



Pergamon

Progress in Oceanography 53 (2002) 369–387

**Progress in
Oceanography**

www.elsevier.com/locate/pocean

Organic carbon and nitrogen in the northern California current system: comparison of offshore, river plume, and coastally upwelled waters

J.K. Hill ¹, P.A. Wheeler *

College of Oceanic and Atmospheric Sciences, Ocean Admin Building 104, Oregon State University, Corvallis, OR 97331, USA

Abstract

During the first year of the Northeast Pacific GLOBEC program we examined the spatial distributions of dissolved and particulate organic carbon and nitrogen in the surface waters off the Oregon and Washington coasts of North America. Eleven east–west transects were sampled from nearshore waters to 190 km offshore. Hydrographic data and the distribution of inorganic nutrients were used to characterize three distinct water sources: oligotrophic offshore water, the Columbia River plume, and the coastal upwelling region inshore of the California Current. Warm, high salinity offshore water had very low levels of inorganic nutrients, particulate organic carbon (POC) and dissolved organic carbon (DOC). Warm, low salinity water in the Columbia River plume was relatively low in nitrate, but showed a strong negative correlation between salinity and silicate. The river plume water had the highest levels of total organic carbon (TOC) (up to 180 μM) and DOC (up to 150 μM) observed anywhere in the sampling area. Cold, high salinity coastal waters had high nutrient levels, moderate to high levels of POC and particulate organic nitrogen (PON), and low to moderate levels of DOC and dissolved organic nitrogen (DON). Each of these regions has characteristic C:N ratios for particulate and dissolved organic material. The results are compared to concentrations and partitioning of particulate and dissolved organic carbon and nitrogen in other regions of the North Pacific and North Atlantic Oceans. © 2002 Elsevier Science Ltd. All rights reserved

Contents

1. Introduction	370
2. Methods	371
2.1. Study areas	371
2.2. Hydrographic data	371
2.3. Sample collection	371
2.4. Chlorophyll	372

* Corresponding author. Tel.: +1-541-737-0558; fax: +1-541-737-2064.

E-mail address: pwheeler@oce.orst.edu (P.A. Wheeler).

¹ Present address: International School of Tanganyika, Dar es Salaam, Tanzania

2.5.	Particulate organic carbon and nitrogen	373
2.6.	Inorganic nutrients	373
2.7.	Total nitrogen	373
2.8.	Total organic carbon	374
2.9.	Dissolved organic nitrogen	374
2.10.	Dissolved organic carbon	374
3.	Results	375
3.1.	Hydrography and inorganic nutrients of the spatial survey	375
3.2.	Chlorophyll and particulate organic carbon and nitrogen for the spatial survey	377
3.3.	Total organic carbon and nitrogen for the spatial survey	377
3.4.	Dissolved organic carbon and nitrogen for the spatial survey	378
3.5.	Time series at the coastal station (NH-5)	380
3.6.	Excess POC, DOC, PON and DON production during the upwelling period	381
4.	Discussion	382
4.1.	Oceanic water in the subarctic/transition domain of the northeast Pacific	383
4.2.	Influence of the Columbia River	383
4.3.	Influence of coastal upwelling	385
4.4.	Effects of El Niño and other climate variations	385
4.5.	Conclusions	386

1. Introduction

In marine systems most dissolved organic carbon is ultimately derived from phytoplankton and released directly or indirectly into seawater. The labile and semilabile forms of dissolved organic carbon and nitrogen are essential sources of energy and nutrient for heterotrophic bacteria and protists. Over the last decade, it has become clear that although the cycling of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) are important, these key components of the carbon and nitrogen cycles in the upper layers of the water column often remain unmeasured (Carlson, Ducklow, & Michaels, 1994; Williams, 1995; Peltzer & Hayward, 1996). In coastal systems, terrestrially derived organic carbon is also released by river runoff (Maybeck, 1982). This terrestrially derived carbon differs both chemically and nutritionally from marine sources (Benner, 1998; Benner, Pakulski, McCarthy, Hedges, & Hatcher, 1992).

The distribution of organic material, especially dissolved organic matter (DOM) in the waters off the Oregon coast has received little attention prior to this study. Our goal has been to describe its distribution in both space and time and to begin to look at possible correlations between organic matter, especially DOM concentrations, and other biological, chemical, and physical properties. To investigate these variations, we conducted a wide spatial survey over a period of around two weeks during July 1997, which focused on distribution patterns in the surface waters off the coasts of southern Washington and Oregon.

The general circulation in the northeast Pacific Ocean is described by Hickey (1989). The North Pacific Current carries surface water across the North Pacific towards the Washington coast. Summer winds from the north drive the California Current, which flows southward along the Oregon and California coastline. The Columbia River releases significant amounts of freshwater into nearshore waters off Oregon. This freshwater is observable as a surface lens of low-salinity water that is carried further offshore and southward during the upwelling season (Landry, 1989). The month of July occurs at the midpoint of the historical upwelling season (May–October) along the Oregon and Washington coasts. Upwelling during this time period is sporadic, occurring in ‘events’ lasting from a few days to a few weeks (Huyer, 1976; Small & Menzies, 1981).

Because of the overall complexity of the oceanographic system in this region, it was beneficial to examine a large area in order to distinguish the major domains with different sources of surface water. Three regions were of specific interest, the offshore oligotrophic region, the Columbia River plume, and the region of coastal upwelling. Another part of our work included a year-long time series that focused on seasonal changes in the distribution of organic matter in the surface water at a site near Newport, Oregon.

2. Methods

Sampling for the spatial survey took place between 9 and 21 July 1997. Samples were collected in conjunction with a National Marine Fisheries Service (NMFS) project led by Robert Emmett using the NMFS research vessel *Sea Otter*. Physical properties of the upper water column were measured by NMFS and a subset of the hydrographic data is presented here. NMFS also collected zooplankton and chlorophyll samples. Most of the chlorophyll data presented were analyzed and made available by NMFS.

2.1. Study areas

Samples for the spatial survey were collected along eleven transects extending westward from the coast (Fig. 1). The transects varied in length, most of them extending from the coast to approximately 190 km offshore. The northernmost transect was near Grays Harbor, Washington (47°N) and the southernmost was near Cape Blanco, Oregon (43°N), giving a north–south range of 450 km. We started collecting samples from the northernmost sites and proceeded south as each transect was completed. Samples were collected as soon as we reached each site, regardless of the hour.

Our study site for the time series was NH-05 (44.65°N, 124.18°W) with a water depth of 58 m, located 9 km offshore of Newport, Oregon. We visited this station from 27 June 1997 to 6 July 1998 using the R/V *Sacajawea*, a small vessel maintained by the Hatfield Marine Science Center in Newport, OR and four cruises aboard the R/V *Wecoma*. For the trips using the R/V *Sacajawea*, samples were collected between 0800 and 1100 and were processed in the shore-based laboratory within a few hours.

2.2. Hydrographic data

Physical data for the spatial survey were collected using a pumped SeaBird Model 19 CTD. Collection and processing of the physical data was completed by NMFS. A subset of the physical data is presented subsequently. Sea surface temperature data were also collected in situ using a standard mercury thermometer. CTD data for the transect at 44.6°N were lost because of an equipment problem. Another cruise, led by Dr. Jack Barth of OSU, collected CTD data from the same general area later in the month, 28–30 July (R/V *Wecoma*, cruise number W9707b, data unpublished). W9707b data have been used for our transect at 44.6°N. Physical data for the time series sampling were collected concurrently with water sampling using a SeaBird Model 19 CTD aboard the *Sacajawea* and using a SeaBird 9/11-plus CTD system aboard the *Wecoma*.

2.3. Sample collection

Water samples were collected from 3 m below the surface using a Niskin bottle. The water was immediately filtered through 335 μm Nitex screen to remove debris and zooplankton. The water was then stored in 1-l polycarbonate bottles from which various subsamples were collected. All subsamples were processed and stored within 6 h of collection, and most were processed within 1 h. Samples waiting to be processed

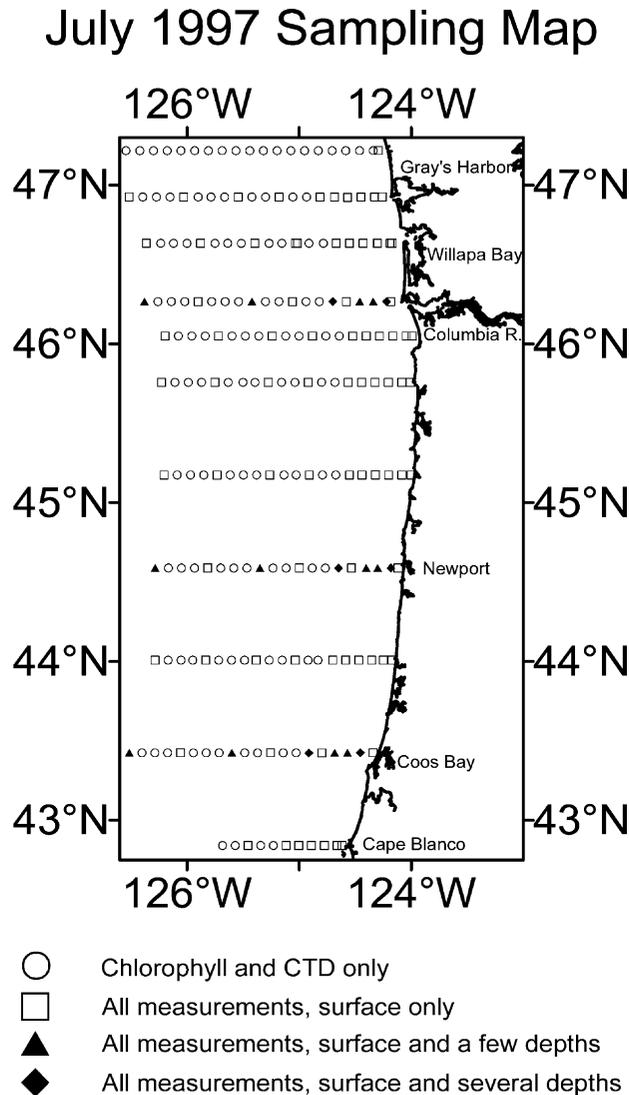


Fig. 1. Map showing sampling sites for the July 1997 spatial survey.

were kept cold in covered coolers. Subsample measurement from the screened water included chlorophyll, total organic carbon, particulate organic carbon/nitrogen, total nitrogen, and nutrients.

For the time series, we collected samples from just below the surface down to 50 m using either 1.8-l Niskin bottles on a steel cable (on the *Sacajawea* cruises) or 5-l Niskin bottles on a 12 bottle rosette (on the *Wecoma* cruises). Water samples were filtered through 335 μm Nitex, stored in 1-l polycarbonate or HDPE bottles in the dark at ambient temperatures before being filtered.

2.4. Chlorophyll

The chlorophyll samples for the spatial survey of surface water were collected and analyzed by NMFS. One 100 ml sample from each station was filtered on pre-combusted 25 mm WhatmanTM GF/F filters using

vacuum filtration. The filters were then stored in plastic centrifuge tubes and kept frozen, until processed on shore after each cruise. On shore, pigments were extracted in 90% HPLC grade acetone in DIW for at least 12 h in a dark freezer before measuring sample fluorescence. Chlorophyll-*a* was calculated from these fluorescence measurements.

Samples for the time series were processed using a method very similar to that described previously, with just two minor differences. First, duplicate samples were collected instead of single samples and secondly the filters were stored in glass Vacutainers™ and were transferred to plastic centrifuge tubes just prior to the extraction step. Fluorescence was measured using Turner Designs™ Model 10-AU fluorometers. The instruments were calibrated within 2 months of the study using Sigma® chlorophyll-*a* powdered standard dissolved in HPLC grade acetone. The calibration was confirmed daily using a preparation of Sigma™ coproporphyrin in HPLC grade acetone and an acetone blank.

2.5. Particulate organic carbon and nitrogen

Particulate material was also collected on 25 mm GF/F filters using vacuum filtration. Five hundred milliliters of seawater was filtered for each station. The filters were frozen immediately after filtration. After fuming with sulfuric acid (to remove calcium carbonate) and drying, the filters were placed in tin boats and analyzed using a Carlo Erba™ CNS analyzer to provide particulate organic carbon (POC) and particulate organic nitrogen (PON) concentrations. Boat blanks, filter blanks and acetonitrile standards were run with each batch of samples.

Recent experiments have questioned the accuracy of POC measurements because of possible adsorption of DOC on filters (Karl, Hebel, Bjorkman, & Letelier, 1998) and the use of small sample volumes (Moran, Charette, Pike, & Wicklund, 1999). For PON, the filter blanks ($1.61 \pm 0.38 \mu\text{g N}$, mean \pm SD) were indistinguishable from empty boat blanks. For POC, the filter blanks ($5.47 \pm 3.82 \mu\text{g C}$, mean \pm SD) were significantly higher than empty boat blanks and varied significantly between runs. Regression of C:N versus POC concentrations showed elevated values for C:N ratios for concentrations $\leq 20 \mu\text{M}$. We assumed that these elevated ratios were the result of absorption of DOC on the filters. An empirical correction of $15 \mu\text{g C}$ was applied to all the POC results as a 'filter adsorption blank'. For the sampling and analytical procedures used here, our detection limits were equivalent to $0.5 \mu\text{M PON}$ and $5\text{--}10 \mu\text{M POC}$ depending on the magnitude of the filter blank for each run. The mean coefficient of variation for replicate samples was $15 \pm 11\%$ for POC and $15 \pm 8\%$ for PON.

2.6. Inorganic nutrients

Nutrient samples were filtered through 25 mm GF/F filter using a syringe and Swinex filter holder. Duplicate samples of ~ 20 ml were stored in HDPE bottles and frozen. These samples were later analyzed for nitrate, nitrite, ammonium, silicate, and phosphate using standard colorimetric methods adapted for an autoanalyzer (Atlas, Hager, Gordon, & Park, 1971). Usually only one of the two samples was measured. The coefficient of variation for duplicates at low nutrient concentrations for our analyses are typically $< 1\%$ for nitrate, phosphate and silicate (Fleischbein, Hill, Huyer, Smith, & Wheeler, 1999) and at high concentrations were close to 2% (Corwith, 2000).

2.7. Total nitrogen

Total nitrogen (TN) samples were collected and measured in triplicate. Ten milliliters of seawater were transferred by pipette into 60 ml HDPE bottles. These samples were frozen until analysis. Organic nitrogen was converted to nitrate using a persulfate wet oxidation method (Libby & Wheeler, 1997; Wheeler, Wat-

lans & Hansing, 1997). Total nitrogen was measured using a single channel autoanalyzer. The mean coefficient of variation for triplicate measurements of 163 TN samples was $2.5 \pm 1.9\%$.

2.8. Total organic carbon

Triplicate total organic carbon (TOC) samples were collected in 8 ml borosilicate vials with Teflon cap liners. Each vial contained 5 ml seawater and was preserved by adding 50 μ l of 90% phosphoric acid. The samples were then stored at room temperature. Later these samples were analyzed using the High Temperature catalytic Combustion (HTC) method on a Shimadzu TOC-500 analyzer. Prior to analysis, the samples were sparged for 5 min using 0.1 grade (ultra-low CO₂) compressed air for the purpose of removing inorganic carbon.

The TOC analyzer was calibrated daily using a DIW blank and four concentrations of an acid potassium phthalate standard solution. A stock solution was kept refrigerated and diluted each day to make the working calibration standards. After the initial calibration, a deep water sample of known TOC concentration was used to test the accuracy of the calibration. Three subsamples of 60 μ l were taken from each of the samples and injected in sequence once the calibration was completed. Standards were injected after every six samples (18 subsample injections) to check for slope and baseline shifts. Using these calibration methods, we saw <1% variance between injections from the same sample vial and a variance of $4.9 \pm 4.4\%$ among triplicate sample vials. We did not use the results if the coefficient of variation was >10% for a set of replicates.

2.9. Dissolved organic nitrogen

DON was determined by subtracting our values for PON and dissolved inorganic nitrogen (DIN) from our TN values, as expressed in Eq. (1). The DIN includes nitrate, nitrite, and ammonium.

$$\text{DON} = \text{TN} - \text{PON} - \text{DIN} \quad (1)$$

The standard deviation for DON was determined by propagation of error (Bevington, 1969) using the measured standard deviation for TN and the estimated deviations for PON (coefficient of variation=15%) and DIN (coefficient of variation=1%). Most of the variance in the propagated error resulted from the standard deviation of the PON measurements.

2.10. Dissolved organic carbon

The concentration of DOC was determined by difference, using the TOC and POC measurements, as shown in Eq. (2).

$$\text{DOC} = \text{TOC} - \text{POC} \quad (2)$$

A more direct approach to the measurement of DOC is to filter the seawater to remove particulates and then to measure the organic carbon in the filtrate. However, filtration can result in cell breakage at elevated DOC values, and we have found that filtration greatly increases the variability of replicated DOC measurements. So we choose to measure TOC in triplicate and to calculate DOC by differences. This method gave us best precision on the TOC measurements and the estimated DOC measurements since it minimized the error of the largest of the two components. The largest variability in our calculated standard error was the precision of the POC measurement and in future we recommend that studies use triplicate POC values to improve further the precision of the DOC determinations.

3. Results

3.1. Hydrography and inorganic nutrients of the spatial survey

The region of coastal upwelling was clearly distinguished by cold temperatures (Fig. 2(a)) and elevated nitrate+nitrite and silicate (Fig. 2(c) and (d)). We use ranges of 9–12 °C in temperature and 32.0–33.5 in

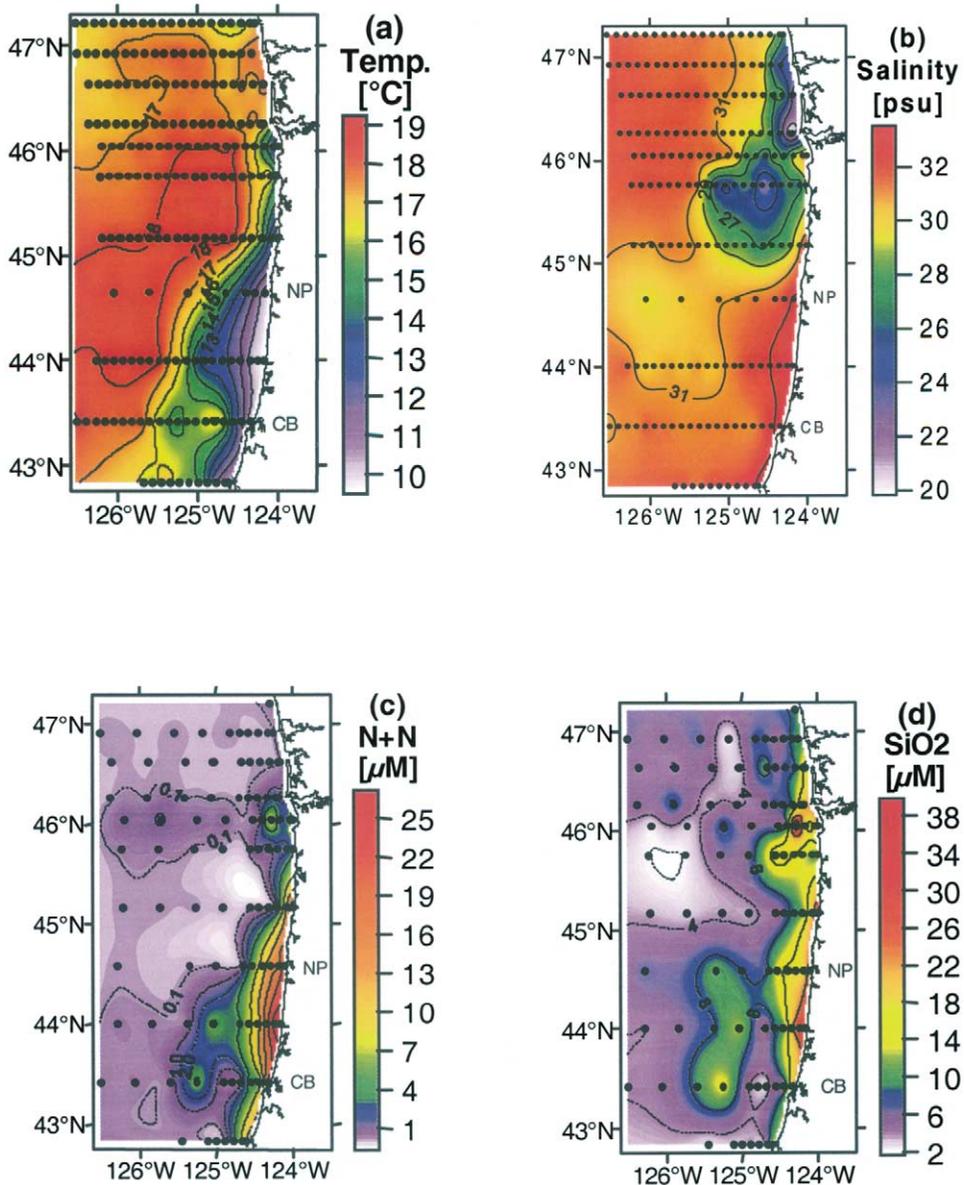


Fig. 2. Contour plots showing (a) temperature, (b) salinity, (c) nitrate+nitrite, and (d) silicate at 3 m depth during July 1997. Closed circles indicate the locations where samples were collected.

salinity (Fig. 3) as the delimiting features of the upwelled water end member in the comparisons reported subsequently.

The Columbia River plume was clearly delineated by the low salinity water that extended from the river mouth (46.3°N) to as far south as 44.7°N (Fig. 2(b)). The river plume extended about 100 km from shore between 46.3 and 45.0°N; further south it was further offshore and wider. We use ranges of 16–19 °C in temperature and 19.8–29.4 in salinity (Fig. 3) as the delimiting features of the river plume end member for the comparisons reported subsequently.

Offshore oceanic water was evident as warm, high salinity water containing low concentrations of nutrients from 47.3 to 46.3°N. It was delineated on its southern boundary by the edge of the river plume (Fig. 2(b)). We used ranges of 16–18 °C in temperature and 31.0–32.4 in salinity (Fig. 3) as the delimiting characteristics of the offshore oceanic water for the comparisons reported subsequently.

Of the inorganic nutrients measured (silicate, nitrate, nitrite and ammonium) silicate was the most useful as a tracer of both upwelled and river plume water. In the upwelled water, silicate was directly proportional to salinity (Fig. 4(a)), while in the river plume silicate was inversely correlated with salinity. Plots of nitrate versus silicate (Fig. 4(b)) showed an Si:N ratio of 1.2 in the upwelled water and a predicted depletion of silicate prior to nitrate. Conversely, in oceanic water and river plume water, nitrate was extremely low, while the lowest measured silicate concentrations were 2 μM (Fig. 4(b)).

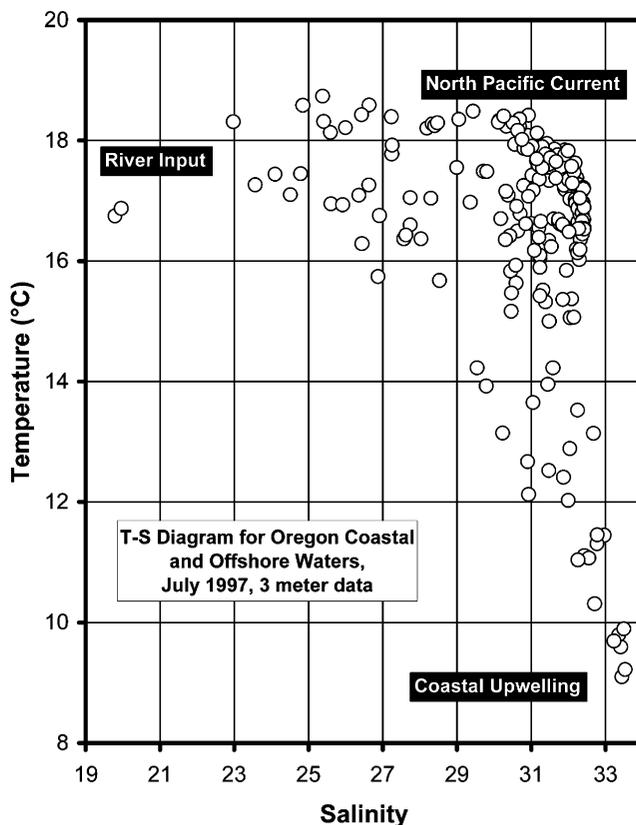


Fig. 3. T-S diagram for the July 1997 spatial survey, all samples from 3 m depth.

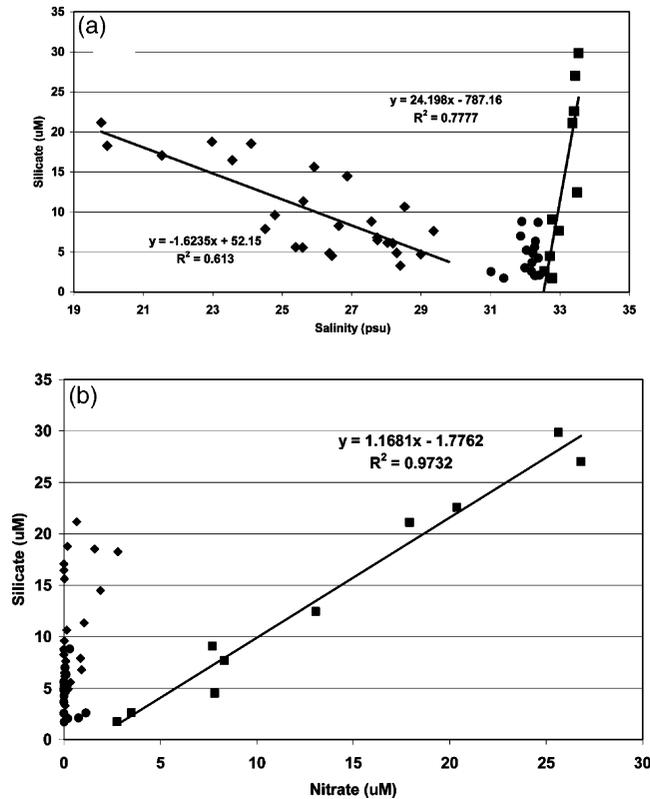


Fig. 4. Property–property plots for oceanic (circles), river plume (diamonds) and coastal upwelling (squares) end member stations. (a) Silicate versus salinity and (b) silicate versus nitrate.

3.2. Chlorophyll and particulate organic carbon and nitrogen for the spatial survey

Fig. 5 shows the surface distribution of Chlorophyll, TOC, POC and PON each of which was derived from direct measurements. Chlorophyll, POC and PON were generally distributed in similar patterns, i.e. high in a narrow coastal band and an extension offshore between 43 and 44°N. TOC on the other hand, showed highest concentrations within the river plume.

Plots of POC versus PON (Fig. 6) had slopes of 6.44 and 7.36 for upwelled and plume water, respectively. These slopes were close to the Redfield ratio, with river plume water being about 15% richer in carbon. Mean POC concentrations were about 3-fold greater in the river plume and coastal upwelled water (42.5 and 37.0 µM, respectively) compared with the oceanic water with a mean POC of 12.6 µM (Table 1). Oceanic water was low in both POC and PON (Fig. 6), and its C:N ratio was elevated (11.8, see Fig. 6).

3.3. Total organic carbon and nitrogen for the spatial survey

A summary of the total organic carbon and nitrogen data is presented in Table 1. TOC was high in both the river plume and coastal water (means of 144 and 140 µM, respectively) and lowest in oceanic water (mean=87 µM). Mean TON concentrations were also high and similar in both the river plume and coastal water (means of 9.4 and 10.6 µM, respectively) and lowest in oceanic water (mean=6.0 µM). The mean

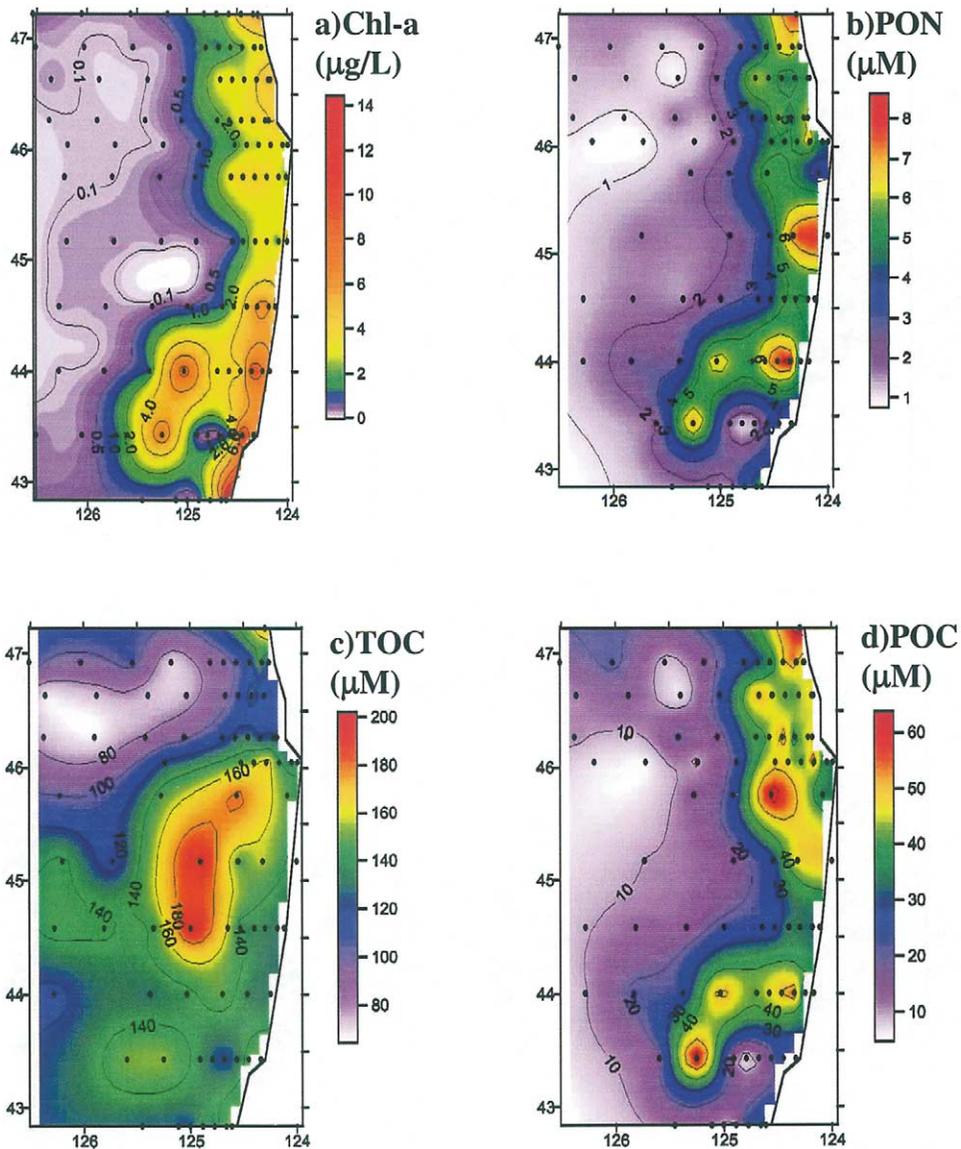


Fig. 5. Contour plots showing (a) chlorophyll, (b) particulate organic nitrogen, (c) total organic carbon, and (d) particulate organic carbon at 3 m depth during July 1997. Closed circles indicate the locations where samples were collected.

C:N ratios for TOC and TON was 13.5 in coastal upwelled water, while the river plume and oceanic water were richer in C with ratios of 17.8 and 17.3, respectively.

3.4. Dissolved organic carbon and nitrogen for the spatial survey

In all the three water types, DOC accounted for 70–85% of TOC and followed the same relative distribution as observed for TOC; being highest in the river plume and coastal water (101 and 105 μM , respectively) and lowest in oceanic water 74 μM (Table 1). DON showed a very different pattern. Highest

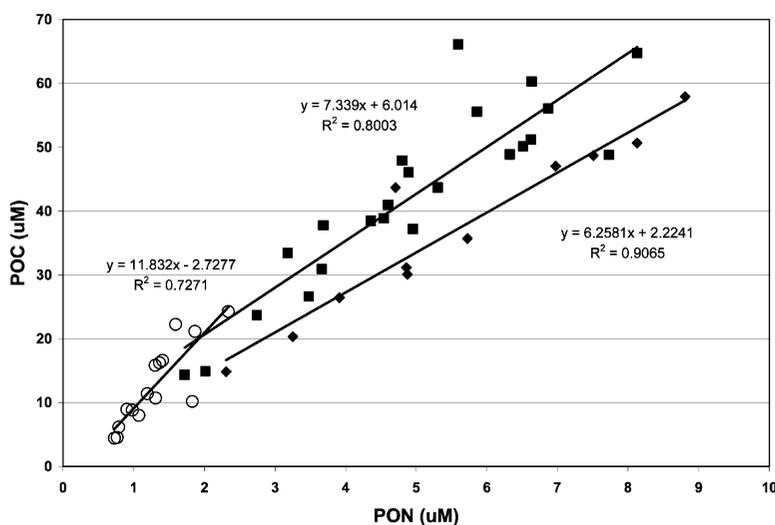


Fig. 6. Particulate organic carbon versus particulate organic nitrogen for oceanic (circles), river plume (diamonds) and coastal upwelling (squares) end member stations.

Table 1
Organic carbon and nitrogen (means and mean SD) in three water types of the northeast Pacific Ocean

Component		Subarctic transitional	River plume	Coastal upwelled
TOC (µM)	Mean	86.8	143.6	140.2
	SE (n)	4.7 (14)	4.7 (20)	4.8 (7)
	Mean SD	3.4	5.6	4.9
TON (µM)	Mean	6.01	9.37	10.6
	SE (n)	0.54 (14)	0.56 (20)	0.8 (8)
	Mean SD	(0.11)	(0.26)	(0.42)
TOC/TON	Mean	17.3	17.8	13.5
	SE (n)	2.0 (14)	1.3 (20)	1.1 (7)
	Mean SD			
POC (µM)	Mean	12.6	42.5	37.0
	SE (n)	1.4 (15)	2.4 (20)	3.9 (7)
	Mean SD	1.9	6.4	5.6
PON (µM)	Mean	1.30	4.97	5.55
	SE (n)	0.19 (15)	0.29 (23)	0.60 (11)
	Mean SD	0.19	0.74	0.83
POC/PON	Mean	9.38	8.64	6.69
	SE (n)	0.54 (15)	0.19 (23)	0.25 (11)
	Mean SD			
DOC (µM)	Mean	74.4	101	105
	SE (n)	5.3 (14)	5 (20)	7.1 (7)
	Mean SD	4.0	9.0	7.5
DON (µM)	Mean	4.72	4.78	6.94
	SE (n)	0.50 (14)	0.43 (20)	0.59 (6)
	Mean SD	0.29	0.79	0.85
DOC:DON	Mean	20.6	29.1	16.8
	SE (n)	3.0 (14)	3.6 (18)	0.6 (5)

concentrations were present in coastal water ($6.94 \mu\text{M}$) and lowest concentrations ($4.7 \mu\text{M}$) in oceanic and river plume water. The C:N ratio for dissolved organic material was high in oceanic and river plume water (21 and 29, respectively) but lower in coastal water (17).

3.5. Time series at the coastal station (NH-5)

Plots of temperature and Chl from the time series (Fig. 7(a)) showed two upwelling/relaxation events, decreases in temperature and increases in Chl, in the summer of 1997. This was followed by a major warming trend with surface water reaching temperatures of $18 \text{ }^\circ\text{C}$. Surface water temperatures decreased throughout the fall 1997, then remained at about $12 \text{ }^\circ\text{C}$ through the winter and spring (days 320–550, Fig. 7(a)). Plots of total, particulate, and dissolved organic carbon and nitrogen (Figs. 7(b) and 8) show similar trends with highest levels during the upwelling period and lowest levels during the winter and spring.

For a quantitative comparison over the time series, we have grouped the data into three periods; upwelling conditions (day 178–226), a warming period (day 233–252), and the winter and spring (day 307–465). Mean concentrations of TOC during the upwelling period were $149 \mu\text{M}$ and then decreased to $132 \mu\text{M}$ during the warming period and still further to $76 \mu\text{M}$ during the winter and spring (Table 2). TON levels showed less variation over the time series, and the decreasing TOC levels resulted in a change in the C:N ratio from 14 during the upwelling period to 8.5 during the winter and spring. Both POC and PON were

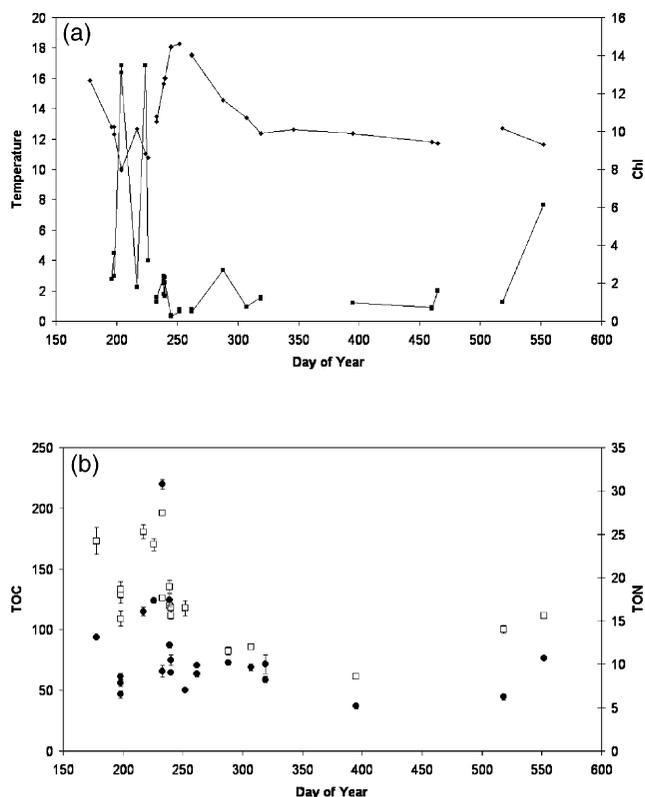


Fig. 7. Time series from 27 June 1997 to 6 July 1998 for temperature (filled diamonds), chlorophyll (filled squares), total organic carbon (open squares) and total organic nitrogen (filled circles) at NH-5, a station 10 km off Newport, Oregon. Day is day since 1 January 1997.

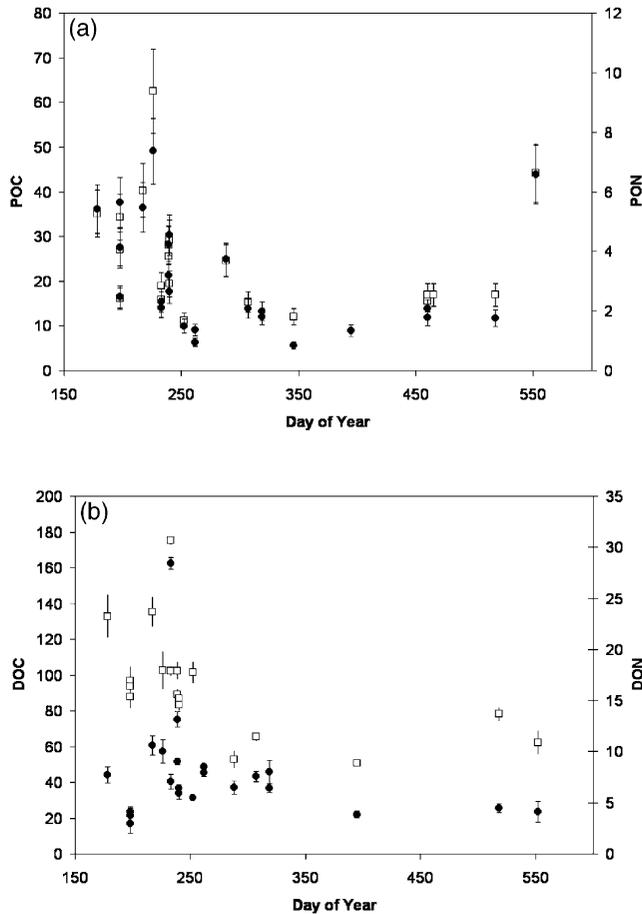


Fig. 8. (a) Time series from 27 June 1997 to 6 July 1998 for particulate organic carbon (open squares), particulate organic nitrogen (filled circles); and (b) Time series for dissolved organic carbon (open squares) and dissolved organic nitrogen (filled circles) at NH-5, a station 10 km off Newport, Oregon. Day is day since 1 January 1997.

highest during the upwelling period (36 and $5.1 \mu\text{M}$, respectively) and decreased by a factor of 2 through the warming period and winter/spring. The C:N ratio for particulate material in the surface water was relatively constant through the time series ranging from 6.9 to 7.5 (Table 2).

Mean concentrations of DOC during the upwelling and warming periods were similar (108 and $106 \mu\text{M}$, respectively). Afterwards DOC concentrations dropped by a factor of 2, to a mean of $56 \mu\text{M}$ during the winter and spring (Table 2). DON levels were variable and showed no distinct pattern, although high concentrations did occur during the upwelling period in 1997. The decrease in DOC, however, resulted in a major change in the C:N ratio for the dissolved organic pool with a mean ratio of 20 during the upwelling period and dropping to 8.4 for the winter/spring mean (Table 2).

3.6. Excess POC, DOC, PON and DON production during the upwelling period

In order to examine net production of organic material during the summer upwelling period, we used the concentrations of water collected from 50 m as an indicator of 'refractory' or deep water levels of organic carbon and nitrogen. These 50 m concentrations are similar to the low values observed during

Table 2

Organic carbon and nitrogen (means and mean SD) in time series sampling of surface water at NH-5 off Newport, OR

Component		Upwelling conditions	Warming period	Winter/spring	50 m water
TOC (μM)	Mean	149.1	132.3	76.5	86.3
	SE (n)	12.0 (6)	11.1 (7)	7.7 (3)	3.9 (8)
	Mean SD	7.0	3.4	1.2	2.8
TON (μM)	Mean	11.6	13.7	8.87	7.66
	SE (n)	1.9 (6)	3.1 (7)	0.67 (7)	0.84 (8)
	Mean SD	0.3	1.82	0.41	0.36
TOC/TON	Mean	13.8	11.1	8.47	11.43
	SE (n)	1.2 (6)	1.35 (7)	0.42 (2)	0.82 (7)
POC (μM)	Mean	35.9	21.2	16.9	15.2
	SE (n)	6.3 (6)	2.5 (7)	1.7 (6)	1.0 (8)
	Mean SD	5.4	3.1	2.5	2.3
PON (μM)	Mean	5.09	2.93	1.79	1.62
	SE (n)	0.67 (6)	0.42 (7)	0.26 (10)	0.10 (8)
	Mean SD	0.76	0.44	0.27	0.24
POC/PON	Mean	6.91	7.49	7.00	9.53
	SE (n)	0.36 (6)	0.34 (7)	0.41 (2)	0.56 (8)
DOC (μM)	Mean	108.2	105.9	56.3	71.0
	SE (n)	8.4 (6)	12.0 (7)	4.6 (3)	3.9 (8)
	Mean SD	9.1	3.9	2.5	3.9
DON (μM)	Mean	6.52	10.79	6.98	5.98
	SE (n)	1.38 (6)	3.10 (7)	0.60 (7)	0.87 (7)
	Mean SD	0.85	0.50	0.52	0.44
DOC/DON	Mean	19.9	12.0	8.38	12.37
	SE (n)	3.1 (6)	1.6 (7)	0.6 (2)	1.21 (7)

winter and spring in the surface water (Table 2). Subtraction of the 50 m values from the mean values observed in surface waters during the upwelling period (149–86 μM), gave net excess production of TOC of 63 μM . POC production (36–15 = 21 μM) accounted for 36% of this net production and DOC production (108–71 = 37 μM) accounted for 63% of the net carbon excess produced during the upwelling period. Net production of TON was 4 μM (12–8 μM), of which 86% (3.5 μM) was PON and 14% (0.5 μM) was DON.

4. Discussion

One of the primary purposes of this research was to determine the levels of organic carbon and nitrogen in the main water domains in the northeast Pacific Ocean off the coast of Oregon. The complex physical dynamics of the California Current System were most recently studied as part of the Coastal Transition Zone Project (Brink and Cowles, 1991). The main flow in this system is the southward flowing California Current, the core of which may be the same as the baroclinic coastal jet (Huyer et al., 1991). The biological effect of this jet is to define a region next to the coast that contains much of the nutrient rich water (Strub, Kosro, & Huyer, 1991). Our broad spatial survey in July 1997 allowed us to identify the three major sources of water with distinct hydrochemical and organic signatures. The present paper is the first published work reporting simultaneous measurement of total organic carbon and nitrogen in this oceanographic system. This information allows delineation of regions where particular physical and biological processes may

interact in the production, utilization and redistribution of organic carbon and nitrogen in an eastern boundary current and wind-driven upwelling system.

4.1. Oceanic water in the subarctic/transition domain of the northeast Pacific

The offshore water of the northeast Pacific is derived from the Subarctic Current as it bifurcates to flow either northward as the Alaska Coastal Current or southward as the California Current. There are large nitrate gradients in the eastward flowing water and during the summer nitrate is usually depleted east of 140°W (Anderson, Parsons, & Stephens, 1969; Whitney & Freeland, 1999). The oceanic water sampled in this study north of 45°N originates from the subarctic and the ‘transition domain’ between the subarctic boundary at about 42°N and the Subarctic Current System at about 48°N (Favorite, Dodimead, & Nasa, 1976). This oceanic water had low concentrations of POC, PON and DOC compared with the river plume and coastal water sampled in this study, but much higher levels of POC and PON than subtropical water off Hawaii (Table 3). In north Pacific subtropical water, POC and PON are minor components of the total organic carbon and nitrogen pools (4 and 7%), respectively (Table 3). In the subarctic/transition domain, POC and PON both appear to be 5-fold higher than in subtropical water (Table 3). The same magnitude of difference was found by Pak, Kiefer and Kitchen (1988) in a meridional comparison of transmittance and fluorescence in surface waters of the Pacific from 23 to 57°N along 155°W. Their meridional variation in fluorescence ranged from 0.5 v in the subtropical water to levels of 2–4 v north of the subarctic boundary (42°N). Similarly, the beam attenuation coefficient increased from a low of 50 in subtropical waters to levels in excess of 250 north of the subarctic boundary (42°N). DOC is about 20% higher and DON 10%

Table 3
Regional comparison of the partitioning of organic carbon and nitrogen

Region	Latitude	POC	PON	C:N	DOC	DON	C:N	POC/ TOC	PON/ TON	Reference
Pacific Oceanic										
Subtropical	23N	2.39	0.31	7.71	62	4.35	14.2	0.04	0.07	HOTS data
Transition Domain	42N		2.97							Shiomoto et al., 1990
Subarctic	45–47N	12.60	1.30	9.40	74	4.72	20.6	0.14	0.22	This study
	45–50N	14.45	1.79	8.16						POC, Maldonado and Price, 1999; PON, Shiomoto et al., 1990
	50 N	17.30	1.75	9.77						POC, Maldonado and Price, 1999; PON, Wheeler, 1993
	50 N	10.50	1.75	6.00						POC, Maldonado & Price, 1999; PON, Wheeler, 1993
Coastal Oregon Atlantic Oceanic										
	43–47 N	37.00	5.55	6.69	105	6.94	16.8	0.26	0.50	This study
	32 N	1.96	0.29	6.76	101	5.95	17.2	0.02	0.05	BATS data
	35 N	5.00	1.00	5.00	65	6.00	10.8	0.02	0.05	Kahler and Koeve, 2001
	40 N	10.00	2.00	5.00	63	5.90	10.7	0.07	0.14	Kahler and Koeve, 2001
	45 N	20.00	3.00	6.67	60	5.80	10.3	0.14	0.25	Kahler and Koeve, 2001
	50 N	35.00	5.00	7.00	58	5.70	10.2	0.25	0.34	Kahler and Koeve, 2001
Coastal Spain										
	42 N	28.00	4.00	6.60	100	6.80	15.0	0.22	0.45	Doval et al., 1997

higher in the transition domain compared with the subtropical water in the Pacific (Table 3). In the subtropical waters only 4–7% of TOC and TON is present in the particulate phase, whereas in the subarctic/transition zone 14–22% of the TOC and TON is present as particles (Table 3).

Kähler and Koeve (2001) and Körtzinger, Koeve, Kähler and Mintrop (2001) have recently examined the distribution of dissolved and particulate organic carbon and nitrogen in the northeast Atlantic Ocean from 33 to 60°N along the 20°W meridian and their results are included in Table 3. POC increased from 5 to 35 μM along the transect, while DOC decreased only slightly from 65 to 58 μM (Kähler & Koeve, 2001). In the northeast Atlantic, POC accounted for <7% of TOC in the subtropical water and 25% of TOC at 50°N (Kähler & Koeve, 2001). Similar south to north differences were seen for PON and DON, and these resulted in PN accounting for 14% of TON in the subtropical Atlantic and 34% of TON in temperate water at 50°N. As argued by Körtzinger et al. (2001), the partitioning and cycling of organic carbon and nitrogen vary across meridional sections that are characterized by trophic gradients in nutrient supply. How these differences affect the dynamics in the California Current system off Oregon remains to be determined. Our results indicate that the oceanic surface water in the subarctic/transition domain contained higher relative amounts of both POC and PON than subtropical Pacific water and also had higher C:N ratios in both the particulate and dissolved phases. The higher C:N ratios may be part of a seasonal variation that has not been examined yet in the oceanic northeast Pacific.

4.2. *Influence of the Columbia River*

Riverine inputs are also expected to play a large role in the DOC distribution in the northeast Pacific. The large plume of TOC extending from the Columbia River mouth, suggests that the Columbia River is exporting a large amount of organic carbon into the North Pacific Ocean. Dahm, Gregory and Park (1981) reported TOC values in the Columbia River for 1973–1974 as 130 μM in the winter and between 200 and 300 μM in the summer. The inverse relationship we observed between salinity and silicate concentrations for Columbia River source water is evidence of conservative mixing. No significant correlations were observed however, between salinity and nitrate, versus TOC, POC or DOC concentrations in the river plume. The Columbia River has a high (about 9) winter silicate to nitrate ratio (Dahm et al., 1981) compared to the ratio of 1.2 that we observed in the upwelled water. Apparently not only is the nitrate more rapidly depleted in the plume than is silicate, but also the river plume can serve as a substantial source of silicate to offshore water. The absence of a correlation between organic carbon and salinity may reflect transformations between the particulate and dissolved phases of organic carbon. Klinkhammer, Chin, Wilson, Rudnicki and German (1997) also report non-conservative behavior of turbidity, dissolved manganese and chlorophyll in the river plume, and attributed this to a chemical front near the plume boundary where reduction of manganese oxides and oxidation of humic ligands take place. Notwithstanding chemical transformation, the observed C:N ratios and high load of carbon clearly distinguish the river plume organic material from the marine material produced in the coastal upwelling band.

4.3. *Influence of coastal upwelling*

From the time series data presented here, it is clear that upwelling strongly influences the distribution of Chl, POC and PON. The analysis of 'excess net production' is a conservative estimate of the amount of particulate and dissolved carbon and nitrogen that is produced in the upwelling region. It is quite striking that in the Oregon coastal region, significant percentages of organic carbon (36%) and organic nitrogen (86%) accumulate as particulate organic matter. In a similar time series study for a temperate embayment affected by coastal upwelling (Doval, Alvarez-Salgado, & Perez, 1997), 60% of the excess organic carbon and 70% of the excess organic nitrogen formed were in the particulate phase. These results for coastal upwelling systems contrast with the results for subtropical Pacific and equatorial Pacific water where the

dissolved pools are a more important component of the ‘excess’ or semilabile pool of organic carbon. However, the coastal systems are similar to the Antarctic systems where more carbon production appears as POC than in the DOC pools (Carlson, Ducklow, Hansell, & Smith, 1998).

4.4. *Effects of El Niño and other climate variations*

By September 1997, the downward sloping isotherms and isohalines off Oregon clearly indicated that the 1997–1998 El Niño had reached the site of our times series sampling (Huyer, Smith, & Fleischbein, 2002). Additionally, in November 1997 and February 1998, there was a much stronger than usual poleward flow inshore of 100 km that extended to depths >200 m (Huyer et al., 2002; Kosro et al., 2001). As a consequence, our sampling during the winter and spring may have reflected characteristics of water from the south that is not usually transported as far north as Oregon. This appeared to be the case for unusually low N:P ratios in water collected from 100 m depth (Corwith, 2000). The California Undercurrent moves to the surface in the winter and spring (Hickey, 1989) and the surface water data presented here for that for winter and spring may reflect water conditions from further south that are not usually seen off Oregon. Sampling is being continued through the NEP GLOBEC Long Term Observation Program to address this question with respect to the seasonal variation in the distributions of particulate and dissolved organic carbon and nitrogen.

Whitney and Freeland (1999) recently reviewed data collected over the past 42 years in the subarctic Pacific at Ocean Station P. Major trends towards warmer and less saline surface waters are apparent in the 1990s compared with the 1970s. These changes were accompanied by lower winter nitrate and silicate levels and less macronutrient utilization in the 1990s compared with the 1970s. The regional comparisons we present in Table 3 are from data collected in the 1990s. However, the magnitudes of seasonal, interannual, and ‘regime shift’ variations remain to be determined. For reasons outlined by Kortzinger et al. (2001) the partitioning of organic material between dissolved and particulate phases should be considered in ecological evaluations of new and export production across the major trophic gradients in the northeast Pacific.

4.5. *Conclusions*

The data set resulting from our wide spatial survey is the first study of the distribution of organic carbon and nitrogen in the coastal and oceanic waters off the coast of Oregon (Hill, 1999). While precision and spatial resolution could be improved in future studies, the data are certainly sufficient to depict the large-scale features discussed here. The oceanic currents from the west clearly bring in subarctic/transition water with much higher levels of particulate carbon and nitrogen than observed in the subtropical gyre. Favorite et al. (1976) noted that temperature and salinity alone were insufficient to distinguish the surface water masses within the transition domain between the subtropical and subarctic water masses. They speculated that other chemical signals might serve as better tracers for water moving from the west to the east across the North Pacific. Shiimoto and Hashimoto (2000) observed higher integrated chlorophyll in the western portion of the Transition Domain compared to the eastern portion. Future studies should analyze gradients in nitrate and organic material for a more complete analysis of new and export production in the eastward flowing current.

The Columbia River plume is an obvious source of organic carbon and dissolved silicate off the coast of Oregon. Although the organic material of riverine origin may be less labile than marine derived material our results and those of Klinkhammer et al. (1997) demonstrate the non-conservative behavior of organic matter within the plume. Biological processes within the plume have not been studied, but could clearly contribute to carbon cycling off the Oregon coast during the summer and waters to the north (off Washington) during the winter and spring.

Finally, during the upwelling season, productive coastal waters produce excess particulate and dissolved carbon and nitrogen. It is noteworthy, that the particulate phase of the total organic material is a much more significant component in this coastally produced organic material than in subtropical and subarctic/transition offshore waters. The seasonal contribution of the particulate and dissolved phases to cross shelf and along-shore transport of organic material remains to be determined in higher resolution spatial and temporal studies.

Acknowledgements

This work was supported by NOAA Contract # A67RJ0151 to Smith, Huyer, Wheeler, Peterson, Kosro and Barth and NSF OCE-9732386 to Smith, Huyer, Kosro and Wheeler. The cooperation, ship support and availability of physical data sets and chlorophyll data from Robert Emmett and NMFS personnel are gratefully acknowledged. This is contribution number 203 of the US GLOBEC Program, jointly funded by the National Science Foundation and National Oceanic and Atmospheric Administration.

References

- Anderson, G. C., Parsons, T. R., & Stephens, K. (1969). Nitrate distributions in the subarctic Northeast Pacific Ocean. *Deep-Sea Research*, 16, 329–334.
- Atlas, E.L., Hager, S., Gordon, L., & Park, P. (1971). *A practical manual for use of the Technicon AutoAnalyzer in seawater nutrient analyses*. Revised O.S.U. Tech. Report 215, Ref. 71-22, Dept. of Oceanography, Oregon State University, Corvallis.
- Benner, R. (1998). Cycling of dissolved organic matter in the ocean. In D. O. Hessen, & L. J. Tranvik (Eds.), (pp. 317–331). *Aquatic humic substances, ecological studies*, 133.
- Benner, R., Pakulski, J. D., McCarthy, M., Hedges, J. I., & Hatcher, P. G. (1992). Bulk chemical characteristics of dissolved organic matter in the ocean. *Science*, 255, 1561–1564.
- Bevington, P. R. (1969). *Data reduction and error analysis for the physical sciences*. In (p. 336). New York: McGraw-Hill.
- Brink, K. H., & Cowles, T. J. (1991). The coastal transition zone program. *Journal of Geophysical Research*, 96, 14637–14647.
- Carlson, C. A., Ducklow, H. W., Hansell, D. A., & Smith, W. O. Jr. (1998). Organic carbon partitioning during spring phytoplankton blooms in the Ross Sea polynya and the Sargasso Sea. *Limnology and Oceanography*, 43, 375–386.
- Carlson, C. A., Ducklow, H. W., & Michaels, A. F. (1994). Annual flux of dissolved organic carbon from the euphotic zone in the northwestern Sargasso Sea. *Nature, London*, 371, 405–408.
- Corwith, H.L. (2000). *El Niño related variations in nutrient and chlorophyll distributions off Oregon and northern California*. MS thesis, Oregon State University, pp. 109.
- Dahm, C. N., Gregory, S. V., & Park, P. K. (1981). Organic carbon transport in the Columbia River. *Estuarine and Coastal Shelf Science*, 13, 645–658.
- Doval, M. D., Alvarez-Salgado, X. A., & Perez, F. F. (1997). Dissolved organic matter in a temperate embayment affected by coastal upwelling. *Marine Ecology Progress Series*, 157, 21–37.
- Favorite, F., Dodimead, A. J., & Nasa, F. (1976). Oceanography of the subarctic Pacific region. *Bulletin of the International North Pacific Fisheries Commission*, 33, 1–134.
- Fleischbein, J.A., Hill, J.K., Huyer, A., Smith, R.L., Wheeler, P.A. (1999). *Hydrographic data from the GLOBEC long-term observation program off Oregon, 1997 and 1988*. Data Report 172, Ref. 99-1, Oregon State University, pp. 288.
- Hickey, B. M. (1989). Patterns and processes of circulation over the Washington continental shelf and slope. In M. R. Landry, & B. M. Hickey (Eds.), *Coastal Oceanography of Washington and Oregon* (p. 607). *Elsevier Oceanography Series*, 47. New York: Elsevier.
- Hill, J.K. (1999). *The distribution and partitioning of dissolved organic matter off the Oregon coast: A first look*. Master's Thesis, Oregon State University pp. 118.
- Huyer, A. (1976). A comparison of upwelling events in two locations: Oregon and northwest Africa. *Journal of Marine Research*, 34, 531–546.
- Huyer, A., Kosro, P. M., Fleischbein, J., Ramp, S. R., Stanton, T., Washburn, L., Chavez, F. P., Cowles, T. J., Pierce, S. D., & Smith, R. L. (1991). Currents and water masses of the coastal transition zone off northern California, June to August 1988. *Journal of Geophysical Research*, 96, 14809–14831.

- Huyer, A., Smith, R.L., Fleischbein, J. The coastal ocean off Oregon and northern California during the 1997-8 El Niño. *Progress in Oceanography*, 2002.
- Kähler, P., & Koeve, W. (2001). Marine dissolved organic matter: Can its C:N ratio explain carbon overconsumption? *Deep-Sea Research I*, 48, 49–62.
- Karl, D. M., Hebel, D. V., Bjorkman, K., & Letelier, R. M. (1998). The role of dissolved organic matter release in the productivity of the oligotrophic North Pacific Ocean. *Limnology and Oceanography*, 43, 1270–1286.
- Klinkhammer, G. P., Chin, C. S., Wilson, C., Rudnicki, M. D., & German, C. R. (1997). Distributions of dissolved manganese and fluorescent dissolved organic matter in the Columbia River estuary and plume as determined by in situ measurement. *Marine Chemistry*, 56, 1–14.
- Körtzinger, A., Koeve, W., Kähler, P., & Mintrop, L. (2001). C:N ratios in the mixed layer during the productive season in the northeast Atlantic Ocean. *Deep-Sea Research I*, 48, 661–688.
- Kosro, P.M., (2002). A poleward jet and an equatorward undercurrent observed off Oregon and northern Oregon, during the 1997–98 El Niño, *Progress in Oceanography*, in press
- Landry, M. R. (1989). Broad scale distributional patterns of hydrographic variables on the Washington/Oregon shelf. In M. R. Landry, & B. M. Hickey (Eds.), *Coastal Oceanography of Washington and Oregon* (p. 607). *Elsevier Oceanography Series*, 47. New York: Elsevier.
- Libby, P. S., & Wheeler, P. A. (1997). Particulate and dissolved organic nitrogen in the central and eastern equatorial Pacific. *Deep-Sea Research I*, 44, 345–361.
- Maldonado, M. T., & Price, N. M. (1999). Utilization of iron bound to strong organic ligands by plankton communities in the Subarctic Pacific Ocean. *Deep-Sea Research II*, 46, 2447–2473.
- Maybeck, M. (1982). Carbon, nitrogen, and phosphorus transport by world rivers. *American Journal of Science*, 282, 401–450.
- Moran, S. B., Charette, M. A., Pike, S. M., & Wicklund, C. A. (1999). Differences in seawater particulate organic carbon concentration in samples collected using small- and large-volume methods: The importance of DOC adsorption to the filter blank. *Marine Chemistry*, 67, 33–42.
- Pak, H., Kiefer, D. A., & Kitchen, J. C. (1988). Meridional variations in the concentrations of chlorophyll and microparticles in the North Pacific Ocean. *Deep-Sea Research*, 35, 1151–1171.
- Peltzer, E., & Hayward, N. (1996). Spatial distribution and temporal variability of total organic carbon along 140°W in the equatorial Pacific Ocean in 1992. *Deep-Sea Research II*, 43, 1155–1180.
- Shiomoto, A., & Hashimoto, S. (2000). Comparison of east and west chlorophyll standing stock and oceanic habitat along the Transition Domain of the North Pacific. *Journal of Plankton Research*, 22, 1–14.
- Small, L. F., & Menzies, D. W. (1981). Patterns of primary productivity and biomass in a coastal upwelling region. *Deep-Sea Research*, 28, 123–149.
- Strub, P. T., Kosro, P. M., & Huyer, A. (1991). The nature of the cold filaments in the California Current System. *Journal of Geophysical Research*, 96, 14743–14768.
- Wheeler, P. A., Watkins, J. M., & Hansing, R. L. (1997). Nutrients, organic carbon and organic nitrogen in the upper water column of the Arctic Ocean: Implications for the sources of dissolved organic carbon. *Deep Sea Research II*, 44, 1571–1592.
- Williams, P. J. leB (1995). Evidence for the seasonal accumulation of carbon-rich dissolved organic material its scale, in comparison with changes in particulate material and the consequential effect on net C/N ratios. *Marine Chemistry*, 51, 17–29.
- Whitney, F. A., & Freeland, H. J. (1999). Variability in upper ocean water properties in the NE Pacific Ocean. *Deep-Sea Research II*, 46, 2351–2370.