Riverine input of macronutrients, iron, and organic matter to the coastal ocean off Oregon, USA, during the winter

Michael S. Wetz1,*
Burke Hales1
Patricia A. Wheeler1
Zanna Chase1
Michael M. Whitney1, 2

*Corresponding author

1College of Oceanic and Atmospheric Sciences
Oregon State University
104 COAS Admin. Bldg.
Corvallis, OR 97331
mwetz@coas.oregonstate.edu

2Now at Department of Marine Sciences
University of Connecticut at Avery Point
1080 Shennecossett Road
Groton, CT 06340

Running head: River influence on coastal ocean
Acknowledgements:

We thank J. Wetz, J. Arrington, J. Harman, L. Bandstra, J. Jennings, P. Covert, R. Schwartz, and L. Baker for technical assistance at sea and in the laboratory. M. Levine, T. Boyd, M. Kosro, J. Moum, and A. Perlin are gratefully acknowledged for providing us with some of their unpublished data. This research was supported by a NSF Graduate Research Fellowship to MSW, NSF grant OCE-9907854 to BH and PAW, and NSF grant OCE-9907953 to A. Van Geen.
ABSTRACT

Little is known about wintertime biogeochemical cycles or ecosystem function in eastern boundary current systems. Three cross-shelf transects were conducted off northern Oregon in early February 2003, within a few days of one another and coincident with a flood event, but under different wind and current conditions. During downwelling favorable winds, low salinity (~ 25 psu) river-influenced water was located in a ca. 5 km wide band near the coast. Associated with the low salinity water were significantly elevated macronutrient, dissolvable iron (dFe), and total organic carbon (TOC) concentrations. As winds relaxed and switched to upwelling favorable conditions, the low salinity water spread out at the surface extending to the shelf break and carried with it elevated levels of nutrients and organic carbon. Riverine input of nitrate and silicate increased those pools in the upper 10 m of the coastal ocean by 20-50% and 80-190%, respectively. Riverine dFe flux to the coastal ocean was also high, and given that downwelling conditions during winter tend to minimize cross-shelf transport, dFe supplied by the rivers may remain over the shelf and then become available to spring and summer phytoplankton. Finally, in comparison to the Pacific Northwest’s largest river, the Columbia, the smaller coastal rivers can increase the supply of terrestrial TOC to the coastal ocean by 15-20%. These results show that small coastal rivers, key features during the wintertime but rarely studied in eastern boundary current systems, can significantly alter coastal biogeochemical cycles and influence ecosystem structure.
INTRODUCTION

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 (Huyer 1977; Huyer et al. 1979; 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 (Huyer 1977; Huyer et al. 1979; Allen and Newberger 1996; Austin and Barth 2002). In the region of the front, the water column can be vertically homogenous (Barth et al. 2004). Currents inshore of the front are predominately to the north, and cross-shelf circulation is believed to be minimal (Huyer et al. 1975; Huyer et al. 1978; 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 and are interspersed between periods of weaker winds and even southward, upwelling favorable winds (Huyer et al. 1978; Huyer et al. 1979; 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, recent wintertime incubation studies using natural phytoplankton communities collected over the Oregon shelf demonstrated that the phytoplankton were capable of growth at surface light intensities, but suggested that deep mixing associated with downwelling cycles likely prevents significant growth in situ (Wetz et al. 2004). Nonetheless, results from several field studies indicate that a small, but ecologically important, late winter phytoplankton bloom is a common feature. Elevated levels of chlorophyll $a$ (~4 to 5.5 µg l$^{-1}$) were observed in surface waters over most of the shelf off Newport, Oregon, in mid-February of both 2002 and 2003 (Wetz et al. 2005). Additionally, Peterson and Miller (1977) observed clogging of their zooplankton sampling nets by a dense bloom of the diatom *Thalassiosira* sp. in late February 1970. These blooms are potentially an important food source for zooplankton emerging from diapause (Peterson and Miller 1977). However, the timing of the blooms precedes 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).

The Coast Range rivers in Oregon tend to have high nutrient and organic matter concentrations (Wigington et al. 1998; Colbert and McManus 2003; Compton et al. 2003; Sigleo and Frick 2003). Discharge from the rivers is highest in the winter and much lower 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 late October through March (Colbert and McManus 2003; M.M. Whitney submitted manuscript). Because of their high nutrient and organic matter concentrations, the rivers have the potential to influence coastal ocean biogeochemistry and food web dynamics. However, wintertime studies of nutrient and
organic matter dynamics are rare in these types of systems. Here we present results from three cross-shelf transects that coincided with a flood event and 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 carbon were conducted off northern Oregon (45.00 N, ~124.05 to 124.40 W; Fig. 1) aboard the R/V Revelle on three dates in 2003; 1 Feb, 2 Feb, and 5 Feb. 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 ca. 7 to 8 hours to complete. The 1 Feb transect began at 1300 local time, and the 2 and 5 Feb transects began at 0800 local time. Additional CTD cast stations were occupied from 21 Jan to 1 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 was collected from a buoy deployed over the mid-shelf (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) (Boyd et al. 2005). Current velocities were sampled every 120 s in 2-m bins over the water column depth. Vertical profiles of salinity and density were obtained using a loosely tethered profiler equipped
with temperature, salinity, and pressure sensors (Perlin et al. in press). Those data were provided courtesy of the OSU Mixing group (A. Perlin and J. Moum).

Streamflow Information- Daily streamflow from the Siletz River (station 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. Wintertime river discharge into shelf waters from all of Oregon’s coastal rivers was estimated from data provided by the Oregon State University Streamflow Research Project (http://cwest.oregonstate.edu/streamflow/mainpage/hydro.htm). Briefly, annual river discharge rates for each of five coastal watersheds was multiplied by the area of each watershed to get an annual average discharge for all of Oregon’s coastal rivers. Since nearly all of the discharge occurs during a 6-month period from mid- October through mid- April (Colbert and McManus 2003; M.M. Whitney, unpublished data), we doubled the annual discharge to estimate a wintertime discharge rate (~2570 m$^3$ s$^{-1}$ or 4.00 x 10$^{10}$ m$^3$ winter$^{-1}$).

Chemical Analyses - High-speed macronutrient analyses were performed following the WOCE/JGOFS protocols of Gordon et al. (1995, as amended in 2000; http://chemoc.coas.oregonstate.edu/~lgordon/), 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 (Hales et al. In press), but in this instance supplied by ship's surface intake line. Samples were analyzed at a frequency of roughly 1 Hz, which, at the typical survey speeds of ca 10 km hr$^{-1}$, represent a horizontal resolution of several meters. Calibrations with artificial seawater solutions of known nutrient concentrations were performed at least once every two hours.
Discrete total organic carbon (TOC) samples were collected in triplicate in acid-washed and pre-combusted (500°C for 5 hours) 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 being processed one to four months later. Samples were analyzed using the High Temperature Catalytic Combustion method on a Shimadzu TOC-5000A analyzer. Standard curves were run twice daily using a DIW 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 (fifteen to twenty subsamples) to check for baseline shifts. In order to ensure that the system was working properly, Certified Reference Materials Program deep seawater (Dec. 2000 batch; obtained from Dr. W. Chen, University of Miami) was injected three times during each run. Average TOC concentration in the CRMP water for the 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 (TN) measurements. Total nitrogen samples were collected in acid washed 60 ml HDPE bottles and immediately frozen at −30°C until laboratory analysis. Samples were processed within four months of collection and were analyzed over four days. Organic nitrogen was converted to nitrate using a persulfate wet oxidation method (Libby and Wheeler 1997), which was then analyzed using a Technicon AA-II. Instrument calibration was performed daily using 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.

Iron was sampled from the R/V Wecoma following the methods described in Chase et al. (2005). 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 5-foot boom on the starboard side of the ship. Measurements were made as the ship was underway at ~ 13 km h$^{-1}$. The sample stream passed through a 20 µm acid-cleaned capsule filter followed by a ~30 second in-line acidification to pH 3.3 ± 0.1 before entering the FIA manifold. The underway analysis results in an operationally defined measurement of iron. We refer to this fraction as dissolvable iron (dFe). The dFe was detected following the method of Measures et al. (1995) without preconcentration. Standards were prepared in acidified low iron seawater and were run at least every 5 hours 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 seawater sample checked against the NASS-5 seawater standard. The surface salinity and temperature associated with each iron 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.

Statistical analyses – Relationships between the various chemical measurements and salinity
were established using 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 1 Feb (Fig. 2).
Surface currents were to the north at > 50 cm s\(^{-1}\) with Ekman transport towards the coast.
Isopycnals sloped downward and intersected the bottom over the mid-shelf (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 1 Feb, streamflow was only slightly lower at 350 m\(^3\) s\(^{-1}\). The
freshwater input, limited to a narrow region nearshore on 1 Feb (Figs. 3, 5), resulted in enhanced
stratification of the upper 40 m of water (Fig. 3). By 2 Feb, winds subsided and began to reverse
direction to being southward (Fig. 2). Streamflow on 2 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 mid-shelf (Fig. 3). By 5 Feb, winds had completely reversed to
being 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 all the way 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 sub-surface) 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 1 Feb, ~124.25-124.40 W on 2 Feb), characterized as having salinities ≥ 32.2 psu, were nearly constant between 1 Feb and 2 Feb (Fig. 7). Highest concentrations of nitrate, phosphate, silicate, ammonium (Fig. 7a-d respectively) and dissolvable iron (Fig. 8b) were found on 1 Feb in the core of the freshwater plume; i.e in the region of lowest salinity. As the plume moved offshore on 2 Feb under relaxing winds, elevated nutrient concentrations were seen out to nearly the mid-shelf (Fig. 7). By 5 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 (ca. 77 to 89 µmol L\(^{-1}\)) were observed on 1 Feb (Fig. 8a) coinciding with the lowest salinity water (Fig. 5). In contrast, TON concentrations were relatively low in the low salinity water (ca. 4-5 µmol L\(^{-1}\)) and were not correlated with salinity (data not shown). A secondary TOC peak (ca. 81 to 82 µmol L\(^{-1}\)) was observed further offshore in the vicinity of the mid-shelf. The TOC concentrations at the shelf break ranged from 63 to 67 µmol L\(^{-1}\). By 2 Feb, a single peak in TOC concentrations (76 to 80 µmol L\(^{-1}\)) was observed over the mid-shelf, 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 5 Feb and ranged from approx. 57 to 64 µmol L$^{-1}$ at the shelf break and inner shelf waters. Mid-shelf TOC concentrations were slightly higher, ranging from ~62 to 65 µmol L$^{-1}$.

Regression analysis of the data from the 1 Feb transect revealed that all of the nutrients, TOC, and dissolved iron 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)$_4^-$ all show some curvature at ~ 30 psu (data not shown), also clearly evident in the NO$_3^-$ and to a lesser extent PO$_4^{3-}$ regressions in Figure 9. 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 data at < 30 psu 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 and dFe 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, but if only data from < 30 psu is used, the estimate becomes 175 µmol L$^{-1}$. The dFe concentrations appeared to be anomalously low between 29.5 and 30.5 psu, coincident with the presence of a slightly warmer water mass (by ca. 0.2° Celsius) than surrounding waters at <29.5 or > 30.5 psu. Thus, river dFe concentrations were estimated using only data from < 29.5 psu. The estimated river dFe concentration was 120 nmol L$^{-1}$.

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 on numerous occasions off Oregon (e.g. Peterson and Miller 1977; Wetz et al. 2005; R. Letelier unpubl. data). However, until now, potential nutrient sources for winter phytoplankton growth had not been characterized, nor had potential mechanisms behind the temporal evolution of favorable hydrographic conditions. We suggest here that coastal rivers could 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 tends to be located in a narrow band along the coast (e.g. Figs. 3, 5; Whitney unpublished data). However, wind relaxation and ultimately reversal to upwelling favorable conditions spreads the river plume and it’s associated materials across the shelf, consistent with theoretical and in situ observations from other systems (e.g. Geyer et al. 2000; Whitney and Garvine 2005).

High streamflow rates and short residence time of water (< 1-2 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 nitrate and silicate in a northern Oregon estuary during the winter. Our estimated concentrations of nitrate (43-52 µmol L⁻¹) and silicate (171-197 µmol L⁻¹) in river water are very similar to wintertime concentrations observed by those authors for rivers that drain into Tillamook Bay (~ 30-75 µmol L⁻¹ nitrate, ~ 200-250 µmol L⁻¹ silicate) and also to observations of Sigleo and Frick (2003) for the Yaquina River, located south of our study site. Additionally, bi-monthly sampling of nitrate from nearly all of Oregon’s coastal rivers by the Oregon Department of Environmental Quality has revealed that nitrate
concentrations are $\geq 40 \mu\text{mol L}^{-1}$ during the winter (Pacific Northwest Water Quality Exchange; http://deq12.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 believed to be due to red alder trees (*Alnus rubra*) that form dense stands in the Coast Range and that have symbiotic N$_2$ fixers associated with their roots (Wigington et al. 1998; 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). The high silicate concentrations are characteristic of intense weathering of rocks in the Coast Range (Karentz and McIntire 1977; Callaway and Specht 1982).

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 have significant ecological implications 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 pre-existing, 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 ($\sim 5.5 \mu\text{mol L}^{-1}$) and silicate ($\sim 5 \mu\text{mol L}^{-1}$) 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 1 Feb or 2 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.
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 the estuarine regeneration was an additional source for those nutrients. They also estimated that there were net exports of those nutrients to the coastal ocean during the winter.

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 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 endmember 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. It is thus likely that an ammonium source is detected in the absence of a clear nitrate source.
Iron is a key element in controlling the growth of coastal phytoplankton, and we have shown that riverine iron is transported into the coastal ocean during high discharge events. The estimated river dFe concentration (120 nmol L\(^{-1}\)) is slightly lower than average dissolved iron concentrations measured by Colbert (2004) in rivers feeding into Tillamook Bay during the winter (~200 nmol L\(^{-1}\)), suggesting that ca. 40 % of riverine dFe is lost within the estuary. However, recent work by Chase (unpublished data) has shown that most of the iron present in the coastal rivers is associated with particles > 20 µm (i.e. iron concentrations approaching 10 \(\mu\)mol L\(^{-1}\)), which were not measured in our study. Thus, despite some loss of iron within the estuary, the flux of both particulate (incl. flocculated material) and dissolved Fe to the coastal ocean is still large. Furthermore, loss of only ca. 40% of riverine dFe within the estuary contrasts with studies from other lower flow estuaries that have shown > 90 % of riverine iron is lost in the estuary through flocculation and sedimentation (e.g. Boyle et al. 1977; Sholkovitz et al. 1978). This relatively small loss of iron can likely be attributed to the quick passage of river water through the estuaries during flood events; i.e. river water has a low (< 1 d) residence time in the estuaries. These large iron supplies could presumably have an immediate impact on the winter/early spring phytoplankton community.

These iron inputs may also affect summertime (upwelling) production in the system as well. Studies off central and northern California have shown that during the upwelling season, phytoplankton growth and nutrient drawdown can be severely limited due to iron limitation (Hutchins et al. 1998; Bruland et al. 2001). Off Oregon however, nitrate (ca. 20-30 \(\mu\)mol L\(^{-1}\)) is frequently drawn down to non-detectable levels by large phytoplankton blooms (i.e. > 10 \(\mu\)g L\(^{-1}\) chlorophyll \(a\)) that develop during upwelling events (Small and Menzies 1981; Corwith and Wheeler 2002; Wetz et al. 2003; Hales et al. in press), and intensive surveys of iron
concentrations suggest that there is ample iron to support phytoplankton requirements and the complete nitrate drawdown (Chase et al. 2002; Chase et al. in press). Most of the iron that supports phytoplankton growth in upwelling systems comes from upwelled water that has been in contact with the bottom boundary layer or continental shelf sediments (Johnson et al. 1999; Chase et al. 2002; Chase et al. in press). However, the source of iron to the continental shelf sediments remains elusive, as rivers discharge relatively little iron to the coastal ocean during the upwelling season and aerosol input is minimal (Duce 1991).

We suggest that off Oregon, the $dFe$ supplied by Coast Range rivers during the winter could be a major iron 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 $4.2-7.8 \times 10^6$ mol winter$^{-1}$. If this iron were to settle to the nearshore sediments upon entering the coastal ocean, downwelling conditions and more specifically the presence of a downwelling front, may prevent it 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 (Hales et al. in press; Perlin et al. 2004), the iron will become available to surface phytoplankton communities.

Another important constituent of the river water is organic material. High TOC concentrations (ca. 77 to 89 µmol L$^{-1}$) were found in the core of the river plume on 1 Feb. This material consisted of ~19 % POC and ~81 % DOC and had an average molar C:N ratio of ca. 19.4, indicative of a terrestrial source. Our estimated zero-salinity river water TOC concentration (175-210 µmol L$^{-1}$) appears to be representative of most of Oregon’s Coast Range rivers, based on bi-monthly sampling by the Oregon Department of Environmental Quality (Pacific Northwest Water Quality Exchange; http://deq12.deq.state.or.us/pnwwqx). If we
multiply that estimate by the annual wintertime discharge rate for all of the rivers (4.00 x 10^{10} m^3 winter^{-1}), we get a mean wintertime TOC input to the coastal ocean of approximately 1.0 x 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 x 10^{11} g TOC year^{-1}. Thus, despite their small size and short discharge period, Oregon’s Coast Range rivers can increase the total annual river input of TOC by 15.5-18.5%. If this material is labile, it has the potential to serve as a supplement to the coastal microbial food web and could alter system metabolism. Alternatively, if the material is refractory and is ultimately transported to deeper water, then it (the riverine TOC) 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, 2005), although the transport mechanism itself was not determined. Given the general lack of cross-shelf transport in the winter, we suggest that the TOC may accumulate over the shelf during downwelling conditions. Upon return to upwelling conditions, some of the material may be transported offshelf through mixing to deeper waters and advection. However, Hales et al. (submitted) recently determined that transport through the bottom boundary layer is the dominant mechanism for offshelf export of sedimented upwelling phytoplankton bloom carbon, and this could presumably be the primary mechanism for export of the river carbon, especially the POC and flocculated DOC components.

CONCLUSIONS
Small mountainous rivers influence the physical structure and biogeochemistry of coastal waters off Oregon on short time scales (days to weeks) following heavy precipitation and discharge events that occur during the winter. Input of freshwater leads to buoyant surface waters and increased stratification. Macronutrient and dFe inputs elevate concentrations in coastal surface waters, and if retained over the shelf, the dFe inputs may be important for summertime (upwelling) production in the system. 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. Further work is clearly needed to characterize wintertime ecosystem dynamics in these types of systems, as they are important in global C, N, and P cycles. Of immediate need are studies to determine the response of marine microorganisms to the riverine nutrient and carbon supplies, and on a broader time scale, 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).

LITERATURE CITED


Callaway, R.J., and D.T. Specht. 1982. Dissolved silicon in the Yaquina Estuary, Oregon,


Table 1. Model II geometric means regression statistics for nutrients, TOC, and dFe vs. salinity on 1-Feb. 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 psu). A more conservative estimate for the error associated with the Y-intercept is the difference the between the < 30 psu Y-intercept and the Y-intercept from the entire observed salinity range (± 11-28%).

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>All data</th>
<th>Slope</th>
<th>Y-int (± 95% conf. limit)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_3^-$ (µmol L$^{-1}$)</td>
<td>All data</td>
<td>-1.14</td>
<td>42.51 (± 0.10)</td>
<td>26794</td>
</tr>
<tr>
<td></td>
<td>&lt; 30 psu</td>
<td>-1.47</td>
<td>51.71 (± 0.06)</td>
<td>4672</td>
</tr>
<tr>
<td>Si(OH)$_4$ (µmol L$^{-1}$)</td>
<td>All data</td>
<td>-5.93</td>
<td>196.98 (± 0.22)</td>
<td>26794</td>
</tr>
<tr>
<td></td>
<td>&lt; 30 psu</td>
<td>-5.03</td>
<td>171.30 (± 0.06)</td>
<td>4672</td>
</tr>
<tr>
<td>PO$_4^{3-}$ (µmol L$^{-1}$)</td>
<td>All data</td>
<td>-0.15</td>
<td>5.48 (± 0.02)</td>
<td>26794</td>
</tr>
<tr>
<td></td>
<td>&lt; 30 psu</td>
<td>-0.13</td>
<td>4.89 (± 0.06)</td>
<td>4672</td>
</tr>
<tr>
<td>NH$_4^+$ (µmol L$^{-1}$)</td>
<td>All data</td>
<td>-0.25</td>
<td>8.20 (± 0.02)</td>
<td>26794</td>
</tr>
<tr>
<td></td>
<td>&lt; 30 psu</td>
<td>-0.33</td>
<td>10.52 (± 0.06)</td>
<td>4672</td>
</tr>
<tr>
<td>TOC (µmol L$^{-1}$)</td>
<td>All data</td>
<td>4.37</td>
<td>209.80 (± 41.80)</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>&lt; 30 psu</td>
<td>3.25</td>
<td>175.36 (± 42.92)</td>
<td>6</td>
</tr>
<tr>
<td>dFe (nmol L$^{-1}$)</td>
<td>&lt; 29.5 psu</td>
<td>-6.31</td>
<td>119.99 (± 25.01)</td>
<td>8</td>
</tr>
</tbody>
</table>
FIGURE LEGENDS

Figure 1. Location of study site off Cascade Head, just north of Lincoln City, OR.

Figure 2. Top panel- Wind velocity and direction at the mid-shelf buoy in late January/early February 2003. Lines pointed up are for northward (i.e. downwelling favorable) winds and lines pointed down are for southward (i.e. upwelling favorable) winds. Bottom panel- Alongshore current velocity measured at inner shelf mooring (45.00 N, 124.07 W). Vertical dashed lines indicate sampling dates from this study (from left to right- 1 Feb, 2 Feb, and 5 Feb respectively).

Figure 3. Across shelf salinity distributions (colors) and isopycnals (solid lines) on 1 Feb (top), 2 Feb (middle), and 5 Feb (bottom). Note that due to 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 psu, see Figs. 5,6) is not indicated on this figure.

Figure 4. Daily river discharge measured at the USGS station on the lower Siletz River (station 14305500). Data were obtained from the USGS website (http://waterdata.usgs.gov).

Figure 5. Surface salinity on 1 Feb (black line), 2 Feb (blue line), and 5 Feb (green line).

Figure 6. Temperature vs. salinity characteristics of surface water on 1 Feb (diamonds), 2 Feb (squares), 5 Feb (triangles), and from late January CTD casts (crosses).

Figure 7. Distributions of nitrate (A), phosphate (B), silicate (C), and ammonium (D) in surface waters on 1 Feb (black line), 2 Feb (blue line), and 5 Feb (green line).

Figure 8. Distributions of TOC (A) in surface waters on 1 Feb (diamonds), 2 Feb (squares), and 5 Feb (triangles), and distribution of dFe (B) on 1 Feb.

Figure 9. Model II geometric means regression of nitrate (A), phosphate (B), silicate (C), ammonium (D), TOC (E), and dFe (F) vs. salinity on 1 Feb. Regressions performed using all data are indicated in red and regressions performed using only data at salinities <30 psu (or < 29.5 psu for dFe) are indicated in blue.
Figure 1

Wetz et al.

Newport, OR

Cascade Head

Newport, OR
Figure 2

Velocity (m s\(^{-1}\))

Day of Year (2003)
Wetz et al.

Figure 3

Depletion (m)

Salinity (psu)

1-Feb

2-Feb

5-Feb

Longitude

Wetz et al.

Figure 3
Daily Mean Stream Flow (m$^3$ s$^{-1}$)

Date

19-Jan 21-Jan 23-Jan 25-Jan 27-Jan 29-Jan 31-Jan 2-Feb 4-Feb 6-Feb
Figure 5

Salinity (psu)

Longitude

1 Feb
2 Feb
5 Feb
Figure 6

Salinity (psu)

Temperature (°Celsius)

River plume core water

Offshore, non-river influenced water

Sub-surface water

1-Feb

2-Feb

5-Feb

Pump Stations

Wetz et al.

Figure 6
Wetz et al
Figure 7