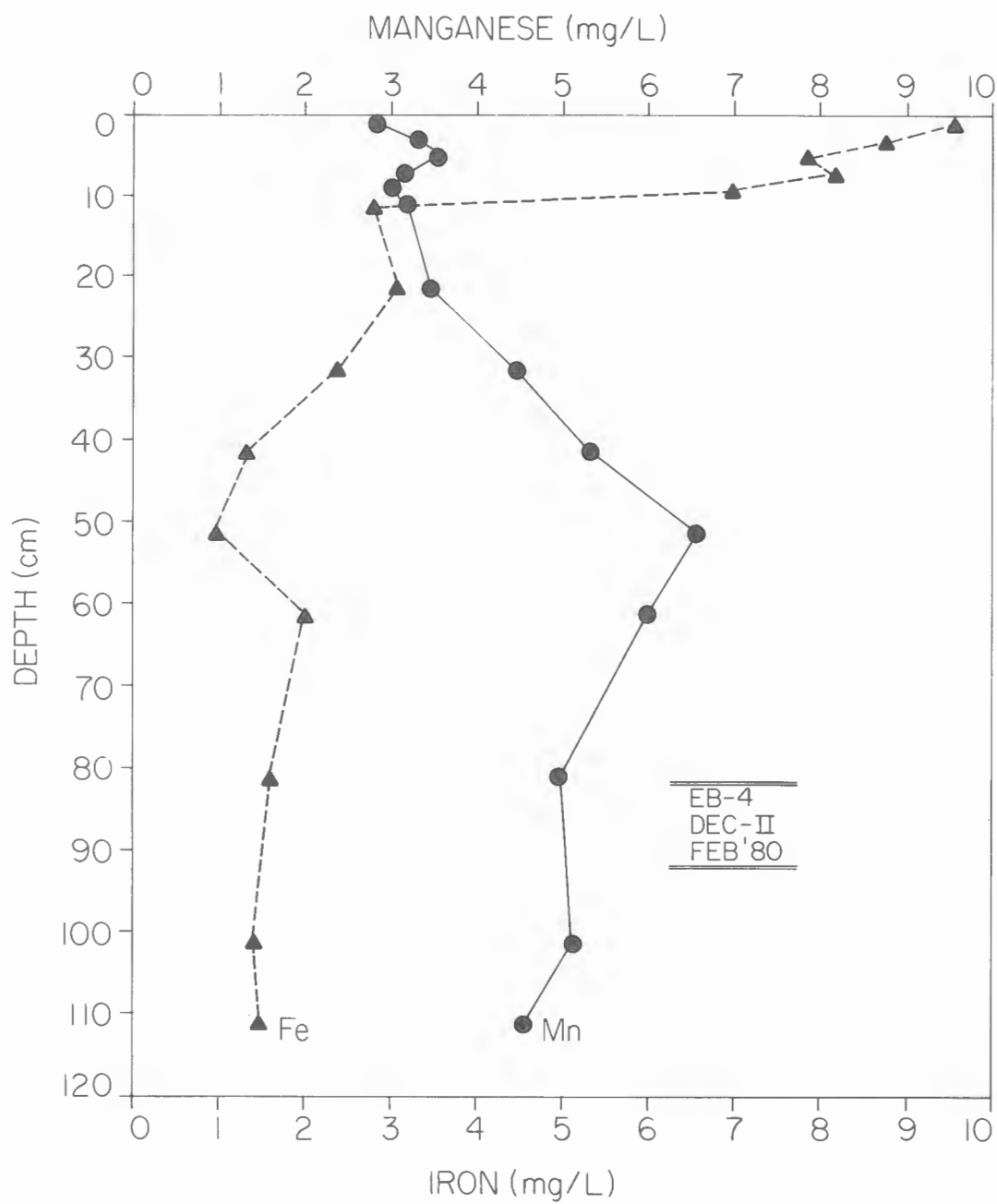
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Figure 3.13.   Profiles of the distributions of total dissolved Mn and Fe in pore fluids of a sediment core from station EB-4 in Elliott Bay.

particles in the bottom subsurface layer can be estimated from the data of Baker (1981). Assuming an average integrated concentration of approximately 110 g suspended matter m^{-2} in the subsurface layer, and an average removal rate of 31 g suspended matter m^{-2} day^{-1} (based on the sediment trap data), a residence time of 3.5 days is obtained for the particulate matter in the subsurface layer. This value is somewhat lower than the value of 8 days estimated by Schell et al. (1977) from ^{210}Pb data. This difference is probably due to the difference in time scales involved with the individual measurements and, as such, probably provide a useful range of residence times for subsurface suspended matter in the bay. Thus, there should be ample time for the particles to interact with the dissolved Mn that is diffusing out of the sediments.

4. DISCUSSION

4.1 Duwamish River Estuary

The flocculation of trace elements in the Duwamish River estuary is a major factor affecting the geochemistry and, very probably, the ecology of the local marine environment. As stated previously, the laboratory studies of Feely et al. (in press) indicate that anywhere from 18 percent to 62 percent of the dissolved-trace-element burden of the Duwamish River is transformed from a dissolved state to an organic-rich flocculant during estuarine mixing. A large fraction of the flocculated material settles to the bottom of the lower estuary and significantly increases the trace metal burden of these sediments as indicated by the enrichments of the concentrations of Cr, Cu, Zn, and Pb in the suspended matter and sediments. The enrichments of the trace elements in the sediments of the Duwamish River estuary and Elliott Bay are several times higher than corresponding sediments from the central basin of Puget Sound (Malins et al., 1980), which suggests that the removal and sedimentation processes are relatively rapid and primarily confined to the local, nearshore environment.

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The possible ecological consequences of these findings should be viewed in the light of a number of recent studies. From laboratory studies with benthic bivalves, Louma and Jenne (1977) reported that some benthic organisms accumulated trace elements in direct proportion to the concentrations of organically bound metals in the sediments. Similar results were indicated by other investigators who studied metal concentrations in some organisms feeding on polluted sediments and sewage waste water (Louma and Bryan, 1978; Furr et al., 1981; Young et al., 1981). Malins et al. (1980) compared trace metal concentrations in bottom sediment from several Puget Sound embayments, including the Duwamish River and Elliott Bay, with a number of fish and shellfish population indices for benthic organisms sampled from the same locations. They found significant correlations between abundances of several trace elements in the sediments and taxon richness values for the benthic communities, indicating a possible causal relationship. If the organic-rich flocculants from the Duwamish River are the major source of the enriched trace elements in the sediments, then it is probable that the flocculants also provide the trace elements to the organisms as well. The marine organisms sampled by these authors were also found to have the largest percentages of incidences of lesions and tumors when compared with marine organisms from other polluted Puget Sound embayments. Although the exact cause-effect relationships for these diseases have not been established, the disease incidences are cause for concern and point out the need for a better understanding of how metals are associated with specific particle phases and how they are bio-accumulated in edible forms of fish and shellfish.

4.2 Elliott Bay

The distributions of particulate trace elements in Elliott Bay delineate the sources and transport pathways for anthropogenic contaminants. Trace elements that are discharged from the RSTP are rapidly scavenged by particulate matter in the Duwamish River estuary and are significantly enriched in the near-surface

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particulate matter of Elliott Bay. This material traverses the bay and is advected to the north and west along the northern shore.

The evidence for significant enrichments of particulate Mn in the subsurface waters of Elliott Bay strongly indicates the occurrence of scavenging reactions involving Mn in Elliott Bay and possibly the central basin of Puget Sound. This result is highly significant since several other trace elements (i.e., Cr, Ni, Cu, Zn, and Pb) appear to be scavenged by the newly formed Mn oxides in the subsurface particulate matter (fig. 3.12). In order to investigate this possibility further, we have calculated interelement correlation coefficient matrices for the near-surface and subsurface particulate matter from Elliott Bay (tables 3.4 and 3.5). The major elements--C, Ti, and Fe--have been included to provide information on the relationships between the trace elements and the major solid phases that contain them. Carbon is used to show relationships with organic matter. Usually Al is used to show relationships with inorganic aluminosilicate matter (Price and Calvert, 1973; Feely et al., 1981a). However, since the Al data for the Elliott Bay samples are incomplete, the Ti data have been used for this purpose (the recent data of Feely et al., 1981a, have shown that in coastal suspended matter, both Ti and Al are derived from terrestrial aluminosilicate material and their ratio in suspended matter remains relatively constant at about 0.04-0.07, which is the same as the ratio for average shales). Fe is used to indicate relationships with flocculated material and oxide coatings. In the near-surface suspended matter the trace elements show little correlation with particulate C but are highly correlated with Fe and Ti. These data indicate that the trace elements are primarily associated with both the flocculated materials and the aluminosilicate rock material from the Duwamish River estuary. Since the trace elements correlate most highly with Fe, the flocculant material is probably the dominant phase containing the trace elements in the near-surface particulate matter.

The situation is dramatically reversed in the subsurface particulate matter (table 3.5). The most significant correlations

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Table 3.4. Interelement correlation coefficient matrix for near-surface (< 3 m) suspended matter from Elliott Bay.[1] Samples were collected on February 20, 1980.

	C	Ti	Cr	Mn	Fe	Ni	Cu	Zn	Pb
C	1.000	0.250	0.604*	0.074	0.511	0.381	0.226	0.312	0.458
Ti		1.000	0.447	-0.314	0.522	0.396	0.540	0.583	0.441
Cr			1.000	-0.101	0.542	0.815*	0.511	0.579	0.298
Mn				1.000	-0.607*	-0.255	-0.440	-0.667	-0.455
Fe					1.000	0.588*	0.551	0.740*	0.652*
Ni						1.000	0.553	0.639*	0.317
Cu							1.000	0.641*	0.447
Zn								1.000	0.587
Pb									1.000

[1] Eighteen samples were used in this analysis. At the 99 percent confidence level a correlation coefficient of 0.590 or higher is significant.
* Significant at the 99 percent confidence level.

Table 3.5 Interelement correlation coefficient matrix for subsurface (> 10 m) suspended matter from Elliott Bay.[2] Samples were collected on February 20, 1980.

	C	Ti	Cr	Mn	Fe	Ni	Cu	Zn	Pb
C	1.000	0.001	0.581*	0.752*	0.097	0.438	0.409	0.459	0.452
Ti		1.000	0.427	0.103	0.887*	0.641*	0.266	0.355	0.355
Cr			1.000	0.831*	0.487*	0.848*	0.628*	0.693*	0.680*
Mn				1.000	0.119	0.654*	0.481*	0.570*	0.454
Fe					1.000	0.651*	0.362	0.350	0.377
Ni						1.000	0.623*	0.781*	0.652*
Cu							1.000	0.766*	0.488*
Zn								1.000	0.578*
Pb									1.000

[2] Twenty-nine samples were used in this analysis. At the 99 percent confidence level a correlation coefficient of 0.470 or higher is significant.
* Significant at the 99 percent confidence level.

exist between the trace elements and Mn. For Cr, Ni, Cu, and Zn the correlations are significant at the 99 percent confidence level or higher, indicating that hydrous Mn oxide coatings are the dominant phases controlling the trace element distributions. The high degree of correlation between some of the trace elements, notably Ni and Fe, indicates that hydrous Fe oxide coatings may also be important. The lowest correlations are with Ti for all elements except Ni. These data suggest that in the subsurface waters the trace element concentrations in the particulate matter are primarily controlled by scavenging processes involving hydrous Mn and Fe oxide coatings.

These findings are highly significant from both geochemical and ecological points of view. In the field of geochemistry, the data are important because they suggest that Mn recycling from recent sediments can play a major role in sequestering other trace elements in estuarine and coastal environments. In order to evaluate this possibility the relative contributions of Mn from various sources must be determined. This calculation can be made if the dissolved Mn concentrations and flow data are known or can be estimated. Baker (1981) states that at the time of his study the mean discharge of the Duwamish River was approximately 44 m^3 s^{-1}. Assuming an average concentration of dissolved Mn in the Duwamish River of 54 µg/L (based on measurements made in our laboratory) and an average flocculation of 40 percent of the Mn during estuarine mixing (Feely et al., in press), approximately 1.2 x 10^5 g Mn day^{-1} was discharged from the river in the dissolved form. The Mn released from the sediments can be estimated from the pore water data. Using an average concentration of 4340 µg Mn/L in the top few centimeters of the sediment column (based on the data in fig. 3.15 and other pore water data from Elliott Bay cores) and applying Fick's first law of diffusion:

$$F_{Mn} = D_{Mn} \frac{dc}{dz} \qquad (1)$$

where F_{Mn} is the flux of Mn in units of µg cm^{-2} sec^{-1}, $\frac{dc}{dz}$ is the concentration gradient of Mn at the seawater sediment interface in

units of μg Mn cm^{-4} and D_{Mn}, the diffusion coefficient for Mn, is
4.85 x 10^{-6} cm^2 sec^{-1} (Li and Gregory, 1974), the flux of Mn to
the bottom waters is 1.9 μg Mn cm^{-2} day^{-1}. Multiplied by the area
of fine-grained sediments in Elliott Bay (~20 km^2) this value
yields a daily input of 3.8 x 10^5 g Mn from the sediments, which
is about three times higher than the input from the Duwamish
River. Estimates of Mn inputs from the central basin are more
difficult to obtain because of the uncertainties about water
circulation in the Bay. However, if the maximum excursion time--
approximately 8 days (Sillcox et al., 1981)--is combined with
average dissolved Mn concentrations at middepth in the central
basin ($\cong$ 1.0 μg/L, Curl et al., 1981), an input rate of about 2.6
x 10^5 g Mn day^{-1} is obtained. Thus, the total input of dissolved
Mn to Elliott Bay is estimated to be about 7.6 x 10^5 g Mn day^{-1}.
Of this amount, approximately 50 percent is derived from the
sediments, 34 percent is derived from the central basin, and 16
percent is derived from the Duwamish River. These calculations
are obviously tenuous and errors as large as the numbers them-
selves are probably not unrealistic. However, the results do
point out that the Mn contribution from the sediments is at least
as large as or larger than Mn contributions from other sources and
explain, in part, why the Mn enrichments are highest in the sub-
surface waters: the two major sources for Mn are also located in
subsurface regions. Thus, it is not unreasonable that the major
scavenging reactions involving Mn occur in the subsurface waters.

From an ecological point of view these results are also
important because trace elements associated with Mn oxides are not
readily assimilated by particle-feeding organisms. For example,
Louma and Jenne (1977) conducted laboratory experiments with the
detritus-feeding clam, *Macoma balthica,* to show that metals bound
to detrital organic matter were more easily assimilated by the
clams than metals bound to Mn and Fe oxides. Similarly, Louma and
Bryan (1978) found that the amount of Pb in the bivalve *Scarbi-
calaria plana* inversely varied with the amount of Fe in the under-
lying sediments of several European estuaries, indicating that
sediment-bound Pb is not readily available to benthic organisms

when the Pb is bound to Fe oxides. These findings provide a foundation for evaluating the ecological significance of the trace element scavenging processes that occur in the Duwamish River-Elliott Bay region which can reduce the potential for bioaccumulation of trace elements in the indigenous marine organisms. Since trace elements bound to Mn oxides appear to be less available to organisms than trace elements bound to organic materials (e.g., organic flocculants), it seems prudent to identify those regions where formation of organic flocculants and Mn oxides are maximized with the intent to provide possibly useful recommendations about where waste-water dischargers, particularly those containing elevated concentrations of trace elements, ought to be located. For example, our data indicate that organic flocculants are formed in the low-salinity regions of the Duwamish River estuary and that a portion of the flocculants settle out in the estuary and in nearshore regions of Elliott Bay. Although the formation of organic flocculants reduces the potential toxicity of trace elements to free-swimming organisms, they apparently increase the potential for bioaccumulation of trace elements to suspension- and detritus-feeding benthic organisms. In contrast, in the deeper waters of Elliott Bay the scavenging of trace elements by Mn-Fe oxides and the subsequent sedimentation of this material may reduce the potential for bioaccumulation of trace elements in both free-swimming and detritus-feeding organisms. Thus, in light of this simple analysis, locating waste-water dischargers may be more advantageous in areas where Mn-Fe oxides are forming in the water column than in regions where organic flocculants are forming, such as the Duwamish River estuary. However, it is important to point out that this analysis does not include the potential effects of diagenesis of particle-bound trace elements in the underlying sediments which can cause remobilization of some trace elements back into the water column (Curl et al., 1981). A thorough study of the distributions of the trace elements in the underlying sediments is, therefore, imperative before any specific recommendations can be put forward about where future dischargers ought to be located in Puget Sound.

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Acknowledgments

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