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Application of a chemical leach technique for estimating labile particulate aluminum, iron, and manganese in the Columbia River plume and coastal waters off Oregon and Washington

Carolyn J. M. Berger,[1] Sherry M. Lippiatt,[1] Michael G. Lawrence,[1] and Kenneth W. Bruland[1]

[1] In order to determine the total concentration of bioavailable trace metals in seawater, measurement of both the dissolved and labile particulate fractions is necessary. Comparison of labile particulate metal concentrations from various researchers is limited because of differing definitions of the fraction that is potentially available to phytoplankton on a time frame of generations. A comparison experiment was conducted on coastal and riverine suspended particulate matter to determine the difference between several commonly used techniques that operationally define the labile particulate trace metal fraction. Furthermore, we compared two leach techniques for surface transect samples from within the Columbia River plume and water offshore of Oregon and Washington, United States. The particulate trace metal concentration in the leachate was determined by high-resolution inductively coupled plasma–mass spectrometry. From this comparison, one chemical leach was chosen to best define the labile particulate fraction of Al, Fe, and Mn: a weak acid leach (25% acetic acid at pH 2) with a mild reducing agent (0.02 M hydroxylamine hydrochloride) and a short heating step (10 min 90–95°C). This leach was applied to three surface transects within the Columbia River plume. These coastal waters were found to be rich in labile particulate trace metals that are directly delivered from the Columbia River and indirectly supplied via resuspension from upwelling over a broad continental shelf.

1. Introduction

[2] The distribution and productivity of phytoplankton in the oceans is fundamentally related to the sources and concentrations of biologically available, essential trace metals in surface waters [*Bruland et al.*, 1991; *Morel et al.*, 2004]. Though trace metals in the dissolved phase (<0.4 μm) are traditionally considered the most biologically accessible [*Wells et al.*, 1995], particulate matter (>0.4 μm) contains another potentially important reservoir that can be solubilized and made available to phytoplankton on timescales of days. In order to determine the total biologically available concentration of trace metals, both dissolved and particulate phases must be considered.

[3] Rivers are an important source of trace metals to coastal regions [*Gibbs*, 1973; *Martin and Meybeck*, 1979]. However, because of nonconservative behavior during estuarine mixing, part of the riverine-derived dissolved metal pool is removed to the particulate phase [*Mackenzie and Garrels*, 1966]. For example, the majority of the dissolved iron found in rivers associated with humic acids flocculates and is removed to the particulate phase within estuaries [*Sholkovitz*, 1978]. In coastal waters and near the sediment-water interface, the particulate concentrations of trace metals such as iron and aluminum can greatly exceed the dissolved concentrations [*Johnson et al.*, 1997, 1999, 2001; *Bruland et al.*, 2001; *Fitzwater et al.*, 2003], but the biologically available fraction is not well constrained.

[4] The bioavailability of particulate trace metals is dependent on the solubility and/or remineralization of the solid phases. Various mechanisms lead to the dissolution of particulate metals in seawater. For example, redox conditions can be important in solubilizing particulate metals. In particular, manganese oxide solid phases are reduced in suboxic conditions in the water column [*Landing and Bruland*, 1987], and both iron and manganese oxides are reduced and solubilized in anoxic sediment [*Trefry and Presley*, 1982; *Canfield*, 1989]. These oxide minerals are effective scavengers of other trace metals, which are subsequently released into solution during reductive mineral dissolution of the carrier phase [*Warren and Zimmerman*, 1994]. In addition, trace metals bound to easily dissolved phases such as calcium and magnesium carbonates are

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available for solubilization [*Tessier and Campbell*, 1987]. Aeolian dust offers another source of labile particulate metals; aerosol iron oxyhydroxides are solubilized via photochemical dissolution in the presence of siderophores and other efficient electron donors [*Sunda et al.*, 1983; *Barbeau et al.*, 2001; *Borer et al.*, 2005]. Furthermore, trace metals can be associated with organic matter of biogenic origin. The organic matter carrier phase can be oxidized or respired and remineralized, releasing the associated trace metals to solution in concert with carbon, nitrogen and phosphorus. *Hutchins and Bruland* [1994] used metal radioisotopes in grazing experiments to demonstrate that zooplankton grazers are able to remineralize biogenic iron, manganese, and zinc over a time frame of hours. Additionally, *Hutchins and Bruland* [1995] suggested that the dissolution of trace metals during cell lysis is an important mechanism for regeneration of the biogenic particulate phase. As is commonly recognized in the biogeochemical cycling of nitrogen, particulate trace metals associated with the plankton community can be recycled and reused in a regenerated form [*Hutchins and Bruland*, 1994]. Recently, *Hurst and Bruland* [2007] used a stable isotope of iron as a tracer to demonstrate that solubilization of labile particulate iron in growout experiments in the Bering Sea was the major source of available iron to the phytoplankton community.

[5] Aside from the uptake of trace metals solubilized from particulates, phytoplankton and bacteria can directly access certain forms of particulate trace metals [*Bruland et al.*, 1991; *Wells et al.*, 1995; *Fitzwater et al.*, 2003]. In addition, filter-feeding organisms and the feeding vacuoles of protozoans have been suggested to provide a low-pH (pH 2–3) environment for solubilization of ingested calcium and magnesium carbonate minerals, iron oxyhydroxides, and intracellular trace metals associated with bacteria and picoplankton [*Barbeau et al.*, 1996; *Barbeau and Moffett*, 2000]. Last, mixotrophic phytoplankton species can assimilate particulate trace metals via the ingestion of bacteria [*Bird and Kalff*, 1986; *Maranger et al.*, 1998].

[6] An insoluble portion of the particulate trace metal pool is unavailable to phytoplankton even on long timescales. These metals exist in a refractory fraction locked within mineral lattices, such as alumino-silicate minerals and crystalline iron oxyhydroxides [*Jenne*, 1977]. Because of the unavailability of refractory metals, measurements of the total concentration of particulate trace metals overestimate the labile or potentially bioavailable portion [*Michalke*, 2003].

[7] Operationally defining the bioavailable particulate trace metal fraction is not straightforward [*Wells et al.*, 1995]. No chemical leach technique will be able to perfectly mimic natural processes. Some researchers have used multiple sequential leaches of particulate samples to characterize specific portions of the labile trace metal pool. While these sequential leaches are useful to understanding trace metal partitioning in particles and geochemical cycles [*Koschinsky et al.*, 2001; *Turner and Millward*, 2002], they are unfavorable for quantifying bioavailable trace metals in suspended particulate matter. Although sequential methods result in a number of operationally defined particle phases [*Martin et al.*, 1987], the selectivity of a given extraction step for a specific metal phase is not absolute [*Shannon and White*, 1991]. In addition, these sequential extraction

methods are extremely labor intensive and costly. Alternatively, leach methods which involve a single leach step to solubilize the labile particulate trace metal pool have the advantage of simplicity and save substantial time and expense in both sample processing and analyses [*Wells and Mayer*, 1991]. A single step extraction that provides a total concentration of labile trace metals is desirable. Single step leach methods reduce experimental error and result in one operationally defined labile metal concentration. The goal of this research is to improve on existing single step leach methods in order to provide a chemically defined measure of the portion of the particulate trace metal pool that is potentially bioavailable on the time frame of phytoplankton generations (days).

[8] One of the most widely used single step leaches of marine sediment is that of *Chester and Hughes* [1967]. In their method, marine sediment is leached with a solution of 25% (vol/vol) acetic acid (HAc, a weak acid maintaining the pH at ~2), and 1 M hydroxylamine hydrochloride (a reducing agent) for 4 hours at room temperature with shaking. Researchers have applied numerous versions of the HAc leach to both bottom sediment and suspended particulate matter in a multitude of environments. Table 1 is a list of publications referencing *Chester and Hughes'* [1967] leach.

[9] *Martin et al.* [1989] used a traditional 25% HAc leach [*Landing and Bruland*, 1987] to estimate the labile particulate iron phase and recognized that this leach would not account for the portion of the particulate iron associated with biogenic material. In order to quantify the total labile iron concentration, the authors calculated "excess" refractory iron – the biogenic fraction – by subtracting lithogenic iron (estimated via the Fe/Al ratio) from the measured refractory iron concentration. Furthermore, *Hurst and Bruland* [2007] recently performed grow out experiments using stable isotopes of iron and zinc as tracers, confirming that the commonly used 25% HAc leach at room temperature underestimates the potentially bioavailable portion of the particulate iron pool. A portion of their iron and zinc isotope amendments were detected in the operationally "refractory" particulate fraction, which was defined as the particulate metals that are not solubilized by the 25% HAc leach. The authors suggested that the room temperature, weak HAc leach (pH 2) did not release a portion of the more tightly bound biogenic metals associated with phytoplankton. Intracellular proteins (e.g., ferritin) can contain an important portion of the particulate iron pool that is available to phytoplankton and should be included in a leach designed to measure labile trace metals. This problem of differentiating between biogenic trace metals and truly refractory trace metals could be avoided if the leach method were able to solubilize the entire labile particulate phase, particularly including the iron associated with phytoplankton.

[10] *Chester and Hughes* [1967] also demonstrated that even a 100°C, 25% HAc leach that lacks a reducing agent will not completely dissolve iron oxides. Thus, it is apparent that a traditional room temperature HAc leach can lead to significant underestimation of the labile metal concentration, particularly in coastal zones with high biomass and abundant terrigenous particles with iron coatings.

[11] This study compares several adaptations of *Chester and Hughes'* [1967] HAc leach. Four different leaches were

Table 1. Chronological Review of Publications Referencing the *Chester and Hughes* [1967] Leach Method[a]

Publication	Location		Leach	
	Environment	Type	Hours	Reducing Agent
Duinker et al. [1974]	marine	SP	18	yes
Bolger et al. [1978]	marine	SP	2	no
Tessier et al. [1979]	river	SED	2	yes
Kitano and Fujiyoshi [1980]	marine	SED	3	yes
Forstner and Stoffers [1981]	marine	SED	2	yes
Gordon et al. [1982]	marine	SP	2	no
Orians and Bruland [1986]	marine	SP	2	no
Landing and Bruland [1987]	marine	SP	2	no
Martin and Gordon [1988]	marine	SP	2	no
Canfield [1989]	river	SED	8	yes
Martin et al. [1989]	marine	SP	2	no
Landing and Lewis [1991]	marine	SP	4	no
Bruland et al. [1994]	marine	SP	2	no
Baruah et al. [1996]	river	SED	2	yes
Jung et al. [1996]	intertidal flat	SED	2	yes
Stamoulis et al. [1996]	river	SED	2	yes
Marin et al. [1997]	marine	SED	2	yes
Gordon et al. [1998]	marine	SP	2	no
Wells et al. [2000]	marine	SP	2	no
Bruland et al. [2001]	marine	SP	2	no
Dho and Lee [2003]	marine	SED	4	yes
Fitzwater et al. [2003]	marine	SP	2	no
Hatje [2003]	estuary	SP	2	yes
Poulton and Canfield [2005]	river, glacial	SED	2	yes

[a]The 25% HAc leach method was used on either suspended particles (SP) or sediment (SED). Some researchers also used a reducing agent. All leaches were at room temperature, except that of *Kitano and Fujiyoshi* [1980], who maintained their leach at 100°C.

applied to replicate suspended particulate samples collected in the Columbia River plume. The plume samples were rich in both riverine particles and coastal phytoplankton. In addition to the Columbia River samples, two of the four HAc leach techniques were applied to replicate riverine samples collected from the San Lorenzo River in Santa Cruz, CA. An optimal leach technique was chosen on the basis of the results of the comparison experiments. The application of this leach to samples collected along three surface transects within the Columbia River plume is discussed.

2. Methods

2.1. Sample Collection and Processing

[12] All facets of sampling, processing, and storage were performed with rigorous trace metal clean techniques [*Bruland et al.*, 1979]. In July 2004 (during a spring tide), surface seawater was collected along three transects within the Columbia River plume (Figure 1) (hereafter referred to as the "surface transect" samples). Individual samples were pumped using a trace metal clean surface tow-fish system [*Bruland et al.*, 2005], and collected in 2 L low-density polyethylene (LDPE) bottles within a Class-100 clean area. Underway salinity, temperature, and depth measurements were obtained using a YSI 600 OMS CTD sonde attached to the PVC fish [*Lohan and Bruland*, 2006; *Aguilar-Islas and Bruland*, 2006]. The near-field (NF) transect crosses a NF plume formed during spring tide. The salinity minimum (18.8) and silicic acid maximum (~80 μM) of the NF transect was observed ~20 km southwest of the Columbia River mouth on 2 July 2004 (Figure 1). An intermediate-field (IF) transect (Figure 1) was located ~40 km south of the Columbia River mouth and included an IF plume with a salinity minimum of 21.9 and silicic acid maximum of

69 μM. During the IF transect on 30 June 2004, upwelling favorable winds were ~10 m/s from the north/northwest. The far-field (FF) transect was completed on 20 June 2004 100 km south of the Columbia River mouth (Figure 1). Winds were upwelling favorable (~15 m/s north/northeast) during and for several days prior to the transect.

[13] During the RISE-2 (River Influence on Shelf Ecosystems) cruise in June 2005 a seawater sample for the leach comparison experiment was collected at 46°25.01′N, 124°10.70′W (Figure 1) (hereafter referred to as the "coastal" sample). The coastal sample was collected from within the surface mixed layer at a depth of four meters. Site selection for the coastal sample was based on proximity to the mouth of the Columbia River, a source of terrestrial trace metals and region of coastal upwelling [*Chase et al.*, 2002]. The area was rich in suspended particulate matter and phytoplankton, as indicated by high fluorescence and beam attenuation values (Figure 2). A 20 L carboy of seawater was filled over a 10 min interval and thoroughly shaken prior to and during transfer into a series of acid-cleaned 2 L low-density polyethylene (LDPE) bottles.

[14] In addition to the seawater samples, river water samples were collected from the San Lorenzo River in Santa Cruz, California (hereafter referred to as the "river" sample). River samples were collected directly into acid-cleaned 2 L LDPE bottles. The samples are considered replicates as each 2 L sample was collected at the same location in the river within minutes of one another. The river sample was collected in January 2006, during a flood event at the end of a winter storm.

[15] All water samples were kept cold and in the dark prior to filtration under trace metal clean conditions. Samples were filtered within a few hours of collection using an inline filtration apparatus pressurized with filtered nitrogen
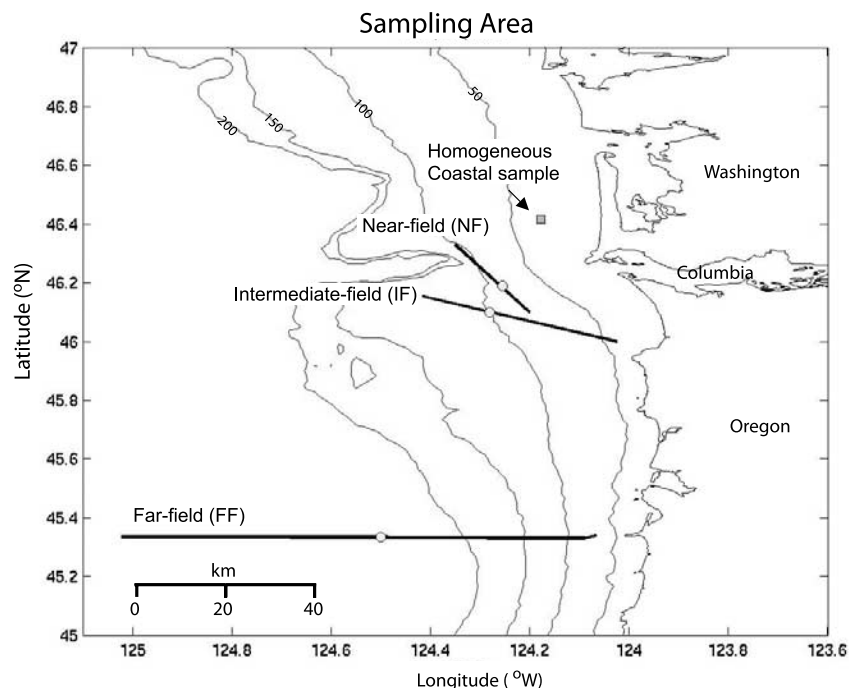
Figure 1. A map of the study area illustrating the location of the coastal homogeneous surface sample (taken in a 20 L carboy for the leach comparison experiment) and the surface transects (near-, intermediate-, and far-field). The open circle in each transect delineates the salinity minimum. Fifty meter isobaths are shown up to the 200 m shelf break.

gas. Sample passed through 47 mm diameter 10 μm then 0.4 μm pore size Nuclepore™ polycarbonate track-etched membrane filters (Whatman) mounted in polypropylene filter sandwiches (Millipore™). Filters were folded into eighths and placed in 2 mL high-density polyethylene

(HDPE) acid-cleaned vials and stored frozen. The total sample volume filtered ranged from 250 to 2140 mL. Filter blanks were processed as described above, except no sample passed through the filters.
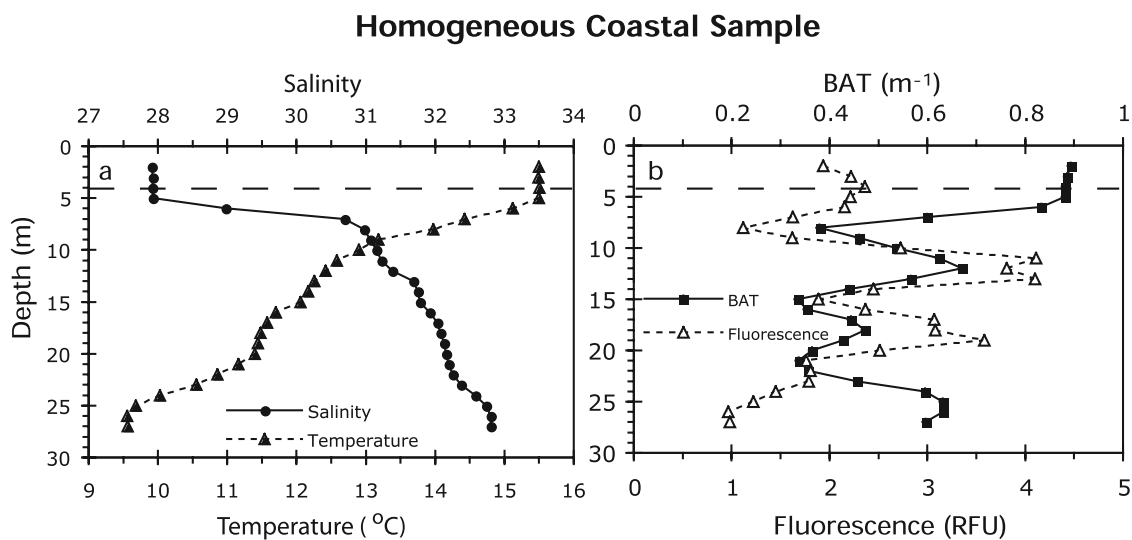

Figure 2. Vertical profile at the homogeneous coastal sample location. (a) Salinity and temperature and (b) beam attenuation (BAT) and fluorescence. The coupling of BAT and fluorescence indicates that a high percentage of suspended particles are biogenic. Dashed line indicates the 4 m depth at which the sample was collected.

Table 2. Leach Applied to Each Filter[a]

Sample	Filters Collected (0.4 μm/10 μm)	Leach Protocol	Time in 25% HAc (hours)				Reducing Agent
			RT	90–95°C	60°C	30°C	
Coastal homogeneous	3/3	HAc	2				no
	3/3	$HAc + HAc_{T*}$	2	0.5	1.5		no
	3/3	$HAc + HAc_{T*} + HAc_{T*+R}$	2	1	3		yes
	2/2	HAc_{T*+R}		0.5	1.5		yes
	3/3	HAc_{T+R}		0.2		1.8	yes
River homogeneous	3/3	HAc	2				no
	3/3	$HAc + HAc_{T+R}$	2	0.2		1.8	yes
	3/3	HAc_{T+R}		0.2		1.8	yes
Marine surface transect	numerous	HAc	2				no
	numerous	$HAc + HAc_{T+R}$	2	0.2		1.8	yes
BCR 414	4[b]	$HAc + HAc_{T+R}$	2	0.2		1.8	yes

[a]Leach HAc: 25% acetic acid (HAc) for 2 hours at room temperature (RT); leach HAc_{T*}: 25% HAc for 2 hours with a heating step (0.5 hours 90–95°C, 1.5 hours 60°C); leach HAc_{T*+R}: 25% HAc and 0.02 M hydroxylamine hydrochloride for 2 hours with a heating step (0.5 hours 90–95°C, 1.5 hours 60°C); leach HAc_{T+R}: 25% HAc and 0.02 M hydroxylamine hydrochloride for 2 hours with a heating step (0.2 hours 90–95°C, 1.8 hours 30°C). Some filters were releached, indicated by, e.g., $HAc+HAc_{T*}$.
[b]For BCR 414 samples, only 0.4 μm filters were collected.

2.2. Leachable Particulate Trace Metal Analyses

[16] In all leach procedures 1 mL of reagent was added to a 2 mL HDPE vial containing a folded 47 mm Nuclepore filter (Table 2). During all leaches the filter vials remained upright without agitation. Filter blanks were leached following the same protocol as the samples.

[17] Four different variations of the *Chester and Hughes* [1967] leach were applied to the filters; the total time in contact with the leach solution remained constant at 2 hours per leach. In the first leach, "HAc," 25% HAc was added to the vial at room temperature. The second leach, "HAc_{T*}" consisted of 25% HAc with heating. For the duration of the heating step, filters were held upright in a Teflon™ filter tray within a water bath heated to 90–95°C for 0.5 hours, then gradually cooled to 60°C for the remainder of the leach. The third leach procedure, "HAc_{T*+R}," used the same heating protocol as the second leach, but with the addition of 0.02 M hydroxylamine hydrochloride in the 25% HAc. The fourth leach, "HAc_{T+R}," used the same leach solution as the third, but with a shorter 10 min heating step at 90–95°C followed by gradual cooling to 30°C.

[18] All filters collected from surface transect samples were leached first with leach HAc, then releached with the fourth leach, HAc_{T+R}. A subset of filters from the coastal sample were sequentially leached using the HAc, HAc_{T*}, and HAc_{T*+R} protocols. Two other subsets of coastal sample filters were leached with either the third leach, HAc_{T*+R}, or the fourth, HAc_{T+R}. The river sample was divided into two subsets; one was leached with leach HAc and then releached with HAc_{T+R}, while the second was leached with only HAc_{T+R}. A summary of the leaches applied to the different groups of filters is shown in Table 2.

[19] For all leaches, at the end of the 2 hour leach time the 1 mL of leachate was processed according to the procedure of *Landing and Bruland* [1987]. Briefly, the leachate was transferred to a quartz beaker and the filter rinsed with four 0.5 mL aliquots of subboiled quartz distilled water (Q-H$_2$O). The solution was acidified with 100 μL of subboiled quartz distilled concentrated nitric acid (Q-HNO$_3$) and heated to dryness. The residue was digested using 100 μL of Q-HNO$_3$ and heated to dryness a second time. The remaining residue was dissolved in 1 N Q-HNO$_3$ and quantitatively transferred to an acid cleaned 15 mL LDPE bottle.

[20] Ideally, it would be beneficial to evaluate the effectiveness of these leaches for a well-characterized reference material. However, there is a dearth of phytoplankton reference materials available for comparison of the leaches. Nonetheless BCR-414, although not certified for Fe and Al, does have published reference values, and was used as the best available material. BCR-414 is a freshwater phytoplankton reference material containing ~50% by volume clay [*Quevauviller et al.*, 1993] and should have significant concentrations of trace elements in both the easily leachable (nominally bioavailable), and refractory phases. Two subsets of four filters were prepared by depositing 10 mg of sample onto 0.4 μm filters. The filters were folded into eighths and treated as described above. The first subset of filters was leached with HAc followed by HAc_{T+R}; the second subset was leached only with HAc_{T+R}.

2.3. Refractory Particulate Trace Metal Analysis

[21] All leached filters (with the remaining refractory particulate fraction) were microwave bomb digested with 1 mL concentrated trace metal grade (TMG) nitric acid

Table 3. Results for Varying the Leaching Protocol for Filter Replicates From the Coastal Homogeneous Sample[a]

Element	Leach				
	HAc (n = 3)	$HAc + HAc_{T*}$ (n = 3)	$HAc + HAc_{T*} + HAc_{T*+R}$ (n = 3)	HAc_{T*+R} (n = 2)	HAc_{T+R} (n = 3)
Al (nM)	88.6 ± 8.6	228 ± 27	301 ± 42	235 ± 4	206 ± 12
Fe (nM)	73.8 ± 10.1	180 ± 16	240 ± 30	232 ± 7	217 ± 12
Mn (nM)	11.4 ± 1.1	13.4 ± 1.1	13.7 ± 1.1	13.9 ± 0.9	13.1 ± 1.4

[a]Values are mean total (>0.4 μm) leachable particulate concentrations and standard deviations. The sum of the 0.4 μm and 10 μm filter fractions represents total > 0.4 μm leachable particulate fraction.

Table 4. Results for Varying the Leaching Protocol for Filter Replicates From the San Lorenzo River Homogeneous Sample[a]

	Leach		
Element	HAc (n = 3)	$HAc + HAc_{T+R}$ (n = 3)	HAc_{T+R} (n = 3)
Al (nM)	247 ± 6	943 ± 49	900 ± 11
Fe (nM)	1515 ± 43	2725 ± 74	2614 ± 187
Mn (nM)	41.0 ± 3.9	53.6 ± 4.8	54.9 ± 6.9

[a]Values are mean total (>0.4 μm) leachable particulate concentrations and standard deviations. The sum of the 0.4 μm and 10 μm filter fractions represents total > 0.4 μm leachable particulate fraction.

(HNO$_3$), 2 mL concentrated TMG hydrochloric acid, and 50 μL concentrated TMG hydrofluoric acid, in perfluoroalkoxy (PFA) Teflon bombs outfitted with pressure relief valves (Savillex, Minnetonka, MN) [*Hurst and Bruland*, 2007, 2008]. The resulting solution was quantitatively transferred to an acid cleaned 15 mL LDPE bottle and diluted to 1N TMG HNO$_3$. *Hurst and Bruland* [2007] have previously shown that the microwave bomb digestion has good agreement with reference materials.

2.4. ICP-MS Analysis

[22] The concentrations of elements (Al, Fe, and Mn) associated with the leachable and refractory particulate fractions were measured using a Thermo-Electron Element 1 high-resolution inductively coupled plasma–mass spectrometer (ICP-MS) [*Hurst and Bruland*, 2007, 2008]. Leachate and digestion solutions were transferred to acid-cleaned 7 mL HDPE vials and spiked with an internal standard solution (final concentration, 0.1 ppb Rh and 1 ppb Ga). Instrument response was quantified against external calibration curves ranging from 0.1 ppb to 25 ppb (Mn) or 1 ppb to 500 ppb (Al and Fe). Multielement standards were prepared in 1 M TMG HNO$_3$ from 1000 ppm stock solutions (SPEX, Edison, NJ; Fisher Scientific). The sample introduction system utilized an HF-compatible PFA-ST nebulizer (Elemental Scientific, Omaha, NE) and PFA spray chamber which minimized blank contamination.

3. Results

3.1. Leach Comparison

[23] In the particle and chlorophyll-rich coastal sample, the concentration of solubilized particulate trace metals varied considerably among the different leach protocols. Table 3 shows the mean concentration of leached particulate trace metals >0.4 μm (the sum of concentrations measured on the 0.4 μm and 10 μm filters) from processing coastal sample filters with a series of three leaches, beginning with leach HAc (n = 3). The addition of heated leach HAc_{T*} to the already HAc leached filters accounted for an increase of

the mean solubilized particulate concentration for aluminum, iron, and manganese (Table 3) (Δ[Al]: 157%, Δ [Fe]: 144%, Δ [Mn]: 18%). The addition of the reducing agent leach HAc_{T*+R} to the previously HAc and HAc_{T*} leached filters accounted for an additional increase of the mean solubilized particulate concentration (Table 3) (Δ[Al]: 32%, Δ [Fe]: 33%, Δ [Mn]: 2%). The leachable particulate manganese fraction had been virtually completely solubilized in the previous two leaches. In the subset of coastal sample filters leached with only HAc_{T*+R} (n = 2), the mean solubilized particulate concentration of iron and manganese was within the range of error of metal concentrations for the $HAc + HAc_{T*} + HAc_{T*+R}$ leach sequence. Conversely, the mean solubilized particulate concentration of aluminum for HAc_{T*+R} was lower compared to the leach sequence $HAc + HAc_{T*} + HAc_{T*+R}$ (Table 3) (Δ[Al]: -22%). Similarly, in the third subset of coastal sample filters which was processed with only leach HAc_{T+R} (n = 2), leachates had mean solubilized particulate concentrations within the range of error of filters leached with only HAc_{T*+R} for iron and manganese, but not aluminum (Table 3). HAc_{T*+R} leached filters had [Al] = 235 ± 4 nM compared to [Al] = 206 ± 12 nM for HAc_{T+R} leachates (Δ[Al]: -12%).

[24] The San Lorenzo river samples were used for comparison of leaches HAc and HAc_{T+R} (Table 4). Solubilized particulate aluminum, iron, and manganese concentrations increased with the addition of HAc_{T+R} on already HAc leached filters (Δ[Al]: 282%, Δ [Fe]: 80%, Δ [Mn]: 31%). When replicate filters were leached with only HAc_{T+R}, the mean solubilized particulate concentrations fell within the range of error of the sequence $HAc + HAc_{T+R}$ concentrations (Table 4). Filter blanks for HAc and HAc_{T+R} protocols were comparable (Table 5).

[25] The first subset of BCR 414 samples was leached with the sequence $HAc + HAc_{T+R}$. The addition of HAc_{T+R} solubilized a substantial amount of additional aluminum and iron, but a negligible amount of manganese (Δ[Al]: 72%, Δ [Fe]: 43%, Δ [Mn]: 6%). Nearly all of the labile particulate manganese was dissolved with the HAc leach. The second subset of samples was leached with only HAc_{T+R}. As in the river sample, mean total solubilized particulate metal concentrations for the single HAc_{T+R} leach and the $HAc + HAc_{T+R}$ leach sequence were comparable (Table 6). Total (leachable plus refractory) particulate iron and manganese concentrations agree well with the reference concentrations for the reference material [*Quevauviller et al.*, 1993].

3.2. Application of Leaches

3.2.1. Near-Field Transect

[26] Decoupled fluorometer and beam attenuation data (in conjunction with consistently low fluorescence) indicated a

Table 5. Average Leach Filter Handling Blanks and Standard Deviations for Particulate Trace Metals (nM)[a]

	HAc			HAc_{T+R}		
Element	0.4 μm (n = 3) (nmol)	10 μm (n = 3) (nmol)	0.4 + 10 μm (nM)	0.4 μm (n = 12) (nmol)	10 μm (n = 11) (nmol)	0.4 + 10 μm (nM)
Al	1.6 ± 2.5	0.59 ± 0.82	2.2 ± 3.3	1.3 ± 1.8	3.7 ± 4.1	5.0 ± 5.9
Fe	0.69 ± 1.4	0.29 ± 0.43	0.98 ± 1.8	0.27 ± 0.25	0.30 ± 0.20	0.57 ± 0.45
Mn	0.029 ± 0.024	0.012 ± 0.0071	0.041 ± 0.0311	0.020 ± 0.022	0.016 ± 0.0089	0.0066 ± 0.0027

[a]The two columns labeled 0.4 + 10 μm have blank values and standard deviations converted to nM by assuming 1000 mL filtered.

Table 6. Average (n = 4) Leachable and Refractory Particulate Metal Concentrations From Reference Material BCR 414[a]

		HAc	$HAc + HAc_{T+R}$	HAc_{T+R}	Refractory	Total
Subset 1	Al (mol/kg)	67 ± 28	182 ± 46	-	2436 ± 399	2618 ± 445
	Fe (mol/kg)	267 ± 61	649 ± 84	-	1321 ± 196	1969 ± 280
	Mn (mol/kg)	234 ± 8.8	249 ± 13	-	13 ± 2	262 ± 16
Subset 2	Al (mol/kg)	-	-	181 ± 62	1926 ± 247	2107 ± 309
	Fe (mol/kg)	-	-	608 ± 109	1244 ± 200	1852 ± 309
	Mn (mol/kg)	-	-	231 ± 5	18 ± 3	248 ± 7

[a]Subset 1 was leached with the sequence $HAc + HAc_{T+R}$, and subset 2 was leached with HAc_{T+R}. All samples were bomb digested to determine the refractory concentration.

high concentration of nonbiological suspended particles within the NF transect salinity minimum [*Aguilar-Islas and Bruland*, 2006]. The plume salinity minimum of the NF transect (124.22°W longitude) contained the maximum leachable particulate trace metal concentration ($HAc + HAc_{T+R}$) among the three surface transects for aluminum, iron, and manganese (Table 7). Within the plume salinity minimum of the NF transect the $HAc + HAc_{T+R}$ leachate concentration was appreciably greater than the concentration for HAc alone for aluminum and iron; only small increases were observed for manganese (Figure 3).

3.2.2. Intermediate-Field Transect

[27] Within the plume core of the IF transect the $HAc + HAc_{T+R}$ leach concentration was significantly greater than the HAc leach alone for iron and aluminum, while no appreciable change in leachable manganese concentration was seen with the addition of HAc_{T+R} (Figure 4). As was seen in the NF transect, leachable ($HAc + HAc_{T+R}$) and refractory particulate trace metal concentrations were greatest in the plume core (Figure 4, Table 8). On the basis of wind, water temperature, and salinity conditions, the western portion of the IF and FF transects were designated as being within a nearshore upwelled water mass (Figures 4 and 5).

3.2.3. Far-Field Transect

[28] In the FF transect, the increase in solubilized particulate metal concentration with the addition of HAc_{T+R} to the already HAc leached filters was the greatest for iron (Figure 5). In the salinity minimum of the FF transect, the addition of the HAc_{T+R} leach increased the leachable particulate iron concentration by 320% (from 8.2 to 34.4 nM), while leachable particulate aluminum concentration increased by only 35% (25.8 to 34.8 nM) (Figure 5). Furthermore, the addition of the HAc_{T+R} leach at 124.05°W longitude (within the nearshore upwelled water mass) led

to a significant increase in leachable particulate iron (from 1.1 to 7.3 nM); HAc_{T+R} did not, however, increase leachable particulate aluminum or manganese concentrations within the FF upwelled water mass (Figure 5). Leachable ($HAc + HAc_{T+R}$) and refractory particulate metal concentrations were appreciably higher in the FF transect plume core relative to 125.30°W longitude in the California Current water mass (salinity > 29.4) (Table 9). All leachable and refractory metal concentrations were elevated in the nearshore upwelled water (124.05°W longitude) compared to California Current water at 125.30°W (Table 9).

4. Discussion

4.1. Leach Comparison

[29] The ideal leach to quantify the labile portion of suspended particulate matter would solubilize only those trace metals available to phytoplankton on the time frame of generations (days). This fraction includes trace metals associated with biogenic material, both living and dead, and abiotic particulate material such as iron, manganese and aluminum oxyhydroxide phases or metals bound to the surface of alumino-silicate clay minerals. While it is argued that primarily the dissolved phase is available to phytoplankton at a given moment [*Wells et al.*, 1995], the leachable particulate pool can become bioavailable to the phytoplankton community over a time frame of days via processes such as grazing [*Hutchins and Bruland*, 1994, 1995], photochemistry [*Sunda et al.*, 1983; *Barbeau et al.*, 2001; *Borer et al.*, 2005], redox processes, and ligand-assisted dissolution [*Buck et al.*, 2007].

[30] Although the HAc leach is commonly used for marine suspended particulate matter analysis (Table 1), at room temperature and a pH of 2 the leach is unable to access all the intracellular protein bound trace metals (e.g.,

Table 7. Leachable Particulate ($HAc + HAc_{T+R}$) and Refractory Particulate Data From the Near-Field Surface Transect[a]

	CC			Near-Field River Plume		
Longitude (°W)	124.32	124.30	124.28	124.22	124.19	124.18
Latitude (°N)	46.32	46.30	46.27	46.20	46.17	46.14
Salinity (psu)	30.5	23.8	21.2	24.0	26.0	26.4
Fluorescence (RFU)	1.34	1.12	1.15	1.53	1.59	2.05
Silicic acid (μM)	10.4	64.7	70.8	70.3	54.6	50.3
LP Al (nM)	75.5	458	664	920	378	220
RP Al (nM)	894	3340	6019	7735	2652	1723
LP Fe (nM)	77.9	427	640	898	334	212
RP Fe (nM)	258	908	1620	2170	735	494
LP Mn (nM)	4.67	21.3	30.5	31.6	31.8	27.6
RP Mn (nM)	1.70	6.75	12.9	16.8	5.15	3.10

[a]Samples were taken offshore within the California Current (CC) (salinity >29.4) and from inside a near-field river plume. psu, practical salinity unit; RFU, relative fluorescence units; LP, leachable particulate; RP, refractory particulate.
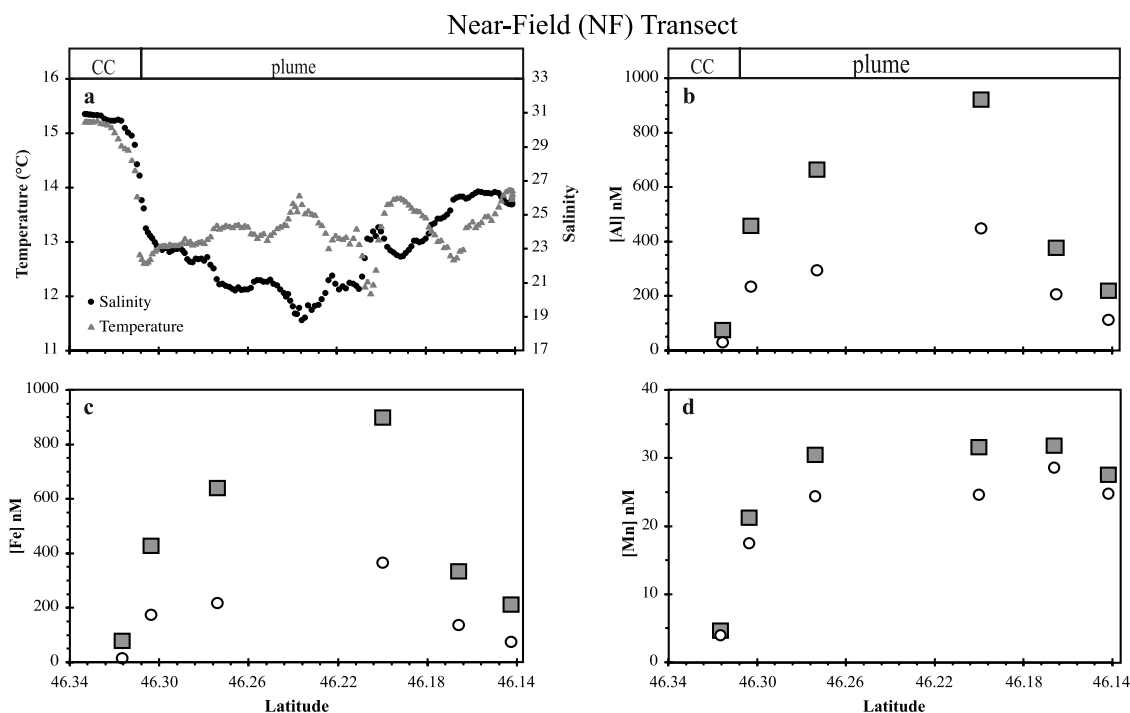
Near-Field (NF) Transect

Figure 3. Leach *HAc* and leach *HAc* + *HAc*$_{T+R}$ in the near-field transect for total (>0.4 μm) leachable particulate trace metal concentrations. Includes (open circles) data from the *HAc* leach and (solid squares) data from the additional trace metals leached when the filter was releached with the *HAc*$_{T+R}$ leach (*HAc* + *HAc*$_{T+R}$). Latitude (°N) versus (a) temperature and salinity, (b) aluminum, (c) iron, and (d) manganese. Observations were within California Current (CC) water (salinity >29.4) and a Columbia River plume.
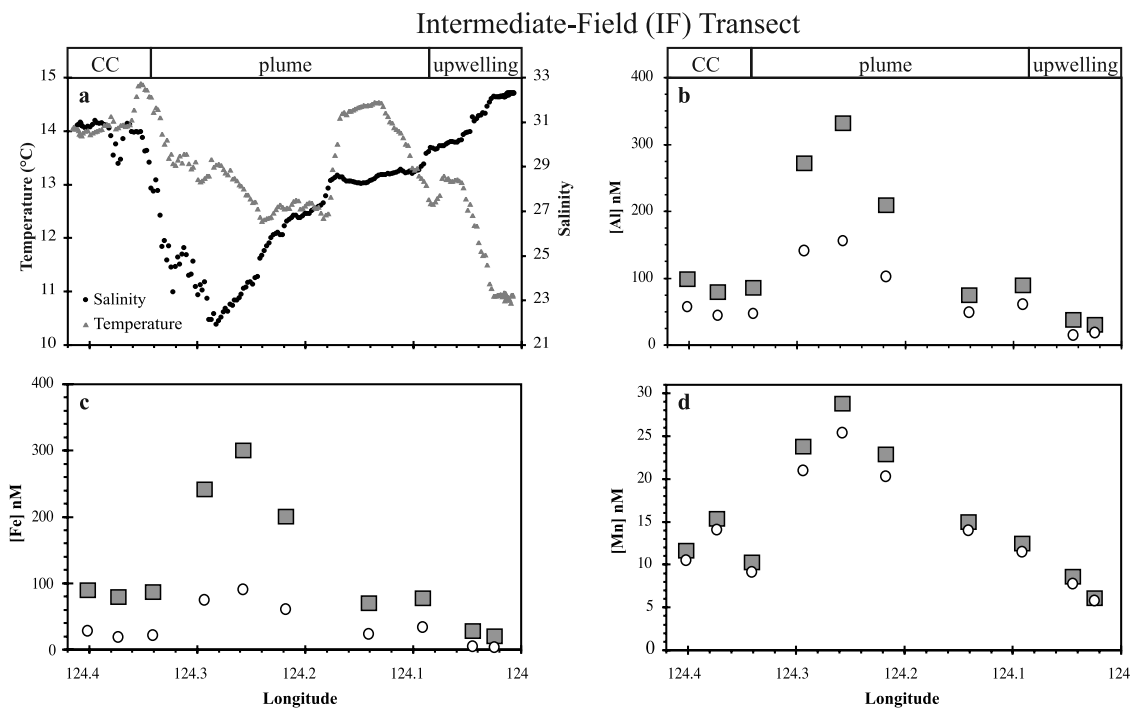
Intermediate-Field (IF) Transect

Figure 4. Leach *HAc* and leach *HAc* + *HAc*$_{T+R}$ in the intermediate-field transect for total (>0.4 μm) leachable particulate trace metal concentrations. Includes (open circles) data from the *HAc* leach and (solid squares) data from the additional trace metals leached when the filter was releached with the *HAc*$_{T+R}$ leach (*HAc* + *HAc*$_{T+R}$). Longitude (°W) versus (a) temperature and salinity, (b) aluminum, (c) iron, and (d) manganese. Observations were within CC water (salinity >29.4), a slightly offshore aged Columbia River plume, and a nearshore upwelling event.

Table 8. Leachable Particulate ($HAc + HAc_{T+R}$) and Refractory Particulate Data From the Intermediate-Field Surface Transect[a]

	CC			Intermediate-Field River Plume					Upwelling	
Longitude (°W)	124.40	124.37	124.34	124.29	124.26	124.22	124.14	124.09	124.04	124.02
Latitude (°N)	46.15	46.14	46.13	46.11	46.10	46.08	46.05	46.03	46.01	46.00
Salinity (psu)	30.8	29.1	27.9	23.8	23.5	26.6	28.4	29.1	31.0	32.1
Fluorescence (RFU)	1.35	1.51	1.09	1.36	1.09	1.59	1.63	1.87	2.96	4.12
Silicic acid (μM)	10.0	9.2	19.0	44.3	56.6	46.2	46.8	20.3	9.4	12.4
LP Al (nM)	98.5	79.2	85.4	272	332	209	74.6	89.4	38.0	30.8
RP Al (nM)	634	535	734	2047	2016	1417	537	520	286	269
LP Fe (nM)	89.5	79.6	86.6	241	300	200	70.0	77.6	28.3	23.1
RP Fe (nM)	188	179	216	564	639	438	157	151	90.3	87.2
LP Mn (nM)	11.6	15.3	10.3	23.8	28.8	22.9	15.0	12.5	8.55	6.10
RP Mn (nM)	1.23	1.11	138	3.81	4.23	2.91	0.950	0.930	0.537	0.564

[a]Samples were taken within upwelled water, in the Columbia River plume, and offshore within the California Current (CC) (salinity >29.4).

ferritin) [*Hurst and Bruland*, 2007]. Proteins are denatured in more acidic solutions (i.e., 1 M hydrochloric acid [*Castruita et al.*, 2006]), but such strong acids have been shown to access refractory particulate metals that are unavailable to phytoplankton [*Agemian and Chau*, 1976; *Turner and Olsen*, 2000]. Rather than changing to 1 M HCl (a strong acid) and decreasing the pH, a heating step was added to our leach comparison experiment in order to denature the proteins while maintaining the pH 2, 25% HAc weak acid leach. *Chester and Hughes* [1967] noted that in their 3 hour, 100°C, 25% HAc and 1 M hydroxylamine hydrochloride leach of marine sediment, the iron and manganese oxide phases were 94% (iron) and 100% (manganese) dissolved. Maintaining the leach at 100°C for 3 hours, however, caused some dissolution of trace metals associated with refractory alumino-silicate phases [*Chester and Hughes*, 1967].

[31] Our relatively short heating step was designed so that it would not appreciably dissolve the refractory portion, but would access intracellular trace metals. The addition of the heated HAc_{T*} leach (which has a longer, higher-temperature heating step than HAc_{T+R}) to previously HAc leached coastal filters resulted in an increase of the mean total solubilized particulate concentrations for aluminum, iron, and manganese. The coastal sample location had high surface fluorescence ($\sim$2 relative fluorescence units) (Figure 2), indicative of elevated phytoplankton biomass. As expected, the added heating step dissolved more of the particulate phase, mainly intracellular metals. However, the HAc_{T*} leach solubilized a greater molar amount of particulate aluminum
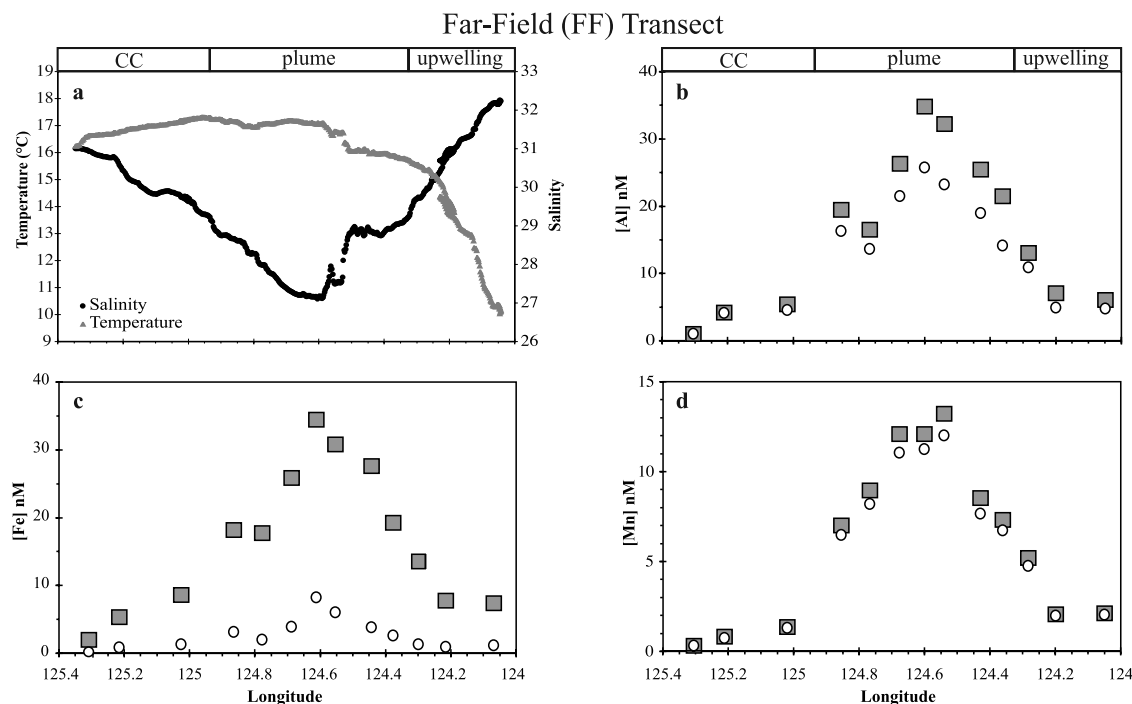

Figure 5. Leach *HAc* and leach $HAc + HAc_{T+R}$ in the far-field transect for total (>0.4 μm) leachable particulate trace metal concentrations. Includes (open circles) data from the *HAc* leach and (solid squares) data from the additional trace metals leached when the filter was releached with the HAc_{T+R} leach ($HAc + HAc_{T+R}$). Longitude (°W) versus (a) temperature and salinity, (b) aluminum, (c) iron, and (d) manganese. Observations were within CC water (salinity >29.4), an offshore very aged Columbia River plume, and a nearshore upwelling event.

Table 9. Leachable Particulate ($HAc + HAc_{T+R}$) and Refractory Particulate Data From the Far-Field Surface Transect[a]

			CC					Far-Field River Plume						U
Longitude (°W)	125.30	125.21	125.02	124.85	124.77	124.68	124.60	124.54	124.43	124.36	124.28	124.20	124.05
Latitude (°N)	45.33	45.33	45.33	45.33	45.33	45.33	45.33	45.33	45.33	45.33	45.33	45.33	45.33
Salinity (psu)	30.9	30.6	29.7	28.6	28.0	27.2	27.2	27.6	28.8	29.0	29.8	30.8	32.2
Fluorescence (RFU)	0.44	0.46	0.52	0.67	0.69	0.77	0.88	0.89	0.92	0.89	0.86	0.80	1.46
Silicic acid (μM)	5.5	7.2	10.2	15.7	19.2	22.7	25.1	24.9	14.3	13.9	10.8	5.9	16.0
LP Al (nM)	1.00	4.17	5.38	19.5	16.5	26.3	34.8	32.3	25.4	21.5	13.0	7.04	6.09
RP Al (nM)	12.1	31.5	57.5	107	120	206	205	233	212	172	113	56.3	79.3
LP Fe (nM)	1.98	5.33	8.56	18.1	17.7	25.8	34.4	30.7	27.6	19.2	13.5	7.71	7.34
RP Fe (nM)	3.41	9.36	17.1	33.1	38.8	67.5	63.0	74.7	62.7	56.7	32.6	16.3	24.4
LP Mn (nM)	0.315	0.832	1.36	7.02	8.96	12.1	12.1	13.2	8.52	7.32	5.21	2.05	2.13
RP Mn (nM)	0.014	0.036	0.070	0.138	0.160	0.322	0.272	0.343	0.312	0.273	0.196	0.139	0.215

[a]Samples were taken within upwelled water (U), in the Columbia River plume, and offshore within the California Current (CC) (salinity >29.4).

than iron, suggesting that the longer heating step (30 min) also dissolved a portion of the refractory alumino-silicate phase.

[32] In addition to heat, the HAc leach lacks a reducing agent, which is necessary to access a portion of the labile particulate trace metal pool (e.g., iron oxyhydroxide coatings). *Chester and Hughes* [1967] recommend a reducing agent similar to the 0.02 M hydroxylamine hydrochloride used in our HAc_{T*+R} and HAc_{T+R} leaches. The addition of the HAc_{T*+R} leach to the previously HAc and HAc_{T*} leached coastal filters solubilized a remaining portion of the labile particulate aluminum and iron pools (Table 3). For iron in particular, each leach step in the sequence $HAc + HAc_{T*} + HAc_{T*+R}$ solubilized an additional portion of the particulate phase: 74 nM with HAc, an extra 106 nM with HAc_{T*}, and an additional 60 nM from the HAc_{T*+R} leach (Table 3). Comparable molar amounts of aluminum and iron were solubilized during the coastal sample $HAc + HAc_{T*} + HAc_{T*+R}$ leach sequence (Table 3). This is probably due to the release of labile aluminum hydroxide phases with the reduction and dissolution of iron coatings, solubilization of refractory alumino-silicates, or a combination of both processes. As discussed, the more intense heating step of HAc_{T*+R} compared to HAc_{T+R} appears to access a portion of the refractory aluminum fraction.

[33] The increase of the leachable particulate metal concentration in the coastal sample leachate through the $HAc + HAc_{T*} + HAc_{T*+R}$ sequence can be attributed to the addition of a heating step ($HAc + HAc_{T*}$), the addition of a reducing agent ($HAc + HAc_{T*} + HAc_{T*+R}$), and/or the exposure of filters to an extra 4 hours of leach time from two additional leaching steps. Leaching coastal and riverine filters with only HAc_{T*+R} and/or HAc_{T+R} removed the effect of additional leach time. In the coastal sample, significantly more aluminum was leached in the three-step $HAc + HAc_{T*} + HAc_{T*+R}$ sequence versus the single leach steps (Table 3), particularly in the 0.4–10 μm size fraction. Particulate aluminum solubilization from small size-fraction particles was more affected by longer leach time than particulate iron and manganese. In the river sample, the extended leach time from the two-step $HAc + HAc_{T+R}$ sequence had minimal effect on the solubilization of aluminum, iron, or manganese (Table 4). In contrast with the $HAc + HAc_{T*} + HAc_{T*+R}$ sequence, the less intense heating step and shorter leach time of the $HAc + HAc_{T+R}$ sequence did not access the refractory aluminum phase.

[34] In both the coastal and river samples, the HAc_{T+R} leach accounted for more iron and aluminum (primarily in

the 0.4–10 μm size fraction) than the HAc leach. Thus, the reducing agent and heating step of the HAc_{T+R} protocol accesses a greater portion of the labile iron pool along with some of the particulate aluminum phase. We can only speculate whether this is due to solubilization of a labile aluminum hydroxide phase along with iron oxyhdyroxides (e.g., coprecipitated or as inclusions within iron oxyhydroxide coatings), or if it is due to leaching some aluminum from the refractory alumino-silicate minerals. In contrast, the stronger HAc_{T*+R} leach was shown to solubilize refractory aluminum. The concentration of particulate aluminum solubilized with the HAc_{T+R} leach was lower than that solubilized with the HAc_{T*+R} leach, while the concentrations of particulate iron and manganese solubilized with the two leaches were within the range of error. The HAc_{T+R} leach more completely accesses the labile iron and manganese phases while solubilizing little, if any, refractory aluminum. The HAc_{T+R} protocol is more effective than the traditional HAc leach at accessing the potentially bioavailable trace metal fraction and has therefore been selected as the most favorable leach. The inclusion of a low-concentration, weak reducing agent (0.02 M hydroxylamine hydrochloride) and a short heating step were found to be essential in accessing the majority of the reducible and protein-bound particulate metal pool.

Table 10. Leachable Particulate Trace Metals as a Percentage of the Total Particulate (Leachable + Refractory) Phase[a]

Location	Leach	Al (%)	Fe (%)	Mn (%)
NF CC	HAc	3.2	4.7	62.3
	HAc_{T+R}	7.8	23.2	73.3
NF core	HAc	4.8	10.9	53.3
	HAc_{T+R}	10.3	28.9	67.6
IF CC	HAc	7.8	10.2	81.6
	HAc_{T+R}	13.4	32.3	90.4
IF core	HAc	6.3	9.5	77.1
	HAc_{T+R}	12.9	31.1	87.3
IF upwelling	HAc	5.3	5.0	85.5
	HAc_{T+R}	11.0	22.5	93.0
FF CC	HAc	7.7	3.1	93.3
	HAc_{T+R}	7.6	36.7	95.7
FF core	HAc	9.6	6.1	89.4
	HAc_{T+R}	12.7	30.7	97.6
FF upwelling	HAc	5.6	3.6	87.1
	HAc_{T+R}	7.1	23.1	90.8

[a]Percentages indicate the amount of the particulate phase solubilized with each leach (HAc and HAc_{T+R}). Data from all three surface transects. Samples were taken within upwelled water, in the Columbia River plume, and offshore within the California Current (CC) (salinity >29.4). NF, near-field; IF, intermediate-field.
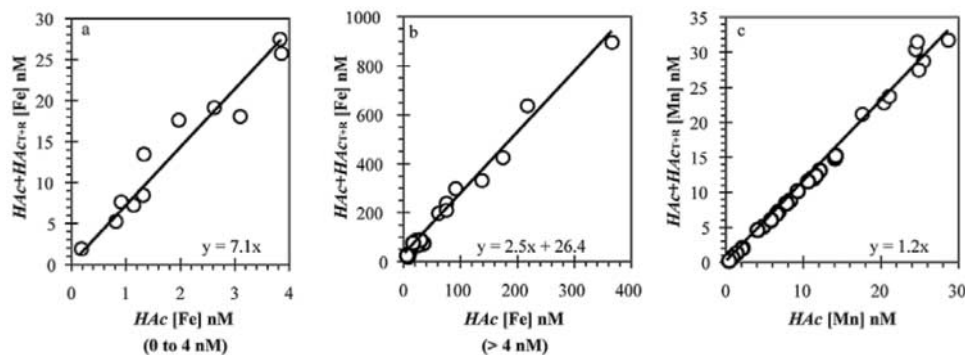
Figure 6. The *HAc* leach versus the *HAc* + *HAc*_{T+R} leach for the marine surface transect samples. The iron data was split into (a) that from the *HAc* leach ranging from 0 to 4 nM and (b) that from the *HAc* leach greater than 4 nM to better represent the low-concentration data. (c) The manganese data is nearly 1:1.

[35] As an additional evaluation of the HAc_{T+R} method, we analyzed a plankton standard reference material – BCR 414. This material is a coastal sample containing a substantial amount of clay. As with our coastal and river samples, it is not possible to determine whether the additional aluminum solubilized with the HAc_{T+R} compared to the HAc leach can be attributed to a labile aluminum hydroxide phase or an alumino-silicate phase. If we assume that the 115 ± 18 moles/kg of aluminum solubilized with the addition of the HAc_{T+R} leach to HAc-leached BCR samples (Table 6) is from alumino-silicates, by using the crustal aluminum:iron ratio (4:1, [*Taylor*, 1964]) a maximum of 29 moles/kg of iron is associated with the terrigenous phase. In fact, 382 ± 23 moles/kg of iron was solubilized with the addition of HAc_{T+R}. This indicates that the leach accessed a portion of the biogenic and/or labile iron hydroxide phases that the HAc leach did not. However, it is likely that a fraction of the 115 ± 18 moles/kg of solubilized aluminum is from a labile aluminum hydroxide phase, which would suggest that an even greater portion of the HAc_{T+R} iron is labile. These results indicate that the potentially refractory portion of the iron solubilized with the addition of HAc_{T+R} is minimal (<8% if all Al is refractory) with respect to the total labile particulate iron concentration.

[36] Recent data from growout experiments conducted in the Gulf of Alaska in August 2007 (M. G. Lawrence, unpublished data, 2007) indicate that the HAc_{T+R} leach recovers 100% of ^{57}Fe isotope amendments. *Hurst and Bruland* [2007] confirmed that over the course of their growout experiments a significant proportion of ^{57}Fe was partitioned into a biogenic phase that was not accessible or leachable by the traditional HAc leach. The results of our Gulf of Alaska growouts confirm that the new HAc_{T+R} leach method is an improvement over the traditional HAc technique.

[37] In addition to being a more complete solubilization of the labile particulate trace metal phase, we argue that the one-step HAc_{T+R} leach presented here is more direct and simple than other methods such as determining the difference between "dissolvable" and dissolved metal concentrations as a measure of leachable particulate metal. Dissolved metal is that found in the filtrate passing through a 0.4 or 0.2 μm pore size filter, whereas dissolvable metal is that observed in an unfiltered sample that has been acidified with a strong acid such as HCl to pH 1.5 to 3.3 and stored

for a period of minutes to months prior to analysis at sea or in the laboratory. The metal concentration solubilized with the dissolvable method depends on a number of variables, including the strength and type of acid, the length of time and temperature of storage, and the type of particles in the unfiltered sample [*Bruland and Rue*, 2001]. Though it is commonly reported in the literature, the dissolvable fraction is very operationally defined; even slight differences in pH and storage time can lead to significant differences in the concentration of dissolvable metals [*Bruland and Rue*, 2001].

[38] The difference between the dissolvable and dissolved measurements should ideally be a measure of the leachable particulate fraction and be comparable to what we determine directly with the HAc_{T+R} leach. *Johnson et al.* [2005] performed a comparison of historical dissolvable, dissolved, and particulate iron data from Ocean Station Papa in the Subarctic Pacific. *Johnson et al.* [2005] measured dissolvable iron from an unfiltered sample that was acidified to pH 1.5 with HCl, stored for >7 months, and then microwaved just prior to analysis (they called this measurement "total iron"). The authors estimated a leachable particulate fraction by subtracting the dissolved value (filtered, acidified to pH 1.5, stored for >7 months– they called this measurement "total dissolved iron") from the dissolvable or "total" iron concentration. Although they expected their calculated leachable particulate iron concentrations to correspond to *Martin et al.*'s [1989] *HAc* leachable particulate iron values, they were instead much higher than the *HAc* leachable values of Martin and coworkers and just slightly less than *Martin et al.*'s [1989] total (leachable + refractory) particulate iron values. Although 11 years separate the two groups' studies, it can be concluded that either the traditional *HAc* leach greatly underestimated leachable iron, the dissolvable minus dissolved method overestimated the leachable particulate fraction, or both. While all methods used to determine the labile particulate trace metal fraction (both dissolvable and leach methods) are useful, none is completely accurate. There is inevitably some similarity in the chemical strength required to solubilize intracellular proteins and refractory mineral phases. Nevertheless, on the basis of evidence that the traditional *HAc* leach is too weak [*Hurst and Bruland*, 2007], some dissolvable methods may be too harsh [*Johnson*
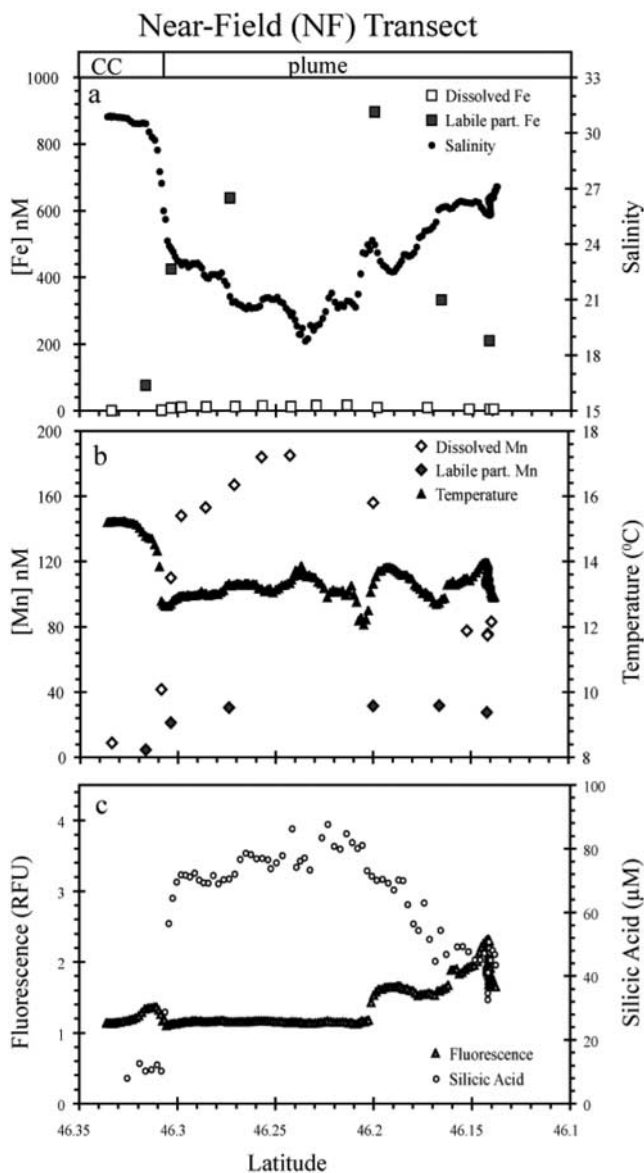
Figure 7. The near-field transect. Latitude (°N) versus (a) dissolved iron, leachable (HAc + HAc_{T+R}) particulate iron, and salinity; (b) dissolved manganese, leachable (HAc + HAc_{T+R}) particulate manganese, and temperature; and (c) fluorescence and silicic acid.

et al., 2005], and data presented here, we argue that the HAc_{T+R} leach is an improvement over existing methods.

4.2. Surface Transects

[39] The salinity minimum of all three surface transects represents the core of the Columbia River plume advecting southwestward off the coast of Oregon under upwelling conditions. The addition of the HAc_{T+R} leach to already HAc leached filters from the NF, IF, and FF plume core samples led to an increase in the percentage of the total particulate iron pool that is leachable: from 10.9%, 9.5%, and 6.1% to 28.9%, 31.1%, and 30.7% respectively (Table 10). While the percentage of HAc leachable iron decreases with distance from the river mouth, the percentage of HAc_{T+R} leachable iron remains constant at about 30%. The increase

in the percentage of particulate aluminum that is leachable with the addition of the HAc_{T+R} leach to the NF, IF, and FF plume core samples was much lower than that of iron: from 4.8%, 6.3%, and 9.6% to 10.3%, 12.9%, and 12.7% respectively (Table 10). The percentage of the total particulate aluminum pool that was HAc_{T+R} leachable was much smaller than that for iron and manganese. While comparable molar concentrations of particulate iron and aluminum were HAc_{T+R} leachable, the percentage of leachable metal relative to the total particulate load was much greater for iron.

[40] The addition of the HAc_{T+R} leach to FF transect samples within the nearshore upwelling water mass led to a marked increase in only the solubilized particulate iron concentration; the other metals were not significantly affected by the additional leach. In particular, the HAc_{T+R}
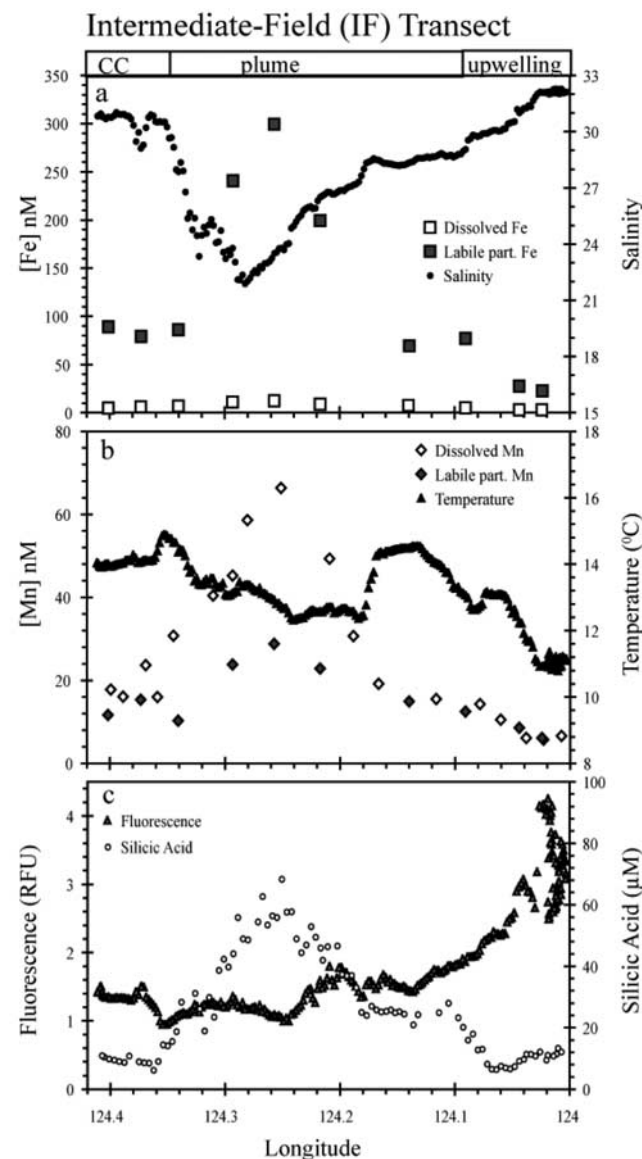

Figure 8. The intermediate-field transect. Longitude (°W) versus (a) dissolved iron, leachable (HAc + HAc_{T+R}) particulate iron, and salinity; (b) dissolved manganese, leachable (HAc + HAc_{T+R}) particulate manganese, and temperature; and (c) fluorescence and silicic acid.
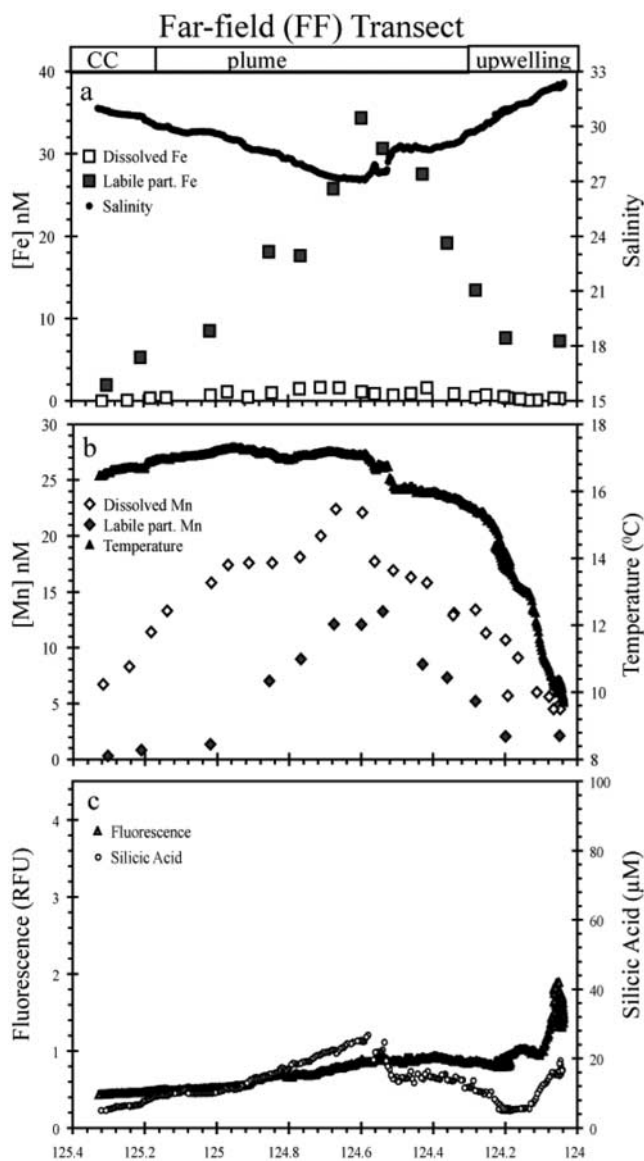
Figure 9. The far-field transect. Longitude (°W) versus (a) dissolved iron, leachable (HAc + HAc_{T+R}) particulate iron, and salinity; (b) dissolved manganese, leachable (HAc + HAc_{T+R}) particulate manganese, and temperature; and (c) fluorescence and silicic acid.

method solubilizes a greater amount of iron within the surface transect salinity minimums and in nearshore upwelled waters. In the three surface transects the HAc + HAc_{T+R} leach solubilized 7.1 times more iron from filters with low iron concentrations (0 to 4 nM) and 2.5 times more iron from filters with higher iron concentrations (>4 nM) (Figure 6). The addition of the HAc_{T+R} leach had much less influence on manganese concentrations; 1.2 times more manganese was leached from surface transect samples in the HAc + HAc_{T+R} sequence compared to HAc alone (Figure 6). The HAc leach appeared adequate to access the bulk of the leachable particulate Mn. The HAc + HAc_{T+R} leach is especially effective at accessing the total leachable particulate iron pool in low-iron regions, such as in the FF transect.

4.3. Coastal Particulate Aluminum

[41] In the NF Columbia River plume core particulate aluminum was primarily in the refractory phase (∼90%) (Table 7). The total particulate aluminum load (leachable + refractory) in the IF plume core was only 27% of that found in the NF plume core, while the FF plume core was only 3% of that found in the NF (Tables 7 and 8). It is apparent that particulate aluminum decreases dramatically in concentration with distance from the source. Physical processes such as plume dilution and particles settling out of the surface layer are primary causes of the observed decline.

4.4. Coastal Iron

[42] This study adds to the evidence supporting the solubilization and bioavailability of leachable particulate iron. Though particulate iron in the Columbia River plume core was primarily refractory, a substantial percentage was leachable (NF: 28.5%, IF: 30%, FF: 35.3%); leachable particulate iron concentrations (898 nM, 300 nM, 34.4 nM respectively) were over 1 order of magnitude greater than dissolved iron concentrations (18 nM, 12 nM, 1.18 nM respectively) [*Lohan and Bruland*, 2006] (Figures 7, 8, and 9). In a Columbia River plume drifter study, *Lohan and Bruland* [2006] observed that dissolved iron decreased with distance from the river mouth; the authors suggested that the measured dissolved iron concentration was not sufficient to sustain the observed biomass in the aging plume. Considering the comparatively low dissolved iron concentrations, leachable particulate iron concentrations measured in the Columbia River plume are significantly greater and must be considered as a factor affecting phytoplankton productivity in this region. Such an observation is consistent with the hypothesis that coastal phytoplankton are able to access labile particulate iron via the solubilization of iron rich riverine and upwelled particles. Similarly, *Chase et al.* [2002] noted a decrease of particulate iron and constant fluorescence with distance from the Oregon shelf; the authors suggested this as evidence of biological removal of the particulate phase. The buoyant Columbia River plume contains a substantial pool of leachable particulate iron that can be transported a great distance from the river mouth (up to 100 km to the location of the FF transect).

[43] *Chase et al.* [2002] observed an aged Columbia River plume containing elevated (10–15 nM) dissolvable iron ("dissolvable" in this case is defined as treating an unfiltered sample with HCl to pH 2 and storage for at least 2 months) ∼165 km from the Columbia River mouth. The authors hypothesized that "the Fe at 45°N associated with the Columbia River plume is probably in a smaller size fraction than Fe associated with resuspended sediment, since larger particles would have settled out of the plume during its ∼20 day [*Huyer*, 1983] transit from the river mouth" [*Chase et al.*, 2002]. In this study, however, the majority of iron in both the leachable (HAc + HAc_{T+R}) and refractory phases that reached the FF plume (45.33°N) or were upwelled in the nearshore upwelling event were in the larger (>10 μm) size fraction (Figure 10).

[44] The fluorescence maxima of the IF and FF transect were found within the nearshore upwelled water mass [*Aguilar-Islas and Bruland*, 2006; *Lohan and Bruland*, 2006]. The upwelled water in the nearshore portion of the FF transect was colder (10.3°C), more saline (salinity of
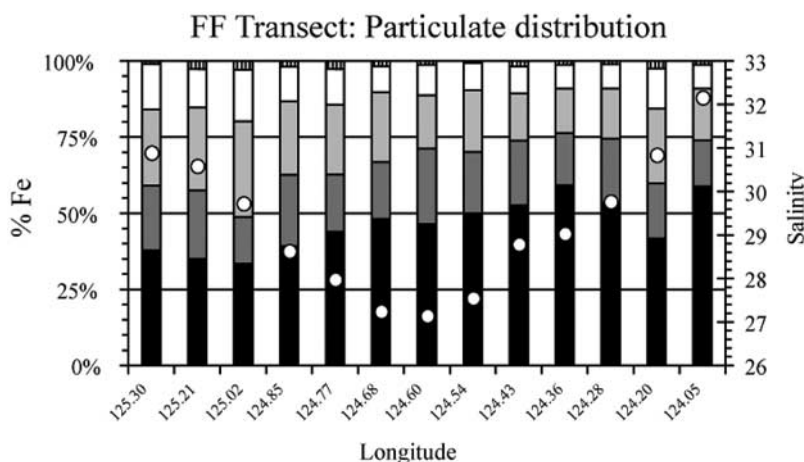
Figure 10. Iron in the far-field transect. Longitude (°W) versus (vertical bars) dissolved [*Lohan and Bruland*, 2006], (white) leachable ($HAc + HAc_{T+R}$) $0.4-10$ μm, (light gray) refractory $0.4-10$ μm, (dark gray) leachable >10 μm, (black) refractory >10 μm, and (open circles) salinity. About 70% of the iron within the plume core is in the >10 μm size.

32.2), and more macronutrient enriched (nitrate 10.7 μM, silicic acid 16.0 μM) than the upwelled water in the IF transect (10.9°C, salinity 32.1, nitrate 9.8 μM, silicic acid 12.4 μM) [*Aguilar-Islas and Bruland*, 2006; *Lohan and Bruland*, 2006]. Even so, the upwelled water in the IF transect had higher dissolved (5.1 nM) and labile particulate iron (23.1 nM) concentrations than the FF upwelled water, which had 0.39 nM dissolved iron [*Lohan and Bruland*, 2006] and 7.3 nM leachable particulate iron. The variation in shelf width between the IF and FF transects (80 and 40 km respectively) provides an explanation for the difference in particulate trace metal concentrations. Broad continental shelves act as traps for particulate iron that becomes entrained in upwelled waters [*Johnson et al.*, 1999]. *Chase et al.* [2007] have correlated river runoff and shelf width along the U.S. West Coast with iron availability and phytoplankton biomass. *Chase et al.* [2005a] hypothesize that beyond a critical shelf width, iron content within upwelled water is relatively uniform. In this study, FF water upwelled over a 40 km wide shelf had leachable particulate (7.3 nM) iron concentrations comparable to "dissolvable" iron concentrations observed during upwelling over a narrower shelf (10 km) offshore of California (6 nM [*Chase et al.*, 2005b], 6.5 nM, [*Fitzwater et al.*, 2003]). *Chase et al.* [2002] report elevated "dissolvable" iron concentrations (15 nM) in waters upwelled over a wider shelf (78 km) offshore of Oregon (44.2°N). In this study, waters upwelled over the 80 km IF shelf (46°N) contained 23 nM leachable particulate iron. This comparison supports the hypothesis that wider continental shelves correspond to high "dissolvable" or leachable particulate iron concentrations in upwelled waters [*Johnson et al.*, 1999].

[45] In terms of methodology, it is important to examine differences between techniques used to measure the labile particulate iron fraction. *Fitzwater et al.* [2003] noted that using the *HAc* leach technique 7% of the total particulate iron in coastal California upwelled water is leachable. Within the FF upwelled water mass in this study the *HAc* leach solubilized a comparable amount of the total particulate iron (5%) while the HAc_{T+R} leach solubilized 25% of the total particulate iron (Figure 5).

4.5. Coastal Manganese

[46] Manganese did not follow the same trends as aluminum and iron. Within the plume core, manganese was found primarily in the dissolved phase (NF: 76%, IF: 67%, FF: 64%) [*Aguilar-Islas and Bruland*, 2006] (Figures 7, 8, and 9). A greater portion of the total manganese was in the leachable particulate phase (NF: 16%, IF: 29%, FF: 35%) compared to the refractory phase (NF: 8%, IF: 4%, FF: 1%). The plume core total particulate (leachable + refractory) manganese was 46% lower in the IF transect than the NF transect, and 72% lower in the FF transect compared to the NF transect. The decrease in particulate manganese with distance from the river mouth was not as drastic as the decrease observed for aluminum and iron. Furthermore, the percentage of particulate manganese in the leachable phase increased away from the source (67.5% at the NF plume core, 86.5% at the IF plume core, and 98.0% at the FF plume core).

[47] As the river plume ages dissolved manganese can be scavenged to the particulate phase via oxidation, biological incorporation, or adsorption onto particles. In addition, particulate manganese can be a source of dissolved manganese via photochemical and microbial processes. The observed decrease in dissolved and particulate manganese and subsequent increase in the percent leachable as the surface plume travels farther away from its source indicates that transfer between the dissolved and particulate phases is drawing dissolved manganese into the leachable particulate pool.

5. Conclusion

[48] This leach comparison experiment was designed to compare commonly utilized leach techniques in order to choose one leach method which best solubilizes the labile particulate trace metal fraction of coastal suspended particles. We recommend leach HAc_{T+R}: the 25% HAc, 0.02 M hydroxylamine hydrochloride leach with a short heating step (10 min 90–95°C). This leach accessed a greater portion of particulate trace metals than the 25% HAc leach commonly used by researchers studying marine suspended particles. In particular, this HAc_{T+R} leach is accessing a

greater concentration of iron associated with oxyhydroxides (via the reducing agent) and intracellular iron (via the heating step).

[49] Using the HAc_{T+R} leach we have shown that the Columbia River and nearshore upwelling events are the primary sources of leachable particulate aluminum, iron, and manganese to this coastal region. In particular, we have addressed the sources of new iron to the coastal zone: upwelling and river input [*Wells et al.*, 1995]. The leachable particulate iron data from this study and the dissolved iron data from *Lohan and Bruland* [2006] contain valuable information on the distribution of iron in coastal zones.

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