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Riverine input of macronutrients, iron, and organic matter to the coastal ocean off Oregon, U.S.A., during the winter

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Abstract

Three cross-shelf transects were conducted off northern Oregon in February, 2003, coincident with flooding of Coast Range rivers, to assess the riverine impact on coastal ocean biogeochemistry. During downwelling conditions, low salinity river-influenced water was located in a narrow band near the coast and contained elevated macronutrient, iron, and organic carbon concentrations. Wind relaxation allowed the river-influenced water to spread out at the surface across the shelf. Nutrients supplied by the rivers could result in winter carbon fixation equating to ~20% of the summer upwelling carbon fixation if conditions are suitable for phytoplankton growth, which is likely on the basis of recent studies. This implies that wintertime production may be significant and requires further study. Iron supplied by the rivers is sufficient to support the entire summer upwelling production and because downwelling conditions prevail during the winter and minimize cross-shelf transport, this iron may be retained on the shelf to support the summer phytoplankton blooms. Of the major eastern boundary current systems, the northern California Current (including Oregon) and Portugal Current (i.e., Iberian Peninsula) have the highest riverine discharge rates normalized to coastline length. In contrast, riverine inputs to the central California, Canary (i.e., northwest Africa), Benguela and Peruvian Current systems averaged only 3–35% of that in Oregon. This patchy riverine input (and narrower shelves) might explain why iron limitation is more widespread off California and Peru than Oregon. These results show that small coastal rivers, characteristic of the U.S. Pacific Northwest, can significantly alter coastal biogeochemical cycles and influence ecosystem structure.

The coastal ocean plays a key role in global biogeochemical cycles and marine food webs. In recent years, advances have been made in linking atmospheric and physical dynamics to ecosystem structure and function during the productive summer season in eastern boundary current systems. Unfortunately, that progress has not been matched by increased study or enhanced understanding of wintertime conditions. In fact, relatively little is known about wintertime biogeochemical or food web conditions in these types of systems.

Results from modeling and field observations show that the wintertime physical dynamics of eastern boundary current systems are quite different than during the summer upwelling season. Off Oregon for example, mean wintertime coastal wind direction is to the north and strong north/northeastward propagating storms frequently occur (Halliwell and Allen 1987; Strub et al. 1987). Northward winds cause onshore Ekman transport of surface waters, leading to development of a downwelling front at the 100–150-m isobath (Allen and Newberger 1996; Austin and Barth 2002). In the region of the front, the water column can be vertically homogenous (Barth et al. unpubl.). Currents inshore of the front are predominately to the north, and cross-shelf circulation is believed to be minimal (Allen and Newberger 1996; Austin and Barth 2002). There can be considerable variability in the duration and direction of the winds, however. Periods of relatively strong (>10 m s^{-1}) northward winds typically last for a few days to a week, but can be interrupted by periods of weaker winds and even southward, upwelling favorable winds (Halliwell and Allen 1987; Strub et al. 1987). The consequences of these wind fluctuations on coastal circulation and ecosystem dynamics are largely unknown.

Phytoplankton biomass, and consequently upper trophic level biomass (i.e., zooplankton) have traditionally been thought to be low during most of the winter off Oregon (e.g., Landry et al. 1989). However, results from recent field studies indicate that a small, but ecologically important, late winter phytoplankton bloom is a common feature. Satellite observations show a phytoplankton bloom occurring in mid-February through early March of nearly every year from 1998–2003 (R. M. Letelier unpubl. data), while shipboard sampling of coastal waters also showed elevated levels of chlorophyll *a* (~4 to 5.5 μg L^{-1}) in surface waters over most of the shelf off Newport, Oregon, in mid-February of both 2002 and 2003 (Wetz et al. 2005). A recent wintertime incubation study that used natural phytoplankton communities collected over the Oregon shelf demonstrated that the phytoplankton were capable of growth at January/February surface light intensities and suggested that stabilization of the water column is key for promoting phytoplankton growth in situ (Wetz et al. 2004). These winter blooms are potentially an important food

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source for zooplankton emerging from diapause (Peterson and Miller 1977). However, the timing of the blooms usually precedes the annual spring transition to upwelling conditions, indicating that nutrients are supplied by some other mechanism and that physical conditions must also be conducive for phytoplankton growth (i.e., reduced mixing).

Numerous small rivers discharge into estuaries and ultimately the coastal ocean off Oregon during the winter (Fig. 1), when discharge from these Coast Range rivers is over an order of magnitude higher than in the summer (e.g., Colbert and McManus 2003; Sigleo and Frick 2003). Wintertime discharge centers on episodic storm events that occur at a frequency of 1–3 per month from November through April (Colbert and McManus 2003; M. M. Whitney unpubl. data). The Coast Range rivers in Oregon tend to have high nutrient and organic matter concentrations (Colbert and McManus 2003; Compton et al. 2003; Sigleo and Frick 2003) and because of this, they have the potential to influence coastal ocean biogeochemistry and food web dynamics. In a comparative analysis of discharge and dispersal from rivers of various sizes, Warrick and Fong (2004) suggest that the importance of small mountainous rivers to coastal oceanographic and biogeochemical conditions may be substantial, even relative to significantly larger rivers. However, there are very few published field studies on the impact of these river systems, and more generally, wintertime studies of nutrient and organic matter dynamics are rare in eastern boundary current systems. Here we present results from three cross-shelf transects that coincided with a flood event and were conducted within a few days of one another but under different wind and current conditions; i.e., downwelling favorable winds, relaxed winds, and weakly upwelling favorable winds. The goals of this study were to examine the impact of small Coast Range rivers on coastal ocean biogeochemistry and to examine the effects of physical forcing on the distribution and movement of river water and its associated materials.

Materials and methods

Sampling surveys for macronutrients and organic matter were conducted off northern Oregon (45.00 N, ~124.05 to 124.40 W; Fig. 1) aboard the RV *Revelle* on three dates in 2003: 01 Feb, 02 Feb, and 05 Feb. Sampling for iron (Fe) was conducted from the RV *Wecoma* and overlapped with the RV *Revelle* on 01 Feb. Macronutrient and organic matter samples were collected from the ship's surface seawater system with an intake mounted at 3 m below the surface. Sampling began at the offshore end of the transect and ended nearshore, taking ~7 to 8 h to complete. The 01 Feb transect began at 13:00 h local time, and the 02 and 05 Feb transects began at 08:00 h local time. Additional conductivity-temperature-depth (CTD) cast stations were occupied from 21 Jan to 01 Feb at fixed locations over the inner, middle, and outer shelf, but only salinity and temperature from those are reported in this paper.

Physical oceanographic data—Wind data were collected from a buoy deployed over the midshelf (45.00 N, 124.15 W). Current data were collected from a mooring with an acoustic Doppler current profiler attached, located on the inner shelf (45.00 N, 124.07 W). Current velocities were sampled every 120 s in 2-m bins over the water column depth. Vertical profiles of salinity and density were obtained by using a loosely tethered profiler equipped with temperature, salinity, and pressure sensors (Perlin et al. 2005).

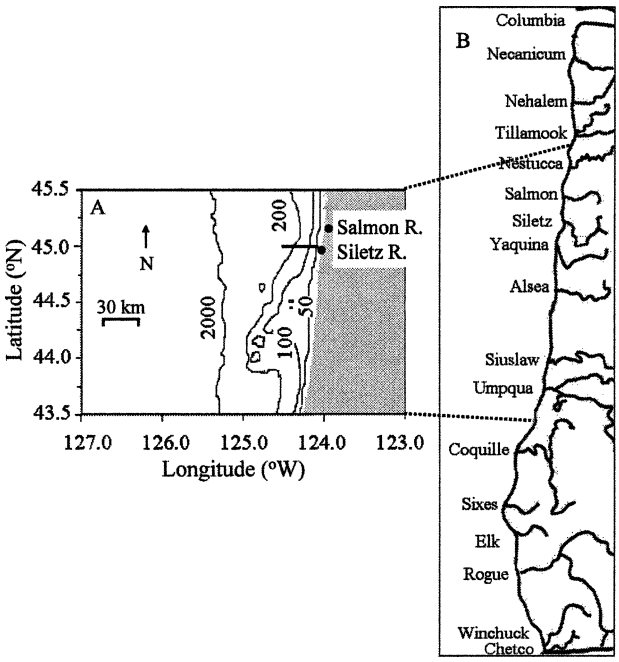

Fig. 1. (A) Location of study site off Cascade Head, adjacent to Lincoln City, OR. (B) Location of rivers along the Oregon coast.

Streamflow information—Daily streamflow from the Siletz River (Sta. 14305500) was obtained from the United States Geological Survey (USGS; http://waterdata.usgs.gov). The gage for the Siletz R. is located at 44.71 N, 123.88 W. Because nearly all of the discharge from Oregon's coastal rivers occurs during a 6-month period from November through April (Colbert and McManus 2003; M. M. Whitney unpubl. data), we refer to that period as "wintertime" discharge and estimate the discharge into shelf waters by using data obtained from Oregon State University's Streamflow Research Project (M. M. Whitney unpubl. data). Briefly, the wintertime discharge rates normalized to watershed area for each of five coastal watersheds were multiplied by the area of each watershed and then summed to get an average wintertime discharge, which equated to ~2,570 $m^3 s^{-1}$. Finally, this average rate was multiplied by 180 d (i.e., the period from November to April) to get a total wintertime freshwater flux to the coastal ocean (4×10^{10} m^3 $winter^{-1}$).

Chemical analyses—High-speed macronutrient analyses were performed following the WOCE/JGOFS protocols of Gordon et al. (1995) with slight modifications. Ascorbic acid was used as the reductant in place of stannous chloride

and hydrazine in the silicate and phosphate analyses, respectively. Sample introduction was modified to draw continuously from a stream of flowing seawater supplied by ship's surface intake line. Samples were analyzed at a frequency of roughly 1 Hz, which, at the typical survey speeds represents a horizontal resolution of several meters. Calibrations with artificial seawater solutions of known nutrient concentrations were performed at least once every 2 h.

Discrete total organic carbon (TOC) samples were collected in triplicate in acid-washed and precombusted (500°C for 5 h) borosilicate vials with Teflon cap liners. Approximately 5–10 mL of seawater was collected in each vial and preserved with 50 μL of 90% phosphoric acid. Samples were stored at room temperature until processed. Samples were analyzed with the high-temperature catalytic combustion method on a Shimadzu TOC-5000A analyzer. Standard curves were run twice daily using a deionized water blank and four concentrations of an acid potassium phthalate solution. Five subsamples were taken from each water sample and injected in sequence. Variance between subsamples averaged 1.7 ± 1.6%. Deep-water standards of known TOC concentration were injected after every three to four samples (15 to 20 subsamples) to check for baseline shifts. Certified Reference Materials Program deep seawater (December 2000 batch) was also injected three times during each run. Average TOC concentration in the CRMP water over 29 runs was 46 ± 5 μmol L^{-1}. In order to eliminate daily variations in instrument response, each day's sample data was then normalized to the mean CRMP concentration of 46 μmol L^{-1}. Average coefficient of variation for all triplicate TOC samples was 4.0%.

Discrete total organic nitrogen (TON) concentrations were estimated by subtraction of inorganic nitrogen concentrations from total nitrogen measurements. Total nitrogen samples were collected in acid-washed 60-mL high-density polyethylene bottles and immediately frozen at −30°C until laboratory analysis. Organic nitrogen was converted to nitrate by using a persulfate wet oxidation method (Libby and Wheeler 1997), which was then analyzed with a Technicon AA-II. Instrument calibration was performed daily with a standard curve prepared from triplicate digested leucine standards at three concentrations. Fresh standards were made prior to each run by diluting a primary standard with artificial seawater. Digested artificial seawater was used as a blank, and the standard curve was corrected for nitrogen content of the blank by determining the concentration of nitrogen in the persulfate solution and then calculating the amount of nitrogen in the artificial seawater. Artificial seawater nitrogen content was estimated as the difference between blank signal and persulfate signal.

Fe was sampled from the RV *Wecoma* following the methods described in Chase et al. (2005*a*). A continuous supply of near-surface (0–5 m) water was peristaltically pumped into the laboratory through acid-cleaned silicone and Teflon-lined polyethylene tubing attached to a brass "fish" (Vink et al. 2000). The fish was deployed off a 1.5-m boom on the starboard side of the ship. Measurements were made as the ship was under way at ~13 km h^{-1}. The sample stream passed through a 20-μm acid-cleaned capsule filter followed by a ~30-s in-line acidification to pH 3.3 ± 0.1 before entering the flow injection analysis manifold. The underway analysis results in an operationally defined measurement of Fe referred to as dissolvable iron (dFe). Along a nearshore transect from Baja to Monterey, California, no systematic offset was found between dFe and dissolved Fe in the upper 20 m, but in deeper waters, dissolved Fe was about half of the dFe (Chase and Johnson unpubl. data). The dFe was detected following the method of Measures et al. (1995) without preconcentration. Standards were prepared in acidified low Fe seawater and were run at least every 5 h and whenever new reagents were prepared. A system blank was assessed by injecting carrier (pH 3 Milli-Q water) as a sample. The blank associated with sample acidification was determined by doubling the addition of acid, and was found to be below detection. The detection limit, calculated as three times the standard deviation of the blank, was 0.5 nmol L^{-1} during the run reported here. Accuracy was assessed by periodically running a large-volume filtered and acidified seawater sample of known concentration (Fe = 3 nmol L^{-1} ± 6%) and was also checked once against the CASS-4 reference standard (13 ± 2 nmol L^{-1} measured vs. 13 ± 1 nmol L^{-1} certified). The surface salinity and temperature associated with each Fe measurement was determined by time-matching with the ship's surface underway system, after correcting for the lag (~1 min) between uptake from the fish and entry into the Fe analytical system.

In addition to the underway analyses, discrete, unfiltered samples were collected from the surface pumping system from 24 Jan to 05 Feb for quantification of total dissolvable iron (tFe). All discrete samples were acidified with 4 mL 6 mol L^{-1} quartz-distilled HCl L^{-1} within 24 h of collection. Samples were stored for ~1 yr before analysis by flow injection analysis.

Statistical analyses—Relationships between the various chemical measurements and salinity were established by the geometric means model II regression (Ricker 1973).

Results

Oceanographic conditions varied dramatically between the three sampling dates of this study. Strong (>10 m s^{-1}) northward, downwelling favorable winds were in place on 01 Feb (Fig. 2). Surface currents were to the north at >50 cm s^{-1} with Ekman transport toward the coast. Isopycnals sloped downward and intersected the bottom over the midshelf (at ~124.15–124.20 W), and a region of vertically homogenous water was located from ~124.10–124.15 W (Fig. 3). Several periods of heavy rain occurred over the northern Oregon coast on 29–31 Jan. Consequently, streamflow from the Siletz River, just south of our transect line, peaked on 31 Jan at ~400 m^3 s^{-1} (Fig. 4). By 01 Feb, streamflow was only slightly lower at 350 m^3 s^{-1}. The freshwater input, limited to a narrow region nearshore on 01 Feb (Figs. 3, 5), resulted in enhanced stratification of the upper 40 m of water (Fig. 3). By 02 Feb, winds subsided and began to reverse direction toward the south

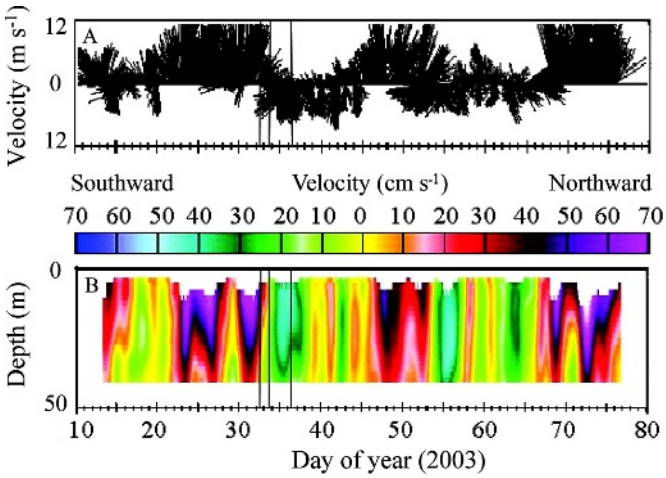

Fig. 2. (A) Wind velocity and direction at the midshelf buoy in late January/early February 2003. Lines pointed up (above zero) are for northward (downwelling favorable) winds and lines pointed down (below zero) are for southward (upwelling favorable) winds. (B) Alongshore current velocity measured at inner shelf mooring (45.00 N, 124.07 W). Vertical lines indicate the three sampling dates from this study.

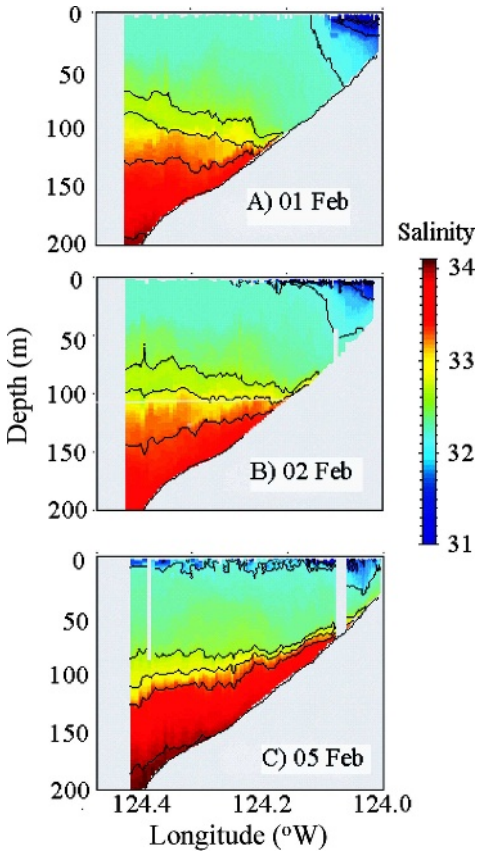

Fig. 3. Across-shelf salinity distributions (colors) and isopycnals (solid lines) on (A) 01 Feb, (B) 02 Feb, and (C) 05 Feb. Note that as a result of interference from the ship's wake, the profiling instrument did not collect data in the upper 3–5 m of the water column. Hence, the lowest-salinity water (i.e., <31; *see* Figs. 5, 6) is not indicated here.

(Fig. 2). Streamflow on 02 Feb had decreased to 175–200 $m^3\ s^{-1}$ (Fig. 4), and although a downwelling front was still evident, relaxing winds allowed the river plume to spread out as a thin layer (<5 to 10 m) at the surface, which visibly increased stratification over the inner and midshelf (Fig. 3). By 05 Feb, winds had completely reversed and were weakly southward, or upwelling favorable, surface currents were to the south (~40 to 50 cm s^{-1}) and offshore (Fig. 2), indicative of weak upwelling conditions, and streamflow had dropped to 75 $m^3\ s^{-1}$ (Fig. 4). The shift to upwelling favorable winds and offshore surface currents spread the plume of freshwater out to the shelf-break region (Figs. 3, 5). By this time, the salinity of the plume had increased considerably from mixing with the higher salinity offshore (and subsurface) waters (Fig. 6).

Nutrient distributions on each of the transects (Fig. 7) were noticeably elevated in regions of lowest salinity (Fig. 5), indicating that the river water was a clear source. Nutrient concentrations in non-plume-influenced offshore water (from ~124.15–124.40 W on 01 Feb, ~124.25–124.40 W on 02 Feb), characterized as having salinities ≥32.2, were nearly constant between 01 Feb and 02 Feb (Fig. 7). Highest concentrations of nitrate, phosphate, silicate, ammonium (Fig. 7A–D, respectively) and dFe (Fig. 8B) were found on 01 Feb in the core of the freshwater plume; i.e., in the region of lowest salinity. As the plume moved offshore on 02 Feb under relaxing winds, elevated nutrient concentrations were seen out to the midshelf (Fig. 7). By 05 Feb, the plume had spread out over the entire shelf in response to upwelling favorable winds and currents (Fig. 5), resulting in elevated nutrient concentrations in surface waters over the entire shelf (Fig. 7). However, mixing with lower nutrient water (noticeable from T-S characteristics, Fig. 6) resulted in lower concentrations in the freshwater plume than on previous days.

Highest TOC concentrations (~77 to 89 μmol L^{-1}) were observed on 01 Feb (Fig. 8A) coinciding with the lowest salinity water (Fig. 5). In contrast, TON concentrations were relatively low in the low salinity water (~4–5 μmol L^{-1}) and were not correlated with salinity (data not shown). A secondary TOC peak (~81 to 82 μmol L^{-1}) was observed further offshore in the vicinity of the midshelf. The TOC concentrations at the shelf break ranged from 63 to 67 μmol L^{-1}. By 02 Feb, a single peak in TOC concentrations (76 to 80 μmol L^{-1}) was observed over the midshelf, although inner-shelf TOC concentrations were still elevated relative to shelf break concentrations (~69 to 76 μmol L^{-1} vs. 60 to 65 μmol L^{-1}). The lowest TOC concentrations of this study were observed on 05 Feb and ranged from approx. 57 to 64 μmol L^{-1} at the shelf break and inner shelf waters. Midshelf TOC concentrations were slightly higher, ranging from ~62 to 65 μmol L^{-1}.

Regression analysis of the data from the 01 Feb transect revealed that all of the nutrients, TOC, dFe and tFe were negatively correlated with salinity (Fig. 9; Table 1). Extrapolation of the regression lines back to zero salinity (i.e., the y-intercept) allows for estimation of the riverine concentrations. Plots of NO_3^-: PO_4^{3-} and NO_3^-: $Si(OH_4)^-$

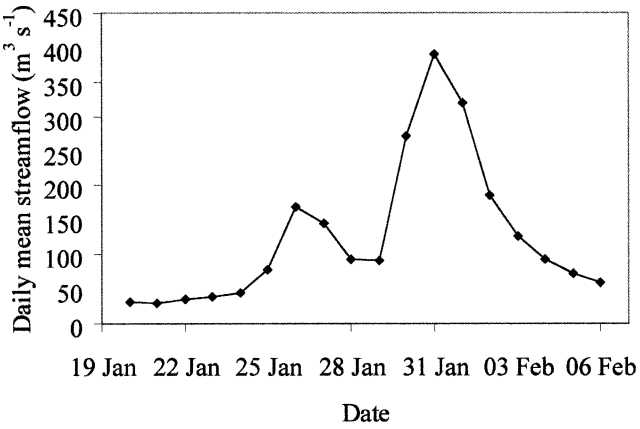

Fig. 4. Daily river discharge from the Siletz River.

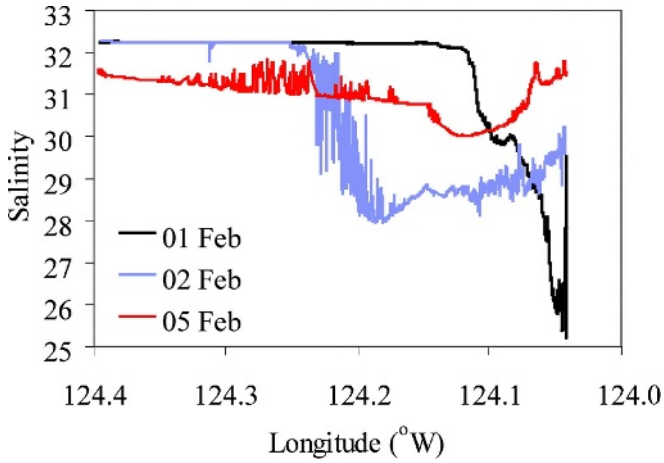

Fig. 5. Surface salinity on 01 Feb, 02 Feb, and 05 Feb.

all show some curvature at a salinity of ~30 (data not shown), also clearly evident in the NO_3^- and to a lesser extent PO_4^{3-} regressions in Fig. 9. It is not clear what the cause of this curvature is, although there is an anomalously warm water mass (by ~0.2–0.3°C) present at salinities of 29.5–30.5. It should also be noted that the curvature is likely not due to productivity, as chlorophyll was <1 μg L^{-1} on 01 Feb. Using all of the data yields estimated river concentrations of 43 μmol L^{-1} NO_3^-, 5.5 μmol L^{-1} PO_4^{3-}, 197 μmol L^{-1} $Si(OH_4)^-$, and 8.2 μmol L^{-1} NH_4^+. Using regressions derived from salinity <30 yields 52 μmol L^{-1} NO_3^-, 4.9 μmol L^{-1} PO_4^{3-}, 171 μmol L^{-1} $Si(OH_4)^-$, and 10.5 μmol L^{-1} NH_4^+. Estimations of TOC, dFe and tFe were not as precise because they were derived from a smaller data set of discrete samples. From those discrete sample measurements at the entire salinity range, the estimated TOC river concentrations was 210 μmol L^{-1} TOC, or if only data from salinity <30 is used, the estimate is 175 μmol L^{-1}. The dFe concentrations appeared to be anomalously low at salinities between 29.5 and 30.5, coincident with the presence of the slightly warmer water mass. Thus, river dFe concentrations were estimated using only data from salinities <29.5. The estimated river dFe concentration was 120 nmol L^{-1} and the estimated tFe was

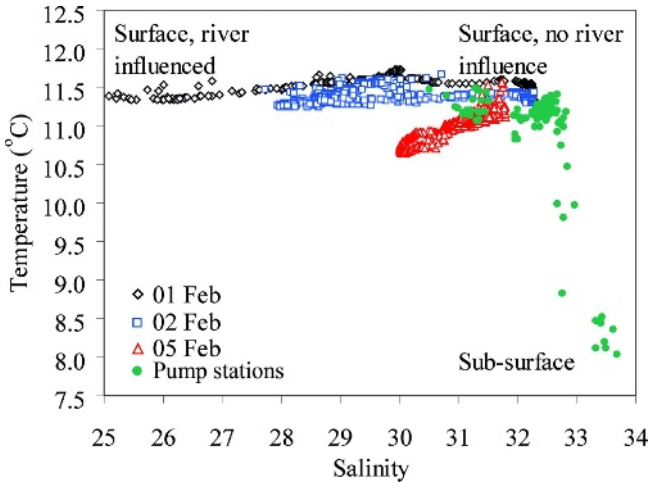

Fig. 6. Temperature versus salinity characteristics of surface water on 01 Feb, 02 Feb, 05 Feb, and from late January CTD casts.

12.8 μmol L^{-1}. Although only one transect of Fe data is presented, it is representative of similar transects conducted at other sites along the Oregon coast during this time period (Z. Chase unpubl. data).

Discussion

Wintertime biogeochemical cycles and ecosystem dynamics have traditionally been overlooked in eastern boundary current systems. Nonetheless, ecologically important late winter phytoplankton blooms have been documented off Oregon (Wetz et al. 2005; R. Letelier unpubl. data). We suggest that coastal rivers supply two key ingredients that might be necessary for wintertime phytoplankton growth: nutrients and buoyant freshwater (leading to stratification and a stable water column). During downwelling favorable conditions, the river plume was located in a narrow band along the coast. However, wind relaxation and/or reversal allowed the plume and its associated materials to spread out across the shelf.

High streamflow rates and short residence time of water (≤1 d; e.g., Colbert and McManus 2003) in Oregon estuaries during the winter means that river water and its constituents can pass through estuaries and enter the coastal ocean relatively unaltered. Colbert and McManus (2003) observed conservative mixing behavior for both silicate and nitrate in a northern Oregon estuary during the winter. Our estimated concentrations of silicate (171–197 μmol L^{-1}) and nitrate (43–52 μmol L^{-1}) in river water are similar to wintertime concentrations observed by those authors for rivers that drain into Tillamook Bay (~200–250 μmol L^{-1} silicate, ~30–75 μmol L^{-1} nitrate,) and also to observations from the Yaquina River, located south of our study site (Callaway and Specht 1982; Sigleo and Frick 2003). Additionally, bimonthly sampling of nitrate from nearly all of Oregon's coastal rivers by the Oregon Department of Environmental Quality has revealed that nitrate concentrations are ≥40 μmol L^{-1} during the winter (Pacific Northwest Water Quality Exchange; http://deq12.

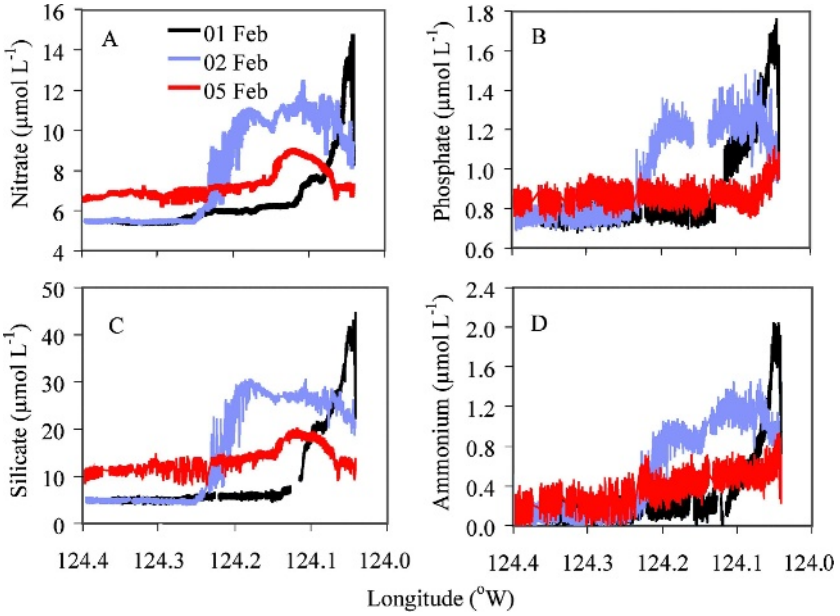

Fig. 7. Distributions of (A) nitrate, (B) phosphate, (C) silicate, and (D) ammonium in surface waters on 01 Feb, 02 Feb, and 05 Feb.

deq.state.or.us/pnwwqx). These high nitrate concentrations, despite the fact that most of Oregon's coastal streams and rivers are relatively pristine, are partly the result of the presence of red alder trees (*Alnus rubra*) that form dense stands in the Coast Range and that have symbiotic N_2 fixers associated with their roots (Compton et al. 2003). The presence of these trees has been shown to substantially increase nitrate concentrations in nearby watersheds in the Oregon Coast Range (Compton et al. 2003). Flow-weighted nitrate concentrations in river water are highest in the winter, indicating that the nitrate is derived primarily from leaching of water out of soils in the Coast Range (Colbert and McManus 2003). Although fixed-nitrogen input from nonalder soil nitrogen fixers cannot be discounted in the other major eastern boundary current systems, red alder are almost exclusively found in the North American Pacific Northwest (Little 1971). Furthermore, even though the southern extent of their range in the western U.S. extends to central California (Little 1971), we have been unable to find information on whether the alder form dense stands there similar to Oregon (Harrington et al. 1994). Thus, depending on the biomass density, alder-derived watershed N inputs to the coastal ocean off Central California may also be different from Oregon.

Results from this study coupled with previous observations in the system imply that that riverine fluxes of nitrate and silicate to the coastal ocean can be significant on relatively short timescales (days to weeks). As these small rivers have been overlooked until now, no studies have compared the magnitude of their nitrate and silicate inputs to preexisting, non-river-influenced surface water nutrient pools. If one compares the amount of nitrate and silicate in the upper 10 m of the water column across the 27.5-km shelf under non-river-influenced conditions (assuming uniform nitrate (~5.5 μmol L^{-1}) and silicate (~5 μmol L^{-1}) concentrations) to the amount of nitrate and silicate in the upper 10 m across the shelf under river-influenced conditions (using the observed nutrient concentrations on 01 Feb or 02 Feb), we estimate that this particular flood event increased the pools of nitrate by 20–50% and silicate by 80–190%, depending on the stage of the flood event. Over the entire winter, we estimate that if all of the riverine nitrate were taken up by phytoplankton at Redfield stoichiometry with carbon, ~1.1–1.4 $\times$ 10^{10} mol carbon would be fixed. That equates to ~18–22% of summertime upwelling production (Hales et al. unpubl. data), implying that wintertime production and controls on that production can no longer be thought of as insignificant. This assumes that conditions are suitable for phytoplankton growth and nitrate utilization. The previously mentioned studies of winter phytoplankton growth off Oregon and recent observations by Álvarez-Salgado et al. (2005) of large winter diatom blooms in the eastern boundary current system off Spain suggest that there are periods when the light and mixing regimes in these types of systems are conducive for phytoplankton growth during winter.

Our estimated ammonium and phosphate river water concentrations are higher than estimates by Colbert and McManus (2003) and Colbert (2004) (8–10.5 μmol L^{-1} vs. ~1.5–2.5 μmol L^{-1} ammonium, 4.9–5.5 μmol L^{-1} vs. ~0.5–1.5 μmol L^{-1} phosphate). However, those authors found considerable positive deviations from a conservative mixing line between river water and seawater for both phosphate and ammonium, indicating that estuarine regeneration was an additional source for those nutrients. Release of phosphate and ammonium is likely enhanced during wintertime high-discharge events that are the result of increased sediment resuspension and pore water flow. It is not surprising that phosphate and ammonium show evidence of strong estuarine remineralization while nitrate and silicate do not. Silicate and, to a lesser extent, nitrate are enriched in river water over wintertime high-salinity

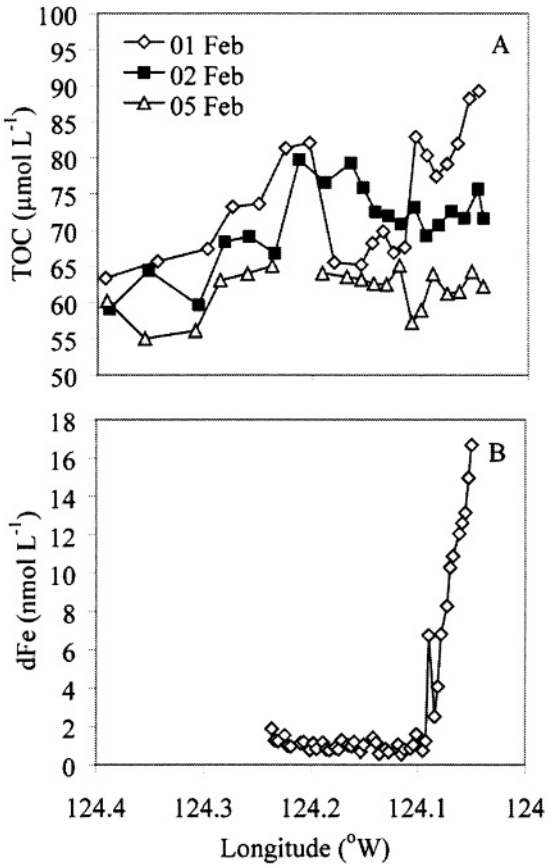

Fig. 8. Distributions of (A) TOC in surface waters on 01 Feb, 02 Feb, and 05 Feb, and distribution of (B) dFe on 01 Feb.

coastal waters. In the case of silicate, which is 40-fold enriched in river water over coastal ocean waters, an addition of a few μmol L^{-1} in the estuary would be hardly noticeable relative to the 200 μmol L^{-1} river water. The same is largely true for nitrate, as we would be hard-pressed to distinguish between an extrapolated zero-salinity intercept of 52 μmol L^{-1} and a true river end member of 45 μmol L^{-1}. There is, however, another possible explanation for the lack of an obvious remineralized nitrate signal. Advection of high nutrient upwelled water from the coastal ocean into the estuaries frequently occurs during the summer (Sigleo et al. 2005), spurring intense phytoplankton production and organic matter deposition in the estuary during that time. Thus, remineralization in these sediments probably proceeds to a large extent by suboxic processes, all of which release organic nitrogen in the form of ammonium rather than nitrate. Nitrate reduction, the first suboxic diagenetic process to occur after oxygen depletion, actually consumes nitrate. Thus, an ammonium source is detected in the absence of a clear nitrate source.

Fe is a key element in controlling the growth of coastal phytoplankton, and we have shown that riverine Fe is transported into the coastal ocean during high-discharge events. The estimated river dFe concentration (120 nmol L^{-1}) is slightly lower than average Fe concentrations measured by Colbert (2004) in rivers feeding into Tillamook Bay during the winter (~200 nmol L^{-1}), suggesting that at least 40% of riverine dFe is lost within the estuary. However, without concurrent measurements of dissolved (<0.2 μm) Fe in the river and ocean over several tidal cycles, we cannot yet say whether Fe losses in Oregon's estuaries are anomalously small relative to other lower flow estuaries that have shown >90% of riverine dissolved Fe is lost in the estuary through flocculation and sedimentation (e.g., Boyle et al. 1977; Sholkovitz et al. 1978). One possibility is that the short residence time ($\leq$1 d) of river water through Oregon's estuaries in winter results in a larger fraction of dissolved Fe escaping the estuary and reaching the shelf. Although some dissolved Fe is certainly lost in these estuaries, our more limited measurements of tFe (i.e., dissolved + particulate) suggest this tFe is largely conserved through estuarine mixing. Our measurements extrapolate to a river value of about 12.8 μmol L^{-1}, which is within the range of values reported by the USGS for tFe in the Alsea River (USGS gauging and water quality Sta. 14306500; http://nwis.waterdata.usgs.gov/or/nwis/qwdata), and similar to the value extrapolated from our own in-estuary measurements of tFe (Chase unpubl. data). Conservative behavior of total Fe has been noted for several estuaries in Maine (Mayer 1982).

Riverine Fe inputs could have an immediate affect on the winter/spring phytoplankton, and quite possibly on the summertime (upwelling) production in the system as well. Studies off central California have shown that during the upwelling season, phytoplankton growth and nutrient drawdown can be severely limited as a result of Fe limitation (Hutchins et al. 1998; Bruland et al. 2001; Chase et al. 2005*b*). Off Oregon, however, nitrate (~20–30 μmol L^{-1}) is frequently drawn down to nondetectable levels by large phytoplankton blooms (>10 μg L^{-1} chlorophyll *a*) that develop during upwelling events (Corwith and Wheeler 2002; Hales et al. 2005), and intensive surveys of Fe concentrations suggest that there is ample Fe to support phytoplankton requirements and the complete nitrate drawdown (Chase et al. 2005*a*). Most of the Fe that supports phytoplankton growth in upwelling systems comes from upwelled water that has been in contact with the bottom boundary layer and continental shelf sediments (Johnson et al. 1999; Chase et al. 2005*a*,*b*). However, the source of Fe to the continental shelf sediments has not been characterized, as rivers discharge relatively little Fe to the coastal ocean during the upwelling season and aerosol input is minimal (Duce and Tindale 1991).

As suggested by Bruland et al. (2001) for central California, we believe that the Fe supplied by Oregon's Coast Range rivers during the winter could be a major Fe source to the shelf sediments. Using the estimated river dFe concentration from this study, the total winter input of dFe to the coastal ocean is on the order of 4.8×10^6 mol $winter^{-1}$. Assuming a high-end estimate of Fe : C requirements for coastal diatoms (100 μmol Fe : mol C; Bruland et al. 2001), we estimate that enough Fe is supplied just by the dFe in the coastal rivers to support the entire upwelling season productivity. Furthermore, this dFe fraction does not include Fe associated with particles >20 μm, which contain Fe concentrations that are two orders of magnitude higher than the dFe (i.e., the tFe,

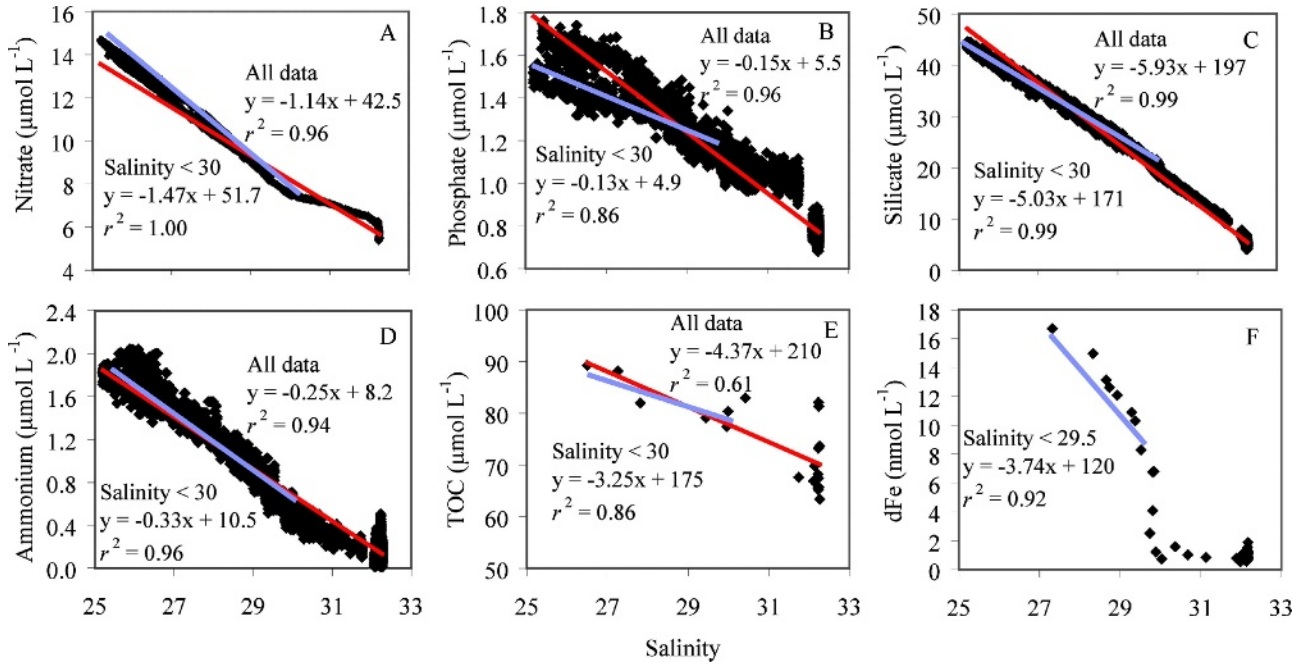

Fig. 9. Model II geometric means regression of (A) nitrate, (B) phosphate, (C) silicate, (D) ammonium, (E) TOC, and (F) dFe versus salinity on 01 Feb. Regressions performed using all data are indicated in red, and regressions performed using only data at salinities <30 (or <29.5 for dFe) are indicated in blue.

Table 1.). That the winter Fe can support summertime blooms is dependent on the Fe remaining on the shelf. Warrick et al. (2004) found that during flooding of a small coastal southern California river, a significant portion of the particles and sediment associated with that river water rapidly settled to the inner-shelf seafloor. This could be a mechanism by which the particle-associated Fe, i.e., the tFe reported here, is deposited on the shelf. Downwelling conditions and more specifically the presence of a downwelling front will likely prevent shelf-sedimented and/or flocculated Fe from being transported offshore (e.g., Austin and Barth 2002). Thus, once upwelling begins in March or April (Huyer et al. 1979), and assuming that upwelled waters come into contact with the bottom boundary layer (Hales et al. 2005; Perlin et al. 2005), the Fe will become available to surface phytoplankton communities. Downwelling conditions may also limit offshelf transport and dilution of the water column Fe (i.e., the nonsedimented or "dissolved" fraction).

On a global scale, striking differences in riverine discharge are apparent between the major eastern boundary current systems, with implications for biogeochemical cycles. Discharge rates normalized to coastline length during high-flow periods are highest in the northern California Current system from northern California to Washington followed by the Portugal Current off the Iberian Peninsula (Table 2.). The southern end of Vancouver Island (British Columbia), which experiences seasonal

Table 1. Model II geometric means regression statistics for nutrients, TOC, dFe and tFe vs. salinity. Data are from 01 Feb transect except for tFe, which is from 24 Jan to 05 Feb transects. Note that the 95% confidence limits for the macronutrients are <1% of the mean Y-intercepts for the observed salinity range (ca. 25 to 30 or 32). A more conservative estimate for the error associated with the Y-intercept is the difference the between the <30 Y-intercept and the Y-intercept from the entire observed salinity range (±11–28%).

		Slope	Y int (±95% conf. limit)	*n*
NO_3^- (µmol L^{-1})	All data	−1.14	42.5(±0.1)	26,794
	Salinity <30	−1.47	51.7(±0.1)	4672
$Si(OH)_4^-$ (µmol L^{-1})	All data	−5.93	197.0(±0.2)	26,794
	Salinity <30	−5.03	171.3(±0.1)	4672
PO_4^{3-} (µmol L^{-1})	All data	−0.15	5.48(±0.02)	26,794
	Salinity <30	−0.13	4.89(±0.06)	4672
NH_4^+ (µmol L^{-1})	All data	−0.25	8.20(±0.02)	26,794
	Salinity <30	−0.33	10.52(±0.06)	4672
TOC (µmol L^{-1})	All data	−4.37	209.8(±41.8)	20
	Salinity <30	−3.25	175.4(±42.9)	6
dFe (<20 µm) (nmol L^{-1})	Salinity <29.5	−3.74	120.0(±25.0)	8
tFe (unfiltered) (nmol L^{-1})	All data	−399.50	12,800(±1900)	44

Table 2. Average discharge rates during high flow periods for coastal rivers of the major eastern boundary current systems.

Current system	Discharge ($m^3\ s^{-1}$)	Coastline normalized discharge ($km^3\ s^{-1}\ km^{-1}$)	Coastline normalized discharge relative to Oregon (%)
California current off Oregon*	2570	5.47×10^{-9}	
Portugal current†	1800	2.61×10^{-9}	48
Central California current‡	1299	2.49×10^{-9}	35
−San Francisco Bay Rivers	257	4.93×10^{-10}	7
Canary current§	1890	6.96×10^{-10}	13
Peruvian current‖	1240	6.84×10^{-10}	13
Benguela current¶	200	1.43×10^{-10}	3

* Coastline normalized discharge rate is representative of Northern California (40.5°N to Oregon border) and Washington state ($4.11–9.26 \times 10^{-9}$ $km^3\ s^{-1}\ km^{-1}$).

† Includes Muros, Arosa, Pontevedra, Vigo, Lima and Mira Rivers; wintertime discharge rates were assumed to average 50 $m^3\ s^{-1}$; see Varela et al. (2005). Also includes Minho, Douro, Mondego, Tejo, and Sado Rivers; discharge rates were multiyear wintertime averages obtained from the Oak Ridge National Laboratory River Discharge project (ORNL) (http://www-eosdis.ornl.gov/RIVDIS/rivdis.html).

‡ From 34.5°N to 40.5°N; includes Mattole, Noyo, Navarro, Russian, Guadalupe, Coyote, Alameda, Sacramento, San Joaquin, San Lorenzo, and Salinas Rivers; data obtained from the USGS.

§ From Senegal to northern Morocco including Ouergha, Sebou, Ourn el Rebia, Gambia, Casanance, and Senegal Rivers; data obtained from the ORNL.

‖ Includes Chira and Santa Rivers; data obtained from ORNL. Also includes Jequetepeque and Chicama Rivers; data obtained from Marengo and Tomasella (1998). Note there were at least 14 other rivers from which we could find no discharge data. For those, an arbitrary average discharge rate of 50 $m^3\ s^{-1}$ was assigned, which is likely an overestimate for small rivers.

¶ Includes Orange and Doring Rivers; data obtained from ORNL.

upwelling, also has numerous small rivers draining to the Pacific coast, and may be similar to Oregon, Washington, and northern California with regard to riverine effects on the coastal ocean. For the central California Current, the wintertime coastline length normalized discharge rate is only 35% of that in Oregon. Exclusion of the river input to San Francisco Bay, which is a large but localized source of freshwater to the coastal ocean, further reduces the central California discharge to 7% of that in Oregon. This implies that although most of the coastal ocean off Oregon receives significant riverine input and its associated Fe and nutrients, central California receives a smaller, more localized and patchy supply of freshwater. Thus, the limited riverine input to the coastal ocean in conjunction with the narrower shelves in central California may be a major reason why Fe limitation is much more widespread there than off Oregon. Similar results are obtained for the Peruvian, Benguela, and Canary Current systems, where coastline normalized discharge is ~3–13% of that in Oregon. It should be noted though that the Benguela and Canary Current systems may still receive significant Fe inputs through atmospheric dust deposition (Duce and Tindale 1991; Mahowald et al. 2005).

Another important constituent of the river water is organic material. High TOC concentrations were found in the core of the river plume on 01 Feb. This material consisted of ~20% POC and ~80% DOC and had an average molar C : N ratio of ~19.4, indicative of a terrestrial source (e.g., Hedges et al. 1997). Our estimated river water TOC concentration (175–210 $\mu mol\ L^{-1}$) appears to be representative of most of Oregon's Coast Range rivers on the basis of bimonthly sampling by the Oregon Department of Environmental Quality (Pacific Northwest Water Quality Exchange; http://deq12.deq.state.or.us/pnwwqx). Multiplying that estimate by the annual wintertime discharge rate for all of the rivers gives a mean wintertime TOC input to the coastal ocean of approximately 1.0×10^{11} g TOC. In comparison, the annual TOC input from the Columbia River, estimated using discharge rates and TOC concentrations in Hopkinson et al. (1998), is approximately 5.5×10^{11} g TOC yr^{-1}. Thus, despite their small size and short discharge period, Oregon's Coast Range rivers can increase the total annual river input of TOC (over that of the Columbia R.) by 16–19%. If the estimated riverine TOC concentrations for Oregon's rivers are also representative of rivers in North California and Washington, the total annual input of TOC from these small mountainous rivers to the northern California Current may be closer to 30–40% of that from the Columbia River. Some of this material may be labile (e.g., Hedges et al. 1997), and thus it has the potential to serve as a supplement to the coastal microbial food web and affect the metabolism of the northern California Current. The more recalcitrant or rapidly sinking components, if transported to deeper water, could be a sink for terrestrial carbon.

Recent work off northern California supports the notion of an offshelf carbon sink, as it was determined that a considerable amount of organic carbon derived from mountainous coastal rivers is transported to an adjacent abyssal site with a time lag of roughly 2–4 months (Hwang et al. 2004), although the transport mechanism itself was not determined. Given the general lack of cross-shelf transport in the winter, we suggest that some of the organic carbon may accumulate over the shelf during downwelling conditions. Upon return to upwelling conditions, the material may be transported offshelf through mixing to deeper waters and advection. For the POC component and other sedimented components of the riverine carbon, a more likely mechanism would be through movement of organic matter-laden parcels of water from the bottom boundary layer to deeper waters, which has recently been shown to be the dominant mechanism for offshelf export of sediment upwelling phytoplankton bloom POC off Oregon (Hales et al. in press).

Small coastal rivers influence the physical structure and biogeochemistry of coastal waters off Oregon on short timescales (days to weeks) following heavy precipitation and discharge events that are common during the winter. On the basis of river discharge data, we believe that the riverine input is not unique to Oregon but is representative of most of the northern California Current. Input of this riverine freshwater leads to buoyant surface waters, increased stratification, and elevated macronutrient and Fe concentrations in coastal surface waters. If retained over the shelf, the Fe inputs may be important for summertime (upwelling) production. Finally, the rivers carry a large supply of terrestrial organic matter to the coastal ocean that could either: 1) serve as a supplement to the coastal microbial food web and possibly alter system metabolism, or 2) be a major sink for terrestrial carbon if it is refractory and is transported to the deep ocean. Because of the importance of eastern boundary current systems in global biogeochemical cycles, further work is clearly needed to characterize wintertime ecosystem dynamics and to examine conditions that lead to differences between the major systems. Also needed are studies to determine the response of marine microorganisms to the riverine nutrient and carbon supplies, and on a broader timescale, to determine the influence that El Niño/La Niña cycles and other atmospheric fluctuations might have on winter precipitation and ultimately the riverine inputs and ecosystem response (e.g., Sigleo and Frick 2003).

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