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DIAGNOSTIC MODELING OF OCEANIC BIOGEOCHEMICAL FLUXES USING A GENERAL OCEAN TURBULENCE MODEL (GOTM) AND TIME-SERIES TRACER MEASUREMENTS

A Dissertation in
Meteorology
by
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ABSTRACT

This work addressed the ocean biogeochemical context of two climate-relevant gases: carbon dioxide (CO₂) and dimethylsulfide (DMS). We combined time-series measurements and a model of ocean physics to conduct two diagnostic modeling studies.

The objective of the first case study was to estimate gross biological DMS production rates in the coastal Southern Ocean, west of the Antarctic Peninsula, near Palmer Station. A combination of field measurements from the 2005–2006 DMS sampling season and a physical model of ocean mixing were combined into a diagnostic model of DMS production. The average DMS production rate in the water column was estimated at 3.3 ± 0.5 nM d⁻¹. When diagnosed production rates were normalized by DMSP concentrations, we found a strong similarity between our estimates and the results obtained by others in a contrasting biogeochemical environment, the North Atlantic subtropical gyre. We, therefore, propose that the average DMSP to DMS conversion rate might be independent of the biogeochemical environment and place our estimate at 0.07 ± 0.01 (nM DMS d⁻¹)/(nM DMSP).

In the second case study, hydrographic and biogeochemical field measurements from the 1996–1998 sampling seasons at the European Station for Time-series in the Ocean, Canary Islands (ESTOC) were used together with a physical model of ocean mixing to diagnose net biological fluxes of nutrients, oxygen, and carbon. On the annual basis ESTOC appeared to be close to metabolic balance, with interannual fluctuations between net autotrophy and net heterotrophy. Our results suggest that export production at the site is indistinguishable from zero.
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CHAPTER 1

INTRODUCTION

This work addressed the ocean biogeochemical context of two climate-relevant gases: carbon dioxide (CO$_2$) and dimethylsulfide (DMS). We combined time-series measurements and a model of ocean physics to conduct two diagnostic modeling studies. The first, the Palmer Station case study, was focused on estimating gross biological production of DMS at two coastal sites in the Southern ocean. The second, the Canary Island case study, was focused on estimating fluxes of carbon and related elements in the eastern subtropical North Atlantic gyre.

Conceptually, diagnostic modeling is not a new approach and our contribution lies primarily in the implementation. We explicitly resolved mixed layer dynamics while estimating tracer budgets and employed unique time-series measurements to constrain tracer variability. The rationale behind the indirect approach to quantifying tracer fluxes from tracer concentration data was that direct measurement of ocean fluxes is difficult and, as a consequence, flux data are scarce and are prone to large measurement errors. In comparison, tracer concentration measurements are more reliable, have a broader spatial and temporal coverage, and integrate over larger space and time scales.
CHAPTER 2

DIAGNOSTIC MODELING OF DIMETHYLSULFIDE (DMS) PRODUCTION AT TWO SITES
WEST OF THE ANTARCTIC PENINSULA, NEAR PALMER STATION

2.1 INTRODUCTION

In this study we address the ocean biogeochemical context of dimethylsulfide (DMS) – a climate-relevant gas product of sulfur metabolism in the marine food-web, thought to be formed from the precursor compound dimethylsulfoniopropionate (DMSP). Because DMS is volatile, it escapes from the ocean surface to the atmosphere, where it reacts with a variety of oxidizing trace species to produce a range of sulfur products, most importantly non-sea-salt sulfate. Compelling observational and modeling evidence suggests that DMS is the largest biogenic source of sulfur to the atmosphere (Kettle and Andreae 2000) and that DMS-derived aerosols influence the global radiation budget by scattering incoming photons directly and by acting as cloud condensation nuclei, thus increasing cloud albedo (Charlson et al. 1987, Ayers and Gillett 2000). Because atmospheric DMS and its oxidation products are highly reactive, their concentrations strongly depend on local DMS flux from the ocean, which in turn depends on the sea-surface DMS distribution resulting from a combination of physical, chemical, and biological processes in the upper ocean. The central problem in understanding and modeling the DMS-climate connection is the lack of understanding of the dynamics of the marine DMS cycle. In particular, the most fundamental quantity in the DMS budget – the production flux – is not well constrained.

The goal of this study was to quantify gross biological DMS production at two coastal sites in the Southern Ocean using *in situ* estimates of chemical and biological loss terms in the DMS budget and the observed variability of DMS and related tracers.
DMS VARIABILITY IN THE UPPER OCEAN

DMS variability in the upper ocean is driven by biological processes involving the entire marine food web, as well as physical and chemical processes in the water column. A detailed summary of the current understanding of the marine DMS cycle is given in Gribble et al. (2001). To first approximation, DMS is produced by algal and bacterial cleavage of DMSP. DMS loss processes include biological consumption by bacteria, conversion to non-volatile species by photochemical oxidation, and removal from the ocean surface by ventilation to the atmosphere. The biological functions of DMS and DMSP production by algae are not entirely clear. DMSP is believed to regulate osmotic pressure in the cells and to prevent cells from freezing; DMSP and DMS may also be a part of an antioxidant mechanism (Sunda et al. 2001) and a defense mechanism against grazers (Wolfe et al. 1997). Despite the long history of DMS research, the details of DMS production remain elusive and the magnitude of the production flux is poorly constrained. While robust approaches exist for measuring microbial and photochemical removal of DMS from the water column, direct measurement of biological production is difficult because incubation experiments are affected by grazing and light exposure (Bailey et al. 2008).

Toole and Siegel (2004) proposed existence of two regimes for DMS cycling: a stress regime and a bloom regime. The bloom regime refers to highly productive ocean regions, where highest DMS concentrations are observed during a peak in primary production (usually characterized as a peak in chlorophyll, which is used as a proxy for phytoplankton abundance). The stress regime describes conditions when DMS and chlorophyll are decoupled, and DMS production occurs in response to oxidative stress, as proposed by Sunda et al. (2001). Such conditions exist, for example, in the subtropical gyres, where low nutrient content and high solar radiation exert oxidative stress on marine organisms. Bailey et al. (2008) conducted a diagnostic DMS study in the western part of the North Atlantic subtropical gyre, i.e., the Sargasso Sea, which is an ocean environment corresponding to the stress DMS regime. In the
present study, which is an extension of work by Bailey et al. (2008), we address DMS production in the highly productive coastal environment of the Southern Ocean, which we think corresponds to the bloom DMS regime. We expect that DMS production at Palmer station should be closely correlated with chlorophyll and DMSP concentrations.

CONCEPTUAL FRAMEWORK FOR THE DIAGNOSTIC APPROACH

Diagnostic modeling of biogeochemical fluxes that is at the core of this study is based on the Reynolds-averaged statement of tracer conservation in a turbulent flow. Let \( \bar{C} \) represent an instantaneous concentration of some tracer that can be decomposed into a mean (\( C \)) and a fluctuating (\( c \)) component:

\[
\bar{C} = C + c .
\]

(1)

Tracer concentration at any location in the flow is controlled by physical processes of advection and diffusion, as well as by a number of sources and sinks of biogeochemical origin. Therefore, three-dimensional tracer conservation can be formulated as follows:

\[
\frac{\partial C}{\partial t} = -U_i \frac{\partial C}{\partial x_i} - \frac{\partial}{\partial x_i} \left( u_i c \right) + J_{\text{constrained}} + J \quad (i = 1, 2, 3),
\]

(2)

where \( U_i \) is the mean component of the flow, \( u_i \) is the fluctuating component of the flow, and \( J \) is a composite biogeochemical source term, which can be further subdivided into constrained (i.e., \( J_{\text{constrained}} \)) and unconstrained (\( J \)) flux components, if applicable. A quantitative estimate of the unknown biogeochemical processes can be obtained if we find the means to constrain all terms except \( J \) in (2) with observations and theory and solve for \( J \) as the only unknown.

The underlying motivation behind this approach to quantify tracer fluxes from tracer concentration data is that direct measurement of ocean fluxes is difficult and, as a consequence, flux data are scarce and are prone to large measurement errors. In comparison,
tracer concentration measurements are more reliable, have a broader spatial and temporal coverage, and integrate over larger space and time scales. In addition, the theory describing the physical processes is more advanced and reliable compared with the theory behind prognostic biogeochemical modeling.

While the approach is straightforward conceptually, it becomes challenging in practical application. The challenges arise because the potential uncertainties in the diagnosed source terms are strongly dependent on the quality of the physical simulations and on the availability and quality of the data used to constrain the temporal and spatial tracer gradients.

Conceptually, diagnostic modeling is not a new approach and our innovative contribution lies primarily in the implementation. We explicitly resolved mixed layer dynamics with a physical model of ocean mixing and used unique time-series measurements obtained during the summer 2005–2006 DMS field campaign at Palmer station, Antarctica, to simulate known biogeochemical source terms and the temporal and spatial tracer gradients. The DMS field campaign measurements are discussed next.
2.2 STUDY AREA AND FIELD MEASUREMENTS

The study area is located in the coastal waters of the Southern Ocean, to the west of the Antarctic Peninsula, near Palmer Station. Starting in 1990, the Long Term Ecological Research (LTER) program has continuously operated a sampling network in the vicinity of Palmer station (http://pal.lternet.edu). Stations B (64.78° S, 64.07° W) and E (64.82° S, 64.04° W) from the LTER network are the focus of the present study (Figure 2.1). Total water column depth is about 80 m at station B and 172 m at station E.

The DMS field campaign was coordinated with the LTER 2005–2006 summer sampling season. Routine LTER sampling was conducted from a zodiac boat, approximately every two to three days, when the weather conditions were safe. Conductivity-temperature-depth (CTD) measurements were collected with a SeaBird SBE 19 SEACAT instrument and processed with the SeaBird software to produce temperature (\(T\)) and salinity (\(S\)) profiles at 1-m resolution. Underwater irradiance profiles were measured with a BSI PRR-800 Profiling Reflectance Radiometer at 16 wavelengths. Discrete water samples were analyzed for chlorophyll (\(Chl\)) by fluorometry, and for nitrate (\(N\)) by colorimetric spectroscopy. From November to February, in addition to routine LTER sampling, water samples were collected from approximately six depths for DMS-related analyses. DMS and DMSP concentrations were determined with a Shimadzu GC-14 gas chromatograph according to the procedure described in Kiene and Service (1991). Microbial consumption rate constants were determined according to the \(^{35}\)S tracer method of Kiene and Linn (2000). Absorption coefficients of chromophoric dissolved organic matter (CDOM) and apparent quantum yields were measured in order to determine photolysis rate constants. CDOM absorption coefficients were determined for the wavelength range from 190 nm to 750 nm using a Hewlett Packard 8453 UV-Vis photodiode array spectrophotometer. Apparent quantum yields were determined using filtered water samples, collected on 24
January 2006, which were incubated in polychromatic incubators at eleven wavelengths, from 290 to 400 nm. DMS loss was quantified using the $^{35}$S tracer method (Kiene and Linn, 2000), and the photon fluxes were determined by nitrate chemical actinometry (Jancowski et al. 2000). The results were scaled to 1-nM DMS concentration to produce spectral apparent quantum yields – the number of moles of DMS lost per 1 mole of photons absorbed in a 1-nM DMS solution (Toole et al. 2003).
2.3 METHODS

GENERAL MODEL CONFIGURATION

To address the DMS budget problem at LTER stations B and E, we reformulated the one-dimensional form of Equation 2 as

\[
\frac{\partial C}{\partial t} = J_{\text{mix}} + J_{\text{mic}} + J_{\text{phot}} + J_{\text{prod}},
\]

where \( C \) [nM]\(^*\) is the DMS concentration, \( J_{\text{mix}} \) [nM s\(^{-1}\)] represents the rate of DMS gain or loss due to turbulent mixing, and the composite biogeochemical source term is separated into three components: the rate of microbial consumption, \( J_{\text{mic}} \) [nM s\(^{-1}\)]; the rate of photochemical oxidation, \( J_{\text{phot}} \) [nM s\(^{-1}\)]; and the rate of gross biological production, \( J_{\text{prod}} \) [nM s\(^{-1}\)], the latter being the objective of the diagnostic calculations. Horizontal advection was assumed negligible compared with the other source terms.

For numerical implementation, we embedded a DMS module into the framework of the General Ocean Turbulence Model (GOTM), which is a one-dimensional physical model that, given the surface forcing, simulates vertical mixing in the water column and solves the one-dimensional transport equations for momentum, salt, and heat energy. Complete GOTM documentation is available online at http://gotm.net.

Model domain depth was set to 60 m, with depth resolution of 2 m, and the positive z coordinate directed upward. The model was initialized with observed profiles of \( T \), \( S \), and DMS, and integrated from 1 January 2006 (Julian day 1) through 1 March 2006 (Julian day 60) using a 30-min time step, with the biological production term excluded from the DMS budget. At

\(^*\) 1M = 1 mol L\(^{-1}\)
each time step, gross biological production for a given vertical level was diagnosed from the difference between the observed and modeled DMS concentrations:

\[ J_{\text{prod}}(t, z) = \frac{C_{\text{obs}}(t, z) - C_{\text{mod}}(t, z)}{\Delta t}, \]  

(4)

where \( C_{\text{mod}} \) [nM] is the DMS concentration calculated by the model, \( C_{\text{obs}} \) [nM] is the DMS concentration produced by linearly interpolating measured DMS concentration profiles to the model vertical and temporal grid, and \( \Delta t \) [s] is the model time step. Following each diagnostic calculation, model DMS concentrations were restored to the observations at that time before proceeding to the next model iteration.

The specific treatment of each rate term in Equation 3 is discussed next.

RATE OF TURBULENT MIXING

The rate of vertical mixing was modeled in terms of turbulent eddy diffusivity:

\[ J_{\text{mix}}(t, z) = \frac{\partial}{\partial z} \left( \overline{wc} \right) = \frac{\partial}{\partial z} \left( \nu(t, z) \frac{\partial C(t, z)}{\partial z} \right), \]  

(5)

where \( \overline{wc} \) [nM m s\(^{-1}\)] is the vertical turbulent flux of DMS, and \( \nu \) [m\(^2\) s\(^{-1}\)] is the vertical eddy diffusivity. In all base-run calculations, we used the K profile parameterization (KPP) turbulence closure of Large et al. (1994) for the vertical eddy diffusivity. An alternative turbulence closure of Mellor and Yamada (1982) was used in error analysis calculations.

RATE OF GAS EXCHANGE

Air-sea DMS flux due to gas exchange, \( F_{\text{gas}} \) [nM m s\(^{-1}\)], was included into the mixing term in the surface grid box and acted as a surface boundary condition:
\[-v(t, z = 0) \frac{\partial C(t, z = 0)}{\partial z} = F_{\text{gas}}(t) \, .\]  

(6)

For gas flux calculations, we used the stagnant film model, in which, following Kettle and Andreae (2000), we assumed the equilibrium ocean surface DMS concentrations to be negligibly small compared with the actual surface ocean concentrations:

\[F_{\text{gas}}(t) = k_w(t)C(t, z = 0) \, ,\]  

(7)

where \(k_w\) [m s\(^{-1}\)] is the gas transfer velocity for DMS. To parameterize \(k_w\) we used the formulation of Wanninkhof (1992):

\[k_w = \gamma U_{10}^2 (Sc / 600)^{-0.5} \, ,\]  

(8)

where \(\gamma = 0.31\) [(cm hr\(^{-1}\))/(m\(^2\) s\(^{-2}\))] is an empirical constant, \(U_{10}\) [m s\(^{-1}\)] is the wind speed at 10 m above sea-surface and \(Sc\) is the dimensionless Schmidt number. The relationship gives \(k_w\) in units of [cm hr\(^{-1}\)]. The Schmidt number for DMS was calculated from sea-surface \(T\) according to the polynomial fit of Saltzman et al. (1993), and the wind speed observations were obtained from the automated weather system located at Palmer Station (see MODEL FORCING section).

RATE OF MICROBIAL CONSUMPTION

Rate of microbial consumption was modeled as a first-order process with rate constant, \(k_{\text{mic}}\) [s\(^{-1}\)], constrained by \textit{in situ} measurements that were linearly interpolated to match the model depth and time grid:

\[J_{\text{mic}}(t, z) = -k_{\text{mic}}(t, z)C(t, z) \, .\]  

(9)

When depth extrapolation was necessary, we assumed zero \(k_{\text{mic}}\) at 100-m depth.
RATE OF PHOTOLYSIS

Photochemical oxidation was also modeled as a first-order process dependent on the integrated photolysis rate constant, $k_{\text{phot}}$ [s$^{-1}$]:

$$J_{\text{phot}}(t, z) = -k_{\text{phot}}(t, z)C(t, z).$$ (10)

Our calculations of the integrated photolysis rate constant followed the algorithm of Toole et al. (2003):

$$k_{\text{phot}}(t, z) = \int_{\lambda_1}^{\lambda_2} a_{\text{CDOM}}(\lambda, t)E_0(\lambda, t, z)\Phi(\lambda)d\lambda,$$ (11)

where $\lambda$ [nm] is the wavelength, $a_{\text{CDOM}}$ [m$^{-1}$] is the CDOM absorption coefficient, $E_0$ [E m$^{-2}$ s$^{-1}$ nm$^{-1}$] is the scalar irradiance (coming from all directions), and $\Phi$ [m$^3$ E$^{-1}$] is the apparent quantum yield (moles of DMS lost per one mole of photons absorbed by CDOM, normalized by DMS concentration). The integration limits are $\lambda_1 = 290$ nm and $\lambda_2 = 600$ nm. CDOM absorption coefficients and quantum yields were determined on the basis of field measurements at each station. Measured quantum yield dependence on wavelength was fit with an exponential relationship, which was then used to calculate $\Phi(\lambda)$ at required wavelength resolution. Similarly, surface $a_{\text{CDOM}}$ dependence on wavelength was fit with an exponential relationship at each measurement time. The fit coefficients were then linearly interpolated in time to produce $a_{\text{CDOM}}(\lambda, t)$ fields of required temporal resolution. Following Toole et al. (2003), $E_0$ irradiance was set to 1.2 $I$ (after accounting for unit conversion):

$$E_0 = \frac{1.2I}{h\nu N_{\lambda}},$$ (12)

* 1 E = 1 mole of photons
where $I [W \text{ m}^{-2} \text{ nm}^{-1}]$ is the measured downwelling spectral irradiance, $h = 6.6262 \times 10^{-34}$ Js is Plank’s constant, $\nu \ [\text{s}^{-1}]$ is the frequency, and $N_A = 6.022 \times 10^{23}$ mol$^{-1}$ is Avogadro’s number. To compute the downwelling underwater spectral irradiance fields we combined the surface downwelling spectral irradiance measurements of high temporal resolution (from spectral pyranometer at Palmer Station, see MODEL FORCING section) and the spectral attenuation coefficients $k_\nu$ [m$^{-1}$] calculated by fitting exponential decay curves to the measured spectral underwater irradiance profiles of lower temporal resolution:

$$I(\lambda, t, z) = \beta I(\lambda, t, 0) \exp[k_\nu(\lambda)z], \quad (13)$$

where, $\beta = 0.96$ is the wavelength independent light transmission across the air-sea interface, following Bailey et al. (2008).

MODEL FORCING

GOTM was forced with wind velocity, atmospheric temperature, pressure, humidity, precipitation, and downwelling shortwave radiation (Figure 2.2). We used 30-min averaged atmospheric measurements from the PALMOS automated weather system located at Palmer Station and operated by the Antarctic Meteorological Research Center; the data are available online at ftp://ice.ssec.wisc.edu/pub/palmer/observations. For downwelling shortwave radiation forcing, we used 30-min averaged integrated (0.285 – 2.8 μm) solar radiation measured with an Eppley Laboratory Precision Spectral Pyranometer operated by Biospherical Instruments, Inc., at Palmer Station; the data are available online at http://www.biospherical.com/nsf.

Given that GOTM is one-dimensional, all horizontal gradients must be obtained outside the model for horizontal advection processes to be included into the model. Because the spatial coverage of our field measurements was limited to only two stations, prescribing observed horizontal tracer gradients for GOTM was not feasible and we chose to use a simple
nudging method to account for the horizontal advection of $T$ and $S$. The measured profiles of $T$ and $S$ were linearly interpolated to the model vertical and temporal grid and, at each time step, the model was relaxed towards the observations using a one-day relaxation time-scale, i.e. the following nudging source term was added to both $T$ and $S$ conservation equations:

$$J_{nudg} = -\frac{1}{\tau} (Y_{\text{mod}} - Y_{\text{obs}}),$$

(14)

where $\tau$ is the nudging time scale and $Y$ represents $T$ or $S$.

PROCESSING OF MODEL OUTPUTS AND ERROR ESTIMATION

Model outputs at the original 30-min and 2-m resolution were sampled to return to the time resolution of in situ measurements and then averaged by depth intervals. To streamline the analyses of the vertical structure, we divided the model water column into three intervals: the 0 m to 20 m interval is referred to as the surface interval (SFC) and approximately corresponds to the mixed layer, the 20 m to 40 m layer is referred to as the middle interval (MID); and the 40 m to 60 m layer is referred to as the bottom interval (BOT). The entire model water column, from 0 m to 60 m, is referred to as the total column (TOT).

To provide a measure of the significance of the final results we selected a number of model input variables that we believe contributed appreciably to the final error in the model output. We assigned standard errors to these independent variables, combining available information about the measurement errors and our best judgment about the uncertainty in the model parameters (Table 2.1), and used a standard Taylor series expansion approach to propagate the errors into the final results (Squires 2001). That is, for a general case of some variable $Z$ dependent on several input variables, $Z = Z(A, B, ...)$, the standard error in the dependent variable, $\Delta Z$ can be approximated from the known standard errors in the input variables, $\Delta A, \Delta B$, etc.:
\[(\Delta Z)^2 = (\Delta Z^4)^2 + (\Delta Z^8)^2 + \ldots, \tag{15}\]

where \(\Delta Z^4 = \frac{\partial Z}{\partial A} \Delta A\) is the change in the dependent variable when the input variable \(A\) is changed by the amount of its standard error, holding the other input variables constant, and so on. The implicit assumption in Equation 15 is that the error-contributing independent variables are uncorrelated so that their co-variances are negligible (Squires 2001). We calculated the model output errors due to each error-contributing independent variable as the difference between the base-run \((R0)\) and five error-runs \((R1\) through \(R5)\), in which the independent variables were altered, one at a time, as described in Table 2.1. Increasing or decreasing the input variables by the assigned amount resulted in approximately symmetric error in the output; that is error of approximately equal magnitude and opposite sign. The summary of the error propagation calculations is given in Table 2.2.

For the observations, the standard errors in the means were estimated as follows: (1) the observation time-series were averaged by depth-intervals, each 20-m thick; (2) for each depth-averaged time-series we calculated the mean and the standard deviation; (3) the standard error of the mean was estimated as the standard deviation divided by the square root of the number of elements in the time-series (Squires 2001).
2. 4 RESULTS AND DISCUSSION

The DMS field campaign samples were collected at irregular depth and time intervals; therefore, where applicable, both the individual measurements and the interpolated fields are plotted to illustrate the extent of interpolation. All temporal averaging was done for the entire modeling period from 1 January 2006 (Julian day 1) to 1 March 2006 (Julian day 60). Plotted error bars show one standard error of the mean and are intended as an aid in data comparison: the greater the overlap in the error bars, the less meaningful is the observed difference in the mean quantities.

PHYSICAL AND BIOGEOCHEMICAL CHARACTERISTICS

Hydrographic observations for the modeling period are summarized in Figure 2.3. Measured profiles of $T$ and $S$ were used to calculate profiles of density ($\sigma_z$), referenced to sea-level pressure, from the equation of state (Millero and Poisson 1981). Mixed layer depth (MLD) was calculated as the depth at which in situ $\sigma_z$ exceeded the sea-surface $\sigma_z$ value by 0.125 kg m$^{-3}$. Station B is slightly colder and fresher compared with station E, most likely because it is located closer to a glacial melt-water source. Mixed layer depth is on the order of 10 m at station B and varies between 10 m and 30 m at station E.

Biogeochemical characteristics are summarized in Figure 2.4. For depth extrapolation we assumed zero nM DMS and DMSP concentrations, zero mg m$^{-3}$ Chl concentrations, and 30 $\mu$M $N$ concentrations at 100-m depth. Based on observed Chl concentrations, station B was slightly more productive than station E. Higher productivity induces greater $N$ drawdown at the surface at B; however, as expected, $N$ concentrations remain high even during the phytoplankton bloom events. Surface layer DMSP concentrations are clearly lower at station B,
but the differences in DMS concentrations are very minor. This observation suggests that it is reasonable to assume that horizontal DMS gradients in the region are close to zero, which then can serve as a justification for neglecting the horizontal advection term in the DMS budget, as we have chosen to do.

DIAGNOSED DMS BUDGETS

Time and depth-interval averaged base-run DMS budget parameters, i.e. rate constants for microbial consumption ($k_{mic}$) and photolysis ($k_{pho}$), vertical eddy diffusivity ($v$), and gas transfer coefficient ($k_w$), are summarized in Figure 2.5. Similarly to other station characteristics, the differences in the budget parameters are observed mostly in the surface layer. On average, $k_{mic}$ is greater at station B, where higher primary productivity is likely conducive to higher bacterial activity. Average $k_{pho}$ is non-zero only in the surface layer for both stations, and is greater at station E, which has lower light attenuation because of lower primary productivity. On average, model $v$ is larger and more variable at station B. Average $k_w$ is slightly larger at station B, consistent with lower average surface water temperatures that enter in the denominator of the $k_w$ calculations through the Schmidt number.

Figure 2.6 presents a summary of the diagnosed budgets for stations B and E. In the surface layer, plotted rate of mixing is a combination of two processes: turbulent mixing and gas exchange. As before, we see that the differences between the stations are slight and occur mostly in the surface interval. Mixing can lead to both gains and losses of DMS, depending on the direction of eddy movement and the DMS concentration gradient. When averaged, mixing rates at both stations are very close to zero in the interior and is a minor loss of DMS at the surface. At both stations, microbial consumption is the dominant loss term in the budget. DMS
loss to microbial consumption is stronger at station B, while photolysis loss is stronger at E. The production rate is slightly higher at E in the mixed layer, and the situation is reversed in the interior. However, averaged over the entire water column, DMS production is approximately equal at both stations.

From our diagnostic analysis, the scale for all of the source terms in the DMS budget is on the order of (~) 1 to 10 nM d\(^{-1}\). We use this scale information to provide additional justification for omitting the horizontal advection term in the DMS budget. The horizontal advection rate, \(J_{\text{adv}}\), in Equation 2 can be scaled as

\[
J_{\text{adv}} \sim U \frac{\Delta C}{\Delta X},
\]

where \(U\) is the horizontal velocity scale and \(\frac{\Delta C}{\Delta X}\) is the scale for the horizontal gradient in the DMS concentrations. As Smith et al. (1999) and Klinck et al. (2004) indicate, the surface currents in the region are \(\sim 0.01\) m s\(^{-1}\). We use the average DMS concentration difference between stations B and E from our analysis to approximate \(\Delta C \sim 0.1\) nM, and the horizontal distance between the stations is approximately \(\Delta X \sim 1000\) m. We estimate the scale for the horizontal advection rate \(J_{\text{adv}} \sim 0.1\) nM d\(^{-1}\), which is between one and two orders of magnitude smaller than the other source terms in the DMS budget.

DIAGNOSED RATES OF PRODUCTION

Figure 2.7 shows total-column averaged time-series of DMS production in comparison with the biogeochemical parameters. The patterns emerging from this comparison are similar for both stations. Notwithstanding the uncertainty, there are two peaks in the production rates – around Julian days 25 and 40 – reaching close to 8 nM d\(^{-1}\), while the background rate is below 5 nM d\(^{-1}\). The peaks in production are well aligned with the peaks in DMSP and \(Chl\) and with the
minima in $N$ concentrations. This suggests that at both stations B and E we are observing the DMS bloom regime discussed by Toole and Siegel (2004).

Figure 2.8 gives a depth-interval summary of the diagnosed production rates, and also production rates normalized by DMSP and by $Chl$ concentrations. At both stations, average production rate in the mixed layer is about three times higher than in the interior. While the two stations do not show marked differences in terms of production rates, some dissimilarities emerge when production rates are normalized by DMSP and $Chl$. In the mixed layer, station E produces more DMS per unit of $Chl$, but the situation is reversed in the interior. As a result, averaged over the entire column, the efficiencies of $Chl$ to DMS conversion at both stations are $\sim 1$ (nM DMS d$^{-1}$)/(mg Chl m$^{-3}$). On the other hand, production rates normalized by DMSP are approximately equal at both stations in the mixed layer, but station B shows higher rates in the interior. Averaged over the entire column, the efficiency of DMS to DMS conversion is $0.10 \pm 0.04$ (nM DMS d$^{-1}$)/(nM DMSP) for station B and $0.04 \pm 0.02$ (nM DMS d$^{-1}$)/(nM DMSP) for station E.

We estimate the time scale for the DMS cycling from a scale analysis of our results. Averaged over the entire water column, our estimate of the gross production is $\sim 3$ nM d$^{-1}$ for both stations. Combining this estimate with the average observed DMS concentration of $\sim 3$ nM, we estimate DMS replacement time – DMS concentration divided by gross production rate – on the order of one day.
2.5 SUMMARY AND CONCLUSIONS

The observed peaks in diagnosed production rates at two stations follow maxima in \( Chl \) concentrations, consistent with the bloom regime of DMS production proposed by Toole and Siegel (2004). Combining the results for both stations, average DMS production rate in the water column that we inferred through our diagnostic approach is \( 3.3 \pm 0.5 \text{ nM d}^{-1} \).

In Table 2.3 we compare our results with the results of a diagnostic DMS study in the North Atlantic subtropical gyre by Bailey et al. (2008), referred to as B08 hereafter. The B08 study used a similar modeling approach to estimate gross biological DMS production in two eddies in the Sargasso Sea - a downwelling ocean region, characterized by low nutrient concentrations and extremely low primary productivity. Therefore, B08 and the present study of the coastal Southern Ocean region describe two contrasting biogeochemical ocean environments. Average gross production in the water column estimated in this study is about three times greater than in B08. Our estimated replacement time scale of one day is smaller than in B08, where the reported replacement time is between 4 and 9 days, suggesting a faster DMS turnover in the Southern Ocean. Gross production in B08 is greatest below the mixed layer, whereas in this study gross production is greatest in the mixed layer. Compared to our estimates, gross production normalized by \( Chl \) is about an order of magnitude higher in B08. We find, however, a striking similarity in production rates normalized by DMSP concentrations, suggesting a strong underlying similarity between two contrasting biogeochemical environments in terms of DMSP to DMS conversion rate. Combining the results of B08 with the results of the present study, our estimate of the average DMSP to DMS conversion rate, independent of the biogeochemical environment, is \( 0.07 \pm 0.01 \text{ (nM DMS d}^{-1})/(\text{nM DMSP}). \)
### 2.6 TABLES

**Table 2.1:** Summary of the error-estimation runs and the errors assigned to the input variables.

<table>
<thead>
<tr>
<th>Model run number</th>
<th>Altered input variable</th>
<th>Method of error assignment</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>C [nM]</td>
<td>fractional error = ±10%</td>
<td>Estimated from the reported DMS measurement errors</td>
</tr>
<tr>
<td>R2</td>
<td>ν [m² s⁻¹]</td>
<td>used alternative turbulence closure scheme</td>
<td>Subjective selection of Mellor and Yamada (1982) turbulence model</td>
</tr>
<tr>
<td>R3</td>
<td>k_u [m s⁻¹]</td>
<td>fractional error = ±50% assigned to empirical γ coefficient in the Wanninkhof (1992) formulation</td>
<td>Subjective estimate</td>
</tr>
<tr>
<td>R4</td>
<td>k_{mic} [s⁻¹]</td>
<td>fractional error = ±16%</td>
<td>Estimated from the reported measurement errors</td>
</tr>
<tr>
<td>R5</td>
<td>k_{phao} [s⁻¹]</td>
<td>fractional error = ±50%</td>
<td>Subjective estimate</td>
</tr>
</tbody>
</table>
Table 2.2: Propagation of errors, assigned to the input variables, into the uncertainty estimation for the dependent variables. $R0$ is the model base-run. $R1$ through $R5$ are model error-runs as described in Table 2.1. The error notation follows Equation 15.

<table>
<thead>
<tr>
<th>Dependent variable</th>
<th>Input variables</th>
<th>Partial errors in the dependent variable due to each input variable</th>
<th>Combination of the partial errors into the total error in the dependent variable</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_{mix}$</td>
<td>$C$</td>
<td>$\Delta J_{mix}^C = J_{mix,R1} - J_{mix,R0}$</td>
<td>$(\Delta J_{mix}^C)^2 = (\Delta J_{mix}^C)^2 + (\Delta J_{mix}^v)^2$</td>
</tr>
<tr>
<td></td>
<td>$v$</td>
<td>$\Delta J_{mix}^v = J_{mix,R2} - J_{mix,R0}$</td>
<td></td>
</tr>
<tr>
<td>$J_{gas}$</td>
<td>$C$</td>
<td>$\Delta J_{gas}^C = J_{gas,R1} - J_{gas,R0}$</td>
<td>$(\Delta J_{gas}^C)^2 = (\Delta J_{gas}^C)^2 + (\Delta J_{gas}^{k_w})^2$</td>
</tr>
<tr>
<td></td>
<td>$k_w$</td>
<td>$\Delta J_{gas}^{k_w} = J_{gas,R3} - J_{gas,R0}$</td>
<td></td>
</tr>
<tr>
<td>$J_{mic}$</td>
<td>$C$</td>
<td>$\Delta J_{mic}^C = J_{mic,R1} - J_{mic,R0}$</td>
<td>$(\Delta J_{mic}^C)^2 = (\Delta J_{mic}^C)^2 + (\Delta J_{mic}^{k_{mic}})^2$</td>
</tr>
<tr>
<td></td>
<td>$k_{mic}$</td>
<td>$\Delta J_{mic}^{k_{mic}} = J_{mic,R4} - J_{mic,R0}$</td>
<td></td>
</tr>
<tr>
<td>$J_{phot}$</td>
<td>$C$</td>
<td>$\Delta J_{phot}^C = J_{phot,R1} - J_{phot,R0}$</td>
<td>$(\Delta J_{phot}^C)^2 = (\Delta J_{phot}^C)^2 + (\Delta J_{phot}^{k_{phot}})^2$</td>
</tr>
<tr>
<td></td>
<td>$k_{phot}$</td>
<td>$\Delta J_{phot}^{k_{phot}} = J_{phot,R4} - J_{phot,R0}$</td>
<td></td>
</tr>
<tr>
<td>$J_{prod}$</td>
<td>$C$</td>
<td>$\Delta J_{prod}^C = J_{prod,R1} - J_{prod,R0}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$v$</td>
<td>$\Delta J_{prod}^v = J_{prod,R2} - J_{prod,R0}$</td>
<td>$(\Delta J_{prod}^C)^2 = (\Delta J_{prod}^C)^2 + (\Delta J_{prod}^v)^2 +$</td>
</tr>
<tr>
<td></td>
<td>$k_w$</td>
<td>$\Delta J_{prod}^{k_w} = J_{prod,R3} - J_{prod,R0}$</td>
<td>$(\Delta J_{prod}^{k_w})^2 + (\Delta J_{prod}^{k_{mic}})^2 + (\Delta J_{prod}^{k_{phot}})^2$</td>
</tr>
<tr>
<td></td>
<td>$k_{mic}$</td>
<td>$\Delta J_{prod}^{k_{mic}} = J_{prod,R4} - J_{prod,R0}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$k_{phot}$</td>
<td>$\Delta J_{prod}^{k_{phot}} = J_{prod,R4} - J_{prod,R0}$</td>
<td></td>
</tr>
</tbody>
</table>
Table 2.3: Diagnosed rates of DMS production, normalized production rates, and DMSP and Chl concentrations from the present study of the coastal Southern Ocean (B and E) in comparison with results from the Sargasso Sea study (C1 and A2) by Bailey et al. (2008).

<table>
<thead>
<tr>
<th>Interval</th>
<th>Station</th>
<th>$J_{prod}$ [nM d$^{-1}$]</th>
<th>DMSP [nM]</th>
<th>$J_{prod}$/DMSP [(nM d$^{-1}$)/nM]</th>
<th>Chl [mg m$^{-3}$]</th>
<th>$J_{prod}$/Chl [(nM d$^{-1}$)/ (mg m$^{-3}$)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-60</td>
<td>B</td>
<td>3.3 ± 0.6</td>
<td>47 ± 10</td>
<td>0.10 ± 0.04</td>
<td>6 ± 1</td>
<td>1.1 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>E</td>
<td>3.2 ± 0.7</td>
<td>69 ± 14</td>
<td>0.04 ± 0.02</td>
<td>3.3 ± 0.7</td>
<td>1.0 ± 0.2</td>
</tr>
<tr>
<td>TOT</td>
<td>C1</td>
<td>0.73 ± 0.09</td>
<td>15.5</td>
<td>0.047 ± 0.006</td>
<td>0.063</td>
<td>12 ± 1</td>
</tr>
<tr>
<td></td>
<td>A2</td>
<td>0.9 ± 0.12</td>
<td>10.4</td>
<td>0.087 ± 0.014</td>
<td>0.044</td>
<td>20 ± 3</td>
</tr>
<tr>
<td>0-20</td>
<td>B</td>
<td>6 ± 1</td>
<td>82 ± 14</td>
<td>0.08 ± 0.04</td>
<td>9 ± 1</td>
<td>1.0 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>E</td>
<td>7 ± 2</td>
<td>127 ± 22</td>
<td>0.05 ± 0.03</td>
<td>5.1 ± 0.9</td>
<td>1.6 ± 0.2</td>
</tr>
<tr>
<td>SFC</td>
<td>C1</td>
<td>0.64 ± 0.09</td>
<td>10.8</td>
<td>0.058 ± 0.008</td>
<td>0.040</td>
<td>15 ± 2</td>
</tr>
<tr>
<td></td>
<td>A2</td>
<td>0.78 ± 0.09</td>
<td>7.5</td>
<td>0.104 ± 0.012</td>
<td>0.033</td>
<td>22 ± 3</td>
</tr>
<tr>
<td>20-40</td>
<td>B</td>
<td>2.7 ± 0.5</td>
<td>36 ± 7</td>
<td>0.11 ± 0.04</td>
<td>5 ± 1</td>
<td>1.3 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>E</td>
<td>1.8 ± 0.4</td>
<td>49 ± 9</td>
<td>0.03 ± 0.02</td>
<td>2.9 ± 0.7</td>
<td>0.71 ± 0.2</td>
</tr>
<tr>
<td>MID</td>
<td>C1</td>
<td>0.91 ± 0.14</td>
<td>14.5</td>
<td>0.062 ± 0.010</td>
<td>0.055</td>
<td>15 ± 3</td>
</tr>
<tr>
<td></td>
<td>A2</td>
<td>1.14 ± 0.16</td>
<td>9.5</td>
<td>0.120 ± 0.017</td>
<td>0.040</td>
<td>28 ± 4</td>
</tr>
<tr>
<td>40-60</td>
<td>B</td>
<td>1.4 ± 0.3</td>
<td>23 ± 5</td>
<td>0.10 ± 0.03</td>
<td>3.5 ± 0.8</td>
<td>1.2 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>E</td>
<td>1.0 ± 0.2</td>
<td>31 ± 6</td>
<td>0.04 ± 0.02</td>
<td>1.9 ± 0.5</td>
<td>0.9 ± 0.3</td>
</tr>
<tr>
<td>BOT</td>
<td>C1</td>
<td>0.64 ± 0.10</td>
<td>21.3</td>
<td>0.030 ± 0.005</td>
<td>0.095</td>
<td>7 ± 1</td>
</tr>
<tr>
<td></td>
<td>A2</td>
<td>0.78 ± 0.15</td>
<td>14.1</td>
<td>0.055 ± 0.011</td>
<td>0.059</td>
<td>13 ± 3</td>
</tr>
</tbody>
</table>
Figure 2.1: Map of the study area. Palmer Station and the LTER basin sampling stations B and E are shown as black triangles.
Figure 2.2: Summary of 30-min averaged GOTM forcing data. Meteorological measurements are from the PALMOS automated weather system located at Palmer Station. Integrated shortwave irradiance measurements are from a spectral pyranometer located at Palmer Station.
Figure 2.3: Temperature, salinity and density at sea-level pressure at stations B and E. Interpolated fields are shown in color. Observations are indicated by light vertical lines. Calculated mixed layer depth is shown as a thick white line. The last column compares the physical characteristics by depth interval, averaged over the entire modeling period. The error bars give one standard error of the means.
Figure 2.4: DMS, DMSP, chlorophyll, and nitrate concentrations at stations B and E. Interpolated fields are shown in color and the observations are indicated in grey. The last column compares the biogeochemical characteristics by depth interval, averaged over the entire modeling period. The error bars give one standard error of the means.
Figure 2.5: Summary of DMS budget parameters used in the base-run budget calculations for stations B and E. The rate constants for microbial consumption ($k_{mic}$) and photolysis ($k_{phot}$), vertical eddy diffusivity ($\nu$), and gas transfer coefficient ($k_w$) are averaged by depth interval and over the entire modeling period. The error bars give one standard error of the means.
Figure 2.6: Diagnosed DMS budgets for stations B and E. DMS production rate ($J_{\text{prod}}$), combined rate of mixing and gas exchange ($J_{\text{mix}}$), microbial consumption rate ($J_{\text{mic}}$), and photolysis rate ($J_{\text{phot}}$) are averaged by depth interval and over the entire modeling period. The error bars give estimated uncertainty in model outputs calculated by propagation of errors from the model input variables.
Figure 2.7: Time-series of the diagnosed DMS production rate ($J_{prod}$), DMSP, chlorophyll ($Chl$), and nitrate ($N$) for stations B and E. The time-series are averaged over the entire model water column (0 m to 60 m). For $J_{prod}$, the error bars give estimated uncertainty in model output calculated by propagation of errors in the model input variables. For DMSP, $Chl$, and $N$ the error bars give one standard error of the means.
Figure 2.8: The diagnosed DMS production rates ($J_{\text{prod}}$), production rates normalized by DMSP ($J_{\text{prod}} / \text{DMSP}$), and production rates normalized by chlorophyll ($J_{\text{prod}} / \text{Chl}$) for stations B and E. The rates are averaged by depth interval and over the entire modeling period. For $J_{\text{prod}}$ the error bars give estimated uncertainty in model output calculated by propagation of errors from the model input variables. For normalized rates, the error bars give the combined error due to the uncertainty in $J_{\text{prod}}$ and the standard error of the mean DMSP and Chl.
2.8 REFERENCES


CHAPTER 3

DIAGNOSTIC MODELING OF BIOLOGICAL PUMP PROPERTIES IN THE EASTERN
SUBTROPICAL NORTH ATLANTIC GYRE AT THE EUROPEAN STATION FOR TIME-
SERIES IN THE OCEAN, CANARY ISLANDS (ESTOC)

3.1 INTRODUCTION

The ocean and the atmosphere exchange mass, momentum, and energy at the air-sea interface. These exchanges connect marine biogeochemistry to climate and climate change. The changing state of the atmosphere alters the physical state of the ocean, which ultimately has an effect on ocean biogeochemical processes. Changes in ocean biogeochemistry, in turn, affect the exchange processes at the air-sea interface. According to recent estimates, carbon dioxide (CO₂) uptake by the oceans and terrestrial biosphere are approximately similar in magnitude and remove about 50-60% of anthropogenic emissions (Solomon et al. 2007). The uptake of CO₂ by the ocean depends on the CO₂ partial pressure (pCO₂) gradient across the air-sea interface, which is primarily controlled by the variability in the ocean surface pCO₂ because, compared with the ocean, the atmospheric CO₂ distribution is relatively uniform. Therefore, in the context of climate change, it is important to understand the processes that determine the ocean surface CO₂ distribution. The term ocean biological pump is used to describe the photosynthetic CO₂ uptake at the surface followed by export of organic carbon to the deep ocean (Sarmiento and Gruber 2006). In steady state, a net downward flux of dissolved and particulate organic carbon (the strength of the biological pump) is approximately compensated by a net upward flux of dissolved inorganic carbon, which is produced in deep waters through remineralization of organic matter back to the inorganic constituents (Sarmiento and Gruber 2006). How the changing atmospheric CO₂ concentrations and ocean temperatures
might affect the strength of the biological pump, relative to the upward inorganic carbon flux, has important implications for the net uptake of atmospheric CO$_2$ by the ocean and, consequently, for climate change. A number of related concepts and terms are used interchangeably in the biogeochemical literature to characterize the biological pump — export production, new production, and net community production (Jin et al. 2007) — because steady state between downward export of organic carbon and the upward flux of dissolved inorganic carbon is usually implicitly assumed. All the above terms refer to the net production of organic matter, that is, after accounting for destruction of organic matter by remineralization. In contrast, primary production refers to the gross biological production of organic matter.

Subtropical gyres — the largest of ocean biomes, covering about 65% of the ocean surface — have traditionally been considered less important to the global biological pump than the more productive high latitude regions but emerging evidence suggests that the subtropics may potentially play a much greater role in the marine carbon cycle than previously thought (Emerson et al. 2001, Neuer et al. 2002a). These new developments provide a strong motivation to understand and quantify the biological pump in the subtropics.

In this study we combine hydrographic and biogeochemical measurements from the European Station for Time-Series in the Ocean, Canary Islands (ESTOC) and a one-dimensional model of ocean physics into a diagnostic model of the local biological pump properties. In particular, we are interested in a number of important fluxes, such as export production and net calcification, processes that are difficult to measure directly. The diagnostic approach employs tracer distributions, which can be accurately measured, the tracer conservation equation, and a model of physical processes to infer, by difference, net biogeochemical fluxes. This approach has been used in numerous marine biogeochemical studies of the upper ocean with varying levels of complexity in quantifying physical processes. Najjar et al. (1992) and Anderson and Sarmiento (1994) used an ocean general circulation model in combination with a climatology of surface ocean phosphate observation to diagnose
the global distribution export production from the upper ocean. A similar approach was taken by 
Gnandesikan (1999) to estimate particulate silicon export. Ono et al. (2001) used a climatology 
of dissolved inorganic carbon, nitrate, and dissolved oxygen measurements to infer net 
photosynthesis and remineralization below the mixed layer in the Sargasso Sea. Our approach 
builds on that of Ono et al. (2001) by (1) applying a mechanistic upper ocean mixing model, (2) 
extending the domain to the surface, (3) attempting to resolve monthly and interannual 
variability in a three-year time series. It differs from Ono et al. (2001) in that we apply the 
technique to measurements in the eastern subtropical North Atlantic Ocean.

The ESTOC site has been characterized as a typical oligotrophic environment with low 
phytoplankton biomass compared with more productive ocean regions (Neuer et al. 2007). 
Neuer et al. (2002a) estimated 1996–1998 primary production of organic matter at ESTOC at 
11.9 mol C m$^{-2}$ yr$^{-1}$, by applying a bio-optical model to monthly in situ chlorophyll and 
temperature. Three puzzles have emerged regarding the carbon cycle at ESTOC. The first 
regards the amount of export production. Shallow particle organic carbon (POC) flux, 
determined with surface-tethered sediment traps located at 200 m depth, was used to estimate 
export production at 0.2 mol C m$^{-2}$ yr$^{-1}$. Neuer et al. (2002a) pointed out that while ESTOC 
primary production was very similar to the estimates at the two other subtropical locations that 
were examined in the study, the export production was four to five times smaller. In contrast, 
Gonzalez-Davila et al. (2007) estimated net community production in the mixed layer at 3.3 ± 
0.8 mol C m$^{-2}$ yr$^{-1}$ by using a ten-year (1995–2004) ESTOC time-series of upper-ocean 
dissolved inorganic carbon (DIC)$^1$ observations. Therefore, export production estimates based 
on surface water column observations appear higher than those based on sediment trap 
observations. The difference could be partially due to the fact that the estimates correspond to

$^1$ DIC = $[H_2CO_3^+] + [HCO_3^-] + [CO_3^{2-}]$, where $[H_2CO_3^+]$ represents the sum of aqueous $CO_2$ and 
carbonic acid, which are not distinguished operationally.
different depths and there is some remineralization between the mixed layer base and 200 m, so that the amount of particulate organic matter reaching the sediment traps is reduced compared with what was exported from the mixed layer. For example, if we assume that sediment trap fluxes follow a power law dependency on depth with an exponent of about -1 (e.g., Kwon and Primeau, 2006) then the particle flux at 200 m is half that at 100 m. In addition, there could potentially be a downward flux of dissolved organic carbon across 200 m, which the sediment traps would not account for but which would be linked to a DIC uptake in the mixed layer (Hansell and Carlson 1998) and vertically migrating zooplankton, which actively export carbon from the euphotic zone to depth (Steinberg et al. 2000). Finally, sediment traps can be subject to large collection biases because of difficulty in collecting horizontally moving particles and of contamination by swimming organisms (Buesseler et al. 1994).

The second puzzle concerning the carbon cycle at ESTOC (and in subtropical waters in general) is about the metabolic status of the surface layer. Systems where photosynthesis exceeds remineralization are termed autotrophic; systems where remineralization exceeds photosynthesis are termed heterotrophic (see for example Alvarez and Alvarez-Salgado 2007, Hansell et al. 2004, Maixandeau et al. 2005). It has been suggested that the ocean surrounding ESTOC might be net heterotrophic (Alvarez and Alvarez-Salgado 2007), in contrast to the conclusions of Neuer at al. (2007) and Gonzalez-Davila et al. (2007), based on the analysis of DIC concentrations in the mixed layer, that the system was net autotrophic. Therefore, estimates of export production from different sources not only vary by more than an order of magnitude, but there is even a disagreement whether organic matter is exported at all.

The third puzzle about carbon cycling at ESTOC is about the degree of calcification, which is the process by which marine organisms use DIC to form shells and skeletons through precipitation of calcium carbonate. Calcification is an important component of the marine carbon cycle because it strongly influences the alkalinity of sea water, which is linked to ocean pH and DIC speciation. Calcification increases surface ocean CO₂ concentration, and thus the
**rain ratio** — the export ratio of inorganic (calcium carbonate) to organic carbon. The rain ratio is a useful metric for assessing the relative importance of calcification and photosynthesis on surface ocean CO₂ levels. Sarmiento et al. (2002) suggested an average rain ratio of 0.014 ± 0.019 for the Subtropical North Atlantic gyre, based on the observations of the vertical gradients of alkalinity and nitrate in the upper 100 m. Neuer et al. (2002b) reported an average winter rain ratio at ESTOC of 0.4 and an average fall rain ratio of 0.6 from the analysis of 1997–1998 shallow sediment traps at 330 m depth. These authors also determined that calcium carbonate accounted for 53% of total particle mass in the winter, and for 65% in the summer, while biogenic opal accounted for less than 2% in both seasons. Sprengel et al. (2002) reported that coccolithophorids² are one of the main primary and carbonate producers in the Canary Islands region and estimated that on average one third of total carbon sedimentation at 750 m is contributed by coccolithophorids, with highest values in winter up to 96%. Compared with coccolithophorids, diatoms³ are rare and contribute between 2% and 25% to total microplankton abundance (Neuer et al. 2007). The apparent prevalence of coccolithophorids over diatoms suggested by the above discussion implies that calcium carbonate fluxes must play a prominent role in carbon cycling at ESTOC and must be explicitly included in carbon budget calculations.

The **goal** of the present study was to diagnose local nutrient, carbon, and oxygen fluxes in order to assess the magnitude of carbon export production at the ESTOC site in the eastern subtropical North Atlantic gyre and, hence, contribute an independent estimate to the previously published studies that used ESTOC time-series measurements to infer biological pump properties (e.g. Neuer et al. 2007, Gonzalez-Davila et al. 2007). The important characteristic of our method is that we used a one-dimensional model of ocean mixing to explicitly resolve mixed

---

² Coccolithophorids are unicellular phytoplankton that precipitate calcium carbonate inside their cells to form calcite scales (coccoliths) that are used to make hard cell-walls (coccoospheres).

³ Diatoms are mostly unicellular phytoplankton that precipitate biogenic opal from dissolved silicate to build hard cell-walls (frustules).
layer dynamics at ESTOC, and attempted to characterize calcium carbonate precipitation and dissolution separately from photosynthesis and remineralization of organic carbon.
3.2 STUDY AREA AND FIELD MEASUREMENTS

ESTOC (29.15°N, 15.5°W) is located in the eastern subtropical North Atlantic gyre about 100 km north of the Island of Gran Canaria. The subtropical gyres are vast ocean regions characterized by downwelling circulation, low supply of nutrients, and low chlorophyll concentrations. Figure 3.1 shows the location of the ESTOC site superimposed on the climatology of surface chlorophyll a concentrations in the North Atlantic subtropical gyre, derived from satellite measurements — the gyre is clearly visible as the area of low concentrations. The station has a water depth of 3600 m and is located on the edge of the Canary current, which is a weak eastern boundary current. Regular water column observations and carbon system measurements have been carried out mainly from the Spanish research vessel BO Taliarte starting in 1996 (Neuer et al. 2007). For the diagnostic modeling we used hydrographic and biogeochemical measurements collected monthly at the ESTOC site from 1996 to 1998. In-depth discussion of the observations and of the measurement techniques are presented in Cianca et al. (2007), Gonzalez-Davila (2003), Gonzalez-Davila (2007), and Neuer et al. (2007).
3.3 METHODS

The diagnostic modeling approach used in this study was based on the Reynolds-averaged statement of tracer conservation in a turbulent flow. Tracer concentration at any location in the flow is controlled by physical processes and by local sources and sinks of biological origin. A quantitative estimate of the net biological processes can be obtained if we find the means to constrain tracer time-tendency and the physical terms with observations and theory and solve for the net biological source as the only unknown. The potential uncertainty in the diagnosed source term depends on the quality of the physical simulations and on the availability and quality of the time-series data, making the practical application of the conceptual approach a challenging process.

We applied the diagnostic approach to the following tracers: nitrate ($NO_3^-$), phosphate ($PO_4^{3-}$), oxygen ($O_2$), and two carbon tracers – a tracer for calcium carbonate ($C_{\text{inorg}}^*$) and a tracer for organic carbon ($C_{\text{org}}^*$), which are used to quantify two biologically-mediated DIC pathways, calcification and photosynthesis. The carbon tracers were calculated from the observations of alkalinity ($Alk$), $DIC$, and $NO_3^-$:

$$C_{\text{inorg}}^* = \frac{1}{2} (Alk + [NO_3^-]) \frac{35}{S}$$  \hspace{1cm} (1)

and

$$C_{\text{org}}^* = DIC \frac{35}{S} - C_{\text{inorg}}^* ,$$  \hspace{1cm} (2)

where the fraction $\frac{35}{S}$ is the salinity correction factor. Addition of freshwater by precipitation decreases tracer concentrations by dilution, while removal of freshwater by evaporation causes concentrations to increase. For $DIC$ and $Alk$, variations in tracer concentrations caused by
addition and removal of freshwater through precipitation and evaporation are comparable in magnitude to the biologically-induced variations and can be removed by salinity normalization, with the assumption that variations due to freshwater fluxes are directly proportional to changes in salinity (Najjar 1992). The formulation for \( C_{\text{inorg}}^* \) is similar to the concept of potential alkalinity, which was first introduced by Brewer et al. (1975), and has been used extensively in marine biogeochemistry studies (Sarmiento and Gruber 2006). Theoretical considerations for the derivation of (1) and (2) are as follows. Alkalinity is the acid-neutralizing capacity of the solution, and thus can be chemically represented as the net excess of base cations over acid anions. For sea water, Sarmiento and Gruber (2006) give the following definition of alkalinity, leaving out trace constituents:

\[
Alk = [Na^+] + [K^+] + 2[Mg^{2+}] + 2[Ca^{2+}] + [NH_4^+] - [Cl^-] - 2[SO_4^{2-}] - [Br^-] - [NO_3^-].
\] (3)

From the measured composition of marine phytoplankton, the stoichiometric formula for organic matter production and remineralization according to Redfield et al. (1963) and amended by Anderson (1995) is

\[
106CO_2 + 16HNO_3 + H_3PO_4 + 78H_2O \Leftrightarrow C_{106}H_{175}O_{42}N_{16}P + 150O_2.
\] (4)

The idealized formula for calcification is (Sarmiento and Gruber 2006):

\[
2HCO_3^- + Ca^{2+} \Leftrightarrow CO_2 + CaCO_3 + H_2O.
\] (5)

Therefore, from an Alk standpoint, biologically-mediated processes affect only calcium and nitrate concentrations and the time rate of change of Alk due to biological processes is

\[
\frac{\partial Alk}{\partial t} = 2 \frac{\partial [Ca^{2+}]}{\partial t} - \frac{\partial [NO_3^-]}{\partial t}.
\] (6)

Solving for the time rate of change of calcium, we have

\[
\frac{\partial [Ca^{2+}]}{\partial t} = \frac{\partial}{\partial t} \left[ \frac{Alk + [NO_3^-]}{2} \right],
\] (7)
which gives us the definition of the tracer for calcium carbonate, or equivalently, for the amount of $DIC$ used during calcification, which we called $C_{inorg}^*$ in Equation 1. The amount of $DIC$ used during photosynthesis can then be determined by difference, which is $C_{org}^*$ in Equation 2.

**DIAGNOSTIC MODEL CONFIGURATION**

We reformulated the general Reynolds-averaged tracer conservation into a one-dimensional form as follows:

$$\frac{\partial C}{\partial t} = J_{adv} + J_{mix} + J_{bio}, \quad (8)$$

where $C$ [mmol m$^{-3}$] is the concentration of any of the five tracers, $J_{adv}$ [mmol m$^{-3}$ s$^{-1}$] represents tracer flux due to vertical advection by mesoscale eddy pumping, $J_{mix}$ [mmol m$^{-3}$ s$^{-1}$] represents tracer flux due to turbulent mixing, and $J_{bio}$ [mmol m$^{-3}$ s$^{-1}$] is the net biological source term that is the objective of the diagnostic calculations. Horizontal advection was assumed negligible compared with the other source terms.

For the numerical implementation, we embedded an individual module for each tracer into the framework of the General Ocean Turbulence Model (GOTM), which is a one-dimensional physical model that, given the surface forcing, simulates vertical mixing in the water column and solves the one-dimensional transport equations for momentum, salt, and heat energy. The advantage of this framework is that it allows for a variety of turbulence closure schemes. Complete GOTM documentation is available online at http://gotm.net (Burchard and Bolding 2001).

The model depth domain was set to 0–200 m, with a depth resolution of 2 m, and the positive $z$ coordinate directed upward. The model was initialized with observed profiles of temperature ($T'$), salinity ($S'$), and the tracers, and integrated from 1 January 1996 through 1
January 1999, using a 30-min time step, with the net biological term excluded from the tracer budgets. At each time step, the net biological source term for a given vertical level for each tracer was diagnosed from the difference between the observed and modeled tracer concentrations:

$$J_{bio}(t, z) = \frac{C_{obs}(t, z) - C_{mod}(t, z)}{\Delta t},$$

(9)

where $C_{mod}$ [mmol m$^{-3}$] is the tracer concentration calculated by the model, $C_{obs}$ [mmol m$^{-3}$] is the tracer concentration produced by linearly interpolating measured tracer concentration profiles to the model vertical and temporal grid, and $\Delta t$ [s] is the model time step. Following each diagnostic calculation, model tracer concentrations were restored to match the observations before proceeding to the next model iteration.

RATE OF TURBULENT MIXING

The rate of vertical mixing was modeled using

$$J_{mix}(t, z) = -\frac{\partial}{\partial z} \left( \overline{wC} \right) = \frac{\partial}{\partial z} \left( \nu(t, z) \frac{\partial C(t, z)}{\partial z} \right),$$

(10)

where $\overline{wC}$ [mmol m$^{-2}$ s$^{-1}$] is the vertical turbulent flux of the tracer, and $\nu$ [m$^2$ s$^{-1}$] is the vertical eddy diffusivity of salinity, which was assumed to be representative of the tracer eddy diffusivities. In all primary calculations, we used the K profile parameterization (KPP) turbulence closure of Large et al. (1994) for the vertical eddy diffusivity. An alternative turbulence closure scheme based on the dynamic dissipation rate equation of Rodi (1987) was used in error analysis calculations.
AIR-SEA FLUX

We assumed the rainwater inputs of all tracers negligibly small, and considered only gas exchange of \(O_2\) and \(CO_2\) at the air-sea interface. Thus, in the model, only \(O_2\) and \(C_{org}^*\) have non-zero air-sea fluxes. Diffusive gas exchange depends on the difference between the observed sea-surface concentration of the gas and the concentration required for equilibrium with the atmosphere. Diffusive gas exchange of \(O_2\) and \(CO_2\) was parameterized using the stagnant film model:

\[
F_{gas}^{diff} = k_w (C - C_{eq}),
\]

where \(F_{gas}^{diff}\) [mmol m\(^{-2}\) s\(^{-1}\)] is the net upward diffusive gas flux at the air-sea interface, \(k_w\) [m s\(^{-1}\)] is the gas transfer velocity, and \(C_{eq}\) [mmol m\(^{-3}\)] is the equilibrium concentration.

To parameterize \(k_w\) we used the formulation of Wanninkhof (1992):

\[
k_w = \gamma U_{10}^2 \left(\frac{Sc}{600}\right)^{-0.5},
\]

where \(\gamma = 0.31\) (cm hr\(^{-1}\))/(m\(^2\) s\(^{-2}\)) is an empirical constant, \(U_{10}\) [m s\(^{-1}\)] is wind speed at 10 m above sea-surface, and \(Sc\) is the dimensionless Schmidt number for the appropriate gas. The relationship gives \(k_w\) in units of [cm hr\(^{-1}\)].

NCEP Reanalysis 2 Gaussian grid 6-hr average wind data (http://www.cdc.noaa.gov), interpolated to the ESTOC location, were used for \(U_{10}\). The Schmidt numbers for \(O_2\) and \(CO_2\) were calculated from sea-surface \(T\) according to Wanninkhof (1992).

The formulation of Garcia and Gordon (1992) was used to calculate \(C_{eq}\) for \(O_2\) from sea surface \(T\) and \(S\) measurements at ESTOC.
For $CO_2$ flux calculations, Equation 11 was reformulated in terms of a solubility parameter, $\alpha$ [mmol m$^{-3}$ μatm$^{-1}$], atmospheric partial pressure, $pCO_2^{air}$ [μatm], and water partial pressure, $pCO_2^{water}$ [μatm]:

$$F_{gas}^{diff} = -k_1 \alpha (pCO_2^{air} - pCO_2^{water}).$$

We approximated $pCO_2^{water}$ with fugacity measurements collected at ESTOC. The Weiss and Price (1980) formulation was used to calculate $\alpha$ from measured sea-surface $T$ and $S$.

We calculated $pCO_2^{air}$ using the mole fraction of $CO_2$ in dry air, $xCO_2$, from GLOBALVIEW-CO2 (2009) at weekly resolution and the pressure of dry air, $P_{dry}$ [μatm], that was approximated as the difference between NCEP reanalysis 6-hr average atmospheric pressure, $P$, and equilibrium water vapor pressure, $e_s$, assuming that water vapor is at saturation in the vicinity of the air-sea interface:

$$pCO_2^{air} = xCO_2 P_{dry} \approx xCO_2 (P - e_s).$$

The formulation of Weiss and Price (1980) was used to calculate equilibrium water vapor pressure from measured $T$ and $S$.

For $CO_2$ we assumed that the total air-sea gas exchange flux equaled the diffusive flux, $F_{gas}^{diff}$. For $O_2$, which is much less soluble than $CO_2$, we assumed that the total air-sea gas exchange flux was the sum of the diffusive flux and the flux due to air-injection by entrained bubbles, $F_{gas}^{ai}$, which has been suggested to contribute substantially to the air-sea flux of low-solubility gases (Stanley et al. 2006, Sarmiento and Gruber 2006). We used the parameterization of air-injection by bubbles summarized in Stanley et al. (2006). The details are given in Appendix A.
All input data used in the gas exchange calculations were linearly interpolated in time and all calculations were performed at the 30-min time resolution.

The calculated total air-sea flux was included into the mixing term in the surface grid box and acted as a surface boundary condition:

$$-\mathbf{v}(t, z = 0) \frac{\partial \mathbf{C}(t, z = 0)}{\partial z} = F_{\text{gas}}(t).$$  \hspace{1cm} (15)

RATE OF VERTICAL ADVECTION

Previous studies indicated non-zero vertical velocities present in the subtropical gyres due to mesoscale eddy activity (Mourino-Carballido and Neuer 2008, Siegel et al. 1999, Cianca et al. 2007). To approximate vertical advection of the tracers due to isopycnal displacement induced by mesoscale eddies, we estimated eddy vertical velocity, \( w \) [m s\(^{-1}\)], from the observed density anomaly distribution at ESTOC. Our calculations are similar to the algorithm outlined in Siegel et al. (1999) and Cianca et al. (2007), but we modified the approach by removing the seasonal cycle from the density distribution. Hydrographic measurements (\( T \) and \( S \)) were used to calculate the density distribution at sea-level pressure (Millero and Poisson 1981). The time rate of change of density was assumed to result from the vertical advection of isopycnal surfaces from their mean location:

$$\frac{\partial \sigma_i(t, z)}{\partial t} = -w(t, z) \frac{\partial \bar{\sigma}_i(z)}{\partial z},$$  \hspace{1cm} (16)

where \( \bar{\sigma}_i(z) \) [kg m\(^{-3}\)] is the mean density profile calculated from \( \sigma_i(t, z) \). Rearranging, the displacement of isopycynals from their mean location, \( \eta \) [m], was calculated as

$$\eta(t, z) = -\frac{\sigma_i(t, z) - \bar{\sigma}_i(z)}{\frac{\partial \bar{\sigma}_i(z)}{\partial z}}.$$  \hspace{1cm} (17)
The assumption in Equation 20 does not take into account seasonal heating and cooling of the water column that also displaces isopycnal contours. To correct for seasonal effects, we calculated the monthly mean climatology of estimated $\eta$ and, at each depth, fit a mean seasonal cycle curve to the climatology, assuming a sinusoidal shape. The resulting relationships were used to calculate the seasonal isopycnal displacement distribution, $\eta_{\text{seas}}$ [m]. The eddy component of isopycnal displacement, $\eta_{\text{eddy}}$ [m], was then calculated as:

$$\eta_{\text{eddy}}(t, z) = \eta(t, z) - \eta_{\text{seas}}(t, z). \quad (18)$$

The time-rate-of-change of $\eta_{\text{eddy}}$ averaged below the mixed layer was used to calculate the time-series of $w$. The calculated velocity values were interpolated to the model 30-min time-step and were assigned to occur at 90 m depth in the model, corresponding to the average base of the mixed layer, and to decrease linearly to zero at the top and bottom of the model domain. All model fields, except the turbulent quantities, were then advected with this vertical velocity:

$$J_{\text{adv}} = -w \frac{\partial C}{\partial z}. \quad (19)$$

MODEL FORCING

NCEP Reanalysis 2 Gaussian grid, 6-hour average data (http://www.cdc.noaa.gov) were used to force the model. The following fields were linearly interpolated from the four nearest NCEP grid points to the ESTOC location: wind velocity components, atmospheric temperature, atmospheric pressure, relative humidity, precipitation rate, and fractional cloud cover. The surface turbulent fluxes of heat energy, moisture, and momentum were calculated using bulk formulae of Large and Pond (1982). Incident short-wave radiation was calculated from time-of-day, latitude, longitude, and cloud fraction following Simpson and Paulson (1979). Net long-
wave radiation was calculated as a function of cloud fraction following Clark et al. (1974). A constant heat flux correction of -110 W m\(^{-2}\) (energy removed from the ocean) was added to improve the agreement between the modeled and observed heat-energy content of the total water column. Short-wave radiation was not used as a surface boundary condition, but rather a vertical profile with depth was parameterized according to Ohlmann and Siegel (2000), with a prescribed constant chlorophyll value of 0.1 mg m\(^{-3}\), and used as a local energy source at each depth level.

Given that GOTM is one-dimensional, for horizontal advection processes to be included into the model, the horizontal gradients must be obtained outside the model. Because the spatial coverage of our time-series data was limited to a single location, we chose to use a simple nudging method to account for the horizontal advection of \(T\) and \(S\), and, as stated earlier, assumed that horizontal advection of the biogeochemical tracers was negligibly small compared with the other terms in the conservation equations. The measured profiles of \(T\) and \(S\) were linearly interpolated to the model vertical and temporal grid and, at each time step, the model was relaxed towards the observations using a five-day relaxation time-scale, i.e. the following nudging source term was added to both \(T\) and \(S\) conservation equations:

\[
J_{\text{nudge}} = -\frac{1}{\tau}(Y_{\text{mod}} - Y_{\text{obs}}),
\]

where \(\tau\) is the nudging time scale and \(Y\) represents \(T\) or \(S\).

PROCESSING OF MODEL OUTPUT FIELDS AND ERROR ESTIMATION

All model output fields at the original 30-min and 2-m resolution were averaged daily and then all days were averaged between each two consecutive times when the water column was actually sampled (Table 3.1); these monthly-averaged model outputs were used in all subsequent analyses and are referred to as model outputs in the following discussion. We
separated the total model water column (TOT, 0–200 m) into two intervals: the 0 m to 100 m interval is referred to as the surface interval (SFC) and approximately corresponds to the mixed layer and the euphotic zone, and the 100 m to 200 m layer is referred to as the bottom interval (BOT). The mixed layer depth was calculated from \( T \) observations as the depth where the \textit{in situ} \( T \) exceeded the 10-m value by 1 °C. This criterion was selected subjectively because it best represented the extent of the surface mixing that was visually noticeable in the measured hydrographic and biogeochemical tracer fields. The average calculated mixed layer depth was about 90 m.

To provide a measure of uncertainty for the model results we assumed that air-sea gas exchange, vertical advection, and mixing calculations were the main contributors to the error in the model output. According to Gonzales-Davila et al. (2003), measurement error was less than 1% for nutrients and carbon parameters; therefore the measurement error was assumed negligibly small in comparison with the modeling uncertainty. We subjectively assigned \( \pm 50\% \) error to the total air-sea flux and the rate of vertical advection; the mixing rate error was estimated as the difference in the mixing rates given by the KPP and Rodi (1987) turbulence models. The standard Taylor series expansion approach was used to propagate the errors assigned to the model input variable into the final results (Squires 2001). That is, the diagnosed biological source term was assumed dependent on three error-contributing input variables, \( J_{bio} = J_{bio} (w, v, F_{gas}^{tot}) \), and the standard error in the dependent variable, \( \Delta J_{bio} \), was calculated from the assumed standard errors in the input variables, \( \Delta w \), \( \Delta v \), and \( \Delta F_{gas}^{tot} \)

\[
(\Delta J_{bio})^2 = (\Delta J_{bio}^w)^2 + (\Delta J_{bio}^v)^2 + (\Delta J_{bio}^{F_{gas}})^2,
\]

where \( \Delta J_{bio}^w = \frac{\partial J_{bio}}{\partial w} \Delta w \) is the partial error, or change in the dependent variable when the input variable \( w \) is changed by the amount of its standard error, holding the other input variables constant, and so on. The implicit assumption in Equation 21 is that the error-contributing
independent variables are uncorrelated so that their co-variances are negligible (Squires 2001). Error-estimation model runs corresponding to the errors assigned to the model input variables are summarized in Table 3.2. The partial errors were calculated as the difference between the base-run ($R0$) and the individual error-estimation runs ($R1$ through $R3$)

\[
\Delta J_{bio}^{w} = J_{bio,R1} - J_{bio,R0},
\]

(22a)

\[
\Delta J_{bio}^{v} = J_{bio,R2} - J_{bio,R0},
\]

(22b)

\[
\Delta J_{bio}^{w} = J_{bio,R3} - J_{bio,R0}.
\]

(22c)

For the total air-sea flux and the rate of vertical advection, increasing and decreasing the input variable by the assigned amount resulted in approximately symmetric error in the output, that is, the errors of approximately equal magnitude and opposite sign. The error-estimation algorithm was applied to the model outputs directly and also to the annual and climatiological summaries.
3.4 RESULTS AND DISCUSSION

Monthly and depth-interval average net biological source terms, diagnosed from the five addressed biogeochemical tracers, are shown in Figures 3.2 through 3.6. During photosynthesis (Equation 4, direction from left to right), inorganic nitrate, phosphate, and carbon are consumed, while molecular oxygen is produced. Therefore, in our model output, net photosynthesis (i.e., its excess over remineralization) is signaled by negative $J_{bio}$ for nitrate, phosphate, and $C^*_\text{org}$, and by positive $J_{bio}$ for oxygen. By analogy, net remineralization is signaled by positive $J_{bio}$ for nitrate, phosphate, and $C^*_\text{org}$, and by negative $J_{bio}$ for oxygen. From the idealized formula for calcium carbonate skeleton and shell formation (Equation 5), in our model output, net calcification is signaled by negative $J_{bio}$ for $C^*_\text{inorg}$ and net dissolution is signaled by positive $J_{bio}$ for $C^*_\text{inorg}$. Depth-interval average biological source terms were characterized by large seasonal and inter-annual variability and were subject to large uncertainties, calculated by the error-propagation algorithm (not shown for clarity considerations of the plots). The depth-interval average model outputs were further summarized as discussed below.

ANNUAL BIOLOGICAL FLUXES

We calculated average biological fluxes per unit area by multiplying the depth-interval average biological source terms, which had units per unit volume, by the thickness of the corresponding depth intervals. The fluxes were then averaged annually for each of the simulation years (1996, 1997, and 1998) and the climatology was calculated as the average of the annual fluxes. To ease the comparison between the tracers, we used the stoichiometric
ratios for $C:N:P:O_2$ of 106:16:1:-150 from Equation 4 to convert all annual fluxes to carbon units; these ratios are referred to as **Redfield ratios** through the rest of the discussion. After the unit conversion, photosynthesis corresponded to a negative flux for all tracers. Table 3.3 gives a summary of the annual biological fluxes and the total propagated uncertainty. The contribution of the individual model input variables to the total uncertainty in the final result is summarized in Figures 3.7 through 3.11. The mixing term is the largest contributor to the total error, especially for the annual fluxes during the year 1996, which was characterized by strong mixing and deepest mixed layer in comparison with the other model years. As a result, the uncertainty in the climatological averages is largely due to the uncertainty encountered during 1996. The uncertainty due to mixing was minimized, when the annual fluxes were averaged over the entire model water column.

**SENSITIVITY OF THE DIAGNOSTIC APPROACH IN THE OLIGOTROPHIC ENVIRONMENT**

The key conclusion from the results presented in Table 3.3 is that the sensitivity of the diagnostic method we used was low, when applied to the oligotrophic ESTOC environment: some fractional errors on the diagnosed annual fluxes greatly exceeded 100%. In the diagnostic method we based our calculations on differences between quantities that were close in magnitude, so that the calculated result was relatively small in magnitude, compared with the input, and the fractional error was greatly magnified (Squires 2001, p. 49). Characterizing an oligotrophic ESTOC environment is extremely challenging precisely because the biological fluxes are low and, thus, comparable in magnitude to the other terms in the budgets. This problem was clearly articulated in the study by Kortzinger et al. (2001) that based new production estimates on the uptake of carbon and nitrogen along 20°W in the northeast Atlantic Ocean. The authors were able to obtain conclusive results in the eutrophic part of the transect.
but the approach was not sufficiently sensitive for a quantitative description of a more
glitrophic environment to the south of 42°N.

METABOLIC STATUS IN VIEW OF THE ENCOUNTERED UNCERTAINTY

We focused on the sign of the diagnosed annual fluxes averaged over the total model
water column to assess the net metabolic status of the marine system – the balance between \textit{in situ} production of organic matter and its consumption. The picture that emerged from Table 3.3
was that the site appeared to fluctuate annually between net autotrophy and net heterotrophy,
based on nitrate, phosphate, and $C^*_\text{org}$ flux estimates; while oxygen biological fluxes consistently
pointed towards net autotrophy. The climatological flux estimates for nitrate, phosphate, and
$C^*_\text{org}$ pointed to net remineralization in the total water column, while oxygen indicated net
photosynthesis. With regards to $C^*_\text{inorg}$, two out of the three years were characterized by net
dissolution of calcium carbonate, and one year — by net calcification, which resulted in
climatological net dissolution.

Gas exchange parameterizations that we used might have overestimated outgassing
and thus generated a bias in the biological source terms calculated in the mixed layer from
oxygen and $C^*_\text{org}$, both of which were affected by gas exchange. If this were the case, then our
overestimation of oxygen loss to the atmosphere resulted in the overestimation of the mixed
layer biological production of oxygen, which, converted to carbon units, produced the negative
bias, leading to overestimation of photosynthesis. If we overestimated $CO_2$ loss to the
atmosphere, this would have resulted in the overestimation of the mixed layer biological
production of $C^*_\text{org}$, which would have produced the positive bias, leading to overestimation of
remineralization.
The notion of net heterotrophy is difficult to reconcile with the idea that there must be a source of organic carbon, other than local biological production: in other words, organic matter must be imported. Lateral advection is an obvious possible mechanism of organic matter import; as stated earlier, horizontal advection was not included in our model. It has also been proposed that the atmosphere-ocean exchange of dissolved organic carbon might be an important component of the upper ocean carbon budget. For example, Dachs et al. (2005) reported that average gaseous diffusive fluxes of organic carbon from the atmosphere to the ocean (9 mol C m$^{-2}$ yr$^{-1}$) exceeded inputs by dry aerosol deposition (0.43 mol C m$^{-2}$ yr$^{-1}$) and net CO$_2$ input (2.3 mol C m$^{-2}$ yr$^{-1}$) during their study in the NE Subtropical Atlantic, part of which was conducted in close proximity to ESTOC (transect along 26°N, starting form the Island of Gran Canaria).

Based on our analysis and notwithstanding the uncertainty of the estimates, on the annual basis ESTOC appears to be close to metabolic balance, with interannual fluctuations between net autotrophy and net heterotrophy. This conclusion is in disagreement with the net annual export production of 3.3 ± 0.8 mol C m$^{-2}$ yr$^{-1}$ estimated in the mixed layer by Gonzalez-Davila et al. (2007) from a ten-year (1995–2004) time-series of upper-ocean DIC observations. The discrepancy could be due to the fact that our estimates were based on a shorter three-year time-series. Given the interannual variability that we noticed in the metabolic status, examination of a ten-year record could feasibly yield a very different result. In addition, Gonzales-Davila et al. (2007) made the assumption that the calcification contribution to the carbon budget was negligible, while we explicitly included the calcification tracer in our analysis. However, this difference is likely insignificant because our climatological estimate points to net dissolution of calcium carbonate. Another possible reason for the disagreement between the present study and the Gonzales-Davila et al. (2007) study is the difference in the treatment of the physical components of the carbon budget. In contrast to mixing, gas exchange, and vertical advection terms used in our study, Gonzales-Davila et al. (2007) used diffusive flux,
entrainment due to mixed layer deepening, and gas exchange. The carbon budgets are compared in Table 3.4.

We calculated the ratios of the diagnosed climatological fluxes for the total water column to estimate $C:N$ remineralization ratio at $6 \pm 4$ and $N:P$ remineralization ratio at $19 \pm 4$. Our estimates are in good agreement with the canonical $C:N:P$ Redfield ratios of 106:16:1. We were not able to provide a quantitative estimate of the inorganic to organic carbon uptake — the rain ratio due to the low sensitivity of the calculation method. Qualitatively, however, our results suggest that $C_{\text{org}}^*$ and $C_{\text{inorg}}^*$ are comparable in magnitude, indicating that that calcification is an important component of the carbon budget at ESTOC.

SCALE ANALYSIS OF HORIZONTAL ADOVENTION

As stated earlier, horizontal advection was not included in our one-dimensional calculations. For any tracer, horizontal advection, $J_{\text{hadv}}$, depends on the $u$ and $v$ velocity components of the flow and on the horizontal gradients of the tracer

$$J_{\text{hadv}} = -u \frac{\partial C}{\partial x} - v \frac{\partial C}{\partial y}.$$  \hspace{1cm} (23)

ESTOC time-series measurements are an extremely valuable research tool for one-dimensional analysis, but these measurements do not supply information for estimation of horizontal tracer gradients, necessary to constrain horizontal advection of the tracers. We conducted a scale analysis of horizontal advection at ESTOC, using tracer measurements from the research cruises conducted in the vicinity of the site. The horizontal advection rate in Equation 23 can be scaled as

$$J_{\text{hadv}} \sim U \frac{\Delta C}{\Delta L},$$  \hspace{1cm} (24)
where $U$ is the horizontal velocity scale and $\frac{\Delta C}{\Delta L}$ is the scale for the horizontal gradient in tracer concentrations.

Neuer et al. (2007) calculated geostrophic transport at ESTOC using cruise data from 1997 and 1998. Net meridional transport was predominantly southward during all seasons and the station appeared to be located in a relatively calm area of the Canary Current. Pelegri et al. (2005) reported predominantly southward surface currents in the region up to 0.1 m s$^{-1}$. We used AVISO absolute geostrophic velocity data products from merged satellite altimeter data (data available online at http://www.aviso.oceanobs.com) to estimate root-mean-square magnitude of the geostrophic velocity components at ESTOC. Using altimeter data from 1992 to 2009, the calculation resulted in 4.0 cm s$^{-1}$ for the zonal component and 3.8 cm s$^{-1}$ for the meridional component. From the above, we assumed that $U \sim 0.01$ m s$^{-1}$ was a representative horizontal velocity scale for the ESTOC site.

To estimate the scale of horizontal gradients, we used tracer measurements collected during the Meteor 06MT19970107 research cruise; the data are available online as part of the CARINA project (Perez and Muller 2007). To estimate tracer gradients we used cruise station 42 (29.17°N, 15.5°W, occupied on 10 January 1997), which approximately corresponded to the ESTOC location, and cruise station 59 (32.25°N, 15.17°W, occupied on 16 January 1997), which was located almost directly to the north of ESTOC. We chose to use the north-south direction, because the predominant Canary current flow direction is from the south (Neuer et al. 2007). The horizontal distance between the two cruise stations was approximately 300 km, resulting in $\Delta L \sim 1 \times 10^5$ m for the horizontal distance scale. To scale the horizontal change in tracer concentrations, $\Delta C$, we used concentration measurements averaged over the upper 200 m of the water column.

The estimated horizontal advection scales for each of the five tracers are summarized in Table 3.5. The table also shows the scales for the five diagnosed biological terms, for the
comparison. According to our estimates, horizontal advection rates for the tracers are approximately one order of magnitude lower, than the diagnosed biological production rates.
3.5 SUMMARY AND CONCLUSIONS

We combined hydrographic and biogeochemical measurements from the European Station for Time-Series in the Ocean, Canary Islands (ESTOC) and a one-dimensional model of ocean physics into a diagnostic model that allowed us to examine biological pump properties at the site. The sensitivity of the diagnostic method was low, when applied to the oligotrophic ESTOC environment where the biological fluxes are comparable in magnitude to the other terms in the budgets. Such setup strongly amplifies the errors propagated to the final results from the model input. Notwithstanding the uncertainty of the estimates, on the annual basis ESTOC appears to be close to metabolic balance, with interannual fluctuations between net autotrophy and net heterotrophy and no signal of export production.

Assuming that the ESTOC site is typical of the subtropical ocean, the large uncertainties that we encountered in quantifying the biological pump properties at the ESTOC site are representative of the challenges presented by the oligotrophic ocean environments in general: because the biological fluxes are very low, they are comparable in magnitude to the other terms in tracer budgets, and are very difficult to quantify. The implications of our analysis are that it is uncertain whether the subtropical regions serve as a source or a sink of carbon in the global climate system. It is likely that the status of the subtropics might fluctuate, as at ESTOC, based on the ambient physical conditions. Subtropical gyres are vast ocean regions that account for about 65% of the ocean surface. Because of their large size and despite of the low biological productivity, the subtropical gyres are an integral part of the climate system by virtue of their vastness, and it is imperative to improve our understanding of these environments in order to assess their role in the global climate.
### 3.6 TABLES

**Table 3.1:** List of dates used for averaging the model output fields, corresponding to the dates when the water column was sampled at ESTOC.

<table>
<thead>
<tr>
<th>No.</th>
<th>Date</th>
<th>No.</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24-Jan-1996</td>
<td>16</td>
<td>02-Jul-1997</td>
</tr>
<tr>
<td>2</td>
<td>10-Feb-1996</td>
<td>17</td>
<td>22-Aug-1997</td>
</tr>
<tr>
<td>3</td>
<td>13-Mar-1996</td>
<td>18</td>
<td>14-Sep-1997</td>
</tr>
<tr>
<td>5</td>
<td>15-May-1996</td>
<td>20</td>
<td>02-Nov-1997</td>
</tr>
<tr>
<td>6</td>
<td>12-Jun-1996</td>
<td>21</td>
<td>01-Dec-1997</td>
</tr>
<tr>
<td>7</td>
<td>09-Jul-1996</td>
<td>22</td>
<td>20-Jan-1998</td>
</tr>
<tr>
<td>8</td>
<td>27-Sep-1996</td>
<td>23</td>
<td>17-Feb-1998</td>
</tr>
<tr>
<td>10</td>
<td>17-Dec-1996</td>
<td>25</td>
<td>24-Apr-1998</td>
</tr>
</tbody>
</table>
Table 3.2: Summary of the error-estimation model runs and the errors assigned to the input variables.

<table>
<thead>
<tr>
<th>Model run number</th>
<th>Altered input variable</th>
<th>Method of error assignment</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R1a$ $R1b$</td>
<td>$w$ [m s$^{-1}$]</td>
<td>fractional error = +50%</td>
<td>Subjective estimate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>fractional error = -50%</td>
<td></td>
</tr>
<tr>
<td>$R2$</td>
<td>$v$ [m$^2$ s$^{-1}$]</td>
<td>used alternative turbulence closure scheme</td>
<td>Subjective selection of Rodi (1987) turbulence model</td>
</tr>
<tr>
<td>$R3a$ $R3b$</td>
<td>$F_{gas}^{tot}$ [s$^{-1}$]</td>
<td>fractional error = +50%</td>
<td>Subjective estimate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>fractional error = -50%</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.3: Summary of average annual biological fluxes in the surface layer (SFC, 0–100 m), bottom layer (BOT, 100–200 m), and for the total model surface water column (TOT, 0–200 m). All fluxes were converted to carbon units using Redfield ratios. For nitrate, phosphate, $C^\text{org}$, and oxygen negative flux corresponds to photosynthesis; for $C^\text{inorg}$ negative flux corresponds to calcification. Letters in parentheses mark estimated net process for the total column.

<table>
<thead>
<tr>
<th>Tracer flux [mol C m$^{-2}$ yr$^{-1}$]</th>
<th>Depth interv.</th>
<th>1996</th>
<th>1997</th>
<th>1998</th>
<th>CLIMATOLOGY</th>
</tr>
</thead>
<tbody>
<tr>
<td>nitrate</td>
<td>SFC</td>
<td>0 ± 34</td>
<td>0.3 ± 0.9</td>
<td>0.0 ± 0.6</td>
<td>0 ± 12</td>
</tr>
<tr>
<td></td>
<td>BOT</td>
<td>-1 ± 35</td>
<td>-0.3 ± 0.2</td>
<td>2.3 ± 2.0</td>
<td>0 ± 11</td>
</tr>
<tr>
<td></td>
<td>TOT</td>
<td>-1 ± 1 (P)</td>
<td>0.0 ± 0.7 (B)</td>
<td>2.2 ± 2.6 (R)</td>
<td>0.5 ± 0.7 (R)</td>
</tr>
<tr>
<td>phosphate</td>
<td>SFC</td>
<td>-0.2 ± 0.9</td>
<td>0.4 ± 0.7</td>
<td>0.2 ± 0.6</td>
<td>0.1 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>BOT</td>
<td>-0.4 ± 0.4</td>
<td>0.1 ± 0.7</td>
<td>1.2 ± 1.3</td>
<td>0.3 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>TOT</td>
<td>-0.5 ± 1.2 (P)</td>
<td>0.5 ± 1.4 (R)</td>
<td>1.3 ± 1.8 (R)</td>
<td>0.4 ± 0.7 (R)</td>
</tr>
<tr>
<td>$C^\text{org}$</td>
<td>SFC</td>
<td>0 ± 64</td>
<td>0 ± 1</td>
<td>0 ± 11</td>
<td>0 ± 25</td>
</tr>
<tr>
<td></td>
<td>BOT</td>
<td>0 ± 66</td>
<td>0 ± 1</td>
<td>1 ± 8</td>
<td>0 ± 25</td>
</tr>
<tr>
<td></td>
<td>TOT</td>
<td>0 ± 2 (B)</td>
<td>-0.2± 0.4 (P)</td>
<td>2 ± 3 (R)</td>
<td>0.4 ± 0.3 (R)</td>
</tr>
<tr>
<td>oxygen</td>
<td>SFC</td>
<td>-7 ± 35</td>
<td>-9 ± 5</td>
<td>-6 ± 5</td>
<td>-7 ± 15</td>
</tr>
<tr>
<td></td>
<td>BOT</td>
<td>-1 ± 38</td>
<td>0.6 ± 0.3</td>
<td>1.3 ± 0.3</td>
<td>0 ± 13</td>
</tr>
<tr>
<td></td>
<td>TOT</td>
<td>-8 ± 4 (P)</td>
<td>-8 ± 5 (P)</td>
<td>-4 ± 6 (P)</td>
<td>-7 ± 4 (P)</td>
</tr>
<tr>
<td>$C^\text{inorg}$</td>
<td>SFC</td>
<td>0.9 ± 0.2</td>
<td>0.3 ± 0.2</td>
<td>-0.4 ± 1.4</td>
<td>0.3 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>BOT</td>
<td>0.0 ± 1.8</td>
<td>0.0 ± 0.1</td>
<td>0.1± 0.6</td>
<td>0.0 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>TOT</td>
<td>0.8 ± 1.9 (D)</td>
<td>0.2 ± 0.2 (D)</td>
<td>-0.3 ± 0.8 (CF)</td>
<td>0.3 ± 0.4 (D)</td>
</tr>
</tbody>
</table>

Key:

B = balance
P = net remineralization
R = net photosynthesis
CF = net calcification
D = net dissolution
Table 3.4: Comparison of estimated carbon budgets. The present study results are based on three-year climatology (1996–1999) of the upper 200 m. Gonzales-Davila et al. (2007) results are based on ten-year climatology (1995-2004) for the mixed layer.

<table>
<thead>
<tr>
<th>Carbon budget flux</th>
<th>Gonzales-Davila et al. (2007) [mol C m$^2$ yr$^{-1}$]</th>
<th>Present study [mol C m$^2$ yr$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>biological</td>
<td>-3.3 ± 0.8</td>
<td>0.4 ± 0.3</td>
</tr>
<tr>
<td>mixing</td>
<td>Diffusive: 0.2 ± 0.03</td>
<td>0.0 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>Entrainment: 3.4 ± 1.1</td>
<td></td>
</tr>
<tr>
<td>gas exchange</td>
<td>0.05 ± 0.02</td>
<td>-0.1 ± 0.2</td>
</tr>
<tr>
<td>vertical advection</td>
<td>not used</td>
<td>0.3 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>0.35</td>
<td>0.6</td>
</tr>
</tbody>
</table>
Table 3.5: Scale analysis of horizontal advection using tracer concentration measurements collected at stations 42 and 59 during 06MT19970107 cruise. The measurements were averaged over 0–200 m depth interval. Horizontal advection scale was calculated according to Equation 24 assuming $\Delta L \sim 1 \times 10^5$ m horizontal distance scale and $U \sim 0.01$ m s$^{-1}$ horizontal velocity scale.

<table>
<thead>
<tr>
<th>Tracer</th>
<th>Observed concentration difference [mmol m$^{-3}$]</th>
<th>Scale estimate for concentration difference [mmol m$^{-3}$]</th>
<th>Calculated horizontal advection scale [mmol m$^{-3}$ mo$^{-1}$]</th>
<th>Scale of the diagnosed biological source, for comparison [mmol m$^{-3}$ mo$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>nitrate</td>
<td>1.49</td>
<td>$\sim$1</td>
<td>$\sim$0.1</td>
<td>$\sim$1</td>
</tr>
<tr>
<td>phosphate</td>
<td>0.0023</td>
<td>$\sim$0.001</td>
<td>$\sim$1$\times 10^{-4}$</td>
<td>$\sim$0.01</td>
</tr>
<tr>
<td>$C_{\text{org}}^*$</td>
<td>0.99</td>
<td>$\sim$1</td>
<td>$\sim$0.1</td>
<td>$\sim$1</td>
</tr>
<tr>
<td>oxygen</td>
<td>7.40</td>
<td>$\sim$10</td>
<td>$\sim$1</td>
<td>$\sim$10</td>
</tr>
<tr>
<td>$C_{\text{inorg}}^*$</td>
<td>1.98</td>
<td>$\sim$1</td>
<td>$\sim$0.1</td>
<td>$\sim$1</td>
</tr>
</tbody>
</table>
Figure 3.1: Map of the North Atlantic subtropical gyre, showing the location of the ESTOC site and surface chlorophyll $a$ [mg m$^{-3}$] climatology from satellite measurements from 1997-2008 (produced with the Giovanni online data system, http://gdata1.sci.gsfc.nasa.gov).
Figure 3.2: Summary of the net biological source ($J_{bio}$) diagnosed from nitrate: (a) time-series of $J_{bio}$ averaged over the surface layer (SFC, 0–100 m); (b) time-series of $J_{bio}$ averaged over the bottom layer (BOT, 100–200 m); (c) time-series of $J_{bio}$ averaged over the total water column (TOT, 0–200 m).
Figure 3.3: Summary of the net biological source ($J_{bio}$) diagnosed from phosphate: (a) time-series of $J_{bio}$ averaged over the surface layer (SFC, 0–100 m); (b) time-series of $J_{bio}$ averaged over the bottom layer (BOT, 100–200 m); (c) time-series of $J_{bio}$ averaged over the total water column (TOT, 0–200 m).
Figure 3.4: Summary of the net biological source ($J_{bio}$) diagnosed from the $C_{org}^*$ tracer: (a) time-series of $J_{bio}$ averaged over the surface layer (SFC, 0–100 m); (b) time-series of $J_{bio}$ averaged over the bottom layer (BOT, 100–200 m); (c) time-series of $J_{bio}$ averaged over the total water column (TOT, 0–200 m).
Figure 3.5: Summary of the net biological source ($J_{bio}$) diagnosed from oxygen: (a) time-series of $J_{bio}$ averaged over the surface layer (SFC, 0–100 m); (b) time-series of $J_{bio}$ averaged over the bottom layer (BOT, 100–200 m); (c) time-series of $J_{bio}$ averaged over the total water column (TOT, 0–200 m).
Figure 3.6: Summary of the net biological source ($J_{bio}$) diagnosed from the $C^*_{\text{inorg}}$ tracer: (a) time-series of $J_{bio}$ averaged over the surface layer (SFC, 0–100 m); (b) time-series of $J_{bio}$ averaged over the bottom layer (BOT, 100–200 m); (c) time-series of $J_{bio}$ averaged over the total water column (TOT, 0–200 m).
Figure 3.7: Estimated uncertainties in the diagnosed nitrate annual biological fluxes resulting from the propagation of errors assigned to the model input variables. The partial errors due to vertical advection (W) and mixing (MIX) were calculated as the differences between the annual fluxes computed in the base-run and the error-estimation runs defined in Table 3.2. The total error (TOT) was calculated from the sum of squares of the partial errors. All fluxes were converted to carbon units using Redfield ratios.
Figure 3.8: Estimated uncertainties in the diagnosed phosphate annual biological fluxes resulting from the propagation of errors assigned to the model input variables. The partial errors due to vertical advection (W) and mixing (MIX) were calculated as the differences between the annual fluxes computed in the base-run and the error-estimation runs defined in Table 3.2. The total error (TOT) was calculated from the sum of squares of the partial errors. All fluxes were converted to carbon units using Redfield ratios.
Figure 3.9: Estimated uncertainties in the diagnosed $C_{\text{org}}^*$ annual biological fluxes resulting from the propagation of errors assigned to the model input variables. The partial errors due to vertical advection (W), mixing (MIX), and gas exchange (GAS) were calculated as the differences between the annual fluxes computed in the base-run and the error-estimation runs defined in Table 3.2. The total error (TOT) was calculated from the sum of squares of the partial errors.
Figure 3.10: Estimated uncertainties in the diagnosed oxygen annual biological fluxes resulting from the propagation of errors assigned to the model input variables. The partial errors due to vertical advection (W), mixing (MIX), and gas exchange (GAS) were calculated as the differences between the annual fluxes computed in the base-run and the error-estimation runs defined in Table 3.2. The total error (TOT) was calculated from the sum of squares of the partial errors. All fluxes were converted to carbon units using Redfield ratios.
Figure 3.11: Estimated uncertainties in the diagnosed $C_{\text{inorg}}^*$ annual biological fluxes resulting from the propagation of errors assigned to the model input variables. The partial errors due to vertical advection (W) and mixing (MIX) were calculated as the differences between the annual fluxes computed in the base-run and the error-estimation runs defined in Table 3.2. The total error (TOT) was calculated from the sum of squares of the partial errors.
3.8 APPENDIX A. AIR-INJECTION PARAMETERIZATION

\( F_{\text{gas}}^{ai} \) is calculated as the sum of two processes: air injection due to bubbles that are completely dissolved, \( F_c \), and air injection due to bubbles that are partially dissolved, \( F_p \).

If \( U_{10} < 2.27 \text{ m s}^{-1} \), \( F_c = 0 \), otherwise it is given by:

\[
F_c = -\gamma_c A_c (U_{10} - 2.27)^3 \nu_a \frac{pC_{\text{air}}}{RT_{\text{air}}},
\]

where \( \gamma_c \) is a tunable parameter (set to 1), \( A_c = 1.4 \times 10^{-3} \), \( \nu_a \) is the air-entrainment velocity (set to 0.1 m s\(^{-1}\)), \( pC_{\text{air}} \) [Pa] is the partial pressure of oxygen in the atmosphere (calculated from the atmospheric pressure, assuming a constant mole fraction of oxygen, \( xO_2 = 0.2095 \), \( R = 8.31 \text{ [Pa m}^3\text{ mol}^{-1}\text{ K}^{-1}] \) is the universal gas constant, and \( T_{\text{air}} \) [K] is air temperature.

If \( U_{10} < 2.27 \text{ m s}^{-1} \), \( F_p = 0 \), otherwise it is given by:

\[
F_p = -\gamma_p A_p (U_{10} - 2.27)^3 \nu_a \beta D^{2/3} \frac{pC_{\text{bubble}} - pC_{\text{water}}}{RT_{\text{air}}},
\]

where \( \gamma_p \) is a tunable parameter (set to 1), \( A_p = 2 \times 10^5 \), \( \beta \) is the Bunsen solubility coefficient (we used parameterization of Weiss (1970) form sea-surface \( T \)), \( D \) is oxygen diffusivity in water (we used a constant value of 1.97 \( \times 10^{-2} \text{ m}^2 \text{ s}^{-1} \)), \( pC_{\text{bubble}} \) [Pa] is the partial pressure of gas in the bubbles, and \( pC_{\text{water}} \) [Pa] is the partial pressure in the water (calculated from observed sea-surface oxygen concentrations and Bunsen solubility coefficient). Partial pressure in the bubbles was approximated as:

\[
pC_{\text{bubble}} = xC(P_{\text{dry}} + \rho gh_{\text{bubble}}),
\]

where \( xC = 0.2095 \) is the mole fraction of oxygen in dry air, \( P_{\text{dry}} \) [Pa] is the atmospheric pressure of dry air (calculated from observed atmospheric pressure and equilibrium vapor pressure, assuming saturation with respect to water vapor), \( \rho \) [kg m\(^{-3}\)] is the water density, \( g = 9.81 \text{ m s}^{-2} \) is the gravitational acceleration, and \( h_{\text{bubble}} \) [m] is the average dissolution depth of the bubbles (approximated as \( h_{\text{bubble}} = 0.5(0.3U_{10} - 1.1) \)).
3.9 REFERENCES


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VITA

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EDUCATION

Ph. D. in Meteorology, 2010, Pennsylvania State University

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U. S. Global Ocean Carbon and Repeat Hydrography Program A13.5 Research Cruise

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PRESENTATIONS AND PUBLICATIONS

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Meteorology Department, the Pennsylvania State University
Title: Diagnostic modeling of oceanic biogeochemical fluxes using a general ocean turbulence model (GOTM) and time-series tracer measurements

Feb 2009

Oral presentation, open to public
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Meteorology Department, the Pennsylvania State University
Title: Gross biological production of DMS at two coastal sites west of the Antarctic Peninsula

Nov 2008

Poster presentation
IMPETUS 2008 Workshop: Techniques in Polar Ocean Observation and Monitoring, St. Petersburg, Russia
Title: DMS production at two coastal sites west of the Antarctic Peninsula

Jun 2008

Poster presentation
Advances in Marine Ecosystem Modeling Research (AMEMR) Symposium 2008
Plymouth Marine Laboratory, Plymouth, United Kingdom
Title: Diagnosis of gross biological production of dimethylsulfide (DMS) at two coastal sites west of the Antarctic Peninsula near Palmer station

Mar 2008

Poster presentation
2008 Ocean Sciences Meeting, Orlando, FL
Title: DMS production at two coastal sites west of the Antarctic Peninsula