

Dissolved iron speciation in two distinct river plumes and an estuary: Implications for riverine iron supply

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Abstract

Dissolved iron (Fe) speciation in the Columbia River plume, the San Francisco Bay plume, and the Columbia River estuary was investigated using competitive ligand exchange–adsorptive cathodic stripping voltammetry (CLE-ACSV) with the added ligand salicylaldoxime. A stronger L₁-type Fe-binding ligand class was measured in all surface samples, and in the Columbia River estuary. A weaker L₂-type ligand class was present in the far-field Columbia River plume and the San Francisco Bay plume but was not observed in the low-salinity ($S = 1.4$ – 22.5) waters of the near-field Columbia River plume or estuary. Concentrations of total dissolved Fe were correlated with the concentrations of the stronger L₁-type ligand in nonestuarine ($S > 13$) surface samples. Leachable particulate ($>0.4 \mu\text{m}$) Fe concentrations in the Columbia River plume were measured to supplement existing data from the San Francisco Bay plume. There is a large concentration of readily leachable particulate Fe in the two plumes, yet it is the concentration of ambient L₁-type ligands that appears to dictate the concentration of dissolved Fe in these waters and, consequently, the supply of dissolved Fe to neighboring coastal waters. The correlation between dissolved Fe and L₁ ligand concentrations in both plume waters, as well as in California Current and upwelled surface waters, suggests that this relationship will persist in other coastal environments and should be considered when evaluating and modeling coastal Fe cycling and supply.

Recent global models have estimated that primary productivity in nearly 40% of the world's oceans is limited by a lack of sufficient iron (Fe; Moore et al. 2002). While total dissolved Fe concentrations are low ($[\text{Fe}_T] < 0.1 \text{ nmol L}^{-1}$) in open ocean high-nutrient low-chlorophyll (HNLC) regions, coastal environments are much closer to continental Fe sources and would seem unlikely to be limited by Fe. Yet low Fe concentrations have been observed to limit productivity in coastal upwelling zones off central California (Hutchins and Bruland 1998; Hutchins et al. 1998) and Peru (Hutchins et al. 2002; Bruland et al. 2005).

A gradient of Fe concentrations is frequently observed in surface transects from the coast offshore, with dissolved Fe concentrations in coastal waters orders of magnitude greater than those in open ocean environments (Martin and Gordon 1988; Bruland et al. 2001; Bruland et al. 2005). This gradient results from the increased input of Fe at coastal margins from river outflow and the upwelling of

suspended shelf sediments (Bruland et al. 1991; Kuma et al. 1996). Rivers can indirectly supply dissolved Fe to nearshore ecosystems by exporting Fe-rich particles to the coastal shelf area that are subsequently upwelled to the surface (Johnson et al. 1999), where Fe may be remineralized from these particles in the presence of light and Fe-binding ligands (Borer et al. 2005). The upwelling of bottom boundary layer (BBL) sediments, particularly from midshelf mudbelt deposits (Xu et al. 2002), has been identified as the predominant source of Fe to shelf surface waters along the California coast (Johnson et al. 1999; Fitzwater et al. 2003).

In both open ocean and coastal marine environments, dissolved Fe(III) is $>99\%$ complexed by strong (high-affinity) organic Fe-binding ligands (Rue and Bruland 1995; van den Berg 1995). The concentrations of these ambient ligands vary widely in the marine environment but are ubiquitously in slight excess of dissolved Fe concentrations (Bruland and Rue 2001; Cullen et al. 2006). The physicochemical speciation of Fe, including the concentrations ($[\text{L}_1]$ and $[\text{L}_2]$) and thermodynamic conditional stability constants ($K_{\text{FeL}_1, \text{Fe}'}^{\text{cond}}$ and $K_{\text{FeL}_2, \text{Fe}'}^{\text{cond}}$) of natural Fe-binding ligands, has been measured using electrochemical techniques (Bruland and Rue 2001). Two classes of Fe(III)-binding organic ligands have been identified: stronger L₁ ligands and weaker L₂ ligands. The stronger L₁ ligands are classified by ($K_{\text{FeL}_1, \text{Fe}'}^{\text{cond}}$ values of 10^{11} – $10^{13} \text{ mol L}^{-1}$, while the weaker L₂ ligands have $K_{\text{FeL}_2, \text{Fe}'}^{\text{cond}}$ values of generally less

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Acknowledgments

We thank Ana Aguilar-Islas, Bettina Sohst, and Geoffrey Smith for sampling assistance. Chlorophyll data were provided by Raphael Kudela, with funding from National Science Foundation grant OCE-0230347. This work was funded from an Ida Benson Lynn Graduate Fellowship in Ocean Health and NSF grants OCE-0238347 and OCE-0526601. The authors thank two anonymous reviewers for their insightful comments.

than 10^{11} mol L⁻¹. It is important to note that these ligand classes are operationally defined, and they represent the average values for a continuum of possible Fe(III)-binding organic molecules assuming that 1:1 Fe(III)-L_i complexes are formed.

In the absence of organic Fe-binding ligands, the solubility of Fe(III) in seawater (pH ~ 8.1) is very low, 0.08 nmol L⁻¹ or less (Wu et al. 2001), and the dominant species of dissolved inorganic Fe are largely hydrolysis products (such as Fe(OH)₃⁺) of sparing solubility. Complexation by Fe(III)-binding ligands stabilizes elevated dissolved Fe concentrations near sources, since without these ligands most inorganic dissolved Fe(III) quickly forms hydroxides that may precipitate out, resulting in consistently low concentrations of dissolved Fe (Wu et al. 2001). Thus, the concentration of these ligands may well determine dissolved Fe concentrations in coastal environments and near Fe sources.

Here we present the dissolved Fe speciation from June and July 2004 in the Columbia River estuary, as well as in the plumes of the Columbia River and San Francisco Bay outflow and their surrounding coastal surface waters. We also present the leachable particulate Fe concentrations of suspended particles in the Columbia River plume, complementing a similar data set obtained by our collaborators in the San Francisco Bay plume (Hurst and Bruland unpubl. data) and providing a larger context for understanding the role of dissolved Fe speciation in the supply of Fe from these two very different river systems.

The Columbia River, on the U.S. Northwest coast, is the second largest river in the United States, discharging an average of ~7,000 m³ s⁻¹ freshwater (Hickey 1998). This high discharge results in low salinity values and short residence times for water (1–3 days) within the estuary (Jay and Smith 1990). San Francisco Bay is a broad shallow estuary in central California with a lower discharge (generally <100 m³ s⁻¹ in summer) than that of the Columbia River (Flegal et al. 1991). Tidal flushing in the San Francisco Bay estuary is far greater than river discharge, resulting in estuarine salinities that are correspondingly much higher in San Francisco Bay in the summer, rarely falling below 30. This hydrology of San Francisco Bay results in residence times for water here that are long—weeks to several months (Flegal et al. 1991).

Our objectives were to determine the dissolved Fe speciation in these two distinct river plume systems and in the low-salinity ($S < 6$) Columbia River estuary, as well as in surrounding surface waters, enabling us to examine the role of ambient Fe-binding organic ligands in the supply of Fe to coastal regions. To date, the Columbia River estuary data presented here represent the first reported Fe speciation data from a low-salinity ($S < 6$) estuary, although Fe speciation has been reported in a freshwater mountain lake in Japan (Nagai et al. 2004). Overall, this research was conducted as part of a larger collaborative effort, providing the opportunity for assessing the role of ambient ligands in terms of both dissolved and leachable particulate Fe concentrations.

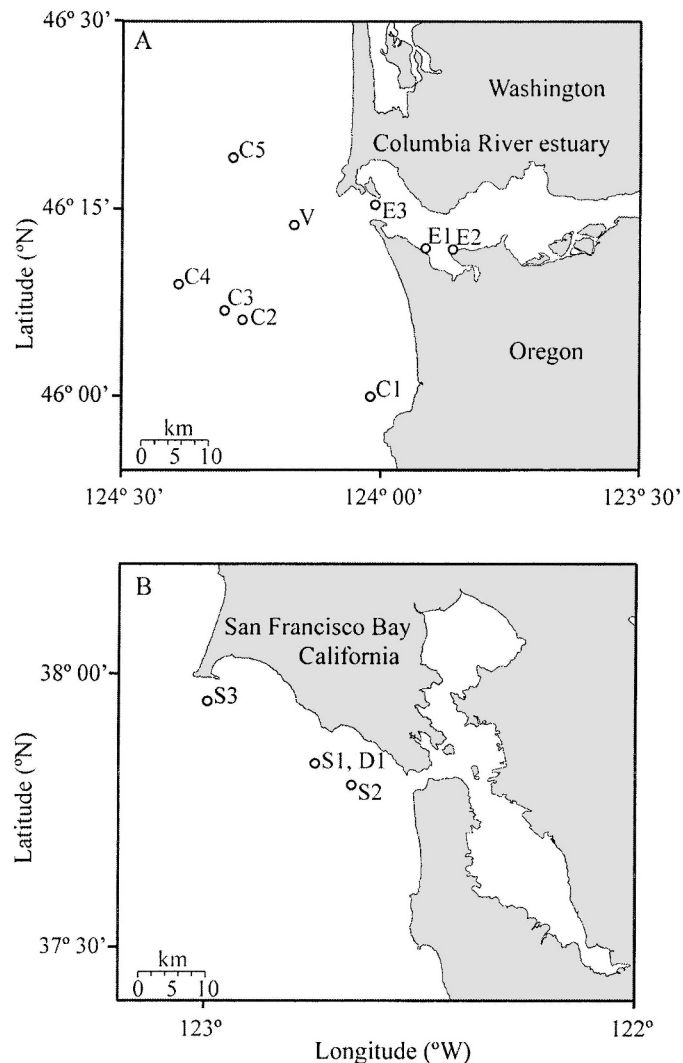


Fig. 1. (A) Surface sampling sites in the Columbia River plume system (C1–C5) and Columbia River estuary (E1–E3), as well as a vertical sampling station (V) in the Columbia River plume system. (B) Surface sampling sites (S1–S3) and deep sample (D1) station in San Francisco Bay plume system.

Materials and methods

Sample collection—Surface samples from the Columbia River (Fig. 1A) and San Francisco Bay (Fig. 1B) plume systems, including shallow (to 20 m) vertical profiles through the Columbia River plume, were collected with a clean surface pump “sipper” system (Bruland et al. 2005) aboard the R/V *Point Sur* in June and the R/V *Wecoma* in July 2004. Columbia River estuary samples and the BBL sample from outside San Francisco Bay were collected using 30 L Teflon™ coated GO Flo™ bottles (General Oceanics) attached to Kevlar™ hydroline (Bruland et al. 1979). Samples from the R/V *Wecoma* in July 2004 were obtained in collaboration with the interdisciplinary river influences on shelf ecosystems (RISE) study.

Samples for leachable particulate Fe, dissolved Fe and dissolved Fe speciation were collected from the Columbia

River estuary (E1–E3) on 30 June 2004. Outside the estuary, samples were collected as vertical profiles (to 20 m) in the near-field plume at station V (Fig. 1A) during consecutive flood and ebb tides in July 2004; particulate Fe samples were collected here only for the plume waters (upper two depths of each profile). Samples were also obtained from the far-field plume (C2–C3, C5) and surrounding California Current (C4) and upwelled subsurface (C1) waters off Oregon and Washington. In the San Francisco Bay plume system, samples were collected within the San Francisco Bay plume and surrounding upwelled subsurface waters. These samples overlap with particulate trace metal samples analyzed by Hurst and Bruland (unpubl. data).

Reagents—Adsorptive cathodic stripping voltammetry (ACSV) reagents: A 5 mmol L⁻¹ salicylaldoxime (SA; Aldrich, ≥98% purity) solution was prepared in quartz-distilled methanol (Q-MeOH) and stored in the refrigerator; SA was stable in Q-MeOH for at least 1 month and did not require any further cleaning prior to use. A final concentration of 25 μmol L⁻¹ SA was used for all speciation and total dissolved Fe measurements. A 1.5 mol L⁻¹ borate buffer was made in 0.4 mol L⁻¹ quartz-distilled ammonium hydroxide (Q-NH₄OH) as previously described (Ellwood and van den Berg 2000). Fe standards were diluted from a 1,000 ppm AA standard with pH 1.8 quartz-distilled hydrochloric acid (Q-HCl).

Flow injection analysis (FIA) reagents: An eluting acid of 1.5 mol L⁻¹ Q-HCl was prepared in Milli-Q water (18 MΩ). A supersaturated ammonium acetate solution was prepared by bubbling anhydrous ammonium gas into quartz-distilled acetic acid. A 3.5 mol L⁻¹ ammonium acetate buffer was then made from the ammonium acetate solution and the pH was adjusted to 9 with Q-NH₄OH. A 1.5 mol L⁻¹ ammonium acetate rinse solution was also prepared from the ammonium acetate solution and adjusted to pH 3.5 with Q-HCl. A 0.05 mol L⁻¹ solution of *N,N*-dimethyl-*p*-phenylenediamine (4-amino-*N,N*-dimethylamine) dihydrochloride (DPD) (Fluka) was made daily by dissolving DPD in Milli-Q (Lohan et al. 2006).

Calibration reagents: A 0.04 mol L⁻¹ ethylenediamine-tetraacetic acid (EDTA; Aldrich) stock solution was prepared in Milli-Q (18 MΩ). The pH of the EDTA solution was adjusted to neutral (~7) before further dilution with Milli-Q. A supersaturated KCl (Suprapur KCl, Merck) solution was prepared in Milli-Q for adjusting the diluted estuarine samples to a salinity of 1.

Total dissolved Fe analyses—All Fe speciation and total dissolved Fe samples were filtered through acid-cleaned 0.45-μm pore size Teflon™ membrane polypropylene capsule filters (Calyx™, MSI) following the cleaning techniques outlined in Bruland et al. (2005). Total dissolved Fe concentrations were measured using two comparable methods: adsorptive cathodic stripping voltammetry (ACSV) and FIA. For both methods, samples were acidified to pH 1.8 with 4 mL L⁻¹ 6 mol L⁻¹ Q-HCl following collection and filtration.

In the ACSV method, samples were microwaved 2 × 15 s at 1,100 Watts to release dissolved Fe from ambient organic matter (Bruland et al. 2005), neutralized once cool with 1 mol L⁻¹ Q-NH₄OH, and buffered to pH 8.2 with a borate buffer. Once buffered, SA and appropriate Fe additions were immediately made, and following ACSV analysis, Fe concentrations were determined from a linear regression of the standard addition curve. The detection limit for the ACSV method was 0.01 nmol L⁻¹, calculated from three times the standard deviation of a 0.05 nmol L⁻¹ Fe addition to UVSW (Macrellis et al. 2001), since no peak was observed in either our Milli-Q or ultraviolet-oxidized seawater (UVSW) at deposition times of up to 900 s. Deposition times for sample analyses here were between 10 and 600 s, depending on ambient dissolved Fe and ligand concentrations.

Total dissolved Fe was also determined using a custom FIA system with a chelating (NTA Superflow) resin (Quiagen), which allowed samples to be analyzed directly at pH 1.8 without inline buffering (Lohan et al. 2005, 2006). The detection limit for this method was 0.02 nmol L⁻¹, calculated from three times the standard deviation of the blank. All total dissolved Fe measurements were determined using the FIA method onboard ship, with a subset of measurements also made using the ACSV method described above. These two methods were extensively compared in both open ocean and coastal waters on an intercalibration cruise (SAFe: Sampling and analysis of Fe, Oct/Nov 2004 R/V *Melville*), and these comparisons indicated that the two methods agree within 3% over the range of 0.1 to ~1 nmol L⁻¹ total dissolved Fe.

Fe speciation analyses—Following collection, speciation samples were frozen and returned to our shore-based laboratory for analysis. Samples were thawed and vigorously shaken to ensure homogeneity before the dissolved Fe speciation was determined using a competitive ligand exchange–adsorptive cathodic stripping voltammetry (CLE-ACSV) method with SA as the added ligand (Rue and Bruland 1995). Here this method has been modified for analysis on a BioAnalytical Systems (BAS) controlled growth mercury electrode (CGME) interfaced with a CV-50 W voltammetric analyzer. A 0 V deposition potential was used for all speciation analyses, as this potential provided the highest sensitivity in laboratory experiments (Fig. 2). See Table 1 for a complete list of voltammetric parameters used in this study.

For each titration, 10-mL sample aliquots were made into lidded Teflon™ Savillex vials (17 mL flat bottom). Aliquots were then buffered to pH 8.2 with a borate buffer before the addition of dissolved inorganic Fe. This added Fe was allowed to equilibrate for at least 120 min with the ambient ligands, following laboratory studies suggesting that long (>90 min) equilibration times were necessary (Fig. 3). To minimize the loss of added inorganic Fe to the vial walls once the ambient ligands have been titrated, the vials were conditioned to the specific Fe additions and the seawater matrix.

Once equilibrated with the Fe additions, 25 μmol L⁻¹ SA was added and allowed to equilibrate 15 min prior to

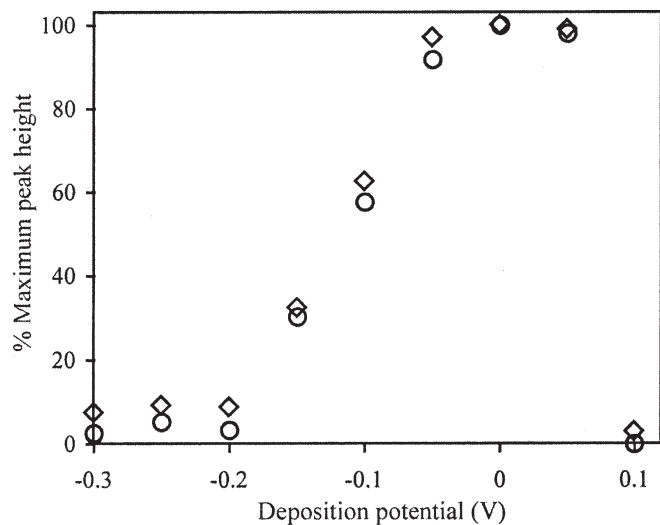


Fig. 2. Effect of changing deposition potential on current response. The two symbols (diamonds and circles) represent duplicate experiments conducted in ambient coastal seawater samples. Maximum peak height was consistently achieved at a deposition potential of 0 V, and this deposition potential was used for all measurements.

analysis. Vials were equilibrated one at a time to avoid a dip in sensitivity observed in lengthy (deposition times >300 s) titrations (data not shown), presumably from loss of the $\text{Fe}(\text{SA})_2$ complex to vial walls at high Fe additions. The linear current response achieved, with increasing Fe additions, after the titration of ambient ligands (Fig. 4) indicates that the loss of Fe to vial walls or colloidal aggregates was insignificant, or at least reversible, such that any lost Fe was recovered by the addition and equilibration of SA in the samples.

Low-salinity ($S < 5$) estuarine samples were diluted 10-fold with Milli-Q (18 M Ω), as suggested by Nagai et al. (2004), in order to improve the method sensitivity in freshwaters and prevent mercury drop saturation at the elevated dissolved Fe concentrations of the estuarine sample titrations (Nagai et al. 2004). Following the dilution of estuarine samples and adjustment to salinity of 1, the sensitivity of this method was improved to nearly 16 nA nmol⁻¹ L min⁻¹, which is comparable to the

Table 1. CLE-ACSV parameters used for all Fe speciation measurements.

CSV parameter	Setting
Mode	Differential pulse
Initial potential	0 V
Final potential	-0.85 V
Scan rate	0.03 V s ⁻¹
Sample width	17 ms
Pulse amplitude	0.05 V
Pulse width	35 ms
Pulse period	200 ms
Quiet time	15 s
Sensitivity	10 $\mu\text{A V}^{-1}$
Stir rate	600 RPM
Drop size	14 (large)

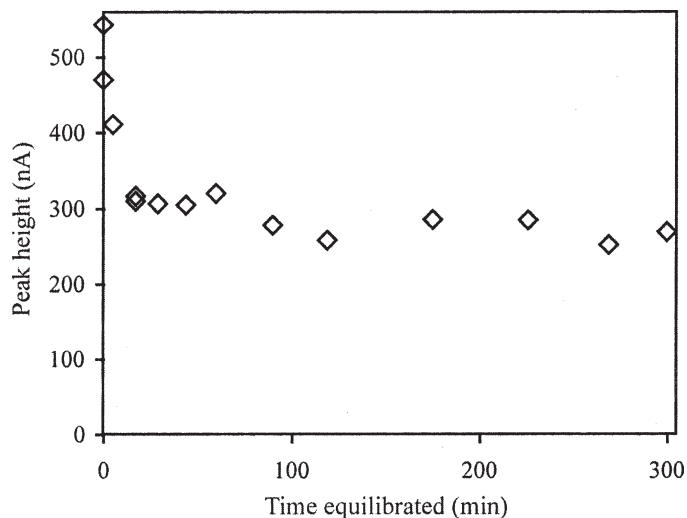


Fig. 3. Time to reach equilibrium between added inorganic Fe and ambient Fe-binding ligands. Current response was steady after ~90 min of equilibration, and we used 120 min for equilibration throughout this study.

sensitivity of this method in seawater (15–30 nA nmol⁻¹ L min⁻¹).

In the current literature, SA has only been calibrated for oceanic salinities (Rue and Bruland 1995). In order to get accurate data over the range of salinities encountered here, SA was calibrated against EDTA following the methods of Gledhill and van den Berg (1994) for 1-nitroso-2-naphthol (NN) and Rue and Bruland (1995) for SA to obtain appropriate stability constants for the $\text{Fe}(\text{SA})_2$ complexes in these samples. To calibrate the SA, ultraviolet (UV)-oxidized seawater that had organic ligands and trace metals removed (Donat and Bruland 1988) was diluted with Milli-Q to achieve salinities of 1, 11, 21, and 36 (Orion conductivity meter, model 130). At each salinity, water was aliquoted to Savillex vials and spiked with 1.5 mol L⁻¹ borate buffer, 25 $\mu\text{mol L}^{-1}$ SA, and 10 nmol L⁻¹ Fe. A

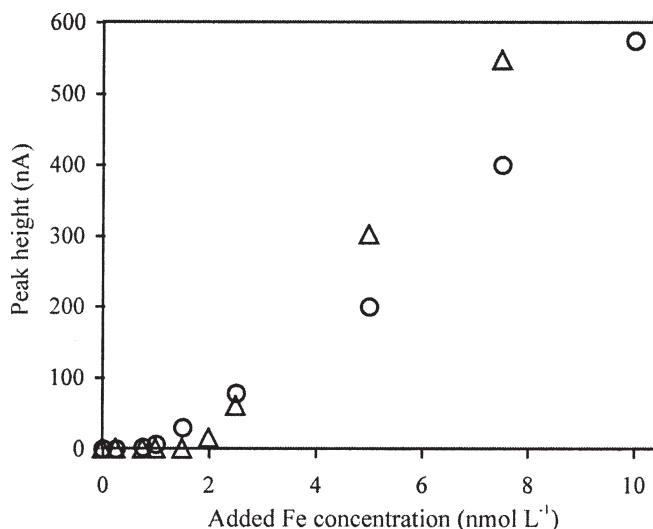


Fig. 4. Peak height as a function of added dissolved Fe concentration in titrations of S3 (circles) and E1 (triangles).

range of EDTA concentrations (1 nmol L^{-1} to $100 \text{ } \mu\text{mol L}^{-1}$ final concentrations) was then added to the vials and allowed to equilibrate with the SA for 5 h. Following equilibration, each vial was analyzed at 4-min deposition times. The theory behind these calibration techniques has been extensively documented elsewhere (e.g., Gledhill and van den Berg 1994; Rue and Bruland 1995).

Raw speciation data were then interpreted using the Scatchard and van den Berg/Ružic' linearization methods to calculate the concentrations of ambient Fe-binding ligands and the conditional stability constants of these ligands (Ružic' 1982; van den Berg 1982). With these linearization techniques, the data fit to a single line when one ligand class was observed, and in the case of two or more ligand classes the data were depicted as two distinct lines. Figure 5A,B illustrates the van den Berg/Ružic' and Scatchard linearizations, respectively, of an estuary sample (one ligand class observed) and a coastal surface (two ligand classes) sample. The mean and standard deviation of results was calculated from these two linearization techniques.

Leachable particulate Fe analyses—Columbia River plume system samples were also collected for leachable particulate Fe analyses. These samples were filtered at sea, using an inline filtration rig pressurized with nitrogen gas ($\sim 35 \text{ kPa}$), through acid-cleaned 47-mm diameter Nuclepore™ polycarbonate track-etched membrane filters (Whatman, $10\text{-}\mu\text{m}$ and $0.4\text{-}\mu\text{m}$ filters in series) mounted in Teflon™ filter sandwiches (Millipore™). Following filtration, filters were folded and stored frozen in polyethylene vials. Back in our shore-based laboratory, filters were subjected to a 2-h room temperature 25% acetic acid leach (Chester and Hughes 1967; Landing and Bruland 1987). The 25% acetic acid leach is a pH 2 weak acid leach, used to provide an estimate of the readily leachable (or easily soluble) Fe associated with the particles. After the leach was complete, the leachate was then analyzed for Fe using high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS; Thermo-Electron Element 1) as described in Hurst and Bruland (unpubl. data). The leachable particulate Fe concentrations presented here for both the Columbia River plume (this work) and the San Francisco Bay plume (Hurst and Bruland unpubl. data) were measured following this method.

Results

Stations where dissolved Fe speciation samples were collected are identified for the Columbia River (Fig. 1A) and San Francisco Bay plume systems (Fig. 1B). Hydrographic data and station locations for Fe speciation samples are summarized in Table 2. Dissolved Fe speciation results from all samples are presented in Table 3. Salinity values were used to distinguish the Columbia River plume ($S < 29.4$) from neighboring California Current ($S = 29.4\text{--}32$) and upwelled/subsurface ($S > 32$) waters. The near-field Columbia River plume was sampled at a time-

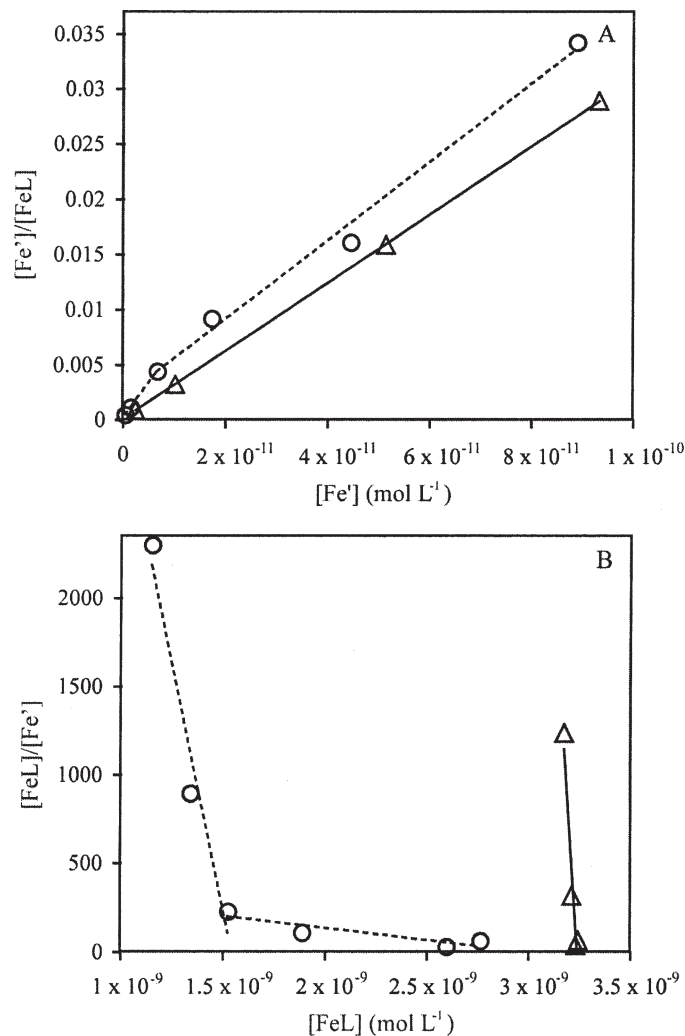


Fig. 5. (A) van den Berg/Ružic' linearization results from titrations of S3 (circles) and E1 (triangles). The long dashed lines represent the best linear fit in the two-ligand system seen in sample S3 (circles). The dotted line represents the best linear fit for the one-ligand system observed in sample E1 (triangles). (B) Scatchard linearization results from S3 (circles) and E1 (triangles) titrations. The long dashed lines indicate the best linear fit for the two-ligand system (S3), and the single dotted line indicates the best linear fit for the one-ligand system (E1).

series station (Sta. V) for vertical profiles just outside the estuary mouth over an 18-h time period (Fig. 1A).

Three surface samples (S1–S3) and one deep sample (D1) were obtained from the San Francisco Bay plume system (Fig. 1B) on 23 June 2004. Surface samples were collected from upwelled subsurface ($S > 33.7$) waters (S1, S3) and the San Francisco Bay plume ($S < 33$; S2) in this system (Table 2). The deep sample (D1) was taken from the BBL just outside the San Francisco Bay, as was indicated by the lower percentage beam transmission observed here (data not shown).

SA calibration—The conditional stability constant for SA with Fe, $\beta_{\text{Fe}(\text{SA})_2, \text{Fe}^3}^{\text{cond}}$, was calibrated against EDTA at four different salinities (1, 11, 21, 36). The results from this

Table 2. Sampling station information and hydrographic data for all samples. Water types include subsurface (SS), California Current (CC), San Francisco Bay plume (SFP), Columbia River plume (CRP), and Columbia River estuary (CRE) waters.

Sample	Date	Depth (m)*	Tide	Latitude (°N)	Longitude (°E)	Salinity	Type
S1	23 Jun 04	Surface	Ebb	37.84	-122.70	33.8	SS
S2	23 Jun 04	Surface	Ebb	37.80	-122.70	32.7	SFP
S3	23 Jun 04	Surface	Ebb	37.95	-122.99	33.8	SS
D1	22 Jun 04	31	Ebb	37.91	-122.92	33.9	SS
E1	30 Jun 04	2	Ebb	46.20	-123.92	5.6	CRE
E2	30 Jun 04	2	Ebb	46.19	-123.83	1.4	CRE
E3	30 Jun 04	2	Ebb	46.25	-124.01	4.9	CRE
C1	30 Jun 04	Surface	Spring ebb	46.00	-124.02	32.1	SS
C2	30 Jun 04	Surface	Spring ebb	46.10	-124.27	22.8	CRP
C3	30 Jun 04	Surface	Spring ebb	46.11	-124.30	23.6	CRP
C4	30 Jun 04	Surface	Flood	46.15	-124.39	31.0	CC
C5	02 Jul 04	Surface	Spring flood	46.32	-124.29	22.5	CRP
V1	13 Jul 04	2.2	Flood	46.23	-124.17	26.7	CRP
V1	13 Jul 04	4.2	Flood	46.23	-124.17	28.6	CRP
V1	13 Jul 04	9.7	Flood	46.23	-124.17	31.7	CRP
V1	13 Jul 04	15.7	Flood	46.23	-124.17	32.5	SS
V2	14 Jul 04	0.9	Ebb	46.23	-124.18	13.0	CRP
V2	14 Jul 04	1.7	Ebb	46.23	-124.18	20.9	CRP
V2	14 Jul 04	4.1	Ebb	46.23	-124.18	31.4	CRP
V2	14 Jul 04	14.9	Ebb	46.23	-124.18	32.8	SS

* Depth at which sample was acquired, where "Surface" samples were obtained with the sipper fish at depths averaging 2 m.

calibration are summarized in Table 4 and illustrated in Fig. 6A,B. The effect on peak height of varying the concentrations of EDTA is depicted in Fig. 6A. The value of $\log \beta_{\text{Fe}(\text{SA})_2, \text{Fe}'}^{\text{cond}}$ was found to vary linearly with \log salinity, as shown in Fig. 6B, such that $\log \beta_{\text{Fe}(\text{SA})_2, \text{Fe}'}^{\text{cond}} = -0.37 \log \text{salinity} + 11.59$. This relationship was determined from a linear regression of the calibration data and was used to calculate $\beta_{\text{Fe}(\text{SA})_2, \text{Fe}'}^{\text{cond}}$ for each sample. The

effect of salinity on $\beta_{\text{Fe}(\text{SA})_2, \text{Fe}'}^{\text{cond}}$ was found to be quite small, and speciation results were not greatly affected by new $\beta_{\text{Fe}(\text{SA})_2, \text{Fe}'}^{\text{cond}}$ values at low salinities.

Vertical profiles—Vertical profiles of salinity, as well as dissolved Fe, L₁-type ligand, and L₂-type ligand concentrations, in the upper 20 m of the water column in the Columbia River plume system, collected at Sta. V (Fig. 1A)

Table 3. Dissolved Fe speciation results from all samples and corresponding chlorophyll data. The concentrations of L₁ and L₂ ligands are expressed as averages and standard deviations of van den Berg/Ruzic' and Scatchard results.

Sample	[Fe] (nmol L ⁻¹)	[L ₁] (nmol L ⁻¹)	$\log K_1$	[L ₂] (nmol L ⁻¹)	$\log K_2$	Chl <i>a</i> (μg L ⁻¹)
S1	5.3±0.1	5.6±0.2	12.7	2.3±0.4	11.8	nda
S2	8.2±0.1	8.3±0.3	12.8	3.2±0.1	11.1	9.42
S3	1.2±0.06	1.6±0.02	12.9	1.3±0.02	11.3	12.57
D1	6.2±0.2	19.3±0.02	12.9	5.0±1	11.1	nda
E1	13.3±0.1	32.4±0.02	13.9	nd	nd	nda
E2	22.4±0.1	45.7±0.3	13.3	nd	nd	6.26
E3	16.8±0.1	55.8±0.6	12.7	nd	nd	nda
C1	2.0±0.04	2.9±0.06	12.6	3.2±0.2	11.4	24.64
C2	3.6±0.04	5.4±0.9	12.0	9±5	10.7	nda
C3	2.1±0.04	3.8±0.2	11.8	2.3±0.4	11.1	nda
C4	1.4±0.04	2.4±0.01	11.9	1.1±0.02	11.4	nda
C5	7.0±0.07	6.6±0.04	12.3	2.6±0.09	11.2	nda
V1	1.6±0.03	3.5±0.3	11.9	nd	nd	2.08
V1	2.1±0.03	2.6±0.08	12.7	nd	nd	8.79
V1	0.6±0.03	1.0±0.1	12.1	nd	nd	10.40
V1	1.1±0.03	1.8±0.1	12.0	0.4±0.4	11.3	nda
V2	5.2±0.04	5.2±0.2	11.8	nd	nd	7.00
V2	3.0±0.04	3.2±0.2	12.5	nd	nd	6.26
V2	0.8±0.04	1.7±0.5	11.1	nd	nd	0.89
V2	0.8±0.04	1.1±0.1	12.5	0.5±0.1	11.7	12.61

Here, "nd" refers to the ligand class as "not detectable" in these analyses and "nda" refers to "no data available" for chlorophyll.

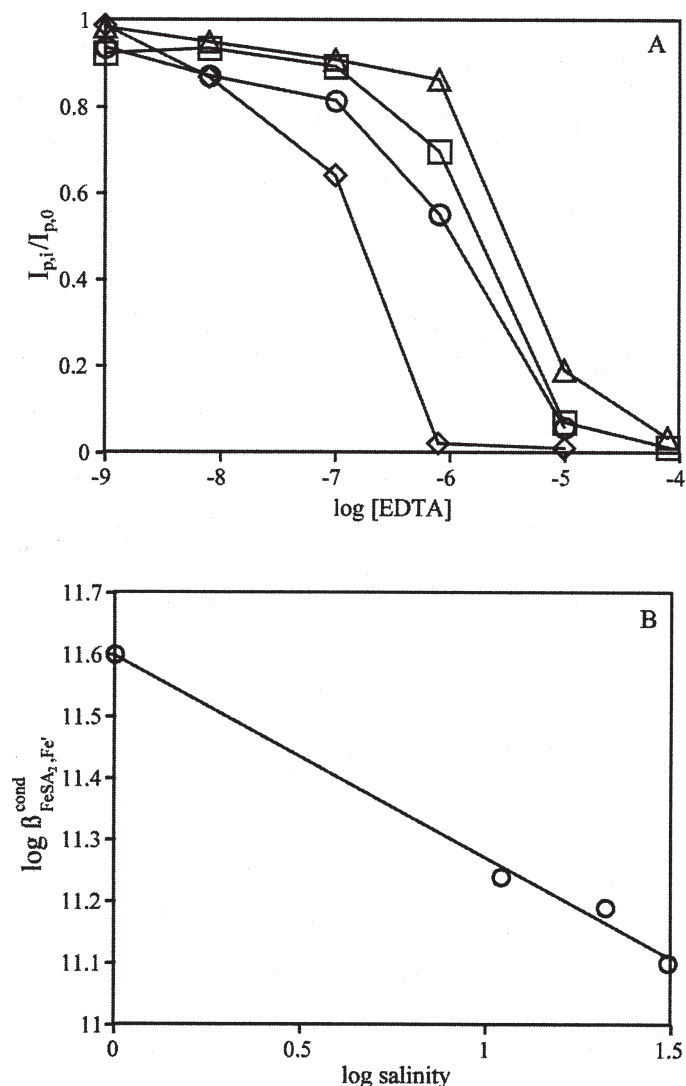


Fig. 6. (A) Change in peak height as a function of added EDTA concentrations over a range of salinities in UVSW/Milli-Q solutions spiked with $10 \text{ nmol L}^{-1} \text{ Fe}$ and $25 \mu\text{mol L}^{-1} \text{ SA}$. Peak height is expressed here as the ratio of current in samples with EDTA over the current in samples with no EDTA added ($i_{p,i}/i_{p,0}$) for salinities of 1 (diamonds), 11 (circles), 21 (squares), and 36 (triangles). (B) Plot of relationship between $\log \beta_{\text{Fe}(\text{SA})_2, \text{Fe}}^{\text{cond}}$ and $\log \text{salinity}$ deduced from calibration against EDTA.

during a neap tidal sequence, are shown in Fig. 7A for the flood tide and in Fig. 7B for the ebb tide. The concentrations of the stronger L_1 -type ligands in both profiles (Fig. 7A,B) were higher ($3.5\text{--}5.2 \text{ nmol L}^{-1}$) in the surface waters, with the highest concentrations (5.2 nmol L^{-1}) in the shallow low-salinity plume lens of the outflowing ebb tide profile (Fig. 7B). Within these vertical profiles, the weaker L_2 -type ligands were not present in the plume or mixed surface waters (Fig. 7A,B) and were only detected in the deepest samples (15–16 m). Dissolved Fe concentrations were also highest in the plume and mixed surface waters of both profiles (Fig. 7A,B), and during the ebb tide the concentration of dissolved Fe saturated the L_1 ligand

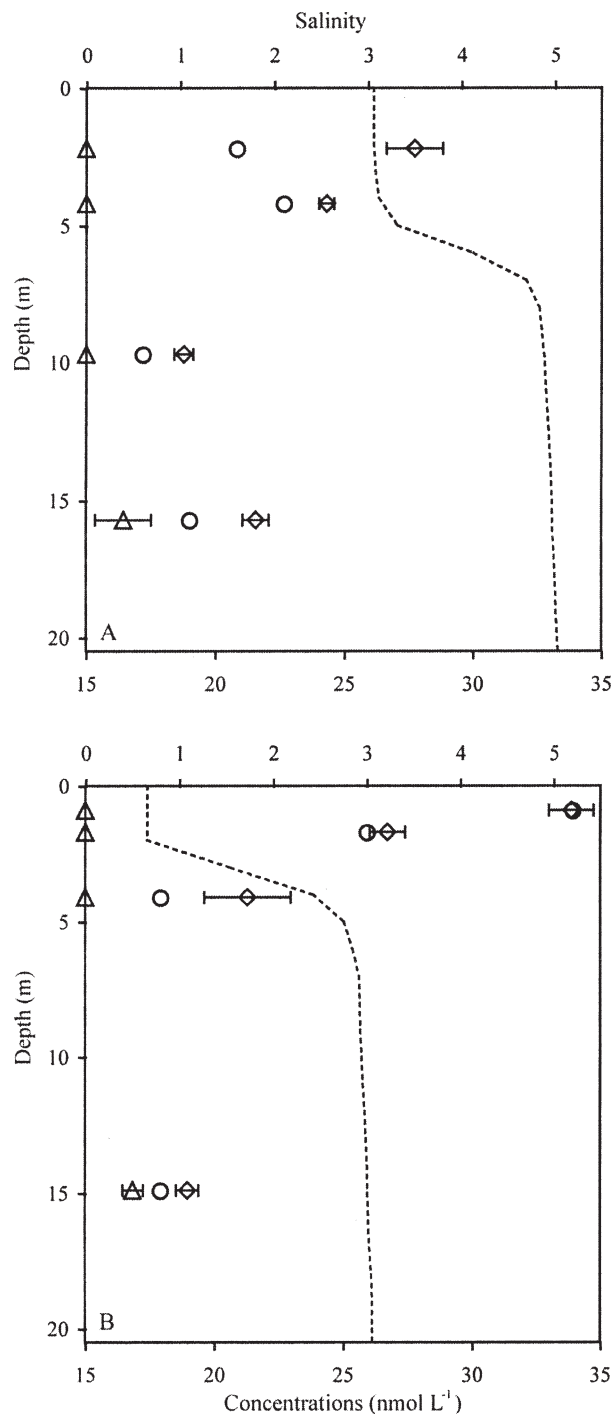


Fig. 7. Vertical profiles of salinity (dotted line), dissolved Fe (circles), stronger L_1 ligand (diamonds), and weaker L_2 ligand (triangles) concentrations for a consecutive (A) flood and (B) ebb tide from Sta. V in the near-field Columbia River plume system.

concentrations ($[\text{Fe}] = [\text{L}_1] = 5.2 \text{ nmol L}^{-1}$) in the Columbia River plume lens (Fig. 7B).

Mixing lines—Dissolved Fe and Fe-binding ligand concentrations of all data from both plume systems are plotted against corresponding salinity values in Fig. 8.

Table 4. Conditional stability constants for salicylaldoxime with respect to Fe' from calibration against EDTA. Values for $\alpha_{\text{FeEDTA, Fe}'}$ were obtained from Martell and Smith (1974) as described by Gledhill and van den Berg (1994) and Rue and Bruland (1995).

Salinity	$\log \alpha_{\text{FeEDTA, Fe}'}$	$\log \beta_{\text{Fe(SA)}_2, \text{Fe}'}$ ^{cond}
1	2.40	11.6
11	2.04	11.24
21	1.99	11.19
36	1.90	11.1

Dissolved Fe concentrations and stronger L₁-type ligand concentrations were highest in the Columbia River estuary (Fig. 8), with a large excess of L₁ ligands observed here (Table 3). As seen in previous studies of dissolved Fe and humic acids (Sholkovitz 1976; Boyle et al. 1977), most of the dissolved Fe (and L₁ ligands) measured in the estuary (E1–E3; [Fe] = 13.3–22.4 nmol L⁻¹, [L₁] = 32.4–55.8 nmol L⁻¹) was lost before the near-field plume station (V; [Fe] = 0.6–5.2 nmol L⁻¹, [L₁] = 1.0–5.2 nmol L⁻¹), presumably because of a combination of flocculation and subsequent dilution with coastal seawater. At the near-field plume station (V; *S* = 13), the dissolved Fe saturated the L₁ ligand concentrations, with no ligand excess observed (Table 3). The weaker L₂ ligands were not apparent in any samples with salinity less than 22 (Fig. 7), with many of the Columbia River plume samples having no observed L₂ ligands and all of the San Francisco Bay plume system samples having an excess of L₂-type ligands (Table 3).

The freshwater end member of the Columbia River was not sampled on the RISE cruise in 2004, but it was sampled for dissolved Fe concentrations on a subsequent RISE cruise in summer 2005. The dissolved Fe data presented in Fig. 9 depict the results from mixing experiments of

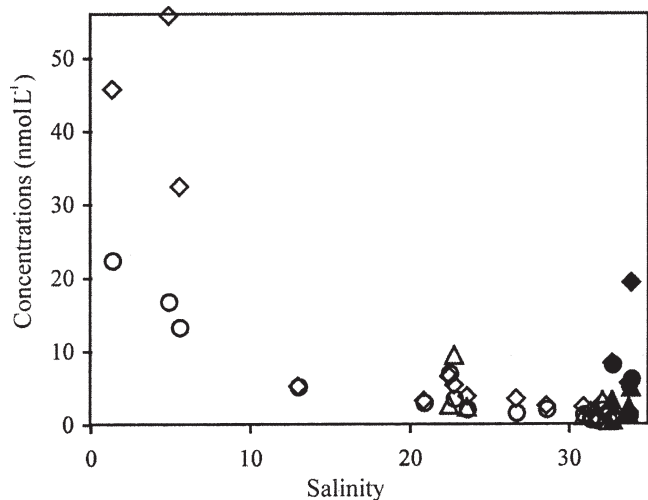


Fig. 8. Dissolved Fe (circles), L₁ ligand (diamonds), and L₂ ligand (triangles) concentrations versus salinity for all samples in the Columbia River system (open symbols) and the San Francisco Bay system (closed symbols).

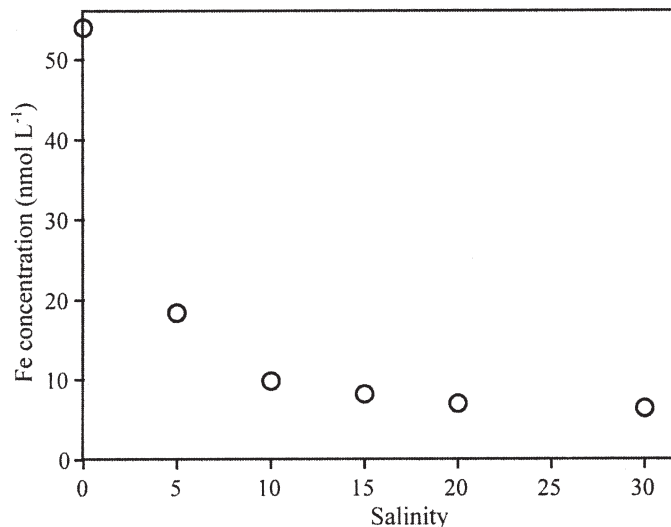


Fig. 9. The concentration of dissolved Fe as a function of salinity from mixing experiments of Columbia River and California Current waters. These samples were collected and analyzed in the summer of 2005 following the same procedures reported here.

dissolved Fe over a range of salinities from 0 salinity in the lower Columbia River to a salinity of 30 in the adjacent California Current. The mixing experiment was designed using similar protocols to Sholkovitz (1978), with filtered (0.4 μm) as for leachable particulate work; see *Methods*) California Current seawater mixed with varying volumes of Columbia River water (collected 25 miles upriver from estuary mouth) to produce six solutions ranging in salinity from 0 to 30. These samples were left for 6 h following mixing before filtering (0.4 μm) to collect the flocculants. As shown in Fig. 9, dissolved Fe concentrations were highest in the river end member, with 54 nmol L⁻¹ at 0 salinity, and decreased rapidly with increasing salinity to 18 nmol L⁻¹ at a salinity of 5. Further downstream, the dissolved Fe concentrations continue to decrease in the middle and lower estuary salinities, but the decrease is much less pronounced.

[L₁] versus [Fe]—As shown in Fig. 10 for the summer 2004 data, there is a close correlation between the dissolved Fe and ambient L₁ ligand concentrations ($r^2 = 0.84$, $n = 14$, $p < 0.001$; simple linear regression). This data set includes samples from the Columbia River and San Francisco Bay plume systems, as well as surrounding California Current and upwelled subsurface waters (Table 2). There is no correlation between dissolved Fe and L₂ ligand concentrations and a much poorer correlation between the total ligand (L₁ + L₂) concentration and dissolved Fe ($r^2 = 0.32$; data not shown). The 1:1 ($y = x$) line plotted on Fig. 10 demonstrates that while dissolved Fe concentrations approach the concentrations of L₁ ligands, they rarely (and then only slightly) exceed them. In the one case in Fig. 10 where [Fe] slightly exceeds [L₁], the [L₂] plays a small role in maintaining this elevated dissolved Fe concentration (C5, Table 3). No discernible relationship

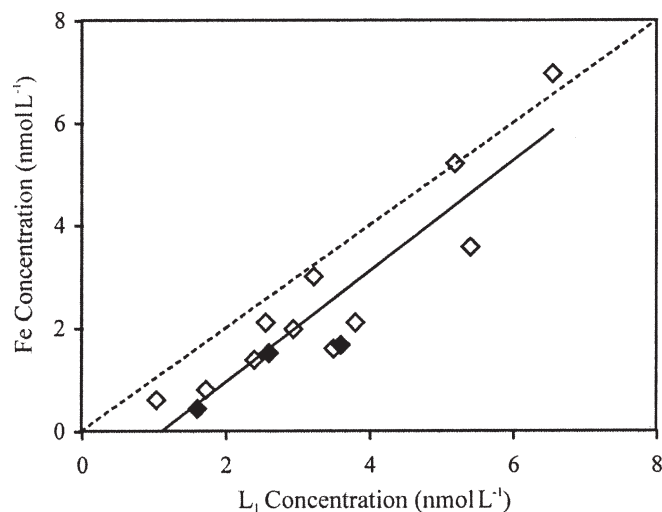


Fig. 10. The concentrations of dissolved Fe as a function of the stronger L_1 -type ligand concentrations for surface samples from the Columbia River system (open symbols) and the San Francisco Bay system (closed symbols). The dashed line represents $y = x$, and the solid line a simple linear regression ($r^2 = 0.84$, $n = 14$, $p < 0.001$; simple linear regression).

was observed between the concentrations of Fe, L_1 , or L_2 ligands and chlorophyll in this study, although chlorophyll data were not available for all samples (Table 3).

Leachable particulate versus dissolved Fe—Dissolved L_1 and total ligand ($L_1 + L_2$) concentrations (this work) have been superposed on leachable particulate Fe versus dissolved Fe data acquired from the San Francisco Bay plume system (Hurst and Bruland unpubl. data) in Fig. 11A and from the Columbia River plume system (this work) in Fig. 11B. Leachable particulate Fe concentrations were much higher in the Columbia River plume region (Fig. 11B) than in the San Francisco Bay plume region (Fig. 11A), although both systems were providing elevated concentrations of leachable particulate Fe to their respective coastal systems. Despite the large pool (up to 360 nmol L^{-1}) of readily leachable particulate Fe present in both plume systems (Fig. 11A,B), dissolved Fe concentrations only reached up to 18 nmol L^{-1} . The inclusion of Fe-binding ligand data in Fig. 11A,B demonstrates that while dissolved Fe concentrations generally increased as leachable particulate Fe increased, they leveled off as their concentrations approached the L_1 ligand concentration. As such, dissolved Fe concentrations did not exceed the L_1 ligand concentrations, despite much larger leachable particulate Fe concentrations and, in some cases, an excess of weaker L_2 ligands present (Fig. 11A,B; Table 3).

Discussion

Within the Columbia River estuary, dissolved Fe speciation is dominated by a large excess of stronger L_1 -type ligands ($\log K_{\text{Fe}L_1, \text{Fe}'}^{\text{cond}} = 12.7\text{--}13.9$). Between the lowest salinity region of the estuary and the near-field plume station (V), the concentrations of both dissolved Fe and L_1

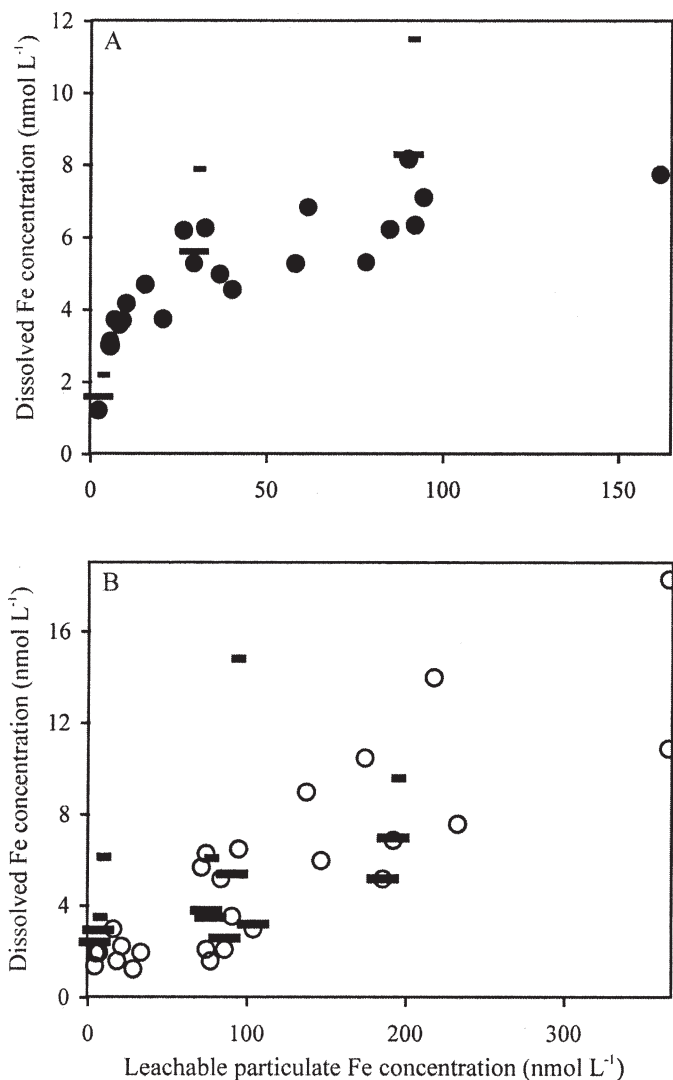


Fig. 11. Leachable particulate Fe concentrations versus dissolved Fe (circles), L_1 ligand (wide black bars), and total ($[L_1] + [L_2]$) ligand (short black bars) concentrations for (A) the San Francisco Bay system and (B) the Columbia River system. Leachable particulate Fe and dissolved Fe concentrations for the San Francisco Bay system from Hurst and Bruland (unpubl.) and for the Columbia River plume system from this work.

ligands decreased dramatically (60% and 80%, respectively; Table 3). Higher resolution of Fe speciation data between the estuary and near-field plume station is required to determine whether the loss in dissolved Fe and L_1 ligands was due to flocculation (nonconservative) or simple dilution (conservative). However, complementary work conducted in this region (Fig. 9) has shown that the loss of dissolved Fe here is most pronounced at low salinities, likely because of flocculation within the estuary, as has been observed in other estuarine environments (Boyle et al. 1977; Sholkovitz 1976, 1978). The remaining decrease between the estuary and the near-field plume station may then be due to a combination of flocculation and dilution. Since the concentrations of dissolved Fe and L_1 ligands are

correlated ($r^2 = 0.84$, $n = 14$, $p < 0.001$; simple linear regression) and the L_1 ligands are saturated with dissolved Fe at the near-field Columbia River plume station, we anticipate that the L_1 ligands are also lost to flocculation in the low-salinity estuary. Indeed, earlier work by Sholkovitz (1976) suggested that dissolved organic matter (e.g., humic acids) plays an important role in the flocculation of Fe during river–ocean mixing.

The Columbia River and San Francisco Bay plume systems are distinctly different. The Columbia River is a high-discharge river system with short (1–3 days) residence times for water, and particles here are largely exported to the coastal shelf waters in a relatively low-salinity plume (Jay et al. 1990; Dagg et al. 2004). San Francisco Bay, on the other hand, has a lower river discharge, and particles in this shallow estuary may be resuspended and recycled in the water column over long (months) hydrologic residence times before being exported to the coast in a relatively high-salinity plume (Flegal et al. 1991).

The differences between these two systems are highlighted in the leachable particulate Fe concentrations measured in their respective plumes (Fig. 11A,B). In the Columbia River plume (Fig. 11B), the concentration of leachable particulate Fe associated with particles is much higher than for the San Francisco Bay plume particles (Fig. 11A)—likely because of the distinct hydrologic characteristics between the Columbia River estuary and San Francisco Bay. Over the range of leachable particulate Fe concentrations associated with particles in each of these plumes, the concentration of dissolved Fe is variable, such that there is no reliable relationship between leachable particulate and dissolved Fe concentrations (Fig. 11A,B).

Despite the wide range in the concentration of leachable particulate Fe between the Columbia River plume and San Francisco Bay plume, the concentrations of dissolved Fe in both systems are dependent on the stronger L_1 -type ligand concentrations. These dissolved Fe concentrations approach, but do not exceed, the ambient concentration of L_1 -type ligands (Fig. 11A,B), and a strong correlation ($r^2 = 0.84$, $n = 14$, $p < 0.001$; simple linear regression) between the concentration of dissolved Fe and the stronger L_1 -type ligands is observed for surface samples obtained from both plumes, as well as from California Current and upwelled subsurface waters (Fig. 10). These results imply that the concentration of ambient L_1 ligands plays a governing role in “capping” dissolved Fe concentrations (at the L_1 concentration) in both of these coastal river plume systems, regardless of the amount of Fe readily available to dissolve from suspended particles determined by the 2-h weak acid (pH 2) leach.

The association between particle recycling (or aging) in San Francisco Bay and the resulting leachable particulate Fe concentrations in the plume has been observed by Hurst and Bruland (pers. comm.). These authors measured leachable particulate Fe concentrations in the San Francisco Bay plume during the winter, when river discharge is high and residence times are much shorter (weeks), as well as during the summer period discussed here. In the winter,

when residence times in the estuary were shorter, the leachable particulate Fe constituted 37% of the particulate Fe pool in the plume, versus 6% under the lower flow and longer residence times of the summer (Hurst and Bruland unpubl. data). Thus, while particles aged in the estuary, leachable Fe was preferentially removed from particles, resulting in a lower percentage leachable particulate Fe associated with particles exported in the plume. By comparison, in the near-field Columbia River plume in summer 2004, ~12% of particulate Fe was in the readily leachable fraction.

Hurst and Bruland (unpubl. data) also found that 30–50% of the dissolved Fe pool was in the colloidal (0.03–0.4 μm) size class in samples collected from the San Francisco Bay plume. Since our speciation samples were collected concurrently with a subset of the Hurst and Bruland (unpubl. data) stations, and dissolved Fe concentrations were strongly correlated ($r^2 = 0.84$, $n = 14$, $p < 0.001$; simple linear regression) with the stronger L_1 ligand concentrations in these speciation samples, a fraction of these L_1 ligands must also have been in the colloidal fraction. In the Columbia River plume, 20% of the dissolved Fe and L_1 ligands were measured in the soluble (<0.03 μm) fraction (this study, data not shown), leaving nearly 80% of each in the colloidal (0.03–0.4 μm) fraction by subtraction. There was no L_2 ligand class present in this sample for comparison. Other studies have also documented the presence of a significant component of dissolved Fe and Fe-binding ligands in the colloidal size fraction, especially in areas with elevated dissolved Fe concentrations (Bruland and Rue 2001; Cullen et al. 2006).

While the identity and sources of ambient ligands cannot be determined from ACSV, the strong L_1 -type ligands measured by this method have been shown in previous work to resemble siderophores based on the comparability of conditional stability constants between strong ambient ligands and siderophores (Witter et al. 2000; Macrellis et al. 2001). However, high conditional stability constants measured for ambient ligands by CLE-ACSV is not conclusively indicative of the presence of siderophores in these samples. Marine siderophores, like their terrestrial counterparts, have recently been shown to play a dissolutive role in obtaining Fe from particles (Borer et al. 2005), a process enhanced in the presence of light and likely due to the photoreactivity of some marine siderophore functional groups (Barbeau et al. 2001).

The association of a fraction (30–50% in San Francisco Bay plume, ~80% in Columbia River plume) of the stronger L_1 ligands with the colloidal fraction is troublesome for any argument for siderophores, since siderophores are low-molecular-weight (300–1,000 Da) ligands and should be in the soluble fraction (Macrellis et al. 2001). However, since marine siderophores have been shown to be associated with particles in the natural environment (Reid et al. 1993), it may be possible that the strong Fe-binding ligands we see in the L_1 ligand class are siderophores associated with colloidal organics. Recent observations of amphiphilic siderophores with long hydrophobic fatty acid chains (Martinez et al. 2003) provides a mechanism by which a fraction of marine siderophores could partition

with organic colloids via tethering with the hydrophobic "tails."

While marine phytoplankton have been shown to produce Fe-binding ligands, including siderophores, there was no correlation between chlorophyll and ambient ligands, either L_1 or L_2 , in this study (Table 3). Similarly, Powell and Wilson-Finelli (2003) did not observe a relationship between ligand and chlorophyll concentrations in the Gulf of Mexico or in the Mississippi River plume. Yet the strong binding constants of the ambient ligands ($\log K_{\text{FeL}_1, \text{Fe}'}^{\text{cond}} = 11.1\text{--}13.9$) make them unlikely to be weaker Fe-binding humic-type material (Hudson et al. 1992).

Since these plume environments are rich in colloids and organic material, the strong Fe-binding ligands observed in the colloidal size fraction may well be organic macromolecules or other colloidal organic matter. High-molecular-weight marine polysaccharides make up a substantial portion of the reactive colloidal dissolved organic matter in marine waters (Santschi et al. 1998). As functional groups on this organic colloidal material could be involved in binding Fe and increasing the solubility of Fe in seawater (Chen et al. 2004), these high-molecular-weight marine polysaccharides may be another source of colloidal Fe-binding ligands. Additionally, the strong organic colloidal ligands may also be cell wall fragments of bacteria and phytoplankton that have retained some high-affinity Fe-binding sites associated with them. Of note, the Fe-binding ligands observed in this study are not interpreted to be purely inorganic Fe colloids because of the curvature observed in sample titrations (Fig. 4) and the loss of these ligands during UV-oxidation of the samples (data not shown). However, it may be possible that these ligands originate from organic matter adsorbed to inorganic Fe oxide colloids, although any effect of Fe oxide colloids on CLE-ACSV measurements remains to be clarified.

The sources and cycling of the weaker L_2 -type ligands are even less understood than those of the L_1 ligands. In this work we have not observed L_2 ligands in low-salinity ($S < 22$) waters (Fig. 8). Rather, L_2 ligands ($\log K_{\text{FeL}_2, \text{Fe}'}^{\text{cond}} = 10.7\text{--}11.8$) were measured in all subsurface waters and in higher salinity ($S > 22$) surface waters (Fig. 8, Table 2, Table 3). The observation of L_2 ligands predominantly at depth in this study is consistent with those of Rue and Bruland (1995) in the North Pacific and Cullen et al. (2006) in the Atlantic.

Laboratory work has shown that the photo-oxidation of L_1 ligands may produce weaker L_2 -type ligands (Barbeau et al. 2001), and fieldwork has documented the photo-destruction of Fe-binding ligands (Powell and Wilson-Finelli 2003) in estuarine and river-to-ocean systems. Since other work has shown that coastal Fe-binding ligands were not affected by UV irradiation (Rijkenberg et al. 2006), the photoreactivity of ambient Fe-binding ligands merits further review. Ambient weaker L_2 ligands have also been suggested to be intracellular Fe-binding ligands (Bruland and Rue 2001), such as porphyrins, that are released from the cell during grazing or lysis (Hutchins et al. 1999). Although there is no definitive relationship between chlorophyll and L_2 ligand concentrations, the concentra-

tions of L_2 ligands were highest at elevated chlorophyll ($>10 \mu\text{g L}^{-1}$) levels (Table 3).

While previous work has documented the strong complexation of dissolved Fe in the marine environment, this study presents the first direct evidence of a significant ($r^2 = 0.84$, $n = 14$, $p < 0.001$; simple linear regression) relationship between the concentrations of dissolved Fe and only the stronger L_1 ligands that bind Fe in coastal waters. These stronger L_1 -type ligands have conditional stability constants similar to those reported for marine siderophores, but the presence of up to 80% of these ligands in the colloidal size fraction in these samples suggests they may be high-molecular-weight macromolecules or other organic colloids.

River discharge along the West Coast of the United States is highly seasonal, with the bulk of flows occurring either during spring freshets in the Northwest or during winter storm events in California. By the late spring and summer, river discharges are lower and upwelling conditions generally dominate the coastal waters of both the Columbia River and San Francisco Bay plume systems. Dissolved Fe concentrations supplied from these two large freshwater sources have been shown here to be independent of leachable particulate Fe loadings in the summer of 2004. However, the leachable particulate Fe concentrations from these two plume systems were orders of magnitude larger than the accompanying dissolved Fe concentrations.

We argue that the discrepancy between the leachable particulate Fe and the dissolved Fe concentrations is due to a capping effect of the stronger L_1 -type Fe-binding ligands, such that while dissolved Fe concentrations approach the saturation of these L_1 ligands they are restricted to the concentration of L_1 . This process results in a larger reservoir of leachable particulate Fe left behind that may settle to the coastal shelf sediments and be upwelled to surface waters during summer months when river supply is minimal. The strong correlation between the concentrations of dissolved Fe and L_1 ligands was observed in all surface samples from both plume systems, the California Current and coastal upwelled waters in this study. Thus, the supply of dissolved Fe from these rivers is likely controlled by the concentrations of strong Fe-binding ligands, and the concentration of these ligands should be considered when evaluating and modeling Fe supply in coastal environments. Further, the ubiquitously strong complexation of dissolved Fe in the marine environment, reported here and elsewhere, would suggest that a similarly close relationship will exist between dissolved Fe and L_1 ligands in other coastal systems.

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Received: 13 June 2006

Accepted: 4 November 2006

Amended: 24 November 2006