

The biogeochemistry of nutrients and trace metals in Hood Canal, a Puget Sound fjord

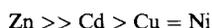
A.J. Paulson^{*,1}, H.C. Curl, Jr.², R.A. Feely

NOAA/Pacific Marine Environmental Laboratory, 7600 Sand Point Way, NE Seattle, WA 98115-0070, USA

(Received 9 August 1991; revision accepted 14 November 1992)

Abstract

The summer stratification of the surface layer of much of Hood Canal (a Puget Sound fjord) results in a surface layer low in nutrients and a deep layer low in dissolved oxygen and enriched in nutrients. Deviations from the dissolved oxygen:nutrient linear relationships are manifestations of several chemical and biological processes. The low dissolved oxygen concentrations (50 μmol) result in the redistributions of Fe in the sediment column while Mn is redistributed within the water column. Trace metals are also taken up by organisms in the surface layer and regenerated in the deep layer in the order



Regenerated Zn is adsorbed on to resuspended bottom sediments that are enriched in Fe oxyhydroxides while Cd is adsorbed throughout the water column. Particulate distributions of Cu and Ni indicate these metals are also participating in biogeochemical cycles, albeit to a lesser extent.

Introduction

Extensive biological and chemical recycling of nutrients and trace constituents occur in most estuaries (Burton and Liss, 1976). Chemical removal of trace metals occurs when fresh water encounters the major cations of seawater (Boyle et al., 1977a; Sholkovitz and Copland, 1981; Feely et al., 1983). Nutrients are also removed from the water column in estuaries during periods of high biological growth (Peterson, 1979; Sharp et al., 1982; Kamatani and Takano, 1984). Although the coupling of nutrient and trace metal cycling has been confirmed in the oceans (Boyle et al., 1977b; Bruland, 1980), few

instances of trace metal removal by biological processes have been observed in estuaries (Church, 1986). In many estuaries, the manifestation of the biological removal of trace metals is probably erased by the vigorous action of physical mixing processes. In this report, we present Hood Canal as a model estuary where biological processes dominate trace metal cycling.

Puget Sound is a conglomeration of many different types of embayments, inlets and estuaries. In each of the estuaries, different physical, chemical and biological processes control trace metal distributions (Fig. 1). The Skagit River estuary is similar to US east coast drowned river estuaries with its extensive salt marshes, in which dissolved Cu is added to the water column (Paulson et al., 1991). Like the Rhone estuary (Guan et al., 1991), most trace metals in Elliott Bay are conservative because of the short residence time of the water in the surface layer (Paulson et al., 1989). In contrast,

* Corresponding author.

¹ Present address: Spokane Research Center, US Bureau of Mines, E. 315 Montgomery Avenue, Spokane, WA 99207-2291, USA.

² Present address: NOS/Hazardous Materials Response Branch, 7600 Sand Point Way, N.E. Seattle, WA 98115-0070, USA.

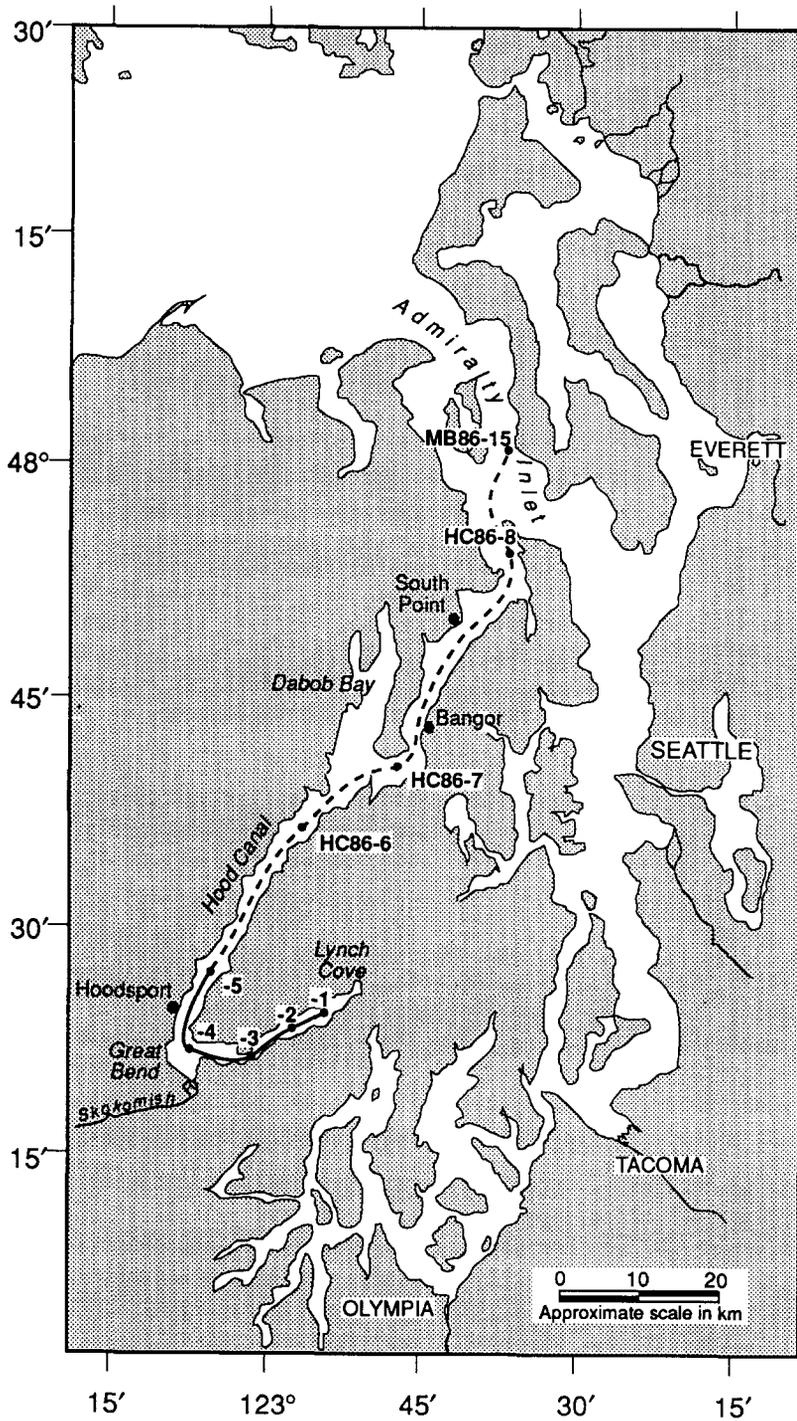


Fig. 1. Puget Sound study area. Along-axis transect between the Great Bend and Lynch Cove is shown as the bold line between stations sampled while the dashed line represents the extended transect through the entire Hood Canal. Names of water bodies are in italics.

the main basin of Puget Sound is a fjord-like estuary (Baker, 1984; Cannon et al., 1990). Although trace metals like Cu and Zn are essentially conservative in the main basin, the oxidation–reduction cycling of Mn produces large quantities of hydrous manganese oxides that adsorb Pb (Paulson et al., 1988). If biological processes were to dominate trace metal cycling anywhere in Puget Sound, Hood Canal would have the highest probability of exhibiting this type of biogeochemical behavior because of its high productivity (Barlow, 1958) and sluggish circulation (Cokelet et al., 1990). In this report, nutrient and trace metal data from a cruise in August 1986 are presented in the context of their oceanic biogeochemical cycles.

Physical setting

The sluggish circulation and stratified water column of Hood Canal produce characteristics that are similar to classic fjords. Hood Canal is 110 km long and is between 2 and 4 km wide throughout most of its length (Fig. 1). Near the entrance to Hood Canal (Fig. 2), bottom water is separated from the main basin of Puget Sound by two deep sills (≈ 50 and 75 m). In this region, average net currents at the depth of the highest flow (60 m) are about 15 cm s^{-1} (Cokelet et al., 1990). Unlike many fjords with shallow sills, Hood Canal does not go anoxic in its deep basin due to periodical renewal of bottom water by intrusions from the Strait of Juan de Fuca over these deep sills. At the time of the cruise in August 1986, an intrusion event probably had not occurred within 4 months (H.O. Mofjeld, personal communication, 1986). Landward of the inner sill, the depths increase to 175 m in central Hood Canal. Although tidal currents may appear vigorous, there is little net advective transport ($\approx 2 \text{ cm s}^{-1}$; Cokelet et al., 1990) and little vertical mixing. In the vicinity of the Great Bend, the bottom shallows to 40 m. Landward of the Great Bend, Lynch Cove is separated from central Hood Canal by a con-

striction in the shore, in which the width decreases to less than 0.7 km. Here, net currents are low ($0.5\text{--}1.5 \text{ cm s}^{-1}$; Cox et al., 1984).

The region surrounding Hood Canal is essentially rural in nature with much of the shoreline around the landward extent of the fjord (Lynch Cove) occupied by vacation homes served by septic tanks. The only National Pollutant Discharge Elimination System (NPDES) permit for Lynch Cove is issued to a small sewage treatment plant serving a resort inn. Freshwater is delivered primarily to the head of the estuary by the Skokomish River with some of the water from this watershed being diverted to a power plant near Hoodspout, Washington. Several smaller rivers draining the Olympic Mountains flow into Hood Canal along the western shore from the Great Bend to Dabob Bay.

Methods

Water samples were collected on 22–23 August 1986 in modified Teflon-coated Go-Flo™ (General Oceanics, Miami, FL, USA) bottles attached to a rosette sampler (nutrient, oxygen, particulate samples) or a Kevlar hydroline positioned on the bow of the NOAA Ship 'Miller Freeman' (dissolved trace metal samples). Salinity samples were collected from each sampling bottle to verify collection at the assumed depth. Oxygen concentrations were determined by Winkler titrations. Nutrient analyses were performed using a Technicon Autoanalyzer 2 according to the method of Whitledge et al. (1981).

All filtration apparatus were acid-cleaned and rinsed with Milli-Q™ (Millipore, Bedford, MA, USA) water. All operations for trace metal samples that were open to the atmosphere were performed in a Class-100 laminar flow hood. Particulates were collected on acid-cleaned 37 mm, $0.4 \mu\text{m}$ Nuclepore (Costar, Cambridge, MA, USA) filters. Total suspended matter (TSM) was determined gravimetrically on Cahn Model 26 electrobalances. Particulate trace metal concentrations were determined by the X-ray

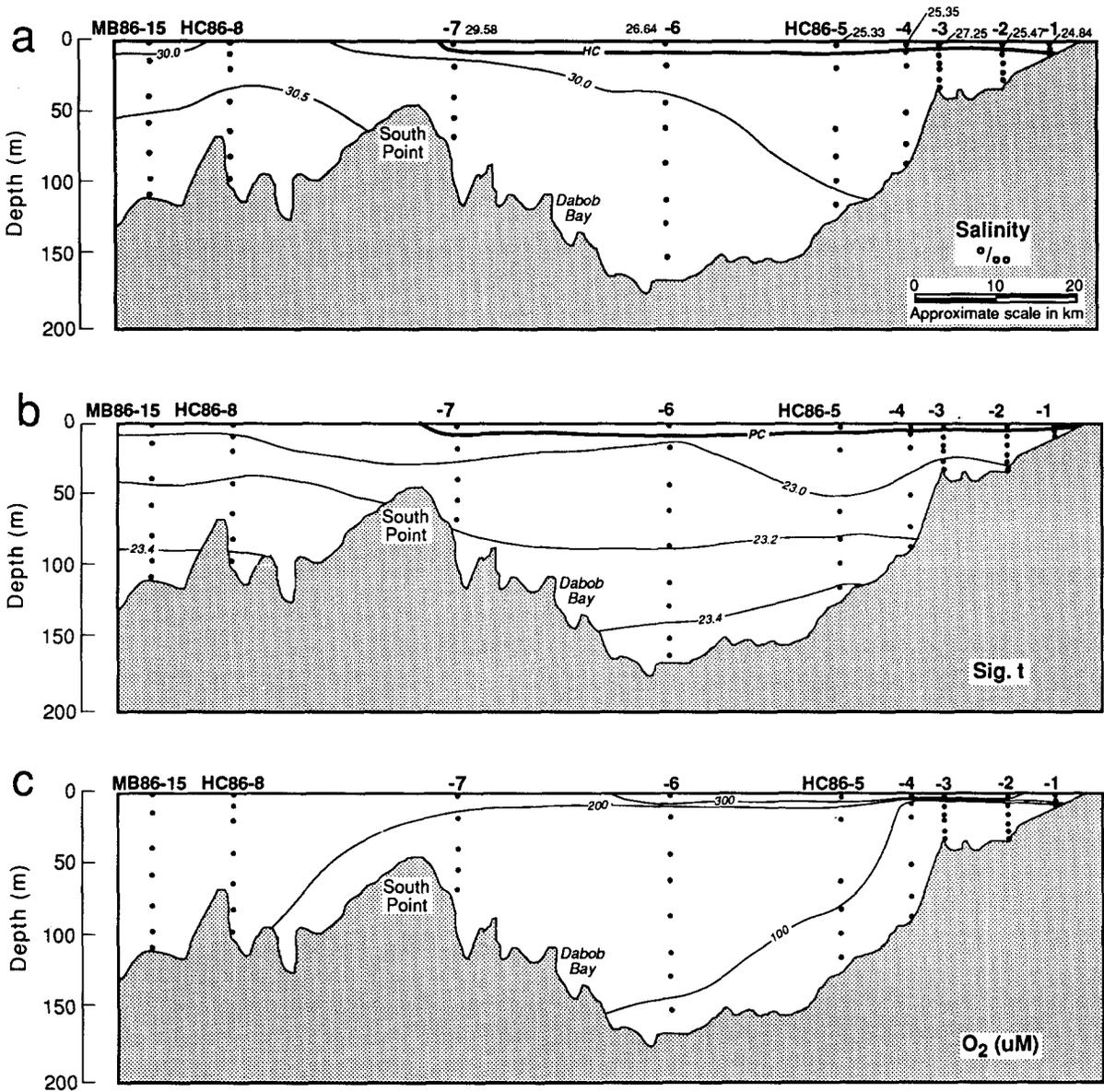


Fig. 2. Salinity (a), density (b), and dissolved oxygen (c) distributions in Hood Canal. Salinity of the surface sample is given by the station number. HC is the halocline between 25 and 27‰ for stations HC86-1 through HC86-6 (a) and PC is the pycnocline (b).

primary- and secondary-emission spectrometry using a Kevex Super 8000-770 X-ray energy spectrometer (Kevex, San Carlos, CA, USA) (Feely et al., 1986). The particulate Cu and Ni concentrations of some Hood Canal surface samples and the particulate Cd concentrations at HC86-5 were determined by graphite furnace atomic absorption spectrometry (GFAAS) following HCl-HNO₃-HF dissolution accord-

ing to Eggimann and Betzer (1976). The determinations Cu, Ni and Cd in the standard BCSS-1 were within the reported tolerance limits (S. Berman, personal communication, 1987).

Dissolved samples were collected in acid-cleaned, high-density polyethylene (HDPE) bottles after filtration through acid-cleaned 50 mm, 0.2 μm Nuclepore filters held in a SavillexTM (Savillex, Minnetonka, MA, USA)

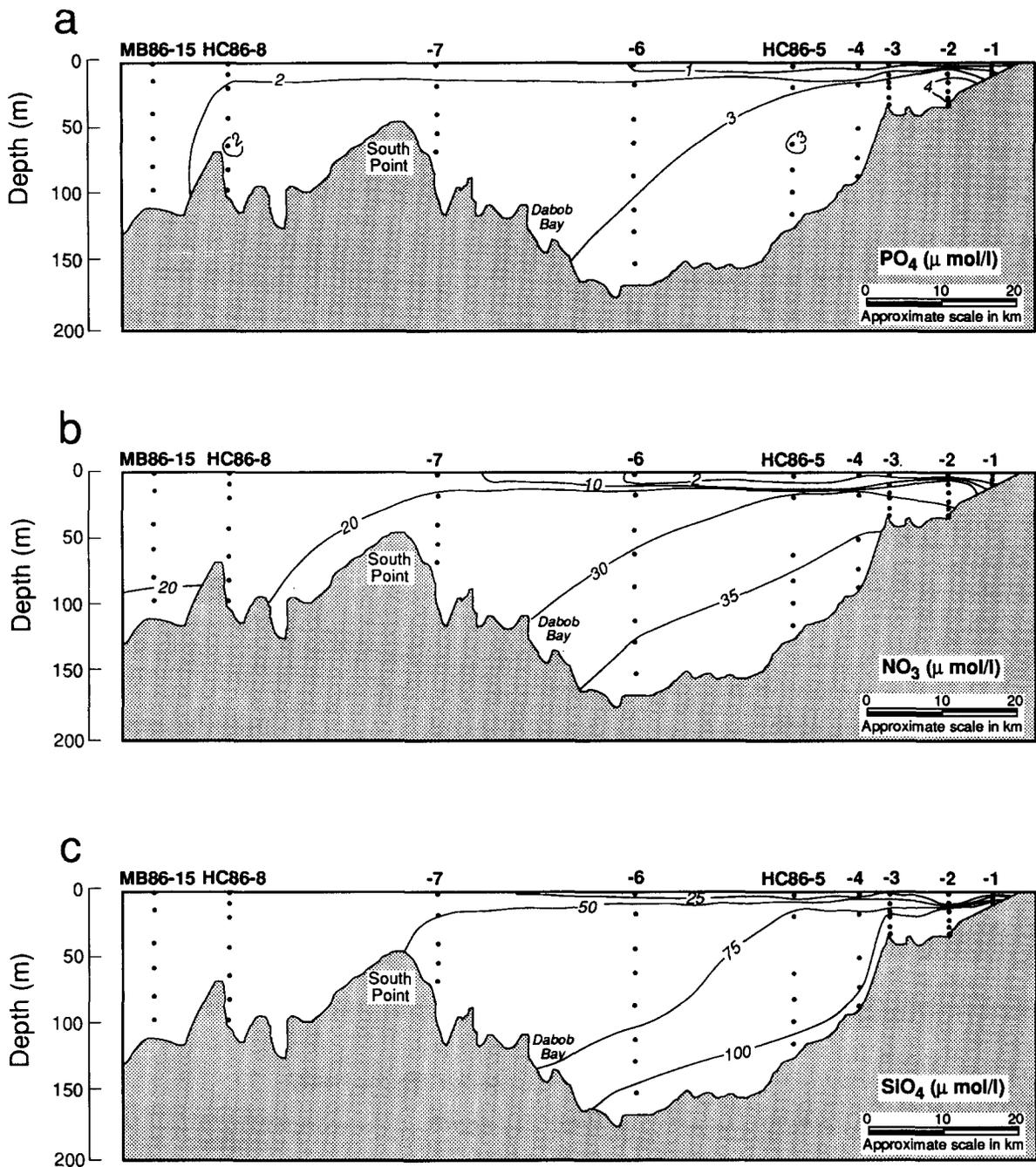


Fig. 3. Distribution of (a) nitrate, (b) phosphate and (c) silicate in Hood Canal.

filter holder and preserved with Seastar (Seastar Chemicals, Sidney, B.C., Canada) high-purity HNO_3 . Dissolved trace metals were analyzed by the GFAAS following preconcentration by the Chelex-100TM (Bio-rad, Richmond, CA, USA)

method of Paulson (1986). The determinations of Mn, Zn, Cd, Ni and Cu in the CASS-1 standard were within the tolerance ranges reported by the National Research Council of Canada (S. Berman, personal communication, 1985). The

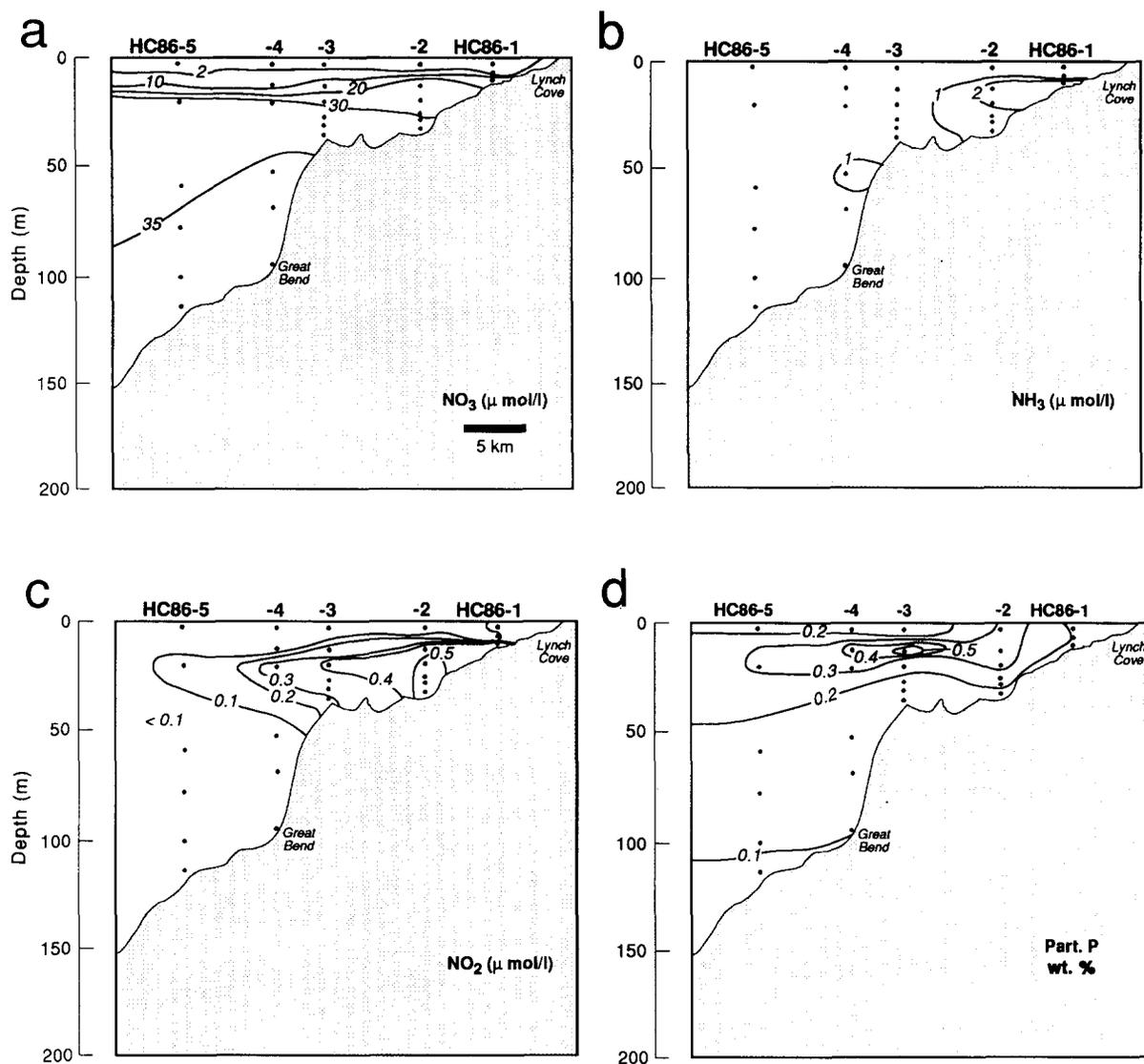


Fig. 4. Nitrate (a), ammonia (b), nitrite (c) and particulate phosphorous (d) between the Great Bend and Lynch Cove.

determination limits for Fe, Mn, Zn, Cd, Cu and Ni were 0.5 nmol, 0.5 nmol, 0.3 nmol, 0.02 nmol, 0.15 nmol and 0.15 nmol, respectively, based on three standard deviations of Q-H₂O filtered in the field (Fe, Mn, Zn and Cd) or based on instrumental detection limits (Cu and Ni). The QA/QC data and tabular results are given in Paulson et al. (1991). Preliminary interpretation of the nutrient and major element (Al, Fe and Mn) distributions are given in Curl and Paulson (1991) and Paulson and Curl (1991).

Results and discussion

Density and oxygen distributions

Water of highest density ($> 23.4\sigma_t$) lay well outside the sill and in the deepest portion of Hood Canal (Fig. 2(a)). The low-salinity surface water layer (25–29‰) extends to the sill (Fig. 2(b)) with a halocline and pycnocline at 10 m or less. Oxygen isopleths under the pycnocline deepen in the seaward direction

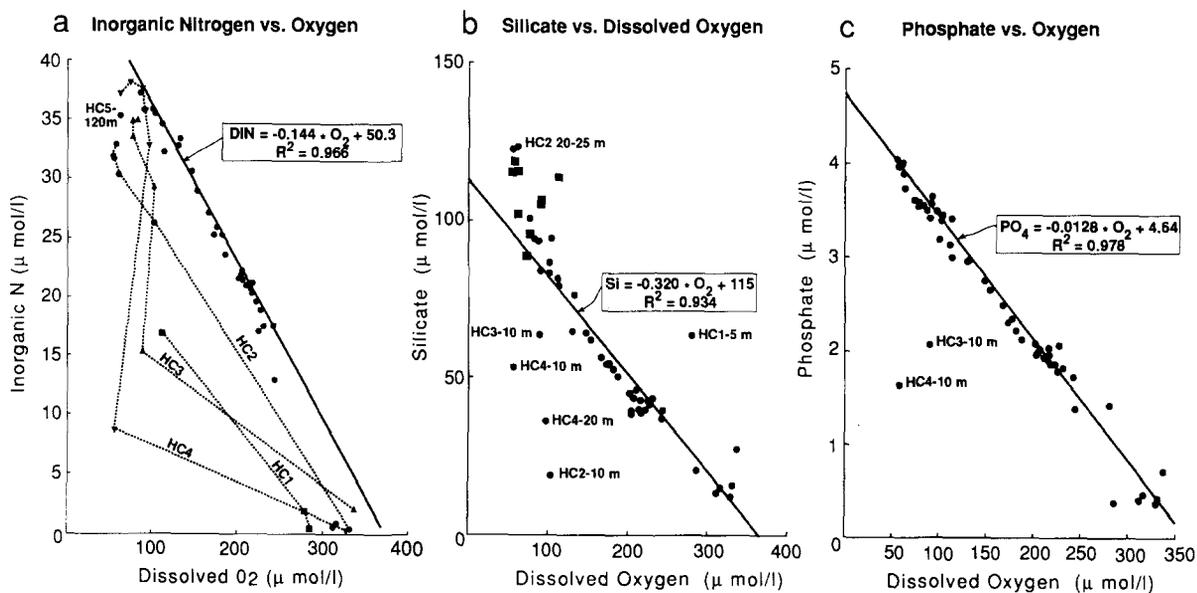


Fig. 5. Nutrient:oxygen relationship. (a) Inorganic nitrogen: samples from stations from Lynch Cove to the Great Bend (HC86-1 to -4) are connected by station and are not included in the regression. (b) Silicate: Lynch Cove (HC86-1&2) stations, near-bottom samples (shown as squares) and seven other identified samples taken from the base of the pycnocline are not included in the regression. (c) Phosphate: two samples taken from the base of the pycnocline are not included in the regression.

providing a horizontal oxygen gradient. This oxygen distribution is suggestive of a major depletion of oxygen during the summer, especially in Lynch Cove (Fig. 2(c)). The minimum values found in the bottom waters near the Great Bend and in Lynch Cove were 30% of saturation ($50 \mu\text{mol l}^{-1}$). The volume of hypoxic water found in 1986 was much greater than that seen in the past (Curl, unpublished data).

Nutrients

Nitrate, phosphate and silicate were depleted in the surface layer as far north as Dabob Bay indicating extensive biological productivity throughout this region (Fig. 3). Nitrate, phosphate and silicate concentrations as low as $0.06 \mu\text{mol l}^{-1}$, $0.38 \mu\text{mol l}^{-1}$ and $11.86 \mu\text{mol l}^{-1}$, respectively, were found at station HC86-4. The settling biological material was remineralized in the water column resulting in bottom water concentrations as high as $4 \mu\text{mol l}^{-1}$ PO_4 and $119 \mu\text{mol l}^{-1}$ SiO_4 at station HC86-2 (Figs. 3(a) and (c)) and $37 \mu\text{mol l}^{-1}$ NO_3 at HC86-4 (Fig. 4(a)). A maximum in NH_3

was found in Lynch Cove (Fig. 4(b)), indicative of early regeneration of settling particulate organic matter. From this locus, a broad tongue of nitrite-enriched water extending as far seaward as Hoodsport suggests seaward advection (Fig. 4(c)). High NH_3 , urea and amino acid concentrations have been found previously in the bottom waters of Lynch Cove in the summer of 1974 (H.C. Curl, unpublished data). These results suggest a sequence of events characteristic of the sedimentation of a recent large plankton bloom as follows: (1) sinking of nutrient-depleted cells (low nutrients in the surface layer, Iverson et al., 1974); (2) landward advection of organic debris and release of labile P (landward displacement of the bottom PO_4 maximum); (3) continued landward advection of organic matter and release of regenerated N (landward displacement of NH_3 maximum); (4) recent conversion of an advected plume of NH_3 to NO_2 (large volume of ephemeral NO_2) (Nixon, 1981); (5) upward mixing and seaward displacement of this NO_2 before its conversion to NO_3 was complete.

The relationships of the nutrients to dissolved

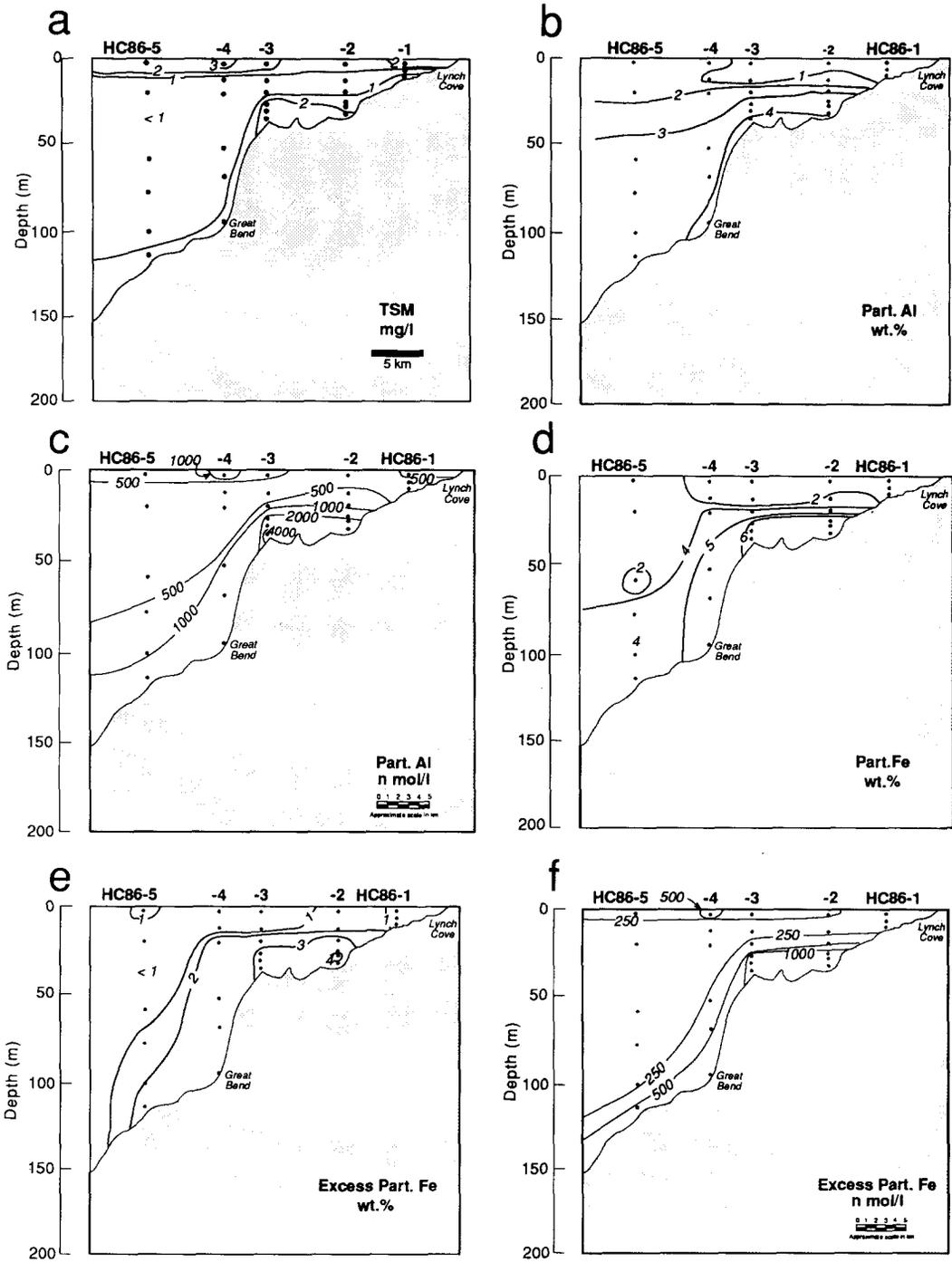


Fig. 6. Distributions of (a) total suspended matter, (b) particulate aluminum (wt. %), (c) particulate aluminum (nmol l^{-1}), (d) particulate Fe, (e) excess particulate Fe (wt. % calculated according to Eq. 1) and (f) excess particulate Fe (in nmol l^{-1} according to Eq. 2).

oxygen also reveal deviations from a simple scenario of biological uptake in the surface waters and regeneration of nutrients from settling organic matter at depth. From station HC86-5 seaward to Admiralty Inlet, dissolved inorganic nitrogen ($\text{NH}_3 + \text{NO}_2 + \text{NO}_3$) is inversely related to dissolved oxygen (Fig. 5(a)). However, from the Great Bend landward to Lynch Cove, dissolved inorganic nitrogen is depleted relative to that which is expected from apparent oxygen utilization. This depletion may be a result of nutrient-starved sinking algae replenishing their nutrient pools (De Manche et al., 1979) or denitrification by chemoautotrophs (Thayer, 1974; Newell, 1984). The phosphate concentrations were inversely related to dissolved oxygen throughout most of Hood Canal including Lynch Cove (Fig. 5(b)). The only deviations from this relationship are two samples depleted in phosphate that are located at the base of the pycnocline. The enrichment of particulate P in these and only these two samples (Fig. 4(d)) indicates an uptake of the regenerated P. This uptake could be a result of a chemical adsorption reaction (Callender, 1982; Day et al., 1989) or, alternatively, a non-photosynthetic biological uptake (De Manche et al., 1979).

Throughout much of Hood Canal, a linear relationship between dissolved oxygen and silicate exists (Fig. 5(b)), which suggests that biogenic opal is being dissolved simultaneous with organic matter remineralization. For samples from the shallow regions of Lynch Cove (HC86-1&2) and most samples within 15 m of the bottom, silicate concentrations were above the $\text{SiO}_4:\text{O}_2$ relationship observed for most of Hood Canal. The proximity of these enrichments to the sediments suggests diffusion of dissolved silicate out of the sediments. Like inorganic N and P, the silicate concentrations of several samples taken from the base of the pycnocline are depleted relative to the general $\text{SiO}_4:\text{O}_2$ relationship.

Total suspended matter and particulate Al

The total suspended matter (TSM) distribution exhibited maximum concentrations in the

surface layer from the Great Bend to Lynch Cove and near the bottom as the depth shallows to the east of the Great Bend (Fig. 6(a)). The Al concentrations of particles (in wt. %; Fig. 6(b)) were low compared with riverine sediments (Feely et al., 1986) and increased towards the bottom. The high TSM and low Al concentrations (in nmol l^{-1} ; Fig. 6(c)) in the surface waters were consistent with the high biological productivity inferred from the nutrient distributions. Likewise, the high TSM and high Al concentrations (Fig. 6(c)) found near the bottom were consistent with the resuspension of bottom sediments with a high aluminosilicate content. Thus, the regions of high TSM originate from two different processes: biological production of organic matter and biogenic silica in the surface layer and resuspension of bottom sediments in the bottom layer.

Iron and manganese

Dissolved Fe concentrations were highest in Lynch Cove ($\approx 30 \text{ nmol l}^{-1}$) and decreased seaward towards the main basin of Puget Sound ($<10 \text{ nmol l}^{-1}$). The dissolved Fe concentrations in Lynch Cove were low compared with anoxic waters in nearby Saanich Inlet ($1 \mu\text{mol}$; Emerson, 1979), which is consistent with the presence of greater than $50 \mu\text{mol}$ dissolved oxygen in bottom waters. Iron concentrations on particles (in wt. %; Fig. 6(d)) were low at the surface compared with Skokomish River suspended matter and increased towards the bottom. Since most particulate Fe in estuaries is associated with aluminosilicates, some of the increases in Fe concentrations near the bottom were probably a result of the increasing aluminosilicate content of the particles (Fig. 6(c)). In order to deconvolute a geochemical signal from changes in particulate bulk composition, a parameter called excess particulate metal was calculated according to the following

$$\{\text{Ex.Part.X}\} = \{\text{Part.X}\} - [\text{X/Al}]\{\text{Part.Al}\} \quad (1)$$

Table 1
Metal concentrations and metal/Al ratios for Skokomish River suspended matter

Metal	Skokomish River suspended matter concentration	Metal/Al ratio (wt./wt.)
Al	4.67 wt. %	
Fe	3.83 wt. %	0.82
Mn	654‰	1.4×10^{-3}
Zn	132‰	2.8×10^{-3}
Cd	1.9‰	3.9×10^{-5}
Cu	52‰	1.1×10^{-3}
Ni	32‰	0.85×10^{-3}

where { } is the particulate or excess particulate concentration of the metal X in the suspended matter (weight of X/weight of suspended sediment) of metal X and X/Al is the metal X to Al (weight/weight) ratio of Skokomish River

suspended matter (Table 1). Excess particulate Fe would represent the Fe oxyhydroxide fraction of the particulate Fe. Excess particulate Fe exhibited a near-bottom maximum in the embayment east of the Great Bend (Fig. 6(e)) in the same vicinity as the TSM maximum. Likewise, the excess particulate metal concentration, [Ex. Part. X], in the water column (in nmol l^{-1}) can be calculated by

$$[\text{Ex. Part. X}] = \text{TSM}\{\text{Ex. Part. X}\}/\text{AW} \quad (2)$$

where AW is the atomic weight of the metal X. Since the concentrations of excess particulate Fe (in nmol l^{-1}) increased in the high TSM region as the sediment bottom was approached (Fig. 6(f)), the primary source of excess particulate Fe was probably resuspended bottom sediment enriched in Fe. It is unlikely that the $> 1000 \text{ nmol l}^{-1}$ of

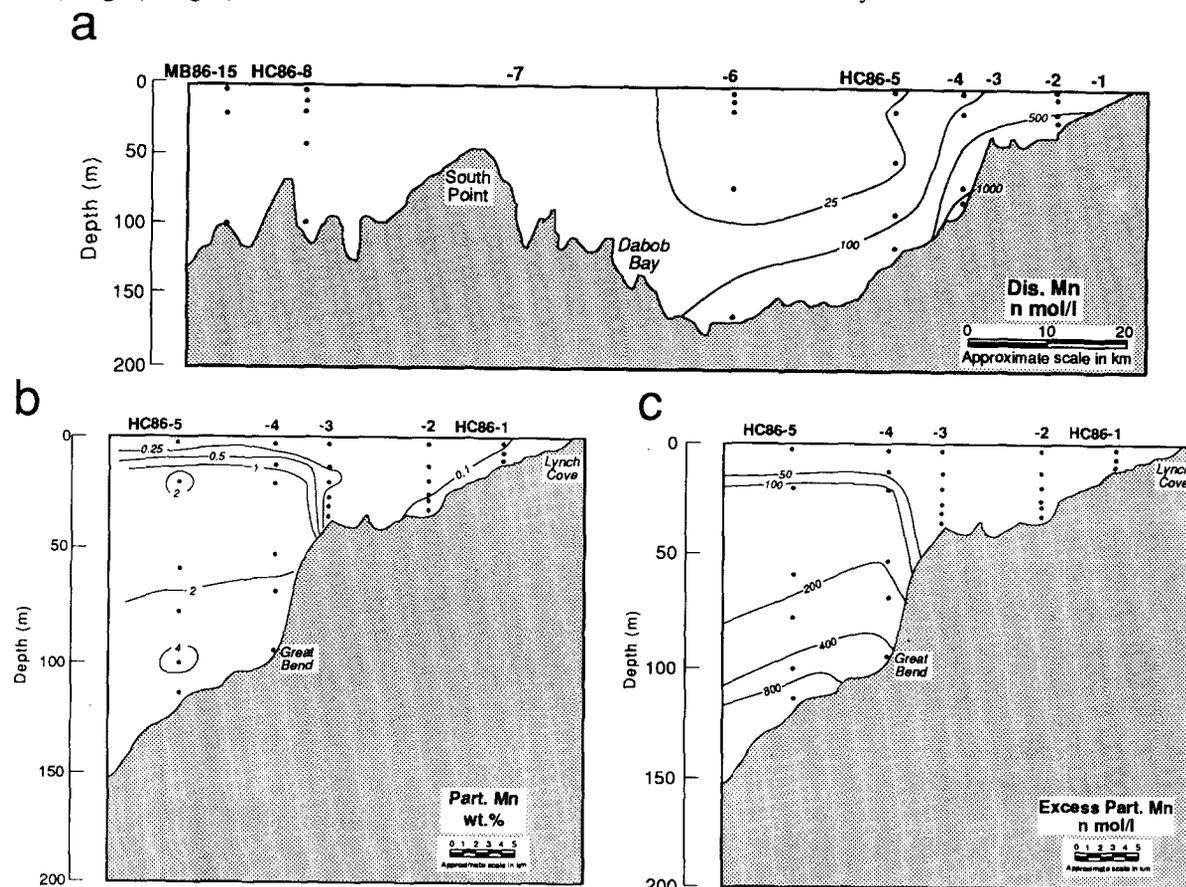


Fig. 7. Distributions of (a) dissolved Mn in Hood Canal and (b) particulate Mn from the Great Bend to Lynch Cove (in micrograms of Mn per gram of suspended sediment); (c) excess particulate Mn (in nanomoles per liter according to Eq. 2).

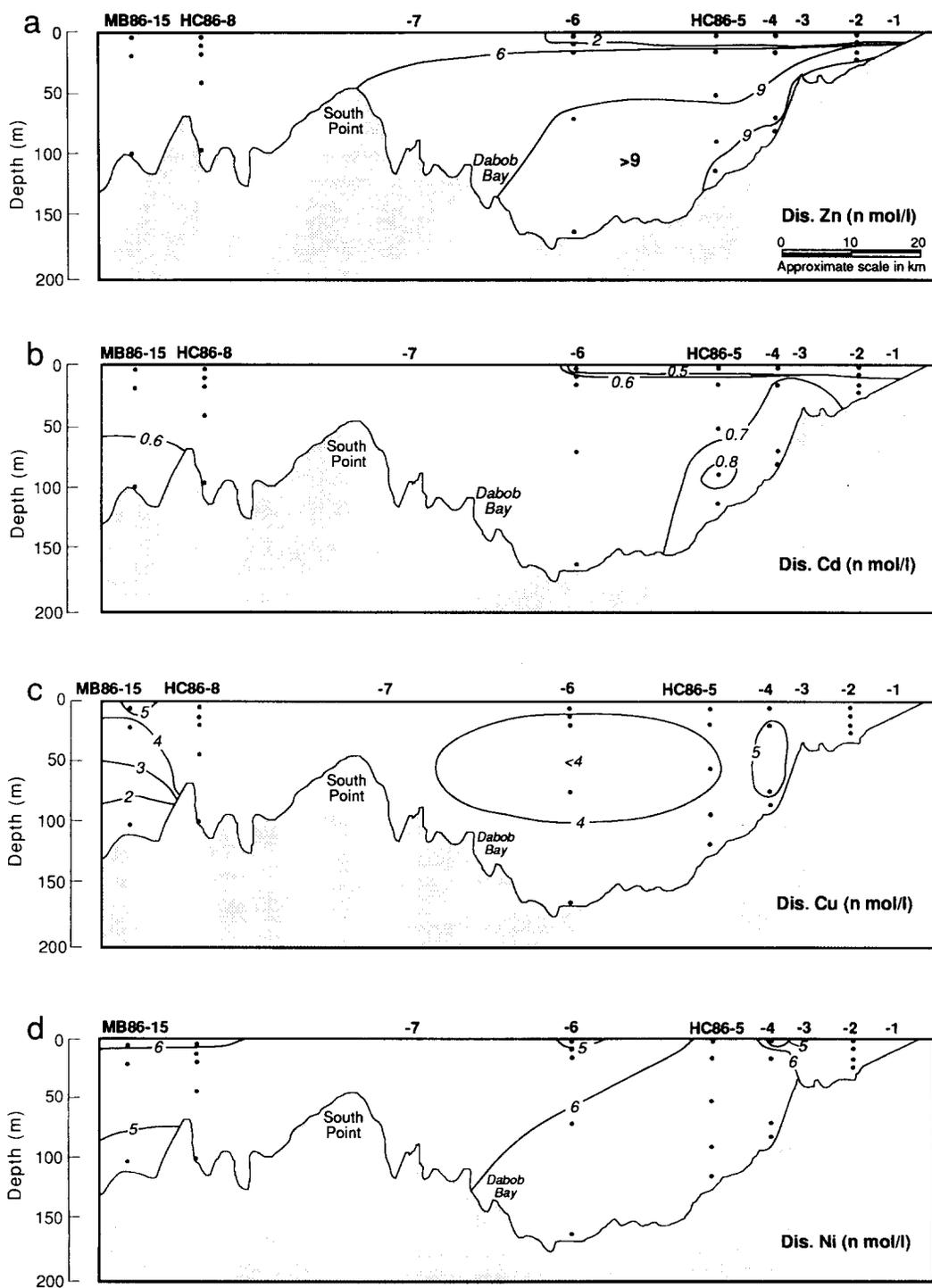


Fig. 8. Distributions of dissolved Zn in units of nmol l^{-1} (a), Cd (b), Cu (c), and Ni (d) in Hood Canal.

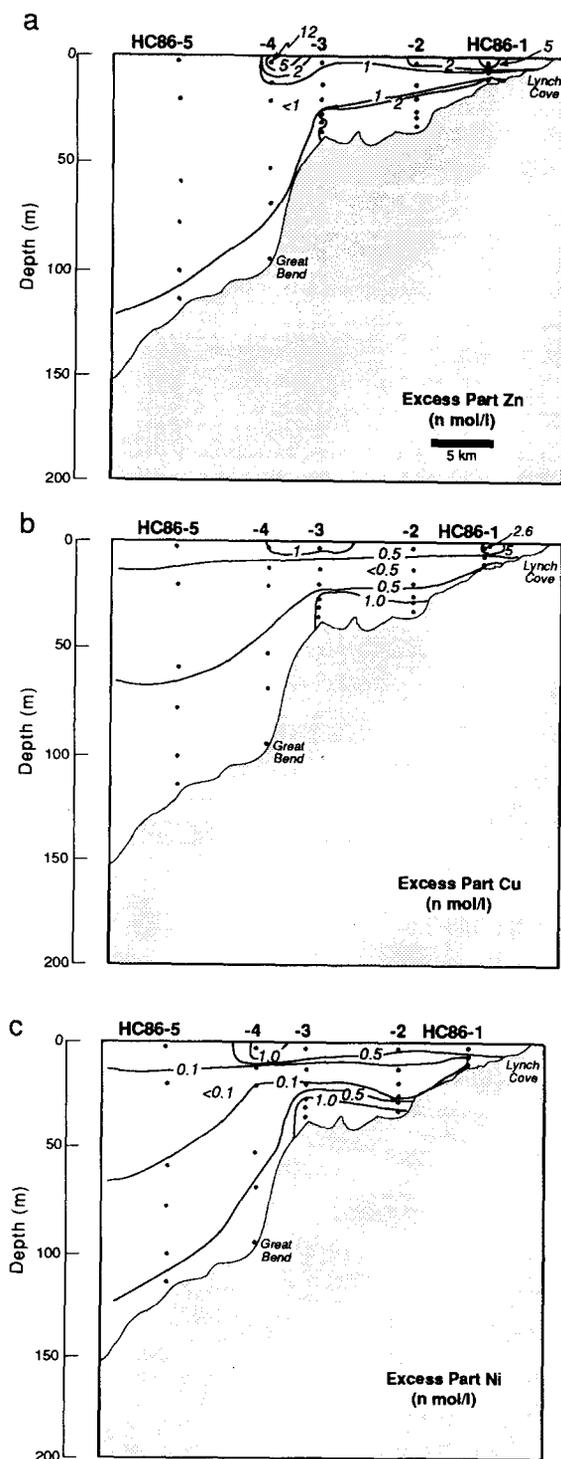


Fig. 9. Distributions of excess particulate Zn in units of nmol l^{-1} (a), Cu (b), and Ni (c) calculated according to Eq. 2.

excess particulate Fe could be derived from in situ precipitation of a standing stock of 30 nmol l^{-1} dissolved Fe. Rather, solid phase Fe, formed from the precipitation of interstitial dissolved Fe, would concentrate in the very surface of the sediments ($<1 \text{ cm}$) due to the probable shallow penetration of oxygen into the sediments, surmised from the low oxygen concentrations in the overlying waters ($\approx 50 \text{ mmol l}^{-1}$). The Puget Sound Ambient Monitoring Program (Tetra-Tech, 1990) observed high surficial Fe concentrations at a station in the Great Bend. Thus, the resuspension of these Fe-rich surficial sediments leads to the high concentrations of excess Fe in the water column observed during our sampling.

Throughout the Great Bend and Lynch Cove areas, dissolved Mn concentrations were greater than 100 nmol l^{-1} (Fig. 7(a)). Very high dissolved Mn concentrations (1000 nmol l^{-1}) were found in the near-bottom waters of the Great Bend. Throughout Lynch Cove (Fig. 7(b)), Mn concentrations on the particulates were low. In the bottom waters of Lynch Cove, the average excess particulate Mn concentration was 20 nmol l^{-1} (Fig. 7(c)). In the Great Bend (the area of the horizontal oxygen gradient), bottom water Mn concentrations on particles increased by 40-fold and excess particulate Mn concentrations ranged between 200 and 850 nmol l^{-1} . These observations were consistent with: (1) the solubilization of particulate Mn in the water or sediment columns of Lynch Cove to the dissolved Mn^{2+} form; (2) diffusion or advection of this dissolved Mn; (3) oxidation/precipitation of this Mn^{2+} in the Great Bend region.

Trace metals

The distributions of several of the trace metals studied seemed to be controlled by biological uptake and bottom water remobilization. Like the nutrients, dissolved Zn was depleted in the surface and was enriched at middepth (Fig. 8(a)). The middepth decrease of excess particulate Zn (in excess of that attributable to aluminosilicates

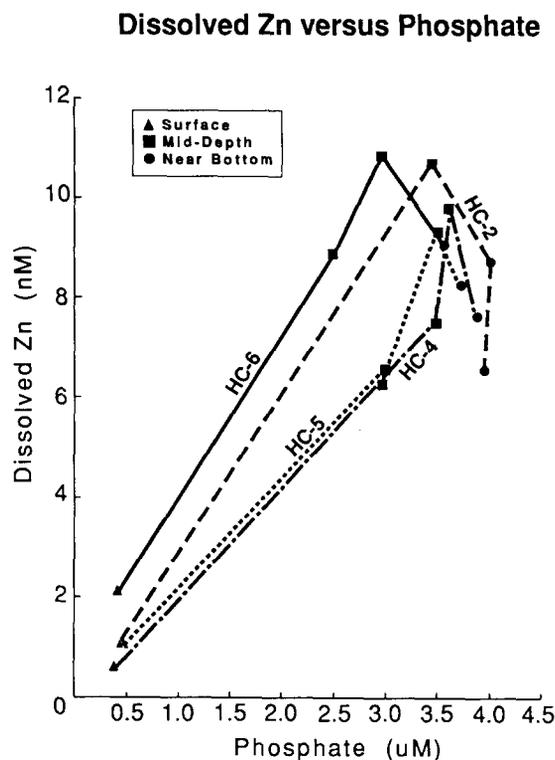


Fig. 10. Dissolved Zn vs. phosphate

according to Eq. 2, Fig. 9(a)) suggests that decomposition of biological material was responsible for the increase of dissolved Zn at middepth. The control of Zn cycling by biological processes has been observed in the oceans and has been correlated with silicate cycling uptake and regeneration (Bruland, 1980; Bruland and Franks, 1983). In estuaries, Zn removal seems only to be observed when nutrients are removed to a significant degree by bio-

logical processes (Church, 1986; Hunter and Tyler, 1987). The near simultaneous decomposition of hard silicate parts and soft organic matter allows us to use phosphate as a parameter that reflects regeneration of both hard and soft biological matter. Dissolved Zn increased with increasing phosphate concentrations at middepth (Fig. 10), which is consistent with biological control of dissolved Zn at the surface and at middepth. However, all near-bottom samples were depleted in dissolved Zn relative to their phosphate concentrations. The near-bottom increases in excess particulate Zn indicate that the regenerated dissolved Zn was adsorbed on to some particulate phase other than biological detritus. The similarity between the excess particulate Zn (Fig. 9(a)) and excess particulate Fe (Fig. 6(f)) distributions suggests that the Zn-adsorbing particulate phase was the Fe oxyhydroxide of the resuspended sediments. The regression of excess particulate Zn vs. excess particulate Fe yields a significant slope of 1.58 Zn per 1000 Fe ($P < 0.05$, Table 2). In contrast, little excess particulate Mn (20 nmol l^{-1} , Fig. 7(c)) was found in the region of high excess particulate Zn. Zinc removal by particulate Fe is also thought to control Zn distributions in the Medway and Maeklong estuaries (Windom et al., 1991).

The distribution of Cd was also affected by biological processes, albeit not to the extent observed for Zn. Dissolved Cd concentrations were low in the surface waters indicating biological uptake (Fig. 8(b)). The middepth increases in dissolved Cd were not as large as those for Zn.

Table 2
Excess particulate metal vs. excess particulate Fe correlations

Metal	Slope	Sign. level	Intercept (nmol l^{-1})	Regression coefficient <i>R</i>
Zn	$1.58 \pm 0.52 \times 10^{-3}$	($P = 0.012$)	0.35	0.67
Cu	$0.59 \pm 0.17 \times 10^{-3}$	($P < 0.01$)	± 0.47 0.17	0.70
Ni	$1.52 \pm 0.27 \times 10^{-3}$	($P < 0.01$)	± 0.17 0.16 ± 0.25	0.85

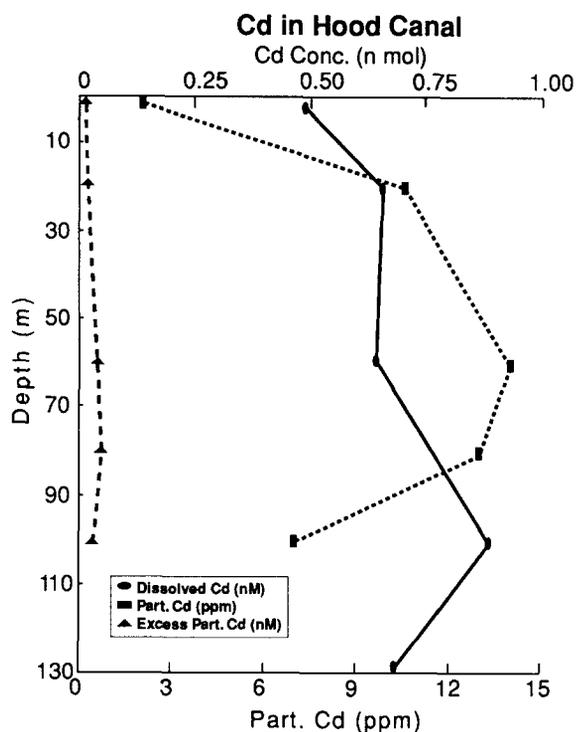


Fig. 11. Cadmium distributions vs. depth at HC86-5. Dissolved Cd in nmol l^{-1} (\bullet — \bullet), particulate Cd in micrograms of Cadmium per gram of suspended matter (ppm) (\blacksquare — \blacksquare); particulate Cd in nmol l^{-1} (\blacktriangle — \blacktriangle) calculated from excess particulate Cd according to Eq. 2.

The middepth dissolved Cd concentrations were depleted relative to the Cd:PO₄ relationship observed in the oceans (Bruland, 1980). At the station with the highest middepth dissolved Cd concentration (HC86-5), Cd concentrations on the particles (in micrograms of Cd per gram of suspended matter) increased with depth (Fig. 11). Near the bottom, Cd-depleted resuspended bottom sediments became a significant fraction of the suspended matter population. To account for this dilution by Cd-depleted resuspended bottom sediment, excess particulate Cd (in units of nmoles of excess particulate Cd per liter) was calculated according to Eq. 2. Excess particulate Cd (triangles in Fig. 11) increases throughout most of the water column, indicating that some of the regenerated Cd was being adsorbed. In nearby Lake Washington (Murray, 1987), the adsorption of the regenerated Cd on to

the more abundant population of particles present in lakes was also suggested as a partial explanation of the lower Cd:PO₄ ratios relative to those of oceanic profiles.

Unlike Zn and Cd, little or no depletion of dissolved Cu and Ni was observed in the surface waters (Figs. 8(b) and (c)). The contrasting biogeochemistry of Cu and Ni relative to that of Cd is consistent with seasonal distributions of these metals in east Atlantic surface waters (Kremling and Pohl, 1987). In June when nutrients were depleted, dissolved Cd was depleted in Atlantic surface waters relative to that found in March, when nutrient concentrations were high. However, no depletion of dissolved Cu and Ni was observed. In mesocosm experiments, Slauenwhite and Wangersky (1991) found that dissolved Cd concentrations decreased dramatically after biomass peaked while little dissolved Cu was lost. The contrasting biogeochemical behavior of Cu and Cd is probably related to their tendency to complex with dissolved organic matter. Marine organisms excrete dissolved organic ligands that complex Cu (McKnight and Morel, 1979, 1980; Zhou and Wangersky, 1985; Schreiber et al., 1990). The complexation of Cu by such excreted dissolved organic ligands has been shown to contribute to the low affinity of dissolved Cu for marine particulate matter in laboratory experiments (Paulson, 1991). In contrast, little Cd was found to complex with dissolved organic matter (Slauenwhite and Wangersky, 1991). Although there were only small variations in the distribution of dissolved Cu and Ni in Hood Canal, these small variations coupled with our understanding of the circulation in Hood Canal suggest that geochemical reactions involving Cu and Ni were occurring in the Hood Canal. Maximums in excess particulate Cu and Ni attributable to biological growth were observed in the surface water (Figs. 9(b) and (c)). However, the magnitude of the maximums in excess particulate Cu and Ni were only 20% and 10%, respectively, of the Zn maximum. Copper and Ni also seem to be have been scavenged by Fe oxyhydroxides in

Lynch Cove. The bottom water Cu and Ni concentrations in Lynch Cove (HC86-2; 4.5 nmol Cu l⁻¹ and 5.5 nmol Ni l⁻¹) were lower than its source water in the bottom waters of the Great Bend area (HC86-4; 5.3 nmol Cu l⁻¹ and 6.2 nmol Ni l⁻¹), indicating loss from the dissolved phase. The maximums of excess particulate Cu and Ni in the bottom waters of Lynch Cove (Figs. 9(b) and (c)) and the significant correlation of excess particulate Cu and Ni vs. excess particulate Fe ($P < 0.01$, Table 2) suggest that the decreases in dissolved Cu and Ni in Lynch Cove were a result of scavenging by Fe oxyhydroxides.

Conclusions

The southern end of Hood Canal is a highly biologically productive region. The oxidation of settling organic matter leads to large areas of hypoxic waters. The hypoxic waters are enriched in nutrients. However, deviations from a linear nutrient:oxygen inverse relationship were observed and attributed to: (1) chemical adsorption; (2) replenishment of nutrient pools of sinking nutrient-deprived algae; (3) denitrification. The Fe concentrations of suspended particulates in Hood Canal are controlled by their aluminosilicate content and the resuspension of Fe-rich sediments formed from the redistribution of Fe within the sediment column. In contrast, dissolved Mn enters the water column in Hood Canal and is oxidized and incorporated into particulate matter near the Great Bend. Biological growth and decay processes control dissolved Zn throughout much of the water column. In near-bottom waters, Zn adsorbs on to resuspended sediments enriched in Fe oxyhydroxide. Cd is also depleted in surface waters and the regenerated Cd is adsorbed on to particles throughout the water column. Although the distributions of dissolved Cu and Ni exhibit only small variations, particulate distributions indicate biological uptake in the surface and near-bottom geochemical scavenging.

Acknowledgments

The authors wish to thank the crew and officers of the NOAA Ship 'Miller Freeman' and Sharon Walker, Marilyn Lamb, Terri Geiselman, James Gendron and Scott Burger of Pacific Marine Environmental Laboratory (PMEL) for sampling assistance. Steve Kelly of PMEL performed the oxygen analysis and Kathy Krogslund of the Department of Oceanography, University of Washington analyzed the nutrients. Karen Conlan prepared the figures. This study was supported by the National Oceanic and Atmospheric Administration.

References

- Baker, E.T., 1984. Patterns of suspended particle distribution and transport in a large fjordlike estuary. *J. Geophys. Res.*, 89(C4): 6553–6566.
- Barlow, J., 1958. Spring changes in phytoplankton abundance in a deep estuary, Hood Canal, Washington. *J. Mar. Res.*, 17: 53–57.
- Boyle, E.A., Edmond, J.M. and Sholkovitz, E.R., 1977a. The mechanism of iron removal in estuaries. *Geochim. Cosmochim. Acta*, 41: 1313–1324.
- Boyle, E.A., Sclater, F.R. and Edmond, J.M., 1977b. The distribution of dissolved Cu in the Pacific. *Earth Planet. Sci. Lett.*, 37: 38–54.
- Bruland, K.W., 1980. Oceanographic distributions of cadmium, zinc, nickel, and copper in the North Pacific. *Earth Planet. Sci. Lett.*, 47: 176–198.
- Bruland, K.W. and Franks, R.P., 1983. Mn, Ni, Cu, Zn, and Cd in the Western North Atlantic. In: C.S. Wong, E.A. Boyle, K.W. Bruland, J. Burton and E.D. Goldberg (Editors), *Trace Metals in Seawater*, NATO Marine Science Series No. 9. Plenum, New York, pp. 395–414.
- Burton, J.D. and Liss, P.S., 1976. *Estuarine Chemistry*. Academic, New York, 229 pp.
- Callender, E., 1982. Benthic phosphorous regeneration in the Potomac River Estuary. In: P.G. Sly (Editor), *Proc. 2nd Int. Symp. on Sediment/Fresh Water Interactions*, Kingston, Ontario, 15–18 June 1981. Junk, The Hague, pp. 431–446.
- Cannon, G.A., Holbrook, J.R. and Pashinski, D.J., 1990. Variations in the onset of bottom-water intrusions over the entrance sill of a fjord. *Estuaries*, 13(1): 31–42.
- Church, T.M., 1986. Biogeochemical factors influencing the residence time of micronutrients in a large tidal estuary, Delaware Bay. *Mar. Chem.*, 18: 393–406.
- Cokelet, E.D., Stewart, R.J. and Ebbesmeyer, C.C., 1990. The annual mean transport in Puget Sound. NOAA

- Tech. Memo. ERL PMEL-92, Pacific Marine Environmental Laboratory, Seattle, WA, 59 pp.
- Cox, J.M., Ebbesmeyer, C.C., Cannon, G.A. and Barnes, C.A., 1984. Synthesis of current measurements in Puget Sound, Washington, Vol. 1, Index to current measurements made in Puget Sound from 1908–1980, with daily record averages for selected measurements. NOAA Tech. Memo. NOS OMS 3, Rockville, MD, 38 pp.
- Curl, Jr., H.C. and Paulson, A.J., 1991. The biogeochemistry of oxygen and nutrients in Hood Canal. In: Proc. of Puget Sound Research '91, Vol. 1. Puget Sound Water Quality Authority, Seattle, WA, pp. 109–115.
- Day, Jr., J.W., Hall, C.A.S., Kemp, W.M. and Yanez-Arancibia, A., 1989. Estuarine Ecology. J. Wiley and Sons, New York, p.116.
- De Manche, J.M., Curl, Jr., H., Lundy, D.W. and Donaghey, P.L., 1979. The rapid response of the marine diatom *Skeletonema costatum* to changes in external and internal nutrient concentrations. Mar. Biol., 53: 2323–2333.
- Eggemann, D.W. and Betzer, P.R., 1976. Decomposition and analysis of refractory oceanic suspended materials. Anal. Chem., 48: 886–890.
- Emerson, S., 1979. Redox species in a reducing fjord: The oxidation rate of manganese II. In: H.J. Freeland, D.M. Farmer and C.D. Levings (Editors), Fjord Oceanography Trace Metals in Seawater, NATO Marine Science Series No. 4. Plenum, New York, pp. 681–688.
- Feely, R.A., Massoth, G.J. and Lamb, R.F., 1983. The effects of sewage effluents on the flocculation of major and trace elements in a stratified estuary. In: C.S. Wong, E.A. Boyle, K.W. Bruland, J. Burton and E.D. Goldberg (Editors), Trace Metals in Seawater, NATO Marine Science Series No. 9. Plenum, New York, pp. 227–244.
- Feely, R.A., Massoth, G.J., Baker, E.T., Gendron, J.F., Paulson, A.J. and Crecelius, E.A., 1986. Seasonal and vertical variations in the elemental composition of suspended and settling particulate matter in Puget Sound, Washington. Estuarine Coastal Shelf Sci., 22: 215–239.
- Guan, D.M., Elbaz-Poulichet, F. and Martin, J.-M. 1991. Low reactivity of trace elements in stratified estuaries: Example of the Rhone River Delta (France). Presented at the Second Int. Symp. on the Biogeochemistry of Model Estuaries: Estuarine Processes in Global Change, 14–20 April 1991, Jekyll Island, Georgia, USA.
- Hunter, K.A. and Tyler, S.R., 1987. The distribution of zinc and reactive silicate in the Otago Harbour, New Zealand. Mar. Chem., 20: 377–387.
- Iverson, R.L., Curl, Jr., H.C. and Saugen, J.L., 1974. Simulation model for wind-driven summer phytoplankton dynamics in Auke Bay, Alaska. Mar. Biol., 28: 169–177.
- Kamatani, A. and Takano, M., 1984. The behaviour of dissolved silica during the mixing of river and sea waters in Tokyo Bay. Estuarine Coastal Shelf Sci., 19: 505–512.
- Kremling, K. and Pohl, C., 1987. Studies on the spatial and seasonal variability of dissolved cadmium, copper and nickel in Northeast Atlantic surface waters. Mar. Chem., 27: 43–60.
- McKnight, D.M. and Morel, F.M.M., 1979. Release of weak and strong copper-complexing agents by algae. Limnol. Oceanogr., 24: 823–837.
- McKnight, D.M. and Morel, F.M.M., 1980. Copper complexation by siderophores from filamentous blue-green algae. Limnol. Oceanogr., 25: 62–71.
- Murray, J.W., 1987. Mechanisms controlling the distribution of trace elements in oceans and lakes. In: R.A. Hites and S.J. Eisenreich (Editors), Sources and Fate of Aquatic Pollutants. American Chemical Society, Washington, DC, pp. 153–184.
- Newell, S.Y., 1984. Bacterial and fungal productivity in the marine environment: A contrastive overview. In: 1st Int. Colloquium on Marine Bacteriology. Colloq. Int. Cent. Natl. Rech. Sci., 331: 133–139.
- Nixon, S.W., 1981. Remineralization and nutrient cycling in coastal marine ecosystems. In: B.J. Neilson and L.E. Cronin (Editors), Estuaries and Nutrients. Humana, Clifton, NJ, pp. 111–138.
- Paulson, A.J., 1986. Effects of flow rate and pre-treatment on the analyses of trace metals in estuarine and coastal seawater by Chelex-100. Anal. Chem., 58: 183–187.
- Paulson, A.J., 1991. Cu interactions between dissolved and particulate organic matter in estuarine waters. Ph.D. Dissertation, University of Washington, Seattle, WA, 252 pp.
- Paulson, A.J. and Curl, Jr., H.C., 1991. The biogeochemistry of trace metals in Hood Canal. In: Proc. of Puget Sound Research '91, Vol. 1. Puget Sound Water Quality Authority, Seattle, WA, pp. 116–122.
- Paulson, A.J., Feely, R.A., Curl, Jr., H.C., Crecelius, E.A. and Geiselman, T., 1988. The impact of scavenging on trace metal budgets in Puget Sound. Geochim. Cosmochim. Acta, 52: 1765–1779.
- Paulson, A.J., Feely, R.A., Curl, Jr., H.C. and Tennant, D.A., 1989. Estuarine transport of trace metals in a buoyant river plume. Estuarine Coastal Shelf Sci., 28: 231–248.
- Paulson, A.J., Curl, Jr., H.C., Feely, R.A., Krogslund, K.A. and Hanson, S., 1991. Trace Metal and Ancillary Data in Puget Sound: August 1986. NOAA Data Report ERL PMEL-32, Pacific Marine Environmental Laboratory, Seattle, WA (NTIS No. PB91-201590), 35pp.
- Peterson, D.H., 1979. Sources and sinks of biologically reactive oxygen, carbon, nitrogen, and silica in northern San Francisco Bay. In: T.J. Conomos (Editor), San Francisco Bay: The Urbanized Estuary. Amer. Assoc. Adv. Sci., San Francisco, CA, pp. 175–193.
- Schreiber, D.R., Millero, F.J. and Gordon, A.S., 1990. Production of an extracellular copper-binding compound by the heterotrophic marine bacterium *Vibrio alginolyticus*. Mar. Chem., 28: 275–284.

- Sharp, J.H., Culbertson, C.H. and Church, T.M., 1982. The chemistry of the Delaware Estuary. General considerations. *Limnol. Oceanogr.*, 27: 1015–1028.
- Sholkovitz, E.R. and Copland, D., 1981. The coagulation, solubility and adsorption properties of Fe, Mn, Cu, Ni, Cd, Co and humic acids in river water. *Geochim. Cosmochim. Acta*, 45: 181–189.
- Slauenwhite, D.E. and Wangersky, P.J., 1991. Behaviour of copper and cadmium during a phytoplankton bloom: a mesocosm experiment. *Mar. Chem.*, 32: 37–50.
- Tetra-Tech, 1990. Marine Sediment Monitoring: Final Report to the Washington Department of Ecology, Bellevue, WA, 255 pp.
- Thayer, G.W., 1974. Identity and regulation of nutrient limiting phytoplankton in the shallow estuaries near Beaufort, N.C. *Oecologia (Berlin)*, 14: 75–92.
- Whitledge, T.E., Malloy, S.C., Patton, C.J. and Wirick, C.D., 1981. Automated Nutrient Analyses in Seawater. Department of Energy and Environment (DE-ACO2-76H00016), Springfield, VA.
- Windom, H., Byrd, J., Smith, Jr., R., Hungprugs, M., Dharmvanij, S., Thumtrakul, W. and Yeats, P., 1991. Trace metal–nutrient relationships in estuaries. *Mar. Chem.*, 32: 177–194.
- Zhou, X. and Wangersky, P.J., 1985. Copper complexing capacity in cultures of *Phaeodactylum Tricornutum*: Diurnal changes. *Mar. Chem.*, 17: 301–312.