

# **Design of OCMIP-2 simulations of chlorofluorocarbons, the solubility pump and common biogeochemistry**

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## **OUTLINE**

1. Introduction
  2. Air-sea gas transfer
    - 2.1. Gas saturation concentrations
    - 2.2. Gas transfer velocity
  3. Carbon dioxide system computations
    - 3.1. Choice of CO<sub>2</sub> dissociation constants
    - 3.2. Governing equations
      - 3.2.1. Equilibrium expressions
      - 3.2.2. Total inorganic species
      - 3.2.3. Definition of alkalinity
    - 3.3. Computational scheme
  4. Direct impact of fresh water fluxes
  5. CFC-11 and CFC-12 simulation design
  6. Solubility pump design
  7. Common biogeochemical model design
    - 7.1. Phosphorus
    - 7.2. Oxygen
    - 7.3. Calcium carbonate
    - 7.4. Dissolved inorganic carbon and alkalinity
    - 7.5. Initial conditions and spin up
- Appendix: Computation of monthly climatology of  $u^2$

## **1. Introduction**

The success of OCMIP-2 depends critically upon carefully designed and coordinated simulations of the carbon cycle and related processes. Two important criteria must be met. First, the biogeochemical parameterizations chosen should be the most appropriate to meet the goals of the simulation. These parameterizations should be based upon a careful survey of the literature and modeling experience. The purpose of this document is to describe and justify the parameterizations chosen for OCMIP-2 simulations of chlorofluorocarbons, the solubility pump and common biogeochemistry. This document will be revised or amended at a later date to include designs of simulations of radiocarbon, anthropogenic CO<sub>2</sub> uptake and “pulse” inputs of CO<sub>2</sub> to the ocean.

The second important criterion to be met is that individual modeling groups use the exact same biogeochemical parameterizations. This will be accomplished via a set of “HOWTO” documents, which will describe, step-by-step, how modeling groups are to code up their models, perform the simulations, save output, and so on.

Before describing the details of each of the simulations, we first describe some parameterizations that are shared by some of the simulations: air-sea gas transfer, carbon dioxide system equilibria and the impact of fresh water fluxes on tracer distributions.

## 2. Air-sea gas transfer

In OCMIP-2, parameterizations are needed for the air-sea gas transfer of CO<sub>2</sub>, oxygen and CFCs. A standard gas transfer formulation is adopted:

$$F = k_w \rho ([A] - [A]_{sat}), \quad (1)$$

where  $F$  is the upward flux of gas A,  $k_w$  is the gas transfer velocity for A,  $\rho$  is the density of surface seawater,  $[A]$  is the surface ocean concentration of A, and  $[A]_{sat}$  is the corresponding saturation concentration, in equilibrium with a water-vapor-saturated atmosphere at a total atmospheric pressure  $P$ . Concentrations throughout are indicated by  $[ ]$  and are in units of  $\mu\text{mol}$  of the chemical species per kg of seawater. Surface density will be computed from the model predicted sea surface temperature and salinity.  $[A]$  is predicted by the model.

### 2.1. Gas saturation concentrations

The saturation concentration can be expressed as

$$[A]_{sat} = K_0 f_A = K_0 K_f p_A = K_0 K_f (P - e_w) x_A, \quad (2)$$

where  $K_0$  is the solubility of A,  $f_A$  is the atmospheric fugacity of A,  $K_f$  is the fugacity coefficient of A,  $p_A$  is the atmospheric partial pressure of A,  $e_w$  is the water vapor saturation pressure and  $x_A$  is the volumetric mixing ratio of A in air. See Weiss and Price (1980), DOE (1994) and Fink *et al.* (1998) for details. Equation (2) can be approximated by

$$[A]_{sat} = \frac{P}{P^\circ} \Phi_A^\circ x_A = \frac{P}{P^\circ} [A]_{sat}^\circ, \quad (3)$$

where  $P^\circ = 1 \text{ atm}$ , the function  $\Phi_A^\circ$ , dependent only on sea surface temperature and salinity, relates  $x_A$  to  $[A]_{sat}$  at one atmosphere total pressure, and  $[A]_{sat}^\circ$  is the saturation concentration at 1 atm total pressure. For CO<sub>2</sub> and CFCs,  $x_A$  is provided as a boundary condition (see sections 5, 6 and 7) and  $\Phi_A^\circ$  is given by the coefficients in Table VI of Weiss and Price (1980) and Table 5 of Warner and Weiss (1985).  $[O_2]_{sat}^\circ$  is taken from Garcia and Gordon (1992). The monthly mean climatology of Esbensen and Kushnir (1981) is used to compute  $P$ , and this will be interpolated linearly to the model timestep. Variations in total pressure are taken into account when computing  $[A]_{sat}$  because these may be important in some regions. Total pressure, for example, decreases by about 3% from 30°S to 60°S, a change that will affect  $p\text{CO}_2$  and  $[O_2]_{sat}$  by about 10  $\mu\text{atm}$  and 10  $\mu\text{mol kg}^{-1}$ , respectively.

### 2.2. Gas transfer velocity

Wanninkhof (1992) has parameterized the instantaneous gas transfer velocity as a function of wind speed at 10 m ( $u$ ) and Schmidt number ( $Sc$ ). Adding the effect of sea ice fraction ( $f_i$ ) to his

formulation yields:

$$k_w = a(1 - f_i) \left( \frac{Sc}{660} \right)^{-1/2} u^2, \quad (4)$$

where  $a$  is a constant adjusted to give the correct global mean gas transfer velocity as deduced from the distribution of natural and bomb radiocarbon and an idealized wind speed distribution. This estimate of the global mean gas transfer velocity has also been found to be consistent with the large scale seasonal variations of oxygen in the surface ocean and the atmosphere (Keeling *et al.*, 1998).  $Sc$  is computed from the model temperature using formulae of Keeling *et al.* (1998), Wanninkhof (1992) and Zheng *et al.* (1998), for  $O_2$ ,  $CO_2$  and CFCs, respectively.

The mean annual cycle at monthly resolution of  $a(1 - f_i)u^2$  will be provided to modelers, and this will be interpolated linearly to the model timestep. The mean annual cycle at monthly resolution of  $f_i$  is taken from Walsh (1978) and Zwally *et al.* (1983). The mean annual at monthly resolution of  $u^2$  is computed from satellite measurements, as described in the Appendix. Note that this monthly climatology includes the effect of short-term (sub-monthly) variations in the wind speed. The value of  $a$  was determined to be 0.336 so that the global and annual mean gas transfer coefficient for carbon dioxide ( $k_w K_0$ ) is equal to  $0.061 \text{ mol m}^{-2} \text{ yr}^{-1} \mu\text{atm}^{-1}$  for preindustrial times, which is based on  $k_w K_0 pCO_2 = 17 \pm 4 \text{ mol m}^{-2} \text{ yr}^{-1}$  estimated by Broecker *et al.* (1986) based on the global bomb radiocarbon budget, divided by the preindustrial  $pCO_2$  of  $280 \mu\text{atm}$ . The value of 0.336 is slightly different from the value of 0.31 derived by Wanninkhof (1992) for “short-term” winds because of the different wind fields used.

Because model temperature and salinity fields will differ from group to group, gas transfer velocities and saturation concentrations will be slightly different among groups. Though this has the disadvantage of complicating the intercomparison, it ensures that each model is as physically consistent as possible. Consider for example, the problem that would occur if a model forms deep water in a place slightly different from the observations. The model may still have the right amount of deep water formation, but the deep CFC concentrations could be off because observed temperatures and salinities were used to compute the solubility at the surface. Model water mass analysis would also be complicated by a mix of model and observed surface temperatures and salinities.

We have chosen to ignore effects of chemical enhancement on the air-sea gas transfer velocity. Under the most favorable conditions (low winds and high temperatures), chemical enhancement increases the transfer velocity by only 4-8% (Wanninkhof and Knox, 1996). This will have an even smaller impact on the air-sea  $pCO_2$  difference, which is largely driven by biological and advective processes.

### 3. Carbon dioxide system computations (with input by C. Sabine and R. Key)

For a variety of simulations in OCMIP-2, modelers will need to compute  $[CO_2^*]$ , the surface ocean concentration of  $CO_2 + H_2CO_3$  (which are difficult to distinguish analytically), in order to compute the air-sea gas flux of  $CO_2$ .  $[CO_2^*]$  will be computed from prognostic variables in their models—most importantly temperature, salinity, dissolved inorganic carbon (DIC) and alkalinity (Alk)—in addition to a set of constants that are solely dependent upon temperature and salinity. (These constants also depend on pressure, but in this application we will be computing the equilibrium constants for the surface ocean, assumed to be at 1 atm total pressure.)

### 3.1. Choice of CO<sub>2</sub> dissociation constants

Unfortunately, there is no universally agreed upon set of constants for computing [CO<sub>2</sub>\*] from [DIC] and [Alk], particularly with regard to the first and second dissociations of CO<sub>2</sub>. Computed CO<sub>2</sub> concentration (and therefore *p*CO<sub>2</sub>) can vary considerably depending on the choice of constants. For example, Lewis and Wallace (1998) find a range of 21 μatm in the computation of *p*CO<sub>2</sub> for typical surface conditions with three different sets of equilibrium constants.

A consensus does seem to be emerging, however, for the specific application mentioned here: computation of [CO<sub>2</sub>\*] from [DIC] and [Alk]. At the first OCMIP-2 meeting in San Diego this past February, Chris Sabine showed computations of the CO<sub>2</sub> fugacity, *f*CO<sub>2</sub>, from measurements of [DIC] and [Alk] using various sets of equilibrium constants and compared those with measured values of *f*CO<sub>2</sub>. *f*CO<sub>2</sub> was measured at temperatures different from *in situ* (4°C or 20°C), and the *f*CO<sub>2</sub> computation from [DIC] and [Alk] was therefore made at the measurement temperature. The following sets of equilibrium constants were compared: Goyet and Poisson (1989), Roy *et al.* (1993), Mehrbach *et al.* (1973), and Hansson (1973a, b). All constants were converted to the seawater pH scale as presented in Millero (1995). (The original reference for the conversions of the last two sets of constants is Dickson and Millero [1987].) Vertical profiles of the computed-measured *f*CO<sub>2</sub> difference for various stations clearly showed that the Mehrbach *et al.* set was the most consistent.

Other supporting evidence for using the Mehrbach *et al.* constants when computing *f*CO<sub>2</sub> from [DIC] and [Alk] comes from work of Wanninkhof *et al.* (1998) and Lueker (1998). Wanninkhof *et al.* (1998) compared measured and computed *p*CO<sub>2</sub> (from DIC and Alk) in surface waters of a wide range of environments in three major ocean basins and found that the Mehrbach *et al.* (1973) constants gave much better results than the other constants mentioned above. For example, the average difference between the observed and computed *p*CO<sub>2</sub> in the North Atlantic was 1.8 μatm using the Mehrbach *et al.* constants compared to the 25.7 μatm difference with the Roy *et al.* (1993) constants. In another study, Lueker (1998) took Sargasso Sea water samples, measured the alkalinity, then equilibrated the water sample with a set *f*CO<sub>2</sub>. [DIC] and *f*CO<sub>2</sub> were measured and the *K*<sub>1</sub>/*K*<sub>2</sub> ratio was computed using the three measurements. The computed *K*<sub>1</sub>/*K*<sub>2</sub> was found to be in very good agreement with that measured by Mehrbach *et al.* (1973).

Based on these considerations, the Dickson and Millero (1987) refit of the Mehrbach *et al.* (1973) constants will be adopted for the OCMIP-2 application described above. We cannot emphasize too greatly that what we describe as an “emerging consensus” could easily change in the future. This is simply, in our opinion, what seems to be the best choice of constants at this time. We also emphasize that we are not suggesting the use of these constants for other applications, like the computation of pH.

Other choices need to be made as well for many of the other constants, but these are less important. What is critical, however, is that these other constants were measured on (or converted to) the same pH scale that the measurements of *K*<sub>1</sub> and *K*<sub>2</sub> were based on, the so-called seawater scale. For this reason, partly, all of the constants adopted here (except for *K*<sub>1</sub> and *K*<sub>2</sub>) are those compiled in the handbook edited by Dickson and Goyet (DOE, 1994). To these we add functions for computing total dissolved inorganic boron, sulfate and fluoride.

### 3.2. Governing equations

The computation of [CO<sub>2</sub>\*] from [DIC] and [Alk] requires the following: (1) equilibrium

expressions for the dissociation of carbonic acid, boric acid, phosphoric acid, silicic acid, water, sulfate and fluoride; (2) relationships between salinity and the concentrations of total dissolved inorganic boron ( $B_T$ ), sulfate ( $S_T$ ) and fluoride ( $F_T$ ); (3) an expression for the alkalinity of seawater; and (4) specification of the concentrations of total dissolved inorganic phosphate ( $P_T$ ) and silicon ( $Si_T$ ). Also see Table 1 in Chapter 2 of DOE (1994). It is also important to include phosphate and silicate dissociation in the calculation. Consider an example from the mixed layer in the South Pacific with  $[Alk] = 2275 \mu\text{eq kg}^{-1}$ ,  $[DIC] = 2150 \mu\text{mol kg}^{-1}$ , temperature =  $1.5^\circ\text{C}$ , salinity = 34 (pss),  $P_T = 2 \mu\text{mol kg}^{-1}$  and  $Si_T = 50 \mu\text{mol kg}^{-1}$ . The computed  $f\text{CO}_2$  is  $384 \mu\text{atm}$ . If phosphate and silicate are set to zero,  $f\text{CO}_2$  is  $7 \mu\text{atm}$  lower, with most of the difference (about  $5 \mu\text{atm}$ ) due to phosphate.

### 3.2.1. Equilibrium expressions

The equilibrium expressions for dissociation are:

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2^*]}, \quad K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}, \quad (5)$$

$$K_B = \frac{[\text{H}^+][\text{B}(\text{OH})_4^-]}{[\text{B}(\text{OH})_3]}, \quad (6)$$

$$K_{1P} = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}, \quad K_{2P} = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}, \quad K_{3P} = \frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]}, \quad (7)$$

$$K_{Si} = \frac{[\text{H}^+][\text{SiO}(\text{OH})_3^-]}{[\text{Si}(\text{OH})_4]}, \quad (8)$$

$$K_W = [\text{H}^+][\text{OH}^-], \quad (9)$$

$$K_S = \frac{[\text{H}^+]_F[\text{SO}_4^{2-}]}{[\text{HSO}_4^-]}, \quad (10)$$

and

$$K_F = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]}. \quad (11)$$

Here  $[\text{H}^+]$  is the total hydrogen ion concentration in seawater and  $[\text{H}^+]_F$  is the free hydrogen ion concentration. The two are related by

$$[\text{H}^+] = [\text{H}^+]_F \left(1 + \frac{S_T}{K_S}\right). \quad (12)$$

References for the equilibrium constants in (5) through (11) are as follows:  $K_1$  and  $K_2$ , Dickson and Millero (1987) using Mehrbach *et al.* (1973) data on the seawater pH scale;  $K_B$ , Millero (1995) using data from Dickson (1990a);  $K_{1P}$ ,  $K_{2P}$ ,  $K_{3P}$  and  $K_{Si}$ , Millero (1995) using data from Yao and Millero (1995);  $K_W$ , Millero (1995) using composite data;  $K_S$ , Dickson (1990b); and  $K_F$ , Dickson and Riley (1979). Note that in all cases the equilibrium constants are given in terms of concentrations, not activities, and that all constants are referenced to the seawater pH scale, except for  $K_S$ , which is on the free pH scale.

### 3.2.2. Total inorganic species

Expressions for total dissolved inorganic carbon, boron, phosphate, silicate, sulfate and fluoride are given by

$$[\text{DIC}] = [\text{CO}_2^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}], \quad (13)$$

$$B_T = [\text{B(OH)}_3] + [\text{B(OH)}_4^-], \quad (14)$$

$$P_T = [\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}], \quad (15)$$

$$Si_T = [\text{Si(OH)}_4] + [\text{SiO(OH)}_3^-], \quad (16)$$

$$S_T = [\text{HSO}_4^-] + [\text{SO}_4^{2-}], \quad (17)$$

and

$$F_T = [\text{HF}] + [\text{F}^-]. \quad (18)$$

[DIC],  $P_T$  and  $Si_T$  are inputs to the calculation. As discussed in later sections, [DIC] is a prognostic quantity,  $P_T$  is either specified or predicted (depending on the simulation) and  $Si_T$  is always specified from observations. The remaining species are proportional to the model salinity using formulations from the following references:  $B_T$ , Uppstrom (1974);  $S_T$ , Morris and Riley (1966); and  $F_T$ , Riley (1965).

### 3.2.3. Definition of alkalinity

The definition of alkalinity used in *this* calculation is the same as that of Dickson (1981), excluding the effect of  $\text{NH}_3$ ,  $\text{HS}^-$  and  $\text{S}^{2-}$ :

$$[\text{Alk}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{OH}^-] + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] \quad (19) \\ + [\text{SiO(OH)}_3^-] - [\text{H}^+]_F - [\text{HSO}_4^-] - [\text{HF}] - [\text{H}_3\text{PO}_4].$$

Other species also make minor contributions to the alkalinity, but these are neglected here.

### 3.3. Computational scheme

Assuming that temperature, salinity, [DIC], [Alk],  $P_T$  and  $Si_T$  are known, Equations (5) through (19) have 18 equations with 18 unknowns:

$[\text{CO}_2^*]$ ,  $[\text{HCO}_3^-]$ ,  $[\text{CO}_3^{2-}]$ ,  $[\text{B}(\text{OH})_3]$ ,  $[\text{B}(\text{OH})_4^-]$ ,  $[\text{OH}^-]$ ,  $[\text{H}^+]$ ,  $[\text{H}_3\text{PO}_4]$ ,  $[\text{H}_2\text{PO}_4^-]$ ,  $[\text{HPO}_4^{2-}]$ ,  $[\text{PO}_4^{3-}]$ ,  $[\text{Si}(\text{OH})_4]$ ,  $[\text{SiO}(\text{OH})_3^-]$ ,  $[\text{HSO}_4^-]$ ,  $[\text{SO}_4^{2-}]$ ,  $[\text{HF}]$ ,  $[\text{F}^-]$  and  $[\text{H}^+]_F$ .

The system of equations is solved using an iterative technique written by Chris Sabine and Bob Key. A “safe” Newton-Raphson method from Press *et al.* (1996) is adopted. Also see page 11 in Chapter 2 of DOE (1994). Individual groups may choose alternative schemes, but the governing equations must be the same.

#### 4. Direct impact of fresh water fluxes

Air-sea fluxes of fresh water can have a significant impact on the concentrations of some chemical species in seawater. This is particularly true for DIC and Alk, which have large background concentrations compared to their variability. In OCMIP-2, we will take into account the impact of fresh water fluxes on DIC and Alk, but not on other chemical species. Water that evaporates from the ocean or falls as precipitation is assumed to have zero concentrations of DIC and Alk. For ocean models with free surfaces, the impact of evaporation and precipitation is therefore straightforward to model.

For models with rigid lids, however, the dilution/concentration effect of evaporation ( $E$ ) and precipitation ( $P$ ) is parameterized as virtual DIC and Alk fluxes (Murnane *et al.*, in preparation), similar to the virtual salt fluxes used in physical ocean GCMs:

$$F_{\text{DIC}} = \rho[\text{DIC}]^\circ(P - E) \quad (20a)$$

$$F_{\text{Alk}} = \rho[\text{Alk}]^\circ(P - E), \quad (20b)$$

where the convention for the direction of the fluxes is positive upward. Here  $[\text{DIC}]^\circ$  and  $[\text{Alk}]^\circ$  are globally-averaged surface concentrations of DIC and Alk in the model and are to be computed at least once per year. Average values are used to insure conservation of DIC and Alk. Care must be taken to insure that the global mean value of  $P - E$  is equal to zero. This can be a problem particularly during spin up of the physical model, when there may be some net salt flux across the sea surface as the model reaches a steady state global salt balance. This is more of a problem for Alk than for DIC, since the inventory of the former will track the global mean salinity if adjustments in  $P - E$  are not made. It is left to the individual modeler how to deal with this, but it could be handled by periodically adjusting the alkalinity distribution with a constant offset or multiplicative factor so that the global mean alkalinity is fixed at its original value.

If the model uses restoring to salinity at the surface in order to parameterize  $P - E$ , we suggest computing  $P - E$  using the following formula from Murnane *et al.* (in preparation):

$$P - E = \left( \frac{S - S^*}{S^\circ} \right) \frac{\Delta z_1}{\tau_S}, \quad (21)$$

where  $S$  is the salinity in the top level of the model,  $S^*$  is the salinity being restored to,  $S^\circ$  is the globally averaged salinity in the top level of the model,  $\Delta z_1$  is the thickness of the top level of the model and  $\tau_S$  is the restoring time scale for salinity.

## 5. CFC-11 and CFC-12 simulation design (with input from J. Bullister)

Chlorofluorocarbon distributions have yielded considerable insight into ocean circulation, particularly those aspects relevant to the uptake of anthropogenic carbon dioxide by the ocean. For this reason, and others, simulations of CFC-11 and CFC-12, two of the more commonly measured chlorofluorocarbons, will be conducted as part of OCMIP-2. Simulation of CFCs is fairly straightforward since CFCs invade the ocean only from the atmosphere, have no natural cycle, and are conservative once in the ocean. In addition to the ocean circulation field, only the following need to be specified: the time history of CFC-11 and CFC-12 in the atmosphere, the air-sea transfer velocity for CFC-11 and CFC-12 and the saturation concentrations of CFC-11 and CFC-12 in seawater. The latter two are specified in Section 2 above, so only the time history is discussed here.

The CFC atmospheric time histories compiled by Stephen Walker, Peter Salameh and Ray Weiss (1998, unpublished document) will be used by OCMIP. These will likely be the same histories used in WOCE CFC synthesis. Since the Walker *et al.* document is unpublished we briefly describe how the reconstructions were made. Time histories from 1931 to 1997 were constructed for the Northern and Southern Hemispheres by using a combination of direct measurements after 1978, estimates of CFC release to the atmosphere from 1931 to 1979, and a simple model of atmospheric CFC lifetime and transport. Northern Hemisphere values are for an average of Mace Head, Ireland (53°N) and Cape Meares, Oregon (45°N) before June 1989 and only Mace Head thereafter. Southern Hemisphere values are for Cape Grim, Tasmania (41°S).

There are significant differences between the hemispheres, so some method must be used to interpolate the point estimates. Atmospheric CFC distributions are generally well mixed within each hemisphere and vary abruptly across the intertropical convergence zone. We assume that each site is representative of its hemisphere poleward of 10° latitude in that hemisphere and varies linearly between 10°S and 10°N. Mid-year values are given for each hemisphere by Walker *et al.* and these will be interpolated to the model timestep. The model will be run from the beginning of 1931 to the end of 1997 with initial concentrations of zero for CFC-11 and CFC-12.

## 6. Solubility pump simulation design

The increase in dissolved inorganic carbon concentration with depth in the ocean is important because it results in atmospheric CO<sub>2</sub> levels that are lower than they would otherwise be, at least for time scales of decades to hundreds of years. Three different processes cause variations of [DIC] in the ocean (Volk and Hoffert, 1985): temperature-dependent solubility and dissociation of CO<sub>2</sub> in seawater (the solubility pump), photosynthesis and respiration (the organic matter pump), and calcium carbonate precipitation and dissolution (the carbonate pump). Clearly, it is important to isolate the different processes if we want to understand the marine carbon cycle and its effect on atmospheric CO<sub>2</sub>. Unfortunately, this is difficult to do using observations alone, largely because of the slow equilibration of CO<sub>2</sub> at the air-sea interface. Models offer an attractive means for estimating the impact of the solubility pump on the marine DIC distribution. For this reason, and others, simulations of the solubility pump will be performed as part of OCMIP-2.

The basic design of the solubility pump model is similar to that used in OCMIP-1. [DIC] is the only prognostic variable in the model, being solely determined by ocean circulation, exchange with an atmosphere of fixed CO<sub>2</sub> dry-air volumetric mixing ratio ( $x_{\text{CO}_2}$ ), and the fresh water flux at the air-sea interface. The air-sea CO<sub>2</sub> flux is parameterized as detailed in Section 2



above. The aqueous  $\text{CO}_2$  concentration, needed for the air-sea flux computation, is computed from model [DIC], temperature and salinity, as discussed in Section 3 above. Alkalinity, phosphate and silicate need to be specified as well. Mean surface values are chosen for phosphate and silicate:  $0.5$  and  $7.5 \mu\text{mol kg}^{-1}$ , respectively (Conkright *et al.*, 1994). For alkalinity, salinity-normalized values are computed using:

$$[\text{Alk}] = \frac{S}{\overline{S}}[\overline{\text{Alk}}] \quad (22)$$

where  $S$  is the modeled salinity and the overbar represents the model’s global horizontal and annual mean surface value. We take  $\overline{[\text{Alk}]}$  to be  $2310 \mu\text{eq kg}^{-1}$  (Sarmiento *et al.*, 1988). The effect of evaporation and precipitation on the DIC distribution is parameterized following Section 4 above.

Model spin up is straightforward: the model will be run to equilibrium from an arbitrary DIC distribution with  $x_{\text{CO}_2}$  fixed at its preindustrial value, 278 ppm.

## 7. Common biogeochemical model design

One of the more challenging tasks facing marine carbon cycle modelers is the formulation of biological processes. Currently there is no universally accepted predictive model of the effect of biological processes on the large scale distribution of carbon in the ocean. As a result, there is a great variety of approaches for simulating the sources and sinks of carbon and related elements in the ocean, ranging from highly parameterized models without any explicit treatment of the biota to extremely complex ecosystem models. Comparing results from different biological models is made difficult by the fact that the ocean circulation models are different as well. To facilitate comparison, it is desirable to have a common biological model, even though such a model is likely to have significant deficiencies.

The purpose of this section is to describe a common biological model to be used in OCMIP-2. A common biological model should satisfy two criteria: it should be able to reproduce the first-order distribution of carbon and related elements in the ocean and should be easy to implement. The simple biological model proposed here has five prognostic variables carried by the circulation field: inorganic phosphate ( $\text{PO}_4^{3-}$ , or  $\text{PO}_4$  for short), dissolved organic phosphorus (DOP), oxygen ( $\text{O}_2$ ), dissolved inorganic carbon (DIC) and alkalinity (Alk). The time evolution equation for one of these variables is given by

$$\frac{\partial C}{\partial t} = L(C) + J_C, \quad (23)$$

where  $C$  is the concentration of the tracer,  $L$  is the linear transport operator defining advection and diffusion and  $J_C$  is the biogeochemical source-sink distribution for  $C$ . Transport will be generated by the individual participants in OCMIP-2 and will be different for each group. Here we describe formulations for  $J_{\text{PO}_4}$ ,  $J_{\text{DOP}}$ ,  $J_{\text{O}_2}$ ,  $J_{\text{DIC}}$  and  $J_{\text{Alk}}$ , as well as the surface and bottom boundary conditions for the five tracers.

### 7.1. Phosphorus

The model describing the cycling of phosphorus is similar to the “nutrient restoring” approach adopted by Najjar *et al.* (1992) and Anderson and Sarmiento (1995). The nutrient restor-

ing approach has the advantage of insuring the correct spatial and temporal distribution of surface nutrients, which is necessary for modeling the correct spatial and temporal distribution of surface ocean  $p\text{CO}_2$  and air-sea  $\text{CO}_2$  transfer—critical criteria that must be met for OCMIP-2. Clearly this diagnostic approach is a temporary solution. If there were a prognostic model that could reproduce the large-scale spatial and seasonal nutrient patterns in the surface ocean, the nutrient restoring approach would be abandoned. Such a model would likely have, at the minimum, explicit treatment of phytoplankton and zooplankton, as well as incorporation of iron limitation. To our knowledge, no such model exists on a global scale. The closest is probably the model of Six and Maier-Reimer (1996), which appears to produce air-sea oxygen fluxes that are consistent with the seasonal variability of the atmospheric  $\text{O}_2/\text{N}_2$  ratio (Stephens *et al.*, 1998).

Phosphate is chosen instead of nitrate as the basic currency of the model so as to avoid the complexities of nitrogen fixation and denitrification. Phosphate also has the advantage of having a greater database of observations for forcing and evaluating the model.

The model described here has two important differences with respect to previous nutrient-restoring models. First, only the so-called semi-labile dissolved organic matter (DOM) pool is considered. This pool is thought to have a lifetime of months. The other two pools commonly considered are the labile pool, with a lifetime of hours to days, and the refractory pool, with a lifetime of hundreds to thousands of years. It is argued that these two pools do not have an appreciable impact on large scale nutrient and carbon distributions because there is very little net organic matter export from the euphotic zone in these dissolved forms. The second important difference is that the model described here is seasonal. Thus, we will be restoring towards a monthly observed climatology of phosphate in the surface ocean (Najjar and Louanchi, in preparation).

To compute  $J_{\text{PO}_4}$ , two regions are defined, separated by the compensation depth,  $Z_c$ , the depth at which photosynthesis is equal to respiration of the whole biological community, as discussed by Smetacek and Passow (1990). We prefer not to use the term “euphotic zone depth,” which is often defined based on an arbitrary percentage (usually 0.1 or 1) of the surface irradiance, because it means something quite different from compensation depth. We will refer to the region above the compensation depth as the production zone and the region below the compensation depth as the consumption zone. In the production zone,  $[\text{PO}_4]$  is nudged towards observations,  $[\text{PO}_4]^*$ , on a timescale  $\tau$ , but only if  $[\text{PO}_4] > [\text{PO}_4]^*$ . Otherwise, there is no nudging. We define this term as  $J_{\text{Prod}}$ , representing the production of organic phosphorus:

$$\begin{aligned} J_{\text{Prod}} &= \frac{1}{\tau}([\text{PO}_4] - [\text{PO}_4]^*), & [\text{PO}_4] > [\text{PO}_4]^* & \\ & & Z < Z_c & \\ J_{\text{Prod}} &= 0, & [\text{PO}_4] \leq [\text{PO}_4]^* & \end{aligned} \quad (24)$$

where  $Z$  is the depth.

It is assumed that a fixed fraction,  $\sigma$ , of the phosphate uptake in the production zone is converted to DOP, which is allowed to be advected and diffused by the circulation field and is consumed everywhere following first-order kinetics. Thus we have the source/sink function for DOP:

$$J_{\text{DOP}} = \sigma J_{\text{Prod}} - \kappa[\text{DOP}], \quad Z < Z_c \quad (25a)$$

$$J_{\text{DOP}} = -\kappa[\text{DOP}], \quad Z > Z_c. \quad (25b)$$

The phosphate not converted to DOP results in an instantaneous downward flux of particulate organic phosphorus at the compensation depth:

$$F_c = (1 - \sigma) \int_0^{Z_c} J_{\text{Prod}} dZ. \quad (26)$$

This flux decreases with depth due to remineralization following a power law relationship:

$$F(Z) = F_c \left( \frac{Z}{Z_c} \right)^{-a}, \quad Z > Z_c. \quad (27)$$

The power law form has the advantage over exponential forms in that it captures the observed increase in remineralization length scale with depth. The source/sink term for phosphate is then:

$$J_{\text{PO}_4} = -\sigma J_{\text{Prod}} + \kappa[\text{DOP}], \quad Z < Z_c \quad (28a)$$

$$J_{\text{PO}_4} = -\frac{\partial F}{\partial Z} + \kappa[\text{DOP}], \quad Z > Z_c. \quad (28b)$$

It is assumed that any flux reaching the sediments is remineralized there and diffused instantaneously back into the water column. Therefore, the bottom box of the model will have an additional source of phosphate beyond that given by Equation (28b).

The assumption that particulate organic phosphorus produced in the production zone is remineralized instantaneously in the consumption zone is reasonable, and is based on the fact that the particle sinking time scale ( $\sim 1$  month) is much shorter than basin-wide advective time scales ( $\sim 1$ -100 years).

Note that remineralization of organic phosphorus is assumed to be independent of the amount of dissolved oxygen present. This may not be strictly true, but clearly there is clear evidence of organic matter decomposition in anoxic regions as a result of denitrification. We simply assume that nitrate is as effective at oxidizing organic matter as oxygen.

We now must choose the parameters  $Z_c$ ,  $\tau$ ,  $\sigma$ ,  $\kappa$  and  $a$ . All of these parameters are likely to have spatial and temporal variability, but in the interest of keeping this model as simple as possible, we will use constant values. For  $Z_c$ , 75 m is used, based on the analysis of seasonal oxygen variations by Najjar and Keeling (1997). They inferred that the summertime compensation depth varies between about 50 and 100 m, depending on the latitude. The choice of  $\tau$  is somewhat arbitrary. We use a value of 30 days, which should be long enough, in most cases, to accommodate differences between observed and modeled circulation, yet short enough to prevent too much of a lag of surface phosphate behind the observations. For  $a$ , we use a value of 0.9, which is close to what sediment traps yield (Martin *et al.*, 1987). Even though there is concern that sediment traps do not properly measure flux in the upper few hundred meters of the water column, other lines of evidence support the rapid drop-off in flux measured by sediment traps. A number of tracer-based estimates of remineralization in the upper few hundred meters of the water column yield remineralization length scales of a few hundred meters (Sarmiento *et al.*, 1990; and references therein), similar to what Equation (27) with  $a = 0.9$  would yield. This value of  $a$  also yields good results for phosphate distributions in GCMs (Yamanaka and Tajika, 1996, 1997).

A variety of studies suggest that  $\kappa$ , the semi-labile DOP consumption rate constant, is between about  $(0.2 \text{ year})^{-1}$  and  $(0.7 \text{ year})^{-1}$ . DOC in the Sargasso Sea at 200 m depth is observed to decrease from about  $62 \mu\text{mol kg}^{-1}$  in February-March to  $52 \mu\text{mol kg}^{-1}$  in July-August (Carlson

*et al.*, 1994), about a five-month time period. Estimating the refractory component of DOC to be the concentration at 1000 m,  $46 \mu\text{mol kg}^{-1}$  (Hansell *et al.*, 1995), the semi-refractory pool decreases from 16 to  $6 \mu\text{mol kg}^{-1}$ . (The labile pool is assumed to be negligibly small.) We can then estimate  $\kappa$  by rearranging (25b), substituting DOC for DOP:

$$\kappa = -\frac{J_{\text{DOC}}}{[\text{DOC}]} \cong -\frac{(-10\mu\text{mol kg}^{-1})/(5\text{mon})}{11\mu\text{mol kg}^{-1}} \cong \frac{1}{0.5\text{yr}}. \quad (29)$$

Mineralization experiments by Hansell *et al.* (1995) give reasonable agreement with this value of  $\kappa$ . They found that DOC in water taken from 200 m depth in the Sargasso Sea decreases at a rate of  $0.044 \mu\text{mol kg}^{-1} \text{ day}^{-1}$ , for a 101 day dark incubation, somewhat less than inferred from the observed decrease at 200 m depth,  $0.067 \mu\text{mol kg}^{-1} \text{ day}^{-1}$  from the Carlson *et al.* (1994) data. This would suggest a semi-labile DOC lifetime of about  $(0.7 \text{ year})^{-1}$ . A 0.5 year lifetime of semi-labile DOC was also estimated by Yamanaka and Tajika (1997) by fitting a three-dimensional model to vertical and horizontal distributions of DOC in the equatorial Pacific measured by Peltzer and Hayward (1996) and Ogawa and Koike (manuscript in preparation). A similar exercise by Archer *et al.* (1997) with a higher resolution GCM found that the semilabile DOC lifetime is somewhat shorter, from 0.1 to 0.3 years, in the equatorial Pacific. Based on these four studies we choose an intermediate value of  $\kappa$  equal to  $(0.5 \text{ year})^{-1}$ .

Estimating a value of  $\sigma$  is difficult because it has not been estimated from observations directly. We use a value of 0.67 for  $\sigma$ , which was determined by Yamanaka and Tajika (1997) in the data-fitting exercise mentioned above. It is important to realize that the fraction of the net downward flux of organic matter across the compensation depth that is in dissolved form is less than  $\sigma$ . This is because DOM is also remineralized above the compensation depth (Equation 25a). For example, with  $\sigma = 0.67$ , Yamanaka and Tajika (1997) found that, on a global scale, DOC accounted for less than 30% of the downward flux of organic matter across 100 m depth.

The 30% figure from Yamanaka and Tajika (1997) can be compared directly with regional observation-based estimates of the fraction of export production that occurs in dissolved form. This should be done with caution, however, because it is likely that this fraction varies spatially. Carlson *et al.* (1994) estimated that downward mixing of DOC accounts for 23-42% of the new production in the Sargasso Sea. In the Equatorial Pacific, a variety of studies estimate DOC export to be roughly one-quarter to one-half of the new production (Murray *et al.*, 1996; Archer *et al.*, 1997; Hansell *et al.*, 1997; Zhang and Quay, 1997; Quay, 1997; Loukos *et al.*, 1997). Thomas *et al.* (1995) find, using DOC and nitrate measurements with a simple box model, that  $20 \pm 15\%$  of the organic matter export in the tropical Atlantic is in dissolved form. Guo *et al.* (1994) used AOU-DOC relationships in the Gulf of Mexico, as well as a simple 1-D model, to estimate that DOC accounts for about 20-30% of the downward flux of organic carbon. Finally, Borsheim and Myklestad (1997) show that the seasonal accumulation of DOC in the mixed layer is 20-60% of the new production in the Norwegian Sea. This fraction is an upper limit on the amount of organic matter exported in dissolved form. All of the observation-based estimates appear to be in reasonable agreement with the Yamanaka and Tajika (1997) estimate based on  $\sigma = 0.67$ .

The final component to be specified for the phosphorus model is  $[\text{PO}_4]^*$ , the observed distribution of phosphate above the compensation depth. The climatological monthly maps of Najjar and Louanchi (in preparation) will be used<sup>1</sup>. These maps were created from the quality-controlled phosphate data of the 1994 World Ocean Atlas (Conkright *et al.*, 1994) using the interpolation/

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1. Surface maps can be viewed by anonymous ftp at ftp.essc.psu.edu in the directory /pub/meteo/ferial.

smoothing technique of Najjar and Keeling (1997). Phosphate values in regions of sparse data coverage were determined from phosphate-temperature relationships. Full details of the maps will be given in Najjar and Louanchi (in preparation).

## 7.2. Oxygen

The oxygen model closely follows that of phosphate, being linked by the Redfield Ratio,  $r_{O_2:P}$ . The main differences are that: (1) oxygen consumption is assumed to be halted below some critical oxygen level  $[O_2]^\circ$  and (2) oxygen crosses the air-sea interface. The latter is a boundary condition and is parameterized as outlined in Section 2 above. Oxygen is likely to go below the critical level below the compensation depth. The ocean will then be a net source of oxygen to the atmosphere because oxygen production above the compensation depth will be greater than oxygen consumption below the compensation depth. This imbalance is probably made up for by nitrogen fixation in surface waters. An estimate of the impact on air-sea oxygen fluxes can be made by converting estimates of global denitrification to a mean air-sea oxygen flux. Unfortunately, global denitrification estimates vary by more than an order of magnitude (Middelburg et al., 1996). Using a value of  $300 \text{ Tg N yr}^{-1}$  for denitrification, at the high end of the estimated range and a  $O_2:N$  Redfield ratio of 10 yields an outgassing of oxygen equal to about  $0.6 \text{ mol m}^{-2} \text{ yr}^{-1}$ , equivalent to an oxygen supersaturation of only  $0.5 \mu\text{mol kg}^{-1}$  given a gas transfer velocity of  $3 \text{ m day}^{-1}$ . Since the impact on the dissolved oxygen distribution in surface waters is so small, we do not include nitrogen fixation in this model. The source/sink term for oxygen is then:

$$\begin{aligned} J_{O_2} &= -r_{O_2:P} J_{PO_4}, & [O_2] > [O_2]^\circ \\ J_{O_2} &= 0, & [O_2] < [O_2]^\circ. \end{aligned} \quad (30)$$

We need now to pick values of  $r_{O_2:P}$  and  $[O_2]^\circ$ . For  $r_{O_2:P}$  we use the value of 170 based on the work of Anderson and Sarmiento (1994). For  $[O_2]^\circ$ , we use a value of  $4 \mu\text{mol kg}^{-1}$ , the oxygen concentration below which zooplankton abundance drops rapidly (Saltzman and Wishner, 1997; and references therein).

## 7.3. Calcium carbonate

The simulation of calcium carbonate cycling is based on the parameterizations of Yamanaka and Tajika (1996). The formation of calcium carbonate in surface waters is tied to the rate of POC production in surface waters. The so-called rain-ratio,  $R$ , the molar ratio of the downward POC flux to the downward  $CaCO_3$  flux at the compensation depth, is assumed to be spatially and temporally constant. Below the compensation depth, the downward flux of  $CaCO_3$ ,  $F_{Ca}$ , is assumed to decrease exponentially with a scale depth  $d$ . Indicating the source-sink function of dissolved calcium as  $J_{Ca}$  we then have

$$\begin{aligned} J_{Ca} &= R r_{C:P} (1 - \sigma) J_{Prod}, & Z < Z_c \\ J_{Ca} &= -\frac{\partial F_{Ca}}{\partial Z}, & Z > Z_c, \end{aligned} \quad (31)$$

where  $r_{C:P}$  is the carbon to phosphorus Redfield Ratio for organic matter cycling.  $F_{Ca}$  is simply

$$F_{Ca} = R r_{C:P} F_c e^{-(Z-Z_c)/d}. \quad (32)$$

Any flux of  $CaCO_3$  reaching the sea floor is assumed to dissolve there instantaneously and diffuse back into the water column.

For  $r_{C:P}$  the value of 117 is adopted, which is based on the analysis of nutrient, DIC and Alk observations in the global ocean by Anderson and Sarmiento (1994). The values of  $R$  and  $d$  that Yamanaka and Tajika (1996) estimate as giving the best fit to the observed alkalinity distribution are 0.08 and 3500 m, respectively. Yamanaka and Tajika (1996) also argue that these parameter choices yield organic/inorganic carbon flux ratios that are broadly consistent with the flux ratios inferred from the analysis of Anderson and Sarmiento (1994) as well as the global synthesis of organic carbon and calcium carbonate sediment trap measurements by Tsunogai and Noriki (1991). We therefore adopt these values, but adjust  $R$  to 0.07 since Yamanaka and Tajika (1996) used  $r_{C:P} = 106$ .

#### 7.4. Dissolved inorganic carbon and alkalinity

DIC and Alk cycling are linked to phosphate and calcium cycling using the standard approach:

$$J_{DIC} = r_{C:P} J_{PO4} + J_{Ca} \quad (33)$$

$$J_{Alk} = -r_{N:P} J_{PO4} + 2J_{Ca}, \quad (34)$$

where  $r_{N:P}$  is the nitrogen to phosphorus Redfield Ratio, taken to be 16 (Anderson and Sarmiento, 1994).

The impact of air-sea freshwater fluxes on DIC and Alk is taken into account following Section 4 above. Air-sea exchange of  $CO_2$  influences the DIC distribution and this is parameterized as discussed in Section 2. The value of the dry-air mixing ratio of  $CO_2$  is taken to be 278 ppm. Finally, aqueous  $[CO_2]$ , needed for the air-sea gas flux computation, is computed from the simulated surface DIC, Alk, phosphate, temperature and salinity distributions as described in Section 3 above. The silicate concentration is also needed for this computation, and we use the annual mean distribution of silicate from Najjar and Louanchi (in preparation).

#### 7.5. Initial conditions and spinup

Choices need to be made for initial conditions. For  $O_2$  and DIC, the initial values are not critical because exchange with the atmosphere will ultimately determine their global steady-state inventories. Alkalinity, phosphate and DOP, however, do not exchange with the atmosphere. The Alk inventory will therefore remain unchanged from the initial condition, as will the sum of the DOP and phosphate inventories. For simplicity, global mean values are chosen for initial conditions:  $2.17 \mu\text{mol kg}^{-1}$  for phosphate (computed from the atlas of Levitus *et al.* [1993]),  $170 \mu\text{mol kg}^{-1}$  for oxygen (Levitus and Boyer, 1994b),  $2370 \mu\text{eq kg}^{-1}$  for alkalinity (Takahashi *et al.*, 1981) and  $2230 \mu\text{mol kg}^{-1}$  for DIC, about 1% lower than the present value (Takahashi *et al.*, 1981). The mean semi-labile DOP concentration can be estimated from the semi-labile DOC distribution,

which decreases from about  $40 \mu\text{mol kg}^{-1}$  at the surface to close to zero around 400 m. Assuming a linear decrease with depth, the above value of  $r_{\text{C,P}}$  and a mean ocean depth of 4000 m yields a mean semi-labile DOP concentration of  $0.02 \mu\text{mol kg}^{-1}$ . The model is will be run from these initial conditions until a steady state is reached.

### **Appendix: Computation of monthly climatology of $u^2$ (by J. Boutin and J. Etcheto, 2/17/95)**

We use the satellite data from the first and second SSM/I (Special Sensor Microwave Imager) which were launched on June 19, 1987 and December 1, 1990 on the U.S. Air Force Defense Meteorological Satellite Program (DMSP) spacecraft F08 and F10 respectively. A complete description of the SSM/I instrument can be found in Hollinger (1989). Its swath is 1400 km wide. At latitudes larger than  $40^\circ$  and at the equator, the coverage is nearly complete after one day; over the global ocean, it is nearly complete after four days (Minster *et al.*, 1992).

We use the wind speed derived by Wentz (1992). The wind speed, originally retrieved at 19.5 m height,  $u_{19.5}$ , is converted into a 10 m height wind speed,  $u$ , using a neutral atmospheric profile and a drag coefficient equal to  $1.5 \times 10^{-3}$ :  $u = 0.939u_{19.5}$ . The resolution of the retrieved wind speed is 25 km. Following the recommendations of Wentz (1989), we discard  $u_{19.5}$  less than  $-4 \text{ m s}^{-1}$  and we consider the  $u_{19.5}$  values between 0 and  $-4 \text{ m s}^{-1}$  to be  $0 \text{ m s}^{-1}$ . We also discard  $u$  when the liquid water content is greater than  $25 \text{ mg cm}^{-2}$ . In order to avoid any pollution by land area, we add a mask around land areas 111 km away from large land masses and 56 km away from islands (diameter less than 150 km) using the method described in Ozieblo and Etcheto (1991).

For SSM/I F08, we use only the “class 0” measurements defined in Wentz (1989) and corresponding to water surface measurements far from ice or land and rain rate less than  $1.5 \text{ mm hr}^{-1}$ . For SSM/I F10, we use the “class 1” measurements newly defined in Wentz (1993) and we add a mask 168 km away from “class 6” measurements which detects sea ice as was suggested by F. Wentz (personal communication) and following the method described in Ozieblo and Etcheto (1991).  $1$  to  $2 \text{ m s}^{-1}$  overestimates of the wind speed in regions of high atmospheric water contents (western equatorial Pacific) as well as  $1$  to  $2 \text{ m s}^{-1}$  underestimates of the wind speeds in some high latitude regions depending on the wind direction have been evidenced (Boutin and Etcheto, December 1994)

The climatology of  $u^2$  is computed from five years of measurements: January 1, 1988 to January 1, 1993. From January 1, 1988 to November 1, 1991, we use the SSM/I F08 measurements. From November 1, 1991 to January 1, 1993, we use the SSM/I F10 measurements.

We compute the monthly average ( $\bar{u}$ ) and standard deviation ( $\sigma$ ) of the satellite wind speed measurements located in a  $2.5^\circ$  box for each of the 60 months; the box is kept only if it contains more than 50 measurements per week. A corresponding time series of the monthly average of  $u^2$  is computed using:

$$\overline{u^2} = \bar{u}^2 + \sigma^2.$$

The monthly climatology of  $u^2$  (the mean annual cycle of  $u^2$  at monthly resolution) is then computed by averaging the monthly  $2.5^\circ$  maps of  $u^2$ .

### **References**

- Anderson, L. A. and J. L. Sarmiento. 1994. Redfield ratios of remineralization determined by nutrient data analysis. *Global Biogeochem. Cycles*, 8, 65-80.
- Anderson, L. A. and J. L. Sarmiento. 1995. Global ocean phosphate and oxygen simulations. *Global Biogeochem. Cycles*, 9, 621-636.
- Archer, D., E. T. Peltzer and D. L. Kirchman. 1997. A timescale for dissolved organic carbon production in equatorial Pacific surface water. *Global Biogeochem. Cycles*, 11, 435-452.
- Borsheim, K. Y. and S. M. Mykkestad. 1997. Dynamics of DOC in the Norwegian Sea inferred from monthly profiles collected during 3 years at 66°N, 2°E. *Deep-Sea Res. I*, 33, 593-601.
- Boutin, J., and J. Etcheto. 1996. Consistency of Geosat, SSM/I and ERS1 global surface wind speeds; comparison with *in situ* data. *Journal of Atmospheric and Oceanic Technology*, 13, 183.
- Broecker, W. S., J. R. Ledwell, T. Takahashi, R. Weiss, L. Memery, T.-H. Peng, B. Jahne and K. O. Munnich. 1986. Isotopic versus micrometeorological CO<sub>2</sub> fluxes: a serious conflict. *J. Geophys. Res.*, 91, 10517-10527.
- Carlson, C. A., H. W. Ducklow and A. F. Michaels. 1994. Annual flux of dissolved organic carbon from the euphotic zone in the northwestern Sargasso Sea. *Nature*, 371, 405-408.
- Conkright, M. E., S. Levitus and T. P. Boyer. 1994. World Ocean Atlas 1994, Volume 1: Nutrients. National Oceanic and Atmospheric Administration, U.S. Dept. of Commerce, Washington, D.C., 150 pp.
- Department of Energy. 1994. Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water; version 2, A. G. Dickson and C. Goyet (eds.) ORNL/CIDAC-74. (Latest version is available on-line at [http://www-mpl.ucsd.edu/people/adickson/CO2\\_QC/](http://www-mpl.ucsd.edu/people/adickson/CO2_QC/))
- Dickson, A. G. 1981. An exact definition of total alkalinity and a procedure for the estimation of alkalinity and total inorganic carbon from titration data. *Deep-Sea Res.*, 28A, 609-623.
- Dickson, A. G. 1990b. Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 318.15 K. *Deep-Sea Res.*, 37, 755-766.
- Dickson, A. G. 1990a. Standard potential of the reaction:  $\text{AgCl(s)} + 1/2 \text{H}_2\text{(g)} = \text{Ag(s)} + \text{HCl(aq)}$ , and the standard acidity constant of the ion  $\text{HSO}_4^-$  in synthetic seawater from 273.15 to 318.15 K. *J. Chemical Thermodynamics*, 22, 113-127.
- Dickson, A. G., and J. P. Riley. 1979. The estimation of acid dissociation constants in seawater media from potentiometric titrations with strong base. I. The ionic product of water— $K_W$ . *Mar. Chem.*, 7, 89-99.
- Dickson, A. G. and F. J. Millero. 1987. A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. *Deep-Sea Res.*, 34, 1733-1743. (Corrigenda *Deep-Sea Res.*, 36, 983)
- Etcheto, J., and L. Merlivat. 1988. Satellite determination of the carbon dioxide exchange coefficient at the ocean-atmosphere interface: a first step. *J. Geophys. Res.*, 93, 15669-15678.
- Garcia, H. E. and L. I. Gordon. 1992. Oxygen solubility in seawater: Better fitting equations. *Limnol. Oceanogr.* 37, 1307-1312.
- Goyet, C., and A. Poisson. 1989. New determination of carbonic acid dissociation constants in seawater as a function of temperature and salinity. *Deep-Sea Res.*, 36, 1635-1654.
- Guo, L., C. H. Coleman Jr. and P. H. Santschi. 1994. The distribution of colloidal and dissolved organic carbon in the Gulf of Mexico. *Mar. Chem.*, 45, 105-119.
- Hansell, D. A., N. R. Bates and K. Gunderson. 1995. Mineralization of dissolved organic carbon in the Sargasso Sea. *Mar. Chem.*, 51, 201-212.



- Hansell, D. A., C. A. Carlson, N. Bates and A. Poisson. 1997. Horizontal and vertical removal of organic carbon in the equatorial Pacific Ocean: A mass balance assessment. *Deep-Sea Res. II*, 44, 2115-2130.
- Hansson, I. 1973a. A new set of acidity constants for carbonic acid and boric acid in sea water. *Deep-Sea Res.*, 20, 461-478.
- Hansson, I. 1973b. The determination of dissociation constants of carbonic acid in synthetic sea water in the salinity range of 20 - 40 ‰ and temperature range of 5 - 30°C. *Acta Chemica Scandinavia*, 27, 931-944.
- Hollinger, J. 1989. DMSP Special Sensor Microwave/Imager calibration/validation, Final report vol 1, Nav. Res. Lab., Washington, D.C.
- Keeling, R. F., B. B. Stephens, R. G. Najjar, S. C. Doney, D. Archer and M. Heimann. 1998. Seasonal variations in the atmospheric O<sub>2</sub>/N<sub>2</sub> ratio in relation to the air-sea exchange of O<sub>2</sub>. *Global Biogeochem. Cycles*, 12, 141-164.
- Loukos, H., B. Frost, D. E. Harrison and J. W. Murray. 1997. An ecosystem model with iron limitation of primary production in the equatorial Pacific at 140°W. *Deep-Sea Res. II*, 2221-2249.
- Levitus, S. and T. P. Boyer. 1994a. NOAA Atlas NESDIS 2, World Ocean Atlas 1994, Volume 4: Temperature. U. S. Government Printing Office, Washington, D. C.
- Levitus S. and T. P. Boyer. 1994b. *NOAA Atlas NESDIS 2, World Ocean Atlas 1994, Volume 2: Oxygen*. U. S. Government Printing Office, Washington, D. C.
- Lewis, E. and Wallace, D. W. R. 1998. Program developed for CO<sub>2</sub> system calculations. Oak Ridge, Oak Ridge National Laboratory.
- Lueker, T. 1998. Ph. D. Thesis. Scripps Institution of Oceanography, University of California at San Diego.
- Martin, J. H., G. A. Knauer, D. M. Karl and W. W. Broenkow. 1987. VERTEX: carbon cycling in the northeast Pacific. *Deep-Sea Res.*, 34, 267-285.
- Mehrbach, C., C. H. Culberson, J. E. Hawley, and R. M. Pytkowicz. 1973. Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnol. Oceanogr.*, 18, 897-907.
- Millero, F. J. 1995. Thermodynamics of the carbon dioxide system in the oceans. *Geochem. Cosmochim. Acta*, 59, 661-677.
- Minster, J. F., D. Jourdan, E. Normant, C. Brossier, and M. C. Gennero. 1992. An improved Special Sensor Microwave Imager water vapor correction for Geosat altimeter data. *J. Geophys. Res.*, 97, 17859-17872, 1992.
- Morris, A. W., and J. P. Riley. 1966. The bromide/chlorinity and sulphate/chlorinity ratio in sea water. *Deep-Sea Res.*, 13, 699-705.
- Murnane, R. J., J. L. Sarmiento and C. Le Quéré. The spatial distribution of air-sea CO<sub>2</sub> fluxes and the interhemispheric transport of carbon by the oceans. Manuscript in preparation.
- Murray, J. W., J. Young, J. Newton, J. Dunne, T. Chapin, B. Paul, J. J. McCarthy. 1996. Export flux of particulate organic carbon from the central equatorial Pacific determined using a combined drifting trap—<sup>234</sup>Th approach. *Deep-Sea Res. II*, 43, 1095-1132.
- Najjar, R. G. 1992. Marine Biogeochemistry. In: *Climate System Modeling*, Trenberth, K. (ed.), Cambridge University Press, Cambridge, England, 241-280.
- Najjar, R. G., J. L. Sarmiento, and J. R. Toggweiler. 1992. Downward transport and fate of organic matter in the ocean: simulations with a general circulation model. *Global Biogeochem. Cycles*, 6, 45-76.
- Najjar, R. G. and R. F. Keeling. 1997. Analysis of the mean annual cycle of the dissolved oxygen

- anomaly in the World Ocean. *J. Mar. Res.*, 55, 117-151.
- Najjar, R. G. and F. Louanchi. A global monthly mean climatology of phosphate, nitrate and silicate in the upper ocean. In preparation.
- Ozieblo, A., and J. Etcheto. 1991. A method for masking microwave radiometer data polluted by the presence of land and ice. *Int. J. Remote Sens.*, 12, 2379-2388.
- Peltzer, E. T. and N. A. Hayward. 1996. Spatial and temporal variation of total organic carbon along 140°W in the equatorial Pacific Ocean in 1992. *Deep-Sea Res. II*, 43, 1155-1180.
- Press, W. H., and others. 1996. Numerical Recipes in FORTRAN. Cambridge University Press, Cambridge, England.
- Quay, P. 1997. Was a carbon balance measured in the equatorial Pacific during JGOFS? *Deep-Sea Res. II*, 44, 1765-1781.
- Riley, J. P. 1965. The occurrence of anomalously high fluoride concentrations in the North Atlantic. *Deep-Sea Res.* 12, 219-220.
- Roy, R. N., L. N. Roy, K. M. Vogel, C. Porter-Moore, T. Pearson, C. E. Good, F. J. Millero, and D. M. Campbell. 1993. The dissociation constants of carbonic acid in seawater at salinities 5 to 45 and temperatures 0 to 45°C. *Mar. Chem.*, 44, 249-267. (1994. Erratum. *Mar. Chem.*, 45, 337; 1996. Erratum. *Mar. Chem.*, 52, 183)
- Saltzman, J. and K. F. Wishner. 1997. Zooplankton ecology in the eastern tropical Pacific oxygen minimum zone above a seamount: 1. General trends. *Deep-Sea Res.*, 44, 907-930.
- Sarmiento, J. L., J. R. Toggweiler and R. G. Najjar. 1988. Ocean carbon-cycle dynamics and atmospheric  $p\text{CO}_2$ . *Phil. Trans. R. Soc. Lond. A* 325, 3-21.
- Sarmiento, J. L., G. Theile, R. M. Key and W. S. Moore. 1990. Oxygen and nitrate new production and remineralization in the North Atlantic subtropical gyre. *J. Geophys. Res.*, 95, 18303-18303-18315.
- Six, K. and E. Maier-Reimer. 1996. Effects of plankton dynamics on carbon fluxes in an ocean general circulation model. *Global Biogeochem. Cycles*, 10, 559-583.
- Smetacek, V. and U. Passow. 1990. Spring bloom initiation and Sverdrup's critical-depth model. *Limnol. Oceanogr.* 35, 228-234.
- Stephens, B. B., R. F. Keeling, M. Heimann, K. D. Six, R. Murnane and K. Caldeira. 1998. Testing global ocean carbon cycle models using measurements of atmospheric  $\text{O}_2$  and  $\text{CO}_2$  concentration. *Global Biogeochem. Cycles*, 12, 213-230.
- Takahashi, T., W. S. Broecker, and A. E. Bainbridge. 1981. Supplement to the alkalinity and total carbon dioxide in the world oceans. In: Bolin, B (Ed.), Carbon Cycle Modelling, SCOPE 16, 159-200, John Wiley & Sons, Chichester.
- Thomas, C., G. Cauwet and J.-F. Minster. 1995. Dissolved organic carbon in the equatorial Atlantic Ocean. *Mar. Chem.*, 49, 155-169.
- Tsunogai, S. and S. Noriki. 1991. Particulate fluxes of carbonate and organic carbon in the ocean: Is the marine biological activity working as a sink of the atmospheric carbon? *Tellus*, 43B, 256-266.
- Uppstrom, L. R. 1974. The boron/chlorinity ratio of deep-sea water from the Pacific Ocean. *Deep-Sea Res.*, 21, 161-162.
- Volk, T. and M. I. Hoffert. 1985. Ocean carbon pumps: analysis of relative strengths and efficiencies in ocean-driven atmospheric  $p\text{CO}_2$  changes. E.T. Sundquist and W.S. Broecker (Eds.), Carbon Dioxide and the Carbon Cycle, Archean to Present, Geophys. Monogr. Ser., vol. 32, 99- 110, AGU, Washington, D.C.
- Walsh, J. 1978. A Data Set On Northern Hemisphere Sea Ice Extent, 1953-76. Glaciological Data,

- World Data Center for Glaciology (Snow and Ice), Report GD-2, 49-51.
- Wanninkhof, R. 1992. Relationship between wind speed and gas exchange over the ocean. *J. Geophys. Res.* 97, 7373-7382.
- Wanninkhof, R. and M. Knox. 1996. Chemical enhancement of CO<sub>2</sub> exchange in natural waters. *Limnol. Oceanogr.*, 41, 689-697.
- Wanninkhof, R., E. Lewis, R. A. Feely and F. J. Millero. 1998. The optimal carbonate dissociation constants for determining surface water pCO<sub>2</sub> from alkalinity and total inorganic carbon. Submitted to *Mar. Chem.*
- Warner, M. J. and R. F. Weiss. 1985. Solubilities of chlorofluorocarbons 11 and 12 in water and seawater. *Deep-Sea Res.*, 32, 1485-497.
- Weiss, R. F. 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Mar. Chem.*, 2, 203-215.
- Wentz, F. J. 1989. User's manual SSM/I geophysical tapes, Tech. Rep. 060989, Remote Sensing Systems, Santa Rosa, CA.
- Wentz, F. J. 1992. Measurement of oceanic wind vector using satellite microwave radiometers, *IEEE Trans. Geosci. Remote Sensing*, 30, 960-972.
- Wentz, F. J. 1993. Revision-2 update for SSM/I geophysical tapes user's manual, Tech. Rep. 040293, Remote Sensing Systems, Santa Rosa, CA.
- Yamanaka, Y. and E. Tajika. 1996. The role of the vertical fluxes of particulate organic matter and calcite in the oceanic carbon cycle: studies using an ocean biogeochemical circulation model. *Global Biogeochem. Cycles*, 10, 361-382.
- Yamanaka, Y. and E. Tajika. 1997. Role of dissolved organic matter in the marine biogeochemical cycle: studies using an ocean biogeochemical general circulation model. *Global Biogeochem. Cycles*, 11, 599-612.
- Zhang, J. and P. D. Quay. 1997. The total organic carbon export rate based on <sup>13</sup>C and <sup>12</sup>C of DIC budgets in the equatorial Pacific region. *Deep-Sea Res. II*, 44, 2163-2190.
- Zheng, M., W. J. DeBruyn, and E. S. Saltzman. 1998. Measurements of the diffusion coefficients of CFC-11 and CFC-12 in pure water and seawater. *J. Geophys. Res.*, 103, 1375-1379.
- Zwally, H. J., J. Comiso, C. Parkinson, W. Campbell, F. Carsey and P. Gloerson. 1983. Antarctic Sea Ice, 1973-1976: Satellite Passive Microwave Observations, NASA, 206 pp.