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Importance of vertical mixing for additional sources of nitrate and iron to surface waters of the Columbia River plume: Implications for biology

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Abstract

The influence of the Columbia River plume on the distributions of nitrate and iron and their sources to coastal and shelf waters were examined. In contrast to other large estuaries, the Columbia River is a unique study area as it supplies very little nitrate ($5 \mu\text{M}$) and iron ($14\text{--}30 \text{ nM}$) at salinities of 1–2 to coastal waters. Elevated nitrate and dissolved iron concentrations (as high as $20 \mu\text{M}$ and 20 nM) were observed, however, in the near field Columbia River plume at salinities of 20. Surface nitrate concentrations were higher than observed in the Columbia River itself and therefore must be added by entrainment of higher nitrate concentrations from subsurface coastal waters. Tidal flow was identified as an important factor in determining the chemical constituents of the Columbia River plume. During the rising flood tide, nitrate and iron were entrained into the plume waters resulting in concentrations of $15 \mu\text{M}$ and 6 nM , respectively. Conversely, during the ebb tide the concentrations of nitrate and total dissolved iron were reduced to $0.3\text{--}3 \mu\text{M}$ and $1\text{--}2 \text{ nM}$, respectively, with a concomitant increase in chlorophyll *a* concentrations. As these plume waters moved offshore the plume drifted directly westward, over a nitrate depleted water mass ($<0.2 \mu\text{M}$). The plume water was also identified to move southwards and offshore during upwelling conditions and nitrate concentrations in this far field plume were also depleted. Iron concentrations in the near-field Columbia River plume are sufficient to meet the biological demand. However, due to the low nitrate in the Columbia River itself, nitrate in the plume is primarily dependent on mixing with nitrate rich, cold, high salinity subsurface waters. Without such an additional source the plume rapidly becomes nitrate limited.

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1. Introduction

The Columbia River plume is a highly productive region with chlorophyll concentrations, on the order of $20 \mu\text{g/l}$ regularly observed (Landry et al., 1989). Ex-

amination of SeaWiFS satellite data shows that the biological productivity originating from the plume extends over a large area (Fielder and Lairs, 1990). The Columbia River is the second largest river in the United States and releases significant amounts of freshwater (mean annual, $7300 \text{ m}^3 \text{ s}^{-1}$ per year) into the nearshore waters off Oregon and Washington (Barnes et al., 1972; Hickey, 1998). This freshwater discharge is observed as a surface lens of low-salinity water (Landry et al., 1989; Hill and Wheeler, 2002). The Columbia

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River plume affects a vast area of the Pacific Northwest not only by reducing salinity, but also by changing the distribution of other water properties such as macro and micronutrients (García-Berdeal et al., 2002). Historical data has suggested that the Columbia River itself provides little nitrate to the coast although it does supply large amounts of silicate (Conomos et al., 1972). Although nitrate concentrations within the River are low, coastal upwelling occurs along the coastline during the spring and summer months and this may supply additional nitrate to these waters. The input of biologically important trace elements such as iron, along with the complex physical structure of buoyant freshwater plumes, leads to a strong gradient in concentrations of and transformations among biogeochemical constituents in plume environments (Dagg et al., 2004).

Along the Pacific Northwest coast chlorophyll concentrations are not uniform, with greater concentrations observed in the Columbia River plume and over the Washington coast, north of the Columbia River (Landry et al., 1989; Thomas and Strub, 2001). Iron availability has been hypothesized as one of the reasons for the differences in observed chlorophyll concentrations (Hickey and Banas, 2003), although data was lacking to test this hypothesis. Concentrations of dissolved iron in river water can be several orders of magnitude greater than open ocean concentrations (Boyle et al., 1977). However, up to 95% of riverine dissolved iron can be lost through estuarine processes such as flocculation and precipitation (Boyle et al., 1977), therefore even large rivers such as the Columbia River may contribute little dissolved iron to the coastal ocean. However, data on iron concentrations and sources of iron from the Columbia River plume is lacking.

The Columbia River may contribute to the shelf sediment source of iron by exporting iron-rich particles from in the estuary (Mayer, 1982; Johnson et al., 2001). A series of recent studies have shown that the primary iron supply in coastal shelf waters is the release, and subsequent upwelling, of dissolved iron from resuspended bottom sediments (Croft and Hunter, 2000; Johnson et al., 1999; Bruland et al., 2001; Chase et al., 2005). As this iron input usually accompanies upwelling of macronutrients (phosphate, silicate and nitrate) from subsurface shelf waters, the potential new growth induced by the added nutrients is not normally iron-limited (Johnson et al., 1999). However, systems with a narrower shelf, such as some parts of the California upwelling system, are now known to be iron-limited and respond to iron addition with increased biomass production (Hutchins and Bruland, 1998; Hutchins et al., 1998; Firme et al., 2003).

The Columbia River plume is large enough to be of regional importance, yet small enough to allow determination of dominant processes affecting and/or resulting from river plumes. This paper describes high-resolution surface and subsurface (down to 20 m) total dissolved iron concentrations and macronutrients measured within the Columbia River plume and examines the sources of both macro and micronutrients to this highly productive plume. Prior to this study, data on dissolved iron concentrations within the plume were lacking and therefore the importance of iron to this region was unknown.

2. Methods

2.1. Sample collection

Seawater samples were collected during two cruises, Pre-RISE (20th of June–3rd of July 2004) onboard the *R/V Point Sur* and RISE (8th of July–28th of July, 2004) onboard the *R/V Wecoma*. Samples for the determination of total dissolved iron and macronutrients (nitrate+nitrite, phosphate, and silicic acid) were collected with a clean surface pump ‘sipper’ system using an all PTFE Teflon™ diaphragm pump (Bruiser™, Osmonics) and PFA Teflon™ tubing mounted to a PVC depressor vane 1 m above a 20-kg PVC fish attached to Yacht-Braid™ dacron line (New England rope). Underway salinity and temperature measurements were obtained using a YSI CTD Sonde attached to the PVC fish. For underway surface sampling at speeds of 4 to 7 knots, the sipper system was deployed off the side of the ship using the ship’s crane to suspend the fish outside of the wake with the intake at a depth of approximately 1.5 m. As the Columbia River plume is very shallow, generally less than 5 m, the fish was also deployed in a ‘vertical’ mode by lowering the ‘fish’ from 1 m down to a maximum depth of 20 m at a speed of approximately 1 knot, thus allowing samples to be collected from both within the surface plume layer and immediately below this layer.

Samples for dissolved iron were filtered through acid-cleaned 0.45 µm Teflon™ membrane polypropylene capsule filters (Calyx™, MSI) (Bruland et al., 2005). As these samples were filtered through 0.45 µm, they represent dissolved iron. Filters were changed on a daily basis and were flushed thoroughly with the new sample prior to collection. Over the salinity range sampled (11–33) iron was not observed to leach from the filters. Samples which were collected in the estuary at salinities of 0.1–8 were filtered through new filters as these filters capsules became clogged after approxi-

mately 10 l. During surface transects, samples for dissolved iron were collected every 10–20 min. Surface water nutrient concentrations were determined underway directly from the outflow of the ‘fish’ every 2 min and analyzed on-line using a LaChat Quick Chem 8000™ Flow Injection Analysis system using standard methods (Parsons et al., 1984). Chlorophyll *a* was determined using a fluorometric technique following the methods outlined in Parsons et al. (1984).

2.2. Dissolved iron analyses

Dissolved iron was determined at sea using a custom-made flow injection system based upon a catalytically enhanced spectrophotometric method (Measures et al., 1995) and the modifications presented in detail by Lohan et al. (submitted for publication). Filtered samples were acidified to pH 1.7 with 6 M quartz suboiled distilled HCl (Q-HCl) immediately upon collection. The flow injection system utilized a chelating resin, NTA Superflow (Qiagen), for the on-line concentration of Fe (III) from acidified samples (pH 1.7–1.8), thereby negating the need to buffer samples in-line prior to pre-concentration as required in previous methods (Lohan et al., 2005). As this chelating resin only binds Fe (III) at low pH, any Fe (II) in the acidified samples was oxidized to Fe (III) by the addition of 10 μM H_2O_2 and allowed to sit for 1/2 an hour prior to analysis (Lohan et al., submitted for publication). Depending on the iron concentration, samples were pre-concentrated on this column for 10 s to 5 min, where the flow rate was 0.8 ml/min. Working standards were prepared by serial dilution of 1000 $\mu\text{g l}^{-1}$ stock solutions (SPEX plasma standard) in acidified UV seawater (UVSW, where trace metals and metal chelating agents are removed see Donat and Bruland, 1988). Iron standards were prepared as standard additions of the working standards to acidified UVSW (pH 1.7). Standards were run at the start and end of each program (typically 20 samples) and concentrations were calculated from these standards using peak area measurement.

Two 500-ml acidified samples were collected during the first cruise, one from Monterey Bay and the other from the Columbia River plume, which were used as control samples and analyzed during every run. Precision was then calculated from these results. The iron concentration obtained over 20 days at sea for the seawater controls was 0.14 ± 0.03 nM and 1.81 ± 0.02 nM, respectively. The precision of this method was 1.4%. The blank utilized in this research was acidified Milli-Q water, which was loaded onto the column for a

similar time as the samples resulted in blank values of 0.08 ± 0.01 nM for 5 min load times. The detection limit of this technique is 0.03 nM was calculated as three times the standard deviation of the blank for 5 min load times.

3. Results

3.1. Surface transects

The locations of the surface transects carried out during Pre-RISE cruise are shown in Fig. 1. Transect 7, located approximately 100 km south of the Columbia River started at 45.35°N , 124.09°W and headed directly offshore along 45.33°N . Recently upwelled water was evident close to shore with a temperature of 10°C , salinity of 32.2 and elevated macronutrient concentrations (~ 13 μM nitrate and ~ 19 μM silicic acid) (Fig. 2). Dissolved iron in this upwelled water was low (0.1–0.5 nM). Offshore, the southern extension of the Columbia River plume was easily identified relative to surrounding surface waters with salinity decreasing to 27 and the silicic acid concentrations increasing to 27 μM . Nitrate concentrations in the Columbia River plume water at this location were depleted (< 0.2 μM), while total dissolved iron concentrations increased to 1.8 nM.

The near-field transect-10a, began north of the plume (46.31°N , 124.32°W) and headed south/south-

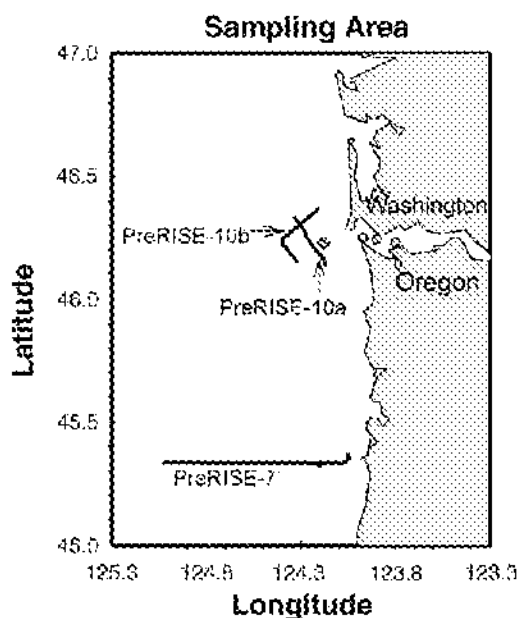


Fig. 1. The location of surface transects (7, 10a and 10b), the time series station (dark grey diamond) and the estuarine stations (light grey circle).

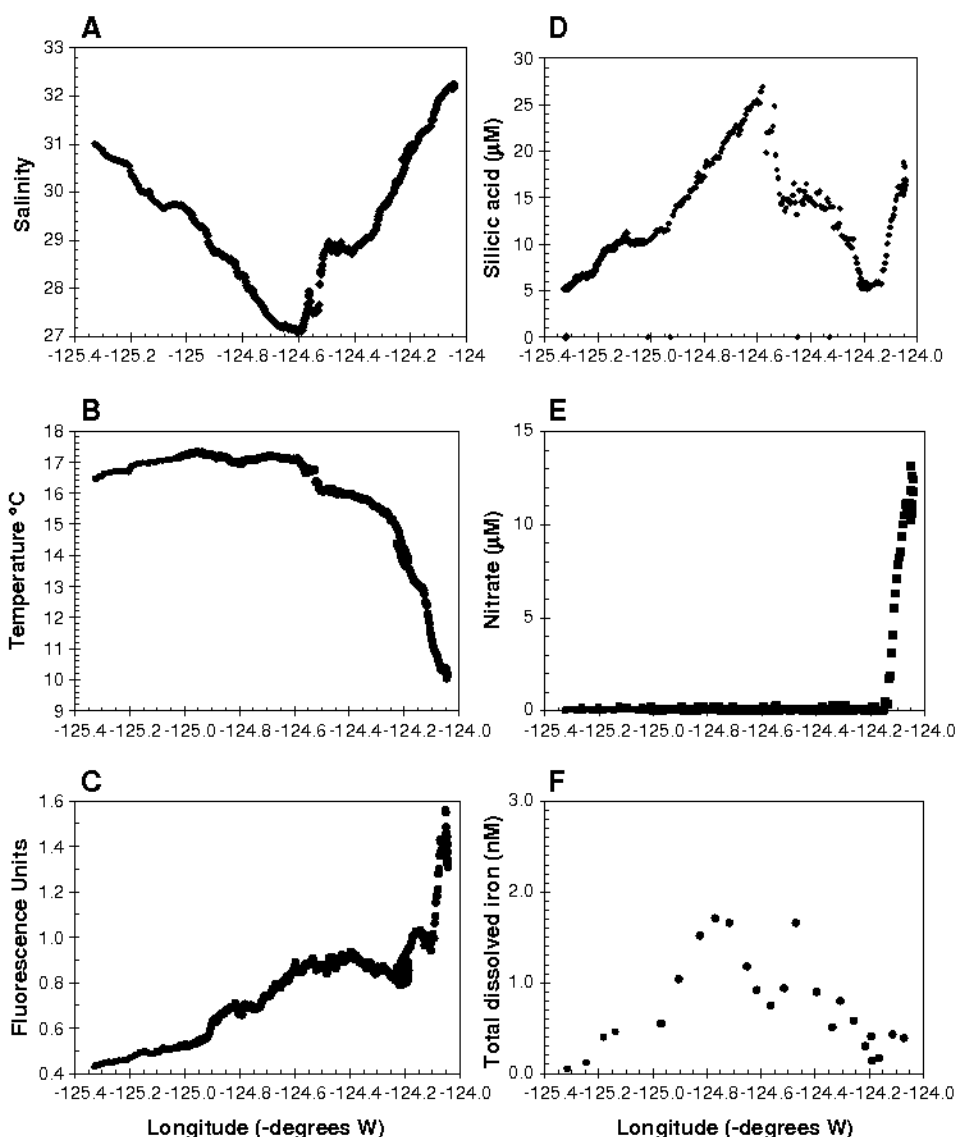


Fig. 2. Data from surface transect 7: (A) salinity, (B) temperature, (C) fluorescence, (D) silicic acid, (E) nitrate and (F) total dissolved iron.

west across the Columbia River plume. Surface water temperatures of 15.2 °C and salinities on the order of 30 were observed at the start of the transect (Fig. 3). Both the temperature and salinity decreased rapidly over a 0.1° change in latitude with temperature decreasing by 3 °C to 12.6 °C and salinities down to 23. Surface water temperatures then began to increase to 14 °C, while salinity continued to decrease to a minimum of 19 (Fig. 3). This near-field transect 10a was sampled during a spring tide resulting in plume waters with low salinities (19), nitrate and silicic acid concentrations of 19 and 88 µM, respectively and high dissolved iron concentrations of 18 nM. A negative correlation of total dissolved iron with % transmittance was observed. Salinities then

began to rise to 26 along the south-easterly transect track with a concomitant decrease in both macro and micronutrients with nitrate and silicic acid concentrations of 6 and 45 µM, respectively, and total dissolved iron concentrations of 6 nM.

As the wind direction had recently shifted from the South, transect 10b started in the northwest direction further offshore than transect 10a (Fig. 1), in order to investigate if the plume waters had headed north off the Washington coast. The transect then changed to the northeast direction to find the northward moving plume. The lowest salinity recorded on transect 10b was 22 with corresponding nitrate and silicic acid concentrations of 15 and 67 µM, respectively, and dis-

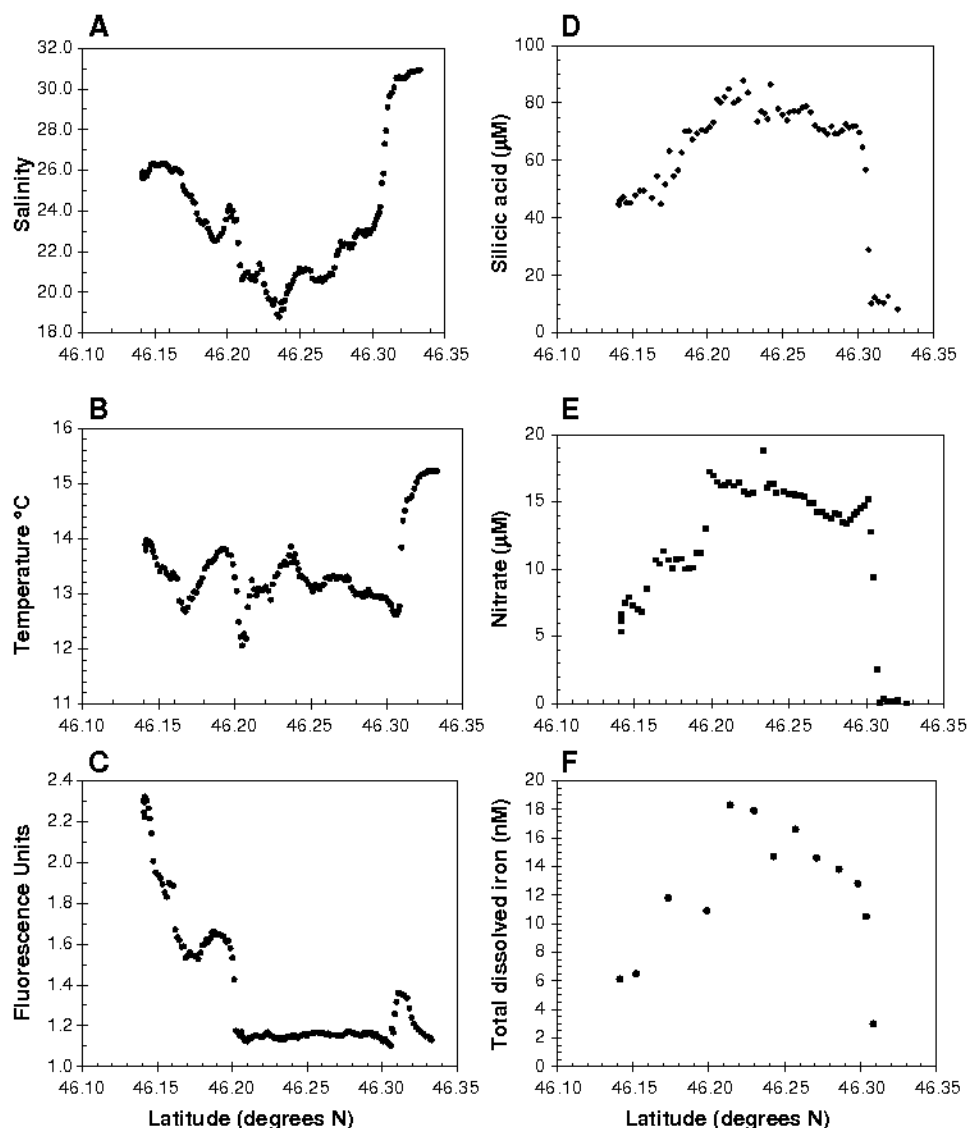


Fig. 3. Data from surface transect 10a: (A) salinity, (B) temperature, (C) fluorescence, (D) silicic acid, (E) nitrate and (F) total dissolved iron. This data was collected during a spring tide tide.

solved iron concentrations of 8.3 nM (Fig. 4). These concentrations are lower than those observed in transect 10a. This could be partly due to the fact the salinity sampled was not as low (22 compared to 19). Further inshore, the salinity and temperature were still only 26 and 13 °C, respectively, indicating that plume waters were present close to shore along the Washington coast.

3.2. Time series

A station close to the mouth of the estuary (46.23°N, 124.18°W, Fig. 1) was occupied over a 35-h period in order to characterize the chemical characteristics of the

Columbia River plume water over three tidal cycles. Approximately every 4 h samples for dissolved iron and nutrients were taken from the fish (4 depths down to a maximum depth of 20 m) and a CTD rosette was deployed down to depths of 30 m from which nutrients and chlorophyll *a* samples were taken. The water depth at this station was 36 m with a shallow plume lens ≤ 4 m. In order to assess the contribution of both macro and micronutrients from the Columbia River, samples for dissolved iron and macronutrients were also analyzed from three stations within the estuary (Fig. 1).

Over the tidal cycle, two distinct mixing lines were observed. Firstly, during the rising flood tide warmer

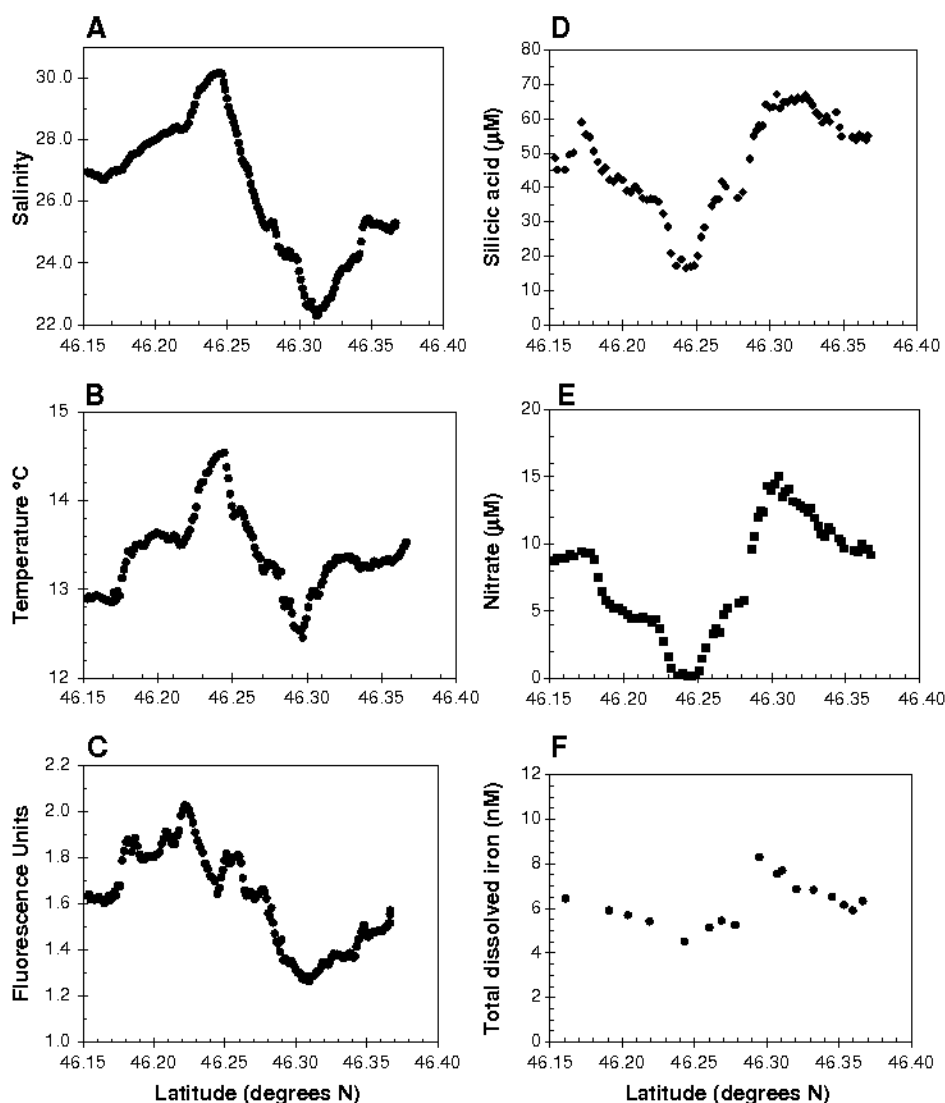


Fig. 4. Data from surface transect 10b: (A) salinity, (B) temperature, (C) fluorescence, (D) silicic acid, (E) nitrate and (F) total dissolved iron.

(22–19 °C), low salinity (2–12) estuarine waters had mixed with colder (8–10 °C), higher salinity (32.5) nutrient rich water resulting in plume water temperatures of 13–14 °C at salinities of 20–25 (Fig. 5B). In contrast, during the falling ebb tide, the warm low salinity water from the estuary mixed with relatively higher temperature (11–13 °C compared to 8–10 °C on the rising flood tide) and relatively lower salinity (30–32 compared to 32.5 on the rising flood tide), and lower nutrient waters resulting in warmer plume waters with temperatures of 16–17 °C at salinities of 20–25 (Fig. 5E).

Nitrate concentrations within the Columbia River are low $\sim 5 \mu\text{M}$ throughout the salinity range from 2 to 12 (Fig. 5C,F and Table 1). During the rising flood tide the

nitrate concentrations within the Columbia River plume were in the range of 12–15 μM , indicative of mixing with cold, higher salinity, higher nitrate concentration waters (20 μM nitrate at salinity of 33) thus adding nitrate to the plume waters (Fig. 5C). Conversely, during the ebb tide the concentration of nitrate within the plume waters was very low ranging from 0.3 to 3 μM at salinities of 20–25 (Fig. 5F). During the ebb tide the plume waters were mixed with warmer, relatively low salinity waters (30–32), which had low nitrate concentrations (3 μM).

Dissolved iron concentrations also varied over a tidal cycle. The concentrations of dissolved iron within the estuary (sampled on three different days) ranged from 0.4 to 32 nM (Table 1). Dissolved iron concentra-

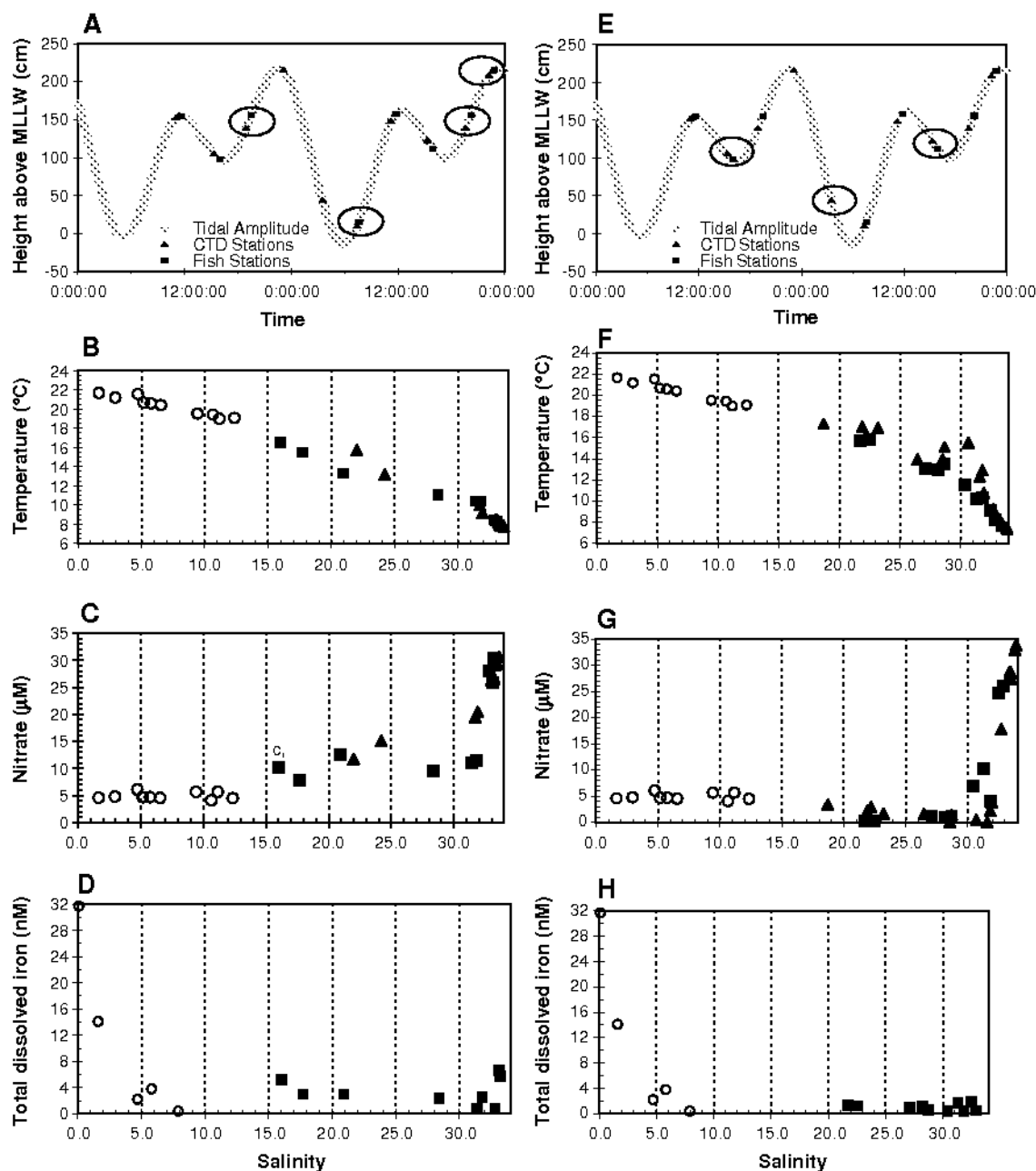


Fig. 5. Property–property diagrams during the flood tide. (A) Tidal amplitude with circles denoting the stations shown in B through D (B), temperature (C), nitrate (D) total dissolved iron vs. salinity and during the ebb tide. (E) Tidal amplitude with circles denoting the stations shown in F through H (F), temperature (G), nitrate and (H) total dissolved iron vs. salinity. Open circles denote estuarine data, closed triangles denote CTD samples and closed squares denote samples taken with the 'Fish'.

tions within the estuary decreased as salinity increased. Similar to nitrate concentrations, dissolved iron concentrations observed were higher during the flood tide than during the ebb tide. During the flood tide, dissolved iron concentrations within the plume ranged from 3 to 6 nM (Fig. 5D) compared to 1–2 nM during the ebb tide (Fig. 5G). Concomitant with the decrease in both nitrate

and iron concentrations within the plume waters during the ebb tide, the chlorophyll *a* concentrations were higher (15–17 µg/l) than that observed in the estuary (~7 µg/l). However, during the flood tide the concentration of chlorophyll *a* was similar to that observed within the estuary ~7 µg/l, which is comparable to that reported by Small et al. (1996).

Table 1
Concentrations of nitrate and total dissolved iron from the Estuary

Location	Date	Salinity	Nitrate (μM)	Dissolved Fe (nM)
Outer Station	7/2/2004	4.9	10	16.8
	7/21/2004	5.8	4.9	3.8
Middle Station	7/2/2004	5.6	10	13.3
	7/20/2004	7.9	9.8	0.4
Inner Station	7/21/2004	1.6	5.2	14.1
	7/2/2004	1.4	5.2	22.4
	7/20/2004	4.7	6.3	2.2
	7/21/2004	0.1	7.8	31.7

All stations are located in the south channel and all samples were taken with a GOFlo at 2 m. The outer station (123.97°W, 46.23°N) is close to the river mouth, the middle station (123.90°W, 46.20°N) is near Young's Bay and the inner station (123.8°W, 46.22°N) is near Astoria Bridge.

3.3. Plume drift

A Brightwater GPS-type surface drifter was deployed in Columbia River plume waters close to the mouth of the estuary to track plume water at 1 m depth. The drifter was followed to gain an insight of both macro and micronutrient concentration changes within plume waters as these waters moved offshore. For the first 31 h samples were taken approximately every 3 h using both the 'fish' deployed from the surface down to a depth of 8 m and a CTD rosette. Sampling was then reduced to every 6 h for another 24 h (Fig. 6). Within 6 h the drifter had traveled approximately 27 km directly offshore in a westward direction and was overlying 500 m of water. At the first sampling point after the drifter was deployed, the salinity of the plume water was 17, nitrate concentrations were 12 μM and the iron concentration was 3.9 nM (Fig. 7). After 2 h the salinity had increased to 23, and the nitrate and dissolved iron concentrations had decreased to 6 μM and 1.8 nM, respectively. At the last sampling time

point (68 h after deployment), the salinity had increased to 30, nitrate and dissolved iron decreased to 0.3 μM and 0.1 nM, respectively (Fig. 7). A salinity of 30 indicated that substantial mixing with coastal waters had occurred.

4. Discussion

4.1. Chemical characteristics of the near-field Columbia River plume

4.1.1. Nitrate

Unlike silicic acid concentrations, which were elevated within the Columbia River Estuary (148–162 μM), nitrate concentrations in the Columbia River Estuary were very low ($\sim 5 \mu\text{M}$). Nitrate in the Columbia River is low compared to other large temperate rivers such as the Mississippi where nitrate concentrations are on the order of 100 μM (Dagg et al., 2004). Instead, nitrate concentrations are comparable to tropical rivers such as the Zaire and the Orinoco (7.2 and 6.6 μM , respectively) (data from Dagg et al., 2004). Nitrate concentrations within the Columbia River plume, however, can still be on the order of 15 μM , indicating that nitrate is being entrained into the plume. Columbia River plume nitrate concentrations are similar to those observed in plume waters of the Santa Clara River, California (12 μM). However, the Santa Clara River is similar to other temperate rivers such as the Mississippi as nitrate concentrations within the river are on the order of 190 μM (Warrick et al., 2005).

As shown in Fig. 5 substantial mixing with cold high salinity, high nitrate waters results in higher nitrate concentrations within the plume. Evidence for entrainment of higher nitrate waters into the plume occurs at the time-series station, during the rising flood tide. During the flood tide, temperatures of $<9 \text{ }^\circ\text{C}$ and salinities of

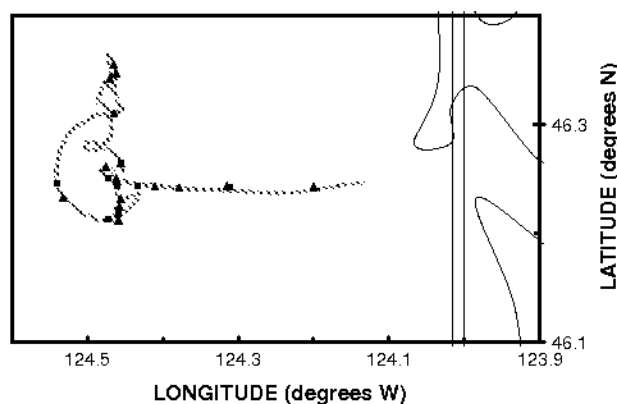


Fig. 6. Drifter track marked with the locations of CTD stations (triangles) and 'fish' stations (squares).

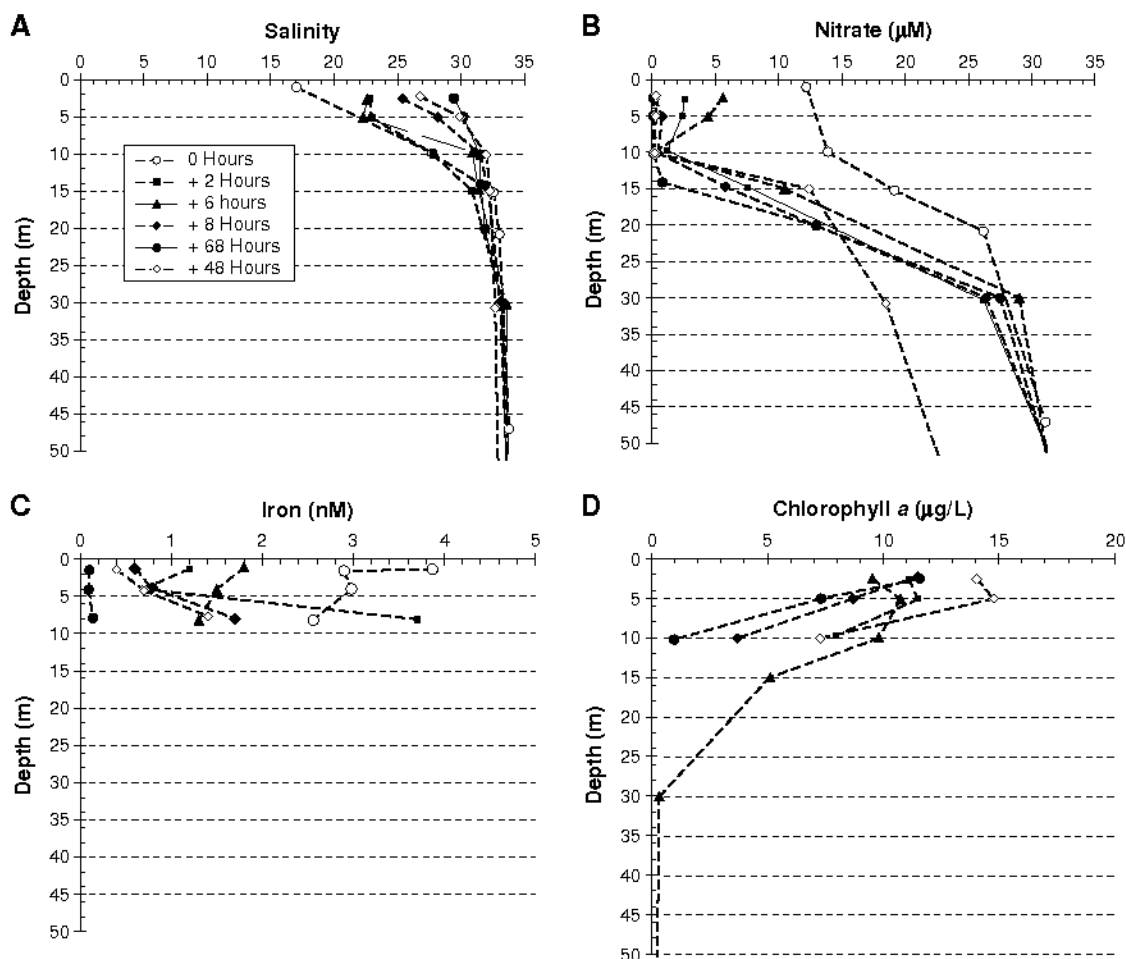


Fig. 7. Data from drifter study (A) salinity, (B) nitrate, (C) total dissolved iron and (D) chlorophyll a .

>32.9 with corresponding nitrate concentrations ranging from 15 to 28 μM were observed at a depth of 5 m. However, during the ebb tide these water mass characteristics were only observed at depths below 15 m. During the ebb tide the Columbia River plume was overlying a water mass with temperatures of 12–14 $^{\circ}\text{C}$ and nitrate concentrations ranging from 0.3 to 8 μM . Fig. 8 shows a conceptual diagram of the two different entrainment processes occurring: entrainment of cold, high salinity nutrient rich upwelling near surface water into the plume during the flood tide and the entrainment of warm, nutrient depleted low iron near surface water into the plume during the ebb tide. Orton and Jay (2005) observed Columbia River plume water mixing with cold subsurface ocean water at the onset of flood tide. Harrison et al. (1991) in a study of the Fraser River in British Columbia observed entrainment of nitrate into the plume waters immediately after spring tides from depth as the plume advected offshore. Nitrate concen-

trations within the Fraser River vary from 2 to 15 μM (Colbert and McManus, 2003) and these concentrations are similar to those offshore, and as such the entrainment of nitrate into the plume is not as large as observed in the Columbia River plume during this study.

During the spring and summer months, the Columbia River plume can be discharged into a coastal upwelling regime. This coastal upwelling would bring cold, nutrient rich deep water directly to the surface near the estuary mouth. In the plume, the characteristics of coastal upwelling would be more evident during the flood tide as cold, nutrient rich water is observed just beneath the plume at a depth of 5 m.

Combining all the surface nitrate concentration data for transect 10a also demonstrates these two mixing regimes (Fig. 9A). Fig. 9A shows the formation of the plume waters with much higher nitrate concentrations than observed in the estuary resulting from the mixing of estuarine water and cold, nutrient

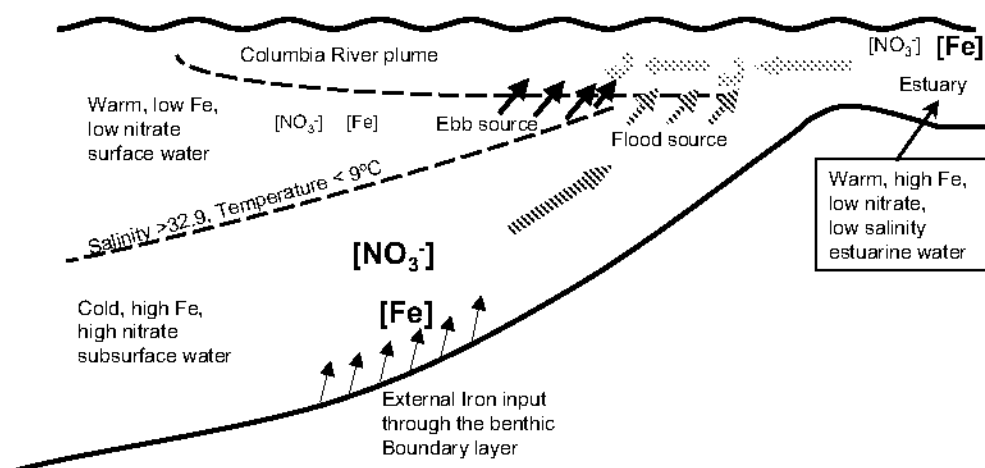


Fig. 8. Conceptual model indicating the two different tidal mixing regimes within the Columbia River plume. During the flood tide, the Columbia River plume is formed from mixing estuarine water with cold, high iron, high nitrate subsurface water (indicated by dark grey arrows). Conversely during ebb tide, estuarine water mixes with warm, low nitrate surface water (indicated by black arrows).

rich subsurface water. These plume waters then mix with lower nitrate surface waters as the plume spreads and moves offshore.

4.1.2. Dissolved iron

Dissolved iron was determined at three stations and on three different days within the estuary (Fig. 1, Table 1). These iron concentrations (32–0.4 nM) are significantly lower than the values of 100–1000 nM reported by Fuhrer et al. (1996) for the Columbia River estuary, and those observed along some east coast estuaries (Boyle et al., 1977). The iron concentrations reported by Fuhrer et al. (1996) were filtered through a 0.45- μ m filter, which is similar to that used in this study and then analyzed by inductively coupled plasma mass spectrometry. The study carried out by Fuhrer et al. (1996) included stations much further upstream and than carried out during this study. However, no blanks or certified reference material were analyzed for iron during their study. Dissolved iron concentrations that we observed within the Columbia River estuary are however, similar to those in the Mississippi where concentrations on the order of 30 nM are observed at low salinities (Ståbler and Boyle, 1991). Similar to that reported for other estuarine environments, total dissolved iron concentrations decreased with increasing salinity. However, with the limited data set obtained within the estuary, there is no conclusive evidence for the non-conservative removal of iron as observed along east coast estuaries (Boyle et al., 1977; Wells and Mayer, 1991). The concentration of dissolved iron within the estuary varied over two consecutive days (Table 1). The extremely low concentrations of dis-

solved iron on the 20th of July 2004 corresponded to sampling just after low tide compared to the higher values observed the next day which were sampled just after high tide.

As observed during the time series with nitrate, dissolved iron concentrations in the plume are also higher during the rising flood tide (Fig. 5D). Estuarine samples taken just after transect 10 (2nd July 2004) show relatively high concentrations of dissolved iron and were sampled just before and immediately after high tide. It appears that tidal influence may have a marked impact on the dissolved iron concentrations observed both within the estuary and the Columbia River plume. The estuary is sufficiently shallow that the effects of bottom friction are felt throughout tidal flow (Jay and Smith, 1990). As the salt wedge moves up the estuary during the flood tide, iron may be resuspended from bottom sediments and mixed into the surface waters. Although the dissolved iron concentrations within the estuary at low salinities (0.1–4) are higher than observed within the plume, at higher salinities of 8 within the estuary, iron concentrations are significantly less than observed within the plume (Table 1). Combining all of the dissolved iron data for transect 10a, the tidal series and samples from 40 to 60 m depth under the influence of the plume, demonstrates the potential for vertical mixing (Fig. 9B). Vertical mixing and/or upwelling and subsequent entrainment of higher dissolved iron concentrations outside the river mouth also increase the dissolved iron concentrations in surface waters as observed during transect 10a where concentrations of 18 nM were observed while concentrations within the estuary were only 13 nM (Fig. 9B).

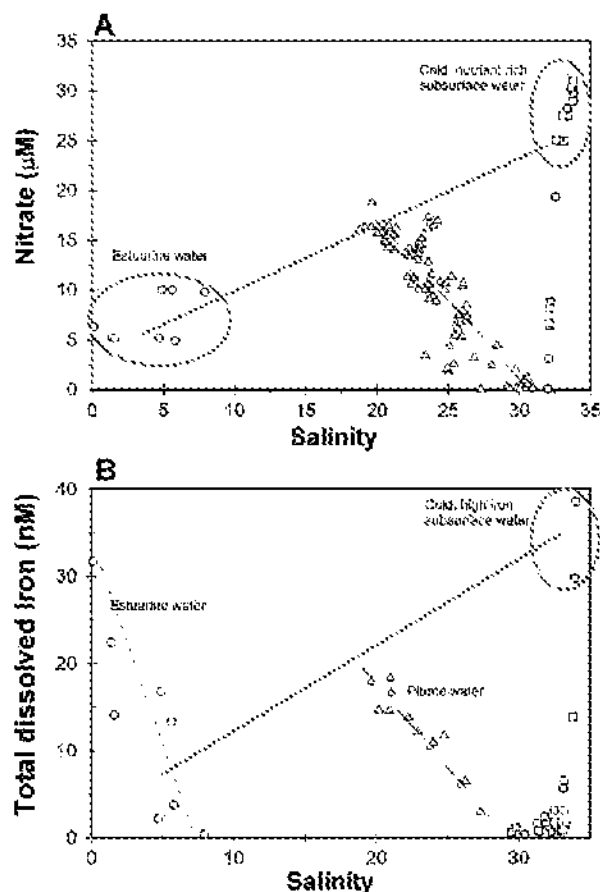


Fig. 9. Property–property diagrams for the near-field surface transect 10a, tidal series and from samples at 40–60 m from within the plume. Open circles denote estuarine data (samples from the estuary), open squares denote coastal data not influenced by the plume (salinity range 30–33), and triangles represent the plume data for transect 10a (salinity range 11–29). (A) Nitrate vs. salinity. The solid line represents conservative mixing between cold, nutrient rich subsurface water and estuarine waters, while the dashed line represents additional mixing of plume water. (B) Total dissolved iron vs. salinity. The dashed line within the estuarine data denotes the removal of total dissolved iron within the inner estuary before entering the plume. The solid line defines the mixing line between the low iron water leaving the estuary and high iron subsurface water which must mix to contribute iron to the observed plume mixtures with warm surface water (dashed line).

4.1.3. Implications for biology

The tidal influence on the chemical characteristics of the freshly formed Columbia River plume is critically important for the distribution of essential macro and micronutrients, nitrate and iron within the plume. Unlike the Californian or Peruvian coasts, where only minimal riverine inputs occur during the summer upwelling season (Bruland et al., 2001; Hutchins et al., 2002), the Columbia River provides a large source of

silicic acid to plume water during the summer upwelling season.

The addition of nitrate and iron to surface plume waters along with the existing elevated silicic acid concentrations allows for extensive blooms of diatoms, resulting in elevated chlorophyll *a* concentrations. Chlorophyll *a* concentrations within the estuary ranged from 5 to 7 µg/l. Concomitant with the decrease in nitrate and iron concentrations within plume waters during the ebb tide, the chlorophyll *a* concentrations increased from ~7 µg/l during the flood tide to 17 µg/l during ebb tide. Therefore, biological drawdown in concert with entrainment of warm, nitrate depleted surface waters resulted in the nitrate depleted (0.3 µM) plume waters during ebb tide. The high phytoplankton biomass of this region as indicated by chlorophyll *a* concentrations of 15–17 µg/l is similar to what has been predicted by satellite images of this area. Due to the mixed semi-diurnal nature of the tides, it appears that both nitrate and iron concentrations within plume waters are enriched on tidal cycles, ensuring that neither nitrate nor iron limitation occurs in the near-field plume.

4.2. Far-field chemical characteristics of the Columbia River plume and implications for the biological demand

A surface drifter was deployed at the mouth of the estuary in order to track a parcel of Columbia River plume water at 1 m depth as it moved offshore. As can be observed in Fig. 6, the plume headed directly offshore before circling over Astoria Canyon. The drifter was deployed after a brief period of upwelling, which caused the plume to move offshore (Garcia-Berdeal et al., 2002). However, immediately after the deployment a strong downwelling event began and remained until the end of the plume drift. Garcia-Berdeal et al. (2002) observed that during downwelling conditions, the Columbia River plume is moved onshore regardless of the direction of the ambient flow, which is typically northward in winter and southward in summer. The currents around Astoria Canyon in combination with the downwelling conditions appeared to have held this parcel of plume water over the canyon.

The plume moved rapidly offshore with a speed of ~1 m s⁻¹ with the majority of mixing occurring over 2–3 h (Nash, personal communication). Due to the nature of the sampling design employed in this study we were unable to resolve the initial mixing of the plume with the surrounding coastal water mass (over the first 2 h). However, the starting sampling point is consistent with that observed during the time series and therefore indi-

cates the initial chemical characteristics of this newly formed plume. Nitrate and dissolved iron concentrations initially in this plume water were indicative of mixing with high salinity, low temperature, nutrient rich water (Fig. 7B,C). As the plume moved offshore both the nitrate and dissolved iron concentrations decreased over time due to mixing with surrounding waters and biological drawdown. Within 2 h the nitrate and dissolved iron had decreased from 12 to 6 μM and from 3.9 to 1.8 nM, respectively (Fig. 7B,C). The salinity had also increased from 17 to 23 (Fig. 7A) thus indicating the large degree of mixing which occurred in the first 2 h.

The salinity of the plume water between 2 and 6 h after deployment however, was similar indicating that, although mixing with surrounding coastal waters had occurred since deployment, this was the same water mass (Fig. 7A). The removal of nitrate and dissolved iron and the simultaneous increase in chlorophyll *a* concentrations during this time period (Fig. 7) indicate that the biological demand is reducing these essential nutrients from the plume. The majority of phytoplankton chlorophyll (>95%) was >5 μm and primarily composed of large chain forming diatoms (Lessard, personal communication). Assuming that coastal diatoms have a cellular Fe/C ratio of 50 $\mu\text{mol}:\text{mol}$ (Bruland et al., 2001; Sunda and Huntsman, 1995) the removal of 3 μM nitrate would require 0.9 nM of iron. A 0.5 nM decrease in dissolved iron was observed, suggesting that iron from other pools may be available such as direct utilization of particle sources (Nodwell and Price, 2001), or utilization of additional dissolved iron produced through photoreduction (Barbeau et al., 2001). Further south, off the coast of Oregon, Chase et al. (2005) observed that during upwelling, the available nitrate was utilized despite low levels of dissolved iron, which would be considered to low to support phytoplankton growth. The balance between solubilization, uptake and sinking of iron was shown to be sufficient to meet phytoplankton demands (Chase et al. 2005).

Within the first 2 h of the plume advecting offshore, the plume was overlying California Current water (Fig. 7), as indicated by a salinity of 29 and sub-micromolar concentrations of nitrate at 10 m. Thus any entrainment from just below the base of the plume (6 m) would not provide an additional source of nitrate. After 8 h the nitrate concentrations at the surface of the plume water were depleted to <0.3 μM while the chlorophyll *a* concentrations increased from 9 to 14 $\mu\text{g/l}$. In addition to the removal of nitrate, dissolved iron concentrations in surface waters of the plume

decreased to 0.4 nM. Although nitrate concentrations are greater than 20 μM at 30 m, without mixing by either upwelling or a storm event, nitrate concentrations in surface waters become depleted due to both mixing with nitrate deplete California Current water and high biological demand.

Unlike nitrate, dissolved iron concentrations were not determined below 8 m, at 5 m values remained relatively constant at 0.7 nM between 2 and 48 h. While at 8 m concentrations decreased from 3.7 nM but were in still excess of 1 nM after 48 h. Although iron concentrations decreased over time due to biological demand and adsorption onto particles, an iron signal still remains in the plume waters. Therefore, it appears that nitrate and not iron will limit biological growth within plume waters as they advect offshore. After 68 h the salinity of the plume water increased to 29.5 by mixing with surrounding coastal waters. Both dissolved iron and nitrate concentrations were also very low <0.1 nM and 0.1 μM , respectively, which is similar to those observed in the California Current water during transect 7 (a far-field plume). Silicic acid concentrations (7 μM) are also similar to those observed in California current water.

During upwelling conditions, the influence of the Columbia River plume was identified by low salinity and high silicate concentrations that extended as far south as 45.33°N, 124.09°W (Fig. 2). Concentrations of silicic acid and dissolved iron in the far-field plume are markedly greater (26 μM and 1.8 nM, respectively) than surrounding surface California Current waters (5 μM and 0.1 nM, respectively), and those observed in upwelled waters that comprised part of transect 7 (18 μM and 0.5 nM, respectively). In contrast, nitrate concentrations of the far-field Columbia River plume were depleted to <0.3 μM , values markedly lower than observed in recently upwelled waters close to shore (13 μM , Fig. 2), or those observed in the near-field plume (15 μM , Fig. 4). The Columbia River plume has high silicic acid to nitrate ratios compared to upwelled waters. During transect 10a, Si/N values range from 31 at salinities of 19 to 7 at salinities of 26 compared to 1.4 in upwelled waters observed during transect 7. Nitrate is more rapidly depleted, while the Columbia River plume serves as a substantial source of silicate to offshore waters as observed in both transect 10 and 7 (Hill and Wheeler, 2002).

Near-field plume waters at a salinity of 19 had nitrate and silicic acid concentrations of 19 μM and 88 μM , respectively (Fig. 3). As this plume moved southwards and offshore, mixing with surrounding surface California Current waters characterized by nitrate

depletion and silicic acid concentrations of 5 μM at salinities of 31 occurred (Fig. 2). During the far-field transect 7, Columbia River plume waters had a salinity of 27 indicating that plume water at a salinity of 19 had mixed with surrounding surface waters at salinities of 31, to give a ratio of one part plume water to two parts surrounding surface waters. The decrease in salinity can be used to constrain the loss of nitrate and silicic acid due to mixing alone. As a result of mixing, the far field Columbia River plume waters would contain 32 μM silicic acid and 6.3 μM nitrate. These values are higher than 27 μM silicic acid and 0.1 μM nitrate observed indicating that some additional biological drawdown contributed to lower the concentrations.

In low iron coastal waters off the coast of California, silicic acid to nitrate assimilation ratios of diatoms are 2–3 but fall to nutrient-replete diatom ratio of ~ 1 (Brzezinski, 1985) when iron is supplied (Hutchins and Bruland, 1998; Fimre et al., 2003). In the case of the Columbia River plume dissolved iron concentrations are elevated (up to 18 nM) compared to coastal waters near California and Oregon (Bruland et al., 2001; Chase et al., 2005) and are therefore not limiting phytoplankton growth. Using a silicic acid to nitrate ratio of 1, the biological drawdown of 19 μM nitrate (observed in transect 10a) would correspond to a decrease in silicic acid concentrations from 88 μM to 69 μM . The effect of both biological removal and mixing with surrounding surface waters in far-field plumes would result in silicic acid concentrations of 26 μM and depleted nitrate concentrations, which is similar to what was observed during transect 7. Therefore, it appears that nitrate is the primary limiting factor for biological growth as these plume waters move offshore.

5. Conclusions

Tidal flow was identified as an important factor in the formation of the chemical constituents of the Columbia River plume. During the rising flood tide, nitrate and dissolved iron concentrations are entrained into plume waters resulting in higher concentrations than observed within the estuary. Conversely, during ebb tide the concentration of both nitrate and dissolved iron decreased in plume waters with a resulting increase in chlorophyll *a* concentrations. In the far field plume, silicic acid is elevated and this signal remains after both biological drawdown and mixing. It appears that neither dissolved iron nor silicic acid concentrations were limiting phytoplankton growth during this study, and that nitrate was the primary limiting factor in plume waters as they moved offshore. Without additional sources of

nitrate from an upwelling event or mixing from below the nitricline these far-field plume waters lack sufficient nitrate to fuel significant phytoplankton growth.

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References

- Barbeau, K., Rue, E.L., Bruland, K.W., Butler, A., 2001. Photochemical cycling of iron in the surface ocean mediated by microbial iron(III)-binding ligands. *Nature* 413, 409–413.
- Barnes, C.A., Pierce, S.D., Morse, B.A., 1972. Circulation and selected properties of the Columbia River effluent at sea. In: Pruter, A.T., Alverson, D.L. (Eds.), *The Columbia River Estuary and Adjacent Ocean Waters*. Univ. of Washington Press, Seattle, WA, pp. 41–80.
- Boyle, E.A., Edmond, J.M., Sholkovitz, E.R., 1977. The mechanism of iron removal in estuaries. *Geochim. Cosmochim. Acta* 41, 1313–1324.
- Brzezinski, M.A., 1985. The Si–C–N ratio of marine diatoms—Inter-specific variability and the effect of some environmental variables. *J. Phycol.* 21, 347–357.
- Bruland, K.W., Rue, E.L., Smith, G.J., 2001. Iron and macronutrients in California coastal upwelling regimes: implications for diatom blooms. *Limnol. Oceanogr.* 46, 1661–1674.
- Bruland, K.W., Rue, E.L., Smith, G.J., DiTullio, G.R., 2005. Iron macronutrients and diatom blooms in the Peru upwelling regime: brown and blue waters of Peru. *Mar. Chem.* 93, 83–103.
- Colbert, D., McManus, J., 2003. Nutrient biogeochemistry in an upwelling-influenced estuary of the Pacific Northwest (Tillamook Bay, Oregon, USA). *Estuaries* 26, 1205–1219.
- Conomos, T.J., Groos, M.G., Barnes, C.A., Richards, F.A., 1972. River-ocean nutrient relations in summer. In: Pruter, A.T., Alverson, D.L. (Eds.), *The Columbia River Estuary and Adjacent Ocean Waters*. Univ. of Washington Press, Seattle, WA, pp. 151–175.
- Chase, Z., Hales, B., Cowles, T., 2005. Distribution and variability of iron input to Oregon coastal waters during the upwelling season. *J. Geophys. Res.* 110, C10512.
- Croot, P.L., Hunter, K.A., 2000. Labile forms of iron in coastal seawater. Otago Harbour, New Zealand. *Mar. Freshw. Res.* 51, 193–203.

- Dagg, M., Benner, R., Lohrenz, S., Lawrence, D., 2004. Transformation of dissolved and particulate material on continental shelves influenced by large rivers: plume processes. *Cont. Shelf Res.* 24, 833–858.
- Donat, J.R., Bruland, K.W., 1988. Direct determination of dissolved cobalt and nickel in seawater by differential pulse cathodic stripping voltammetry preceded by adsorptive collection of cyclohexane-1,2-dione dioxime complexes. *Anal. Chem.* 60, 240–244.
- Fielder, P.C., Laurs, R.M., 1990. Variability of the Columbia River plume observed in visible and infrared satellite imagery. *Int. J. Remote Sens.* 11, 999–1010.
- Firme, G.F., Bruland, K.W., Rue, E.L., Weeks, D.A., Hutchins, D.A., 2003. Spatial and temporal variability in phytoplankton iron limitation along the California Coast and consequences for Si, N and C biogeochemistry. *Glob. Biogeochem. Cycles* 17, 1016.
- Fuhrer, G., Tanner, G., Morance, J., McKenzie, S., Skach, K., 1996. Water quality of the lower Columbia River basin: analysis of current and historical water-quality data through 1994. U.S.G.S., Portland, Or.
- Garcia-Berdeal, I., Hickey, B.M., Kawase, M., 2002. Influences of wind stress and ambient flow on a high discharge river plume. *J. Geophys. Res.* 107, 3130.
- Harrison, P.J., Clifford, P.J., Cochlan, W.P., Yin, K., Stjohn, M.A., Sibbald, M.J., Albright, L.J., 1991. Nutrient and plankton dynamics in the Fraser-River plume, Strait of Georgia, British Columbia. *Mar. Ecol. Prog. Ser.* 70, 291–304.
- Hickey, B.M., 1998. Coastal oceanography of Western North America from the tip of Baja California to Vancouver IS. In: Brink, K.H., Robinson, A.R. *The Sea*, vol. 11. Wiley and Sons, Inc., New York, pp. 345–393.
- Hickey, B.M., Banas, N.S., 2003. Oceanography of the US Pacific Northwest Coastal Ocean and Estuaries with application to coastal ecology. *Estuaries* 26, 1010–1031.
- Hill, J.K., Wheeler, P.A., 2002. Organic carbon and nitrogen in the northern California current system: Comparison of offshore, river plume, and coastally upwelled waters. *Prog. Oceanogr.* 53, 369–387.
- Hutchins, D.A., Bruland, K.W., 1998. Iron-limited diatom growth and Si:N uptake ratios in a coastal upwelling regime. *Nature* 393, 561–564.
- Hutchins, D.A., DiTullio, G., Zhang, Y., Bruland, K.W., 1998. An iron limitation mosaic in the California upwelling regime. *Limnol. Oceanogr.* 43, 1037–1054.
- Hutchins, D.A., Hare, C.E., Weaver, R.S., Zhang, Y., Firme, G.F., DiTullio, G.R., Alm, M.B., Riseman, S.F., Maunicher, J.M., Geesey, M.E., Trick, C.G., Smith, G.J., Rue, E.L., Bruland, K.W., 2002. Phytoplankton and iron limitation in Humboldt current and Peru upwelling. *Limnol. Oceanogr.* 47, 997–1011.
- Jay, D.A., Smith, J.D., 1990. Circulation, density distribution and neap-spring transitions in the Columbia River Estuary. *Prog. Oceanogr.* 25, 81–112.
- Johnson, K.S., Chavez, F.P., Friederich, G.E., 1999. Continental-shelf sediment as a primary source of iron for coastal phytoplankton. *Nature* 398, 697–700.
- Johnson, K.S., Chavez, F.P., Elrod, V.A., Fitzwater, S.E., Pennington, J.T., Buck, K.R., Walz, P.M., 2001. The annual cycle of iron and the biological response in central California coastal waters. *Geophys. Res. Lett.* 28, 1247–1251.
- Landry, M.R., Postel, J.R., Peterson, W.K., Newman, J., 1989. Broad-scale patterns in the distribution of hydrographic variables. In: andry, M.R., Hickey, B.M. (Eds.), *Coastal Oceanography of Washington and Oregon*. Elsevier Press, Amsterdam, Netherlands, pp. 1–10.
- Lohan, M.C., Aguiar-Islas, A.M., Franks, R.P., Bruland, K.W., 2005. Determination of iron and copper in seawater at pH 1.7 with a new commercially available chelating resin, NTA Superflow. *Anal. Chim. Acta* 530, 121–129.
- Lohan, M.C., Aguiar-Islas, A.M., Bruland, K.W., Submitted for publication. Direct determination of iron in acidified (pH 1.7) seawater samples by flow injection catalytic spectrophotometric detection: application and intercomparison. Submitted to *Limnology and Methods*.
- Mayer, L.M., 1982. Retention of riverine iron in estuaries. *Geochim. Cosmochim. Acta* 46, 1003–1009.
- Measures, C.I., Yuan, J., Resing, J.A., 1995. Determination of iron in seawater by flow injection analysis using in-line preconcentration and spectrophotometric detection. *Mar. Chem.* 50, 3–12.
- Nodwell, L.M., Price, N.M., 2001. Direct use of inorganic colloidal iron by marine mixotrophic phytoplankton. *Limnol. Oceanogr.* 46, 765–777.
- Orton, P.M., Jay, D.A., 2005. Observations at the tidal plume front of a high volume river outflow. *Geophys. Res. Lett.* 32, L11605.
- Parsons, T.R., Maita, Y., Lalli, C.M., 1984. *A Manual of Chemical and Biological Methods for Seawater Analysis*. Pergamon Press.
- Shiller, A.M., Boyle, E.A., 1991. Trace elements in the Mississippi River delta outflow region: behavior at high discharge. *Geochim. Cosmochim. Acta* 55, 3241–3251.
- Small, L.F., McIntire, C.D., MacDonald, K.B., Laralara, J.R., Frey, B.E., Amspoker, M.C., Winfield, T., 1990. Primary production, plant and detrital biomass and particulate transport in the Columbia River estuary. *Prog. Oceanogr.* 25, 175–210.
- Sunda, W.G., Huntsman, S.A., 1995. Iron uptake and growth limitation in oceanic and coastal phytoplankton. *Mar. Chem.* 50, 189–206.
- Thomas, A., Strub, P.T., 2001. Cross-shelf phytoplankton pigment variability in the California Current. *Cont. Shelf Res.* 21, 1157–1190.
- Warrick, J.A., Washburen, L., Brzezinski, M.A., Siegel, D.A., 2005. Nutrient contributions to the Santa Barbara Channel, California, from the ephemeral Santa Clara River. *Estuar. Coast. Shelf Sci.* 62, 559–574.
- Wells, M.L., Mayer, L.M., 1991. Variations in the chemical lability of iron in estuarine, coastal and shelf waters and its implications for phytoplankton. *Mar. Chem.* 32, 195–210.