

# Coastal upwelling fluxes of O<sub>2</sub>, N<sub>2</sub>O, and CO<sub>2</sub> assessed from continuous atmospheric observations at Trinidad, California

T. J. Lueker

Scripps Institution of Oceanography, UCSD, La Jolla, CA. 92024-0244 USA

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**Abstract.** Continuous atmospheric records of O<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub>O obtained at Trinidad, California document the effects of air-sea exchange during coastal upwelling and plankton bloom events. The atmospheric records provide continuous observations of air-sea fluxes related to synoptic scale upwelling events over several upwelling seasons. Combined with satellite, buoy and local meteorology data, calculated anomalies in O<sub>2</sub>/N<sub>2</sub> and N<sub>2</sub>O were utilized in a simple atmospheric transport model to compute air-sea fluxes during coastal upwelling. CO<sub>2</sub> fluxes were linked to the oceanic component of the O<sub>2</sub> fluxes through local hydrographic data and estimated as a function of upwelling intensity (surface ocean temperature and wind speed). Regional air-sea fluxes of O<sub>2</sub>/N<sub>2</sub>, N<sub>2</sub>O, and CO<sub>2</sub> during coastal upwelling were estimated with the aid of satellite wind and SST data. Upwelling CO<sub>2</sub> fluxes were found to represent ~10% of export production along the northwest coast of North America. Synoptic scale upwelling events impact the net exchange of atmospheric CO<sub>2</sub> along the coastal margin, and will vary in response to the frequency and duration of alongshore winds that are subject to climate change.

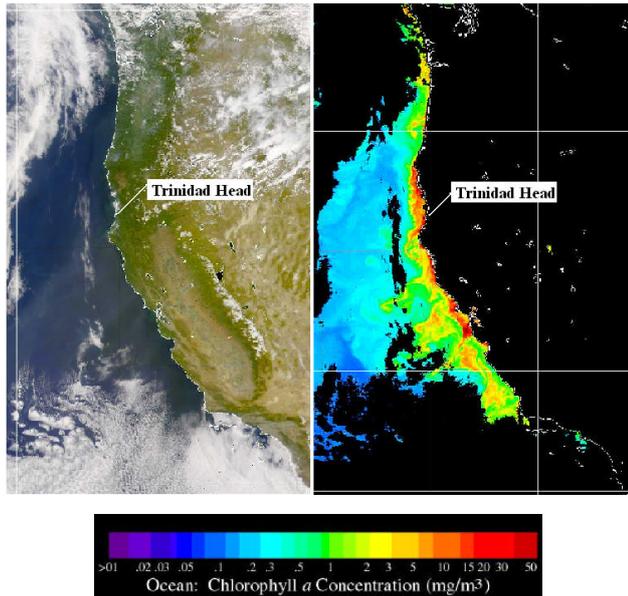
## 1 Introduction

The fate of carbon transported to coastal margins is a subject of increasing interest to biogeoscience and climate researchers. Coastal margins have the potential to absorb and transport atmospheric CO<sub>2</sub> to the interior of the ocean in the forms of organic and inorganic carbon (Walsh, 1991), a process referred to as the “continental shelf pump” (Tsunogai et al., 1999; Frankignoulle and Borges, 2001; Liu et al., 2003; Otsuki et al., 2003; Thomas et al., 2004). Uptake and transport of CO<sub>2</sub> in coastal margins constitutes a potentially large

ocean sink currently underrepresented by ocean carbon cycle models and global pCO<sub>2</sub> surveys (Doney, 1999; Yool and Fasham, 2001; Sarmiento and Gruber, 2002; Takahashi et al., 2002). Ocean circulation in the coastal region is dominated by wind forcing, and susceptible to interannual variability as well as global change (Hayward et al., 1999; Chavez et al., 2002; Schwing et al., 2002a, b; Chavez et al., 2003; Murphree et al., 2003a, b). The forces driving the continental shelf pump also have the potential to impact the mechanisms of carbon sequestration and introduce rapid changes in both CO<sub>2</sub> flux and in the ecosystems involved in the transport of carbon to and from the ocean surface (Mangelsdorf et al., 2000; Alvarez-Salgado et al., 2001; Pacala et al., 2001; Barth et al., 2002; Borges et al., 2003; Miller et al., 2003).

Determining the fate of carbon entering the coastal margin along the west coast of North America is a particularly interesting and challenging topic, currently the subject of intensive observation and modelling efforts (Barth et al., 2002; Friederich et al., 2002; Hales et al., 2003; Ianson et al., 2003; Plattner et al., 2003). Multiple pathways for carbon transport, including upwelling through the release of CO<sub>2</sub> via subsurface ventilation as well as uptake of CO<sub>2</sub> through photosynthesis, ocean currents through the transport of sinking biomass and organic matter, and rivers through the supply of continental biomass and soil carbon, contribute to the uptake and removal of inorganic and organic carbon compounds and CO<sub>2</sub> (Ludwig et al., 1996; Opsahl and Benner, 1997; Aumont et al., 2001; Hill and Wheeler, 2002; Dickens et al., 2004). Limited observations of the processes involved in carbon transport at ocean margins cannot yet provide quantification of carbon fluxes on a seasonal or synoptic event level. The expense of ship time and permanent moored instruments combined with the heterogeneity of ocean margins, particularly the region of the California Current, limits the applicability of oceanographic measurements to the spatial and/or temporal extrapolations necessary for detecting net air-sea exchange of CO<sub>2</sub>. And yet a complete accounting of the

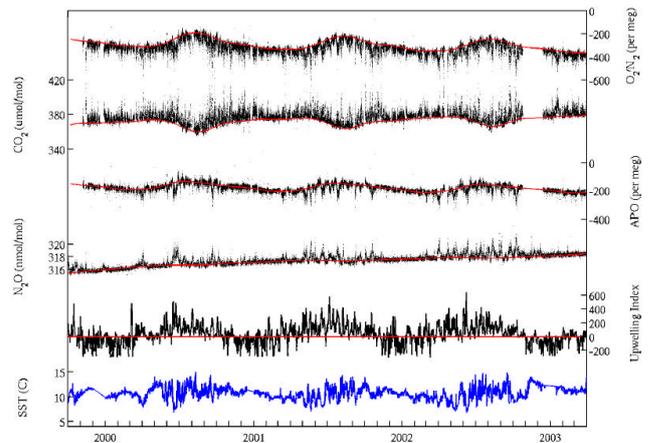
Correspondence to: T. J. Lueker  
(tlueker@ucsd.edu)



**Fig. 1.** Location of Trinidad Head Baseline Air Station (41.05° N, 124.15° W). Temperate forest ecosystems and ocean margin productivity are seen in the true color and Chlorophyll *a* false color images from 1 June 2003 (images courtesy of SeaWiFS and Orbimage).

exchange of carbon at coastal margins is necessary to begin to identify regional sources and sinks, to properly balance global carbon inventories, and to predict future scenarios of the carbon cycle influenced by global change, the goals of national and international programs (Caldeira, 2001; Wofsy and Harriss, 2002).

The oxygen cycle, intimately linked to carbon fluxes through photosynthesis and respiration both on land and in the oceans, provides valuable constraints on several components of the carbon cycle (Keeling and Shertz, 1992; Bender et al., 1998; Battle et al., 2000). The separation of marine and terrestrial oxygen signals can provide further details on the sources of other trace gases, of interest in global change studies, particularly CO<sub>2</sub> and N<sub>2</sub>O (Lueker et al., 2003; Nevison et al., 2004). At Trinidad Head, on the coast in northern California, continuous atmospheric records of O<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>, and N<sub>2</sub>O provide a direct estimate of air-sea fluxes related to coastal upwelling. In particular, monitoring of both O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub> at a coastal site where strong seasonal upwelling, high marine primary production, and rich forest ecosystems converge (Fig. 1), provides the means to detect air-sea interactions of the ocean margin separately from land ecosystems. Although the air-sea CO<sub>2</sub> fluxes are difficult to detect directly due to the large terrestrial signals, the air-sea O<sub>2</sub> fluxes are easily detected, and the associated carbon fluxes can be inferred with the aid of satellite, ocean buoy, and regional hydrographic data.



**Fig. 2.** Time series of atmospheric records from Trinidad Head, CA.  $\delta(\text{O}_2/\text{N}_2)$ , CO<sub>2</sub>, APO, and N<sub>2</sub>O mole fractions shown with Bakun upwelling index at 42° N and SSTs observed at NOAA Buoy 46 027 (41.85° N). Background levels for O<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub> and APO (in red) were computed from daily minimum CO<sub>2</sub> values fit to a 3rd order polynomial and 6 harmonics. N<sub>2</sub>O background data (also in red) were fit to a 3rd order polynomial and 2 harmonics with data 2 sigma above background removed from the fit. Upwelling indices were computed from geostrophic winds derived from six-hourly synoptic and monthly mean surface atmospheric pressure fields provided by NOAA (<http://www.pfeg.noaa.gov/-products/PFEL>), as offshore Ekman transport in units of m<sup>3</sup> s<sup>-1</sup> (100 meters of coastline)<sup>-1</sup>.

## 2 The Trinidad Head Station

Trinidad California is a coastal community located 470 km north of San Francisco and 500 km south of Portland Oregon (41.05° N, 124.15° W) in a region where strong coastal upwelling occurs from March to October (Fig. 1)(Huyer, 1983; Strub et al., 1987a, b; Summerhayes et al., 1994; Pennington and Chavez, 2000). Trinidad Head, a prominent rock outcrop (120 m elevation) on the coast at Trinidad, was selected as a background air observatory in 1995 to monitor trace gases including N<sub>2</sub>O, CH<sub>4</sub>, and CFCs as part of the Advanced Global Atmospheric Gases Experiment (AGAGE) (Prinn et al., 2000) (<http://agage.eas.gatech.edu/home.htm>). The O<sub>2</sub>/N<sub>2</sub> observatory was located adjacent to the Trinidad Head AGAGE site to take advantage of simultaneous observations of atmospheric trace gases. Trinidad Head has also served as the site of aerosol transport and ozone studies and continuing observations conducted by NOAA (<http://www.cmdl.noaa.gov/aero/net/thd/>).

Air is sampled from near the top of the 19 m tall USCG radio antenna tower at the peak of Trinidad Head. The atmosphere is analyzed for CO<sub>2</sub> concentration with a modified LICOR model 6251 CO<sub>2</sub> analyzer. The O<sub>2</sub> concentration is determined using a Servomex paramagnetic oxygen transducer cell (PM1155B) housed in a temperature and motion stabilized environment. Details of the experimental

procedure are published elsewhere (Manning et al., 1999; Lueker et al., 2001). Weather instruments located on the antenna tower provide data on wind direction and velocity, temperature, relative humidity, and photosynthetically active radiation (PAR) averaged over one minute intervals.

Trinidad Head has proven to be an ideal site for atmospheric background observations of many anthropogenic trace gases (Prinn et al., 2000). The CO<sub>2</sub> record displays variations resulting from local meteorology and fluxes from extensive conifer forests to the east as well as local air-sea fluxes (Fig. 2). A diurnal land-breeze sea-breeze pattern dominates the record with winds in the evening to late morning from the east to south-east carrying elevated CO<sub>2</sub> and reduced O<sub>2</sub>/N<sub>2</sub>, the result of terrestrial respiration (Lueker et al., 2001). In the early afternoon the winds shift to the west to north-west, bringing baseline marine air to the station until late evening, when the winds again reverse.

Superimposed over and sometimes overwhelming this diurnal cycle are synoptic weather events that vary by season, often influencing coastal ocean circulation, and sometimes result in coastal upwelling. In spring the northward migrations of the Aleutian low and the north Pacific high result in general strengthening of winds from the North (Strub et al., 1987a, b; Strub and James, 1988; Summerhayes et al., 1994). North winds blowing along the coast combine with the Coriolis force to move surface waters offshore, resulting in the upwelling of deeper waters near shore (Huyer, 1983; Summerhayes et al., 1994). Upwelling events, often associated with large weather systems occurring over several days, can extend up to 2000 km along the west coast of North America. Southerly winds typically weaken in late summer and fall, eventually being superceded by variable winds and extratropical lows associated with winter storms. The air-sea fluxes associated with these upwelling events provide readily interpretable signals of carbon dynamics in the coastal margin (Pennington and Chavez, 2000; Friederich et al., 2002; Hales et al., 2003).

### 3 Description of the data

Atmospheric O<sub>2</sub> is reported as the difference in the ratio of O<sub>2</sub>/N<sub>2</sub> measured against an arbitrary reference, and expressed in per meg units (Keeling et al., 1998).

$$\delta(\text{O}_2/\text{N}_2)(\text{per meg})=[(\text{O}_2/\text{N}_2)_{\text{sample}}/(\text{O}_2/\text{N}_2)_{\text{reference}}-1] \times 10^6 \quad (1)$$

Note that in per meg units addition of 1 μmol of O<sub>2</sub> to 1 mole of dry air (a change of 1 ppm) will result in an increase of 4.8 per meg.

The δO<sub>2</sub>/N<sub>2</sub> measurements reported here are 4 min averages of analyzer data collected every 3 s. CO<sub>2</sub> measurements are the 4 min averages corresponding to the δO<sub>2</sub>/N<sub>2</sub> data. Data are calibrated against compressed gases prepared and measured at the Scripps Institution of Oceanography, trace-

able to global O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub> measurement programs (Keeling et al., 1998) (Lueker et al., in preparation, 2004).

#### 3.1 Oceanic variations in δ(O<sub>2</sub>/N<sub>2</sub>):APO

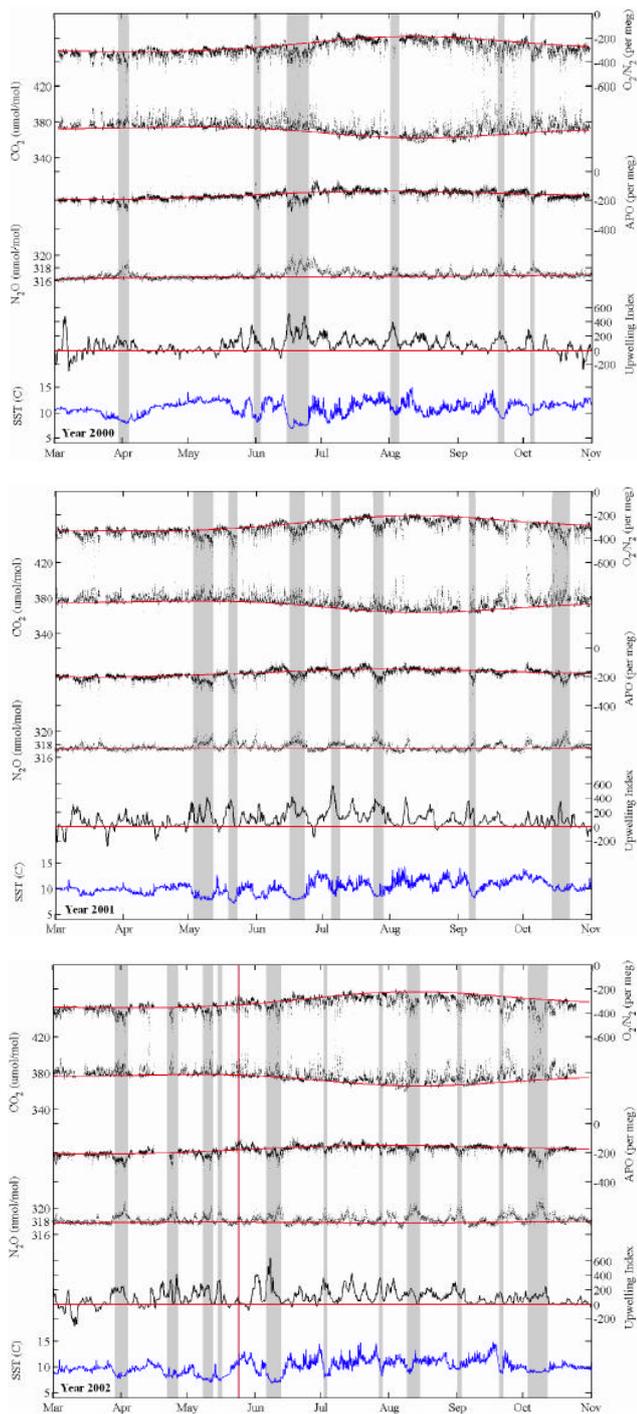
Simultaneous records of O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub> allow separation of marine and terrestrial signals in the δ(O<sub>2</sub>/N<sub>2</sub>) record. Terrestrial photosynthesis and respiration result in contemporaneous gain and release of CO<sub>2</sub> and O<sub>2</sub> to the atmosphere in a consistent exchange ratio. Marine photosynthesis and respiration produce similar variations in dissolved gases, however the CO<sub>2</sub> air-sea exchange is reduced to ~10% of the corresponding O<sub>2</sub> flux due to buffering by the ocean carbonate chemistry. Thus, to a first order, atmospheric CO<sub>2</sub> variations and the corresponding fraction of the O<sub>2</sub>/N<sub>2</sub> variations can be attributed to terrestrial processes, and the remaining O<sub>2</sub> signal attributed to marine processes. To reveal this oceanic signal in the δ(O<sub>2</sub>/N<sub>2</sub>) record, the sum, labeled the potential oxygen of the atmosphere (APO), is computed.

$$\text{APO}=\delta(\text{O}_2/\text{N}_2) + (1.1)(4.8)(\text{CO}_2-350) \quad (2)$$

The factor 4.8 converts CO<sub>2</sub> from mole fraction (μmole/mole) to per meg units, 1.1 is the approximate O<sub>2</sub>:C exchange ratio associated with land photosynthesis and respiration (Lueker et al., 2001), and 350 is an arbitrary reference level. APO effectively reveals the oceanic component of the oxygen variations, because on seasonal and shorter time scales, the main source of variability is the exchange of O<sub>2</sub> across the air-sea interface, with a small contribution (~10%) from air-sea exchange of CO<sub>2</sub> (Keeling et al., 1998; Stephens et al., 1998; Gruber et al., 2001). Biomass burning and wildfires produce little change in APO, as the O<sub>2</sub>:CO<sub>2</sub> ratio seen in fire emissions is similar to the respiration ratio (Lueker et al., 2001). Fossil-fuel burning usually has a negligible effect on APO at Trinidad Head, given the distances to the nearest large population centers. The presence of urban air in the observations at Trinidad is indicated by anthropogenic trace gas species measured at the adjacent AGAGE facility (Prinn et al., 2000), and thus data affected by urban pollution can be removed from the records when necessary.

#### 3.2 Coastal upwelling events

Figure 2 illustrates the seasonal cycles in O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>, as well as the record of marine O<sub>2</sub> variations expressed as APO. Superimposed on the APO record are short (3–10 day) periods of low APO, coincident with elevated levels of N<sub>2</sub>O, and offshore flow and reduced ocean temperatures characteristic of coastal upwelling conditions (Fig. 3). To highlight the upwelling events, we include in Figs. 2 and 3 the AGAGE record of N<sub>2</sub>O, the upwelling index recorded at 42° N provided by the Pacific Fisheries Environmental Laboratory (<http://www.pfeg.noaa.gov/products/PFEL>), and the ocean temperature observations from buoy 46 027 (41.85° N



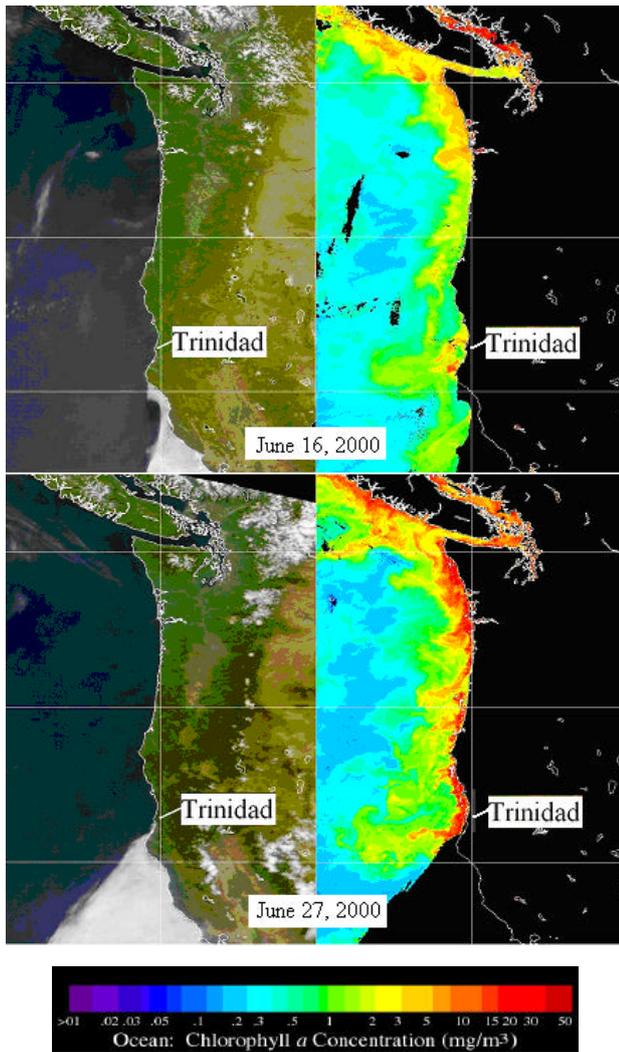
**Fig. 3.** Coastal upwelling events identified in the Trinidad atmospheric records. Periods of anomalously low APO are shaded in the figures for the years 2000–2002. Anomalously low oxygen corresponds to elevated levels of N<sub>2</sub>O, reduced SSTs, and to a lesser extent to the upwelling index at 42° N. Note the Red line in 2002 designates the date of [O<sub>2</sub>] sampling during the Humboldt State University summer field project.

124.38° W) ~100 km north of Trinidad Head operated by the NOAA National Buoy Data Center ([http://www.ndbc.noaa.gov/station\\_page.phtml?station=46027](http://www.ndbc.noaa.gov/station_page.phtml?station=46027)). Reduced APO coincident with elevated N<sub>2</sub>O, positive upwelling index, and colder water temperatures, identified with grey bands, result from the ventilation of shelf water depleted in O<sub>2</sub> and enriched in N<sub>2</sub>O (Lueker et al., 2003). Seen at higher resolution (March to October, 2000–2002, Fig. 3) the upwelling indicators consistently co-vary with anomalies in the atmospheric records. Note as well the diurnal respiration signals in O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>. The ratio of N<sub>2</sub>O to APO variations, ~1:10<sup>4</sup>, is consistent with the ratio of N<sub>2</sub>O excess to O<sub>2</sub> deficit seen in the sub-mixed layer waters of the California Current, and is characteristic of the nitrification of organic matter in the ocean interior (Nevison et al., 2004). The episodic exposure of these subsurface waters leads to N<sub>2</sub>O evasion and O<sub>2</sub> invasion in the roughly the ratio observed in the atmospheric records (Lueker et al., 2002, 2003; Nevison et al., 2003, 2004).

### 3.3 Post upwelling plankton blooms

A closer examination of the APO and N<sub>2</sub>O variations associated with coastal upwelling reveals interesting differences in the response of O<sub>2</sub> and N<sub>2</sub>O. While the upwelling events are uniformly associated with depressions in APO and elevations in N<sub>2</sub>O, the shapes of the onset and termination often differ. Also, periods of positive APO anomalies often follow intense upwelling, e.g. June 2000, June and July 2001, and May 2002 (Fig. 3). SeaWiFS images show that positive APO anomalies are associated with enhanced Chlorophyll *a* in surface waters off northern California (Fig. 4). The injection of nutrients into the euphotic zone during upwelling often supports a plankton bloom within the days or weeks following the cessation of the intense upwelling. The bloom, in turn, can drive a supersaturation of O<sub>2</sub> in the surface mixed layer. The supersaturated N<sub>2</sub>O content of the upwelled surface waters is unaffected by the bloom, even while O<sub>2</sub> is ventilated at the sea surface. The atmospheric APO and N<sub>2</sub>O variations are thus constraining two independent aspects of the coastal biogeochemistry: N<sub>2</sub>O constrains the rate of ventilation of subsurface waters, while APO constrains a combination of subsurface ventilation and mixed-layer biological production.

A limited number of dissolved oxygen [O<sub>2</sub>] samples collected 10–15 km northwest of Trinidad Head in May 2002 indicate that high APO results from marine photosynthesis. Samples to 15 m depths were collected during a period of anomalously high APO corresponding to a high productivity (Lueker et al., 2002) (red stripe in Fig. 3 indicates sampling date, [O<sub>2</sub>] results in Fig. 5). [O<sub>2</sub>] up to 180% of saturation at the surface falling to near saturation at 15 m implies that strong production signals registered in satellite ocean color data were limited to an extremely shallow layer of the ocean. The high production characterized in APO was part of an

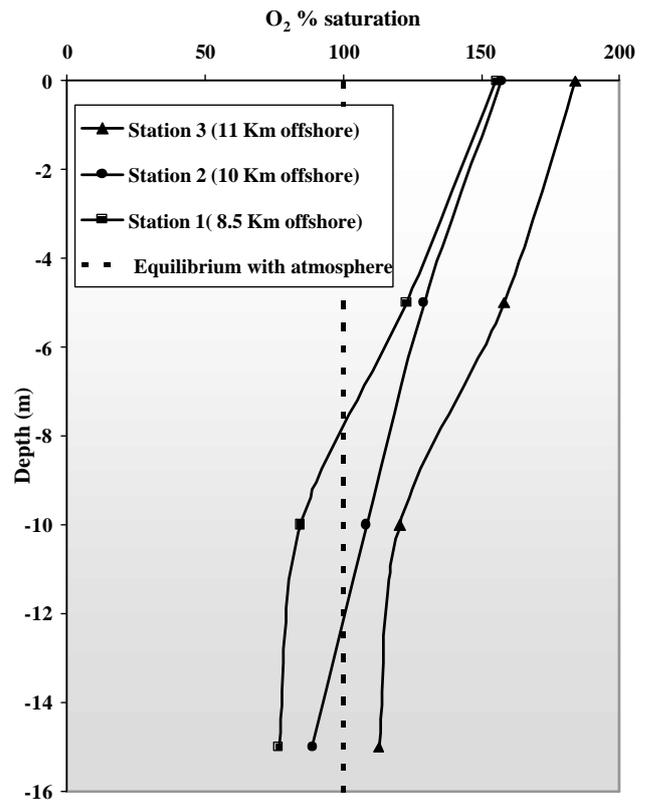


**Fig. 4.** SeaWiFS images (provided by ORBIMAGE). Upper panel: Images from 16 June 2000 during an upwelling event recorded in Fig. 3. Lower Panel: Images from 27 June 2000 during the post-upwelling period correspond to the positive APO anomaly. Note the satellite view was obscured by coastal clouds south of Cape Mendocino.

anonymous period of high CHL<sub>a</sub>, resulting from enhanced Subarctic influence in the California Current in 2002 (Huyer, 2003; Thomas et al., 2003; Wheeler et al., 2003).

#### 4 Estimating fluxes – Lagrangian (Puff) model

Atmospheric observations of the departure of APO and N<sub>2</sub>O from background levels were combined with satellite data on surface winds and SSTs to estimate the air-sea fluxes of O<sub>2</sub>, and N<sub>2</sub>O. We used a simple atmospheric transport (“Puff”) model that represents the flux into a well-mixed column of air moving along the continental margin and QSCAT wind



**Fig. 5.** [O<sub>2</sub>] sampled off Trinidad Head in May 2002. Expressed as % saturation, the data show [O<sub>2</sub>] with the greatest concentrations at the surface, decreasing toward shore and with depth to near or below saturation at 15 m.

data at 0.5° resolution to obtain the distance upwind of the station (fetch) and wind speed.

The air-sea flux into a well mixed moving column of air was represented as (Jacob, 1999)

$$F_t = (\Delta C_t)(h/t_d)/(1 - \exp(-L_{TH}/t_d U)), \quad (3)$$

where  $\Delta C_t$  is the concentration anomaly,  $h$  is a vertical mixing height (height of the column),  $t_d$  is the e-folding lifetime for dilution of the air in the column,  $L_{TH}$  is the fetch and  $U$  is the wind speed over the upwelling area. The atmospheric column height  $h$  was estimated to be 0.4 Km based on Ozone sonds (Wendy Snible, personal communication, data provided by NOAA). The air column dilution parameter ( $t_d$ ) when varied over a range of 12 to 24 h made little difference in the estimated fluxes (Lueker et al., 2003).

A typical O<sub>2</sub> flux for a strong upwelling event recorded in APO was computed to be 1.6 mol m<sup>-2</sup> dy<sup>-1</sup> corresponding to winds of 15 m s<sup>-1</sup> and an atmospheric anomaly of -100 per meg (20 ppm reduction of O<sub>2</sub> from background). An equivalent N<sub>2</sub>O flux was 1.8 × 10<sup>-4</sup> mol m<sup>-2</sup> d<sup>-1</sup> for an anomaly of 2.4 nmol/mol (2.4 ppb increase from background). Atmospheric anomalies in APO and N<sub>2</sub>O were combined with QSCAT wind fields and extrapolated over the coastal region

**Table 1.** Fluxes computed for the upwelling season (March to November) from 35 to 50° N latitude. O<sub>2</sub> fluxes were computed with the atmospheric transport (“Puff”) model for each upwelling event using the upwind fetch and windspeed from QSCAT data. The resulting fluxes were summed from March to November and the sum divided by the area along the coastline from 35 to 50° N latitude with the distance offshore defined by the Rossby radius of deformation (1500×40 km). CO<sub>2</sub> flux was scaled to the integrated O<sub>2</sub> fluxes using air-sea gas exchange relationships [ $F=K\Delta C_a-C_w$ ] predicted from regional hydrographic data (van Geen et al., 2000)(also data from WOCE P17N). Kahru and Mitchell provided satellite derived net primary production (NPP) and export production (EP) data, integrated over the same area from the VGPM model using 9 km gridded data (SeaWiFS, and MODIS) along the continental margin.

Yr	O <sub>2</sub> flux atm. Model	CO <sub>2</sub> flux atm. Model	N <sub>2</sub> O flux atm. Model	NPP	EP	CO <sub>2</sub> flux % of E.P.
	g O <sub>2</sub> m <sup>-2</sup>	g C m <sup>-2</sup>	mmol m <sup>-2</sup>	g C m <sup>-2</sup>	g C m <sup>-2</sup>	%
2000	-86.4	3.2	0.5	67	36	8.9
2001	-80.0	3.0	0.6	71	40	7.5
2002	-124.8	4.7	1.9	80	44	10.7

from 35° to 50° N latitude to provide regional flux estimates. Fluxes were computed and summed over the upwelling seasons (March to November). O<sub>2</sub> and N<sub>2</sub>O fluxes are reported in Table 1 (see also Nevison et al., 2004).

## 5 Estimating upwelling CO<sub>2</sub> fluxes with a gas exchange model and local hydrography

Air-sea fluxes during coastal upwelling result in net uptake of atmospheric O<sub>2</sub> and a concomitant release of marine CO<sub>2</sub>, due to high pCO<sub>2</sub> levels in the upwelled seawater. Estimation of CO<sub>2</sub> fluxes directly from anomalies in the atmospheric record is problematic because of terrestrial CO<sub>2</sub> variations that are an order of magnitude larger than the marine CO<sub>2</sub> flux. However, characterization of the [O<sub>2</sub>] and pCO<sub>2</sub> inventories in upwelled waters enables the CO<sub>2</sub> fluxes to be related to the O<sub>2</sub> fluxes observed in the APO record.

A gas exchange model was applied to observed winds and SSTs during upwelling conditions. The [O<sub>2</sub>] and pCO<sub>2</sub> in freshly upwelled waters were predicted from SSTs based on hydrographic observations along the continental margin of the northwest U.S. (Fig. 6). The available data indicate approximately consistent variation of [N<sub>2</sub>O], [O<sub>2</sub>], and pCO<sub>2</sub> with temperature. The co-variation of these dissolved gases with ocean temperature results from a characteristic balance between remineralization of organic matter, pre-formed gas inventories, and ocean mixing over the geographic area and temperature range of upwelled waters observed between 38° to 43° N. Hydrographic profiles are potentially more consistent than surface observations for characterizing the gas pressure of newly upwelled water, since air-sea gas transfer and

subsequent primary production have not yet altered the gas content of samples collected at depth. Recent observations show large variations occur in nearshore [O<sub>2</sub>] and pCO<sub>2</sub> levels in response to interannual variability in California Current dynamics (Hales et al., 2003; Grantham et al., 2004). While abnormal circulation can bring anomalous [O<sub>2</sub>] and pCO<sub>2</sub> levels to the surface during upwelling conditions, even these extreme departures in [O<sub>2</sub>] off the Oregon coast in 2002 (Wheeler et al., 2003) fall within the data envelopes shown in Fig. 6.

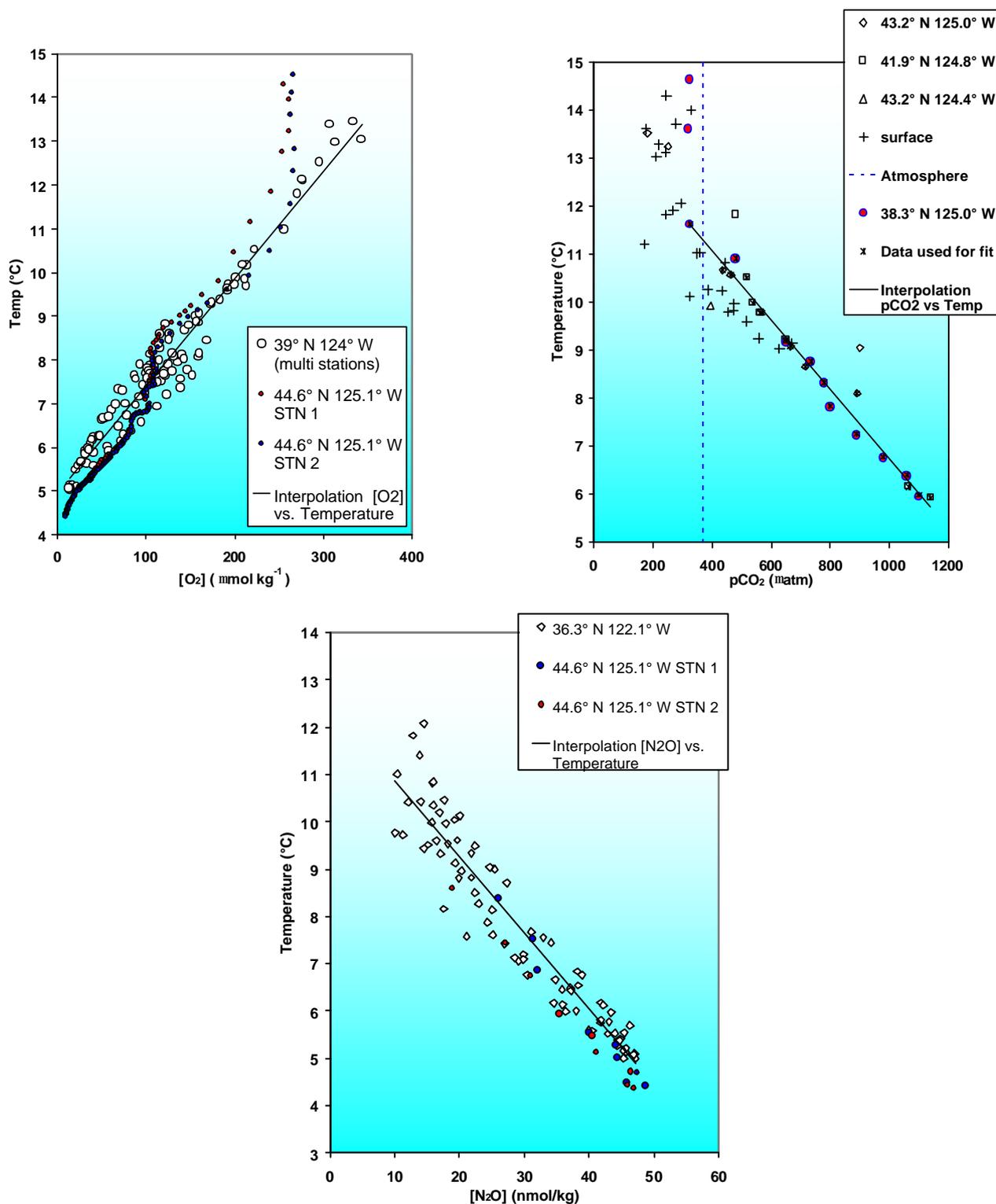
Profiles of N<sub>2</sub>O, O<sub>2</sub> and CO<sub>2</sub>, available for the coastal margin between 35° and 45° N latitude from Van Geen et al., and WOCE leg P17 (van Geen et al., 2000)(<http://whpo.ucsd.edu>), demonstrate the functional relationship with temperature (Fig. 6). The CO<sub>2</sub> flux is then formulated

$$F=K(\Delta p\text{CO}_2), \quad (4)$$

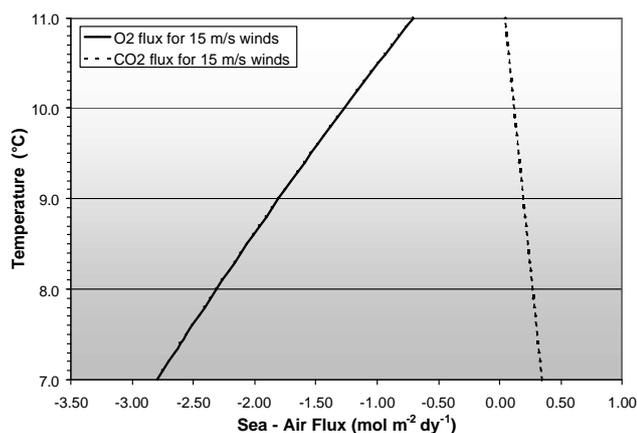
where K, the gas exchange coefficient is a function of SST and wind speed (Wanninkhof, 1992). The gas exchange model was also applied to upwelling N<sub>2</sub>O and O<sub>2</sub> fluxes and was found to give results consistent with estimates based on the “Puff” model (Lueker et al., 2003; Nevison et al., 2004).

To demonstrate the dynamic relationship of air-sea fluxes of O<sub>2</sub> and CO<sub>2</sub> over a range of observed upwelling conditions, fluxes were modeled from observed wind speeds and SSTs (Fig. 7). Dissolved Inorganic Carbon (DIC) and Alkalinity (ALK) profile data were converted to pCO<sub>2</sub> using carbonate dissociation constants experimentally shown to be appropriate for pCO<sub>2</sub> formulations (Lueker et al., 2000). Over the range of observed wind speeds and upwelled ocean temperatures along the coastline, CO<sub>2</sub> flux varies from 12% of the O<sub>2</sub> flux at 7°C to 6% of the O<sub>2</sub> flux at 11°C. Redfield ratios of marine organic matter predict an C:O<sub>2</sub> ratio of 117/170, however the carbonate equilibria in seawater result in much smaller CO<sub>2</sub>:O<sub>2</sub> ratios in the air-sea flux (Keeling et al., 1998; Stephens et al., 1998). CO<sub>2</sub> upwelling fluxes, scaled to the regional O<sub>2</sub> fluxes for the years 2000, 2001 and 2002 are given in Table 1. An APO anomaly of 100 per meg has a predicted CO<sub>2</sub> atmospheric anomaly of about 2 ppm.

It is important to note that the Temperature-pCO<sub>2</sub> relationship shown in Fig. 6 is applicable only below seawater temperatures of 11°C, and only for recently upwelled waters in the California Current. After upwelling, changes in wind driven circulation, warming of the mixed layer, and photosynthesis and/or respiration processes can modify the pCO<sub>2</sub> and temperature at different rates and in different directions. The variability of pCO<sub>2</sub> in surface waters can be seen in the data to the left of the dashed blue line (atmospheric equilibrium) in Fig. 6. Additional examples of the variability of Temperature vs. pCO<sub>2</sub> in surface waters of the California Current have been shown by Hales et al. (2003b, 2004) and Freiderich et al. (2002). In these studies, different correlations between pCO<sub>2</sub> and Temperature are evident, although more scattered due to temporal and special variability, especially in waters from the surface to 20 m depths.



**Fig. 6.** Hydrographic profile data from the Pacific Northwest plotted vs. temperature. Data from several cruises located from Oregon to central California and 1990 to 1998 are represented in plots of [O<sub>2</sub>], [N<sub>2</sub>O] and pCO<sub>2</sub>. Linear fits provide equations for interpolation of chemical species concentrations as a function of upwelled water temperature, shown as lines in the figures. The DIC and ALK data collected on the cruises were converted to pCO<sub>2</sub> to provide a linear relationship with temperature for interpolation of pCO<sub>2</sub> (Lueker et al., 2000).



**Fig. 7.** Modeled  $O_2$  and  $CO_2$  fluxes as a function of SSTs during upwelling conditions.  $[O_2]$  and  $pCO_2$  were inferred as a function of upwelled water temperature from interpolations shown in Fig. 6. Positive flux is to the atmosphere. Upwelling fluxes calculated for 15 m/s winds of 24 h duration and variable SSTs. As colder water upwells to the surface the  $CO_2$  flux relative to  $O_2$  increases from 6% (at 11°C) to 12% (at 7°C).

## 6 Estimates of carbon uptake in coastal waters

How do upwelling  $CO_2$  fluxes compare to the “continental shelf pump” or net air-sea fluxes along the coastal margin of North America? While the direction of net air-sea flux of  $CO_2$  remains a topic of active research and debate, an estimate is provided from satellite ocean color and SST data.

Upwelling  $CO_2$  fluxes were compared to net primary production (NPP) and export production (EP) in the coastal region. Coastal ocean NPP was evaluated from ocean color and SST data (SeaWiFS and MODIS) (M. Kahru, personal communication, 2003, see also Behrenfeld and Falkowski, 1997; Mitchell and Kahru, 1998; Kahru and Mitchell, 2002). Six regions offshore of the west coast of North America were evaluated using a Behrenfeld-Falkowski vertically generalized production model (VGPM) (Laws, 2004a) corresponding to the years of our record at Trinidad Head (2000–2002). Integrating the model productivity over the coastal region from 35°–50° N, NPP was estimated over the same time intervals as the upwelling sea-air flux of  $CO_2$  reported in Table 1. Export production of the coastal margin was also estimated from the combination of satellite ocean color and temperature data. The export production of the coastal area was predicted to be about 55% of NPP. The  $CO_2$  upwelling flux was about 5% of NPP, or 10% of EP. Recent studies suggest the modeled export production might be over-estimated in upwelling areas (Laws, 2004b), so the 10% value might represent a lower limit for ventilation of  $CO_2$  sequestered by export production along the coastal margin.

The  $CO_2$  fluxes reported in Table 1 are the first attempt to quantify the air-sea fluxes related to seasonal upwelling events in the Calcofi Current. In addition to uncertainties

arising from variations in the derived T vs.  $pCO_2$  relationship shown in Fig. 6, the geographical extent of upwelled waters is highly uncertain. Future studies combining satellite SST and scatterometer winds with additional hydrographic  $pCO_2$  data will reduce these uncertainties and provide improved estimates of these significant sea-air  $CO_2$  fluxes.

## 7 Summary

A relevant question for the budgeting of carbon exchange fluxes over the North American concerns the modification of the  $CO_2$  content of air from air-sea fluxes over the continental margins. Upwelling ventilates ocean margin  $CO_2$ , directly impacting the marine air, characterized as “baseline”, as we have documented at Trinidad Head. Furthermore, changes in the frequency and magnitude of wind driven coastal upwelling in response to future climate change are potentially large (Miller et al., 2003). Continuous records of  $O_2/N_2$ ,  $CO_2$  and  $N_2O$  obtained at Trinidad capture the effects of air-sea exchange during coastal upwelling and plankton bloom events. These observations provide direct evidence of the magnitude of air-sea fluxes and demonstrate the importance of synoptic scale events on the overall carbon budget in the coastal margin of western North America. Meteorological and satellite observations of winds and surface ocean temperature provide means to calculate 1st order fluxes on an event by event scale. The consistency of dissolved gas concentrations in subsurface waters of the California Current provides an estimate of  $CO_2$  upwelling fluxes that can be scaled to atmospheric  $O_2/N_2$  observations, providing a means to assess coastal  $CO_2$  fluxes during upwelling events. Upwelling fluxes could represent upwards of 10% of coastal margin export production along the west coast of North America.

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