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THE RATIO OF RESPIRATION TO PHOTOSYNTHESIS IN
LAKE SUPERIOR AND THE NORTH PACIFIC OCEAN:
EVIDENCE FROM STABLE ISOTOPES OF O₂

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**THE RATIO OF RESPIRATION TO PHOTOSYNTHESIS IN LAKE SUPERIOR AND
THE NORTH PACIFIC OCEAN: EVIDENCE FROM STABLE ISOTOPES OF O₂**

By

Mary Elizabeth Russ

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ABSTRACT

THE RATIO OF RESPIRATION TO PHOTOSYNTHESIS IN LAKE SUPERIOR AND THE NORTH PACIFIC OCEAN: EVIDENCE FROM STABLE ISOTOPES OF O₂

By

Mary Elizabeth Russ

A study of respiration to photosynthesis (R:P) ratios in Lake Superior, based on the fraction of O₂ saturation and the isotopic composition of O₂, was undertaken to evaluate spatial and temporal variations in the trophic status of a large oligotrophic freshwater lake. The lake was predominantly net heterotrophic from April to October 2000 (R:P ratios: 1.2-2.5). Uniform R:P ratios of ca. 1.5 with depth and across the lake in April 2000 and 2001 revealed the homogeneity of the water column during spring. A brief period of net autotrophy was observed during summer thermal stratification in 2000 and 2001, and surveys showed this condition to be prevalent and lake-wide in August 2001 (R:P ratios: 0.5-0.9). Strong net autotrophy (R:P ratios: 0.6) was found near Duluth, Minnesota and suggested the potential for the formation of mesotrophic conditions within areas of increased nutrient loadings from urbanization. Respiration and photosynthesis were shown to exert a strong control on O₂ gas exchange within Lake Superior, as evidenced by significant correlations between R:P ratios and O₂ gas exchange during periods of net heterotrophy and autotrophy. This observation was unexpected since [O₂] in the lake appears to be dominated by atmospheric O₂ gas exchange, given that the fraction of O₂ saturation is continuously near levels expected for equilibration with the atmosphere. Furthermore, the relationship between the biological

and physical O₂ fluxes may enable the use of R:P ratios to calculate O₂ gas exchange and ultimately estimate CO₂ fluxes between lakes and the atmosphere.

To evaluate spatial and temporal variations of net heterotrophy and autotrophy within the North Pacific ocean, R:P ratios for a six station transect comprising the oligotrophic North Pacific subtropical gyre (NPSG) to the eutrophic eastern tropical North Pacific (ETNP) were determined. Lower R:P ratios in the summer within the core of the NPSG (R:P ratios: 1.1) as compared to other seasons (R:P ratios: 1.2-1.3) likely reflected a reduction of organic carbon influx from below the pycnocline and an increase in new production supported by N₂ fixation. Within the NPSG, the 1998/2000 La Niña conditions resulted in lower R:P ratios within the upper 100 m (1.1) than during a weak El Niño event in 1990 (R:P ratio: 1.2) from a potential reduction of organic carbon consumption within the euphotic zone. Despite these variations in R:P ratios, the NPSG was net heterotrophic (R:P ratios: 1.1). Net autotrophy at the fringe of the NPSG may provide an external organic carbon source within the NPSG that is transported via horizontal transport and the downwelling conditions within this region. Net heterotrophic conditions also prevailed throughout the ETNP, indicating that expected high rates of photosynthesis were coupled with equally high rates of respiration. Gross O₂ production calculated from ¹⁷O-O₂ data was sufficient to generate net autotrophic conditions within the NPSG and ETNP, given that either external organic carbon inputs decrease or nutrients, from a physical perturbation of the water column, increase. Due to a decoupling in respiration and photosynthesis during storm events within the ETNP, a shift toward a balance in respiration to photosynthesis was the result of the physical redistribution of both organic carbon and nutrients rather than net autotrophy.

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Chapter 1

TEMPORAL AND SPATIAL VARIATIONS IN R:P RATIOS IN LAKE SUPERIOR

Background

Perhaps the most fundamental measure of whole lake metabolism is the balance between the rates of respiration and primary production (R:P). In addition, since respiration in excess of primary production results in the net production of CO₂, the balance between these processes also controls the flux of this important greenhouse gas to the atmosphere from lakes (Cole et al., 1994; del Giorgio et al., 1997). In a closed ecosystem with no external inputs, all of the organic matter generated by primary production may potentially be metabolized by respiration and the rates of these two processes may thus be equal. Natural systems, however, are rarely in balance. R:P ratios less than 1.0 are commonly the result of excessive nutrient loading and occur when autochthonous organic carbon production exceeds that which can be readily metabolized (Odum and Prentki, 1978; del Giorgio and Peters, 1993). This excess organic carbon is either buried or lost from the system by outflowing water. Respiration may exceed photosynthesis in response to allochthonous inputs of organic carbon from rivers or groundwater (Odum and Prentki, 1978; Cole et al., 1989; del Giorgio and Peters, 1993; Cole et al., 2002). Spatial and temporal variation in R:P ratios result because external inputs of organic carbon and nutrients may not be rapidly distributed evenly across a lake and there may be a time variant decoupling of primary production and respiration in response to thermal stratification.

Within the last 10 years R:P ratios in lakes have been shown to correlate with phosphorus and chlorophyll concentrations, and this observation suggests that the primary controls on R:P in lakes are nutrient levels or the magnitude of phytoplankton biomass (del Giorgio and Peters, 1994). In this manner, R:P ratios provide a foundation for evaluating the trophic state of a lake, in which eutrophic systems are characterized by R:P ratios less than 1.0 and oligotrophic systems by values greater than 1.0. The balance between respiration and photosynthesis is not, however, simply affected by nutrient levels but also responds dynamically to external inputs, internal recycling and physical controls such as thermal structure. Since low levels of primary production characterize oligotrophic systems, the delicate balance between primary production and respiration is expected to be particularly sensitive to alterations within these environments.

The main objective of this study is to quantify temporal and spatial variations in the R:P ratios of Lake Superior, the largest of the Laurentian Great Lakes. Low phytoplankton biomass and production, the presence of a deep chlorophyll maximum (DCM), and phosphorus limitation of algal production define Lake Superior as an oligotrophic system (Matheson and Munawar, 1978; Moll and Stoermer, 1982; Guildford et al., 1994). A variety of land-use activities (urban, forest, agriculture, and wetlands) within the drainage basin (Matheson and Munawar, 1978; Phillips, 1978; Weiler, 1978; Robertson, 1997) result in variation in the magnitude of allochthonous organic carbon influx and nutrient levels across the lake. The dimictic nature of Lake Superior affords an opportunity to evaluate the response of R:P to both complete vertical water column mixing and thermal stratification (Bennett, 1978a). In addition, the relatively short mixing time of a few years and the long flushing time of 177 years (Matheson and

Munawar, 1978; Bennett, 1978b) result in a rapid distribution of organic carbon and nutrients across the lake, and a slow return to preconditions following episodic influx events. All these factors indicate that Lake Superior is an ecosystem sensitive to external loadings, and consequently the magnitude of R:P ratios is likely to vary markedly on temporal and spatial scales.

Fluxes of O_2 in Lake Superior are strongly controlled by atmospheric gas exchange in addition to community respiration and phytoplankton photosynthesis. Lake Superior, with a large surface area (82,100 km²), and low rate of primary productivity (Putnam and Olsen, 1966; Fahnenstiel and Glime, 1983; Fee et al., 1992), maintains $[O_2]$ at or near levels in equilibrium with the atmosphere at all times. Little variation in $[O_2]$ occurs seasonally or with depth, and saturation levels are rarely below 80 % or above 110% (Weiler, 1978; Matheson and Munawar, 1978), which reflects the predominance of atmospheric gas exchange as the primary control on $[O_2]$. Previous studies using $\delta^{18}O-O_2$ have been largely focused in eutrophic systems that exhibit a wider range of O_2 saturation values (Quay et al., 1995; Wang and Veizer, 2000). A second objective of this study, therefore, is to utilize $\delta^{18}O-O_2$ and the fraction of O_2 saturation to evaluate the relationship between atmospheric O_2 flux and R:P ratios under oligotrophic conditions in which atmospheric equilibration largely controls O_2 concentrations.

Methods

Study site and sample analysis

To provide detailed temporal and spatial profiles of R:P ratios in Lake Superior, two transects were studied (Figure 1.1). Sampling along the Houghton North (HN) transect was performed on the RV Laurentian in conjunction with Michigan

Technological University and the Keweenaw Interdisciplinary Transport Experiment in Superior (KITES) program (chmac2.chem.mtu.edu/KITES/kites.html). Three stations, one coastal and two offshore, were located northwest of the Keweenaw Peninsula (Figure 1.1, Table 1.1). These stations were sampled monthly from April to October 2000 at five depths: the surface (~5 m), three depths bracketing the chlorophyll maximum, and approximately 5 or 10 m above the bottom. In April and August 2001, a West-East transect was sampled aboard the RV Lake Guardian, during the Environmental Protection Agency's biannual monitoring survey of the Great Lakes (<http://www.epa.gov/glnpo/monitor.html>). Seven stations in April and eight stations in August comprised the West-East transect that extended from Duluth, Minnesota, to outside Whitefish Bay (Figure 1.1, Table 1.1). Each station was sampled at the surface (between 1 and 4 m), three samples within the epilimnion, thermocline, and upper hypolimnion, and two samples at depth (5 and 10 m above bottom). Water column samples for all the stations, from both transects, were analyzed for $[O_2]$, $\delta^{18}O-O_2$, and the $\delta^{18}O-H_2O$.

A SeaBird Electronics CTD profiler determined the temperature and fluorescence as a function of depth within the water column. Water was collected using 5 L lever-action Niskin samplers on the HN transect, and a rosette containing twelve 8 L Niskin samplers on the West-East transect. A modified Winkler method was used to determine $[O_2]$ (Carpenter, 1965; Emerson et al., 1999). The analysis of $\delta^{18}O-H_2O$ was performed by Mountain Mass Spectrometry in Evergreen, Colorado via a MultiPrep and reduction furnace system designed and developed at the facility.

Collection of water samples for determination of the isotopic composition of O_2 and R:P ratios followed the protocol of Emerson et al. (1991;1999). Samples were

collected in pre-evacuated 200 mL glass vessels fitted with high vacuum stopcocks. Prior to use, 1 mL of saturated HgCl_2 was added to each vessel and dried, to eliminate biological activity following water collection. Immediately before and after samples were collected, the vessel inlet was flushed with CO_2 to displace air. Upon returning to the laboratory, headspace gases were equilibrated at a constant temperature water bath ($\sim 24^\circ\text{C}$) for at least 4 hours, under continuous rotation. After equilibration, water was removed by vacuum until 1 mL remained in the vessel and inlets were flushed again with CO_2 to prevent air contamination from potential leakage across the stopcock seals.

Determination of $\delta^{18}\text{O}-\text{O}_2$ was accomplished using a gas chromatograph interfaced to a stable isotope ratio mass spectrometer (Roberts et al., 2000). The sample vessel was connected to an inlet system on the gas chromatograph that consisted of, in series, an ascarite trap to remove water and CO_2 , a 3 mL gas sampling loop between two Valco sampling valves (one 6 port and one 4 port), a vacuum isolation valve, and a vacuum pump. Initially, the inlet system was completely evacuated before closing the isolation valve separating the inlet system from the vacuum pump. The stopcock on the vessel was opened and sample gas was allowed to equilibrate for 10 seconds within the inlet system. Upon rotation of the Valco valves, sample gas was carried by Helium flow onto a 5 m by 1/8" OD molecular sieve 5 Å GC column, and N_2 and O_2 were separated in time. Any residual water or CO_2 entering the GC column was efficiently trapped onto the molecular sieve column and removed later by heating. The effluent of the gas chromatograph was routed to the mass spectrometer and sample isotopic ratios were determined by comparison to a reference pulse of previously characterized pure O_2 tank standard. Stable isotope ratios for O are expressed in per mil (‰) notation:

$$\delta^{18}\text{O} = [(R_{\text{sample}}/R_{\text{standard}})-1] * 1000 \quad (1)$$

where R is the ratio of ^{18}O to ^{16}O . All $\delta^{18}\text{O}$ - O_2 values are expressed with respect to air, which is enriched in ^{18}O by 23.5 ‰ relative to VSMOW, resulting in a $\delta^{18}\text{O}$ value of VSMOW, with respect to air, of -23.5 ‰.

Determination of O_2 gas exchange

The rate of air/water gas exchange was determined from the following relationship (Emerson et al., 1995):

$$F_{\text{O}_2} = - G_{\text{O}_2} ([\text{O}_2] - [\text{O}_2]_{\text{sat}}) \quad (2)$$

where F_{O_2} is the air/water gas exchange rate, G_{O_2} is the gas transfer coefficient, $[\text{O}_2]$ is the concentration of O_2 in the water column, and $[\text{O}_2]_{\text{sat}}$ is the saturation concentration of O_2 (Benson and Krause, 1984; Garcia and Gordon, 1992).

Gas transfer coefficients (G_{O_2}) were calculated from wind speeds using the empirical relations of Clark et al. (1995), with daily wind speeds determined by averaging hourly data generated from Buoy number 45006 (47° 19.06' N, 39° 51.56' W) and compiled by the National Data Buoy Center (<http://www.nodc.noaa.gov/BUOY/bgl.html>).

Determination of R:P ratios

Photosynthesis, respiration and gas exchange at the air/water interface control the concentration and isotopic composition of O_2 (Bender and Grande, 1987; Quay et al., 1995). These three processes are represented by the following equation:

$$d[\text{O}_2]/dt = P - R + F_{\text{O}_2} \quad (3)$$

where $d[O_2]/dt$ is the change in the concentration of O_2 over time, P is the rate of photosynthesis, and R is the rate of respiration.

Air/water gas exchange is generally the primary process controlling the isotopic composition and concentration of O_2 within the water column. The $\delta^{18}O-O_2$ in the atmosphere is defined as 0 ‰ with respect to air. A small fractionation effect during dissolution results in ^{18}O enrichment of O_2 in surface waters by approximately 0.7 ‰ (Knox et al., 1992). The O_2 produced during photosynthesis is derived from water (Stevens et al., 1975; Guy et al., 1993), and the $\delta^{18}O-H_2O$ with respect to the air standard in Lake Superior was determined to have an average isotopic value of -31.5 ± 0.1 ‰ ($n = 30$). Photosynthesis, therefore, not only increases $[O_2]$, but also results in a decrease in $\delta^{18}O-O_2$. In contrast, during respiration, O_2 is consumed and the residual O_2 pool is enriched in ^{18}O by a kinetic isotope effect, in which the lighter ^{16}O isotope is preferentially consumed (Kiddon et al., 1993). Each of these processes uniquely affects both the concentration and isotopic composition of O_2 . In general, $\delta^{18}O-O_2$ values equal to 0.7 ‰ reflect the predominant influences of atmospheric gas exchange, those less than 0.7 ‰ reveal the contribution of O_2 from photosynthesis, and values greater than 0.7 ‰ indicate the effect of O_2 consumption by respiration (Bender and Grande, 1987). The concentration and isotopic composition of the residual O_2 pool will, therefore, reflect the balance of these processes at any depth in the water column.

Based on the influences of photosynthesis, respiration and air/water gas exchange on the concentration and isotopic composition of O_2 , equation 3 is expanded (Quay et al., 1995):

$$d(^{18/16}\text{O})/dt = G_{O_2}/Z \alpha_g \{ ([O_2]_{\text{sat}} ^{18/16}\text{O}_a \alpha_s) - [O_2] ^{18/16}\text{O} \} + P ^{18/16}\text{O}_w \alpha_p - R ^{18/16}\text{O} \alpha_r \quad (4)$$

where Z is depth, $^{18/16}\text{O}_w$ is the measured isotopic composition of H_2O , α_p is the fractionation factor associated with photosynthesis (1.0000; Guy et al., 1993), $^{18/16}\text{O}$ is the measured isotopic ratio of O_2 , α_r is the fractionation factor associated with respiration (0.9770; Luz et al., 2002), α_g is the fractionation factor associated with gas transfer (0.9972; Knox et al., 1992), $^{18/16}\text{O}_a$ is the isotopic ratio of atmospheric O_2 (Kroopnick and Craig, 1972), and α_s is the fractionation factor associated with gas dissolution (1.0073; Benson and Krause, 1984). Fractionation factors are defined here as a ratio of the reaction rates of the heavy, ^{18}O , to light, ^{16}O , isotope.

No measured value of the fractionation factor associated with respiration (α_r) for Lake Superior has been published. The value of α_r may vary depending on the metabolic diversity and planktonic species composition of the system (Kiddon et al., 1993; Luz et al., 2002). Lake Superior's plankton community is generally known to be dominated by various phytoplankton species, however, potentially a large bacterial component may be present due to the oligotrophic state of the lake (Munawar and Munawar, 1978; Scavia and Laird, 1987; del Giorgio et al., 1997; Barbiero and Tuchman, 2001b). Previously published α_r values for bacterially dominated systems are approximately 0.982 (Quay et al., 1995). Lacking an actual evaluation of the relative importance of bacteria and phytoplankton to community respiration, a literature value of 0.977, the annual average α_r for Lake Kinneret, was used for this study (Luz et al., 2002).

R:P ratios are calculated from the measured values of $[O_2]$ and $\delta^{18}O-O_2$ (Quay et al., 1995):

$$R/P = (^{18/16}O_w \alpha_p - ^{18/16}O_g) / (^{18/16}O \alpha_r - ^{18/16}O_g) \quad (5)$$

$$^{18/16}O_g = \alpha_g \{ ^{18/16}O_a \alpha_s - ([O_2]/[O_2]_{sat}) ^{18/16}O \} / \{ 1 - ([O_2]/[O_2]_{sat}) \} \quad (6)$$

R:P ratios greater than 1.0 signify a dominance of respiration, values less than 1.0 indicate a dominance of photosynthesis, and a value equal to 1.0 represent a balance of respiration and photosynthesis (del Giorgio and Peters, 1993; 1994; Quay et al., 1995).

The air/water gas transfer rate (F_{O_2} in equation 2) is no longer included in equations 5 and 6, since steady state of the system is assumed (Quay et al., 1995). At steady state any changes in the concentration or isotopic composition of the residual O_2 pool from the O_2 gas exchange flux will be offset by the biological O_2 fluxes of photosynthesis and respiration, and an equilibrium of the total O_2 flux is reached for the system. The gas transfer rate becomes a function of the fluctuations of the concentration and isotopic composition of O_2 during photosynthesis and respiration and, therefore, is not calculated directly from this method and not required to determine R:P ratios.

Results

HN transect (April through October 2000)

Complete mixing of the water column was evident in April, May and June, resulting in only slight variations in temperature and fluorescence among stations and with depth (Figures 1.2a, 1.3a). The initiation of a fluorescence peak was present in May at stations HN050 and HN090, and all stations had a well-defined fluorescence peak in June. Station HN050 had the highest relative fluorescence value (Figure 1.3a).

Undersaturation of O_2 was prevalent for the entire water column, for all stations, for the

April-June period (Figure 1.4a). Little variation was present in the $\delta^{18}\text{O}-\text{O}_2$ in April and May, and all values in the upper 50 m, at all stations, were greater than 0.7 ‰, representing a predominance of respiration over photosynthesis (Figure 1.5a). Throughout the water column during spring, all stations were net heterotrophic with R:P ratios greater than 1.0, and only a slight decrease in R:P ratios occurred from April to June (Figure 1.6a).

The summer was a period of strong thermal stratification that formed a barrier to gas exchange between the upper epilimnion and lower hypolimnion (Figure 1.2b). In July, the shallowest epilimnion of this study was present. There was a progressive increase in the depth of the epilimnion from July to August (Figure 1.2b). Maximum fluorescence peaks below the thermocline were evident in July, indicating a deep chlorophyll maximum (DCM) was prevalent at all stations. A reduction was apparent in the magnitude of the fluorescence peaks from July to August at all stations, however a DCM was still present (Figure 1.3b). Areas of slight supersaturation of O_2 were evident at all stations within the upper 30 m in July and August, but the depth interval in which supersaturation was present differed among stations (Figure 1.4b). Minimum values of $\delta^{18}\text{O}-\text{O}_2$ were found near areas of supersaturation for all stations (Figure 1.5b). R:P ratios less than 1.0 were also evident within the upper 30 m of the water column, which overlapped the areas of supersaturation and minimum $\delta^{18}\text{O}-\text{O}_2$ (Figure 1.6b). In August, an area of undersaturation of O_2 was present at or below 45 m, for all stations. In this region of the water column, some of the highest $\delta^{18}\text{O}-\text{O}_2$ and R:P ratios for the entire study were evident, signifying strong net heterotrophy (Figure 1.6b).

The water column was in transition between summer stratification and complete fall turnover in September and October. Thermal stratification continued to weaken at all stations during this period, and a decrease in surface water temperature was evident (Figure 1.2c). A reduction in fluorescence was present at all three stations, and in contrast to other months, fluorescence peaks in October were located within the epilimnion (Figure 1.3c). The entire water column became undersaturated in O₂ in September, with the exception of station HN210 at 45 m, which was supersaturated. In October, the fraction of O₂ saturation values were equal to or less than 1.0, for the whole water column at all stations (Figure 1.4c). At all depths, in September, $\delta^{18}\text{O}$ -O₂ values were approximately 0.7 ‰, except station HN210 at 35 and 40 m, where values were less than 0.7 ‰. In October at stations HN090 and HN210, $\delta^{18}\text{O}$ -O₂ values were approximately 0.7 ‰, reflecting a predominance of gas exchange. At station HN050 $\delta^{18}\text{O}$ -O₂ values varied from approximately 0.7 ‰ at 5 and 25 m, to greater than 0.7 ‰ at 20 and 30m (Figure 1.5c). The R:P ratios for all stations in September were greater than 1.0 signifying net heterotrophy, with the exception of station HN210 at 40 m. Variations in R:P ratios among stations were evident in October. All values at stations HN050 and HN210 were greater than 1.0, except at station HN050 at 5 m. At station HN090, R:P ratios were less than 1.0 at 5 and 15 m, and were greater than 1.0 in the remaining upper 50 m (Figure 1.6c).

West-East transect (April and August 2001)

A well mixed water column lacking a distinct fluorescence peak was present for all seven stations of the April 2001 West-East transect, reflecting conditions similar to the April 2000 HN transect (Figure 1.7, 1.8). Once again, the entire water column was

undersaturated in O₂ for all stations (Figure 1.9). All $\delta^{18}\text{O-O}_2$ values were greater than 0.7 ‰, signifying a predominance of respiration, similar to values observed in April along the HN transect (Figure 1.10). The R:P ratios for the West-East transect and the HN transect were also similar, with all individual R:P ratios greater than 1.0, representing net heterotrophy for both transects during this period (Figure 1.11).

Thermal stratification was evident across the transect in August, however, variations in the magnitude and depth of maximum O₂ saturation and minimum $\delta^{18}\text{O-O}_2$ values were apparent among stations from west (SU19) to east (SU01) (Figures 1.7, 1.12). All stations had a similar mixed layer depth of approximately 10 m. A DCM was present at all stations, and the location of the maximum peak increased with depth from west to east (Figure 1.8). Supersaturation of O₂ was apparent at all stations, and was located at or above the thermocline at the western and central stations (SU19 to SU10), and extended below the thermocline at the eastern most stations (SU08 to SU01). The DCM was undersaturated in O₂ at all stations except SU01, the most eastern station (Figures 1.8, 1.12). Values for the $\delta^{18}\text{O-O}_2$ were less than 0.7 ‰ at all stations for the majority of depths sampled, representing a predominance of photosynthesis (Figure 1.13). Net autotrophy was present across the transect at all stations. At stations SU19 through SU10 R:P ratios less than 1.0 were evident at or above the thermocline, and at stations SU08 and SU04, R:P ratios less than 1.0 extended from surface to below the thermocline, and throughout the DCM at station SU01. Finally, R:P ratios greater than 1.0 were present at the DCM for all stations, except for station SU01 (Figure 1.14).

A distinct water column profile of both physical and biogeochemical parameters was present at station SU22B (Figures 1.7, 1.12), in contrast to the other seven stations

that comprised the West-East transect. The epilimnion was deeper, located at 24 m, with a surface water temperature $\sim 18.0^{\circ}\text{C}$, and a fluorescence peak within the epilimnion, near the surface at 7m (Figure 1.7, 1.8). No DCM was present. Supersaturation in O_2 was apparent at or above the thermocline, and the remaining upper 50 m was undersaturated (Figure 1.7, 1.12). The $\delta^{18}\text{O}-\text{O}_2$ values were less than 0.7 ‰ at and above 7m, approximately 0.7 ‰ at the thermocline to 41 m, and greater than 0.7 ‰ at 49 m (Figure 1.13). Minimum R:P ratios less than 1.0 were present at or above the thermocline, signifying strong net autotrophy, and values greater than 1.0, representing net heterotrophy, were evident below the thermocline (Figure 1.14).

Discussion

Two main factors predominantly influence variations in the balance of respiration to photosynthesis within aquatic ecosystems: the flux of organic carbon entering the lake, and the magnitude of primary production within the lake (Wissmar et al., 1977; Odum and Prentki, 1978; Scavia and Laird, 1987; del Giorgio and Peters, 1993; 1994). Temporal and spatial variations in R:P ratios are not only a reflection of the balance of respiration and photosynthesis (del Giorgio and Peters, 1993; 1994) but are also influenced by physical mixing and stratification (Bennett, 1978a). Respiration and photosynthesis also have a strong affect on O_2 , and therefore the concentration and isotopic composition of O_2 provides a basis to determine R:P ratios (Bender and Grande, 1987; Quay et al., 1995). This approach, however, has been rarely applied in a large oligotrophic system on a spatial and temporal scale. This study uses $[\text{O}_2]$ and $\delta^{18}\text{O}-\text{O}_2$ within two multi-station transects in Lake Superior to quantify R:P ratios, and to

understand the factors controlling variations in the ratio within an oligotrophic system on a seasonal and lake-wide basis.

Seasonal variations in R:P ratios

Within temperate lakes extensive mixing during the unstratified period in winter and early spring results in lake-wide homogeneity of biogeochemical and physical characteristics. This trend is evidenced in Lake Superior by constant temperature and fluorescence profiles with depth from April through June along the HN transect (Figure 1.2a, 1.3a). Furthermore, similarities in temperature, fluorescence and $[O_2]$ between the April 2000 HN and April 2001 West-East transects indicate that the homogeneity of water column characteristics is a common feature of early spring and extends across the lake (Figure 1.2a, 1.3a, 1.7, 1.8). Under these conditions of an extensively mixed water column, the $[O_2]$ is expected to be at levels close to equilibrium with the atmosphere. During April and May, however, uniform undersaturation in $[O_2]$ and across lake R:P ratios greater than one are present (Figure 1.4a, 1.6a, 1.9, 1.11), signifying excess respiration over photosynthesis. Prolonged water column mixing may result in resuspension of bottom sediments, potentially releasing organic carbon from past seasons (Phillips, 1978). In addition, influx of allochthonous organic carbon from spring snowmelt and precipitation events adds to the input of organic carbon to the lake during this time (Matheson and Munawar, 1978; Phillips, 1978; Robertson, 1997). The overall result is an excess of respiration over photosynthesis and, thereby, extensive net heterotrophy during April and May. This excess respiration, therefore, results in a period of undersaturated $[O_2]$ throughout the water column and, consequently, a net CO_2 efflux to the atmosphere.

Net autotrophy is expected in June since observations of high diatom biomass and decreases in [Si] suggest increasing levels of productivity in Lake Superior (El-Shaarawi and Munawar, 1978; Matheson and Munawar, 1978; Munawar and Munawar, 1978; Weiler, 1978; Barbiero and Tuchman, 2001b). The observations of a slight increase in fluorescence values, and a decrease in $\delta^{18}\text{O}-\text{O}_2$ values, are consistent with an increase in rates of photosynthesis and the formation of a late spring bloom (Figure 1.3a, 1.5a). Undersaturation in $[\text{O}_2]$ and R:P ratios greater than 1.0, however, seem inconsistent with an increase in diatom biomass (Figure 1.4a, 1.6a). Autochthonous production at this time, therefore, remains insufficient to override the excess respiration over photosynthesis present in April and May. Overall, the result is persistent net heterotrophy during June (Figure 1.6a).

In contrast to the uniformity of the spring water column, variations with depth in temperature, light and nutrient concentrations due to seasonal stratification result in spatial heterogeneity of summer R:P ratios. Regions with low $\delta^{18}\text{O}-\text{O}_2$ values, supersaturated $[\text{O}_2]$, and R:P ratios less than 1.0 are indicative of an overall metabolism in which photosynthesis exceeds respiration. The depth of this net autotrophy within the water column was not consistent, however, between coastal and offshore stations or across the lake (Figure 1.6b, 1.14). At coastal station HN050, R:P ratios less than 1.0 are restricted to the upper epilimnion in July, in contrast to the two offshore stations of the HN transect (Figure 1.6b). In addition, R:P ratios less than 1.0 are confined to the region at or above the thermocline within the western and central portions of Lake Superior (Figure 1.14). These results are consistent with previous studies that show temperature to be a significant variable influencing phytoplankton production in Lake Superior,

especially during periods of thermal stratification (Nalewajko and Voltolina, 1986).

Temperature and R:P ratios were significantly correlated in the western and central regions during summer (Figure 1.15), than in spring ($R^2 = 0.22$, $P = 0.001$, $\alpha = .05$, $df = 18$), indicating a phytoplankton community sensitive to changes in temperature (Nalewajko and Voltolina, 1986). Lake Superior may be similar to many oligotrophic freshwater systems that maintain a large bacterial and phytoplankton community, whose population and/or activity is influenced by temperature (Cotner and Biddanda, 2002; del Giorgio et al., 1997; Currie, 1990; Scavia and Laird, 1987). Earlier coastal warming of the water column in spring may, therefore, lead to accelerated chlorophyll formation and summer phytoplankton production at inshore areas as compared to offshore regions (Bennett, 1978a; Nalewajko and Voltolina, 1986). Community metabolism within the lake may also be enhanced if a large bacterial population is present to respire dissolved organic matter (DOM) and facilitate the transfer of some of this organic carbon to higher trophic levels (Cotner and Biddanda, 2002; Azam, et al., 1983; Azam and Ammerman, 1984; Fuhrman, 1992).

Temperature, in contrast, is not as strong an influence on R:P ratios in the eastern section of Lake Superior (Figure 1.15). Within this region and the offshore stations of the HN transect, R:P ratios less than 1.0 are not restricted to the warmer epilimnion but extend below the thermocline and throughout the DCM (Figure 1.2b, 1.6b, 1.7, 1.14). Other factors, potentially light and/or nutrient concentrations, are the main drivers of lower R:P ratios in the eastern section of the lake (Bennett, 1978b). The 1% light level has been reported as deep as 30 m in the eastern section of Lake Superior and at 20 m off the Keweenaw Peninsula, and therefore, above these depths light may not be a limiting

factor to phytoplankton production (Schertzer et al., 1978). The observation of net photosynthesis below the thermocline may also be the result of low-light adapted phytoplankton that take advantage of higher nutrient concentrations within the hypolimnion (Moll and Stoermer, 1982; Fahnenstiel and Glime, 1983; Fahnenstiel et al., 1984; Barbiero and Tuchman, 2001a). The nutrient concentrations at this depth may be enhanced within the eastern section of Lake Superior as a result of water mass exchange between the lake and Whitefish Bay (Bennett, 1978b). Prior studies of the Straits of Mackinac and the outlets of Lake Huron into Georgian Bay have reported a back flow of water below the thermocline during stratified periods (Saylor and Sloss, 1976; Schertzer et al., 1979). Phosphorus concentrations have been estimated to be 50 % higher entering the St. Mary's River from Whitefish Bay than leaving Lake Superior to the bay (Bennett, 1978b), implying half the St. Mary's River phosphorus influx from Lake Superior and Whitefish Bay is derived within the bay. High nutrient concentrations within Whitefish Bay are suggested to be the result of the large land drainage area to water body area of the bay, hence, the relatively small volume of water in the bay receives nutrient loadings from a large portion of the surrounding drainage basin (Bennett, 1978b). Nutrients from Whitefish Bay, therefore, may enter Lake Superior during summer and become available to phytoplankton within the hypolimnion, ultimately contributing to the summer period of net autotrophy.

In addition to temperature, light and nutrients, another factor resulting in net autotrophy in Lake Superior during the summer is a reduction in the input of allochthonous organic carbon (del Giorgio and Peters, 1993; 1994) from tributary influxes and sediment resuspension. The reduction in the frequency and intensity of

precipitation events during the summer minimizes the magnitude of terrestrial run-off to Lake Superior (Phillips, 1978). This, in turn, lowers the input of total dissolved solids and organic matter from the drainage basin to the lake, resulting in a decrease in the availability of allochthonous organic carbon to fuel heterotrophic microbial respiration (Phillips, 1978; del Giorgio and Peters, 1994; Robertson, 1997). In addition, the development of a thermocline creates a barrier to vertical water movement from the hypolimnion to the epilimnion, further impeding resuspension of sediments (Bennett, 1978a). Thus the supply of allochthonous organic carbon to the epilimnion may limit respiration and, thereby, lower R:P ratios. The upper water column, consequently, becomes extensively net autotrophic (Figure 1.6b, 1.14), augmented by generally higher phytoplankton production in summer within the mixed layer as compared to spring (Fee, et al, 1992). Net autotrophy within the summer, therefore, may result from a period of decreased allochthonous organic carbon fluxes to the upper water column, reducing respiration and not necessarily an increase in phytoplankton production.

Rates of phytoplankton productivity are typically greater in the fall than summer in Lake Superior (Putnam and Olson, 1966; Fahnenstiel and Glime, 1983) as the fall phytoplankton community utilizes nutrients redistributed as stratification deteriorates (Munawar and Munawar, 1978). Indeed, photosynthesis is dominant over respiration in October, at station HN090 (Figure 1.6c). Unexpectedly, respiration remains predominant throughout the upper 50 m at stations HN050 and HN210 in October, and at all stations in September, as signified by R:P ratios greater than 1.0 (Figure 1.6c). Autochthonous organic carbon, from summer net autotrophy in the shallow epilimnion, may become an organic carbon source at depths, since this organic carbon was originally produced at

surface during a period of intense restriction to vertical water movement (Bennett, 1978a). As this organic carbon is redistributed throughout the upper water column during intense mixing in response to surface cooling and increased fall storm events, net respiration prevails throughout the upper 50 m (Figure 1.6c). The spatial heterogeneity of R:P ratios during the fall is, thereby, due to variations in the redistribution of nutrients and/or organic carbon resulting in areas of photosynthesis or excess respiration.

Ecological implications - Duluth, Minnesota (Station SU22B)

One key factor that defines Lake Superior as an oligotrophic system is the presence of a seasonal DCM (Moll and Stoermer, 1982). In August, a DCM was present below the thermocline at all stations, except at the western-most station (SU22B), near Duluth, Minnesota, which had a chlorophyll maximum above the thermocline (Figure 1.7, 1.8). A chlorophyll maximum above the thermocline is consistent with a mesotrophic or eutrophic system, defined by higher rates of phytoplankton productivity than an oligotrophic environment (Moll and Stoermer, 1982). Indeed, some of the lowest R:P ratios of this study are present within the chlorophyll maximum at station SU22B, signifying a strong predominance of photosynthesis over respiration (Figure 1.8, 1.14). Increased nutrient loading from urban areas within the surrounding drainage basin is a likely factor in shifting station SU22B to a mesotrophic state. Previous studies have reported relatively high phosphorus concentrations within the water column near Duluth compared to other regions in Lake Superior, (Matheson and Munawar, 1978; Munawar and Munawar, 1978; Weiler, 1978), potentially affecting trophic state by increasing phytoplankton biomass. In addition, the increased nutrient loading around Duluth, may affect trophic state in other areas of the lake, since the short mixing to long flushing times

of Lake Superior results in a rapid distribution of nutrients across the lake, and a slow return to preconditions following high influx. The duration of this study was not sufficient to resolve such long term alterations to lake-wide trophic state, however, the sensitivity of the trophic state within the region of Lake Superior immediately surrounding the area of increased nutrient loading was revealed.

Ecological implications – the microbial loop and climate change

Previous studies have indicated that the microbial loop is important to nutrient cycling and energy transfer in oligotrophic environments (Fuhrman, 1992; Legendre and Rassoulzadegan, 1995; Biddanda et al., 2001; Cotner and Biddanda, 2002). Bacterioplankton may be a large component of the heterotrophic biomass in oligotrophic systems, and these organisms may dominate community respiration (del Giorgio et al., 1997; Biddanda et al., 2001; Cotner and Biddanda, 2002). Within Lake Superior, greater than 95 % of the less than 1- μm size fraction are heterotrophic bacteria, which perform 82-91 % of planktonic respiration (Biddanda et al., 2001). Growth efficiencies of bacterioplankton in Lake Superior are low, however, ranging from 4-13 % (Biddanda et al., 2001). The heterotrophic community in Lake Superior, therefore, is comprised of a large population of small organisms converting most of the organic carbon from primary production back to CO_2 . Only protozoans less than or equal to 5- μm consume small bacterioplankton, thereby reducing the quantity of organic carbon available for larger sized zooplankton (Ducklow et al, 1986; Legendre and Rassoulzadegan, 1995; Cotner and Biddanda, 2002). In addition, previous studies estimate that greater than 50 % of the phytoplankton biomass in oligotrophic systems is picoplankton, and hence a substantial portion of nutrients released during protozoan grazing on bacterioplankton may be

assimilated by small sized phytoplankton (Ducklow et al., 1986; Legendre and Rassoulzadegan, 1995; Bell and Kalff, 2001). Overall, an active microbial loop foodweb may restrict a large portion of the organic carbon and nutrients to a “closed” microbial community, diverting organic carbon from higher trophic levels within the foodweb, and thereby constraining fishery yields (Legendre and Rassoulzadegan, 1995; Kemp and Smith, 2001; Cotner and Biddanda, 2002).

Climate change within the Great Lakes region has the potential to alter the current foodweb dynamics of Lake Superior. Recent studies have determined that low rates of primary production from picoplankton and high rates of respiration from bacterioplankton result in overall net heterotrophy of oligotrophic lakes (del Giorgio et al., 1997; Bell and Kalff, 2001). Indeed, based on R:P ratios, this study has shown Lake Superior to be net heterotrophic, especially during the long period of spring turnover (Figure 1.2a, 1.6a). Only during a short period of thermal stratification in July and August was the lake net autotrophic (Figure 1.2b, 1.6b). Climate change, however, has increased surface water temperatures and led to reduced ice cover within the Great Lakes during winter. During ice-free periods mixing by winter storms may result in increased nutrient release from sediment resuspension (Hanson et al., 1992; Mortsch and Quinn, 1996; Magnuson et al., 1997). Furthermore, an increase in surface water temperatures may lead to an earlier occurrence of thermal stratification of the water column in spring (Magnuson et al., 1997). An earlier onset of stratification may reduce the period of strong net heterotrophy in spring and increase the duration of the period of summer net autotrophy in Lake Superior. Finally, high nutrient concentrations from prolonged winter mixing would favor phytoplankton as nutrient competitors over bacterioplankton.

Nutrient cycling would thereby be limited in bacterioplankton during spring and the ability of these consumers to utilize the early spring influx of allochthonous organic carbon may be reduced (Bentzen et al, 1992; Cotner and Wetzel, 1992; Coveney and Wetzel, 1995; Cotner and Biddanda, 2002). The overall result would likely be larger sized phytoplankton and zooplankton, which in turn would be directly available to higher trophic levels (Legendre and Rassoulzadegan, 1995). Climate change, therefore, may shift Lake Superior from a foodweb dominated by a microbial community to a shorter foodweb, funneling more organic carbon to higher trophic levels and the potential to increase fish populations. This shift in the foodweb may not occur, however, if a longer period of thermal stratification leads to an earlier depletion of nutrients within the epilimnion (Magnuson, et al., 1997). In this case, the period of net autotrophy may not be extended but merely shifted from summer to early spring, leaving insufficient time for larger sized phytoplankton to develop. Nutrient depletion would ultimately favor bacterioplankton over phytoplankton during nutrient uptake (Bentzen et al., 1992; Cotner and Wetzel, 1992; Coveney and Wetzel, 1995; Cotner and Biddanda, 2002), and hence, reduce phytoplankton production. Indeed, recent studies within Lake Michigan suggest that climate change will follow this second scenario and ultimately lower current rates of offshore primary production (Brooks and Zastrow, 2002). In the future, therefore, climate change is likely to enhance the active microbial community in Lake Superior and further divert organic carbon from higher trophic levels, and ultimately fisheries.

Relationship between O_2 gas exchange and R:P ratios in an oligotrophic lake

An influence of O_2 gas exchange on $[O_2]$ was expected within Lake Superior, however, biological fluxes were shown to equally affect $\delta^{18}O-O_2$ and the fraction of O_2

saturation despite low rates of primary productivity and planktonic biomass in oligotrophic environments. Net autotrophy was evident during July, August and October, and was characterized by supersaturation of O_2 and $\delta^{18}O-O_2$ values less than 0.7‰ signifying a predominance of photosynthesis (Figure 1.16b, 1.16c). A significant correlation was found between R:P ratios and O_2 gas exchange (Figure 1.17) as photosynthesis from summer and fall phytoplankton blooms increased $[O_2]$ to supersaturated levels within the upper water column, and created an O_2 efflux to the atmosphere from the lake. In contrast, net heterotrophy was present in April and May as indicated by an undersaturation of O_2 and $\delta^{18}O-O_2$ values greater than 0.7 ‰ representing a predominance of respiration (Figure 1.16a). R:P ratios and O_2 gas exchange are significantly correlated during this period (Figure 1.17). April and May is a period of extensive water column mixing and low phytoplankton biomass resulting in inputs of atmospheric O_2 and low rates of photosynthesis, respectively. The undersaturation of O_2 , therefore, is from respiration in excess of photosynthesis, which in turn drives the influx of O_2 from the atmosphere to the lake. Finally, June and September are periods in which R:P ratios reveal equal rates of respiration and photosynthesis (Figure 1.16a, 1.16c). At this time a significant correlation was not found between R:P ratios and O_2 gas exchange (Figure 1.17). These periods represent a transition between early spring net heterotrophy and summer net autotrophy and between summer net autotrophy and late fall net heterotrophy, creating a temporary balance between respiration and photosynthesis (Figure 1.16a, 1.16b, 1.16c). Consequently, these are also periods of transition in atmospheric O_2 flux, since biological fluxes are driving the physical flux. During these periods, therefore, a small change in respiration or photosynthesis at one location in the

lake leads to a corresponding small change in the atmospheric O₂ flux. Since the water column is in transition during this time, however, the changes in respiration and photosynthesis that are affecting the variation in the atmospheric O₂ flux at one location in the lake may not be reflected in other parts of the lake. Overall, the spatial variations in respiration, photosynthesis and O₂ gas exchange characteristic of June and September lead to a large scale spatial heterogeneity in R:P ratios and O₂ gas exchange and a poor correlation between the two variables during this time. Significant correlations between R:P ratios and O₂ gas exchange in oligotrophic systems, therefore, are strongly dependent on the biological processes of photosynthesis and respiration even within environments of low primary production. If this relationship between R:P ratios and O₂ gas exchange proves robust in more detailed studies and in other environments, R:P ratios have the potential to be utilized as an indicator of O₂ gas exchange and ultimately could be used to determine the CO₂ flux between a lake and the atmosphere.

Conclusions

Lake Superior, similar to many oligotrophic systems, was found to be predominately net heterotrophic, although the balance of respiration to photosynthesis within the lake shifted on a seasonal basis. The intensity of net heterotrophy was strongest in spring when organic carbon, fueling excess respiration, is more readily available presumably due to resuspension of sediments or high tributary influx. Respiration prevailed even though cold water temperatures were evident and extensive water column mixing indicated that O₂ influx from the atmosphere must have been substantial. Net autotrophy was extensive across the lake in summer, with temperature, light, nutrient concentrations, and the reduction of allochthonous organic carbon inputs

during thermal stratification controlling the intensity and location of these regions. Lake Superior, therefore, was not consistently net heterotrophic on a temporal scale, but the balance between respiration and photosynthesis shifted on a seasonal basis and a short period of lake-wide net autotrophy was observed during summer thermal stratification.

With the exception of the station near Duluth, Minnesota, Lake Superior was spatially homogeneous with respect to R:P ratios. A relatively short mixing time of a few years relative to a long flushing time of 177 years (Matheson and Munawar, 1978; Bennett, 1978b) allows for lake-wide homogeneity of nutrients and organic carbon, resulting in a similar pattern in R:P ratios across the lake. The predominance of net autotrophy near Duluth indicates Lake Superior's potential to develop mesotrophic conditions as a consequence of high nutrient loadings from urbanized areas. A movement toward mesotrophy emphasizes the extreme sensitivity of a predominantly net heterotrophic lake to potential future increases in organic carbon and nutrient loadings, and the ability of $\delta^{18}\text{O}-\text{O}_2$ to monitor these variations.

Results from this study are consistent with a foodweb heavily dominated by an active microbial community, however, climate change may redefine the overall foodweb dynamics of Lake Superior. Other studies have shown that a majority of small sized consumers, grazers and primary producers maintains a large portion of organic carbon and nutrient cycling within a "closed" microbial loop, diverting resources from higher trophic levels, including fish populations. Climate change has increased surface water temperatures within the Great Lakes and may lead to earlier onset and extended periods of thermal stratification. Earlier stratification may create a prolonged period of net autotrophy in the lake that could result in a shorter foodweb and a potential increase in

fishery yield. More likely, an extended period of stratification will result in earlier nutrient depletion in the epilimnion. Our expectation, therefore, is that climate change will enhance metabolism within the microbial community and potentially compromise fishery yields.

Despite the oligotrophic nature and low levels of primary production, biological factors proved significant in controlling the physical flux of O_2 in Lake Superior. The role of O_2 gas exchange within the lake is demonstrated by a clustering of all data around the atmospheric O_2 flux axis (Figure 1.16a, 1.16b, 1.16c). Respiration and photosynthesis drive $[O_2]$ in Lake Superior and thereby create atmospheric O_2 influx during periods of higher respiration to photosynthesis and atmospheric O_2 efflux during periods of lower respiration to photosynthesis. Consequently, a significant relationship between R:P ratios and O_2 gas exchange was found during periods of net autotrophy and net heterotrophy. This correlation may enable the use of R:P ratios as an indicator of O_2 gas exchange and an alternative measurement of CO_2 flux between the atmosphere and freshwater lakes.

SAMPLING SITES

HN TRANSECT

Station	Latitude (N)	Longitude (W)	Maximum Depth (m)	Distance from Shore (km)
HN050	47° 17.2'	88° 36.9'	110	5
HN070	47° 18.1'	88° 37.8'	120	7
HN090	47° 19.0'	88° 38.8'	110	9
HN210	47° 24.3'	88° 44.2'	160	21

WEST-EAST TRANSECT

Station	Latitude (N)	Longitude (W)	Maximum Depth (m)	Distance from Western Shore (km)
SU22B	46° 47.6'	91° 45.0'	55	15
SU19	47° 22.2'	90° 51.2'	192	80
SU16	47° 37.3'	89° 27.7'	184	183
SU12	47° 51.3'	88° 02.5'	243	289
SU10	47° 30.8'	89° 32.7'	159	329
SU08	47° 36.3'	86° 49.0'	307	382
SU04	47° 15.5'	86° 20.8'	149	422
SU01	46° 59.5'	85° 09.9'	96	515

Table 1.1: Latitude and longitude coordinates, maximum depth and distance to shore for all stations along the the HN and West-East transects. Note: Mid-station HN070 was sampled in June instead of HN090.

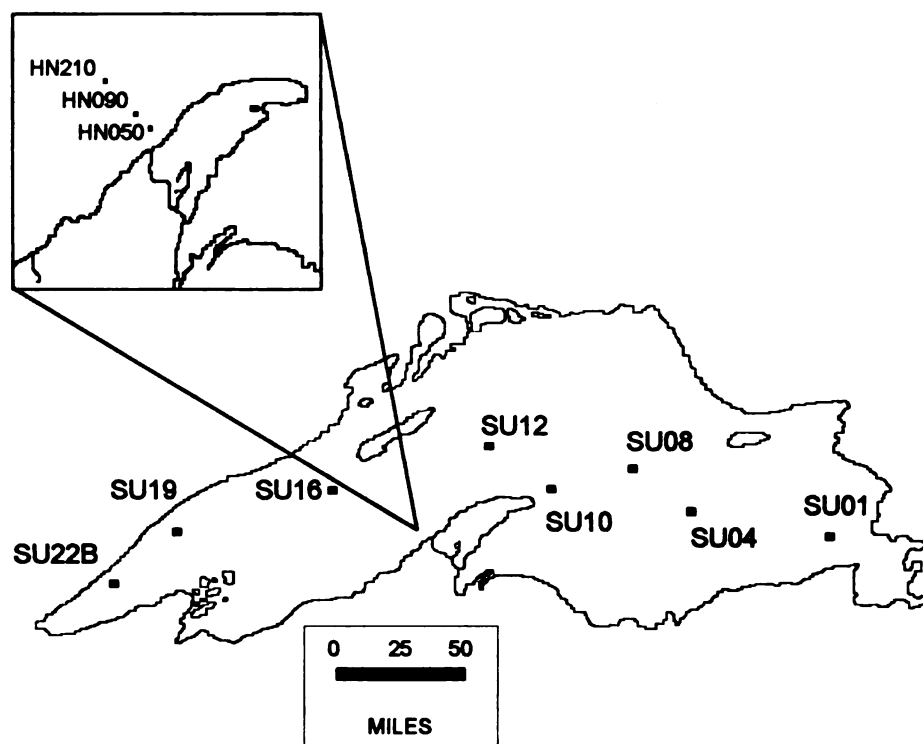


Figure 1.1: Locations of the stations comprising the West-East and HN (insert) transects in Lake Superior.

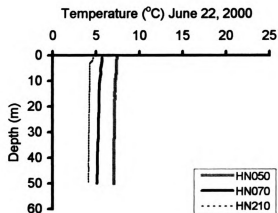
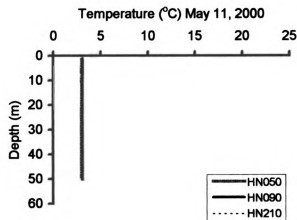
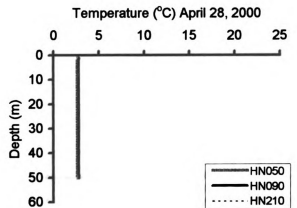


Figure 1.2a: Temperature as a function of depth for all stations along the HN transect in April through June 2000. Note: Mid-station HN070 was sampled in June instead of HN090.

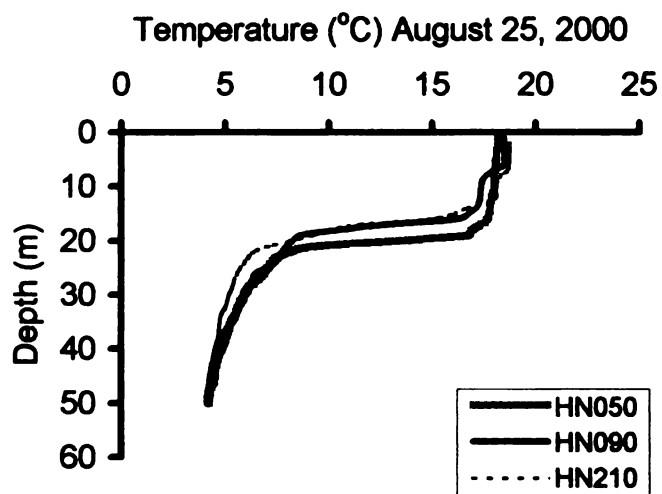
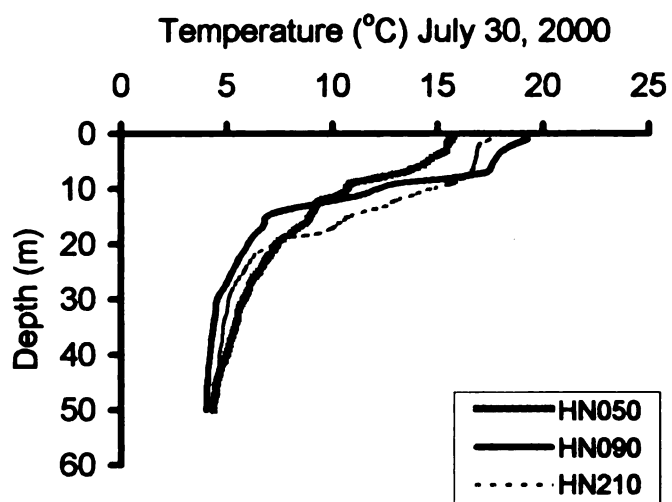


Figure 1.2b: Temperature as a function of depth for all stations along the HN transect in July and August 2000.

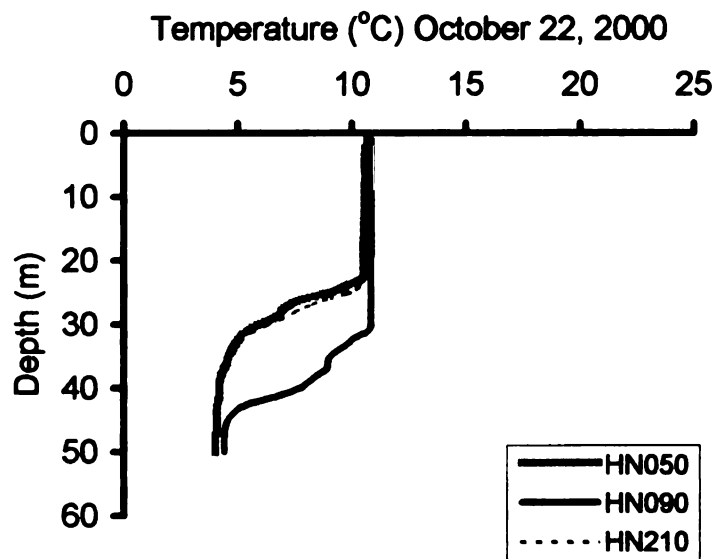
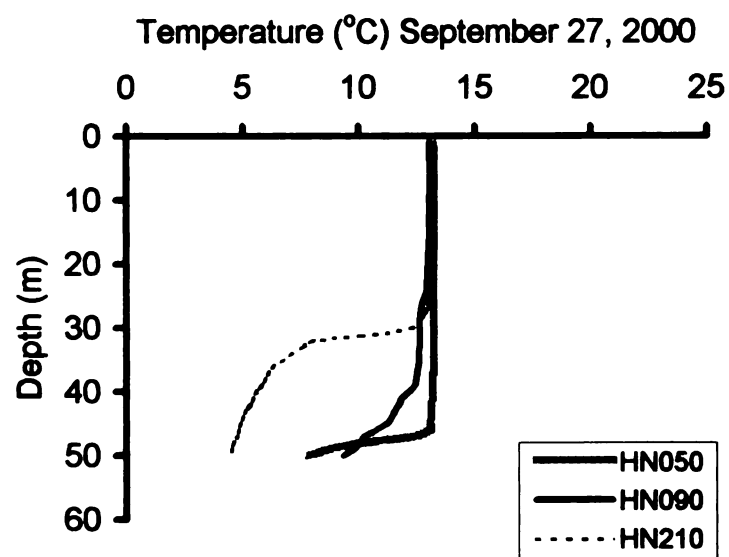


Figure 1.2c: Temperature as a function of depth for all stations along the HN transect in September and October 2000.

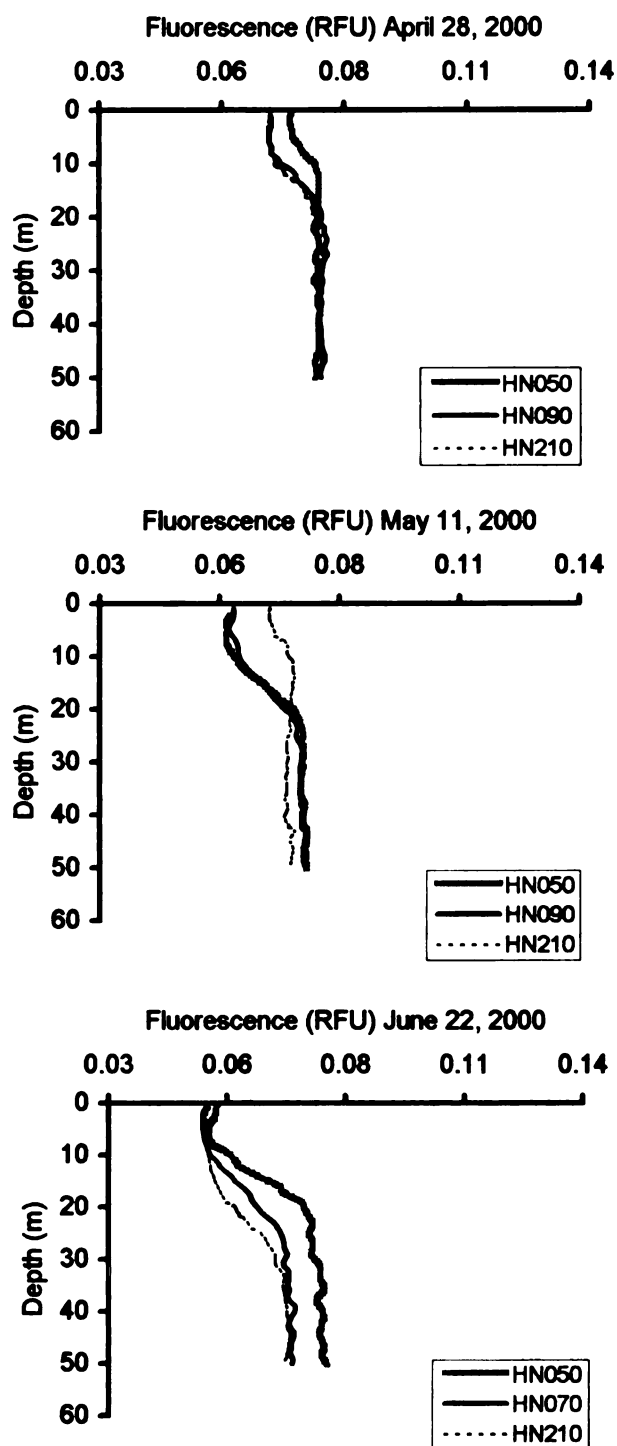


Figure 1.3a: Chlorophyll fluorescence as a function of depth for all stations along the HN transect in April through June 2000. Note: Mid-station HN070 was sampled in June instead of HN090.

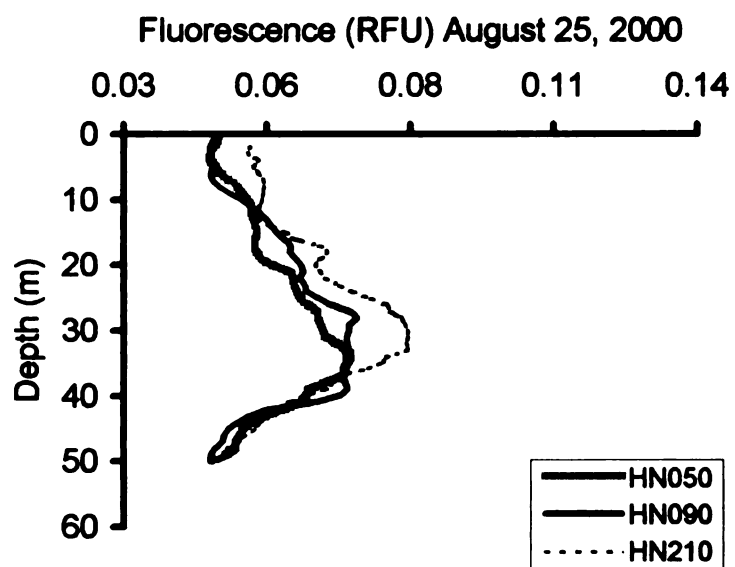
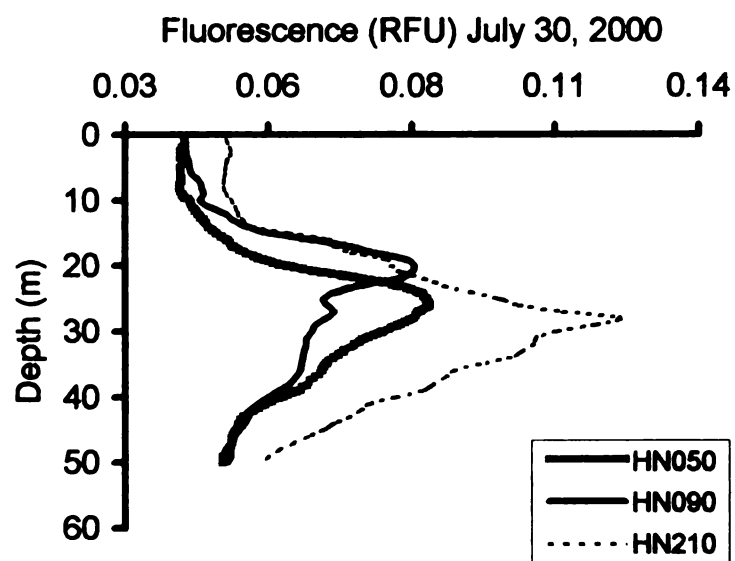


Figure 1.3b: Chlorophyll fluorescence as a function of depth for all stations along the HN transect in July and August 2000.

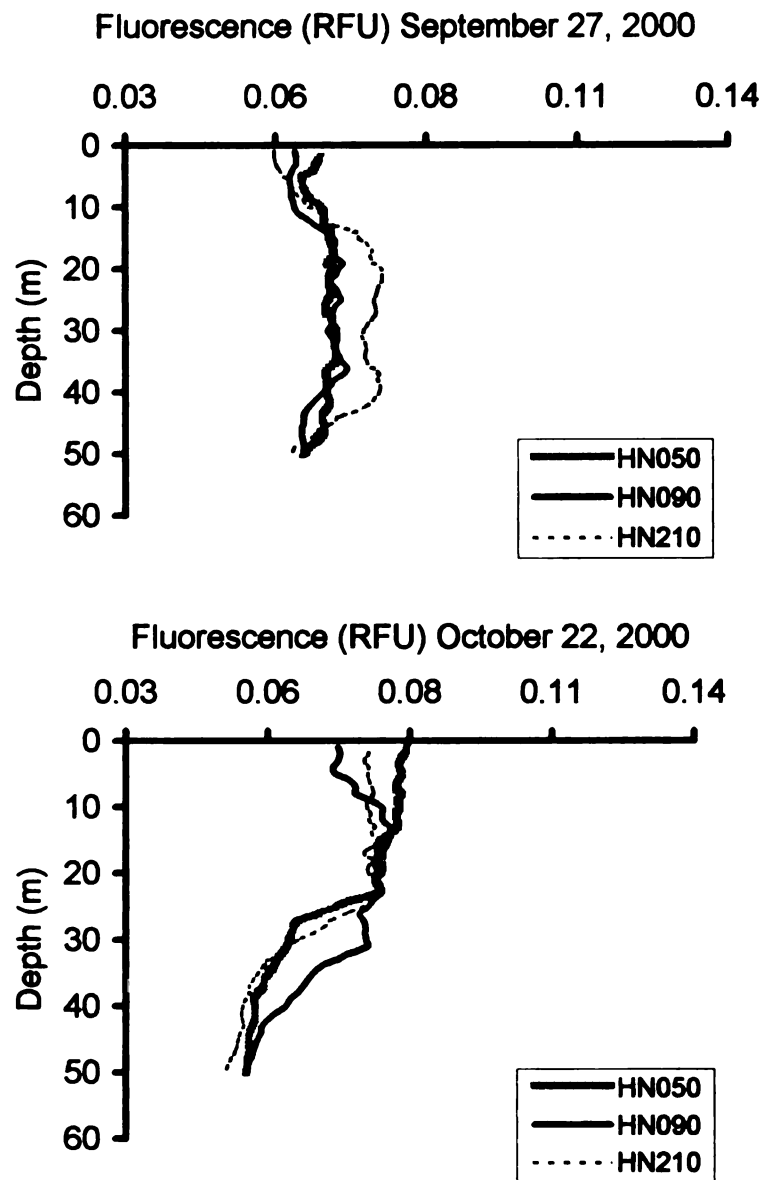


Figure 1.3c: Chlorophyll fluorescence as a function of depth for all stations along the HN transect in September and October 2000.

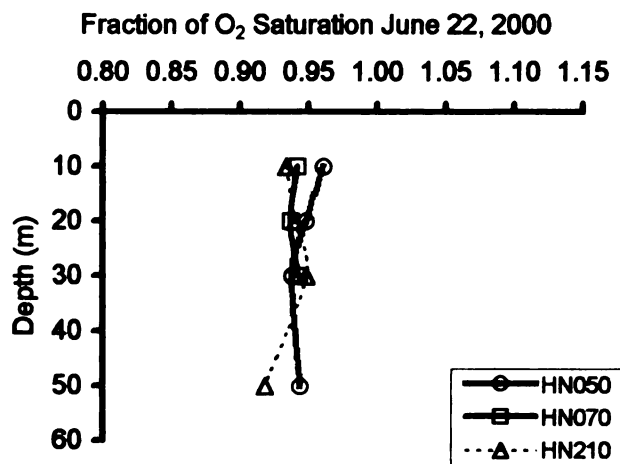
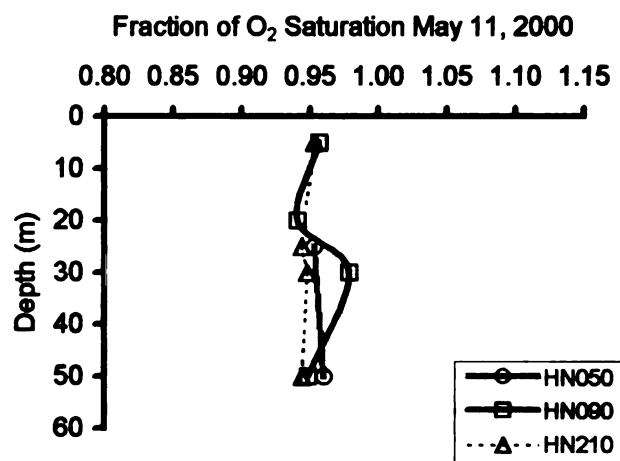
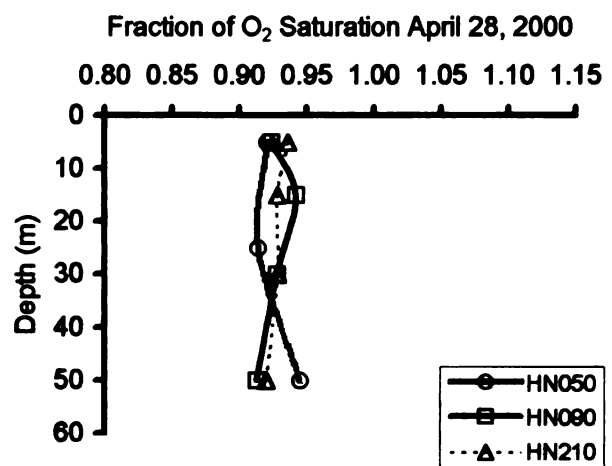


Figure 1.4a: The fraction of O₂ saturation as a function of depth for all stations along the HN transect in April, May and June 2000. Note: Mid-station HN070 was sampled in June instead of HN090.

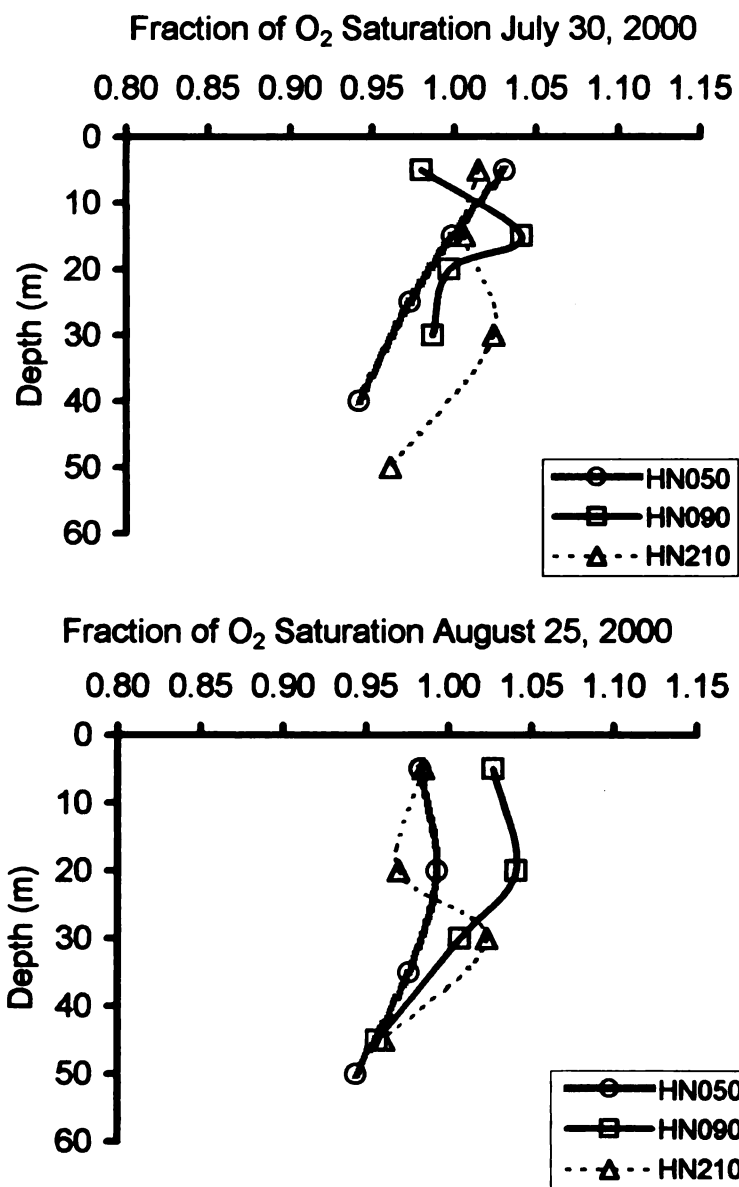


Figure 1.4b: The fraction of O₂ saturation as a function of depth for all stations along the HN transect in July and August 2000.

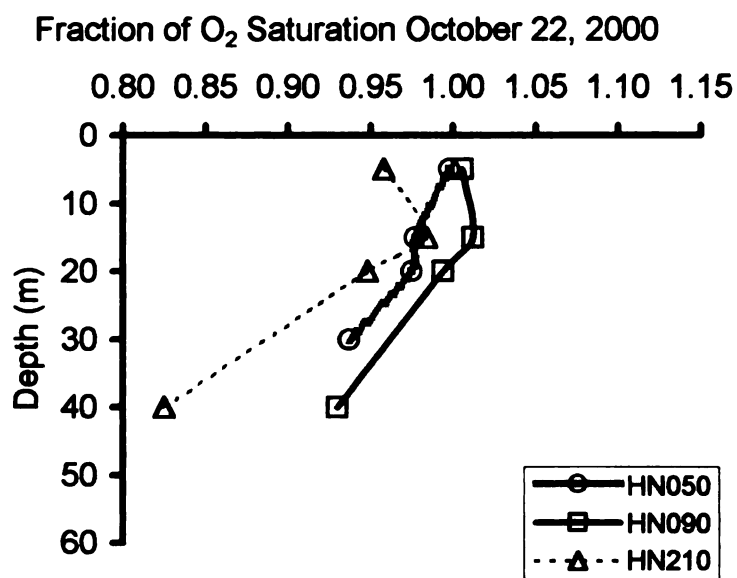
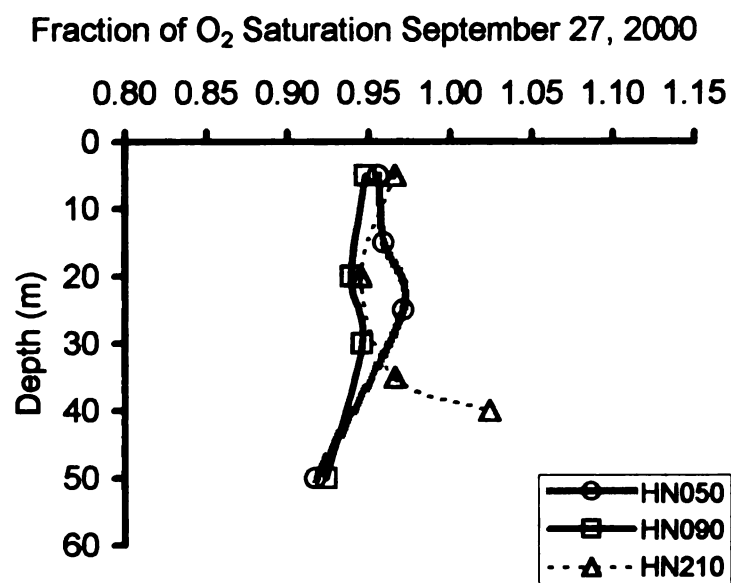


Figure 1.4c: The fraction of O₂ saturation as a function of depth for all stations along the HN transect in September and October 2000.

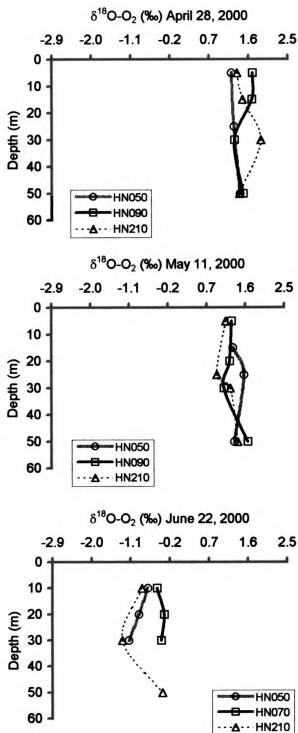


Figure 1.5a: The isotopic composition of O_2 as a function of depth for all stations along the HN transect in April, May and June 2000. Note: Mid-station HN070 was sampled in June instead of HN090.

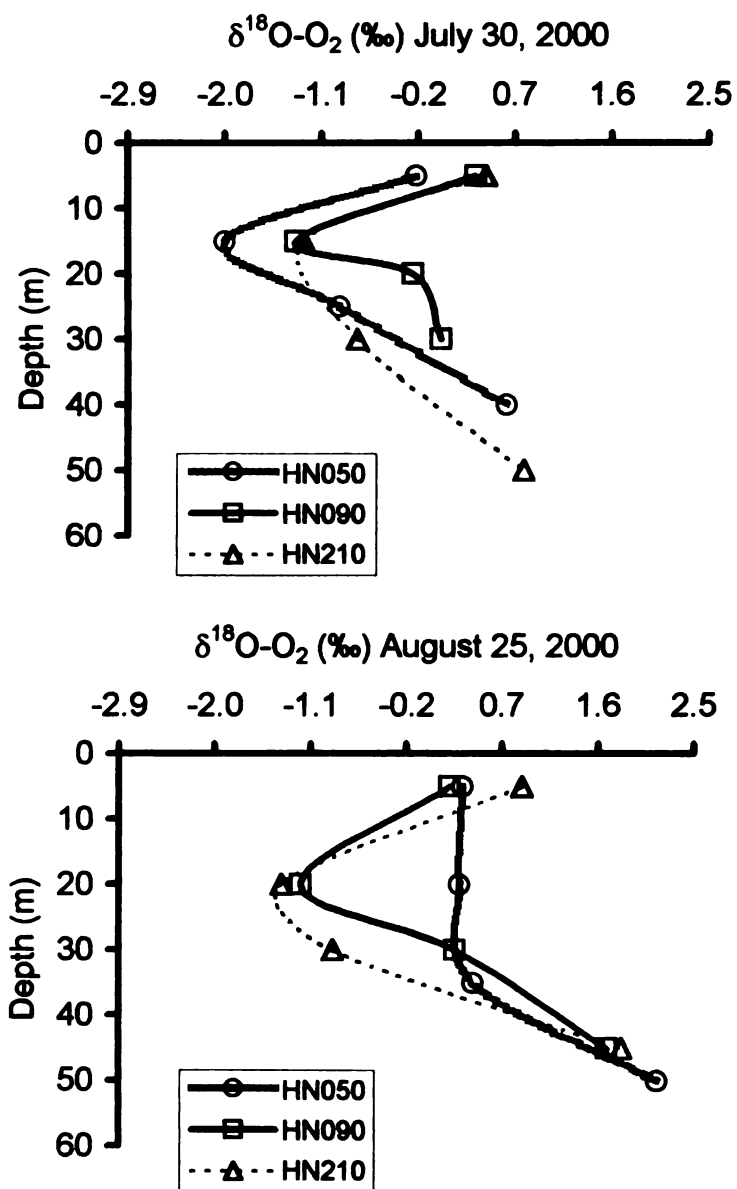


Figure 1.5b: The isotopic composition of O₂ as a function of depth for all stations along the HN transect in July and August 2000.

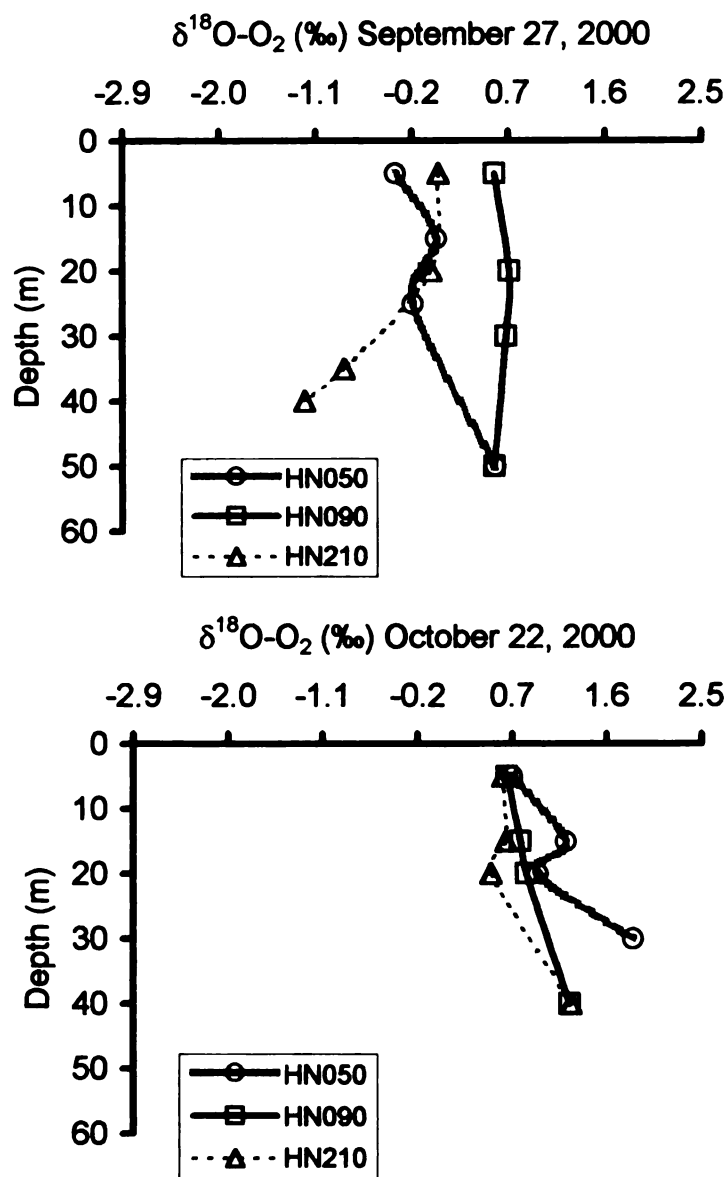


Figure 1.5c: The isotopic composition of O₂ as a function of depth for all stations along the HN transect in September and October 2000.

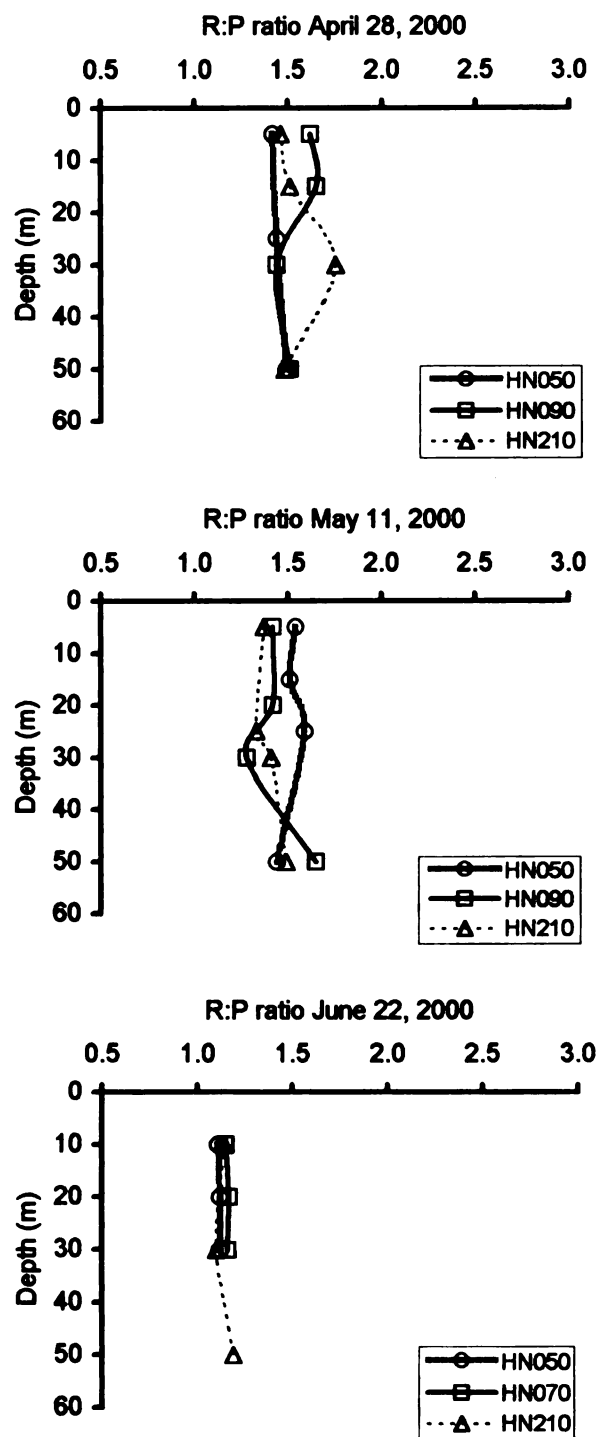


Figure 1.6a: Ratios of respiration to photosynthesis (R:P ratios) as a function of depth at all stations along the HN transect in April through June 2000. Note: Mid-station HN070 was sampled in June instead of HN090.

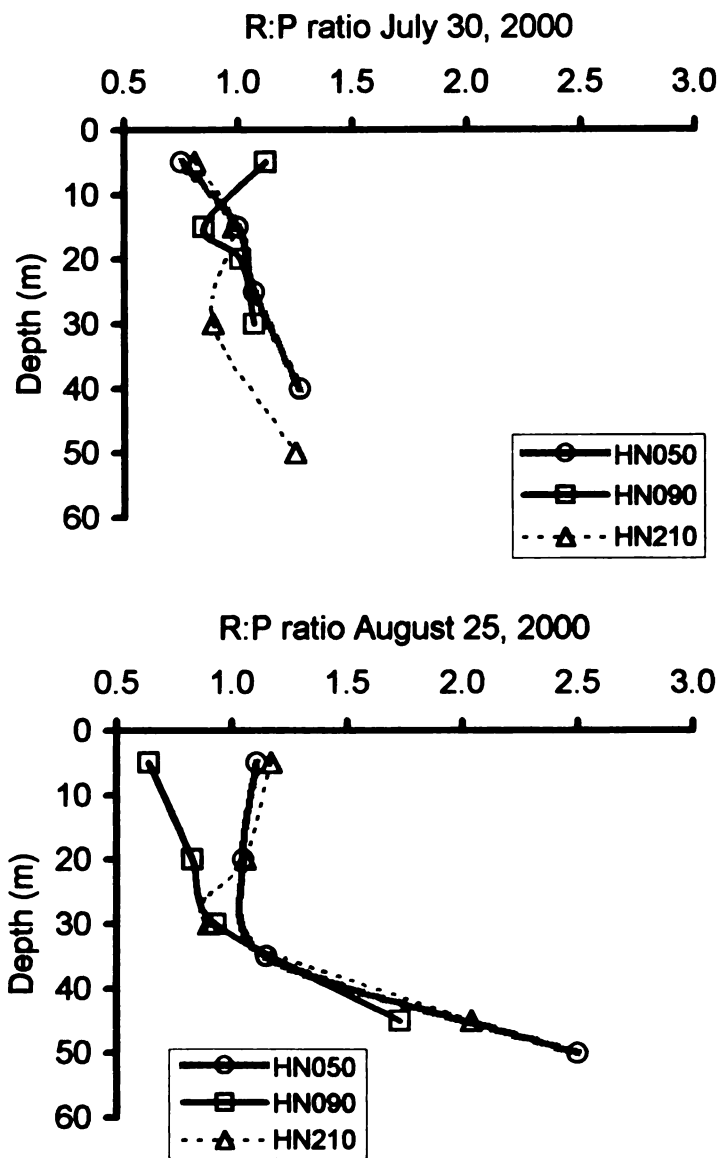


Figure 1.6b: Ratios of respiration to photosynthesis (R:P ratios) as a function of depth at all stations along the HN transect in July and August 2000.

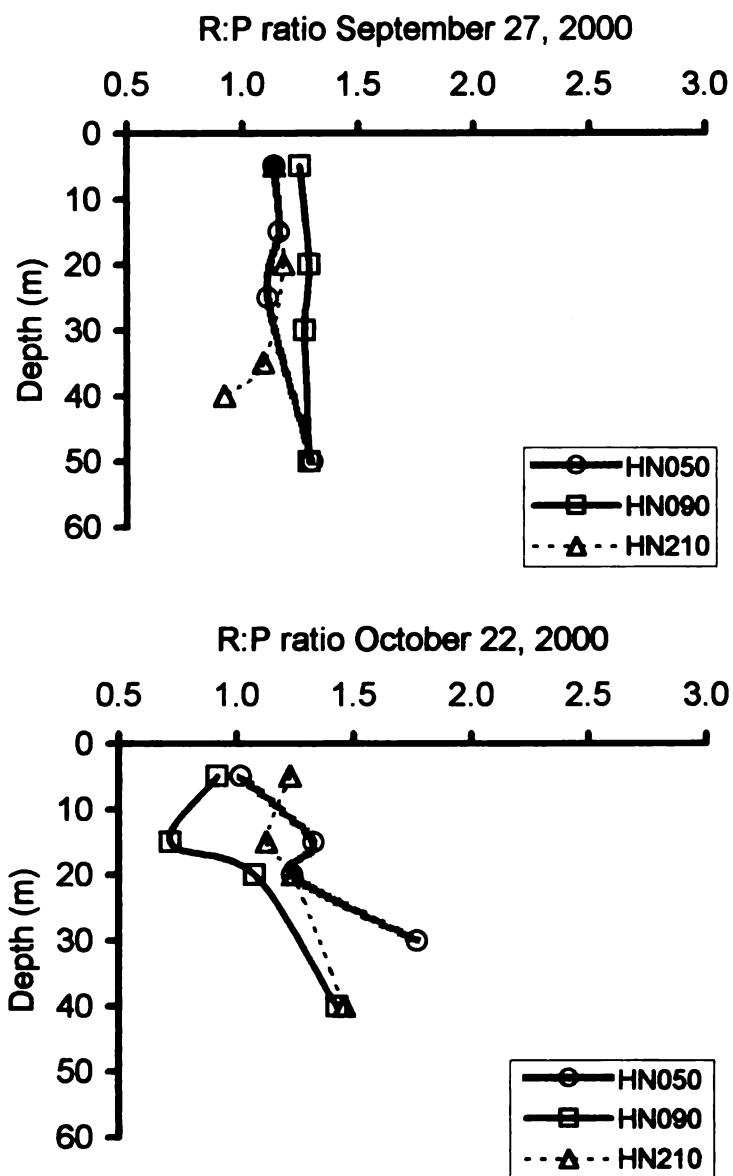


Figure 1.6c: Ratios of respiration to photosynthesis (R:P ratios) as a function of depth at all stations along the HN transect in September and October 2000.

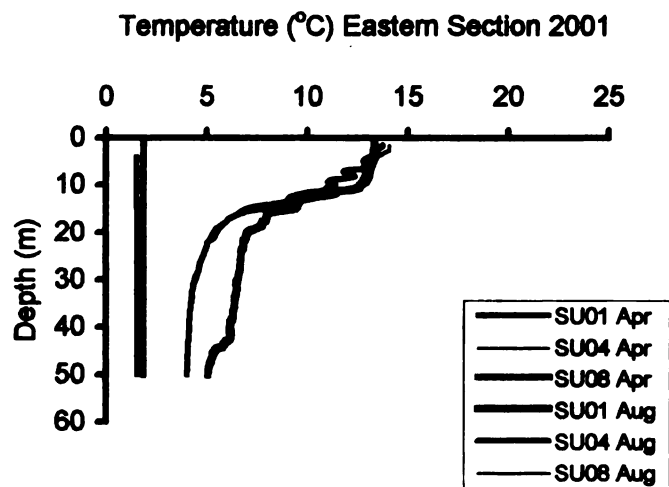
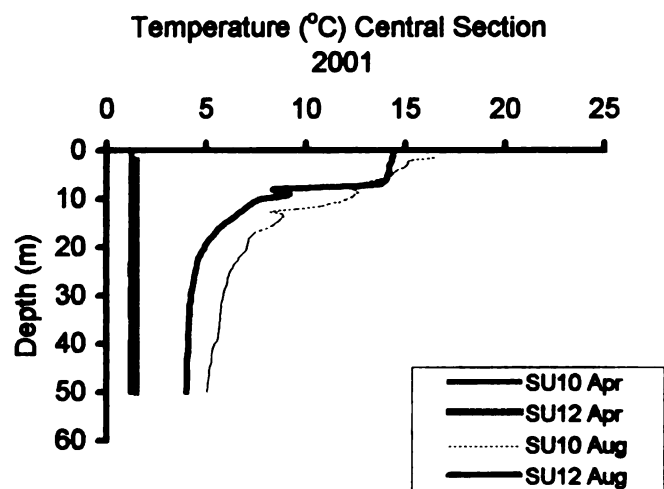
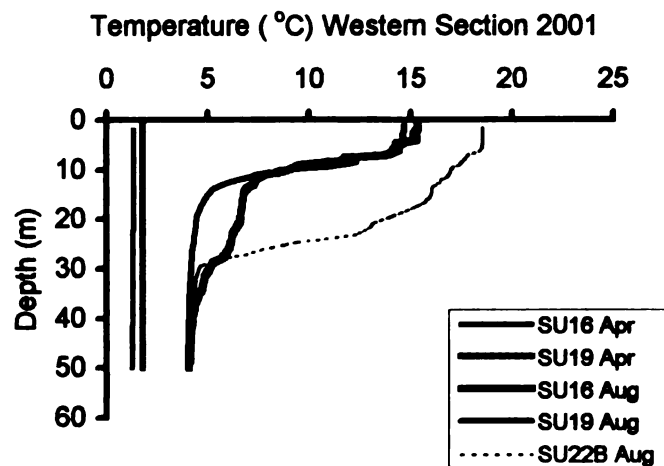


Figure 1.7: Temperature as a function of depth for all stations along the West-East transect in April and August 2001.

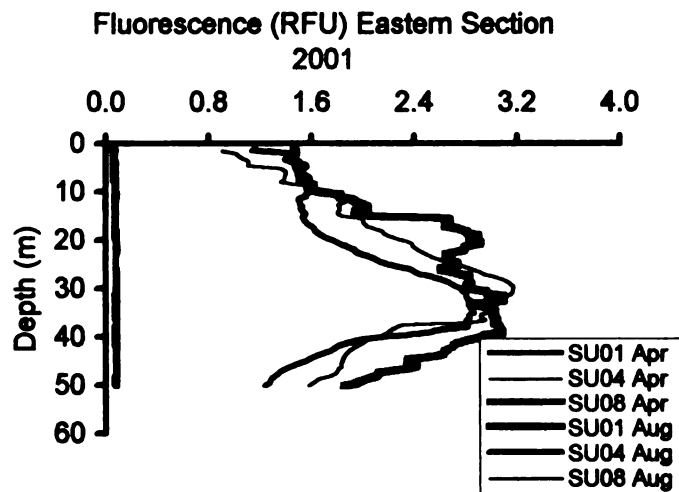
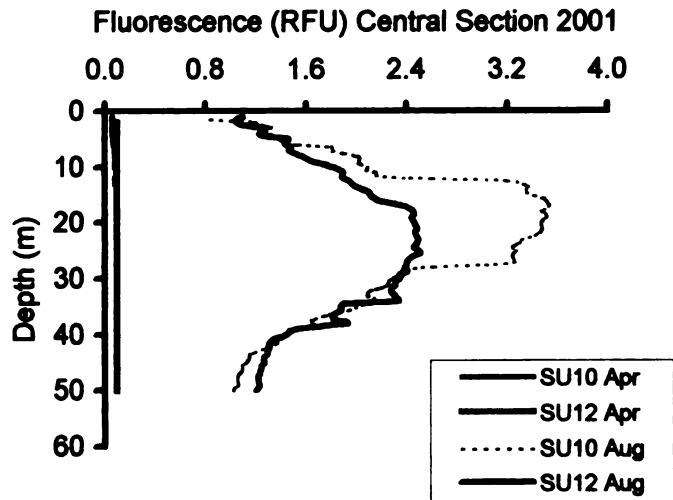
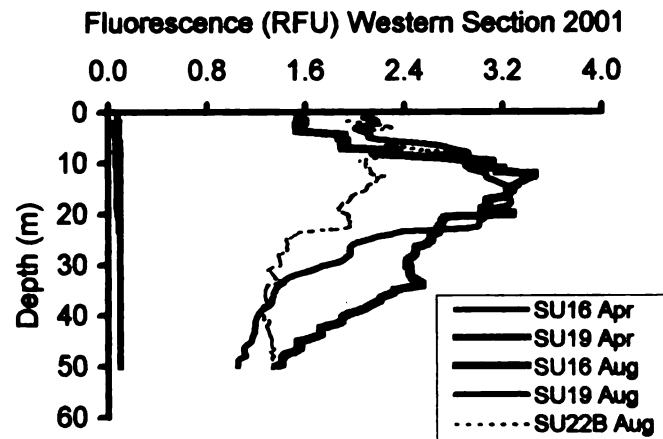


Figure 1.8: Chlorophyll fluorescence as a function of depth for all stations along the West-East transect in April and August 2001.

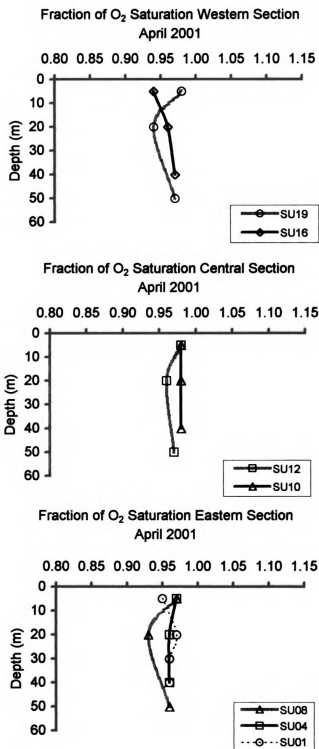


Figure 1.9: The fraction of O_2 saturation as a function of depth for all stations along the West-East transect in April 2001.

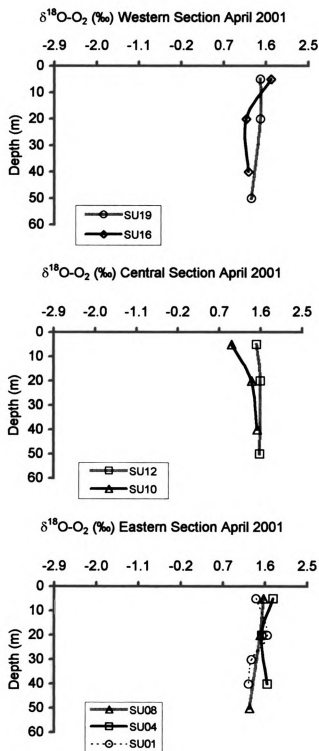


Figure 1.10: The isotopic composition of O_2 as a function of depth for all stations along the West-East transect in April 2001.

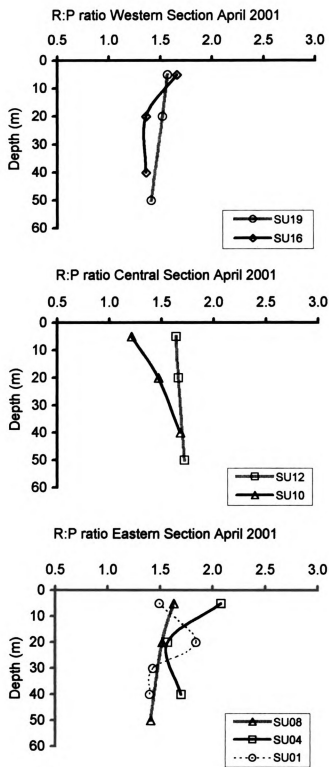


Figure 1.11: The R:P ratios as a function of depth for all stations along the West-East transect in April 2001.

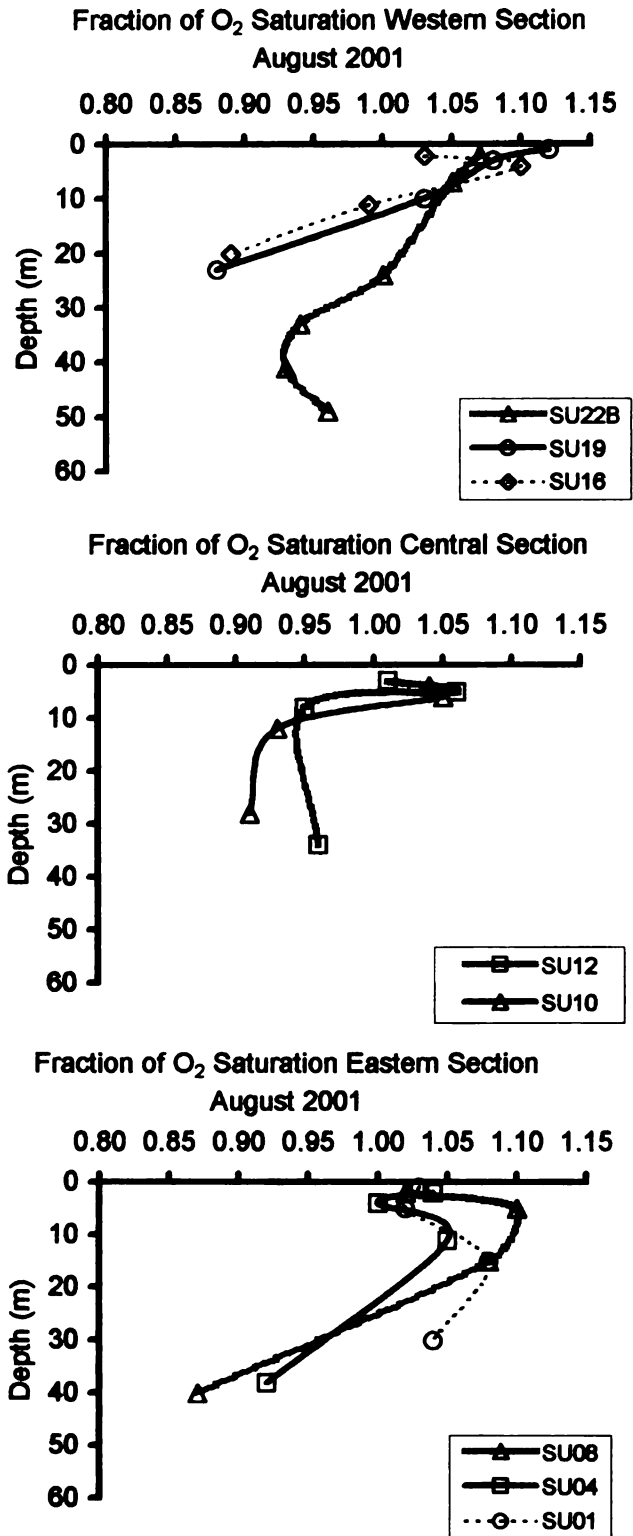


Figure 1.12: The fraction of O₂ saturation as a function of depth for all stations along the West-East transect in August 2001.

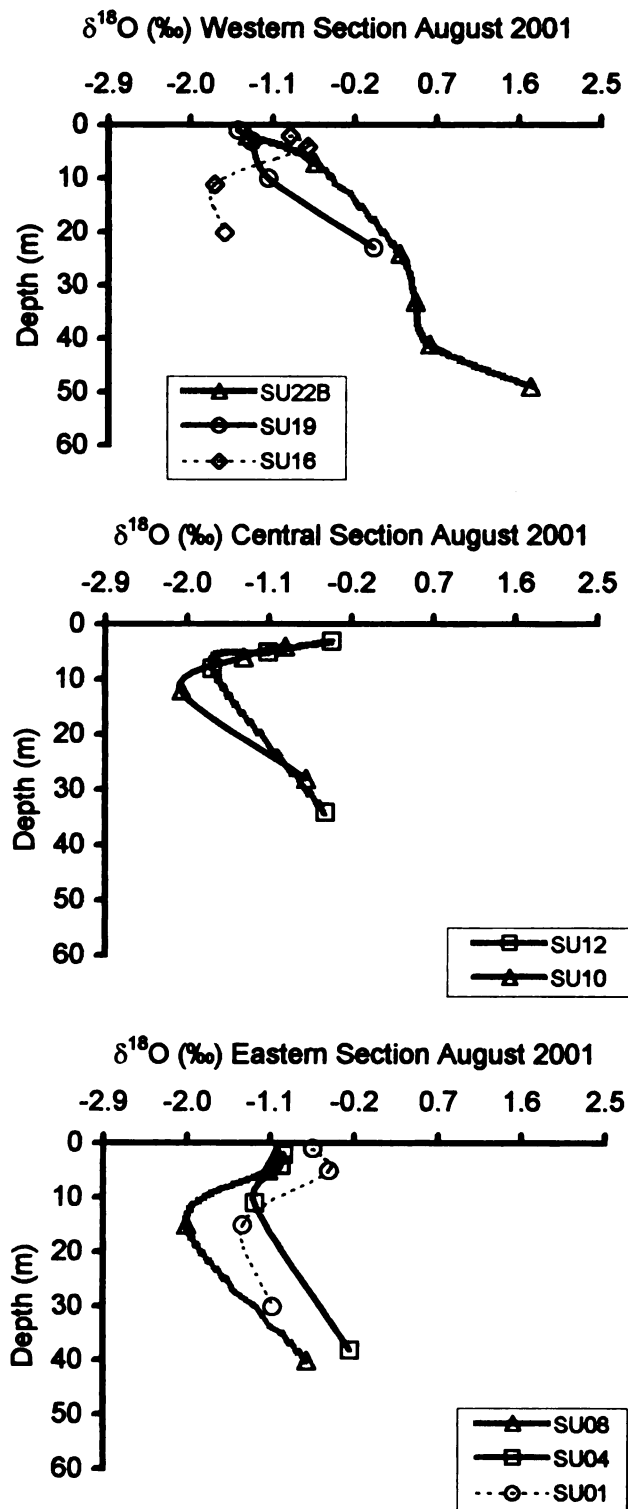


Figure 1.13: The isotopic composition of O_2 as a function of depth for all stations along the West-East transect in August 2001.

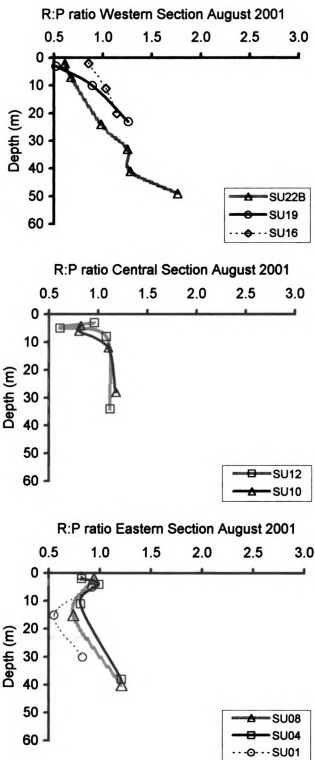
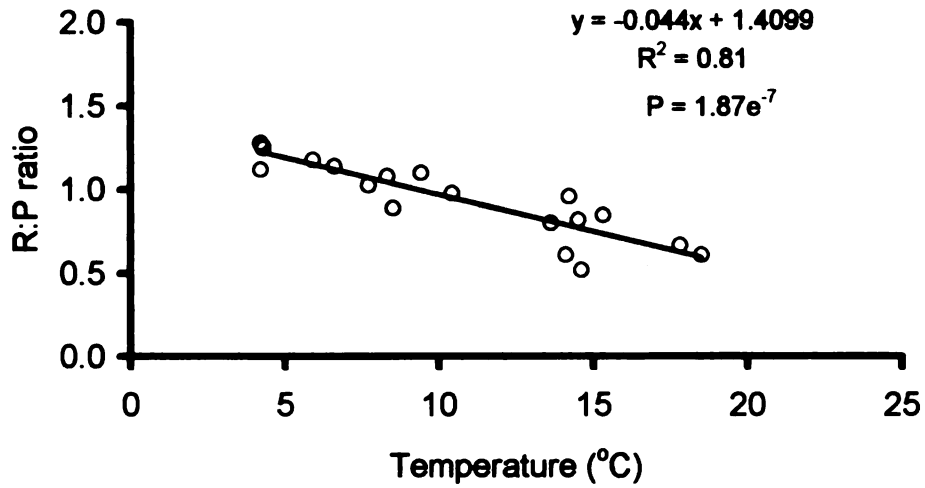


Figure 1.14: The R:P ratios as a function of depth for all stations along the West-East transect in August 2001.

Western and Central Section
Stations SU10, SU12, SU16, SU19, SU22B
August 2001



Eastern Section
Stations SU01, SU04, SU08
August 2001

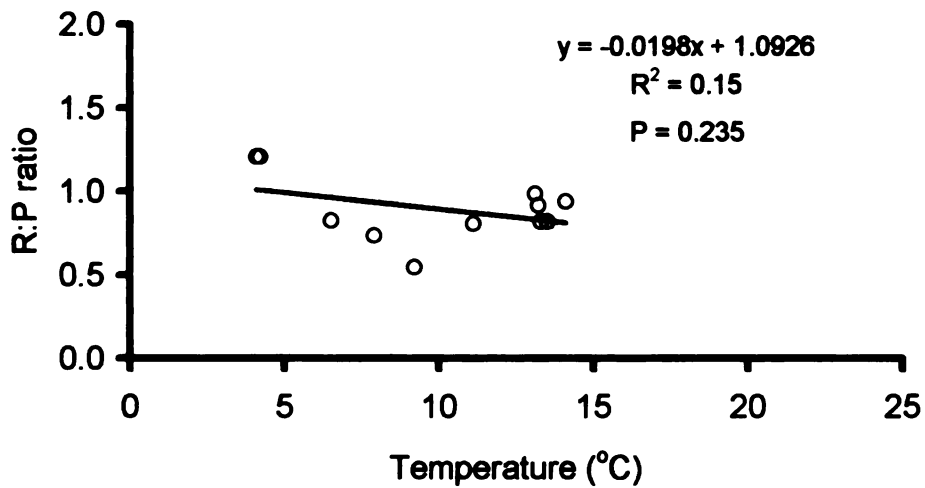
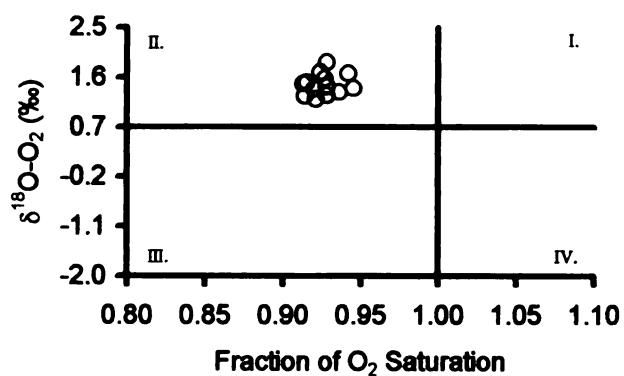


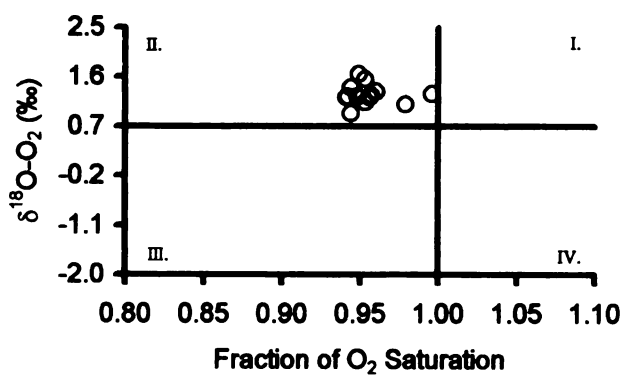
Figure 1.15: R:P ratios as a function of temperature for the western and central sections ($df = 17$, $\alpha = .05$) and the eastern section ($df = 9$, $\alpha = .05$) in August 2001.

Figure 1.16a: The fraction of O₂ saturation as a function of the isotopic composition of O₂ during April, May and June 2000, within the mixed layer along the HN transect. The locus of the fraction of O₂ saturation equal to 1.00 and the isotopic composition equal to 0.7 ‰ represents a system at atmospheric O₂ saturation. Data points within quadrant II represents R:P ratios greater than 1.0 or net heterotrophy, within quadrant III R:P ratios equal to 1.0 or a balance of respiration to photosynthesis, and within quadrant IV R:P ratios less than 1.0 or net autotrophy.

April 28, 2000



May 11, 2000



June 22, 2000

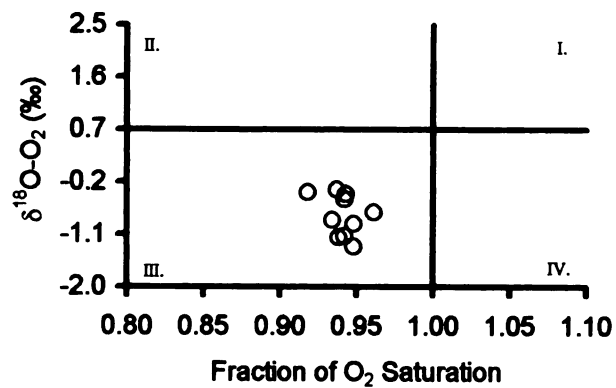
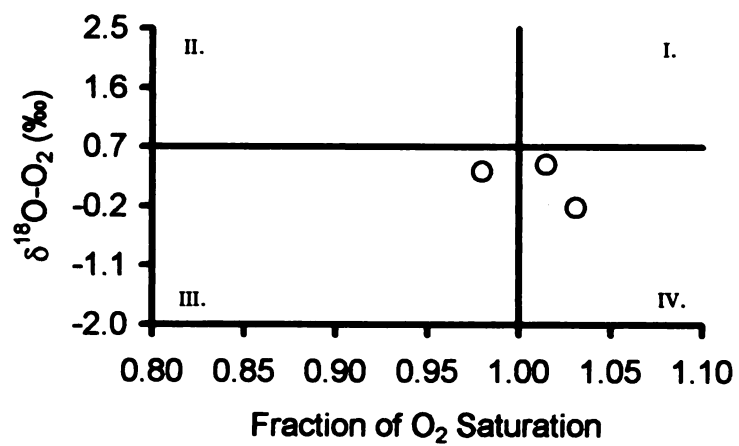


Figure 1.16a

Figure 1.16b: The fraction of O₂ saturation as a function of the isotopic composition of O₂ during July and August 2000, within the mixed layer along the HN transect. The locus of the fraction of O₂ saturation equal to 1.00 and the isotopic composition equal to 0.7 ‰ represents a system at atmospheric O₂ saturation. Data points within quadrant II represents R:P ratios greater than 1.0 or net heterotrophy, within quadrant III R:P ratios equal to 1.0 or a balance of respiration to photosynthesis, and within quadrant IV R:P ratios less than 1.0 or net autotrophy.

July 30, 2000



August 25, 2000

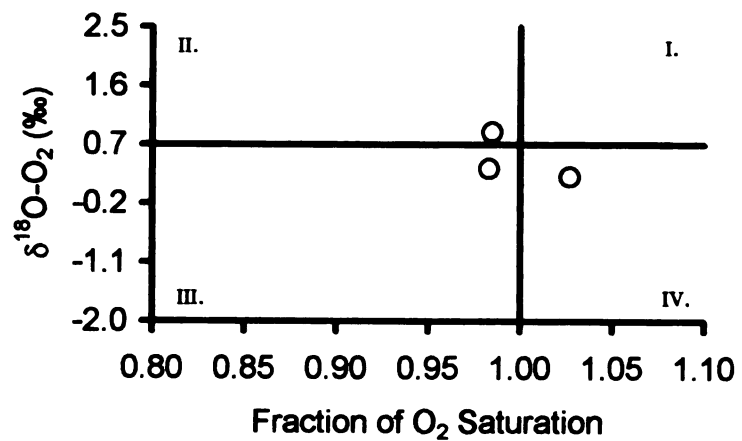
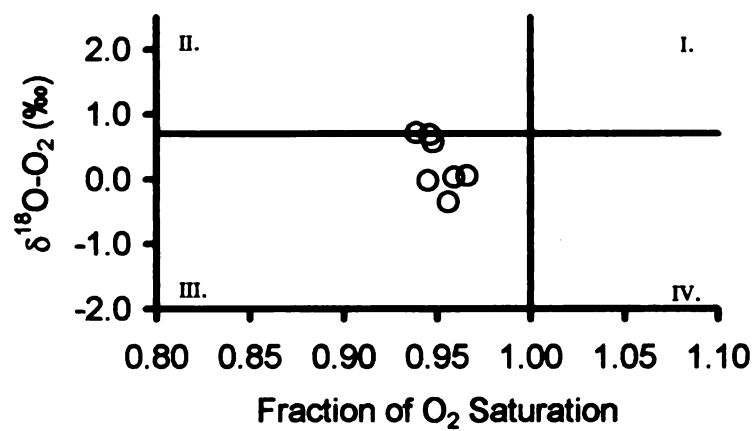


Figure 1.16b

Figure 1.16c: The fraction of O₂ saturation as a function of the isotopic composition of O₂ during September and October 2000, within the mixed layer along the HN transect. The locus of the fraction of O₂ saturation equal to 1.00 and the isotopic composition equal to 0.7 ‰ represents a system at atmospheric O₂ saturation. Data points within quadrant II represents R:P ratios greater than 1.0 or net heterotrophy, within quadrant III R:P ratios equal to 1.0 or a balance of respiration to photosynthesis, and within quadrant IV R:P ratios less than 1.0 or net autotrophy.

September 27, 2000



October 22, 2000

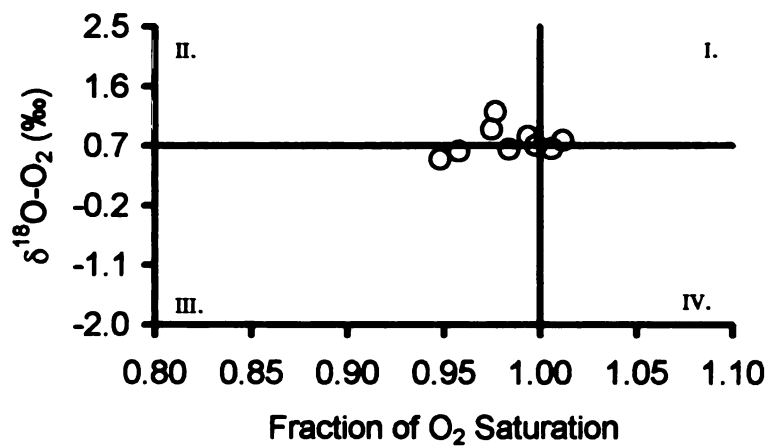


Figure 1.16c

Figure 1.17: O₂ gas exchange as a function of R:P ratios during periods of net autotrophy (df = 2, α = .05), periods of respiration equal to photosynthesis (df = 7, α = .05), and periods of net heterotrophy (df = 7, α = .05) for all depths within the mixed layer for all stations along the HN transect in April through October 2000. Note: For the delineation of each period see Figures 1.16a-c.

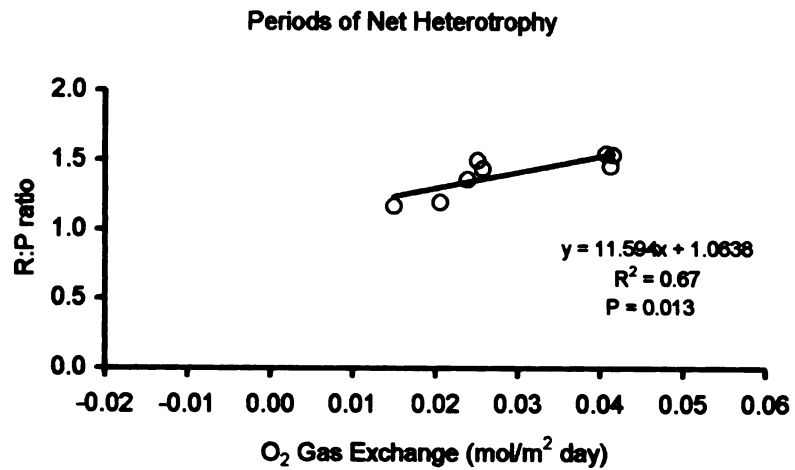
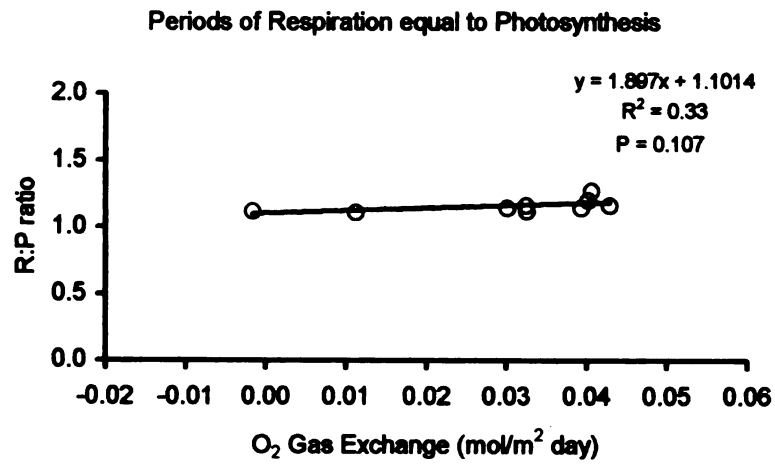
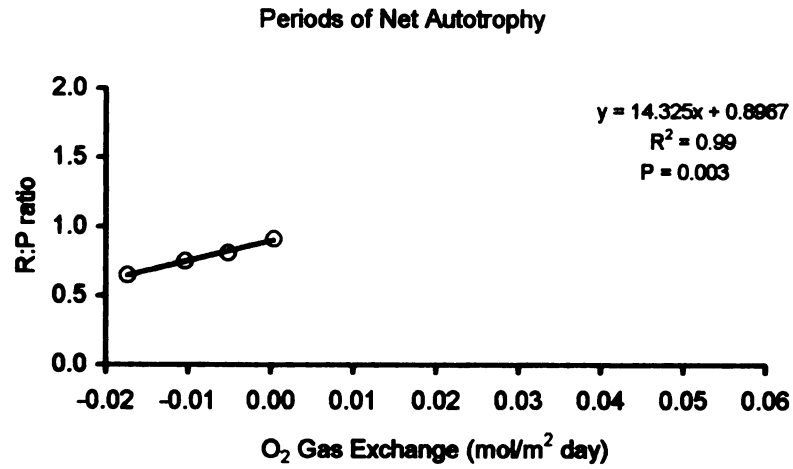


Figure 1.17

Chapter 2

TEMPORAL, SPATIAL AND STORM RELATED CHANGES IN R:P RATIOS IN THE NORTH PACIFIC OCEAN

Background

Phytoplankton photosynthesis within oceanic environments is estimated to contribute approximately one half of total global primary production (Falkowski, 1994; Duarte and Agusti, 1998; Williams, 1998; Karl, 1999). New phytoplankton production within the ocean mixed layer provides, via the biological pump, a source of organic carbon to the water column below the pycnocline, which is then available to fuel heterotrophic respiration at depth (Volk and Hoffert, 1985; Fiedler et al., 1991). In addition, photosynthesis within the ocean surface waters results in atmospheric CO₂ drawdown and the ocean, therefore, acts as a CO₂ sink (Volk and Hoffert, 1985; Sarmiento and Siegenthaler, 1992). Respiration within the mixed layer has the potential to reduce the flux of organic carbon from surface waters to regions below the pycnocline (Geider, 1992). Furthermore, if a predominance of respiration over photosynthesis exists within surface waters, the ocean would be a CO₂ source to the atmosphere (Smith and Mackenzie, 1987; Duarte and Agusti, 1998; Williams, 1998). Previous studies have disagreed on the global ratio of respiration to photosynthesis (R:P ratio) within the upper ocean, claiming both overall net heterotrophy (R:P ratio greater than 1) and overall net autotrophy (R:P ratio less than 1) (Smith and Mackenzie, 1987; Williams, 1998). Duarte and Agusti (1998) further suggest that there exists a spatial variation in R:P ratios, such that oligotrophic environments are net heterotrophic, and eutrophic environments are net autotrophic and that there is an overall balance between respiration and photosynthesis

within the global ocean. The resolution of this debate is required in order to determine the status of the world's ocean as a source or sink of CO₂, especially during the current period of increasing atmospheric CO₂ levels (Lashof and Ahuja, 1990; Falkowski, 1994).

In order to address this question, this study uses the concentration and isotopic composition of O₂ to calculate R:P ratios and gross O₂ production (Bender and Grande, 1987; Quay et al., 1995; Luz et al., 1999; 2000) along a transect from the open ocean oligotrophic waters of the North Pacific subtropical gyre (NPSG) to the coastal upwelling zone of the eastern tropical North Pacific (ETNP). The spatial extent of this transect, across regions of varying nutrient concentrations, [O₂], and degrees of phytoplankton productivity, allows for evaluation and comparison of R:P ratios within contrasting ocean environments. This study, therefore, is an extensive evaluation of the balance between respiration and photosynthesis across a broad spatial scale within the central and eastern North Pacific ocean.

The ETNP is an active area of tropical cyclone formation, with the second highest number of named tropical cyclones compared to all other oceanic regions (Vincent and Fink, 2001). Such episodic disturbances are believed to enhance autotrophic production, as increased wind speeds during storms intensify water column mixing and redistribute nutrients and phytoplankton biomass to surface waters from below the pycnocline (Falkowski, 1994; Karl, 1999). Due to the intensity of the tropical cyclones (Vincent and Fink, 2001), few *in situ* studies of the effects of storm events on phytoplankton production have been attempted within the Pacific ocean (Ditullio and Laws, 1991). During this study, however, two tropical cyclones formed in the ETNP, offering a rare opportunity to quantify variations in nutrient concentrations, [O₂] and the isotopic

composition of O_2 before, during and after a storm event. A second objective, therefore, was to evaluate the effects of an episodic disturbance on the balance of respiration to photosynthesis, and evaluate the impact of storm events on phytoplankton productivity within the ocean mixed layer.

Methods

Sampling during the Eastern Pacific Redox Experiment (EPREX) cruise was performed aboard the RV Roger Revelle, from May 24 to June 28, 2000. Six stations were sampled along a transect consisting of station ALOHA, located 100 km north of the island of Oahu within the NPSG, a station on the fringe of the NPSG, S2, and four stations within the ETNP, located along 16° N from 136° W to 98° W, S3 through S6 (Figure 2.1). Four additional cruises to station ALOHA, three aboard the RV Moana-Wave during, October 17-21, 1998 (HOT98), January 11-15, 1999 (HOT101), and April 12-16, 1999 (HOT104), and the Aka Aka Ea cruise aboard the RV Ka'imikai-O-Kanaloa during July 20-28, 1999 (AKA) were conducted as part of the Hawaii Ocean Time Series study. At each station water was collected at discrete depths throughout the water column for analysis of nutrients, $[O_2]$, and $\delta^{18}O-O_2$, using a rosette containing 24 Niskin sampling bottles. In addition, water was collected during the EPREX cruise at station ALOHA, S3, S4, S5 (prior to the storm) and S6 (after the storm) for $\delta^{17}O-O_2$ analysis. A SeaBird Electronics CTD profiler was deployed to determine temperature, salinity and fluorescence as a function of depth within the water column. A modified Winkler method was used to measure $[O_2]$ (Grasshoff et al., 1983). The analysis of the $\delta^{18}O-H_2O$ was performed at the University of Hawaii, Honolulu, following the method of Epstein

and Mayeda (1953). Water samples from the EPREX cruise were analyzed for $[\text{NO}_3^-]$ by the University of Washington Technical Services, Seattle, Washington.

Collection of water samples for determination of the isotopic composition of O_2 and R:P ratios followed the protocol of Emerson et al. (1991;1999). Samples were collected in pre-evacuated 200 mL glass vessels fitted with high vacuum stopcocks. Prior to use, 1 mL of saturated HgCl_2 was added to each vessel and dried, in order to eliminate biological activity following collection. Immediately before and after samples were collected, the vessel inlet was flushed with CO_2 to displace air. Headspace gases were equilibrated at a constant temperature water bath ($\sim 24^\circ\text{C}$) for at least 4 hours, under continuous rotation. After equilibration, water was removed by vacuum until 1 mL remained in the vessel. Due to limited sampling vessels and storage space, the majority of samples collected during the EPREX cruise were cryogenically transferred within a high vacuum system onto molecular sieve 5 Å 1/16" x 1/4" Alltech pellets and sealed in 10" pyrex tubes for later onshore analysis. Samples not transferred remained in sampling vessels and the inlets were flushed periodically with CO_2 to prevent air contamination from potential leakage across the stopcock seals.

Upon returning to the lab, samples stored on molecular sieve were cryogenically transferred, under vacuum, back to sampling vessels via liquid He, and the determination of $\delta^{18}\text{O}-\text{O}_2$ was accomplished using gas chromatography interfaced to a stable isotope ratio mass spectrometer (Roberts et al., 2000). The sample vessel was connected to an inlet system on the gas chromatograph that consists of, in series, an ascarite trap to remove water and CO_2 , a 3 mL gas sampling loop between two Valco sampling valves (one 6 port and one 4 port), a vacuum isolation valve, and a vacuum pump. Initially, the

inlet system was completely evacuated before closing the isolation valve separating the inlet system from the vacuum pump. The stopcock on the vessel was opened and sample gas was allowed to equilibrate for 10 seconds within the inlet system. Upon rotation of the Valco valves, sample gas was carried by He flow onto a 5 m by 1/8" OD molecular sieve 5 Å GC Alltech column, and N₂ and O₂ were separated in time. Any residual water or CO₂ entering the GC column was efficiently trapped onto the molecular sieve column and removed later by heating. The effluent of the gas chromatograph was routed to the mass spectrometer and sample isotopic ratios were determined by comparison to a reference pulse of previously characterized pure O₂ tank standard. Stable isotope ratios for O are expressed in per mil (‰) notation:

$$\delta^{18}\text{O} = [(R_{\text{sample}}/R_{\text{standard}})-1] * 1000 \quad (1)$$

where R is the ratio of ¹⁸O to ¹⁶O. All δ¹⁸O-O₂ values are expressed with respect to air, which is enriched in ¹⁸O by 23.5 ‰ relative to VSMOW, resulting in a δ¹⁸O value of VSMOW, with respect to air, of - 23.5 ‰. The analysis of δ¹⁷O-O₂ was performed at the Institute of Earth Sciences at the Hebrew University of Jerusalem, Jerusalem, Israel, following the method in Luz et al., (1999; 2000).

Determination of R:P ratios

Photosynthesis, respiration and gas exchange at the air/water interface control the concentration and isotopic composition of O₂ (Bender and Grande, 1987; Quay et al., 1995). These three processes are represented by the following equation:

$$d[\text{O}_2]/dt = P - R + F_{\text{O}_2} \quad (2)$$

where d[O₂]/dt is the change in the concentration of O₂ over time, P is the rate of photosynthesis, R is the rate of respiration, and F_{O₂} is the air/water gas exchange rate.

Air/water gas exchange is generally the primary process controlling the isotopic composition and concentration of O₂ within the upper water column. The δ¹⁸O-O₂ in the atmosphere is defined as 0 ‰ with respect to air. A small fractionation effect during dissolution results in ¹⁸O enrichment of O₂ in surface waters by approximately 0.7 ‰ (Knox et al., 1992). The O₂ produced during photosynthesis is derived from water (Stevens et al., 1975; Guy et al., 1993), and the δ¹⁸O-H₂O at station ALOHA was determined to have an average isotopic value of -23.1 ± 0.5 ‰ (n = 33) with respect to air. Photosynthesis, therefore, not only increases [O₂], but also results in a decrease in δ¹⁸O-O₂. In contrast, during respiration, O₂ is consumed and the residual O₂ pool is enriched in ¹⁸O by a kinetic isotope effect, in which the lighter ¹⁶O isotope, is preferentially consumed (Kiddon et al., 1993). Each of these processes uniquely affects both the concentration and isotopic composition of O₂. In general, δ¹⁸O-O₂ values equal to 0.7 ‰ reflect the predominance of atmospheric gas exchange, those less than 0.7 ‰ reveal the contribution of O₂ from photosynthesis, and values greater than 0.7 ‰ indicate the effect of O₂ consumption by respiration (Bender and Grande, 1987). The concentration and isotopic composition of the residual O₂ pool will, therefore, reflect the balance of these processes at any depth in the water column.

Based on the influences of photosynthesis, respiration and air/water gas exchange on the concentration and isotopic composition of O₂, equation 2 is expanded (Quay et al., 1995):

$$d(^{18/16}\text{O})/dt = G_{O_2}/Z \alpha_g \{ ([O_2]_{\text{sat}} ^{18/16}\text{O}_a \alpha_s) - [O_2] ^{18/16}\text{O} \} + P ^{18/16}\text{O}_w \alpha_p - R ^{18/16}\text{O} \alpha_r \quad (3)$$

where G_{O_2} is the gas transfer coefficient, Z is depth, $[O_2]_{sat}$ is the saturation concentration of O_2 (Weiss, 1970), $[O_2]$ is the concentration of O_2 in the water column, $^{18/16}O_w$ is the measured isotopic composition of water, α_p is the fractionation factor associated with photosynthesis (1.0000; Guy et al., 1993), $^{18/16}O$ is the measured isotopic ratio of O_2 , α_r is the fractionation factor associated with respiration (0.9800; Kiddon et al., 1993), α_g is the fractionation factor associated with gas transfer (0.9972; Knox et al., 1992), $^{18/16}O_a$ is the isotopic ratio of atmospheric O_2 (Kroopnick and Craig, 1972), and α_s is the fractionation factor associated with gas dissolution (1.0073; Benson and Krause, 1984). Fractionation factors are defined here as a ratio of the reaction rates of the heavy, ^{18}O , to the light, ^{16}O , isotope.

Previously published α_r values for marine systems range from 0.9780 for the subarctic Pacific ocean (Quay et al., 1993), to an average value of 0.9800 for specific marine plankton and bacteria (Kroopnick, 1975; Kiddon et al., 1993). The slightly higher averaged value was used in this study because an α_r value reflecting the subarctic Pacific ocean may not be valid in the warm waters of the subtropical/tropical Pacific ocean.

R:P ratios are calculated from the measured values of $[O_2]$ and $\delta^{18}O-O_2$ (Quay et al., 1995):

$$R/P = (^{18/16}O_w \alpha_p - ^{18/16}O_g) / (^{18/16}O \alpha_r - ^{18/16}O_g) \quad (4)$$

$$^{18/16}O_g = \alpha_g \{ ^{18/16}O_a \alpha_s - ([O_2]/[O_2]_{sat}) ^{18/16}O \} / \{ 1 - ([O_2]/[O_2]_{sat}) \} \quad (5)$$

Ratios greater than 1.0, signify a dominance of respiration, values less than 1.0 indicate a dominance of photosynthesis, and a value equal to 1.0 represent a balance of respiration and photosynthesis (del Giorgio and Peters, 1993; 1994; Quay et al., 1995).

The air/water gas transfer rate (F_{O_2} in equation 2) is no longer included in equations 4 and 5, since steady state of the system is assumed (Quay et al., 1995). At steady state any changes in the concentration or isotopic composition of the residual O_2 pool from the O_2 gas exchange flux will be offset by the biological O_2 fluxes of photosynthesis and respiration, and an equilibrium of the total O_2 flux is reached for the system. The gas transfer rate becomes a function of the fluctuations of the concentration and isotopic composition of O_2 during photosynthesis and respiration and, therefore, is not calculated directly from this method and is not required to determine R:P ratios.

Determination of gross O_2 production

A constant relationship between ^{17}O and ^{18}O exists for nearly all materials on Earth, such that the $\delta^{17}O$ of a sample is approximately half that of the $\delta^{18}O$ ($\delta^{17}O = 0.521$ * $\delta^{18}O$) (Luz et al., 1999). Biological processes, such as respiration and photosynthesis, adhere to this linear relationship, and these processes are known as mass dependent fractionation reactions (Luz et al., 1999; 2000). Photochemical reactions within the stratosphere and exchange of O_2 with O_3 and CO_2 , however, result in a slight enrichment in ^{17}O of tropospheric O_2 (0.3 ‰) (Thiemens, 1992; Luz et al., 1999). This anomalous tropospheric O_2 mixes into aquatic ecosystems through air/water gas exchange at the surface waters (Luz et al., 1999). Within the water column, photosynthetically produced O_2 lacks this anomalous enrichment in ^{17}O , and produces O_2 with a $\Delta^{17}O$ value equal to that of the surrounding water:

$$\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.521(\delta^{18}\text{O}) \quad (6)$$

where $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ are the measured isotopic compositions of O_2 (Luz et al., 1999).

The greater the magnitude of photosynthesis, therefore, the closer the $\Delta^{17}\text{O}$ value of O_2 becomes to the maximum $\Delta^{17}\text{O}$ of water, which has been determined to average to 249 per meg [per meg = ‰ * 1000] for all ocean water (Luz et al., 2000). At steady state, any O_2 effluxed to the atmosphere from the ocean will be replaced by O_2 produced during photosynthesis, therefore, by accounting for air/water gas exchange, an estimate of gross O_2 production may be obtained (Luz et al., 2000):

$$\text{GP} = K C_o (\Delta_{\text{diss}} - \Delta_{\text{eq}}) / (\Delta_{\text{max}} - \Delta_{\text{diss}}) \quad (7)$$

where GP is gross O_2 production, K is the gas transfer coefficient, C_o is the saturation

concentration of O_2 , Δ_{diss} is the measured $\Delta^{17}\text{O}$ value of O_2 , Δ_{eq} is the $\Delta^{17}\text{O}$ of

stratospheric O_2 in air/water equilibrium (16 per meg; Luz et al., 2000) and, Δ_{max} is the

$\Delta^{17}\text{O}$ of ocean water (249 per meg; Luz et al., 2000). Gas transfer coefficients (K) were

calculated for this study from the empirical relationship of Clark et al. (1995), with

average daily wind speeds determined from data recorded in the deck logs of the RV

Roger Revelle for the dates sampled.

Results

Transect – station ALOHA to S6 (May 25 to June 22)

Variations in sigma θ , fluorescence and $[\text{NO}_3^-]$ were present from west to east along the transect. A decrease in the density of surface water (5 m) was evident from station ALOHA (23.3) to S6 (21.5) (Figure 2.2). Values of sigma θ greater than or equal to 26, were observed at 300 m at station ALOHA, at 225 m at S2, at 175 m at S3, at 150

m at S4, at 100 m at S5 and at 80 m at S6 (Figure 2.2). This observation is evidence of the upwelling of dense deep water in the eastern portion of the transect, and shallowing of the mixed layer from west to east. A single fluorescence peak was evident at 125 m at station ALOHA and S2, and at 100 m at S3 and S4. Two fluorescence peaks were observed at S5 at 50 and 100 m, and at S6 at 40 and 80 m (Figure 2.3). The deeper peaks at S5 and S6 were present at the surface of the pycnocline. Surface $[\text{NO}_3^-]$ were less than $0.50 \mu\text{M}$ for all stations, however, the nitricline was shallower from west to east (Figure 2.4). At station ALOHA through S4, $[\text{NO}_3^-]$ were highest at or below the pycnocline, in contrast to S5 and S6 where $[\text{NO}_3^-]$ above the pycnocline were greater than or equal to concentrations below the pycnocline.

Distinct water column profiles with depth in $[\text{O}_2]$, the fraction of O_2 saturation, $\delta^{18}\text{O}-\text{O}_2$ and R:P ratios were apparent along the transect. Within the upper 300 m, $[\text{O}_2]$ at station ALOHA fluctuated only slightly around $200 \mu\text{mol/L}$ (Figure 2.3). A reduction in $[\text{O}_2]$ with depth along the transect was apparent at S2 and S3. Minimum $[\text{O}_2]$ were observed at 300 m of $68 \mu\text{mol/L}$ at S2 and $48 \mu\text{mol/L}$ at S3. At S4, S5 and S6 $[\text{O}_2]$ at surface were approximately $210 \mu\text{mol/L}$, however, anoxic zones within the upper 300 m were present at all these station, and anoxia occurred at shallower depths from west to east (Figure 2.5). The fraction of O_2 saturation within the upper mixed layer at station ALOHA, S3, S4 and S6 were approximately 1.0, and in equilibrium with the atmosphere. Supersaturation of O_2 was evident at S2 and S5 at surface (Figure 2.6). A predominance of atmospheric gas exchange at surface was prevalent at station ALOHA, S3 and S4 as indicated by $\delta^{18}\text{O}-\text{O}_2$ values near 0.7‰ (Figure 2.7). In contrast, $\delta^{18}\text{O}-\text{O}_2$ values less than 0.7‰ , indicative of a predominance of photosynthesis, were evident at S2, S5 and

S6, and the lowest $\delta^{18}\text{O}-\text{O}_2$ value of -2.0‰ was present at S6. $\delta^{18}\text{O}-\text{O}_2$ values greater than 0.7‰ , signifying a predominance of respiration, were observed at 250 m at station ALOHA, between 175 and 250 m at S2, between 100 and 150 m at S3, and at 75 m at S5. R:P ratios varied from 0.8 to 2.0 along the transect. Within the upper 100 m, from station ALOHA to S4, respiration was approximately equal to photosynthesis (Figure 2.8). At only five depths in the upper 100 m were R:P ratios slightly less than 1.0, representing a predominance of photosynthesis over respiration; at S2 at 5 and 50 m, at S3 at 50 m and at S5 at 5 and 25 m. At all remaining depths, at all stations, a predominance of respiration over photosynthesis was evident by R:P ratios greater than 1.0. The highest R:P ratio in this study of 2.0 was present at 250 m at station ALOHA.

Storm events – S5 and S6

Strong storm events occurred during the cruise, at S5 from June 14-16, and at S6 from June 19-22. The water column was sampled prior to the storm and after the storm at S5 and S6 and during the storm at S6. Intense water column mixing was apparent from decreased variations in fluorescence, $[\text{NO}_3^-]$, $[\text{O}_2]$, and the fraction of O_2 saturation measured before, during and after storm events (Figure 2.9, 2.10, 2.11, 2.12). A deepening of the pycnocline was evident after the storms, at both stations. In contrast to the sharp, narrow fluorescence peaks prior to the storms at S5 and S6, peaks after the storms were broader and reduced in magnitude (Figure 2.9, 2.10). At S5 and S6, maximum $[\text{NO}_3^-]$ increased in the mixed layer and decreased below the pycnocline after the storm events as compared to prior to the storms (Figure 2.9, 2.10). Overall a deepening of the nitricline in response to the storms was evident at S5, from 30 to 40 m,

and at S6, from 25 to 45 m. Between 25 and 60 m at S6, both $[O_2]$ and the fraction of O_2 saturation were observed to increase as the result of storm (Figure 2.12).

Before the storm at S5, $\delta^{18}O-O_2$ values in the upper 50 m indicated a predominance of photosynthesis, however, below 50 m $\delta^{18}O-O_2$ values greater than 0.7 ‰ were present, signifying a strong predominance of respiration (Figure 2.11). At S6, prior to the storm, $\delta^{18}O-O_2$ values less than 0.7 ‰ were observed at all depths, representing a predominance of photosynthesis, and a minimum value of -2.0 ‰ was found at 25 m (Figure 2.12). A predominance of respiration over photosynthesis was observed at and below 40 m at both stations, as indicated by R:P ratios greater than 1.0 before the storm events (Figure 2.13). During the storm at S6 a predominance of atmospheric gas exchange was present at 5 and 15 m, as indicated by $\delta^{18}O-O_2$ values approximately equal to 0.7 ‰. $\delta^{18}O-O_2$ values less than 0.7 ‰ were observed at 30 and 40 m during the storm, however, $\delta^{18}O-O_2$ values of 3.3 ‰ and 5.6 ‰ indicated a strong predominance of respiration at 50 and 60 m, respectively (Figure 2.12). At S6 R:P ratios throughout the upper 60 m greater than 1.0 were evident during the storm (Figure 2.13). A decrease in the $\delta^{18}O-O_2$ values was evident at 70 m, from 4.5 ‰ prior to the storm and 1.5 ‰ after the storm at S5 (Figure 2.11). After the storm at S6 $\delta^{18}O-O_2$ values, signifying a predominance of photosynthesis, were observed throughout the upper 50 m, and the lowest value of -2.5 ‰ at 50 m (Figure 2.12). At S5, a similar trend in R:P ratios after the storm to those observed before the storm was evident (Figure 2.13). At S6 after the storm, however, R:P ratios equal to 1.0 were observed, representing a balance between respiration and photosynthesis. As expected, atmospheric gas exchange was apparent at the beginning of the storm, however, a predominance of respiration over

photosynthesis during the storm was also observed and was followed by a predominance of photosynthesis throughout the water column after the storm.

Discussion

Transect from the NPSG to the ETNP (station ALOHA to S6)

Variations in the balance of respiration to photosynthesis at station ALOHA within the core of the NPSG, based on our data and that collected 10 years prior (S. Emerson and P. Quay, University of Washington, unpublished data, http://usjgofs.whoi.edu/jg/serv/jgofs/hot/ancillary_measurements/gas_ratio.html), allows for a unique analysis of R:P ratios on a seasonal basis. In 1990, the lowest R:P ratios were present in June and July (1.1) and maximum R:P ratios of 1.3 occurred in February, March, May and December (Table 2.1), and both minimum and maximum R:P ratios signified net heterotrophy. The dominance of respiration over photosynthesis, however, was 20 % lower in the summer than in the spring and winter (Table 2.1). Low R:P ratios in summer are expected within the NPSG, since this is a period of an annual primary production maximum despite also being a period of strong stratification (Karl et al., 1995; Karl, 1999). Stratification is a barrier to mixing and, thereby, the influx of nutrients, organic carbon, and plankton biomass from below the pycnocline to surface is reduced, which potentially decreases both photosynthesis and respiration within the mixed layer. Blooms of the cyanobacteria *Trichodesmium*, however, are reported during periods of strong stratification. N₂ fixation by these organisms contributes approximately half of total new production at station ALOHA (Karl et al., 1995; Karl et al., 1997). Summer within the NPSG, therefore, is a period of reduced respiration and increased photosynthesis, ultimately resulting in lower average R:P ratios as compared to other seasons. This

temporal trend is not evident during 1998/2000, and R:P ratios are approximately 1.0 for all months sampled (Table 2.1). The negligible seasonal variation in R:P ratios may be a consequence of the lack of sufficient sampling during the 1998/2000 season. A second possibility for the dissimilarity between 1990 and 1998/2000 periods is a shift in the balance of respiration and photosynthesis caused by decadal climate fluctuations.

In contrast to a weak El Niño event of 1990, La Niña conditions persisted throughout the 1998/2000 period within the tropical Pacific Ocean (http://www.cpc.noaa.gov/products/analysis_monitoring/ensostuff/enso.years/html). Average R:P ratios at station ALOHA were higher in 1990 (1.2) and indicated a predominance of heterotrophic conditions that contrasts with the balance of R:P ratios during 1998/2000 (Table 2.1). Karl et al. (1995) noted that high primary production and low organic carbon export from the euphotic zone characterizes station ALOHA during El Niño events. This observation may suggest high consumption of organic carbon within the surface waters during El Niño conditions. Indeed, the net heterotrophy in 1990 is indicative of a predominance of respiration over photosynthesis within the upper 100 m (Table 2.1). In comparison, non-El Niño conditions are represented by a relatively high export production from the euphotic zone at station ALOHA (Karl et al., 1995). The balance between respiration and photosynthesis during the La Niña of 1998/2000, therefore, may reflect the reduction in the consumption of organic carbon within the euphotic zone as compared to during the El Niño event. Despite this apparent difference in the balance of respiration to photosynthesis between 1990 and the later samplings the majority of the R:P ratios are equal to or greater than 1.1 and this observation defines station ALOHA as a region of a predominance of respiration over photosynthesis (Table 2.1). This net heterotrophy

requires a supply of organic carbon external to the core of the NPSG, and the primary production in environments at the fringe of the NPSG may provide an organic carbon source that is transported to station ALOHA via horizontal advection.

An external organic carbon source is difficult to reconcile for the NPSG, a region geographically isolated from a direct near-shore terrestrial influx of organic carbon (Smith and Mackenzie, 1987; Kirchman, 1997). One possible source of external organic carbon is horizontal transport from the more productive equatorial fringe of the NPSG (Abell et al., 2000; Emerson et al., 2001). Karl (1999) defines the NPSG as the area from approximately 15° N to 35° N latitude and 135° E to 135° W longitude, thereby, placing S2 on the southeastern edge of this vast oceanic environment (Figure 2.1). Similar depth profiles of sigma θ , [NO₃⁻] and [O₂] for the upper 100 m at station ALOHA and S2 support the characterization of these two stations as part of the same water mass (Figure 2.2, 2.4, 2.5). In contrast to station ALOHA, however, net autotrophy was prevalent throughout the upper 100 m at S2 (Figure 2.8, Table 2.1). Excess organic carbon produced at S2 may be transported to the euphotic zone of station ALOHA by horizontal transport from the edge toward the center of the gyre, due to the effects of downwelling generated from the overall clockwise circulation of the NPSG (Six and Maier-Reimer, 1996; Karl, 1999; Emerson et al., 2001). This downwelling condition of the NPSG that previously defined this region as a homogeneous environment may actually be a necessary mechanism interconnecting carbon cycling between areas, since the primary production within the fringe environment sustains the excess respiration at the core.

In contrast to the downwelling conditions that predominate within the oligotrophic NPSG, the ETNP is a eutrophic environment supported by upwelling of

nutrient rich waters to the surface (Ohman et al., 1982; Barber and Chavez, 1991; Fiedler et al., 1991; Karl, 1999), and thereby net autotrophy might be expected within this region. For all stations sampled along the ETNP transect, however, R:P ratios equal to or greater than 1.0 were observed (Table 2.1). A previous study also noted that within the ETNP, the majority of the organic carbon produced within the euphotic zone was consumed before being exported below the pycnocline (King et al., 1978). We observed regions of net autotrophy within the mixed layer but net heterotrophy above the pycnocline more than balanced any primary production, resulting in average R:P ratios greater than 1.0 within the upper 100 m (Figure 2.8, Table 2.1). Export of excess organic carbon via horizontal advection from east to west (Ohman et al., 1982) from areas of net autotrophy at one station may fuel the net heterotrophy at an adjacent station along the transect from S6 to S3. Despite reported high rates of primary production with the ETNP (Fiedler et al., 1991; Murray et al., 1994), these high rates of photosynthesis appear to be coupled with equal or higher rates of respiration. The ultimate result is not the anticipated extensive net autotrophy but an environment either with respiration and photosynthesis in balance or slightly net heterotrophic.

Pre-storm conditions along the transect (station ALOHA to S6)

Primary production prior to the storm event, based on ^{17}O - O_2 data, increases from west to east along the transect from the oligotrophic NPSG to the eutrophic ETNP (Figure 2.14, Table 2.2). Based on a literature review of the ratio of community respiration to gross primary production in various aquatic environments, Duarte and Agusti (1998) determined the minimum threshold of gross O_2 production required for net autotrophy in an oligotrophic or open ocean environment to be $0.035 \text{ g O}_2 \text{ m}^{-3} \text{ day}^{-1}$.

Both the oligotrophic core of the NPSG at station ALOHA and the open ocean fringe of the ETNP at S3, therefore, had sufficient gross O₂ production for the establishment of net autotrophic conditions within the upper 150 m (Table 2.2). Only at the depth of 50 m at S3 was net autotrophy observed, and all remaining depths at both stations were net heterotrophic (Figure 2.8). This precarious equilibrium between respiration and photosynthesis may be shifted toward net autotrophy either from a decrease in external organic carbon inputs resulting from a reduction in horizontal transport to stations ALOHA and S3, or an influx of nutrients from below the pycnocline during episodic mixing events. Due to the oligotrophic characteristic of these two stations and, therefore, a low threshold of net autotrophy, the balance of respiration to photosynthesis at each station is sensitive to slight variations in the flux of nutrients or organic carbon. In contrast to these oligotrophic environments, in eutrophic coastal regions, with high influxes of terrestrial organic carbon fuelling respiration, a base value of 1.62 g O₂ m⁻³ day⁻¹ is necessary for net autotrophy (Duarte and Agusti, 1998). Indeed, S5, located within the ETNP near the Mexican coast, had sufficient gross O₂ production prior to the storm event for net autotrophy, and R:P ratios less than 1.0 were present within the upper 25 m (Figure 2.8, Table 2.2). Ultimately the variations in R:P ratios along the entire transect from station ALOHA to S6 revealed an overall balance between respiration and photosynthesis within the upper 100 m during the EPREX cruise (Table 2.2). The areas of net heterotrophy and CO₂ efflux from the ocean to the atmosphere, therefore, offset the regions of net autotrophy and CO₂ influx from the atmosphere to the ocean. This balance in R:P ratios and CO₂ flux, however, is sensitive to shifts in the magnitude of primary production, which in turn, may be effected by perturbations to the physical environment.

Storm events – S5 (June 14-16) and S6 (June 19-22)

Strong episodic mixing events redistribute both phytoplankton biomass and nutrients to surface waters and may, thereby, increase rates of primary production within the mixed layer (King, 1986; Hayward, 1987; Falkowski, 1994; Karl, 1999), potentially causing a short-term lowering of the R:P ratio and net autotrophic conditions. The initial impact of storm events at both S5 and S6 was intense mixing of the water column, as indicated by a deepening of the pycnocline, homogeneity in fluorescence, $[\text{NO}_3^-]$ and $[\text{O}_2]$ profiles with depth, and a shift in the isotopic composition of O_2 toward values indicative of gas exchange (Figure 2.9, 2.10, 2.11, 2.12). During the storm, R:P ratios greater than 1.0 between 40 and 60 m at S6 and a corresponding $\delta^{18}\text{O}-\text{O}_2$ value greater than 0.7 ‰ at these depths were followed by after the storm increases in the fraction of O_2 saturation, and low $\delta^{18}\text{O}-\text{O}_2$ values throughout the upper 100 m (Figure 2.11, 2.12, 2.13). These observations were suggestive of a period of predominance of respiration over photosynthesis following the initial storm-induced mixing, which in turn proceeded to a period of net photosynthesis after the storm. A period of net heterotrophy may precede a period of photosynthesis as organic carbon is redistributed with nutrients to the mixed layer from below the pycnocline (Falkowski, 1994). Heterotrophic bacteria present in the mixed layer may consume this newly accessible organic carbon source and initially outcompete phytoplankton, especially during a period of reduced light levels associated with cloud cover. Eventually after the storm, as light returns to pre-storm levels, the increase in the influx of nutrients from below the pycnocline results in an increase in primary production (Ohman et al., 1982; King, 1986).

Despite the apparent increase in primary production following the storm events, however, net autotrophy was not present at S5 and S6 after the storm (Table 2.1). Average R:P ratios indicated slight net heterotrophy at S5, and at S6, shifted toward a balance between respiration and photosynthesis. This balance of respiration to photosynthesis may be a transition period between net heterotrophy during the storm and net autotrophy, but sampling after the storm may have ceased before sufficient time had elapsed for net autotrophy to be established. Furthermore, an increase in photosynthesis from physical redistribution of nutrients does not necessarily equate to net autotrophy, if respiration also increases from a redistribution of organic carbon from below the pycnocline. Indeed, the large increase in primary production recorded by Ditullio and Laws (1991) following a storm event required a nutrient source external to the ocean, and was attributed to atmospheric NO_3^- and Fe deposition and not to redistribution of nutrients from vertical mixing. Ultimately, the storm events in the ETNP resulted not in a shift to net autotrophy due to an increase in primary production as expected, but in a greater balance in R:P ratios due to a temporal decoupling of respiration and photosynthesis. The presence of equal respiration to photosynthesis suggests a minor impact on the net flux of CO_2 between the atmosphere and the ocean following these episodic disturbances, and not a substantial drawdown of atmospheric CO_2 , which may have occurred had expected net autotrophy prevailed after the storms.

AVERAGE R:P RATIOS FOR THE UPPER 100 m

CRUISE	STATION	DATE	R:P RATIO	CRUISE	STATION	DATE	R:P RATIO
HOT13	ALOHA	01/90	1.2	HOT98	ALOHA	10/98	1.0
HOT14	ALOHA	02/90	1.3	HOT101	ALOHA	01/99	1.1
HOT15	ALOHA	03/90	1.3	HOT104	ALOHA	04/99	1.0
HOT16	ALOHA	04/90	1.2	AKA	ALOHA	07/99	1.2
HOT17	ALOHA	05/90	1.3	EPREX	ALOHA	05/00	1.0
HOT18	ALOHA	06/90	1.1				
HOT19	ALOHA	07/90	1.1				
HOT22	ALOHA	12/90	1.3				
AVERAGE:			1.2	AVERAGE:			1.1
STDEV:			0.09	STDEV:			0.09
CRUISE	STATION	DATE	R:P RATIO	CRUISE	STATION	TIME SAMPLED	R:P RATIO
EPREX	ALOHA	05/00	1.0	EPREX	S5	PRIOR TO STORM	1.1
EPREX	S2	05/00	0.9	EPREX	S5	AFTER STORM	1.1
EPREX	S3	06/00	1.1				
EPREX	S4	06/00	1.0	EPREX	S6	PRIOR TO STORM	1.1
EPREX	S5	06/00	1.1	EPREX	S6	DURING STORM	1.3
EPREX	S6	06/00	1.1	EPREX	S6	AFTER STORM	1.0
AVERAGE:			1.0				
STDEV:			0.08				

Table 2.1: Average R:P ratios for the upper 100 m of the water column for past and current cruises, and before, during and after the storm events at stations S5 and S6.

GROSS O₂ PRODUCTION

GP(O ₂) (g m ⁻³ day ⁻¹) station ALOHA		GP(O ₂) (g m ⁻³ day ⁻¹) S3	
Depth (m)		Depth (m)	
100	0.052	5	0.211
125	0.063	100	0.205
150	0.056	125	0.155
		150	0.209

GP(O ₂) (g m ⁻³ day ⁻¹) S5		GP(O ₂) (g m ⁻³ day ⁻¹) S6	
Depth (m)		Depth (m)	
25	2.839	5	0.602
		15	0.160
		30	0.266
		40	0.723
		50	38.555

Table 2.2: The calculated gross O₂ production for stations ALOHA S3, S5 and S6. Station S6 was sampled after the storm event.

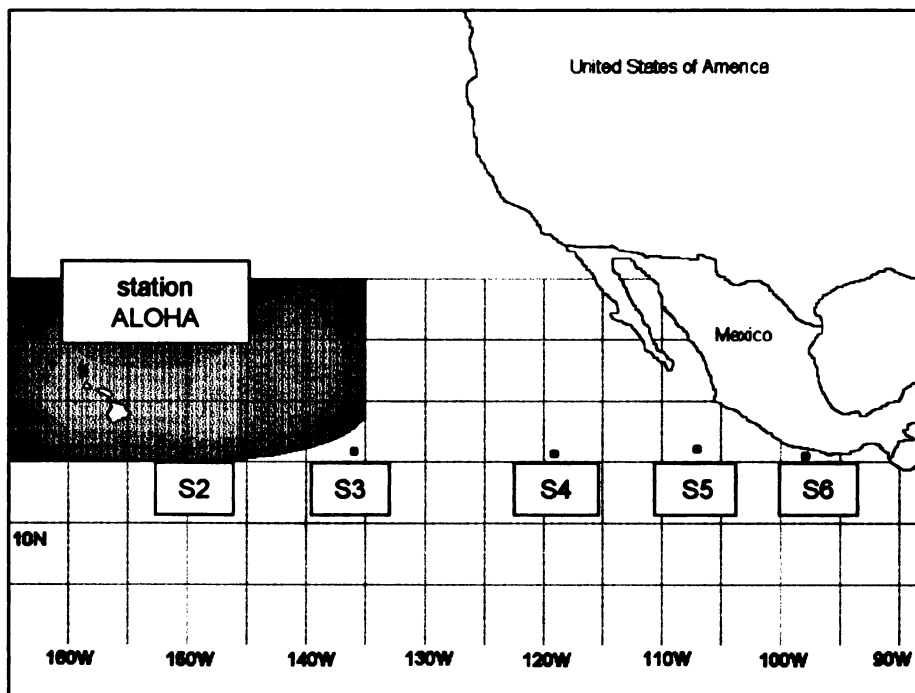


Figure 2.1: The location of all stations comprising the EPREX transect.
Note: The shaded area approximates the NPSG.

Approximate scale: 1:37000000

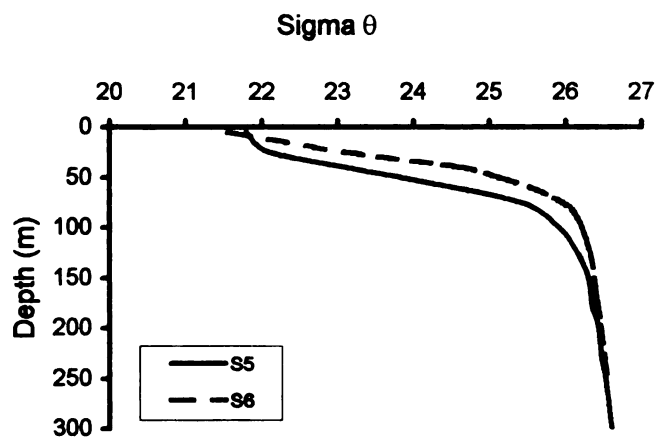
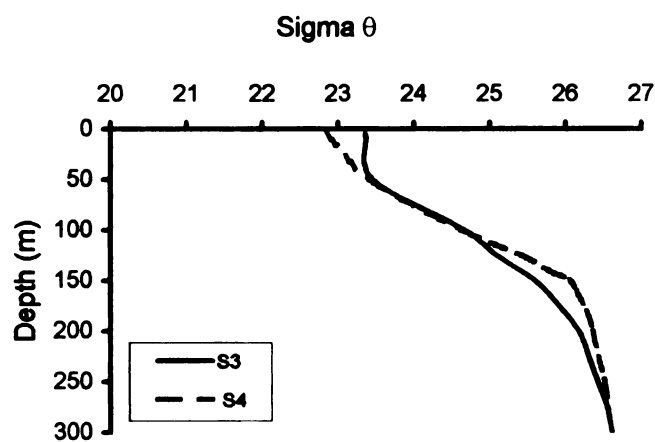
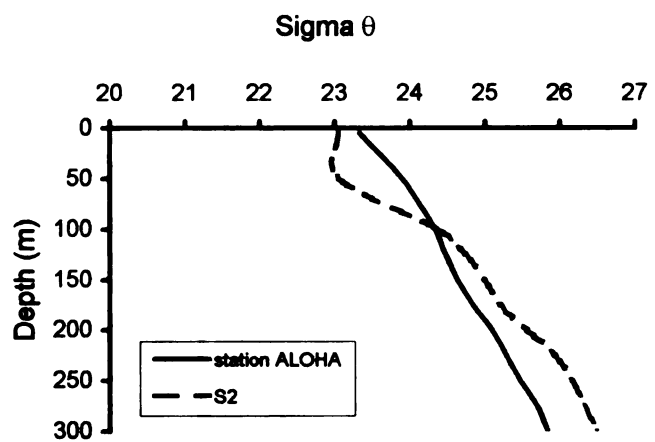


Figure 2.2: Sigma θ as a function of depth for all stations along the EPREX transect from May 24 to June 28, 2000.

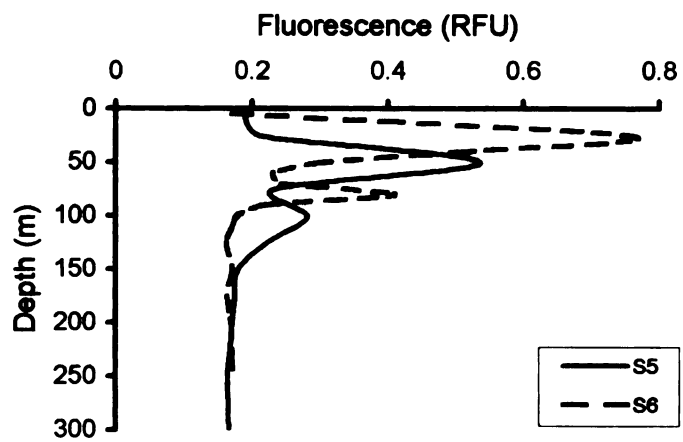
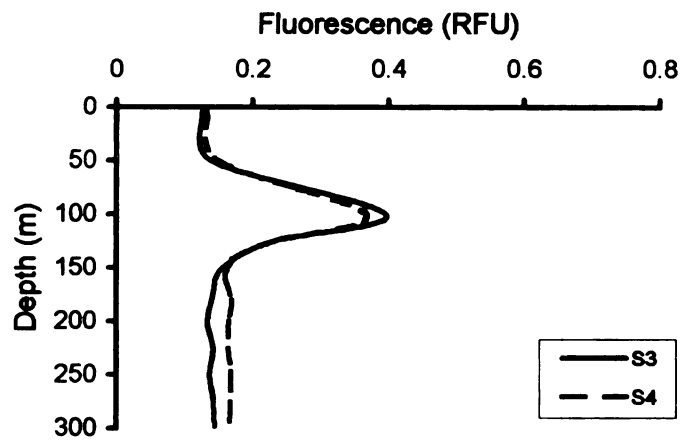
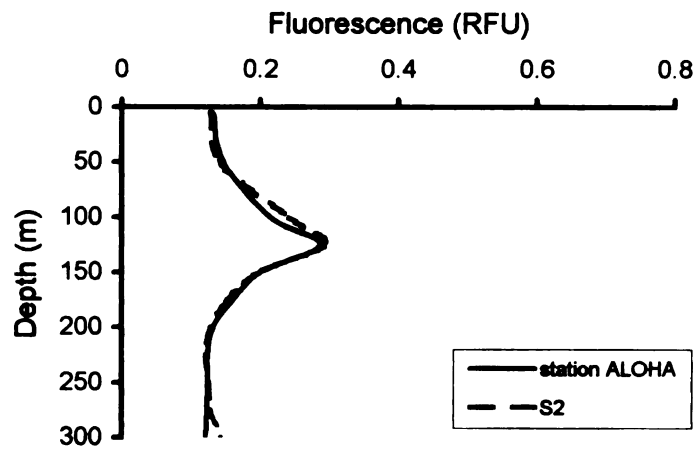


Figure 2.3: Fluorescence as a function of depth for all stations along the EPREX transect from May 24 to June 28, 2000.

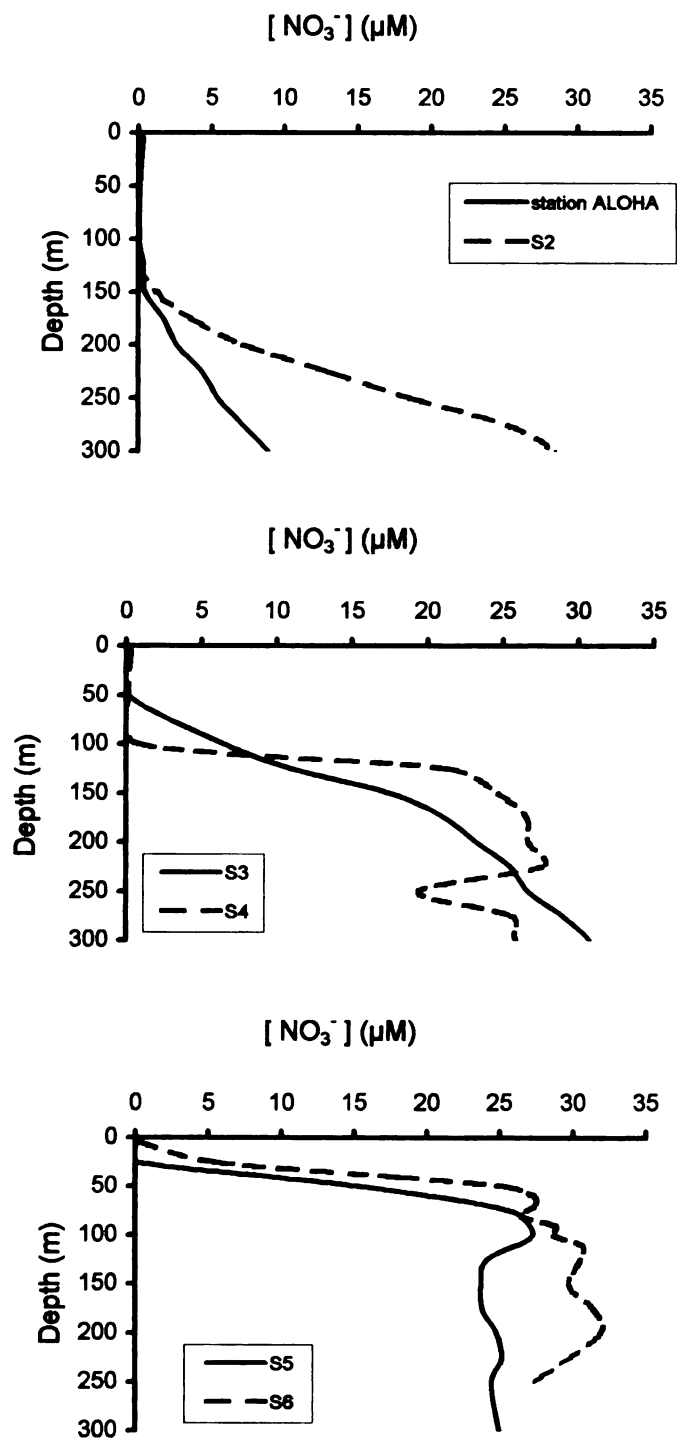


Figure 2.4: $[\text{NO}_3^-]$ as a function of depth for all stations along the EPREX transect from May 24 to June 28, 2000.

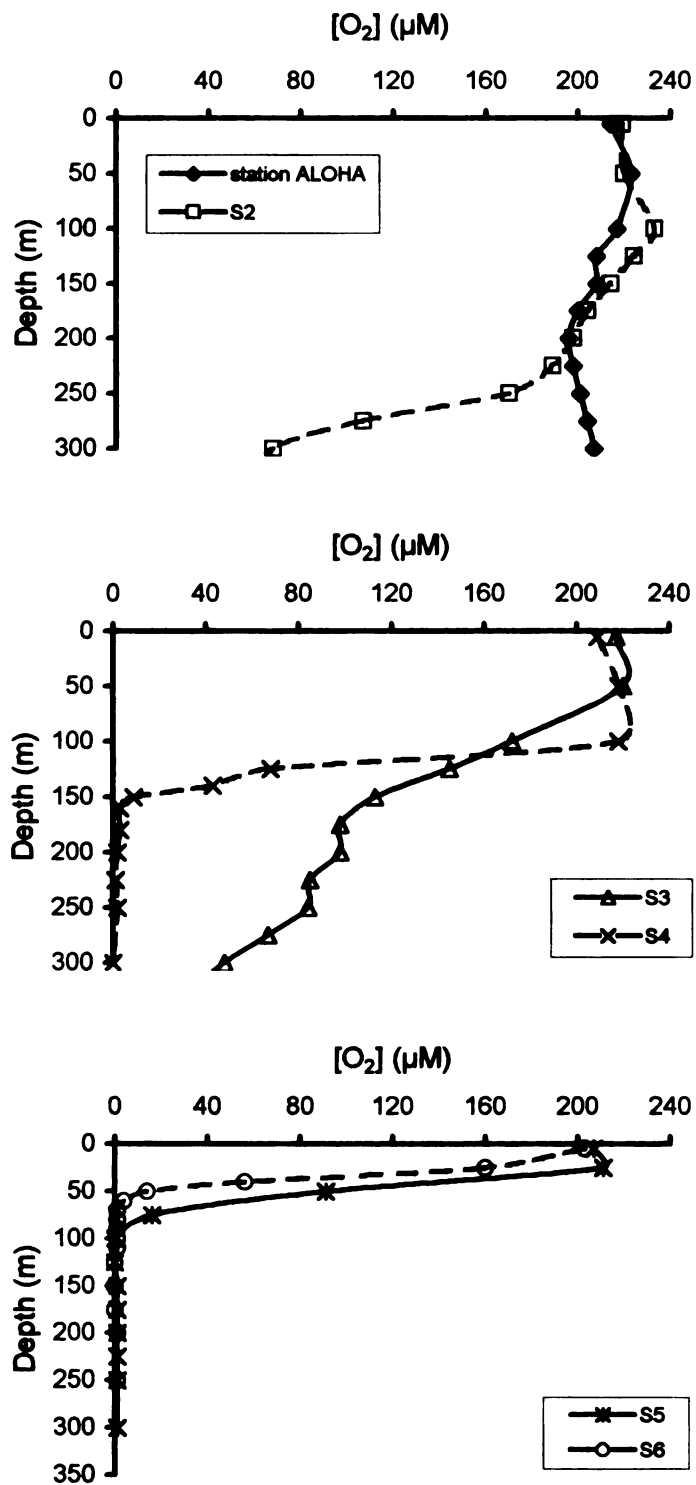


Figure 2.5: $[O_2]$ as a function of depth for all stations along the EPREX transect from May 24 to June 28, 2000.

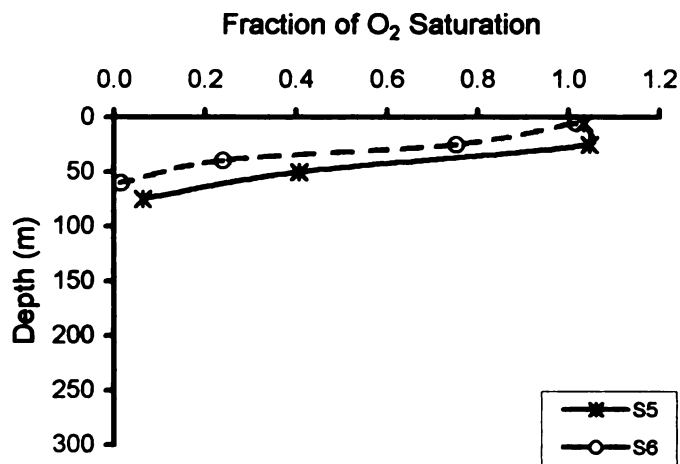
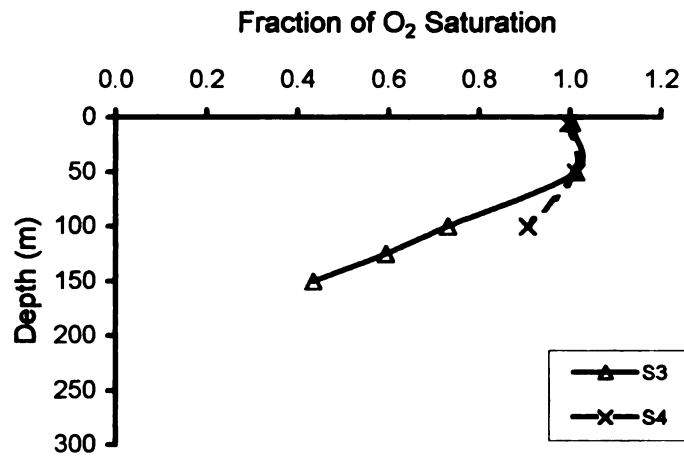
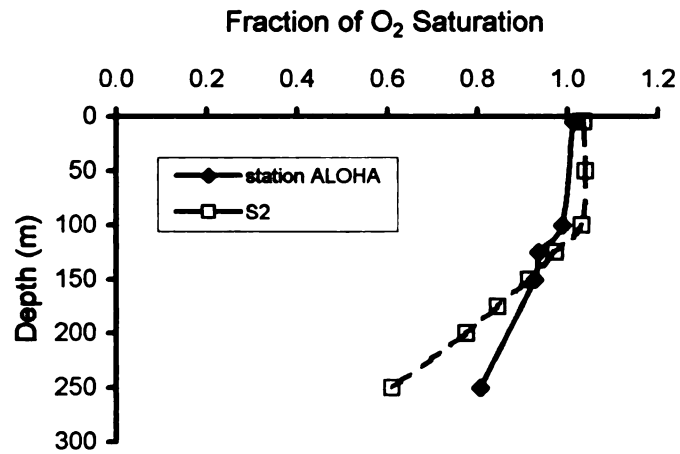


Figure 2.6: The fraction of O_2 saturation as a function of depth for all stations along the EPREX transect from May 24 to June 28, 2000.

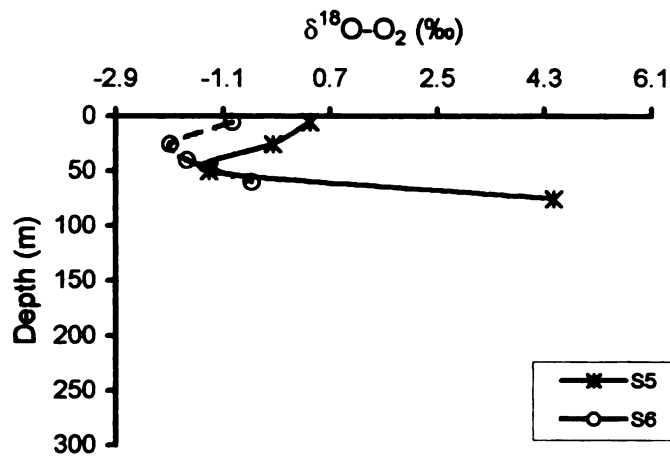
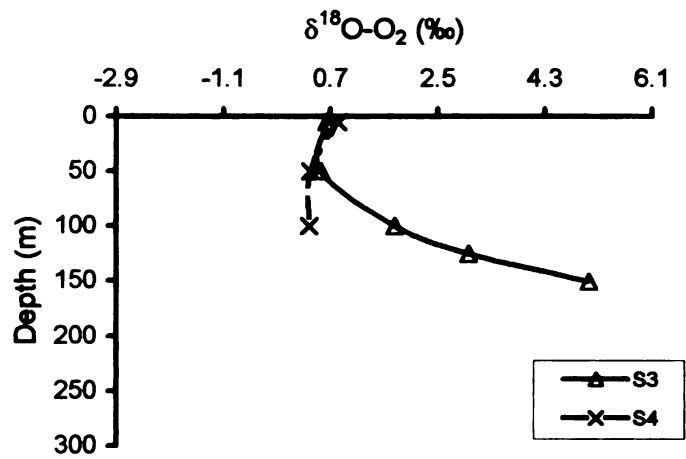
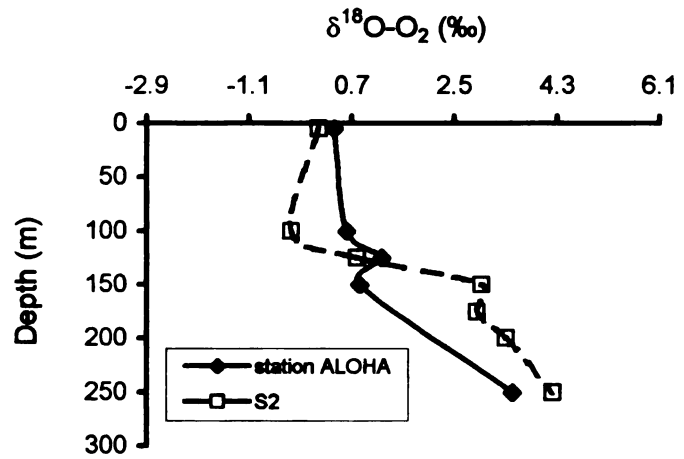


Figure 2.7: The isotopic composition of O₂ as a function of depth for all stations along the EPREX transect from May 24 to June 28, 2000.

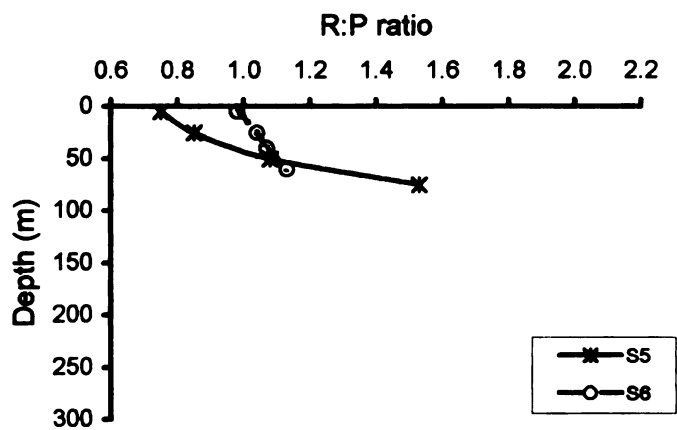
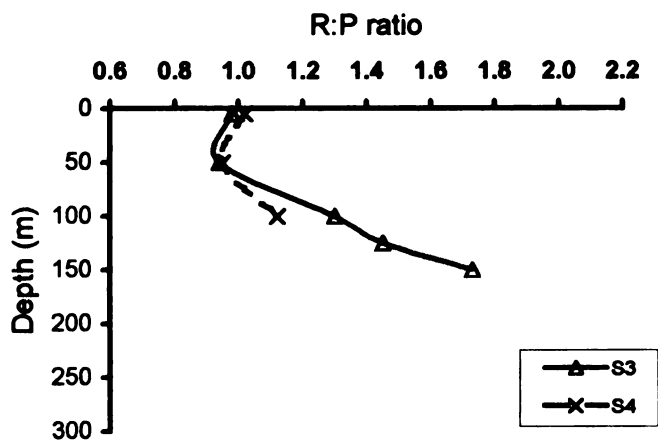
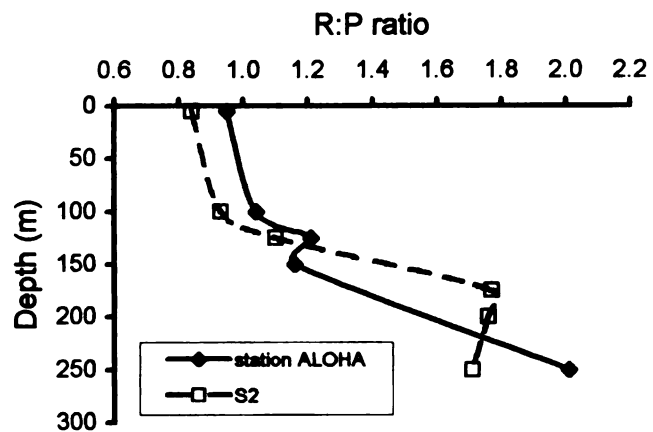


Figure 2.8: Ratios of respiration to photosynthesis (R:P ratios) as a function of depth at all stations along the EPREX transect from May 24 to June 28, 2000.

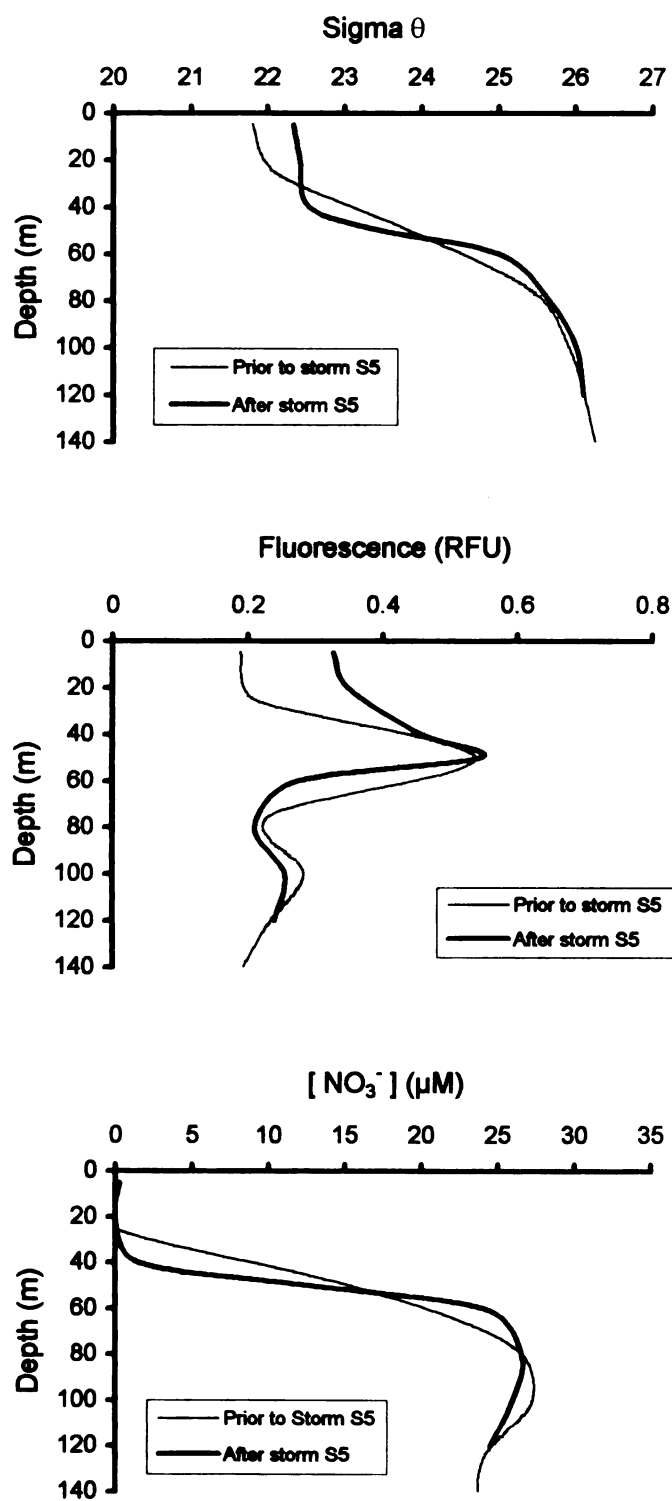


Figure 2.9: Sigma θ , fluorescence and [NO₃⁻] as a function of depth prior to and after the storm at S5 from June 14 to 16, 2000.

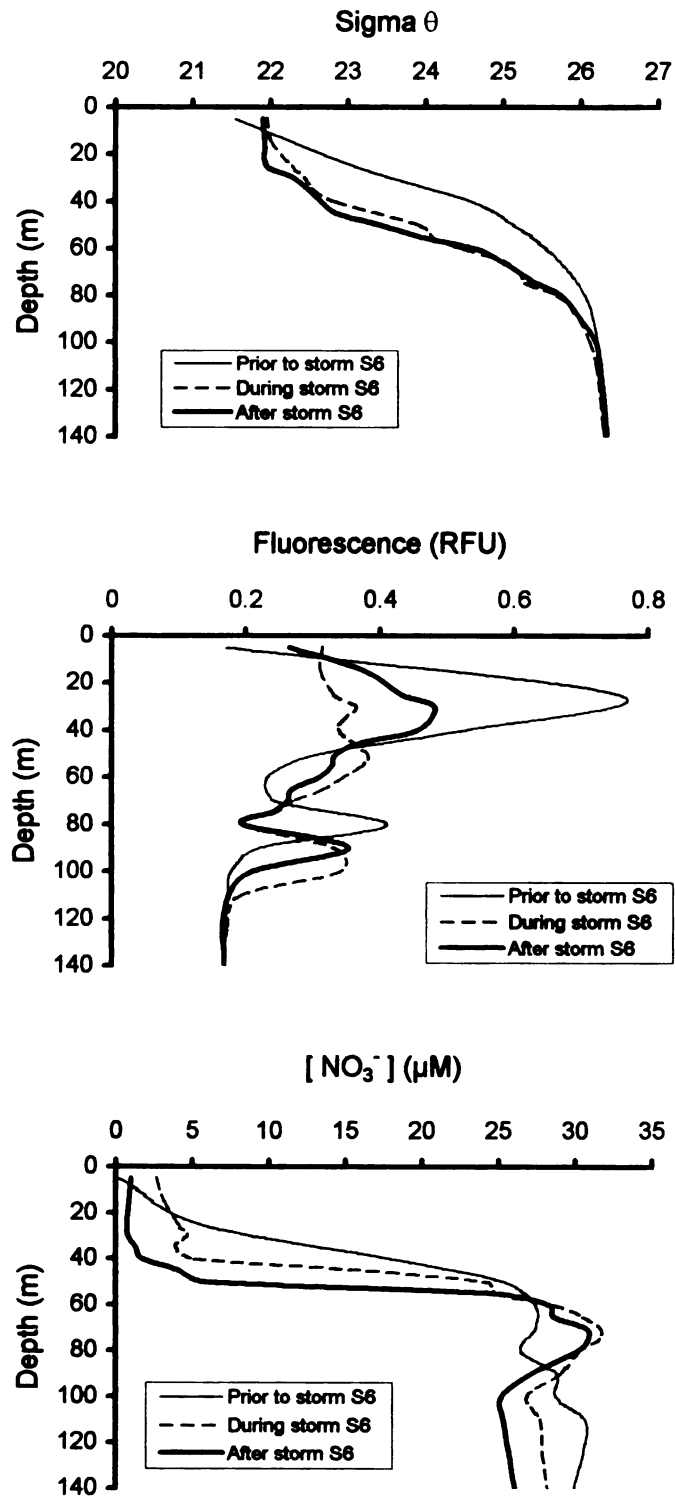


Figure 2.10: Sigma θ , fluorescence and [NO₃⁻] as a function of depth prior to, during and after the storm at S6 from June 19 to 22, 2000.

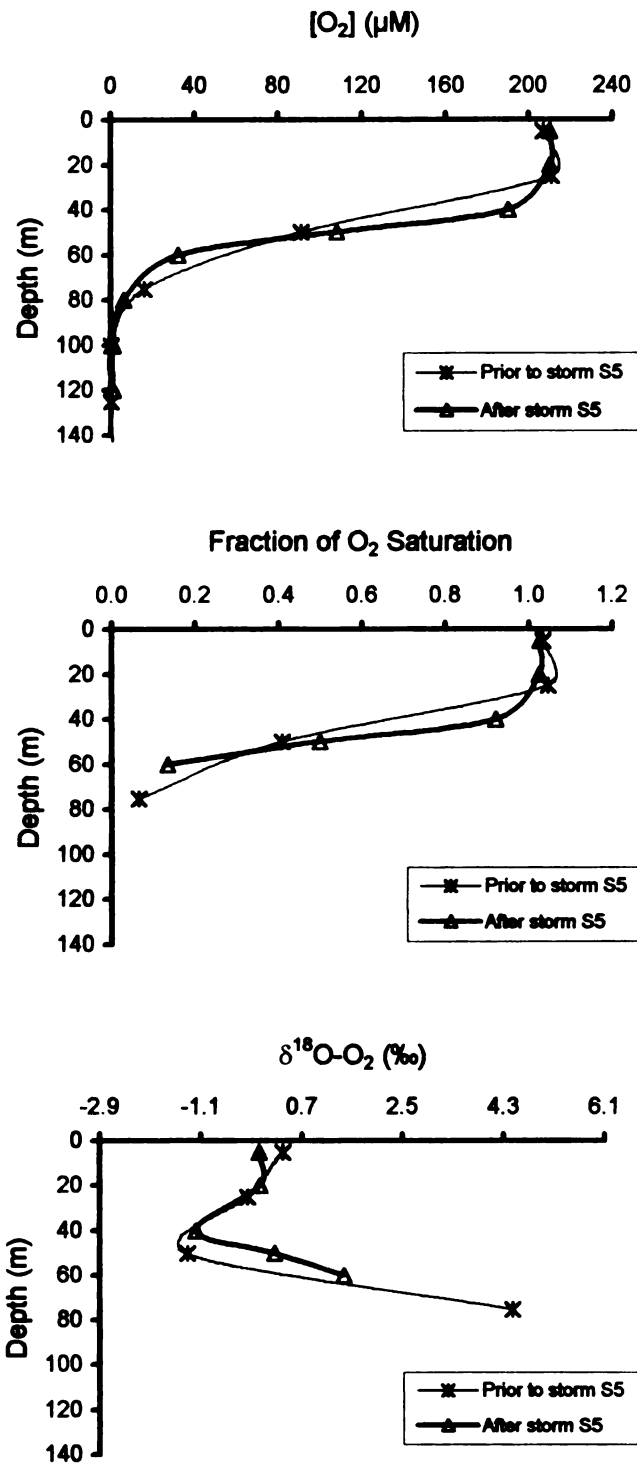


Figure 2.11: $[O_2]$, the fraction of O_2 saturation and the isotopic composition of O_2 as a function of depth prior to and after the storm at S5 from June 14 to 16, 2000.

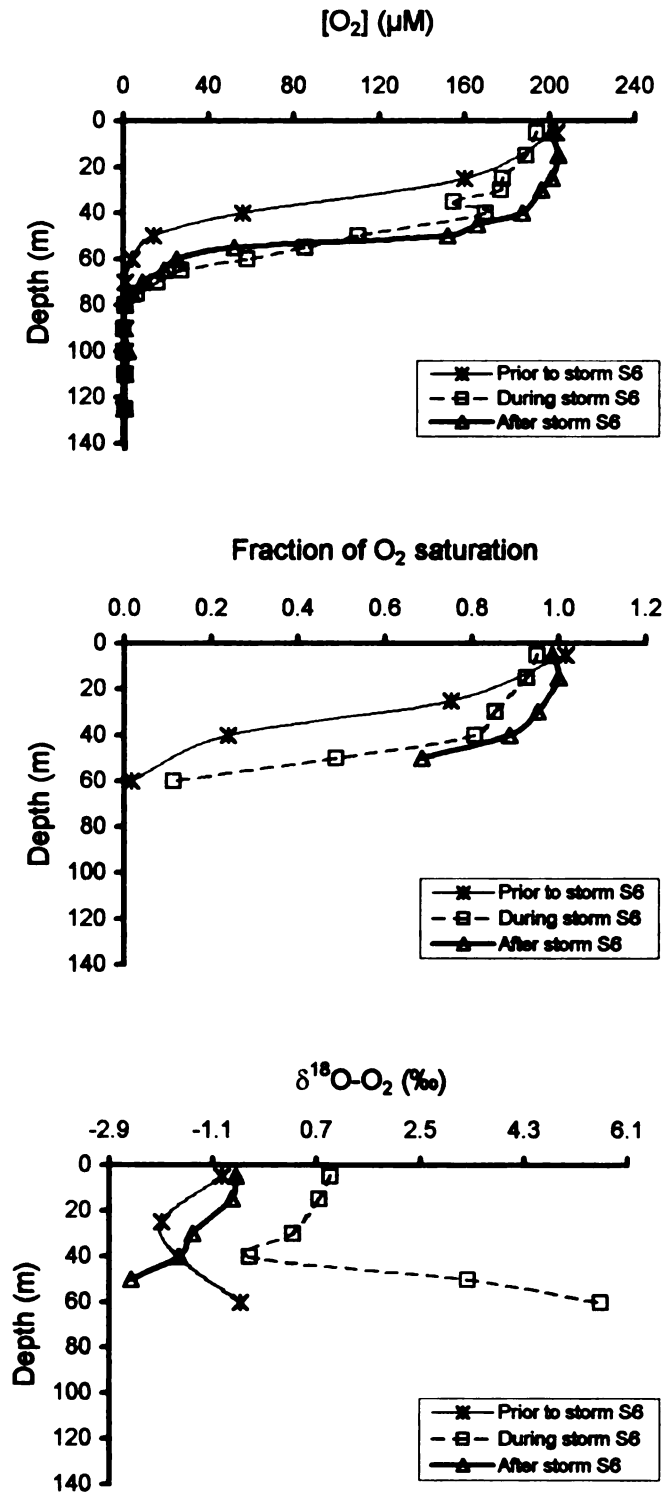


Figure 2.12: $[O_2]$, the fraction of O_2 saturation and the isotopic composition of O_2 as a function of depth prior to, during and after the storm at S6 from June 19 to 22, 2000.

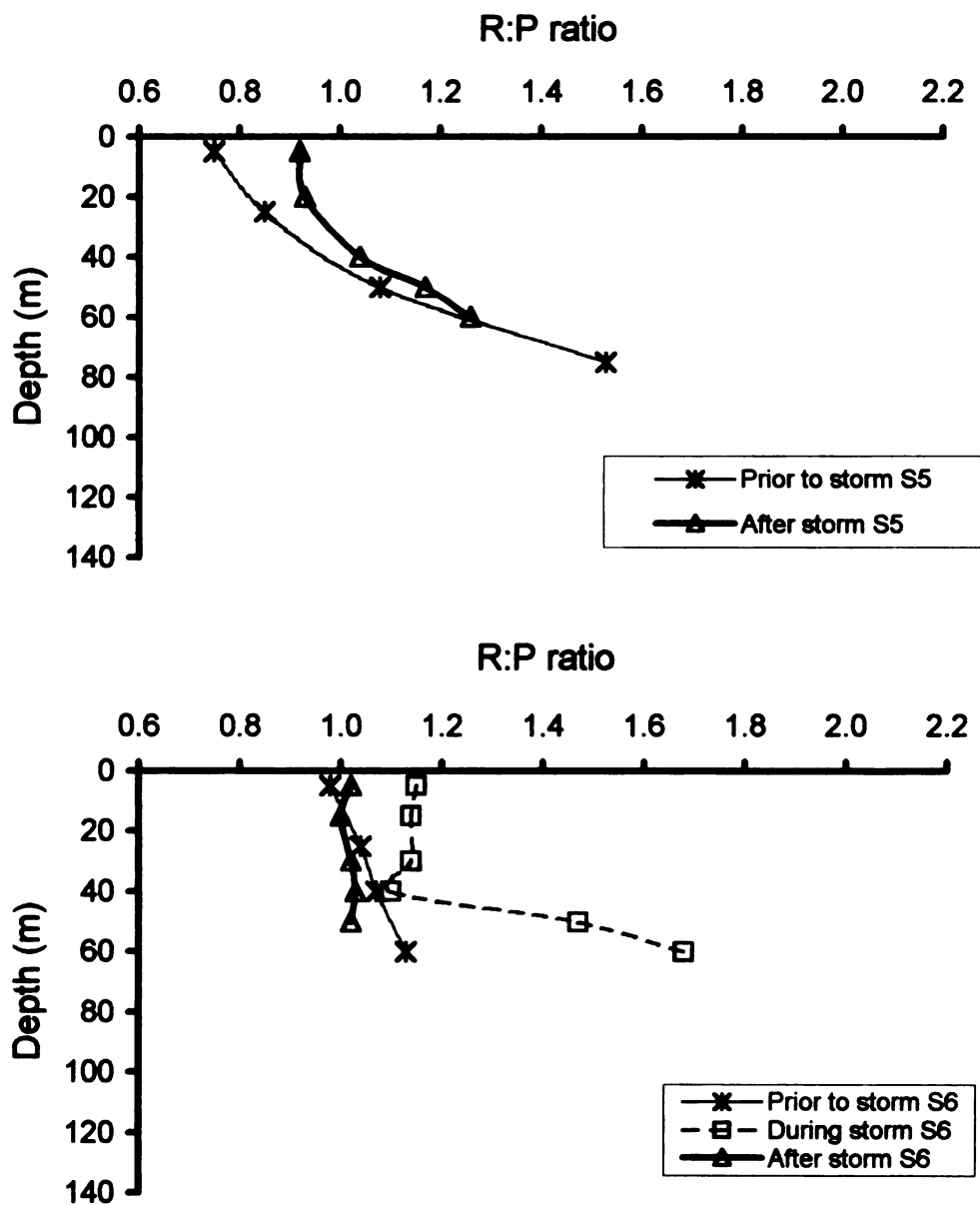


Figure 2.13: Ratios of respiration to photosynthesis (R:P ratios) as a function of depth for storm events prior to and after the storm at S5 from June 14 to 16, 2000 and prior to, during and after the storm at S6 from June 19 to 22, 2000.

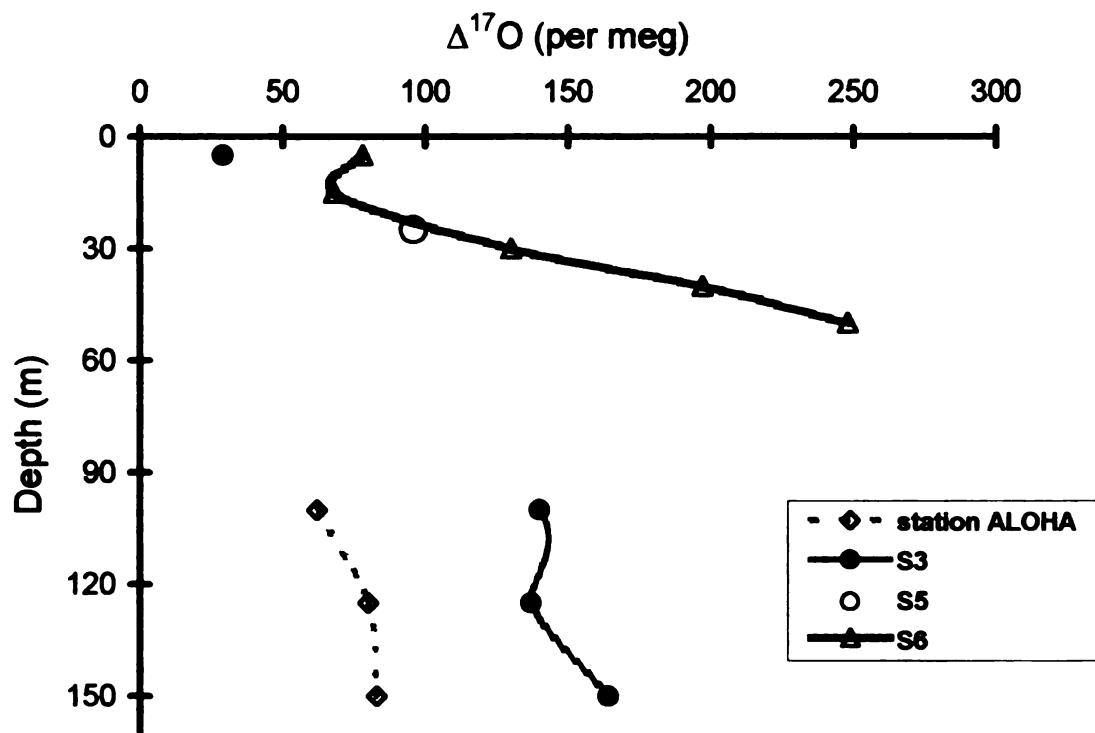


Figure 2.14: The $\Delta^{17}\text{O}$ values of O_2 for stations ALOHA, S3, S5 and S6.

References

- Abell, J., S. Emerson, and P. Renaud, Distributions of TOP, TON and TOC in the North Pacific subtropical gyre: Implications for nutrient supply in the surface ocean and remineralization in the upper thermocline, *Journal of Marine Research*, 58, 203-222, 2000.
- Azam F., and J.W. Ammerman, Mechanisms of organic matter utilization by marine Bacterioplankton, in *Lecture Notes on Coastal and Estuarine Studies*, edited by O. Holm-Hansen, L. Bolis, and R. Gilles, pp. 45-54, Springer-Verlag, New York, New York, 1984.
- Azam, F., T. Fenchel, J.G. Field, J.S. Gray, L.A. Meyer-Reil, and F. Thingstad, The ecological role of water-column microbes in the sea, *Marine Ecology – Progress Series*, 10, 257-263, 1983.
- Barber, R.T., and F.P. Chavez, Regulation of primary productivity rate in the equatorial Pacific, *Limnology and Oceanography*, 36, 1803-1815, 1991.
- Barbiero, R.P. and M.L. Tuchman, Results of the U.S. EPA's biological open water surveillance program of the Laurentian Great Lakes: II. Deep chlorophyll maxima, *J. Great Lakes Res.*, 27, 155-166, 2001.
- Barbiero, R.P. and M.L. Tuchman, Results of the U.S. EPA's biological open water surveillance program of the Laurentian Great Lakes: I. Introduction and phytoplankton results, *J. Great Lakes Res.*, 27, 134-154, 2001
- Bell, T. and J. Kalff, The contribution of picophytoplankton in marine and freshwater systems of different trophic status and depth, *Limnology and Oceanography*, 46, 1243-1248, 2001.
- Bender, M.L. and K.D. Grande, Production, respiration, and the isotope geochemistry of O₂ in the upper water column, *Global Biogeochemical Cycles*, 1, 49-59, 1987.
- Bennett, E., Characteristics of the thermal regime of Lake Superior, *J. Great Lakes Res.*, 4, 310-319, 1978.
- Bennett, E., Water Budgets for Lake Superior and Whitefish Bay, *J. Great Lakes Res.*, 4, 331-342, 1978.
- Benson, B.B. and D. Krause, The concentration and isotopic fractionation of oxygen dissolved in freshwater and seawater in equilibrium with the atmosphere, *Limnology and Oceanography*, 29, 620-632, 1984.

- Bentzen, E., W.D. Taylor, and E.S. Millard, The importance of dissolved organic phosphorus to phosphorus uptake by limnetic plankton, *Limnology and Oceanography*, 37, 217-231, 1992.
- Biddanda, B., M. Ogdahl, and J. Cotner, Dominance of bacterial metabolism in oligotrophic relative to eutrophic waters, *Limnology and Oceanography*, 46, 730-739, 2001.
- Brooks, A.S. and J.C. Zastrow, J.C. The potential influence of climate change on offshore primary production in Lake Michigan, *J. of Great Lakes Res.*, 28, 597-607, 2002.
- Carpenter, J.H., The accuracy of the Winkler method for dissolved oxygen, *Limnology and Oceanography*, 10, 135-143, 1965.
- Clark, J.F., P. Schlosser, H.J. Simpson, M. Stute, R. Wanninkhof, and T.D. Ho, Relationship between gas transfer velocities and wind speeds in the tidal Hudson River determined by the dual tracer technique, in *Air-Water Gas Transfer*, edited by B. Jaehne, and E.C. Monahan, pp. 785-800, Aeon Verlag and Studio, New York, New York, 1995.
- Cole, J.J., N.F. Caraco, D. L. Strayer, C. Ochs, and S. Nolan, A detailed organic carbon budget as an ecosystem-level calibration of bacterial respiration in an oligotrophic lake during midsummer, *Limnology and Oceanography*, 34, 286-296, 1989.
- Cole, J.J., N.F. Caraco, G.W. Kling, and T.K. Kratz, Carbon dioxide supersaturation in the surface waters of lakes, *Science*, 265, 1568-1570, 1994.
- Cole, J.J., S.R. Carpenter, J.F. Kitchell, and M.L. Pace, Pathways of organic carbon utilization in small lakes: Results from a whole-lake ¹³C addition and coupled model, *Limnology and Oceanography*, 47, 1664-1675, 2002.
- Cotner, J.B. and B.A. Biddanda, Small players, large role: Microbial influences on biogeochemical processes in pelagic aquatic ecosystems, *Ecosystems*, 5, 105-121, 2002.
- Cotner, J.B. and R.G. Wetzel, Uptake of dissolved inorganic and organic phosphorus compounds by phytoplankton and bacterioplankton, *Limnology and Oceanography*, 37, 232-243, 1992.
- Coveney, M.F. and R.G. Wetzel, Biomass production, and specific growth rate of bacterioplankton and coupling to phytoplankton in an oligotrophic lake, *Limnology and Oceanography*, 40, 1187-1200, 1995.
- Currie, D.J., Large-scale variability and interactions among phytoplankton, bacterioplankton and phosphorus, *Limnology and Oceanography*, 35, 1437-1455, 1990.

- del Giorgio, P.A. and R.H. Peters, Balance between phytoplankton production and plankton respiration in lakes, *Can. J. Fish. Aquat. Sci.*, **50**, 282-289, 1993.
- del Giorgio, P.A. and R.H. Peters, Patterns in planktonic P:R ratios in lakes: Influence of lake trophic and dissolved organic carbon, *Limnology and Oceanography*, **39**, 772-787, 1994.
- del Giorgio, P.A., J.J. Cole, and A. Cimbleris, Respiration rates in bacteria exceed phytoplankton production in unproductive aquatic systems, *Nature*, **385**, 148-151, 1997.
- Duarte, C.M., and S. Agustí, The CO₂ balance of unproductive aquatic ecosystems, *Science*, **281**, 234-236, 1998.
- Ducklow, H.W., D.A. Purdie, J. LeB. Williams, and J.M. Davies, Bacterioplankton: A sink for carbon in a coastal marine plankton community, *Science*, **232**, 865-867, 1986.
- DuTulio, G.R., and E.A. Laws, Impact of an atmospheric-oceanic disturbance on phytoplankton community dynamics in the North Pacific Central Gyre, *Deep-Sea Research*, **38**, 1305-1329, 1991.
- El-Shaarawi, A. and M. Munawar, Statistical evaluation of the relationship between phytoplankton biomass, chlorophyll a, and primary production in Lake Superior, *Internat. Assoc. Great Lakes Res.*, **4**, 443-455, 1978.
- Emerson, S., P. Quay, C. Stump, D. Wilbur, and M. Knox, O₂, Ar, N₂, and ²²²Rn in waters of the subarctic ocean: Net biological O₂ production, *Global Biogeochemical Cycles*, **5**, 49-69, 1991.
- Emerson, S., P.D. Quay, C. Stump, D. Wilbur, and R. Schudlich, Chemical tracers of productivity and respiration in the subtropical Pacific Ocean, *Journal of Geophysical Research*, **100**, 15873-15887, 1995.
- Emerson, S., C. Stump, D. Wilbur, and P. Quay, Accurate measurement of O₂, N₂, and Ar gases in water and the solubility of N₂, *Marine Chemistry*, **64**, 337-347, 1999.
- Emerson, S., S. Mecking, and J. Abell, The biological pump in the subtropical North Pacific Ocean: Nutrient sources, Redfield ratios, and recent changes, *Global Biogeochemical Cycles*, **15**, 535-554, 2001.
- Epstein, S., and T. Mayeda, Variation of ¹⁸O content of waters from natural sources, *Geochimica et Cosmochimica Acta*, **4**, 89-103, 1953.
- Fahnenstiel, G.L. and J.M. Glime, Subsurface chlorophyll maximum and associated *Cyclotella* pulse in Lake Superior, *Int. Revue ges. Hydrobiol.*, **68**, 605-616, 1983.

- Fahnenstiel, G.L., C.L. Schelske, and A.M. Russell, *In situ* quantum efficiency of Lake Superior phytoplankton, *J. Great Lakes Res.*, **10**, 399-406, 1984.
- Falkowski, P.G., The role of phytoplankton photosynthesis in global biogeochemical cycles, *Photosynthesis Research*, **39**, 235-258, 1994.
- Fee, E.J., J.A. Shearer, E.R. DeBruyn, and E.U. Schindler, Effects of lake size on phytoplankton photosynthesis, *Can. J. Fish. Aquat. Sci.*, **49**, 2445-2459, 1992.
- Fiedler, P.C., V. Philbrick, and F.P. Chavez, Oceanic upwelling and productivity in the eastern tropical Pacific, *Limnology and Oceanography*, **36**, 1834-1850, 1991
- Fuhrman, J., Bacterioplankton roles in cycling of organic matter: The microbial food web, in *Primary Productivity and Biogeochemical Cycles in the Sea*, edited by P.G. Falkowski, and A.D. Woodhead, pp. 361-383, Plenum Press, New York, New York, 1992.
- Garcia, H.E. and L.I. Gordon, Oxygen solubility in seawater: Better fitting equations, *Limnology and Oceanography*, **37**, 1307-1312, 1992.
- Geider, R.J., Respiration: Taxation without representation?, in *Primary Production and Biogeochemical Cycles in the Sea*, edited by P.G. Falkowski and A.D. Woodhead, pp. 333-360, Plenum Press, New York, New York, 1992
- Grasshoff, K., Determination of oxygen, in *Methods of Seawater Analysis*, edited by K. Grasshoff, M. Ehrhardt, and K. Kremling, pp. 61-72, Verlag Chemie, New York, New York, 1983.
- Guildford, S.J., L.L.Hendzel, H.J. Kling, and E.J. Fee, Effects of lake size on phytoplankton nutrient status, *Can. J. Fish. Aquatic Sci.*, **51**, 2769-2783, 1994.
- Guy, R.D., M.L. Fogel, and J.A. Berry, Photosynthetic fractionation of the stable isotopes of oxygen and carbon, *Plant Physiol.*, **101**, 37-47, 1993.
- Hanson, H.P., C.S. Hanson, and B.H. Yoo, Recent Great Lakes ice trends, *Bulletin American Meteorological Society*, **73**, 577-584, 1992.
- Hayward, T.L., The nutrient distribution and primary production in the central North Pacific, *Deep-Sea Research*, **34**, 1593-1627, 1987.
- Karl, D.M., R. Letelier, D. Hebel, L. Tupas, J. Dore, J. Christian, and C. Winn, Ecosystem changes in the North Pacific subtropical gyre attributed to the 1991-92 El Nino, *Nature*, **373**, 230-234, 1995.

- Karl, D., R. Letelier, L. Tupas, J. Dore, J. Christian, and D. Hebel, The role of nitrogen fixation in biogeochemical cycling in the subtropical North Pacific Ocean, *Nature*, 388, 533-538, 1997.
- Karl, D.M., A sea of change: Biogeochemical variability in the North Pacific subtropical gyre, *Ecosystems* #2, 181-214, 1999.
- Kiddon, J., M.L. Bender, J. Orchardo, D.A. Caron, J.C. Goldman, and M. Dennett, Isotopic fractionation of oxygen by respiring marine organisms, *Global Biogeochemical Cycles*, 7, 679-694, 1993.
- King, F.D., The dependence of primary production in the mixed layer of the eastern tropical Pacific on the vertical transport of nitrate, *Deep-Sea Research*, 33, 733-754, 1986.
- King, F.D., A.H. Devol, and T.T. Packard, Plankton metabolic activity in the eastern tropical North Pacific, *Deep-Sea Research*, 25, 689-704, 1978
- Kirchman, D.L., Microbial breathing lessons, *Nature*, 385, 121-122, 1997.
- Knox, M., P.D. Quay, and D. Wilbur, Kinetic isotopic fractionation during air-water gas transfer of O₂, N₂, CH₄, and H₂, *Journal of Geophysical Research*, 97, 20335-20343, 1992.
- Kroopnick, P.M., Respiration, photosynthesis, and oxygen isotope fractionation in oceanic surface water, *Limnology and Oceanography*, 20, 988-992, 1975.
- Kroopnick, P. and H. Craig, Atmospheric oxygen: Isotopic composition and solubility fractionation, *Science*, 175, 54-55, 1972.
- Legendre, L. and F. Rassoulzadegan, Plankton and nutrient dynamics in marine waters, *Ophelia*, 41, 153-172, 1995.
- Lashof, D.A., and D.R. Ahuja, Relative contributions of greenhouse gas emissions to global warming, *Nature*, 344, 529-531, 1990.
- Luz, B., E. Barkan, M.L. Bender, M.H. Thiemens, and K.A. Boering, Triple-isotope composition of atmospheric oxygen as a tracer of biosphere productivity, *Nature*, 400, 547-550, 1999.
- Luz, B. and E. Barkan, Assessment of oceanic productivity with the triple-isotope composition of dissolved oxygen, *Science*, 288, 2028-2031, 2000.
- Luz, B., E. Barkan, S. Yftach, and Y.Z. Yacobi, Evaluation of community respiratory mechanisms with oxygen isotopes: A case study in Lake Kinneret, *Limnology and Oceanography*, 47, 33-42, 2002.

- Magnuson, J.J., K.E. Webster, R.A. Assel, C.J. Bowser, P.J. Dillon, J.G. Eaton, H.E. Evans, E.J. Fee, R.J. Hall, L.R. Mortsch, D.W. Schindler, and F.H. Quinn, Potential effects of climate changes on aquatic systems: Laurentian Great Lakes and Precambrian shield region, *Hydrological Processes*, 11, 825-871, 1997.
- Matheson, D.H., and M. Munawar, Lake Superior basin and its development, *J. Great Lakes Res.*, 4, 249-263, 1978.
- Moll, R.A., and E.F. Stoermer, A hypothesis relating trophic status and subsurface chlorophyll maxima of lakes, *Arch. Hydrobiol.*, 94, 425-440, 1982.
- Mortsch, L.D. and F.H. Quinn, Climate change scenarios for Great Lakes basin ecosystem studies, *Limnology and Oceanography*, 41, 903-911, 1996.
- Munawar, M. and I. Munawar, Phytoplankton of Lake Superior 1973, *Internat. Assoc. Great Lakes Res.*, 4, 415-442, 1978.
- Murray, J.W., R.T. Barber, M.R. Roman, M.P. Bacon, and R.A. Feely, Physical and biological controls on carbon cycling in the equatorial Pacific, *Science*, 266, 58-65, 1994.
- Nalewajko, C. and D. Voltolina, Effects of environmental variables on growth rates and physiological characteristics of Lake Superior phytoplankton, *Can. J. Fish. Aquat. Sci.*, 43, 1163-1170, 1986.
- Odum, W.E., and R.T. Prentki, Analysis of five North American lake ecosystems IV. Allochthonous carbon inputs, *Verh. Internat. Verein. Limnol.*, 20, 574-580, 1978.
- Ohman, M.D., G.C. Anderson, E. Ozturgut, A multivariate analysis of plankton interactions in the eastern tropical North Pacific, *Deep-Sea Research*, 29, 1451-1469, 1982.
- Phillips, D.W., Environmental Climatology of Lake Superior, *J. Great Lakes Res.*, 4, 288-309.
- Putnam, H.D. and T.A. Olson, Primary productivity at a fixed station in Western Lake Superior, *Great Lakes Research Division, Pub. No. 15*, 119-128, 1996.
- Quay, P.D., S. Emerson, D.O. Wilbur, C. Stump, and M. Knox, The $\delta^{18}\text{O}$ of dissolved O_2 in the surface waters of the subarctic Pacific: A tracer of biological productivity, *Journal of Geophysical Research*, 98, 8447-8458, 1993.
- Quay, P.D., D.O. Wilbur, J.E. Richey, A.H. Devol, R. Benner, and B.R. Forsberg, The ^{18}O : ^{16}O of dissolved oxygen in rivers and lakes in the Amazon Basin: Determining the ratio of respiration to photosynthesis rates in freshwater, *Limnology and Oceanography*, 40, 718-729, 1995.

- Roberts, B.J., M.E. Russ, and N.E. Ostrom, Rapid and precise determination of the $\delta^{18}\text{O}$ of dissolved and gaseous dioxygen via gas chromatography-isotope rate mass spectrometry, *Environ. Sci. Technol.*, **34**, 2337-2341, 2000.
- Robertson, D.M., Regionalized loads of sediment and phosphorus to Lakes Michigan and Superior – high flow and long-term average, *J. Great Lake Res.*, **23**, 416-439, 1997.
- Sarmiento, J.L., and Siegenthaler, U., New production and the global carbon cycle, in *Primary Productivity and Biogeochemical Cycles in the Sea*, edited by P.G. Falkowski and A.D. Woodhead, pp. 317-332, Plenum Press, New York, New York, 1992.
- Saylor, J.H. and P.W. Sloss, Water volume transport and oscillatory current flow through the Straits of Mackinac, *Journal of Physical Oceanography*, **6**, 229-237, 1976.
- Scavia, D. and G.A. Laird, Bacterioplankton in Lake Michigan: Dynamics, controls, and significance to carbon flux, *Limnology and Oceanography*, **32**, 1017-1033, 1987.
- Schertzer, W.M., F.C. Elder, and J. Jerome, Water transparency of Lake Superior in 1973, *J. Great Lakes Res.*, **4**, 350-358, 1978.
- Schertzer, W.M., E.B. Bennett, and F. Chiocchio, Water balance estimates for Georgian Bay in 1974, *Water Resources Research*, **15**, 77-84, 1979.
- Six, K.D. and E. Maier-Reimer, Effects of plankton dynamics on seasonal carbon fluxes in an ocean general circulation model, *Global Biogeochemical Cycles*, **10**, 559-583, 1996.
- Smith, E.M. and W.M. Kemp, Size structure and the production/respiration balance in a coastal plankton community, *Limnology and Oceanography*, **46**, 473-485, 2001.
- Smith, S.V., and Mackenzie, F.T., The ocean as a net heterotrophic system: Implications from the carbon biogeochemical cycle, *Global Biogeochemical Cycles*, **1**, 187-198, 1987.
- Stevens, C.L.R., D. Schultz, C. Van Baalen, and P.L. Parker, Oxygen isotope fractionation during photosynthesis in a blue-green and green alga, *Plant Physiol.*, **56**, 126-129, 1975.
- Thiemens, M.H., Mass-independent isotopic fractionations and their applications, in *Isotope Effects in Gas-Phase Chemistry*, edited by J.A. Kaye, pp. 138-153, American Chemical Society, Washington, D.C., 1992.
- Vincent, D.G., and A.H. Fink, Tropical cyclone environments over the Northeastern and Northwestern Pacific based on ERA-15 analyses, *Monthly Weather Review*, **129**, 1928-1948, 2001.

- Volk, T., and M.I. Hofert, Ocean carbon pumps: Analysis of relative strengths and efficiencies in ocean-driven atmospheric CO₂ changes, in *The Carbon Cycle and Atmospheric CO₂: Natural Variations Archean and Present*, edited by E.T. Sundquist and W.S. Broecker, pp. 99-110, American Geophysical Union, Washington D.C., 1985.
- Wang, X. and J. Veizer, Respiration-photosynthesis balance of terrestrial aquatic ecosystems, Ottawa area, Canada, *Geochimica et Cosmochimica Acta*, 64, 3775-3786, 2000.
- Weiler, R.R., Chemistry of Lake Superior, *J. Great Lake Res.*, 4, 370-385, 1978.
- Weiss, R.F., The solubility of nitrogen, oxygen and argon in water and seawater, *Deep-Sea Research*, 17, 721-735, 1970.
- Williams, P.J. le B., The balance of plankton respiration and photosynthesis in the open ocean, *Nature*, 394, 55-57, 1998.
- Wissmar, R.C., J.E. Richey, and D.E. Spyridakis, The importance of allochthonous particulate carbon pathways in a subalpine lake, *J. Fish. Res. Board Can.*, 34, 1410-1418, 1977.

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