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Distributions of dissolved manganese and fluorescent dissolved organic matter in the Columbia River estuary and plume as determined by in situ measurement

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Abstract

We deployed an instrument package consisting of a SeaBird 911 plus CTD, SeaTech 25-cm transmissometer, Chelsea AquaTracka fluorometer/nephelometer, Seapoint turbidity meter and ZAPS UV fluorometer/chemical sensor during a series of tows and lowerings within the Columbia River plume and estuary in 1994 and 1995. Simultaneous in situ measurements of Chl *a*, light attenuation, light scattering, and fluorescent dissolved organic matter (FDOM) or dissolved Mn collected along with CTD information provided new insight into the effects of mixing and non-conservative processes on riverine input to the coastal ocean.

Inter-relationships among these parameters proved to be effective at delineating three coastal water masses: Columbia River Plume Water (CRPW), Shelf Deep Water (SDW), and Shelf Bottom Water (SBW). CRPW had variable amounts of FDOM, dissolved Mn, and Chl *a* as the plume mixed with coastal water. SBW was characterized by high concentrations of Chl *a* and low concentrations of dissolved Mn, suggesting a surface or near-surface source. The properties of SDW were intermediate between humic-rich plume water and turbid bottom water.

FDOM displayed a quasi-linear and inverse relationship with salinity inside the estuary and nearshore coastal plume which supports previous work relating this parameter to the humic-rich terrestrial component of dissolved organic matter (DOM). There was, however, considerable evidence of lower FDOM levels within the estuarine turbidity maximum (ETM) and near the seaward boundary of the plume. There were also elevated levels of FDOM near the bottom at some locations on the shelf, suggesting that there may be a significant benthic flux of this material. Thus FDOM appears to be more reactive than previously thought when looked at in detail.

Dissolved Mn also displayed non-conservative behavior in the estuary and across the plume showing significant input into surface waters. The sharpest Mn gradient on the shelf occurred near the seaward edge of the plume in an area of relatively high turbidity and Chl *a*, and relatively low FDOM. These distributions are consistent with the presence of a chemical front near the plume boundary where Mn-oxides are reduced during the oxidation of humic ligands. This process would release dissolved Mn and promote productivity in the turbid zone associated with the leading edge of the plume jet. This study demonstrates that chemical sensors can provide highly resolved, detailed information on trace substance distribution and variability in marine environments.

Keywords: manganese; fluorescence; dissolved organic matter

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1. Introduction

Turekian (1971, 1977) was one of the first to point out the importance of estuaries in modifying the riverine flux to the oceans. Shifts in pH and ionic strength in estuaries alter the adsorption characteristics of riverine particles while redox changes create new surfaces for scavenging, precipitation, and flocculation. These biogeochemical alterations rearrange the physical partitioning of elements between the solid and dissolved states which in turn affects what happens to this material once it mixes with coastal water. One of the most mobile elements in such environments is Mn (Graham et al., 1976; Morris et al., 1982; Moffett, 1994) which tends to exist as oxide coatings unless acted upon by photoreduction (Sunda and Huntsman, 1994) or microbial activity, most notably during the degradation of organic-rich detritus in sediments (Klinkhammer et al., 1982; Thamdrup et al., 1994). As these latter studies indicate there is often a close association of Mn with organic matter, even though most Mn is not physically bound to organic material or complexed with organic ligands (Whitfield and Turner, 1987).

The association between organic carbon regeneration and Mn mineralization influences the distributions of other elements. Some transition metals such as copper are bound up with labile organic matter and recycled as the organic material is broken down by oxygen (Klinkhammer et al., 1982; Heggie et al., 1987; Chester et al., 1988; Shaw et al., 1990). Other metals such as nickel become associated with metastable manganous coatings and undergo remobilization along with Mn in suboxic environments (Klinkhammer et al., 1982). Still other elements respond independently to variations in reductive intensity brought about by microbial decay, either because they are sensitive to changes in Fe or S as in the case of Cd (Klinkhammer et al., 1982; van Geen et al., 1995), or because they possess their own redox potential as in the case of U (Anderson et al., 1989; C.E. Barnes and Cochran, 1990; Klinkhammer and Palmer, 1991; Shaw et al., 1994).

It is also well known that Mn is one of the trace metals required by phytoplankton as a micronutrient (Bruland et al., 1991; Coale, 1991; Morel et al., 1991; Kolber et al., 1994). Thus Mn and labile organic matter are closely linked and together their cycles affect the partitioning of many elements, determining what regenerates and stays in the water column and what becomes buried in sediments. These cycles are also closely related to the biogeochemical cycling of carbon and nitrogen, especially on continental margins (Walsh, 1991).

The idea behind this study was to use in situ measurements of dissolved Mn and terrestrial organic matter to examine the relationship between degradation and chemical partitioning. While the fundamental processes involved in Mn cycling are well understood (e.g., Graham et al., 1976; Sundby et al., 1981; Morris et al., 1982; Burton et al., 1993; Moffett, 1994; Thamdrup et al., 1994), the evolution of terrestrial organic matter from estuarine to open-ocean environments remains largely unresolved.

Kalle (1949) was the first to demonstrate that dissolved terrestrial organic matter has distinctive fluorescent properties. The distribution of the fluorescent component of DOM, or FDOM, has been examined in estuaries and coastal water (Zimmerman and Rommets, 1974; Laane and Koole, 1982; Willey and Atkinson, 1982; Green and Blough, 1994; Prahl and Coble, 1994), as well as in open-ocean environments (Hayase et al., 1988; Chen and Bada, 1992; Mopper and Schultz, 1993; De Souza Sierra et al., 1994; Green and Blough, 1994). While it seems unclear what processes control the distribution of this property in the oceans (Jerlov, 1976), coastal studies usually find a more-or-less inverse relationship between FDOM and salinity. This observation supports the view that the fluorescence of DOM is influenced strongly by terrestrial humic material in nearshore environments, although the complexities in this relationship leave plenty of room for a reactive component to FDOM. This paper examines FDOM– and dissolved Mn–salinity relationships in detail by using an in situ geochemical package.

2. Methods

Our instrument package consisted of a stainless-steel frame holding a SeaBird 911 plus CTD, SeaTech 25-cm transmissometer, Chelsea Instruments AquaTracka Mk III fluorometer (alternatively nephelometer), Seapoint sensor (backscatter device), ZAPS (*z*ero *a*ngle *p*hoton *s*pectrometer) chemical sensor (alternatively UV fluorometer), magnetically-coupled gear pump, General Oceanic 12 bottle rosette, and Simrad altimeter. Several topside computers regulated data acquisition, digital control of ZAPS, rosette operation, and navigation then transferred the merged data set to an optical disk. A custom-built deck unit supplied the package with 400 V (150 W) of power and supported a 14,400-baud modem channel for digital control of the ZAPS spectrometer and transmission of 4 data channels, as well as the standard 8,640-baud rate SeaBird channel for telemetry of the remaining signals. The data stream was merged with a time stamp and latitude and longitude information from a Garmin GPS unit. Data were displayed in real-time. The same package was used for towing and vertical lowerings.

Details of the ZAPS spectrometer are given elsewhere (Klinkhammer, 1994). Mn concentrations were calibrated by pumping seawater standards through the flow-cell in the laboratory before the cruise. These calibrations underwent minor post-cruise adjustments by comparing the instrumental results with Mn concentrations in water samples collected with the rosette on the package. Filtered aliquots of the rosette samples were analyzed using an inductively coupled plasma mass spectrometer (Fisons VG PlasmaQuad II Plus) interfaced to a Dionex Chelation Concentration Module. In this scheme the elution stream from the Dionex was combined with an In solution using an automated valve and pumped directly into the plasma. The In count rate was used for normalization to eliminate variations in plasma efficiency (Falkner et al., 1995) and the normalized count rates were used to calculate Mn concentrations by comparison with seawater standards.

ZAPS was used to measure FDOM by replacing the chemical cartridges with a filter and exciting the sample stream at 320 nm while monitoring fluorescence at 420 nm. Readings were calibrated back in the laboratory against a standard quinine sulfate solution. A 1.83 μM primary standard was made by weighing 0.70 mg of quinine sulfate monohydrate into 500 ml of acidified quartz-distilled H_2O. A 500-fold dilution of this primary standard was used as the operating standard and the fluorescence of this working solution was defined as 47 fluorescence units (1 fu = 78 pM quinine sulfate) to make our measurements consistent with previous work. Typical FDOM levels in the North Pacific are 8 fu in surface water and 23 fu in deep water (Chen and Bada, 1992; Klinkhammer, 1994). FDOM measurements in the laboratory were made using a bottle adapter specially made for the ZAPS fiber assembly. ZAPS measurements of FDOM were reproducible to $\pm 5\%$.

Temperature, conductivity, and pressure measurements were made with a SeaBird 911 plus CTD. Measured precisions with this unit are ± 0.002°C for temperature, ± 0.003 for salinity (where S is measured on the practical salinity scale), and ± 1 dbar for pressure. Chlorophyll a was determined with a Chelsea AquaTracka Fluorometer. Voltage readings from this instrument were converted to approximate Chl a concentrations using standard solutions and a calibration equation provided by the manufacturer. A limited number of samples from the rosette were analyzed for Chl a by standard procedures. Turbidity was determined with three different techniques: light attenuation, 90° scatter (nephelometry), and backscatter. The Chelsea fluorometer was deployed as a fluorometer in 1994 but converted to a nephelometer (at 420 nm) the following year. A Seapoint backscatter device was also deployed in 1995. The SeaTech Transmissometer (25 cm) was used to measure light transmission during both field seasons. The apparent resolution of this instrument for transmission was $\pm 0.02\%$. Light transmission ($\%T$) was converted to attenuation coefficient or Beam c, where Beam c (m^{-1}) $= -(\ln \%T/100)/0.25$ m. The terms Beam c and turbidity are interchangeable.

3. Study area

The Columbia River estuary and coastal plume have been the subject of several large studies. These results are compiled in Pruter and Alverson (1972), Jay (1984), and Simenstad et al. (1984). The Columbia is the second largest river in North America with respect to length and volume with an annual discharge rate of 2.3×10^{11} m^3 yr^{-1}, or $\sim 60\%$ as much as the Mississippi River. The Columbia is controlled by dams but flow still ranges between 3,000 and 12,000 m^3 s^{-1} with a mean annual value of 7,300 m^3 s^{-1}. Our study periods were at the end of May in both years and discharge rates at these times were somewhat lower than normal. The average rate in 1995 was 8,500 m^3 s^{-1} which was somewhat higher than in 1994 when it was 6,800 m^3 s^{-1}.

Surface currents along the coast are mainly wind-driven and fluctuate during the year (Huyer et al., 1975; Huyer, 1979; Hickey, 1979). As a consequence the Columbia River plume drifts north or south along the coast depending on the seasonal wind pattern (C.A. Barnes et al., 1972; Fiedler and Laurs, 1990). Southerly winds prevail during the winter producing onshore Ekman transport of surface water and downwelling near the coast. These conditions are balanced by northward geostrophic flow which pushes the plume along the Washington coast during the winter. Surface winds begin shifting to a northerly direction during April–May in response to changes in the position of the jet stream. These conditions produce offshore Ekman transport which causes upwelling along the coast. The resulting southward geostrophic flow moves the plume along the Oregon coast during the summer. The system reverts back to winter conditions in September–October. Transitional plumes exist in the late spring and late fall between these extreme patterns.

4. Results

Data for this study were collected during two short cruises of the RV "Wecoma"; each trip consisted of two days in the study area. During the first cruise in May 1994 we focused on the coastal plume. Fig. 1 is a visible satellite image for this sampling

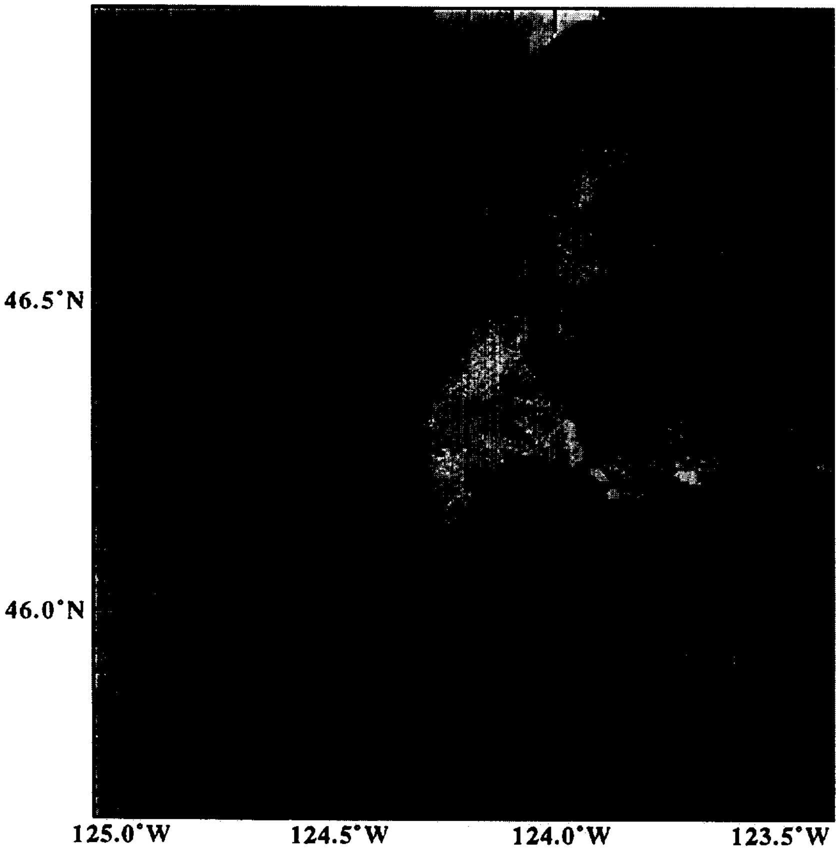

Fig. 1. Enhanced visible satellite image of the coastal region of the northwestern U.S.A. during May 1994. The Columbia River plume is the warmer (*lighter gray*) area extending from the mouth of the river mainly northward along the coast. The track near the seaward plume edge represents the short tows and periodic lowerings discussed in the text. The track in the estuary represents the two surface tows carried out in 1995.

period showing primarily a winter plume flowing north along the Washington coast, but with some penetration to the south. This picture of the plume in transition was essentially identical during our cruise the following year. The 1994 work consisted of a tow-dip operation near the seaward boundary of the plume. Four vertical profiles were carried out along the tow track which is overlain on the satellite image in Fig. 1. The track was due west of the mouth of the estuary, in the main axis of the plume jet. The locations of the surface stations along this line are shown in Fig. 2a which also shows the seaward drift of the ship that occurred during each vertical lowering. This drift was not intentional but the result of

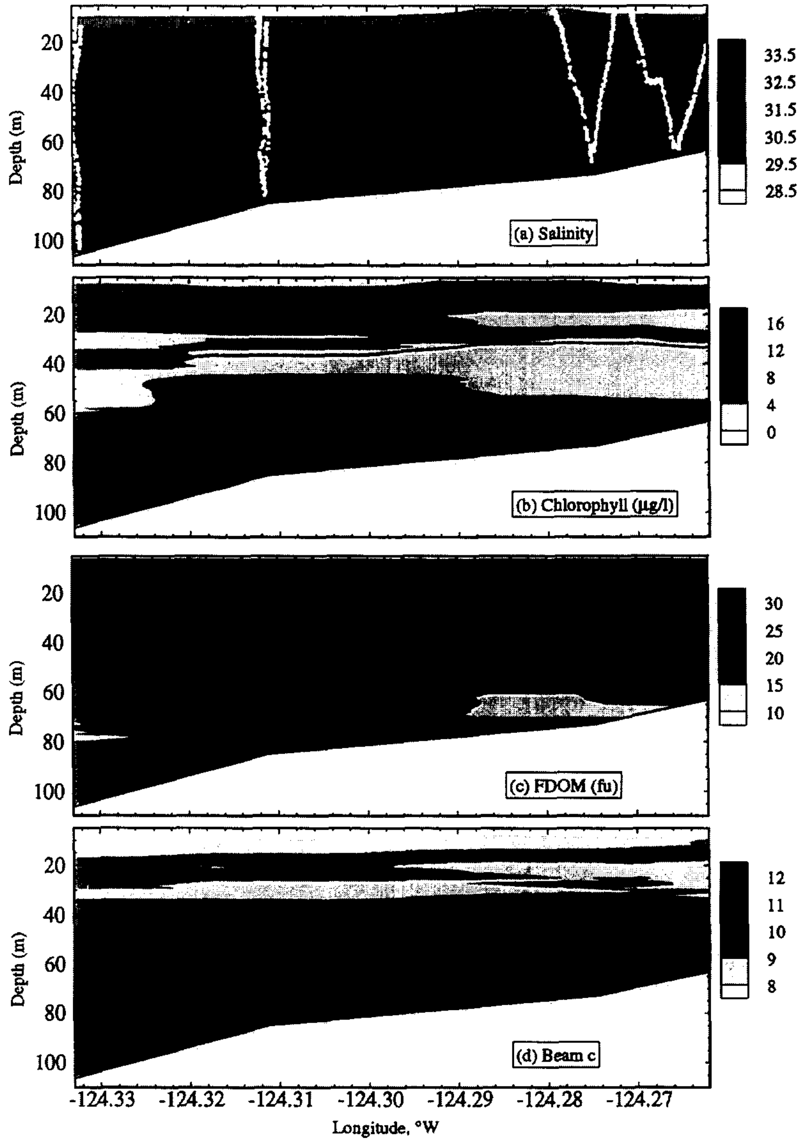

Fig. 2. Contour plots of salinity, Chl *a*, fluorescent dissolved organic matter (FDOM) and the light attenuation coefficient or Beam *c* (turbidity in m^{-1}) for a cross-section of the Columbia River plume directly west of the mouth of the estuary in May 1994. The *dashed line* in each panel is positioned at the $S = 32.5$ isohaline and represents the lower boundary of the plume (C.A. Barnes et al., 1972). The *white traces* in panel (a) are package positions during profile operations near the outer edge of the plume (Fig. 1).

strong offshore currents at our nearshore stations. FDOM and salinity profiles from one near-shore station are shown in Fig. 3. As this figure shows there was a strong inverse relationship between salinity and FDOM in the surface waters of the plume.

In 1995 we carried out operations in the Columbia estuary which consisted of two surface tow tracks, shown as a single line in Fig. 1. Tow SL05 consisted of a short section just off Astoria Harbor carried out during ebb tide. Salinity, dissolved Mn, and light scattering results from this operation are shown vs. longitude in Fig. 4. Tow SL07, also carried out with an ebbing tide, began at the Astoria Bridge and ended just inside the bar at the mouth of the river. The ZAPS UV fluorometer was changed over to measure FDOM for this tow and these results, together with the corresponding Beam *c* data, are shown in Fig. 5. Both tows were carried out in the southern or main shipping (navigation) channel and the package was kept between 4 and 6 m of the

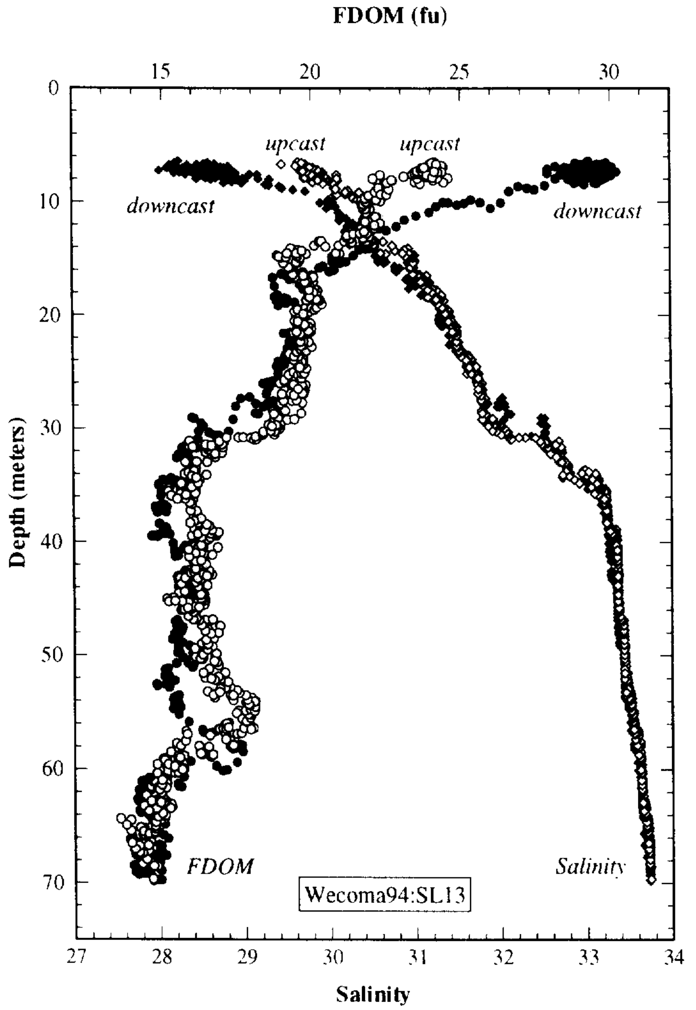

Fig. 3. Vertical profiles of salinity and fluorescent dissolved organic matter (FDOM) within the Columbia River plume. FDOM was measured with the ZAPS chemical sensor. The profiles extend to within 10 m of the bottom. Both sets of profiles diverge near the surface because the ship drifted away from the coast during the operation (Fig. 2a). The base of the plume (CRPW) is at ~ 36 m at this location (the bottom of the halocline) and there is a layer of shelf bottom water (SBW) below 55 m. Intermediate water between these depths is referred to as shelf deep water (SDW) in the text.

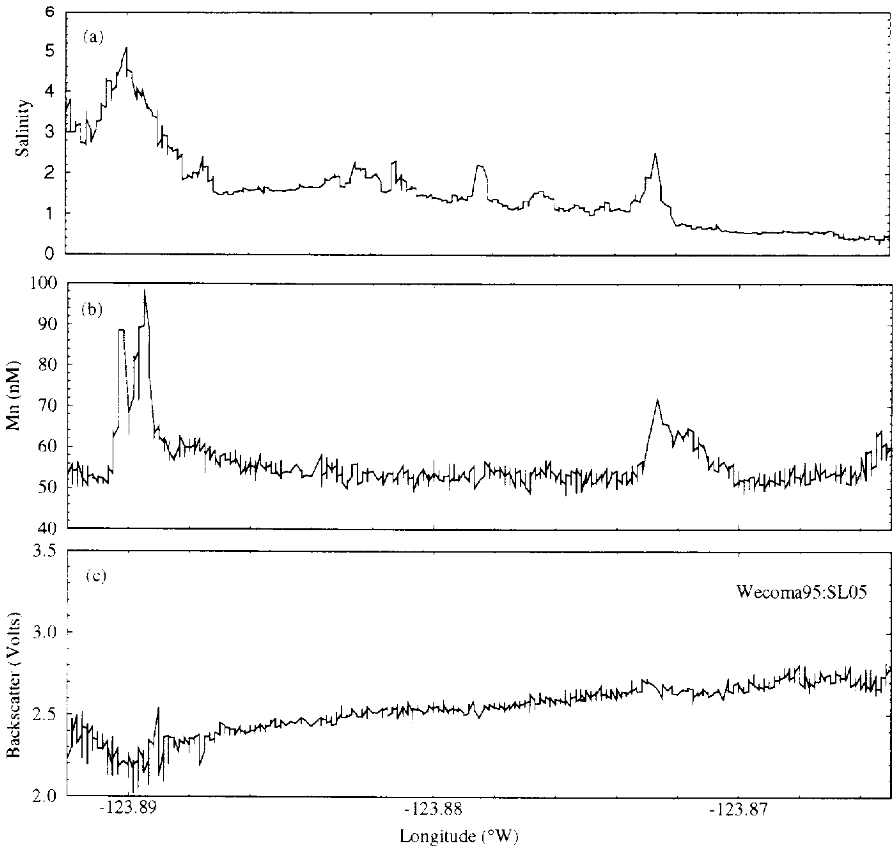

Fig. 4. Salinity, ZAPS dissolved Mn, and light backscatter plotted against longitude for a tow in the surface waters of the lower Columbia River estuary in May 1995. This operation was carried out just off Astoria, Oregon, in the navigation or south channel. The package was kept between 4 and 6 m. The excursions in Mn might represent packets of water originating in shallow embayments just west of this area (Youngs Bay and Baker Bay).

surface. This depth is below the bottom of the estuarine photic zone which is maintained at ~ 2.5 m for most of the year (Lara-Lara et al., 1990).

5. Discussion

5.1. Distributions in the Columbia River estuary

Several positive excursions in dissolved Mn occurred in the estuary during SL05 and these spikes were associated with salinity maxima (Fig. 4). It is difficult to pin down the source of these events given the sketchy nature of this preliminary data set. One possibility is that they were packets of water advected from peripheral bays adjoining the estuary west of this section (Neal, 1972; Prahl and Coble, 1994). Water in these bays has a short residence time before it is flushed into the main channel (Hamilton, 1990; Lara-Lara et al., 1990). It is also well known that Mn-oxides are reduced in the tidal mudflats that characterize such embayments (see references in Morris et al., 1982; Moffett, 1994). However, identifying specific sources will require more extensive surveys.

FDOM data from the longer estuarine tow are plotted against salinity in Fig. 5 along with Beam *c* results. There was generally an inverse relationship between salinity and FDOM, which is consistent with previous studies in the Columbia (Prahl and Coble, 1994) and other estuaries (Kalle, 1949; Zimmerman and Rommets, 1974; Laane and Koole,

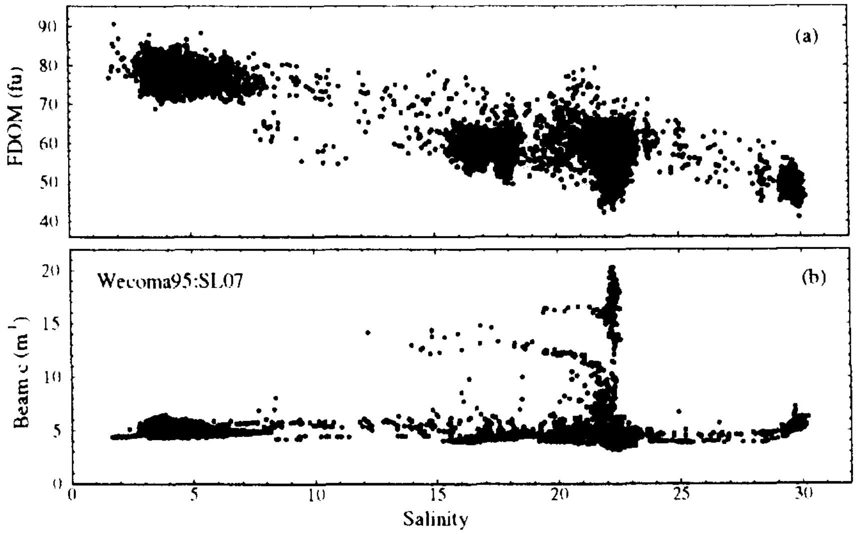

Fig. 5. Light attenuation and fluorescent dissolved organic matter (FDOM) plotted against salinity for a tow in the surface waters of the lower Columbia River estuary in May 1995. The estuary turbidity maximum (ETM) was recorded as high Beam c between $S = 14$ and $S = 23$.

1982; Willey and Atkinson, 1982). If a best-fit straight line is forced through these data it has a freshwater intercept of 82 fu. As we point out later in the discussion, this end-member value is consistent with our work in the coastal plume the previous year. Data from this tow appears to be sorted into several salinity packets which is undoubtedly an artifact of towing at one depth. A turbidity maximum, which appears as a large positive anomaly in Beam c, was encountered at $S = 22$. The location and tidal relationship of this feature is consistent with the estuarine turbidity maximum (ETM) described by Gelfenbaum (1983). Based on measurements in a few discrete samples, Prahl and Coble (1994) were able to conclude that there was reduced fluorescence in surface waters of the ETM. The high-resolution data from ZAPS support this conclusion. That is, if anything FDOM within the ETM is lower than one would expect from simple mixing of high-FDOM river water with low-FDOM coastal water. This result leaves open the possibility that terrestrial organic matter is being degraded in the peripheral bays where this suspended particulate matter originates (Gelfenbaum, 1983), or within the ETM itself. Moreover, we know that the ETM is associated with elevated microbial activity (Baross et al., 1994) increasing the possibility that Mn-oxides are somehow associated with the degradation process.

5.2. Distributions in the Columbia River plume

Historically Columbia River Plume Water (CRPW) is defined as water with a salinity < 32.5 (C.A. Barnes et al., 1972). As illustrated in Fig. 3 this salinity coincides with the halocline which occurred between 30 and 36 m at this station. The next significant shift in salinity below this depth is at $S = 33.6$, which shows up as a small inflection in the T–S relationship (Fig. 6a). For purposes of this discussion, water between $S = 32.5$ and $S = 33.6$ will be defined as shelf deep water (SDW), and water with $S > 33.6$ as shelf bottom water (SBW). As shown in Fig. 2 CRPW extended as deep as 40 m in 1994 while SBW hugged the 60-m isobath. In other words, intermediate SDW was restricted to 20 m of the water column during our study period.

As shown in Fig. 6b and d, there were maxima in turbidity and Chl a in surface waters near the outer edge of the plume ($S = 31.0$). The presence of a turbidity maximum at this boundary seems reasonable as one might expect that suspended particles would begin to fall out and accumulate at the sea-

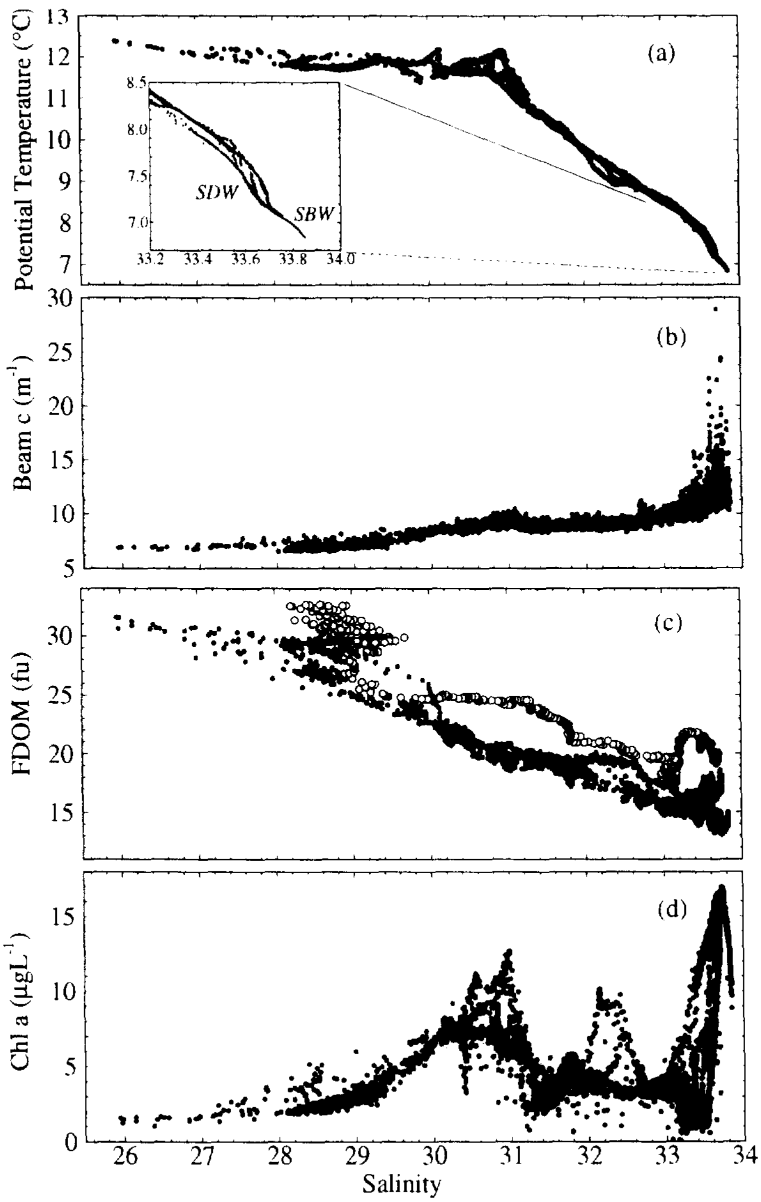

Fig. 6. Potential temperature, Beam *c* or light attenuation, fluorescent dissolved organic matter (FDOM), and Chl *a* plotted against salinity for vertical lowerings in the Columbia River plume in 1994. The base of plume water (CRPW) stands out as decreased scatter in the TS at $S = 32.5$. The TS for shelf deep water (SDW) and shelf bottom water (SBW) are blown-up in the *inset*. FDOM levels at our nearest-shore station (represented by *open circles* in the panel c) were significantly higher.

ward edge of the plume jet (Fig. 1). Moreover, as shown in Fig. 7c, Mn concentrations across this area were higher than expected from mixing of Mn-rich plume water and Mn-poor coastal water. This picture of elevated dissolved Mn concentrations in the presence of suspended particulates is the trend one would expect if Mn-oxides were being reduced, perhaps during the oxidation of organic material as proposed by Sunda and Kieber (1994). In this view the increased concentration and residence time of particles

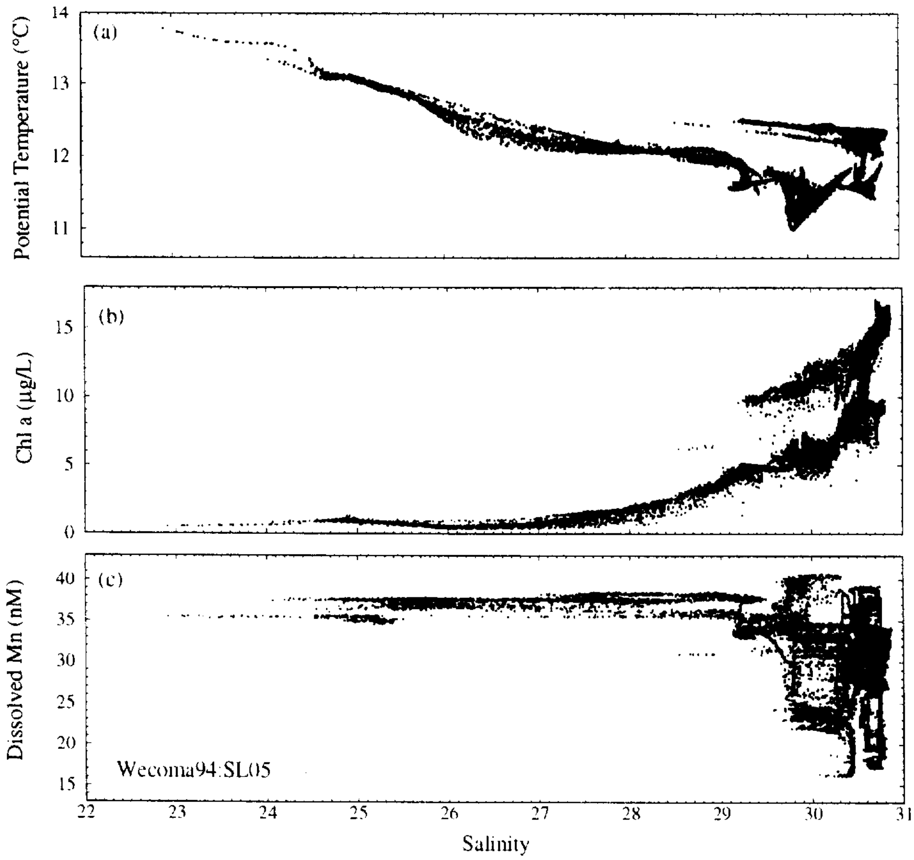

Fig. 7. Potential temperature, Chl *a*, and dissolved Mn data from a surface tow along part of the track shown in Fig. 2a plotted against salinity.

near the plume boundary create a water column more receptive to microbial activity and biogeochemical reaction.

In addition to the Chl *a* maximum in surface water near the plume boundary, there were two subsurface maxima: one at ~ 30 m and another deeper maximum associated with SBW (Figs. 2b, 6d and 8). The shallower of these appears to be related to the seasonal bloom in surface coastal waters (C.A. Barnes et al., 1972). The origin of the anomaly in SBW is more problematic. It is possible that this fluorescence signal was not really Chl *a* at all but fluorescence of other organic ligands, possibly degradation products. This possibility could only be addressed by analyzing fluorescence spectra, which is beyond the scope of this study. Alternatively, similar benthic fluorescence maxima under the Fraser River plume have been attributed to the seeding of bottom waters by sinking freshwater diatoms during lysis (Yin et al., 1995). In some ways a riverine source for the benthic Chl *a* maximum seems reasonable. The highest Chl *a* levels of the year in the Columbia estuary occur in May (Lara-Lara et al., 1990), and there is a Chl *a* maximum in surface waters near the mouth of the estuary (Fig. 2b). On the other hand, the observations that the benthic anomaly coincided exactly with SBW and possessed uniform fluorescence intensity are more consistent with it being an advected feature. Also, as shown in Fig. 8, the deep Chl *a* was associated with a minimum in dissolved Mn further supporting the idea that SBW originated as near-surface coastal water that downwelled and shoaled onto the shelf.

Fig. 6 shows FDOM and other data from the tow

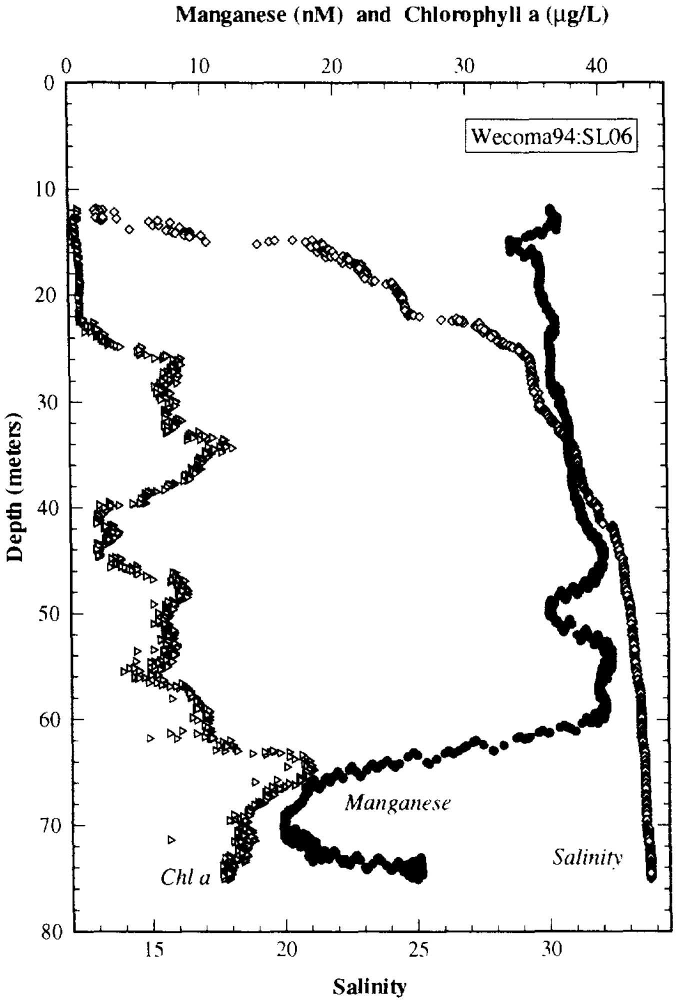

Fig. 8. Profiles of dissolved Mn and Chl *a* within the Columbia River plume in 1994. Shelf bottom water (> 60 m) possesses anomalously high concentrations of Chl *a* and anomalously low concentrations of dissolved Mn consistent with a surface source.

and vertical profiles taken within the plume in 1994. If the FDOM–salt relationship in CRPW surface water ($S < 31.0$ in Fig. 6c) is extrapolated to zero salinity, the predicted FDOM concentration in the riverine end-member is ~ 100 fu. This level is similar to the 82-fu level calculated from the FDOM–salinity relationship within the estuary the following year (Fig. 5). These extrapolated levels become even closer if one takes into account the greater freshwater flow in 1995 and assumes that snow melt has the effect of diluting the FDOM signal.

There is often a FDOM maximum near the bottom (Fig. 6c). Unlike high Chl *a* levels which are closely associated with SBW (Fig. 2b), these FDOM maxima tend to be isolated bottom features suggestive of localized input, probably from the sediment. This observation is consistent with other studies which found high FDOM levels in sediment pore waters (Chen et al., 1993; Benamou et al., 1994).

We have no explanation for the flat Mn concentrations between $S = 23$ and $S = 29$, nor the large amount of scatter near $S = 30$ (Fig. 7c). It is possible that scavenging of dissolved Mn is influencing this trend as seen in other systems (e.g., Morris et al., 1982). It is also evident that some of the scatter in dissolved Mn is matched by structure in the temperature and Chl *a* data. However, complete resolution of this pattern will require more transects across the seaward boundary. The data in this report simply show that this instrumented-package approach has potential for providing highly resolved, detailed information.

6. Conclusions

Dissolved Mn spikes observed in the surface waters of the Columbia River estuary occurred at the same time as salinity spikes. This observation is consistent with the entrainment of packets of water into the main channel from shallow embayments near the mouth of the river. The level of humic organic matter represented by the fluorescent component of dissolved organic matter (FDOM) showed a loose inverse relationship with salinity across the estuary, supporting a primarily terrestrial source for this material. However, there were lower FDOM levels in the surface turbidity maximum, indicating degradation of humic material within the estuary or bordering embayments.

The seaward boundary of the Columbia River plume was characterized by elevated levels of turbidity, dissolved Mn, and Chl *a*. Property–salinity plots suggest that non-conservative processes affected these distributions. One explanation for these observations is that particulate matter from the estuary collects at the seaward edge of the plume jet and acts as a substrate for microbial activity that uses Mn-oxides to break down humic material. This process of remineralization stimulates productivity along the boundary. In this view the leading edge of the river plume is a biogeochemical front where the organic and oxide fractions of terrestrial input are reconstituted, thus altering chemical partitioning. Reaction at the front would act as the final gleaning process for terrestrial material before it becomes part of the oceanic system.

This study demonstrates the potential of using chemical sensors to produce highly resolved oceanographic data sets. Such tools will prove to be especially useful at continental margins where chemical gradients are large and the processes that determine ocean chemistry are in full force.

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