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ELEMENTAL COMPOSITION OF SUSPENDED PARTICULATE MATTER IN THE LOWER DUWAMISH RIVER AND ELLIOTT BAY, WASHINGTON

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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

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

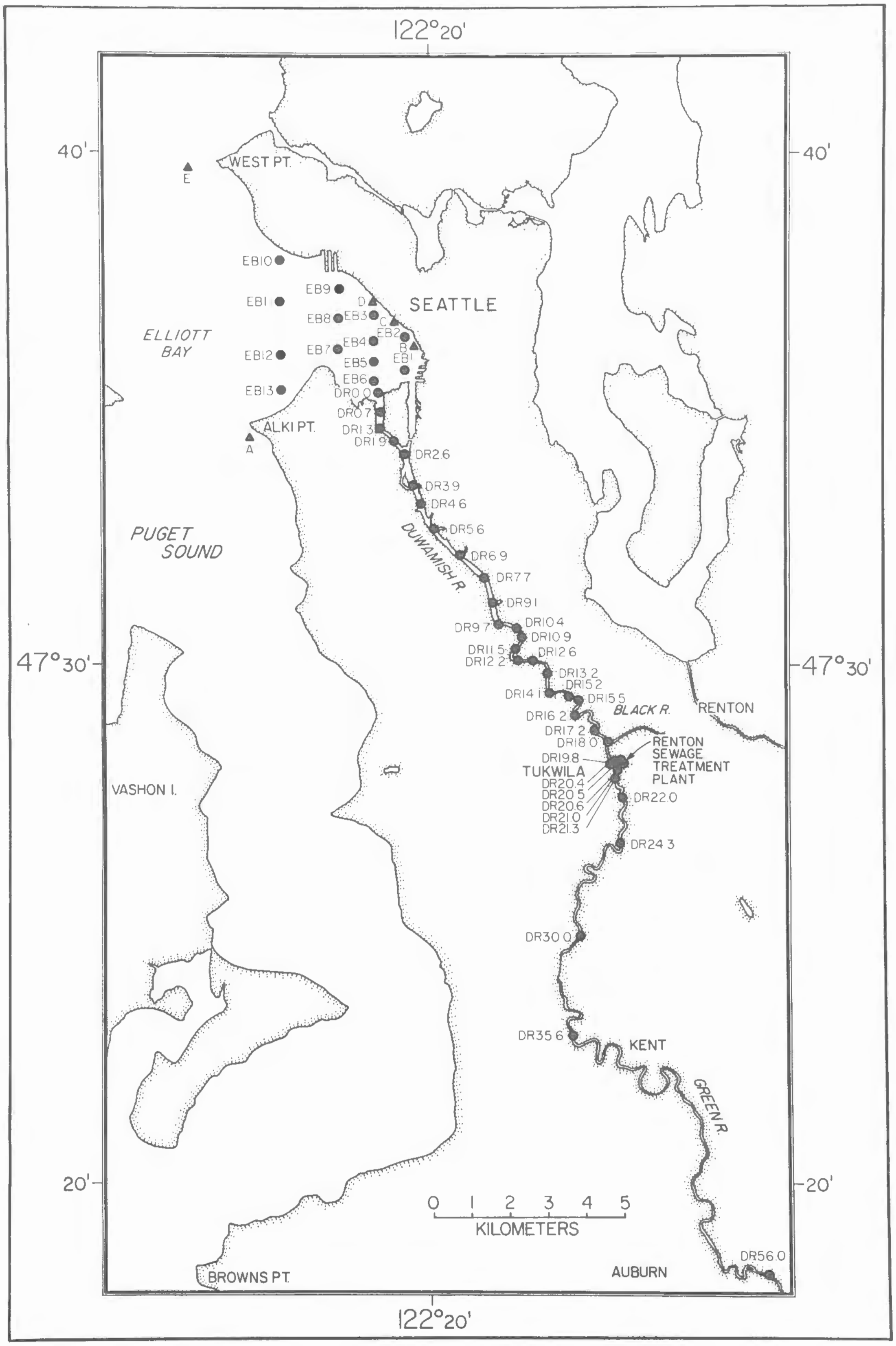

Figure 1.1. Locations of sampling stations in the Duwamish River and Elliott Bay. Stations in the Duwamish River are designated by river kilometer.

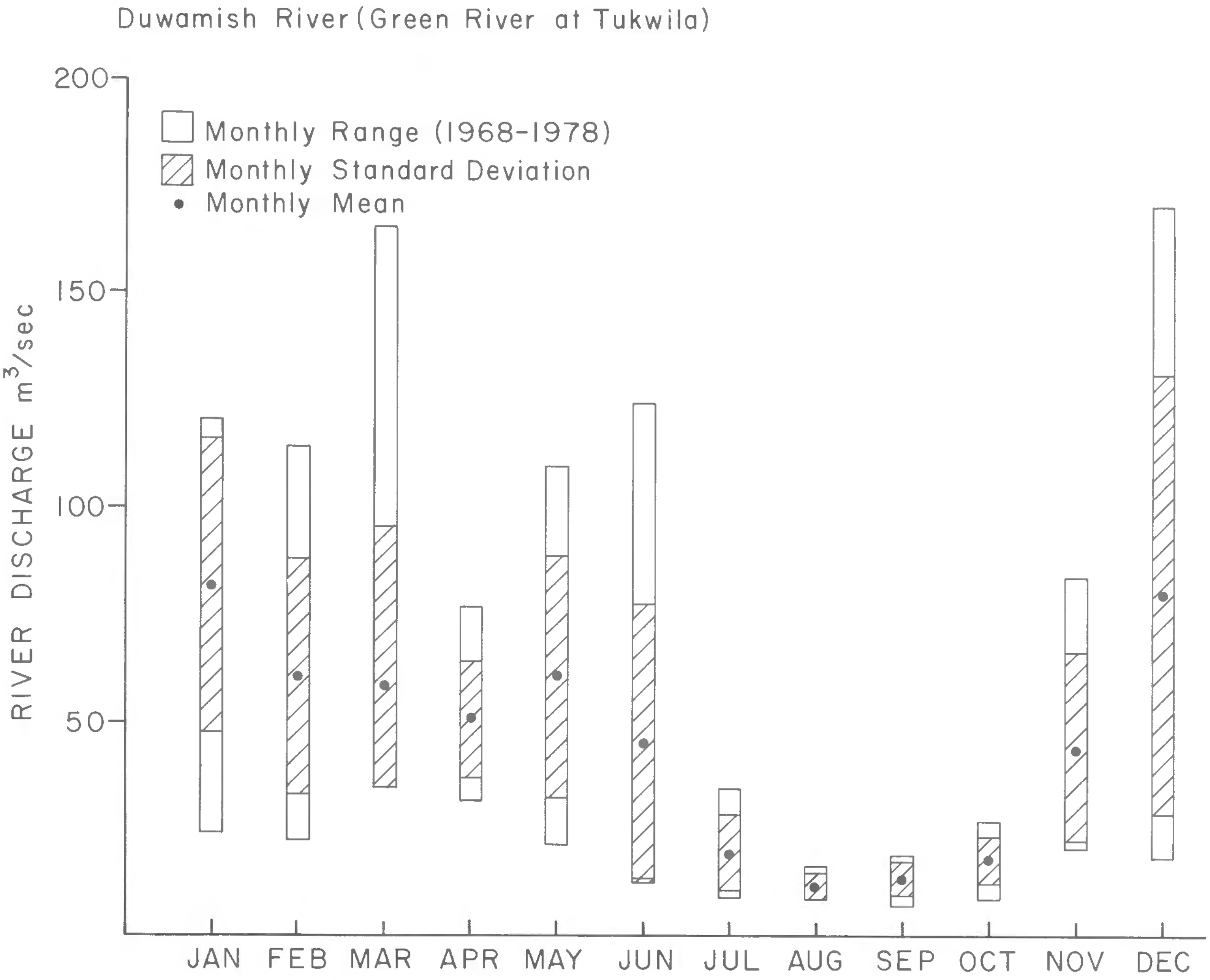

Figure 1.2. Monthly means, standard deviations, and ranges for the Duwamish River discharge. Data compiled from the U.S.G.S. stream flow records obtained at Tukwila for the period 1968-1978.

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 sections of the city of Seattle. The bay has a surface area of approximately 20 km^2 and a total volume of approximately 2.05×10^{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.

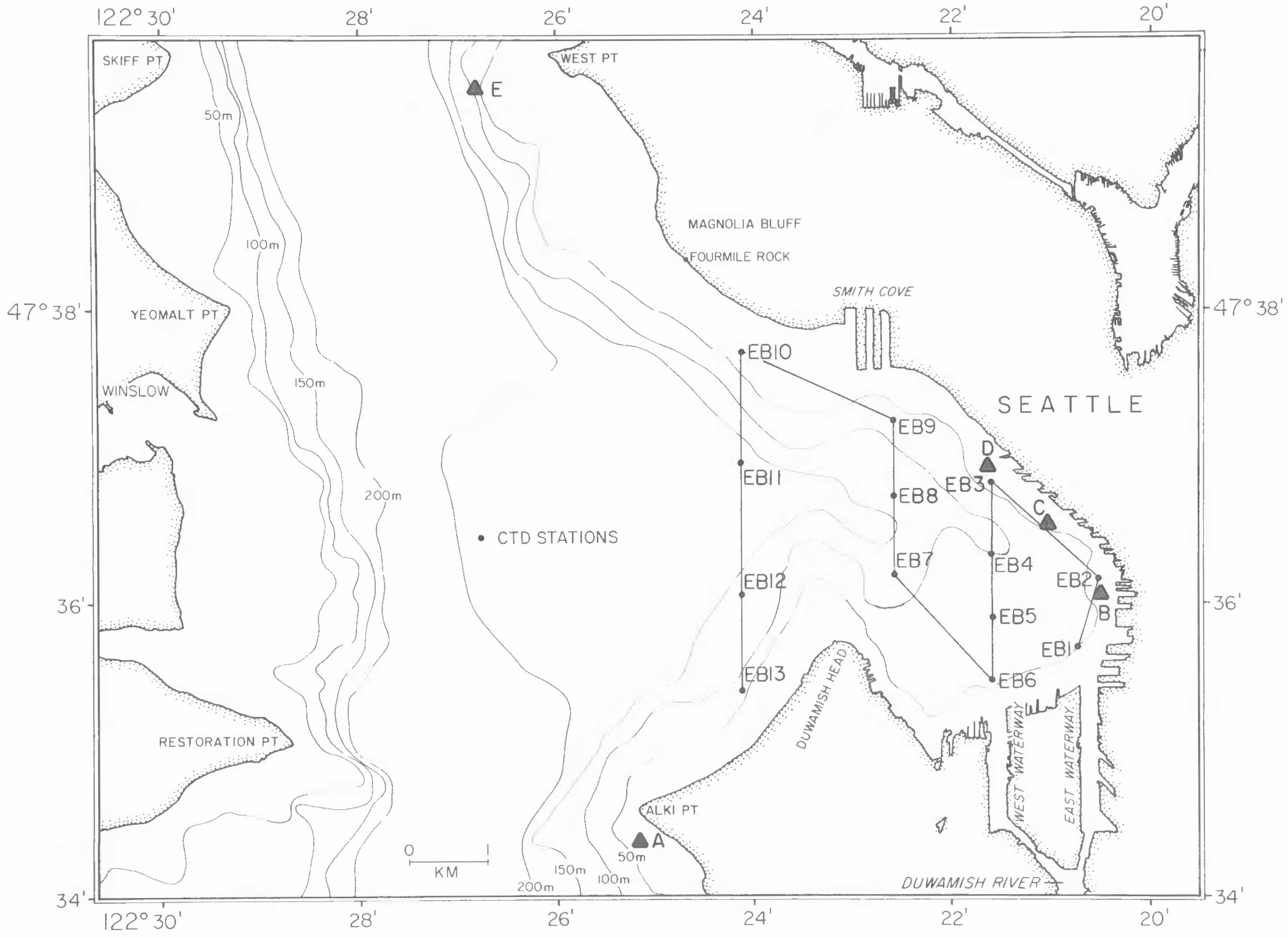

Figure 1.3. Locations of suspended-matter stations in Elliott Bay. The solid line shows the cruise track starting with station EB1 and ending at station EB 13. Outfall stations are indicated as A through E.

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 ($2\sigma = \pm 0.011$ 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 $\mu g\ cm^{-2}$ 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 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 $\leqq 4.0°/_{oo}$). 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

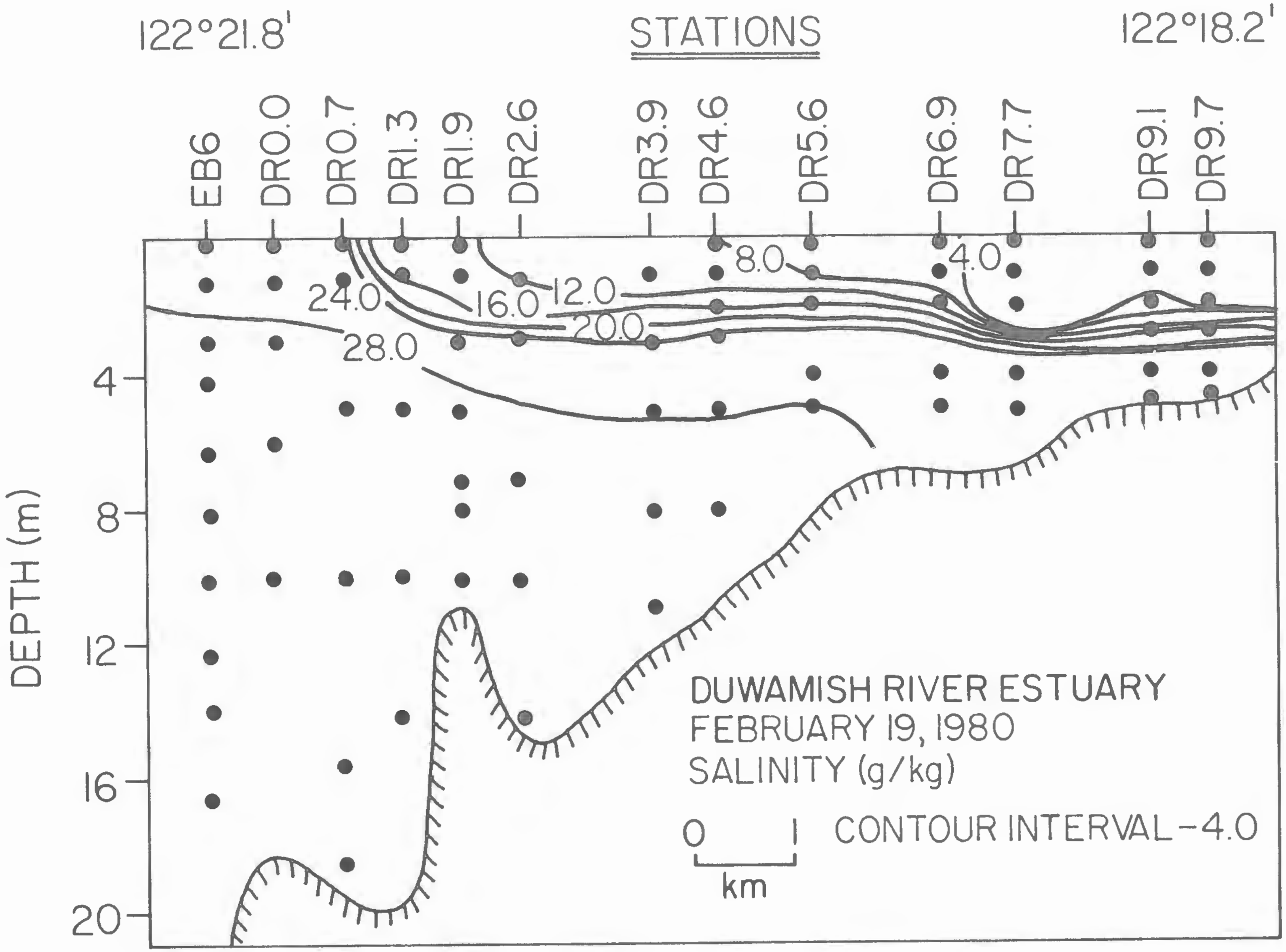

Figure 3.1. Distribution of total suspended matter in the Duwamish River estuary.

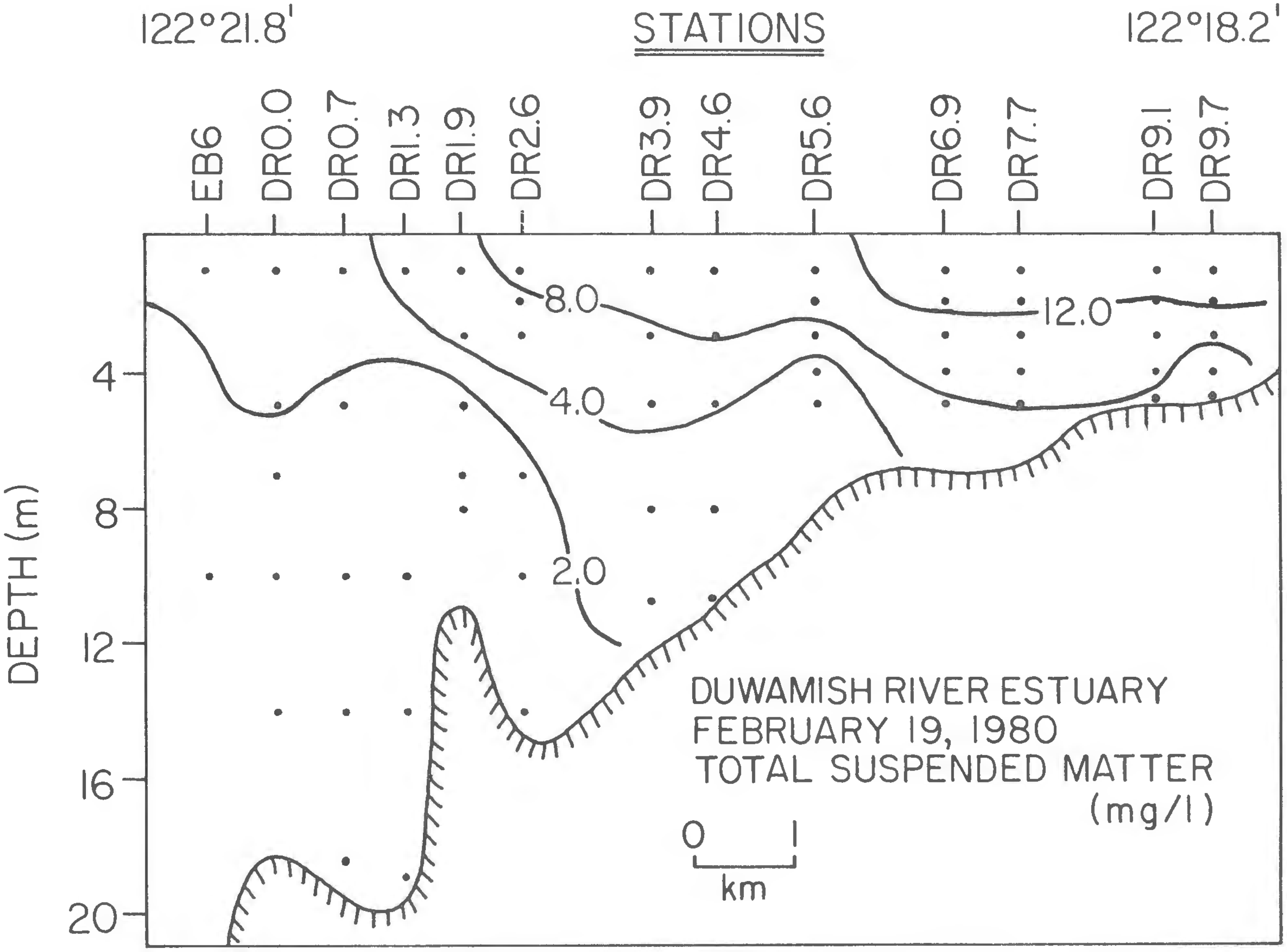

Figure 3.2. Distribution of salinity in the Duwamish River estuary.

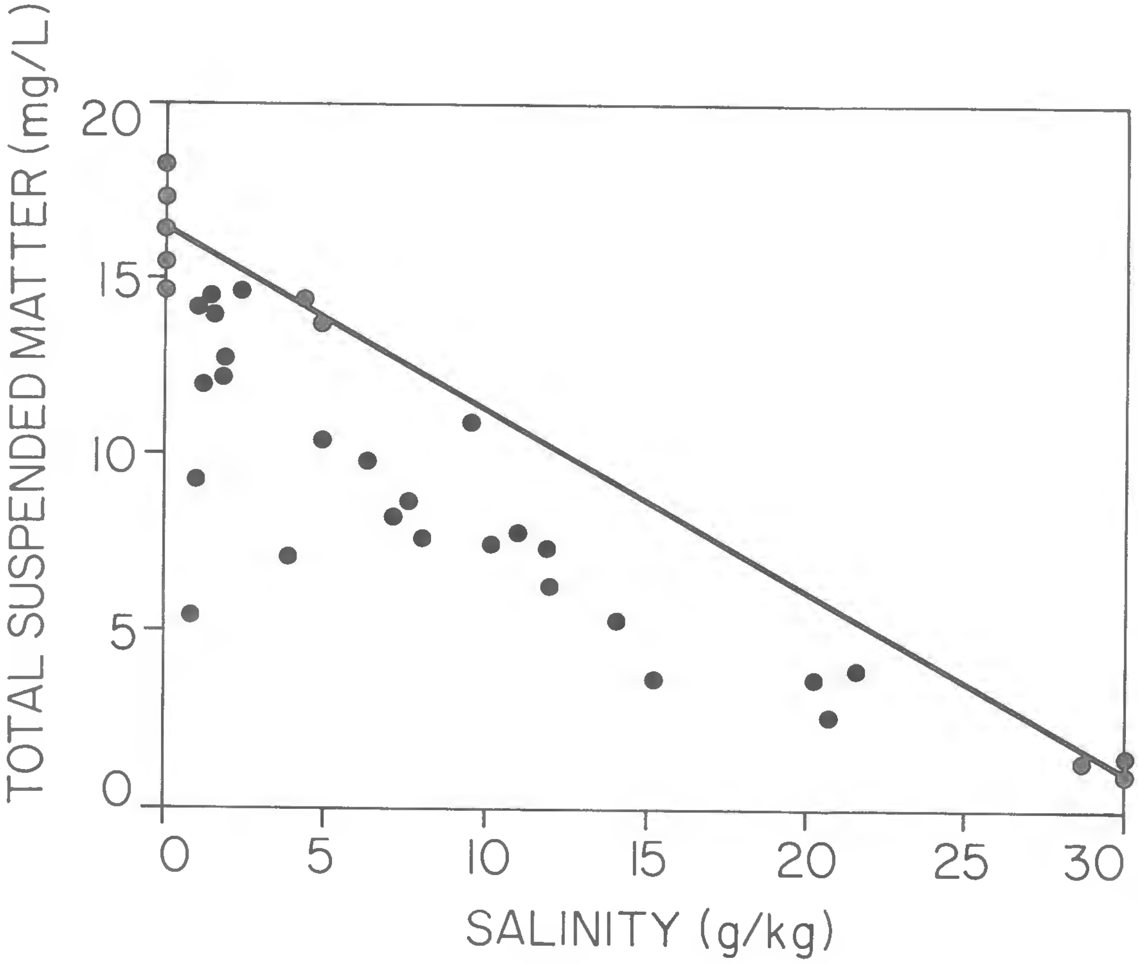

Figure 3.3. Plot of the relationship between total suspended matter and salinity in the Duwamish River estuary. Data collected February 19, 1981. The solid line denotes the theoretical dilution line for conservative mixing.

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 ($< 28.0°/_{oo}$) 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).

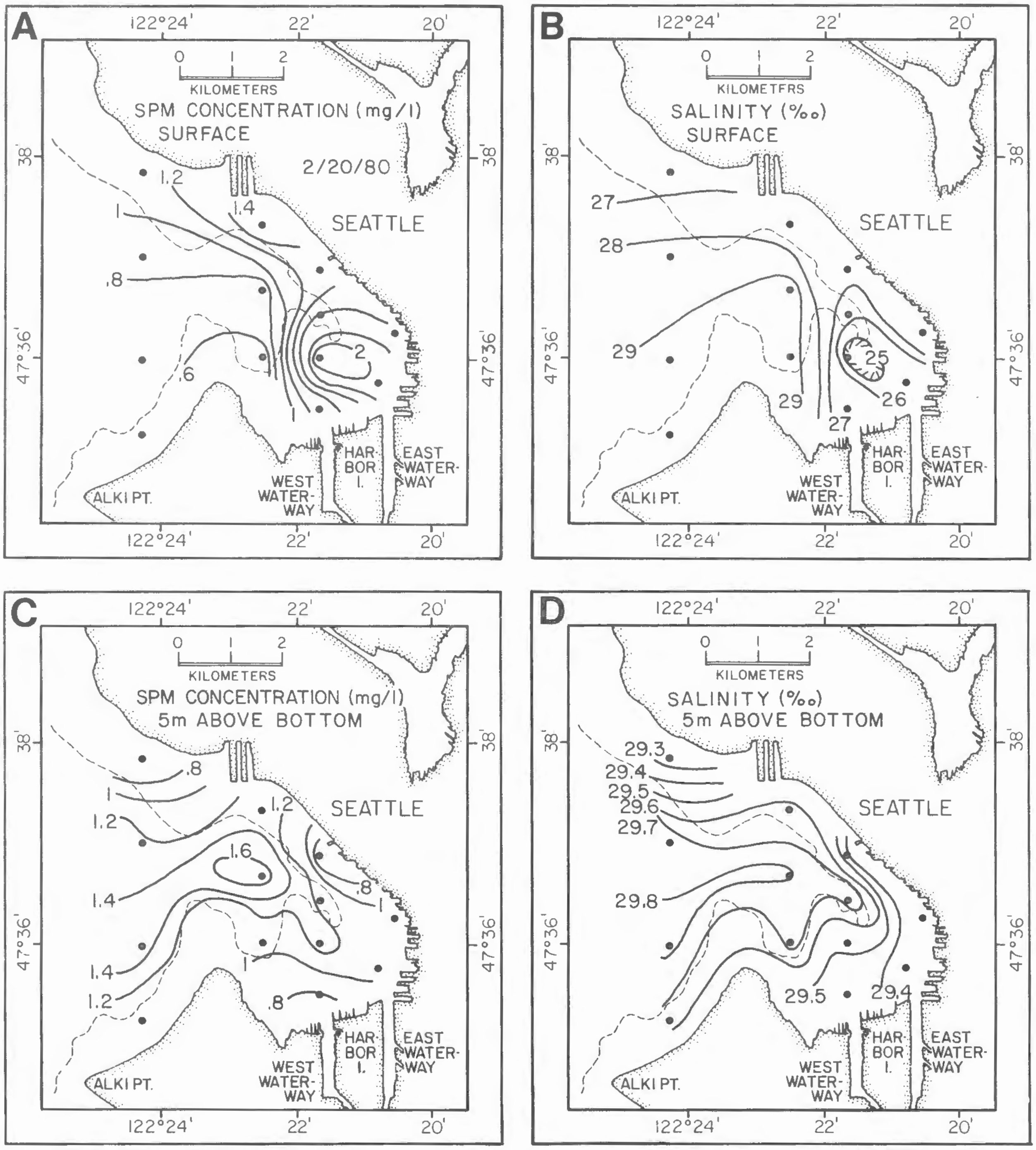

Figure 3.4. Distribution of: A. Total suspended matter B. Salinity at the surface; and C. Total suspended matter, and D. Salinity 5 m above the bottom in Elliott Bay. Data collected February 20, 1980 (after Baker, 1981).

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 ($0\text{-}10^{\circ}/_{oo}$) 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

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	7	$\bar{x}$	8.25	9.26	0.412	6.25	100	1218	53	46	145	66
of RSTP (RK 20.6-		S.D.	±1.80	±1.51	±0.017	±2.06	±14	±221	±7	±7	±20	±14
RK 56.0)												
Samples down-	14	$\bar{x}$	8.46	10.14	0.430	7.80	114	1154	77	60	247	95
stream of RSTP		S.D.	±2.12	±1.17	±.040	±1.04	±32	±135	±22	±26	±85	±37
(RK 20.5-RK 12.2)		%	(+2.5)	(+9.5)	(+4.4)	(+25)	(+14)	(-5)	(+45)	(+30)	(+70)	(+44)
Duwamish River	10	$\bar{x}$	8.28	--	0.439	9.18	154	1087	84	91	298	211
Estuary		S.D.	±2.45	--	±.022	±0.44	±17	±195	±16	±13	±30	±61
(0-10°/$_{oo}$)		%	(+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).

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