



Factors influencing the chemistry of the near-field Columbia River plume: Nitrate, silicic acid, dissolved Fe, and dissolved Mn

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[1] Factors influencing concentrations of nitrate, silicic acid, dissolved Fe, and dissolved Mn in the near-field Columbia River plume were examined during late spring and summer from 2004 to 2006 as part of the River Influences on Shelf Ecosystems program. Under upwelling-active phases, cold, high-nitrate coastal seawater was entrained in the plume, and nitrate concentrations of 16–19 μM were observed with as much as 90% from a coastal seawater origin. Under downwelling-relaxation phases, warm, nutrient-depleted coastal seawater was entrained forming a near-field plume with nitrate concentrations of 2.5–6 μM , with the river as the only source. Elevated silicic acid in the river is the dominant source, with concentrations of 60–80 μM in the near-field plume. During upwelling-active phases, high concentrations of dissolved Fe (as high as 40 nM) in the cold, low-oxygen, nutrient-rich coastal seawater were entrained to form a near-field plume with 15–20 nM dissolved Fe. During downwelling-relaxation phases, dissolved Fe in the intruding underlying warm coastal seawater was 1–3 nM, producing plume concentrations of 2–13 nM, with higher concentrations during the high river flow of May 2006. Dissolved Mn in the near-field plume covaried markedly as a function of increased tidal flushing in the estuary. The use of CORIE (pilot environmental observation and forecasting system for the Columbia River) time series conductivity-temperature-depth data within the estuary, along with data presented in this study, allows extrapolation of the near-field plume chemistry throughout the spring and summer seasons to provide insight into this important source of nutrients to the coastal waters in this region.

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1. Introduction

[2] The Columbia River is the largest river entering the eastern boundary of the North Pacific Ocean [Thomas and Weatherbee, 2006], and during the summer it contributes ~90% of the freshwater entering the California Current system along the U.S. west coast between the Strait of Juan de Fuca and San Francisco Bay [Barnes et al., 1972]. The Columbia River plume is an important feature off the Washington and Oregon coasts, and is characterized by a shallow (~2–20 m) surface lens of low-salinity water. During sustained upwelling conditions this buoyant plume

tends to move offshore and southward, while during downwelling conditions the plume moves northward and nearshore forming a narrow coastal jet [Landry et al., 1989; Hickey et al., 2005]. During wind reversals, the plume can be bidirectional [Hickey et al., 2005, 2008]. With a shift from equatorward upwelling winds to poleward downwelling winds, the southwest plume moves onshore over the Oregon shelf concurrent with the rapid formation of a nearshore northward flowing plume. In contrast, with the onset of upwelling favorable winds, the northward plume advects and mixes offshore over the Washington shelf while a southwest flowing plume is rapidly initiated.

[3] The Columbia River plume is an important source of macro- and micronutrients to the coastal waters off Washington and Oregon [Hill and Wheeler, 2002; Lohan and Bruland, 2006; Aguilar-Islas and Bruland, 2006], thus directly impacting the lowest trophic levels (R. M. Kudela and T. D. Peterson, Influence of a buoyant river plume on phytoplankton nutrient dynamics: What controls standing stocks and productivity?, submitted to *Journal of Geophysical Research*, 2008). The near-field Columbia River plume entering the coastal waters generally has a salinity of 10–25, composed of roughly two-thirds to one-fourth Columbia

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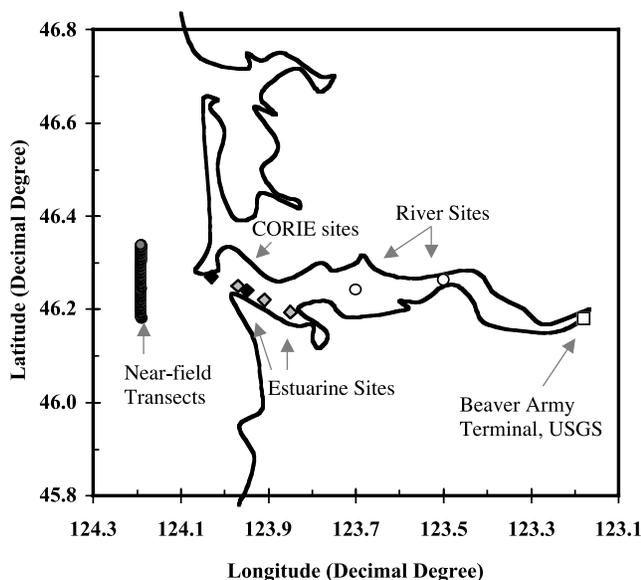


Figure 1. Location of stations used in this study. Surface transect across the near-field plume is indicated by the gray circle. RISE estuarine stations are indicated by the gray diamonds. CORIE CTD stations are indicated by the black diamonds. RISE river stations are indicated by the white circles. USGS NASQAN river station is indicated by the white square.

River water and one-third to three-fourths coastal seawater, varying with the magnitude of both tidal mixing and freshwater river input (J. D. Nash et al., Turbulent mixing in the Columbia River Estuary: Structure and consequences for plume composition, submitted to *Journal of Geophysical Research*, 2008). The entrainment and mixing of this coastal seawater with Columbia River water to form the near-field plume takes place both within, and at or near the mouth of the estuary [Barnes et al., 1972; Nash et al., submitted manuscript, 2008]. The chemistry of the river water coastal seawater, and estuarine water that mix to form the plume vary temporally as a function of season, oceanographic conditions, tidal phase and river flow. As a result, the chemistry of the near-field plume can vary markedly with changes in these conditions.

1.1. Columbia River Freshwater End-Member

[4] The character of the Columbia River varies on a seasonal and interannual basis. Daily values of river discharge and approximately monthly sampling of temperature, nitrate and silicic acid at the Beaver Army Terminal station (RM53), near Quincy, Oregon (Figure 1) over the last decade are reported by the U.S. Geologic Survey's National Stream Water Quality Network (<http://water.usgs.gov/nasqan/data/finaldata/beaver.html>) and are presented in Figure 2. The temperature of the Columbia River increases through the spring to a maximum of 20–23°C in July and August (Figure 2b). Nitrate concentrations in the Columbia River (Figure 2a) are at a maximum in winter (concentrations up to 50 μM), coincident with high winter rainfall and high flow from coastal tributaries draining the coastal subbasin joining the Columbia River west of the Cascade mountain range. Nitrate concentrations decrease markedly

through April and May, and usually reach a minimum of 2–10 μM in June and July (Figure 2a). The silicic acid concentration in the river is high all year (140–240 μM), with minimum concentrations (140–150 μM) in the summer months (Figure 2b). The Columbia River is relatively unique for major rivers in being silicic acid rich and relatively nitrate poor during the summer months, with silicic acid:nitrate ratios ranging from 10 to 50. In contrast, the Mississippi River and other major rivers in North America and Europe have become nitrate rich because of anthropogenic inputs of fixed nitrogen, and their silicic acid:nitrate ratio has dropped to ≤ 1 because of the marked increase in nitrate [Cloern, 2001].

1.2. Coastal Seawater End-Member

[5] The coastal seawater at the mouth of the Columbia River is mixed with river water within and/or near the mouth of the estuary to form the near-field Columbia River plume [Barnes et al., 1972; Jay et al., 1990; Nash et al., submitted manuscript, 2008; E. D. Zaron and D. A. Jay, Mixing in the tidal plume of the Columbia River, submitted to *Journal of Geophysical Research*, 2008]. The seawater source mixing to form the near-field plume is found at depths of 5–20 m near the mouth of the estuary in the core of the entering salt wedge or underlying seawater. Fluctuations in the properties of this coastal seawater end-member correspond to fluctuations in the strength and persistence of regional-scale synoptic winds and local coastal upwelling activity [Hickey et al., 2006]. The upwelling-favorable, equatorward, wind stress can impact the chemistry of the plume by bringing cold, higher-salinity, low-oxygen, nutrient-rich water up the shelf to shallow depths at the mouth of the estuary to be entrained with the river water. Stefansson and Richards [1963] and Hickey et al. [2008] have reported that such upwelling conditions are an important process adding nutrients to the surface waters off the northern Washington coast because of entrainment of nutrient-rich subsurface waters by the estuarine-like circulation in the Straits of Juan de Fuca. Monteiro and Largier [1999], in a study of the Saldanha Bay in the Benguela upwelling system, have referred to this upwelling situation supplying cold, nutrient-rich water to be entrained into the Bay as an “active phase.” The reverse situation was termed the “relaxation phase.” In this situation, downwelling favorable winds can result in warm, lower-salinity, nutrient-depleted coastal surface waters being observed at depths of 5–20 m at the mouth of the estuary.

[6] This variation of the coastal seawater end-member, alternating back and forth between cold, nutrient-rich, higher-salinity waters during upwelling-active phases and warm, nutrient poor, lower-salinity waters during downwelling-relaxation phases, can be ecologically critical in supplying macro and micronutrients to the Columbia River plume (Kudela and Peterson, submitted manuscript, 2008). In addition to influencing the supply of nitrate and silicic acid to the plume [Lohan and Bruland, 2006; Aguilar-Islas and Bruland, 2006], variations in the coastal seawater source can influence dissolved Fe concentrations [Lohan and Bruland, 2006].

[7] The focus of this study is to examine how these changes in the chemistry of river and coastal water end-members, together with the tidal conditions and river

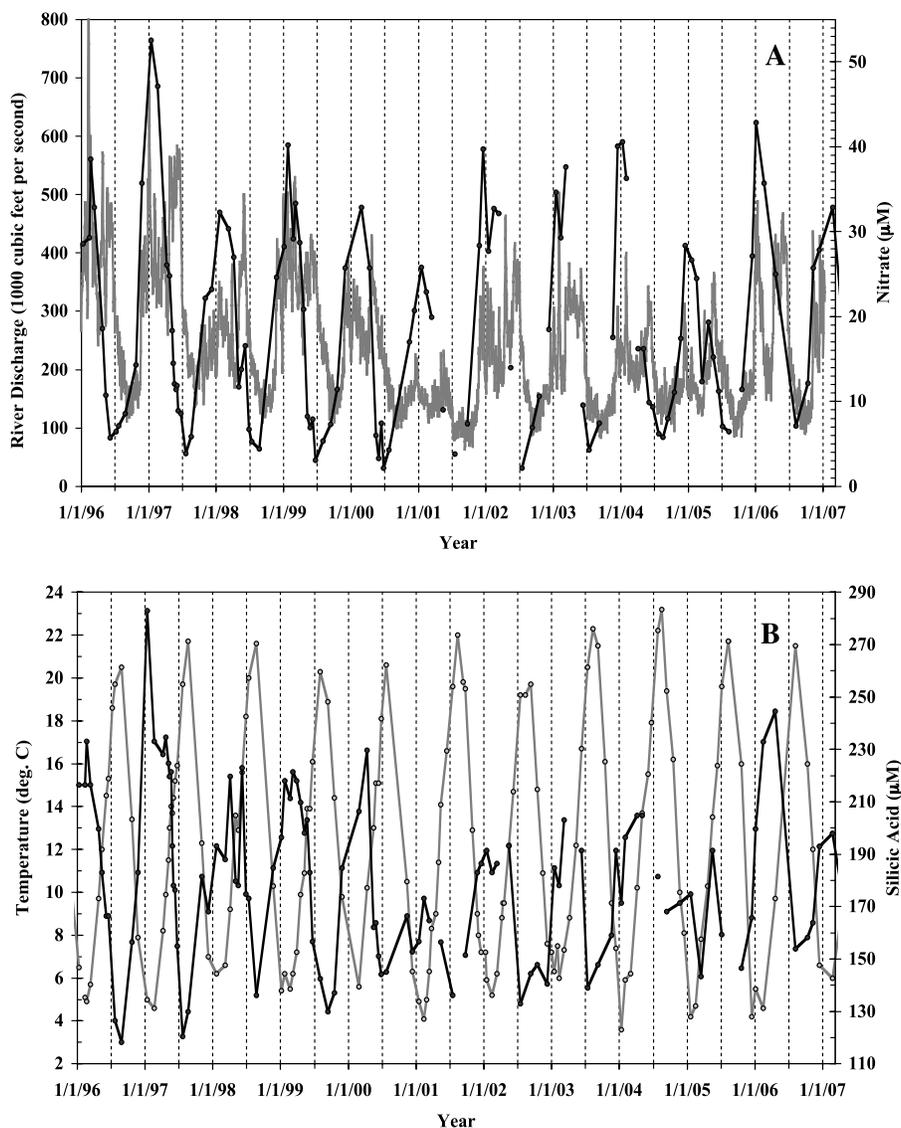


Figure 2. Data from the US Geological Survey’s National Stream Water Quality Network at the Beaver Army Terminal station near Quincy, Oregon. Daily data on (a) river discharge (in gray) and approximately monthly data on nitrate (in black) and (b) temperature (in gray) and silicic acid (in black).

discharge, can influence the macronutrient, and dissolved Fe and Mn chemistry of the near-field Columbia River plume. The coastal ocean processes River Influence on Shelf Ecosystems (RISE) program provided a unique opportunity to examine the formation of the near-field plume during varying conditions in late spring and summer periods of 2004–2006. In addition to the selective observations made during the RISE cruises, the continuous time series of temperature and salinity from conductivity-temperature-depths (CTDs) located at ~ 7 m depth at CORIE (pilot environmental observation and forecasting system for the Columbia River) stations provides information from within the estuary that can be used as an indication of the local upwelling conditions and to predict likely plume nutrient characteristics during longer temporal scales. CORIE [Baptista, 2006] is an end-to-end observatory for the Columbia River estuary and plume, with an extensive observation network of physical parameters coupled with a

semioperational modeling system [Baptista *et al.*, 2005; Y. J. Zhang *et al.*, Daily forecasts of Columbia River plume circulation: A tale of spring/summer cruises, submitted to *Journal of Geophysical Research*, 2008], both served by and integrated through flexible cyberinfrastructure [Howe *et al.*, 2007; L. Bright, D. Maier, and B. Howe, Managing the forecast factory, Proceedings of the 22nd ICDE Workshop on Workflow and Data Flow for Scientific Applications, 2006, available at http://web.cecs.pdx.edu/~bright/papers/factory_final.pdf].

2. Methods

2.1. Sample Collection

[8] Sampling off the coasts of Washington and Oregon was accomplished during five research cruises as part of the collaborative RISE program. The pre-RISE cruise was aboard the R/V *Point Sur* and took place from 27 June to

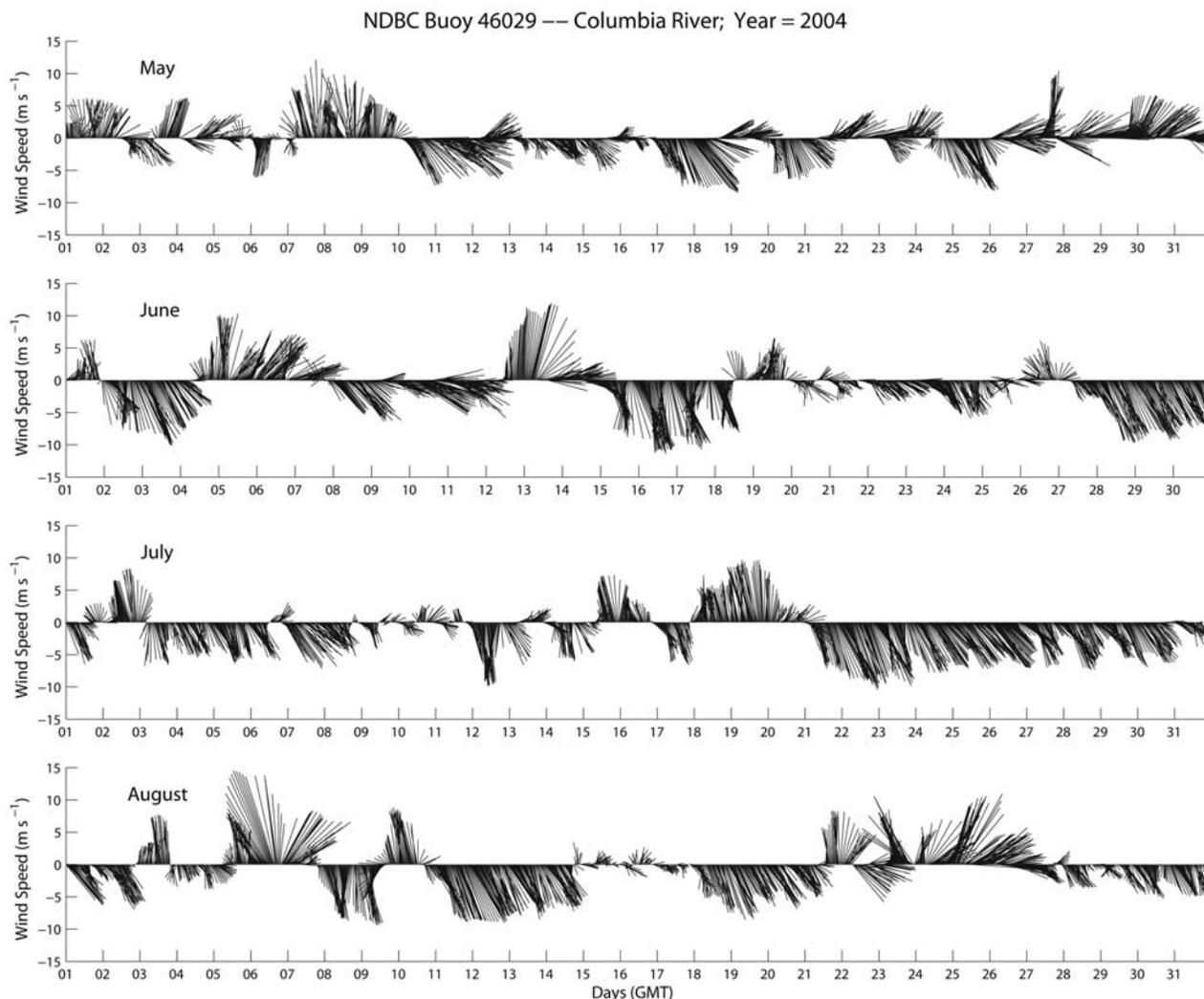


Figure 3a. Wind vector plots at the NDBC Buoy 46029 located just off the mouth of the Columbia River in the vicinity of the near-field plume surface transect. The stick plots depict both the wind speed and direction (positive direction is poleward/downwelling and negative direction is equatorward/upwelling) for the months of May–August for 2004.

2 July 2004. All other research cruises were on board the R/V *Wecoma*, with RISE-1W from 8 to 23 July 2004, RISE-2W from 29 May to 20 June 2005, RISE-3W from 4 to 26 August 2005, and RISE-4W from 21 May to 11 June 2006. Surface samples were collected with a clean surface pump “fish” system [Bruland *et al.*, 2005] equipped with a YSI 600 OMS CTD sonde. The sonde was calibrated against the ship’s calibrated Sea-Bird Electronics SBE 911plus Conductivity, Temperature, and Depth system [Hickey *et al.*, 2008]. Samples for dissolved trace metals were filtered in-line through acid-cleaned 0.45 μm pore size Teflon[™] membrane polypropylene capsule filters (GE Osmonics) [Bruland *et al.*, 2005]. Vertical profiles down to approximately 20 m were collected with the fish, and deeper samples were collected with Teflon[™] coated GO-Flo samplers (General Oceanics) deployed on Kevlar[™] hydro-line [Bruland *et al.*, 1979].

2.2. Analytical Methods

[9] Macronutrients (nitrate + nitrite (referred to herein as nitrate), silicic acid and phosphate) were measured on a Lachat QuikChem 8000 Flow Injection Analysis system using standard colorimetric methods [Parsons *et al.*, 1984]. Samples for the determination of dissolved Fe and Mn were acidified to $\text{pH} \sim 1.7\text{--}1.8$ using subboiled quartz distilled 6 N hydrochloric acid (Q-HCl) (using the equivalent of 4 ml acid per liter of seawater; 0.024 M HCl), and were allowed to sit for at least 30 min after acidification prior to analysis. Dissolved Fe and Mn were determined onboard ship by flow injection (FI) methods involving in-line preconcentration, catalytic enhancement with Fe or Mn acting as a catalyst for the formation of a colored end product, and spectrophotometric detection. Details are found elsewhere (Fe [Lohan *et al.*, 2006] and Mn [Aguilar-Islas *et al.*, 2006]).

[10] Analytical figures of merit for the various techniques include estimates of accuracy within 4% for dissolved Fe

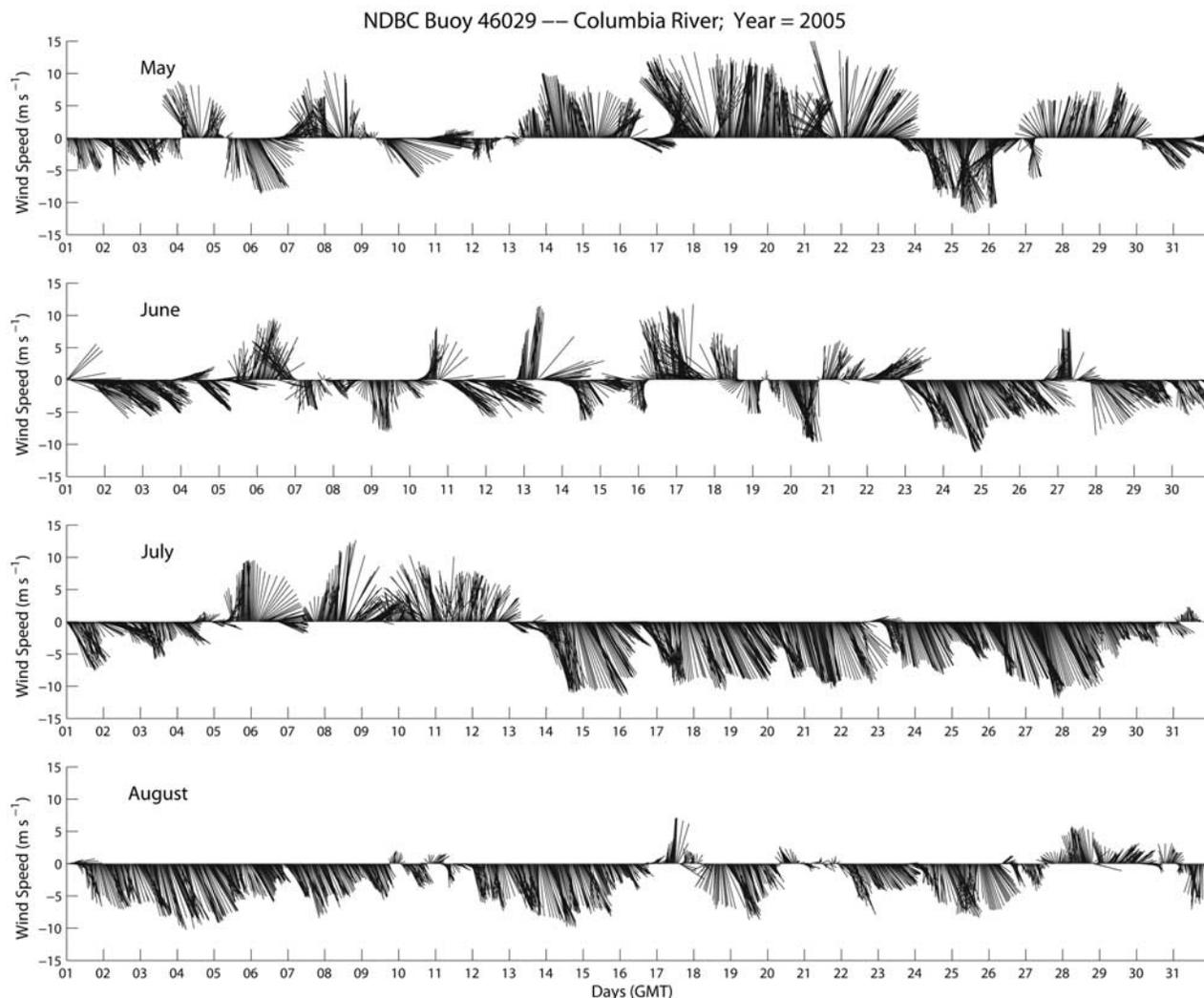


Figure 3b. Wind vector plots at the NDBC Buoy 46029 located just off the mouth of the Columbia River in the vicinity of the near-field plume surface transect. The stick plots depict both the wind speed and direction (positive direction is poleward/downwelling and negative direction is equatorward/upwelling) for the months of May–August for 2005.

based upon analyses of SAFE standards, within 3% for dissolved Mn based upon analysis of NASS-4, and within 4%, 3%, and 5% for nitrate (+nitrite), phosphate and silicic acid (respectively) on MOOS-1, CRM (NRC). Estimates of precision are on the order of 5% for dissolved Fe and Mn, and 2% for macronutrients. Detection limits are 0.02 nM dissolved Fe, 0.5 nM dissolved Mn, 0.05 μM nitrate (+nitrite), 0.03 μM phosphate and 0.2 μM silicic acid.

3. Results

[11] Results from the five RISE cruises are presented in a chronological fashion starting with the pre-RISE cruise in early July 2004 and ending with the RISE-4W cruise in May 2006. The results presented herein consist of data collected in the river, the estuary, and coastal waters in the vicinity of the near-field plume, both within the near-field plume and just outside it (see Figure 1 for station locations). The time series data for winds (Figures 3a–3c) and temperature and salinity from stations within the estuary (e.g., Figures 4, 7, and 11) provide a longer-term perspective

(mid-May–August of each year) to the cruise data collected during selective short time periods of these months. Wind directions and velocities at the Columbia River buoy (B46029) located just offshore of the mouth of the Columbia River for the months of May–August for 2004–2006 provide a measure of the local wind stress and are generally consistent with the regional forcing in this area (Figures 3a–3c). The “stick plots” in the negative direction are equatorward, upwelling favorable winds, while the winds in the positive direction are poleward, downwelling favorable. The temperature of the river increases from May to July, and the maximum temperature observed in the daily estuary time series reflects this increased temperature of the river end-member. There is also a neap/spring tidal cycle with slightly cooler daily temperatures (and higher salinities) observed at these lower estuary stations during spring tides.

3.1. Data From 2004

[12] A time series of temperature data from the estuarine station at Jetty A for mid-May through the end of August 2004 (Figure 4) indicated that an upwelling-active

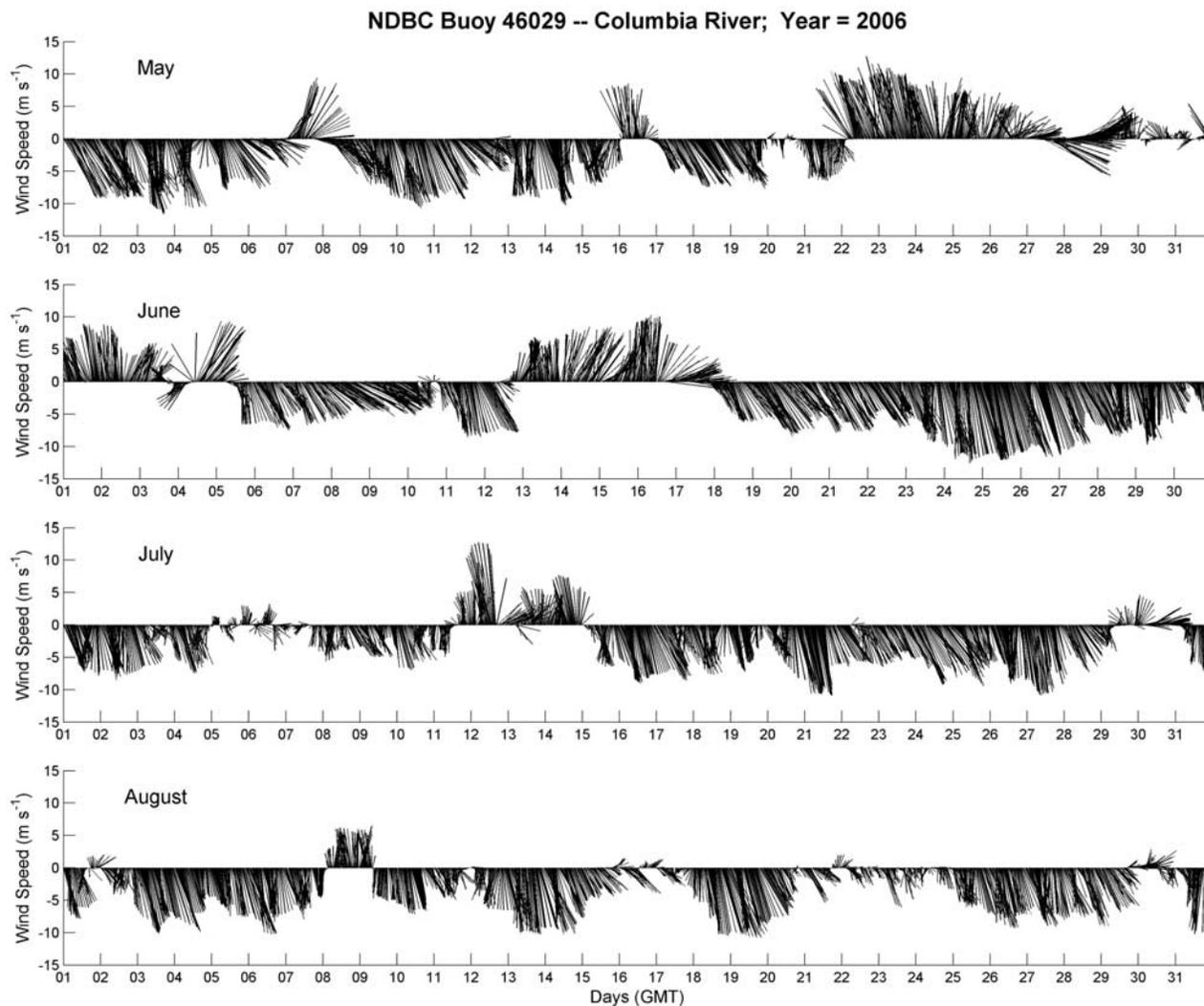


Figure 3c. Wind vector plots at the NDBC Buoy 46029 located just off the mouth of the Columbia River in the vicinity of the near-field plume surface transect. The stick plots depict both the wind speed and direction (positive direction is poleward/downwelling and negative direction is equatorward/upwelling) for the months of May–August for 2006.

phase existed during July, with the exception of a short downwelling-relaxation phase during 20–21 July. Temperature/salinity plots corresponding to our two sampling periods (2 and 21 July) are also presented in Figure 4. A period of strong upwelling favorable winds from the north during 28 June to 2 July preceded the 2 July pre-RISE sampling date and Figure 4 shows that the coastal seawater mixing with the Columbia River water was cold (9°C) with a high salinity (33.5).

[13] A period of strong downwelling favorable winds took place on July 16 and again from 18 to 21 July (Figure 3a). The temperature of the coastal seawater mixing to form the plume rose markedly starting on 18 July (e.g., the rise in daily low temperature within the estuary as shown in Figure 4) with a corresponding drop in salinity, and by 20 July a downwelling-relaxation phase had occurred where the temperature of the coastal seawater being mixed with the river water increased to 14°C and the salinity decreased to 31.5. On 21 July the winds had switched back to be from the north and by 22 July an upwelling-active phase once again

prevailed with cold, higher-salinity coastal seawater mixing with the river water to form the plume. Cruise data from the estuary and near-field plume were obtained on 2 July during the pre-RISE cruise and on 21 July during RISE-1W and correspond to the dates with temperature/salinity plots shown in Figure 4.

[14] The pre-RISE cruise data from 2 July 2004 are representative of the upwelling-active phase prevalent during most of the month of July 2004 and were collected during an intense spring tide. Figure 5a shows that river water of 20.5°C was mixing with cold (8.5° to 9.0°C) coastal seawater intruding into the estuary to form a plume of salinity 20 and a temperature of 13.0 – 13.5°C . In this case 61% of the plume was coastal seawater, and 39% was Columbia River water. Figure 5b shows that silicic acid-rich Columbia River water with a concentration of $155\ \mu\text{M}$ was mixing with cold, nutrient-rich seawater with $35\ \mu\text{M}$ silicic acid to form a plume of salinity 20 with $\sim 80\ \mu\text{M}$ silicic acid. The plume had 74% of its silicic acid from the river source and 26% from the seawater source. The plot of salinity versus nitrate

(Figure 5c) shows river water with only a few μM nitrate mixing with cold, nutrient-rich upwelled water with $\sim 26 \mu\text{M}$ nitrate to form a plume with a salinity of 20 and a nitrate concentration of $\sim 16 \mu\text{M}$. In this case, 95% of the elevated nitrate in the plume had a coastal seawater source associated with the upwelling-active conditions and only 5% came from the Columbia River.

[15] The upwelling-active phase during and preceding the pre-RISE 2 July sampling period, together with the spring tide conditions, resulted in the on-shelf benthic boundary layer transport of low temperature, higher-salinity, low-oxygen, high-nutrient, and high-iron water up onto the inner shelf to depths of 5–20 m near the mouth of the estuary, and it was this upwelled water that was mixing with the Columbia River to form the plume. Figure 5d shows the elevated dissolved iron concentrations of 30–40 nM in this near bottom water being mixed with relatively low dissolved iron water within the estuary. Dissolved Fe behaves nonconservatively within the low-salinity region of the estuary and there is evidence of flocculation and removal of dissolved Fe coming from the river source [Buck *et al.*, 2007]. The plume water at a salinity of 20 has $\sim 16 \text{ nM}$ dissolved iron that appears to be coming primarily from the coastal seawater source in this upwelling-active phase. The dissolved Mn concentrations in the plume were $\sim 200 \text{ nM}$, values much greater than observed in either the river or lower-salinity regions of the estuary, or in the cold, nutrient-rich seawater forming the salt wedge (Figure 5e). Dissolved Mn also behaves nonconservatively within the estuary, but in contrast to dissolved Fe, there is evidence of an estuarine input of dissolved Mn that correlates with tidal amplitude [Aguilar-Islas and Bruland, 2006]. It appears that under intense spring tide conditions the added turbulence within the estuary results in elevated dissolved Mn.

[16] The RISE-1W data from 21 July 2004 are from a downwelling-relaxation phase during a neap tide cycle. Figure 6a illustrates that river water of 22°C was mixing with warm (15°C) coastal seawater to form a plume of salinity 20 with a temperature of $17.0\text{--}17.5^\circ\text{C}$. At a salinity of 20, 60% of the plume was coastal seawater and 40% was Columbia River water. Figure 6b shows that river water of $160 \mu\text{M}$ silicic acid was mixing with warm, nutrient depleted seawater with $< 3 \mu\text{M}$ silicic acid to form a plume of salinity 20 with $\sim 60 \mu\text{M}$ silicic acid. In this case the plume obtained essentially all of its silicic acid from the river source. The plot of salinity versus nitrate (Figure 6c) shows river water with $\sim 5 \mu\text{M}$ nitrate mixing with warm, nutrient depleted water with $< 1 \mu\text{M}$ nitrate to form a plume with a salinity of 20 and a nitrate concentration of $\sim 3 \mu\text{M}$. In this case the source of the low concentration of nitrate present in the plume was from the Columbia River.

[17] The downwelling-relaxation phase during the RISE-1W 21 July sampling period meant that warm, lower-salinity, nutrient-depleted coastal seawater with relatively low dissolved Fe concentrations was being drawn into the Columbia River estuary to mix and form the plume. Figure 6d shows low dissolved iron concentrations of only 1 or 2 nM in this coastal water at depths of 5–20 m being mixed with low dissolved iron water within the estuary. Again, dissolved Fe behaves nonconservatively within the low-salinity region of the estuary, and there is evidence of removal of dissolved Fe coming from the river source. The plume water

at a salinity of 20 has only 2 or 3 nM dissolved Fe. These concentrations are an order of magnitude less than the dissolved iron concentrations observed in the plume during the upwelling-active phase of the pre-RISE cruise. The dissolved Mn concentrations in the plume were $\sim 50 \text{ nM}$, a concentration much lower than observed earlier in the month, but much greater than observed in the warm, nutrient-poor coastal seawater and similar to the concentrations within the low-salinity regions of the estuary (Figure 6e). It appears that, under these lower-energy neap tide conditions, the estuary was a much reduced source of dissolved Mn to the plume.

3.2. Data From 2005

[18] Cruise data were obtained on 5–7 June and 12–13 June during the RISE-2W cruise, and on 18–20 August during RISE-3W. The period in 2005 from mid-May to mid-July was characterized as a downwelling-relaxation phase with warm surface water mixing with the river water (Figure 7). During these two months there were sustained periods of either winds from the south or low winds resulting in the continuous downwelling-relaxation phase (Figures 3b and 7). On 14 July 2005 strong winds from the north picked up and were sustained almost continuously through the rest of July and into mid-August. Within a few days after the initiation of these strong winds from the north, cold, higher-salinity water was observed to be mixing with the river water and the system had entered into an upwelling-active phase.

[19] The RISE-2W data from 5 to 7 June 2005 are within the long-term downwelling-relaxation phase and during an intermediate tidal cycle. During this sampling interval the winds were from the south (Figure 3b). Although there had been a few days preceding this sampling period with relatively weak winds from the northwest, it was not enough for the system to move all the way into an upwelling-active phase (Figure 7). Figure 8a shows that river water of $\sim 16^\circ\text{C}$ was mixing with warm (14°C), low-salinity (~ 30) coastal seawater to form a plume of salinity 12–20 and a temperature of $\sim 15^\circ\text{C}$. Figure 8b shows that river water of $205 \mu\text{M}$ silicic acid was mixing with warm, nutrient depleted seawater with $< 3 \mu\text{M}$ silicic acid to form a plume that at a salinity of 15 had a concentration of $\sim 103 \mu\text{M}$ silicic acid. The plot of salinity versus nitrate (Figure 8c) shows river water with $17\text{--}18 \mu\text{M}$ nitrate mixing with warm, nutrient depleted water with $< 1 \mu\text{M}$ nitrate to form a plume with a salinity of 15 and a nitrate concentration of $\sim 9 \mu\text{M}$. In this case, the nitrate concentration in the river was anomalously high compared with the historical data (Figure 2a) and most of the nitrate in the plume had a river source.

[20] Relatively low dissolved Fe concentrations of 3–5 nM in subsurface waters were being mixed with relatively low dissolved Fe concentrations within the estuary (Figure 8d). The plume water at a salinity of 15 had 8–12 nM dissolved iron. The dissolved Mn concentrations in the plume ranged from 50 to 100 nM with a value of $\sim 80 \text{ nM}$ at a salinity of 15. These dissolved Mn concentrations in the plume were greater than those observed in the warm, nutrient poor seawater and also higher than in the lower-salinity regions of the estuary (Figure 8e).

[21] The RISE-2W data from 12 to 13 June 2005 are also from a downwelling-relaxation phase, but coincided with a

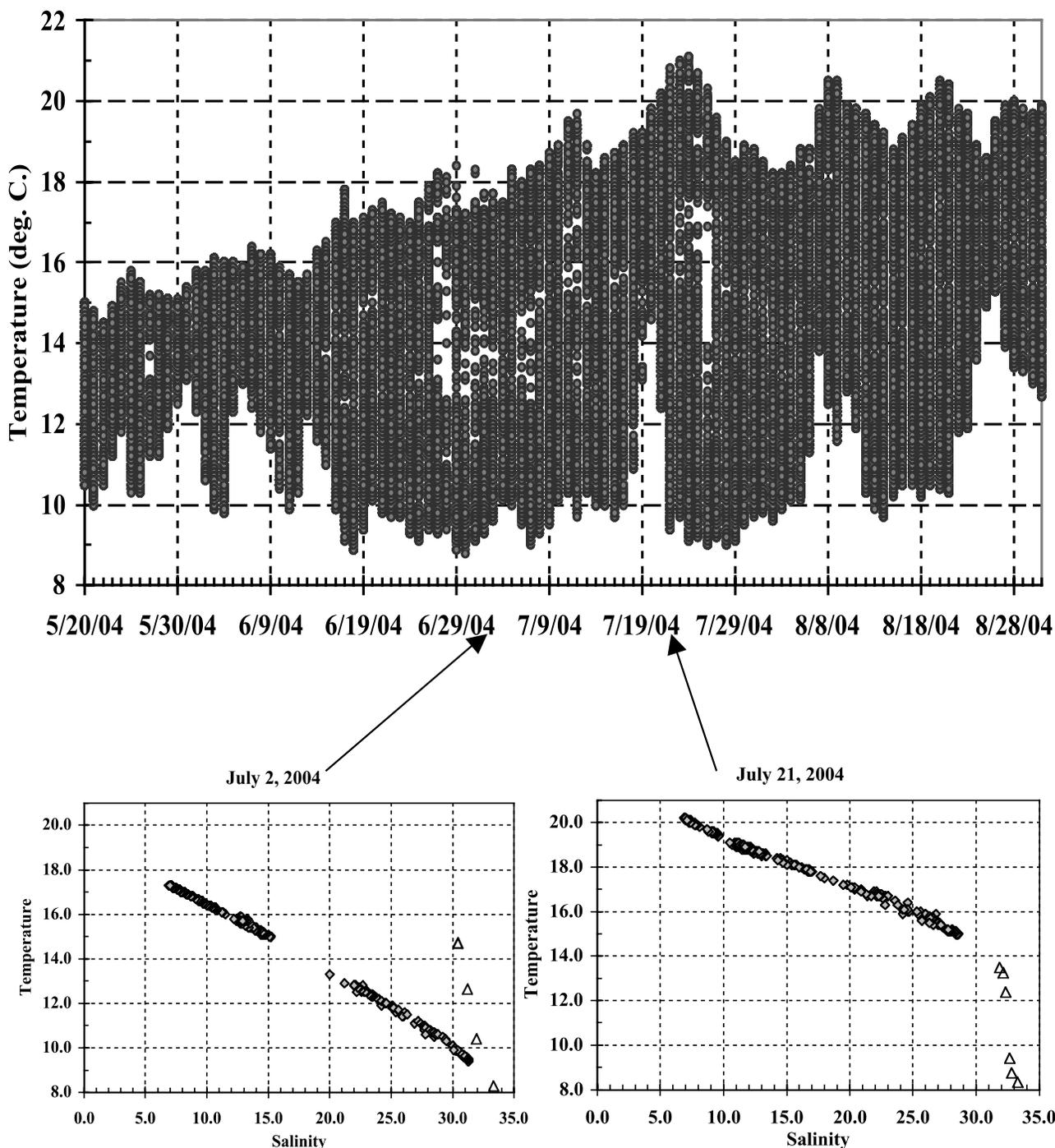


Figure 4. A time series of temperature for a CTD located at 7 m depth just inside the Columbia River estuary at the Jetty A CORIE station for mid-May–August 2004. In addition, temperature-salinity diagrams of the CORIE data for 2 relevant days (2 and 21 July) corresponding to the field studies are also presented. The triangles represent a coastal station within 20 km of the river mouth at close to the same time.

neap tidal cycle. Figure 9a shows that river water of 16°C was mixing with warm (14°C), low-salinity (30) seawater to form a plume with a salinity of 13–20 and a temperature of 15°C. Figure 9b shows that river water of 190 μM silicic acid was mixing with warm, nutrient depleted seawater with <5 μM silicic acid to form a plume with ~ 100 μM silicic acid at a salinity of 15. The plot of salinity versus nitrate

(Figure 9c) shows river water with 13 μM nitrate mixing with warm, nutrient depleted water with <1 μM nitrate to form a plume with a salinity of 15 and a nitrate concentration of ~ 7 μM , with nitrate in the plume coming almost exclusively from the river source. Again, this data shows that the elevated nitrate concentrations in the Columbia

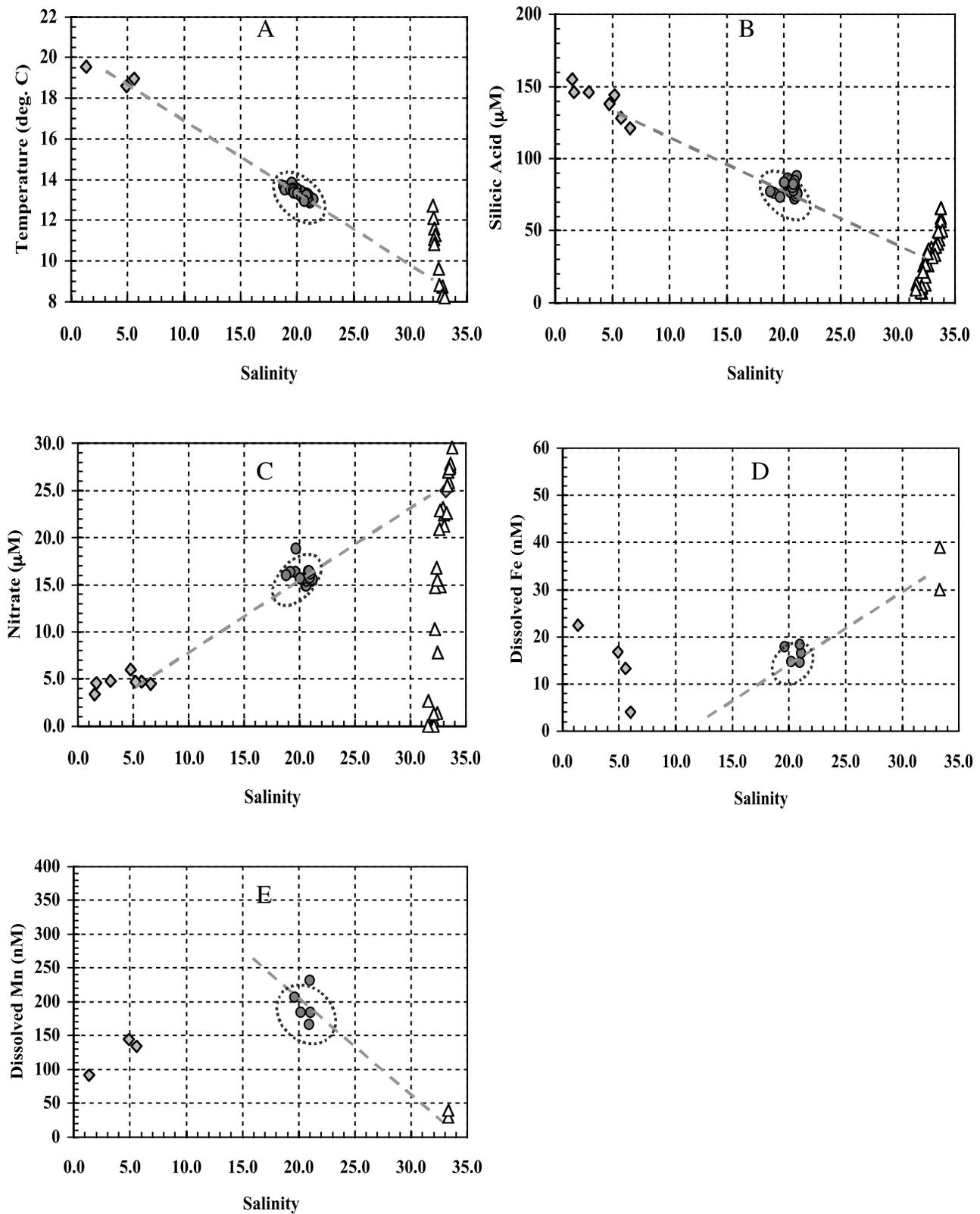


Figure 5. A series of property salinity plots for data collected on the pre-RISE cruise on 2 July 2004 within the estuary (gray diamonds), within the core of the near-field plume (gray circles), and in a vertical profile of nearby coastal seawater (dissolved Fe and Mn data are for the subsurface coastal seawater end-member only (white triangles)). This was during an upwelling-active phase and cold, relatively high-salinity, nutrient-rich coastal seawater was observed at depths of approximately 10 m and was the water entrained together with the river water to form the plume.

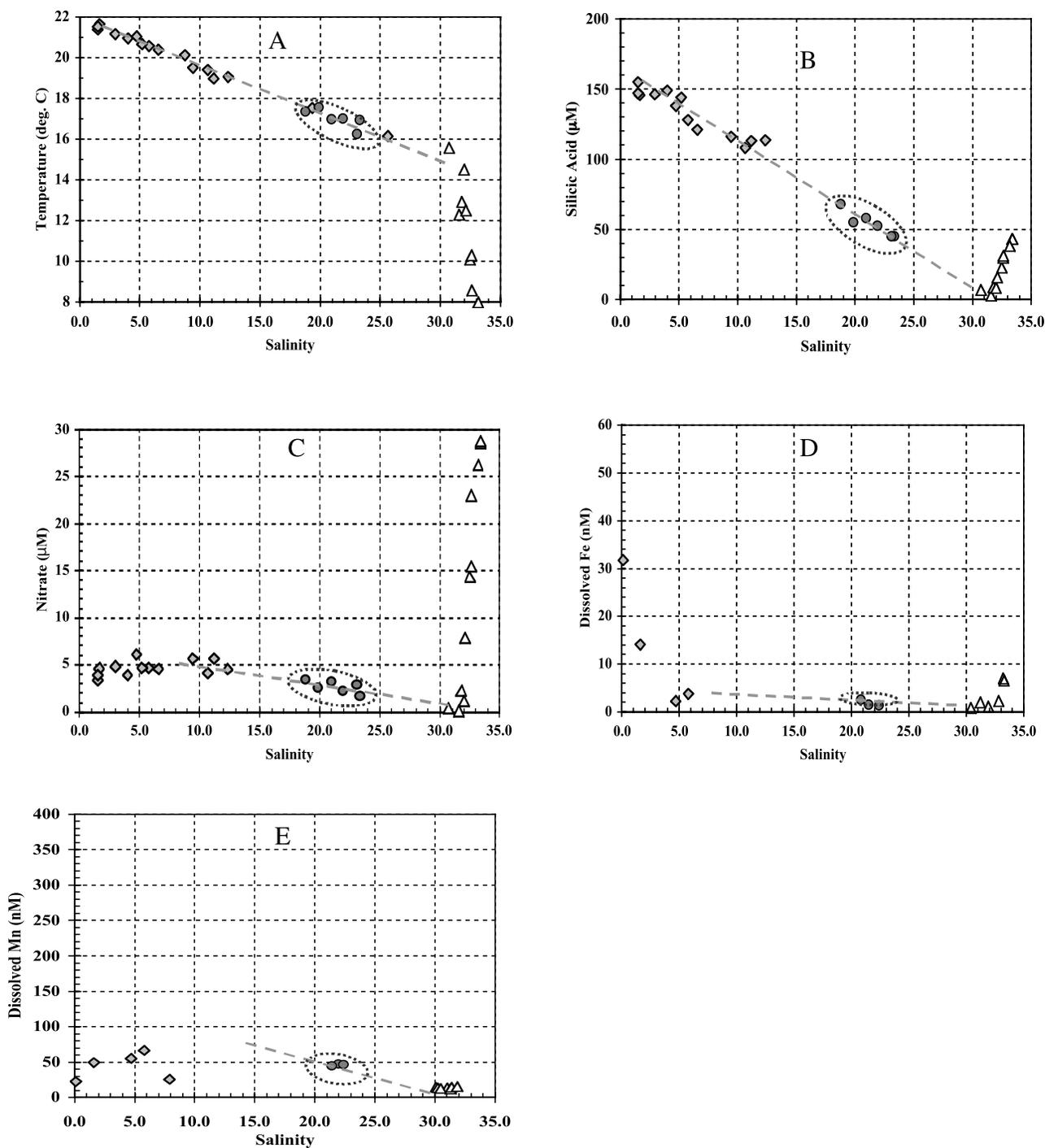


Figure 6. A series of property salinity plots for data collected on the RISE-1W cruise on 21 July 2004 within the estuary (gray diamonds), within the core of the near-field plume (gray circles), and in a vertical profile of nearby coastal seawater (white triangles). This was during a downwelling-relaxation phase and warm, relatively low-salinity, nutrient-depleted coastal seawater was observed at depths of approximately 10 m and was the water entrained together with the river water to form the plume.

River in the summer of 2005 were anomalously high compared to previous years (Figure 2).

[22] Figures 9d and 9f (with increased vertical axis to display all data) show low dissolved iron concentrations of only a few nM in the coastal water at depths of 5–20 m being mixed with relatively low dissolved iron water within

the estuary. The plume water at a salinity of 15 had 6–7 nM dissolved iron. The dissolved Mn concentrations in the plume ranged from 15 to 20 nM with a value of ~ 16 nM at a salinity of 15. These low dissolved Mn concentrations observed in the plume were lower than observed in the warm, nutrient-poor coastal seawater, and approximately

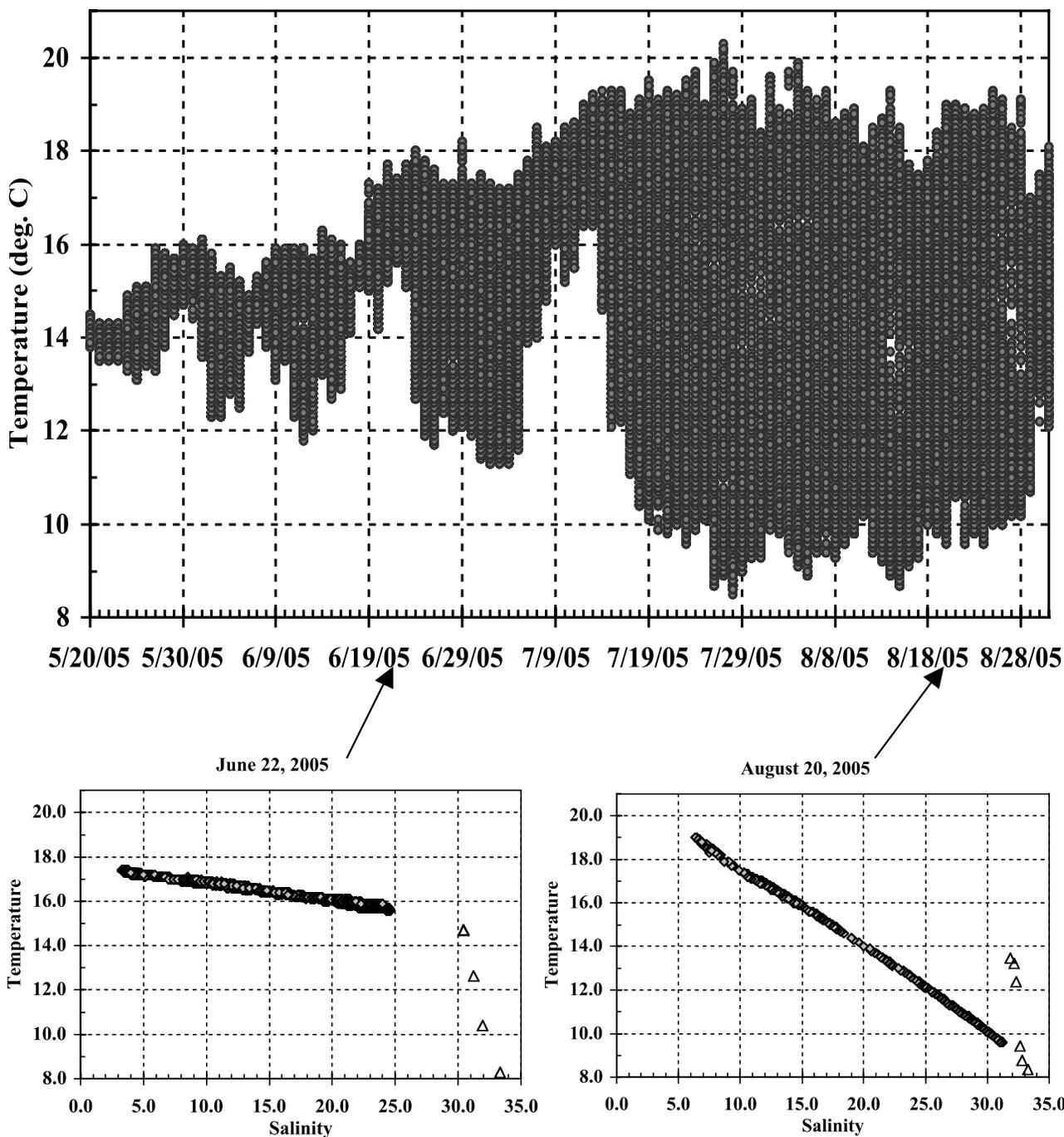


Figure 7. A time series of temperature for a CTD located at 7 m depth just inside the Columbia River estuary at the Desdemona Sands light CORIE station for mid-May–August 2005. In addition, temperature-salinity diagrams of the CORIE data for 2 relevant days (22 June and 20 August) corresponding to the field studies are also presented. The triangles represent a coastal station within 20 km of the river mouth at close to the same time.

the same as observed at salinities of 5–10 within the estuary (Figure 9e).

[23] The RISE-3W data from 18 to 20 August 2005 are from an upwelling-active phase and an intense spring tidal cycle. The winds had been strong and from the north almost continuously for the previous month with only a few 1 day breaks (Figure 3b). Figure 10a shows that warm river water of 21.5°C was mixing with cold (9°C), high-salinity (~33)

coastal seawater to form a plume with a salinity of 20–25 and a temperature of 12–14°C. Figure 10b shows that river water of 150 μM silicic acid was mixing with cold, nutrient rich seawater with $\sim 35 \mu\text{M}$ silicic acid to form a plume of salinity 20 with $\sim 80 \mu\text{M}$ silicic acid. The plot of salinity versus nitrate (Figure 10c) shows river water with $\sim 10 \mu\text{M}$ nitrate mixing with cold, nutrient rich water with $\sim 24 \mu\text{M}$ nitrate to form a plume with a salinity of 20 and a nitrate

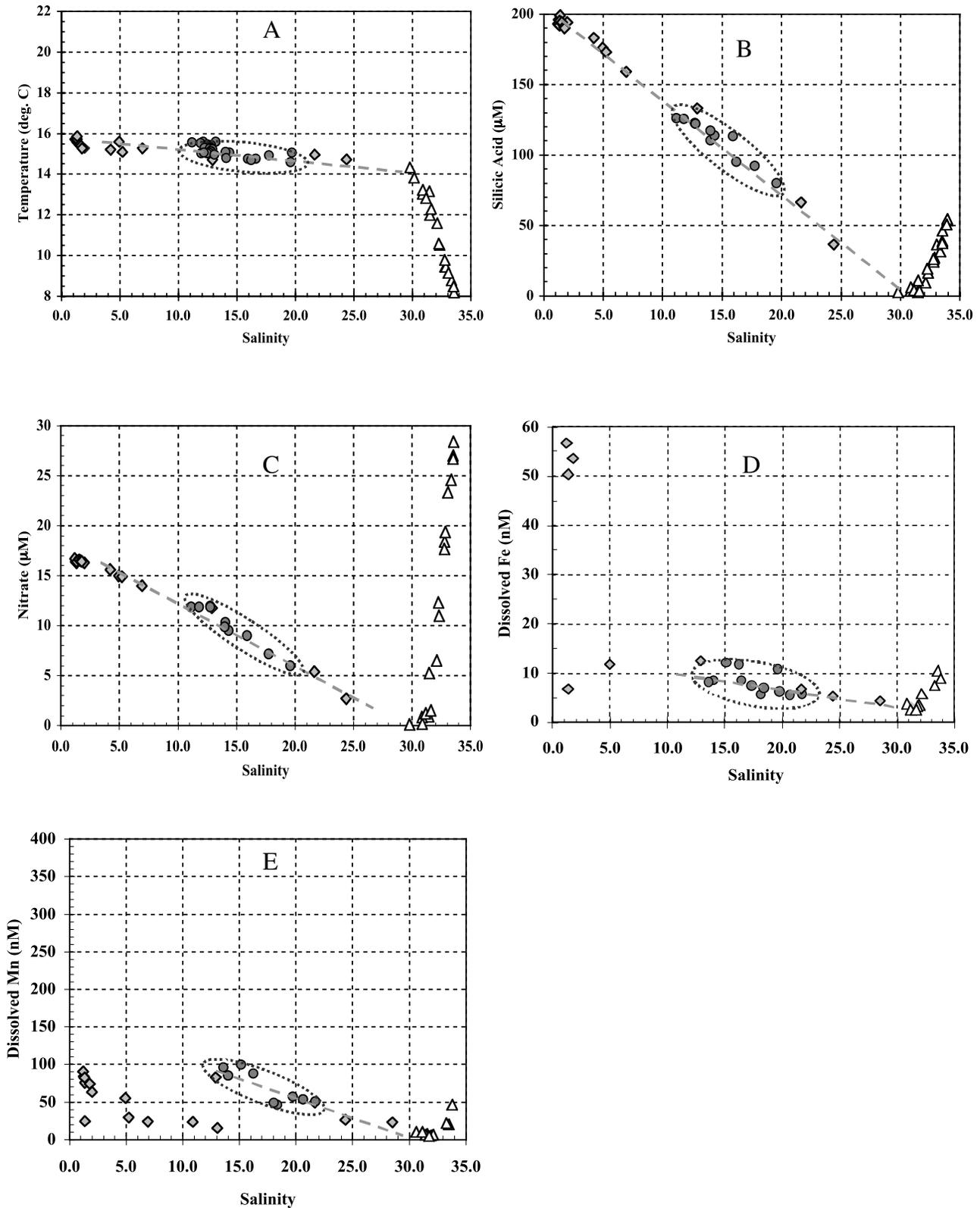


Figure 8. A series of property salinity plots for data collected on the RISE-2W cruise on 5–7 June 2005 within the estuary (gray diamonds), within the core of the near-field plume (gray circles), and in a vertical profile of nearby coastal seawater (white triangles). This was during a downwelling-relaxation phase and warm, relatively low-salinity, nutrient-depleted coastal seawater was observed at depths of approximately 10 m and was the water entrained together with the river water to form the plume.

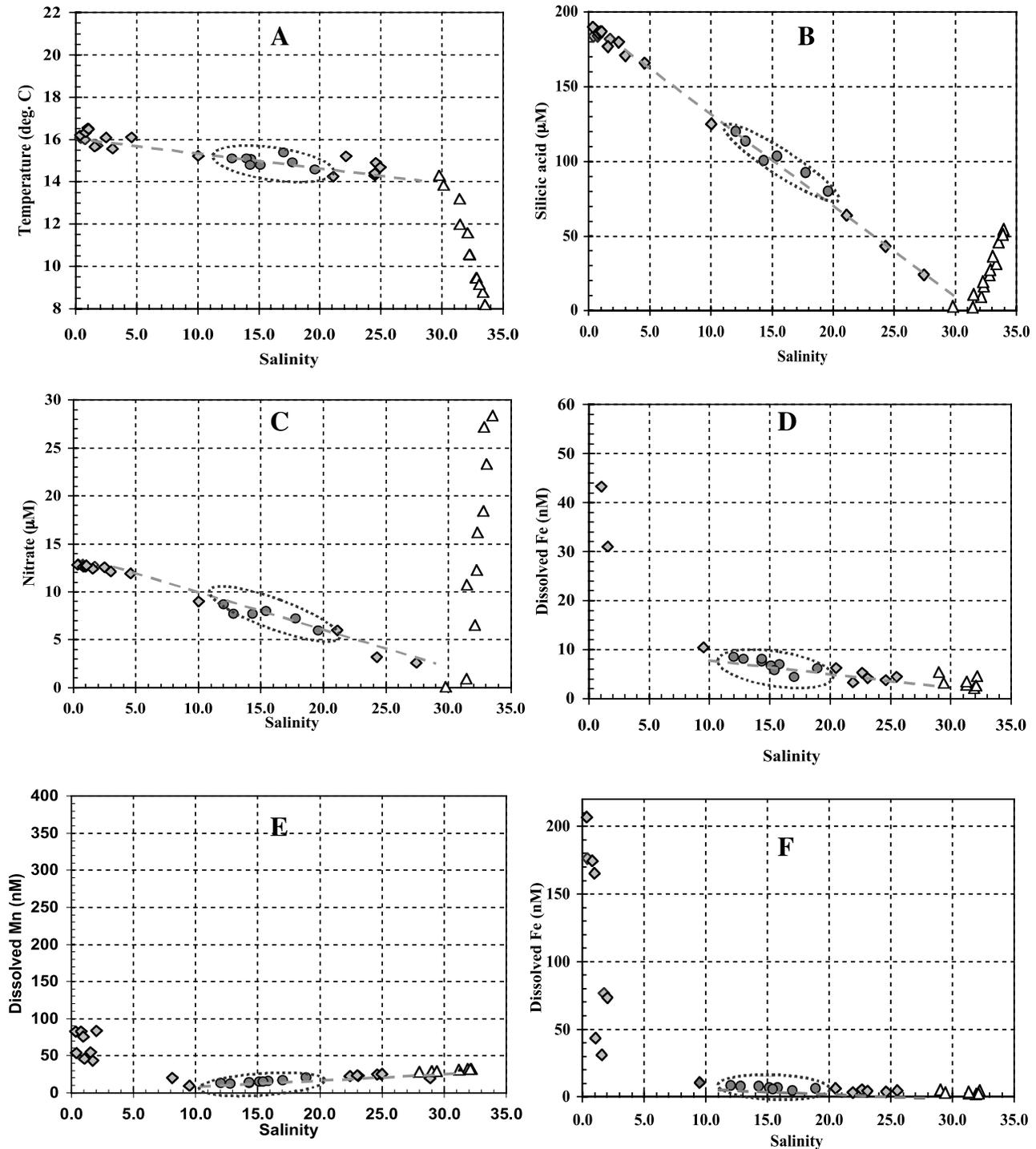


Figure 9. A series of property salinity plots for data collected on the RISE-2W cruise on 12–13 June 2005 within the estuary (gray diamonds), within the core of the near-field plume (gray circles), and in a vertical profile of nearby coastal seawater (white triangles). This was during a downwelling-relaxation phase and warm, relatively low-salinity, nutrient-depleted coastal seawater was observed at depths of approximately 10 m and was the water entrained together with the river water to form the plume.

concentration of 18–19 μM , with 80% of the nitrate in the plume coming from the coastal seawater source.

[24] The upwelling-active phase resulted in cold, high-salinity, nutrient-rich, low-oxygen coastal seawater with

elevated dissolved Fe concentrations of 42–46 nM being drawn into the Columbia River estuary to mix and form the plume. Figure 10d shows high dissolved iron concentrations in this near bottom water at depths of 10–20 m being mixed

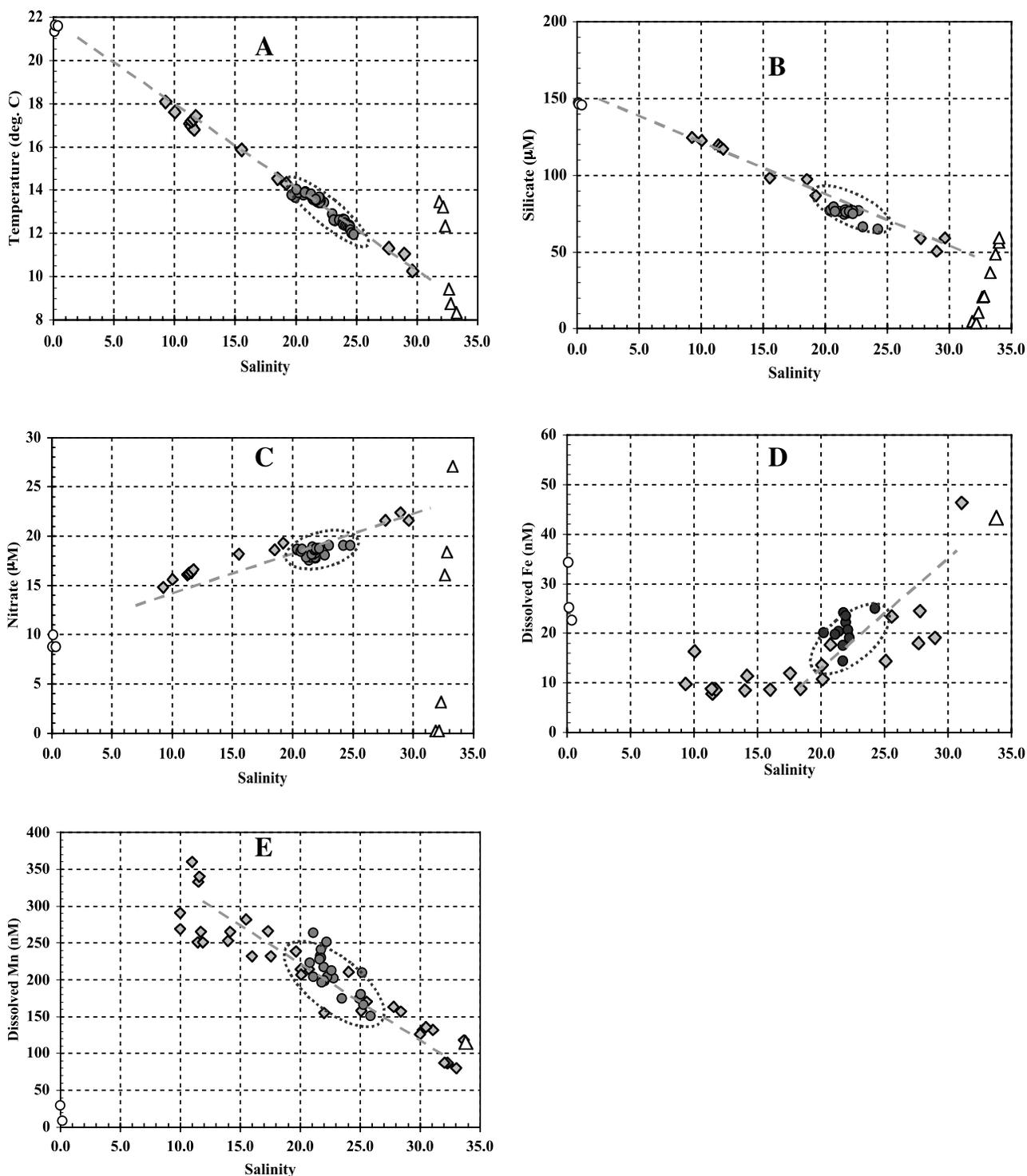


Figure 10. A series of property salinity plots for data collected on the RISE-3W cruise on 18–20 August 2005 within the river (white circles), estuary (gray diamonds), within the core of the near-field plume (gray circles), and in a vertical profile of nearby coastal seawater (the dissolved Fe and Mn data are plotted for the subsurface coastal seawater end-member only (white triangles)). This was during an upwelling-active phase and cold, relatively high-salinity, nutrient-rich coastal seawater was observed at depths of approximately 10 m and was the water entrained together with the river water to form the plume.

with estuarine water with dissolved iron on the order of 10 nM. The plume water at a salinity of 20 has a dissolved Fe concentration of 15–20 nM. The dissolved Mn concentrations in the plume were elevated and ranged from 150 to

250 nM with a value of ~ 230 nM at a salinity of 20. These high dissolved Mn concentrations in the plume fell along a mixing line between the coastal seawater with concentrations on the order of 100 nM and estuarine water at a

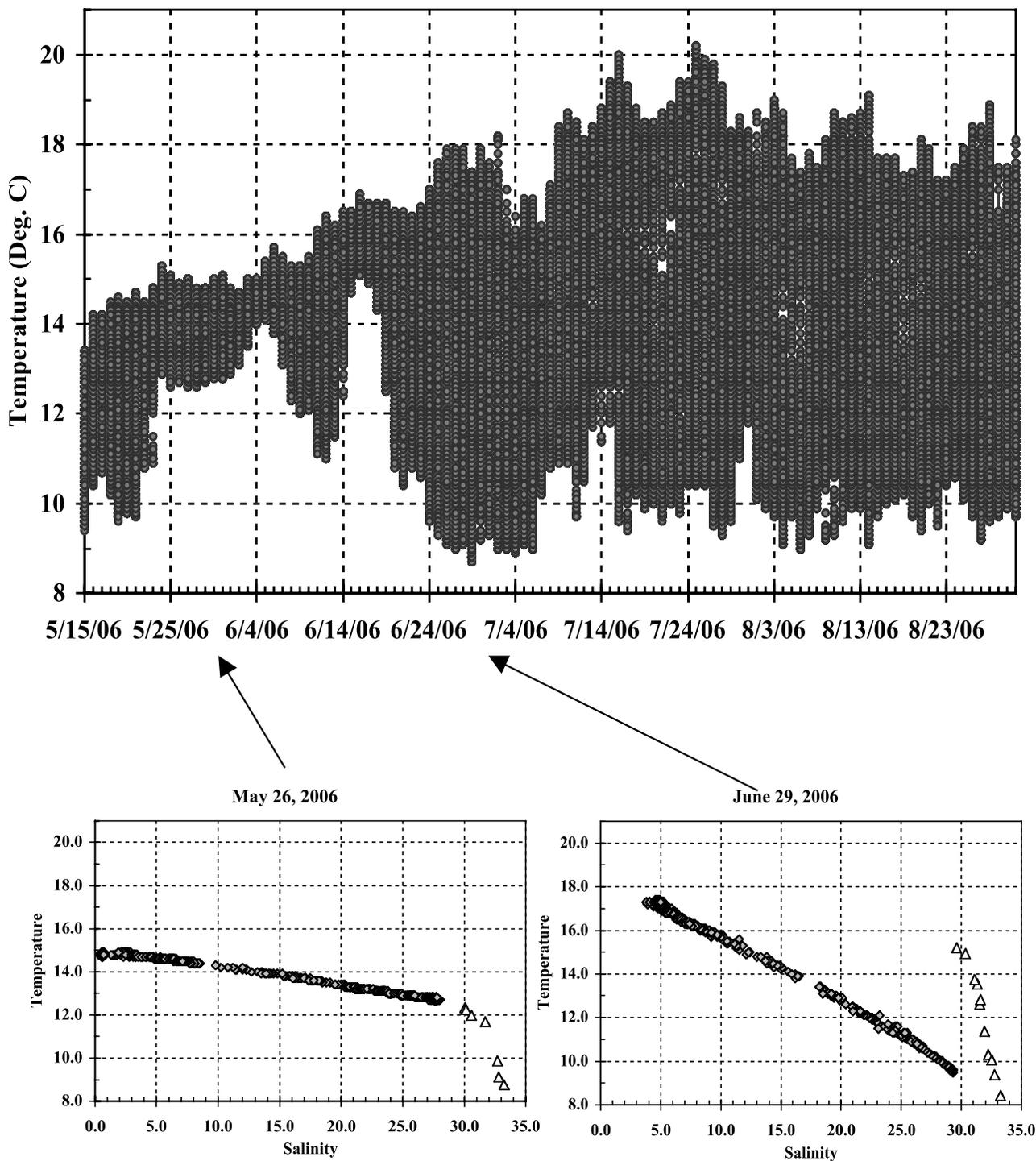


Figure 11. A time series of temperature for a CTD located at 7 m depth just inside the Columbia River estuary at the Desdemona Sands light CORIE station for mid-May–August of 2006. In addition, two temperature-salinity diagrams for the CORIE data for 2 relevant days (26 May and 29 June) are also presented.

salinity of 10 with concentrations of dissolved Mn of roughly 330 nM (Figure 10e). These concentrations are more than an order of magnitude greater than observed in the Columbia River and suggest a major source of dissolved Mn coming from the resuspension of estuarine sediments during the intense spring tide conditions.

3.3. Data From 2006

[25] Cruise data were obtained in 24–28 May during RISE-4W. For the first half of May 2006, the system had been in an upwelling-active phase (Figures 3c and 11). Mid-May was characterized as a downwelling-relaxation phase with generally strong downwelling winds from the south

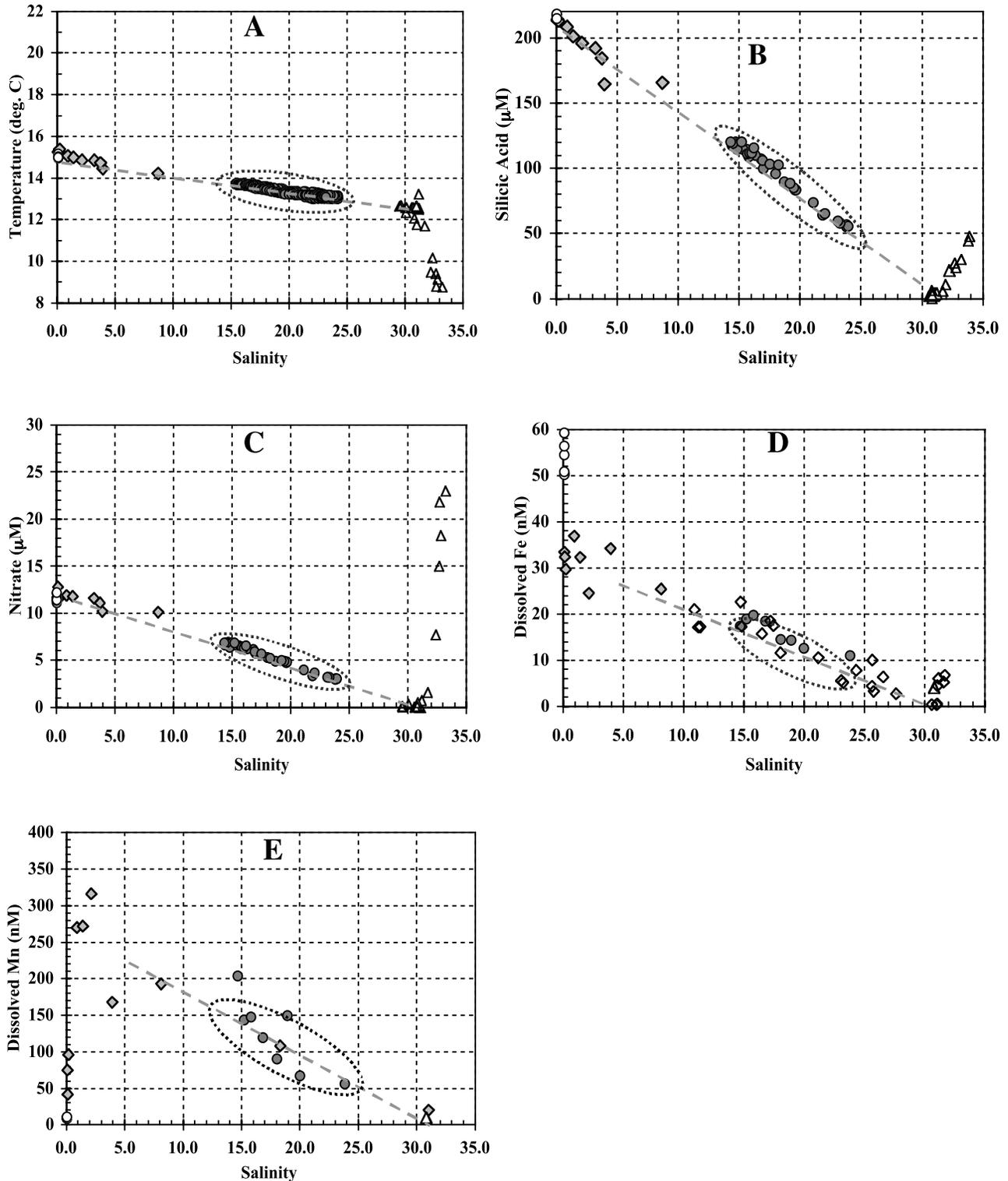


Figure 12. A series of property salinity plots for data collected on the RISE-4W cruise on 24–28 May 2006 within the river (white circles), estuary (gray diamonds), within the core of the near-field plume (gray circles), and in a vertical profile of nearby coastal seawater (the dissolved Fe and Mn data plotted are for the subsurface coastal seawater end-member only (white triangles)). This was during a downwelling-relaxation phase and warm, relatively low-salinity, nutrient-depleted coastal seawater was observed at depths of approximately 10 m and was the water entrained together with the river water to form the plume.

Table 1. Oceanographic, Tidal, and River Conditions for the Different Sampling Periods During the RISE Program

Dates	Upwelling/ Downwelling	Tide Conditions	River Flow (m ³ /s)
<i>Pre-RISE</i>			
2–3 Jul 2004	Upwelling	Intense spring tides	Low (~4000)
<i>RISE-1W</i>			
21–22 Jul 2004	Downwelling	Neap tides	Low (~4000)
<i>RISE-2W</i>			
5–7 Jun 2005	Downwelling	Neap tides	Intermediate (~7000)
12–13 Jun 2005	Downwelling	Low neap tides	Intermediate (~6000)
<i>RISE-3W</i>			
18–20 Aug 2005	Upwelling	Intense spring tides	Low (~4000)
<i>RISE-4W</i>			
24–28 May 2006	Downwelling	Intermediate tides	High (~12,000)

and relatively short periods of only a day or so of relatively weak winds from the north. During this downwelling-relaxation phase plots of salinity versus temperature at the Desdemona Sands CORIE station (Figure 11) indicate that the coastal seawater that was mixing with the Columbia River water was warm (~12.5°C), low-salinity seawater. May 2006 was also a period of relatively high river flow (Figure 2a).

[26] The RISE-4W data from 24 to 28 May 2006 are from a downwelling-relaxation phase, and during an intermediate tidal cycle. During the sampling on 25 May, river water of 15°C was mixing with relatively warm (12.5°C) coastal seawater to form a plume of salinity 15–25 and a temperature of 13–14°C (Figure 12a). Figure 12b shows that river water of 215 μM silicic acid was mixing with warm, nutrient depleted seawater with <3 μM silicic acid to form a plume of salinity 20 with ~80 μM silicic acid. The plot of salinity versus nitrate (Figure 12c) shows river water with ~12 μM nitrate mixing with warm, nutrient depleted water with <1 μM nitrate to form a plume with a salinity of 20 and a nitrate concentration of ~4 μM. In this case, the nitrate in the plume had only a river source.

[27] Figure 12d shows low dissolved iron concentrations of only a few nM in this warm nutrient depleted subsurface water at depths of 5–20 m being mixed with relatively high dissolved iron water within the estuary. It appears that during the high-flow conditions a much greater fraction of the river dissolved Fe was making it through the lower-salinity portion of the estuary. The plume water at a salinity of 20 had ~13 nM dissolved iron. The dissolved Mn concentrations in the plume ranged from 50 to 150 nM with a value of ~100 nM at a salinity of 20. The Mn concentrations observed in the plume were greater than observed in the warm, nutrient poor seawater and higher than observed in the river (Figure 12e). The highest dissolved Mn concentrations within the estuary during these high river flow conditions were observed at salinities of ~2.

4. Discussion

[28] Table 1 presents a summary of the upwelling/downwelling, tides, and river flow for the various field

sampling efforts. Table 2 presents a summary of the chemical characteristics of the Columbia River and coastal seawater end-members during the various sampling intervals, and Table 3 presents a comparison of plume chemistry at a salinity of 20 during each of the RISE sampling periods. Although the salinity of the core for the near-field plume varied from 13 to 20, with lower salinities observed during neap tides and higher river flows and higher salinities observed during spring tides and lower river flows, a salinity of 20 was chosen for comparing plumes in Table 3.

4.1. Columbia River Fresh Water End-Member

[29] The temperature, nitrate and silicic acid concentrations in the Columbia River during the different sampling time periods were generally what was expected on the basis of the 10 year time series presented in Figure 2. During the May–August time period of interest, the temperature of the river was lowest in May and June (15–16°C) and increased to values in excess of 20°C in July and August. This is also apparent in Figures 4, 7, and 11 where the daily upper temperature in the estuary (coincident with the low-salinity value) approached the river temperature on each ebb flow of the tides.

[30] The nitrate concentrations in the Columbia River were higher in May and June and lowest in the July and August sampling interval. The July 2004 nitrate concentration of 4–5 μM was consistent with those observed during the last decade in Figure 2a. The nitrate concentrations of 10–17.5 μM measured in the river in June and August 2005 and in May 2006, although high relative to the longer-term record, were consistent with nitrate concentrations reported by the USGS in the summer of 2005 and 2006 (Figure 2a). Silicic acid concentrations in the river were elevated and ranged from 150 to 215 μM, with the highest concentrations in May and decreasing through the summer to lower values in July and August consistent with the long-term trend (Figure 2b).

[31] Nitrate and silicic acid both appeared to behave conservatively within the Columbia River estuary as evidenced by their linear relationship with salinity (Figures 5b and 5c through 12b and 12c). This conservative behavior is consistent with the short residence time (1 to several days) of water within the Columbia River estuary [Jay and Smith, 1990; Nash et al., submitted manuscript, 2008] relative to the low biological activity within the estuary during the summer (<http://www.columbiaestuary.org/creddp/WATERCOLUMN.pdf> and http://www.columbiaestuary.org/creddp/BENTHIC_PRIMARY_PRODUCTION.pdf). Phosphate (data not shown) also behaved conservatively within the estuary. During RISE-2W and -3W when the nitrate concentration varied between 9 and 17 μM, the phosphate concentration covaried with nitrate, with a nitrate:phosphate ratio averaging 17.3, a value close to a Redfield ratio of 16. This river water, slightly deficient in phosphate relative to nitrate and a Redfield ratio of 16, mixed with coastal seawater that had an excess of phosphate relative to nitrate and a Redfield ratio. Thus, with respect to the requirement of macronutrients by phytoplankton, the summer time plume was nitrate limited.

[32] Dissolved Fe concentrations in the Columbia River itself, or in estuarine waters with salinity less than 1, ranged from 23 to 210 nM. The highest concentrations observed in

Table 2. River Water and Coastal Seawater End-Member Characteristics

Dates	Temperature (°C)		Silicic Acid (μM)		Nitrate (μM)		Dissolved Fe (nM)		Dissolved Mn (nM)	
	River Water	Coastal Seawater	River Water	Coastal Seawater	River Water	Coastal Seawater	River Water	Coastal Seawater	River Water	Coastal Seawater
2–3 Jul 2004	20.5	8.8	155	35	<i>Pre-RISE</i>		...	35	...	30
					3	26				
21–22 Jul 2004	22	15	160	<3	<i>RISE-1W</i>		...	1–2	...	10
					5	<1				
5–7 Jun 2005	16	14	205	<3	<i>RISE-2W</i>		...	3	...	10
12–13 Jun 2005	16	14	190	<3	17.5	<1	...	3	...	25
					13	<1				
18–20 Aug 2005	21.5	9	150	35	<i>RISE-3W</i>		...	44	...	100
					10	24				
24–28 May 2006	15	13	215	<3	<i>RISE-4W</i>		...	3	...	10
					12	<1				

these waters occurred during the 18–20 August 2005 sampling period when concentrations on the order of 200 nM were measured in the Columbia River samples. These are relatively low concentrations of dissolved Fe compared to that reported for rivers in eastern North America where higher concentrations of dissolved Fe exist associated with humic substances [Boyle *et al.*, 1977]. Nothing is known about the seasonal or interannual variation in dissolved Fe in the Columbia River. In each of the sampling periods, a nonconservative behavior of dissolved Fe in the low-salinity region of the estuary was observed, with dissolved iron rapidly decreasing and being removed from solution in the salinity range of 0–5. This is consistent with concentrations of riverine dissolved Fe being associated with humic substances that tend to flocculate and precipitate from the dissolved phase as the river water begins to mix with the coastal seawater [Sholkovitz, 1976; Boyle *et al.*, 1977; Nowostawska *et al.*, 2008]. Sholkovitz and Copeland [1981] and Nowostawska *et al.* [2008] demonstrated that the anionic sites of the humic acids are particularly effective at complexation with the increased Ca^{2+} and Mg^{2+} in seawater, neutralizing their charge and rapidly allowing flocculation and precipitation of the humic acids and their associated complexed Fe. Generally, in the salinity range of 6–10 within the estuary, relatively low dissolved Fe concentrations were observed. In both sampling periods during July 2004 a concentration of 4 nM was observed at a salinity of 6, and in June and August 2005 a concentration of ~10 nM was observed at salinities of ~9. In the high-flow conditions of May 2006, however, the dissolved Fe was ~25 nM in the salinity range of 5–10.

[33] In this case of high river flow observed in May 2006, Fe did not appear to be removed as efficiently at the salinity range of 0–5, with the river concentration of 50–60 nM decreasing to only ~25 nM in the low-salinity region of the estuary. The water in the Columbia River estuary has a short residence time because of the large river flow relative to the small volume of the estuary. The even shorter residence time of water within the estuary during the high-flow conditions may result in higher dissolved Fe still being present at a salinity of 5–10 (Figure 12d), or perhaps under the high-flow conditions the humic acid concentrations were decreased and, as a result, less flocculation occurred. Although the reasons for this are not fully understood, we

did observe a high fraction of the riverine dissolved Fe in the estuary and it was a substantial source to the plume during high river flow during May 2006; whereas during low river flow conditions there appeared to be major removal of dissolved Fe in the low-salinity regions of the estuary and the riverine Fe was only a minor source to the plume.

[34] Dissolved Mn concentrations in the Columbia River or estuary at salinities of less than ~1 ranged from 12 to 95 nM, with concentrations of 12–30 nM observed in the river itself. Once again, reliable data on seasonal or interannual variations in dissolved Mn in the river are lacking. Removal of dissolved Mn was not observed in the estuary, instead an input was observed that coincided with tidal amplitude changes (Figure 13), with higher concentrations during spring tides (as high as ~330 nM (Figure 10e and 13)), when enhanced tidal energy results in greater suspended sediment [Sherwood *et al.*, 1990; Jay *et al.*, 1990; Jay and Smith, 1990] than during neap tides (concentrations as low as ~15 nM, Figure 8e). E. Y. Spahn *et al.* (Particle resuspension in the Columbia River plume near field, submitted to *Journal of Geophysical Research*, 2008) suggest that as the tidal range increases toward the maximum of a spring tide, the estuarine turbidity maximum is supplied with particles from peripheral areas and then exported during the strongest spring tide ebb flows. *Aguilar-Islas and*

Table 3. Near-Field Plume Characteristics at a Chosen Representative Salinity of 20

Dates	Temperature (°C)	Silicic Acid (μM)	Nitrate (μM)	Dissolved Fe (nM)	Dissolved Mn (nM)
		<i>Pre-RISE</i>			
2–3 Jul 2004	13.2	80	16	16	200
		<i>RISE-1W</i>			
21–22 Jul 2004	17.2	6	2.5	3	50
		<i>RISE-2W</i>			
5–7 Jun 2005	15	70	6	7	55
12–13 Jun 2005	15	70	5	5	20
		<i>RISE-3W</i>			
18–20 Aug 2005	14	80	19	14	230
		<i>RISE-4W</i>			
24–28 May 2006	13.5	80	4	13	100

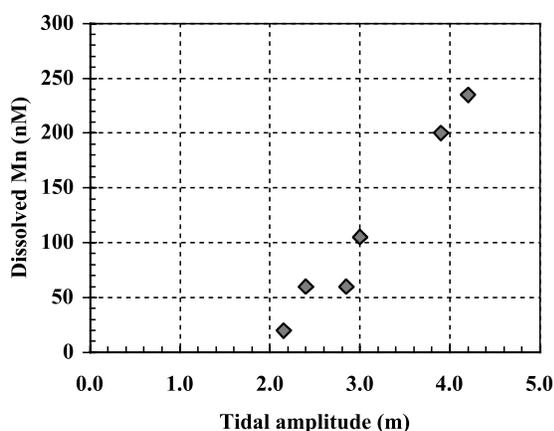


Figure 13. Dissolved Mn (nM) at plume salinity of 20 versus tidal amplitude (m) for the various sampling periods in the RISE program. The tidal amplitude data is from within the estuary at Jetty A.

Bruland [2006] have suggested that dissolved Mn can either be mobilized from suboxic pore waters along with the coexisting sediment during spring tide resuspension events, or alternatively, that the increase in dissolved Mn could be via photo dissolution of manganese oxide coatings of the resuspended sediments.

[35] Sherwood *et al.* [1990] observed a range of ~ 5 – 300 mg L^{-1} in the concentration of suspended particles within the surface waters of the Columbia River Estuary, with the lower suspended loads found seaward during neap tides, and the higher loads found in the middle portion of the estuary during spring tides. The average Mn content in suspended sediment during the summer in the Columbia River is $\sim 1.5 \text{ mg g}^{-1}$ [Covert, 2002]. These values give a range of suspended particulate Mn of 137–8190 nM within estuarine surface waters. A rate of $4.9\% \text{ h}^{-1}$ for the photo dissolution of particulate Mn in estuarine water was obtained by Sunda and Huntsman [1994] during laboratory studies using ^{54}Mn radio labeled manganese oxide particles. A lower dissolution rate in seawater ($2\% \text{ h}^{-1}$) was reported by Matsunaga *et al.* [1995] during laboratory-based experiments. These studies used full sunlight conditions, and lower particle concentrations, therefore a lower Mn photo dissolution rate is likely under natural conditions of changing irradiance, and percent light transmission in surface waters. Allowing for 8 h of intense sunlight, and using $0.5\% \text{ h}^{-1}$ or $5\% \text{ h}^{-1}$ as possible rates of Mn photo dissolution, yields a daily contribution in dissolved Mn to estuarine surface waters from photo dissolution of suspended sediment of 5–55 nM and 328–3280 nM, respectively, for the range of calculated suspended particulate Mn (137–8190 nmol/L) in the surface waters of the estuary. Thus, this photo dissolution process could be the source of the elevated dissolved Mn during the spring tide periods (Figure 13).

4.2. Coastal Seawater End-Member

[36] Although the upwelling-active phase was the dominant mode during the summer months (Figures 4, 7, and 11), only two of our sampling periods coincided with upwelling-active phases (2–3 July 2004 and 18–20 August 2005 (Table 1)). During these two sampling periods, the coastal seawater end-member had a temperature of

8.8 – 9°C , a silicic acid concentration of $35 \text{ }\mu\text{M}$, nitrate concentrations of 24 – $26 \text{ }\mu\text{M}$, dissolved Fe concentrations of 35 – 44 nM , and dissolved Mn concentrations of 30 – 100 nM (Table 2). The other four sampling periods coincided with downwelling-relaxation phases. In these cases the temperature of the coastal seawater end-member was 12.5 – 15°C , the silicic acid was $<3 \text{ }\mu\text{M}$, the nitrate concentration was $<1 \text{ }\mu\text{M}$, dissolved Fe was 2 – 3 nM , and dissolved Mn was 10 – 25 nM . Thus, there was a dramatic variation in the chemistry of the coastal seawater end-member that mixed with river water to form the plume. This variability led to marked differences in the macro- and micronutrient chemistry of the Columbia River plume (Table 3). During upwelling-active phases the plume had elevated nitrate concentrations ranging from 16 to $19 \text{ }\mu\text{M}$ (with 90% from the coastal seawater source), while during downwelling-relaxation phases the plume had nitrate concentrations ranging from 2.5 to $6 \text{ }\mu\text{M}$ (with only the river being a source).

[37] On the basis of historical nutrient data over the last decade for the Columbia River (Figure 2), the low nitrate summer data from 2004 appears to be representative of a typical or average year. In the summer of 2004 the nitrate concentration in the Columbia River plume of salinity 20 during an upwelling-active phase was $16 \text{ }\mu\text{M}$, in marked contrast to a concentration of 2 – $3 \text{ }\mu\text{M}$ in a downwelling-relaxation phase. A plume formed during an upwelling-active phase with $16 \text{ }\mu\text{M}$ nitrate (90% from the coastal seawater source) will have a far greater impact on productivity than a plume formed during downwelling-relaxation phases with only $2.5 \text{ }\mu\text{M}$ nitrate. During the downwelling-relaxation phase in June 2005 the observed nitrate concentration in the plume of 5 – $6 \text{ }\mu\text{M}$ was higher than normal ($2.5 \text{ }\mu\text{M}$) because of the higher-nitrate concentrations observed in the Columbia River during the summer of 2005.

[38] The tidal phase (e.g., spring or neap tides) also has an impact on the nitrate concentrations observed in the plume at a salinity of 20 during an upwelling-active phase. During spring tides there is more seawater drawn into the estuary and the resultant near-field plume has a higher initial salinity than during neap tides. As a result, during spring tide/upwelling-active conditions more cold, high-nitrate water is mixed with the river water to form a high-nitrate plume of salinity 20. During neap tide/upwelling-active conditions, less nitrate-rich seawater is mixed with the river water and the lower-salinity near-field plume (salinity of 13) resulting in a lower nitrate concentration. Thus, summertime plumes with the highest-nitrate concentration are formed during upwelling-active, spring tide conditions. Nash *et al.* (submitted manuscript, 2008) have shown how the magnitude of the river flow also influences the salinity of the plume with lower salinities during high fresh water river flow. Thus, summertime plumes with the highest-nitrate concentrations will be during upwelling-active, spring tide, and low-river-flow conditions. This will be a plume with a relatively high salinity (>20) and the majority of the nitrate provided by the upwelling seawater source.

[39] Although silicic acid concentrations also varied greatly in the coastal seawater end-member (<3 – $35 \text{ }\mu\text{M}$), the concentrations in the Columbia River water are extremely elevated, even during the summer months (150 – $215 \text{ }\mu\text{M}$), therefore the river source always dominated the

silicic acid content of the plume. The Columbia River plume (at a salinity of 20) varied only from 60 to 80 μM , with the higher concentrations occurring during upwelling-active conditions when the silicic acid-rich river water was mixing with cold, nutrient-rich seawater. These elevated and relatively constant concentrations in the near-field plume, makes silicic acid an excellent tracer of both the near-field and far-field plumes [Aguilar-Islas and Bruland, 2006].

[40] The coastal seawater source of dissolved Fe varied dramatically depending upon whether an upwelling-active or downwelling-relaxation phase was present. During the downwelling-relaxation phases, the dissolved Fe concentrations in the coastal ocean end-member were only 1–3 nM. These low concentrations are characteristic of warm, nutrient-depleted, surface coastal seawater in the vicinity of the mouth of the estuary. In contrast, the dissolved Fe concentration in the cold, nutrient rich, low-oxygen coastal seawater end-member during the upwelling-active phase was 35–44 nM. Lohan and Bruland [2008] measured an average of 33 nM dissolved Fe in hypoxic benthic boundary layer waters during upwelling-active phases over the mid shelf in this region; 15 nM Fe(III) was maintained in solution by roughly an equivalent amount of strong Fe(III)-binding organic ligands [Buck *et al.*, 2007], and 18 nM existed as Fe(II) (comprising over 50% of the total dissolved Fe). Lohan and Bruland [2008] suggested that elevated Fe(II) concentrations can develop in hypoxic conditions because of a large source of Fe(II) in anoxic pore waters from the midshelf mud belts to the hypoxic bottom boundary layer, together with the slow oxidation kinetics of Fe(II). The combination of low oxygen, low pH, and low temperature leads to a kinetic stabilization of Fe(II) in the bottom boundary layer [Lohan and Bruland, 2008]. In a time series study at a station located immediately off the mouth of the Columbia River estuary during upwelling-active/spring tide conditions, dissolved Fe concentrations in the near-field plume on the order of 20 nM were observed during ebb tide, with over 50% of this dissolved Fe in the form of Fe(II) [Berger *et al.*, 2008]. Under upwelling-active phases the seawater end-member can consist of this cold, high-salinity, low-oxygen, low-pH, nutrient-rich, and elevated dissolved Fe benthic boundary layer water that is entrained to form the near-field plume. This leads to an iron-enriched plume (concentrations of dissolved Fe on the order of 15 nM at a salinity of 20) with the bulk of the dissolved Fe coming from the hypoxic coastal seawater source.

[41] In contrast, under downwelling-relaxation phases, the summertime plume has lower dissolved Fe concentrations, ranging from 2 to 7 nM, with much of the dissolved Fe from a river/low-salinity estuarine source. However, the May 2006 sampling, under high-flow, downwelling-relaxation conditions, yielded a plume with 13 nM dissolved Fe. Under these high river flow conditions, more of the riverine dissolved iron was making it through the low-salinity region of the estuary and incorporated into the plume.

[42] Concentrations of dissolved Mn in the coastal seawater end-member also varied with upwelling conditions, with values that ranged from 10 to 25 nM under downwelling-relaxation phases, to values of 30–100 nM during upwelling-active phases. However, unlike dissolved Fe, variations in the seawater end-member do not appear

to be the major factor influencing the concentration of dissolved Mn in the Columbia River Plume. Concentrations of dissolved Mn within the near-field plume at a salinity of 20 varied by greater than an order of magnitude, ranging from 20 to 230 nM. The highest concentrations of dissolved Mn were found at lower salinities under spring tide conditions within the estuary and varied greatly with tidal amplitude as described in the previous section. Dissolved Mn in the Columbia River plume appears to be influenced primarily by estuarine inputs associated with tidal conditions [Aguilar-Islas and Bruland, 2006] as illustrated in Figure 13, where the dissolved Mn in the plume at a salinity of 20 is plotted as a function of the tidal amplitude in meters at Jetty A. Although highly variable, the elevated dissolved Mn concentrations in the near-field plume make dissolved Mn an excellent tracer of both the near-field and far-field plumes, and the variable ratio of dissolved Mn and silicic acid is a tracer of the tidal regime [Aguilar-Islas and Bruland, 2006].

4.3. Extrapolation of the Station Data Using the CORIE Time Series

[43] Figures 4, 7, and 11 allow the specific sampling times where nutrient and dissolved Fe and Mn data has been obtained in this study to be extrapolated to a longer time period. In the time series of temperature presented in Figures 4, 7, and 11 the temperature varies with tidal cycles with higher temperatures observed at lower salinities because of the elevated temperature of the river relative to coastal seawater during the summer months. The temperature of the river increases from May to August and the maximum observed reflects this increased temperature of the river end-member. Interestingly, during the winter months the temperature of the river is less than that of the coastal seawater. It is usually during April when the river water warms to be greater than the coastal seawater and in November that it cools to be less than the coastal seawater. The lower daily temperatures during the summer months (May–September) are dependent upon whether an upwelling-active phase or a downwelling-relaxation phase exists. Temperature/salinity plots are presented for two dates (corresponding to our sampling times) in each of the years (Figures 4, 7, and 11) and the extrapolated temperatures at seawater salinities are consistent with the wind patterns in the few days prior to each date (Figures 3a–3c).

[44] For example, colder daily estuarine low temperatures (below $\sim 11^\circ\text{C}$) in Figures 4, 7, and 11 indicate an upwelling-active phase and are observed together with negative wind speed vectors (upwelling winds blowing to the south) in Figures 3a–3c, and warmer daily estuarine low temperatures (above $\sim 13^\circ\text{C}$) indicate a downwelling-relaxation phase and are coincident with positive wind speed vectors (downwelling winds blowing to the north). If the shift from an upwelling-active to a downwelling-relaxation phase is examined, there are three periods with dramatic 4°C increases in the daily estuarine low temperatures in 2004 (20 July, 7 August, and 26 August 2004 (Figure 4)). These events were each associated with 2 days or more of downwelling winds (Figure 3a). The smaller $2\text{--}3^\circ\text{C}$ increases in daily estuarine low temperatures observed on 31 May and 6 June 2004 were also associated with 2 days of downwelling winds. The dramatic increase of $>4^\circ\text{C}$ in the

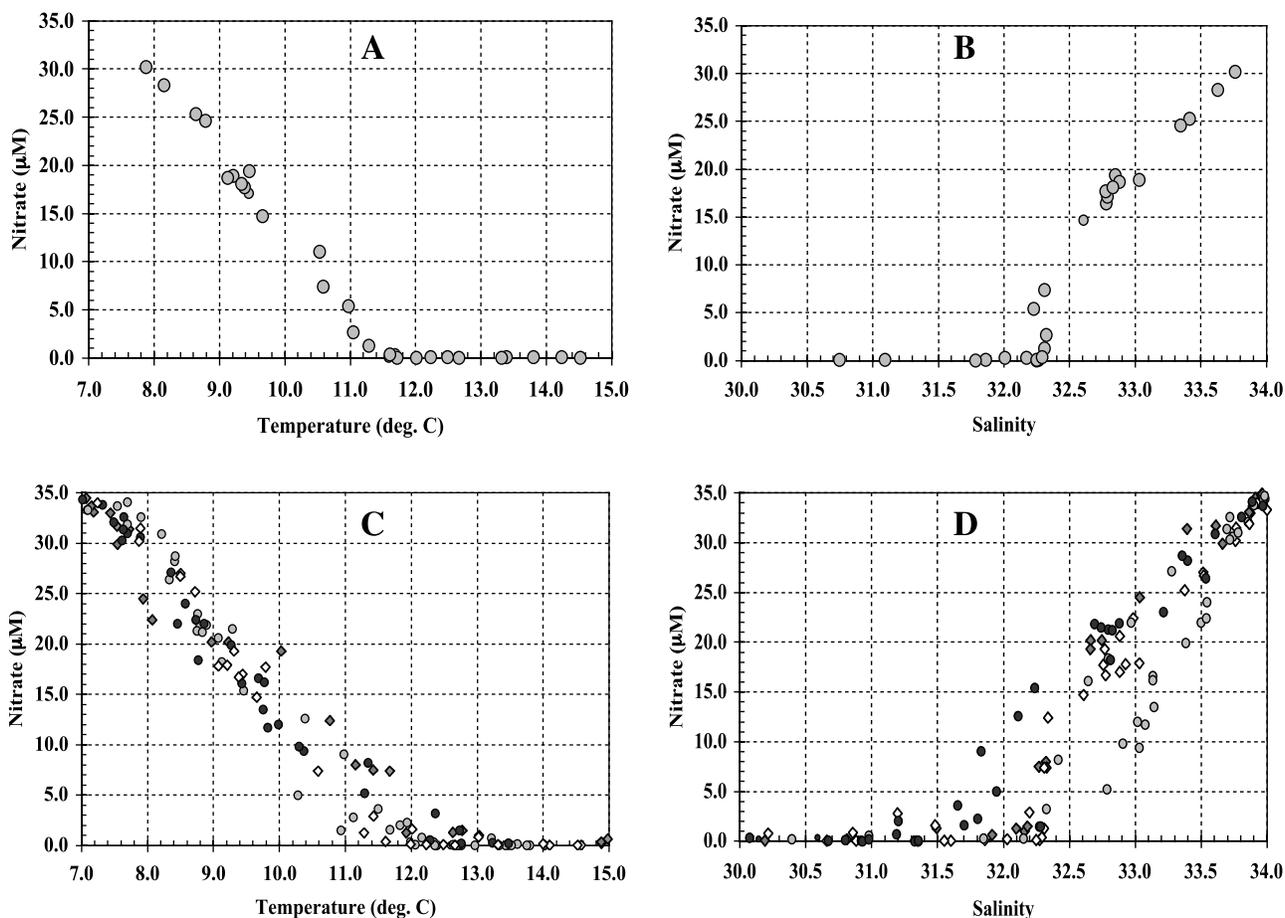


Figure 14. Characterization of (a) nitrate versus temperature and (b) nitrate versus salinity for the coastal seawater end-member during RISE-2W. (c and d) Data for all cruises and all 3 years are plotted. RISE-1W is indicated by white circles, RISE-2W is indicated by white diamonds, RISE-3W is indicated by gray diamonds, and RISE-4W is indicated by gray circles.

daily estuarine low temperature observed on 9 July 2005 (Figure 7) was preceded by 3 days of downwelling winds (Figure 3b), and the warming event of 19 June 2005 was preceded by 2+ days of downwelling winds. In 2006 (Figure 11) the marked warming of the daily estuarine low temperature on 24 May and 15 June 2006 were preceded by 2 days of downwelling winds (Figure 3c). It appears that 2 days of downwelling winds are needed to bring about the dramatic shift from an upwelling-active phase with cold daily estuarine low temperatures to downwelling-relaxation conditions with warm daily estuarine low temperatures.

[45] Similarly, the shift from downwelling to upwelling conditions as indicated by the daily estuarine low temperature was also consistent with the shift in wind directions. In 2004 the dramatic 5°C decrease in daily estuarine low temperature from $>14^{\circ}\text{C}$ to $\sim 9^{\circ}\text{C}$ occurred on 22 July 2004 (Figure 4) after the winds had shifted to strong upwelling winds (Figure 3a). Decreases of $\sim 3^{\circ}\text{C}$ on 14 August, 18 June, and 11 June 2004 each occurred following 2 days of upwelling winds. During 2005, a dramatic decrease in daily estuarine low temperature of more than 6°C on 19 July 2005 (Figure 7) took place over a 5 day period of intense upwelling winds that followed a week of downwelling winds (Figure 3b). The 3°C decrease on 26 June 2005 occurred during 3 days of upwelling winds.

In 2006 there was another dramatic 6°C decrease in daily estuarine low temperature from 15°C to 9°C that occurred over a 2 week period of intense and continuous upwelling winds starting on 14 July and continuing to 28 July 2006 (Figure 11). It appears to take a few days of upwelling winds to decrease the daily estuary low temperatures below 11°C indicative of an upwelling-active phase, and 2 days of downwelling winds to increase the daily estuary low temperature above $\sim 13^{\circ}\text{C}$ exhibited during downwelling-relaxation phases.

[46] Figures 14a and 14b presents plots of nitrate versus salinity and temperature at several vertical stations located over the inner shelf just outside of the plume influence and near the mouth of the Columbia River (within 20 km) during RISE-2W. As the salinity increases above 33 and the temperature decreases below $\sim 9^{\circ}\text{C}$, the nitrate increases to concentrations greater than $20\ \mu\text{M}$. In contrast, at salinities less than 32 or temperatures greater than 12°C , the nitrate is completely depleted to concentrations at the detection limit. Figures 14c and 14d presents plots of nitrate versus temperature and salinity for each of the RISE cruises. If the temperature/salinity data from the estuary CTD presented in Figures 4, 7, and 11 are extrapolated to where it intercepts the temperature/salinity data from the coastal inner shelf samples, an estimate of the temperature and

salinity of the coastal seawater end-member can be obtained. Extrapolating the time series data can provide an estimate of the number of days when an upwelling-active phase or a downwelling-relaxation phase existed. Thus, the CORIE CTD data at stations near the mouth of the estuary can provide an excellent historical record of the derived nitrate concentration in the Columbia River near-field plume.

[47] Generally when the lower daily estuarine temperatures on the temperature time series plots (e.g., Figures 4, 7, and 11) fell below 11°C , the extrapolated values indicated coastal seawater end-member temperatures below 10°C , salinities above 32.6, and nitrate concentrations in excess of $15\ \mu\text{M}$. This is used as the parameter indicative of upwelling-active conditions. In contrast, when the lower estuarine temperature on the daily time series plots was above 13°C , the extrapolated coastal seawater end-member values were temperatures above 12.5°C , salinities below 32, and nitrate concentrations $<0.2\ \mu\text{M}$. This lower daily estuarine temperature of 13°C will be used here as an indicator of a downwelling-relaxation phase. When the lower estuarine temperatures fall between 11° and 13°C it is defined as a transition phase.

[48] During 15 May to 31 August 2004 an upwelling-active phase existed 71% of the time, a downwelling-relaxation phase existed 9% and a transition phase 20% of the time. During the same time period in 2006, conditions were similar with an upwelling-active phase existing 73% of the time, a downwelling-relaxation phase 10% and a transition phase 17% of the time. In marked contrast, during mid-May through the end of August in the summer of 2005, the upwelling-active phase did not start until 18 July and existed only 43% of the time (continuously from 18 July to 29 August). A downwelling-relaxation phase existed 37% of the time during 2005 and was the prevalent phase during the 2 month period from mid-May to mid-July. A transition phase existed 20% of the time during 2005.

[49] During May to September 2004 and 2006 an upwelling-active phase existed during 71–73% of the time and a nitrate-rich and Fe-rich plume developed that, at a salinity of 20, contained 16–19 μM nitrate and 14–16 nM dissolved Fe. Only 9–10 % of the time was the plume produced under a downwelling-relaxation phase with low nitrate and dissolved iron. In contrast, during 2005 the nitrate-rich and Fe-rich, upwelling-active phase was absent from 15 May to 17 July and the downwelling-relaxation phase was dominant. After 18 July, however, an upwelling-active phase was continuous without a break until 29 August.

[50] Under upwelling conditions with winds from the north, the Columbia River plume moves southwest off the Oregon Shelf. This advection of the plume into offshore waters enhances the transport of macro- and micronutrients from what can be provided by upwelling alone, by amplifying the nutrient supply and, most importantly, by rapidly transporting these nutrients farther offshore. An estimate of the flux of nitrate and dissolved iron to this region can be made assuming an average river flow during the summer months of approximately $0.5 \times 10^4\ \text{m}^3/\text{s}$ or $430 \times 10^6\ \text{m}^3/\text{day}$. Since a plume with a salinity of ~ 20 is roughly two thirds coastal seawater and one third river water, the plume will be 3 times the river flow or approximately $1.3 \times 10^9\ \text{m}^3/\text{day}$. At a nitrate concentration of $17.5\ \mu\text{M}$ (mmol/m^3),

this provides 23×10^6 mol nitrate/day. At a dissolved Fe concentration of $15\ \text{nM}$ ($\mu\text{mol}/\text{m}^3$), it provides 20×10^3 mol of dissolved Fe/day. The plume flux of water of $1.3 \times 10^9\ \text{m}^3/\text{day}$ can be compared with coastal upwelling occurring at a rate of $100\ \text{m}^3/\text{sec}/100\ \text{m}$ of coast ($8.6 \times 10^6\ \text{m}^3/\text{day}/100\ \text{m}$ of coast), and the plume, originating from a 3.5 km estuary mouth (R. M. McCabe et al., Ebb tide dynamics and spreading of a large river plume, submitted to *Journal of Physical Oceanography*, 2008), would be equivalent to active upwelling occurring along roughly 15 km of coastline.

[51] Under downwelling-relaxation conditions with winds from the south, the nutrient poor plume is moved northward close to the coastline. It should be noted that unique conditions could occur during the bidirectional stages of the plume. With a shift in the winds to be from the south, the initial plume moving northward continues to form in a nutrient-rich upwelling-active phase for a day or two, and there would be a short period of one or 2 days with a nutrient rich northward flowing plume phasing into a nutrient poor plume. Likewise, approximately the first two days of a southwest flowing plume under new winds from the north would be nutrient poor having formed under a downwelling-relaxation phase, before transitioning into a nitrate-rich and Fe-rich plume as the upwelling-active phase becomes fully established.

[52] In conclusion, the chemistry of the plume during May–September for nitrate and dissolved Fe depends primarily upon whether the coastal ocean is in an upwelling-active or downwelling-relaxation phase, with the plume being enriched in nitrate and dissolved Fe during upwelling-active phases that during 2004 and 2006 existed 71–73% of the time. In 2005, the upwelling-active phase did not appear until 18 July and mid-May–mid-July was characterized as a continual downwelling-relaxation phase. The river concentration for nitrate and dissolved iron was of secondary importance, with the exception of 2005 when the summertime Columbia River had relatively elevated nitrate concentrations and 2006 under high river flow conditions when more of the riverine and dissolved Fe made it through the estuary into the plume. For silicic acid, the elevated concentrations in the river end-member are the primary factor influencing the plume. For dissolved Mn it is the tidal stage that is of primary importance with elevated dissolved Mn appearing within the estuary during high-amplitude spring tides.

[53] Nitrate is arguably the key limiting nutrient in the coastal waters off Oregon and Washington. The nutrient data collected near the river mouth, but outside the influence of the plume provides a range of nitrate values likely to exist in the seawater end-member under different upwelling conditions. The nitrate relationships with salinity and temperature presented in Figure 14 can be used in conjunction with the CORIE time series data (Figures 4, 7, and 11) to obtain an estimate of the nitrate concentration in a newly formed plume. By extrapolating the temperature and salinity data from the CORIE CTD data just within the mouth of the estuary to where it intercepts the temperature/salinity data from the coastal inner shelf samples, it is possible to predict the nitrate concentration of the coastal seawater end-member using Figure 14. This then allows an estimate of the plume nitrate concentration that can be included in future models. The ability to include the concentration of nitrate for a

newly formed plume at any point of time is important for our understanding of the influence of the Columbia River on these coastal waters.

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