The Ocean Carbon Cycle in the Unified Model

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This document is written for the HadOCC model at UM version 4.4.

1 Introduction

The Hadley Centre Ocean Carbon Cycle (HadOCC) model has been developed for use in global ocean carbon cycle modelling. It is implemented as part of the Unified Model ocean component which is based on the Cox (1984) ocean general circulation model. HadOCC simulates the essential aspects of carbonate chemistry and biological production and export. Several extra tracers are carried to model the carbon cycle. These are dissolved inorganic carbon (DIC), total alkalinity (A_T), a nitrogenous nutrient, phytoplankton, zooplankton and sinking detritus. Radioactive ^{14}C is also included in the model. Its implementation is dependent on the air-sea gas exchange of CO_2.

The HadOCC model can be divided conceptually into separate inorganic and biological parts. Inorganic carbonate chemistry and partial pressure physics are well understood and can be reproduced with fair accuracy even in a simple carbon cycle model where assumptions are made about the concentrations of minor ionic species. For a comprehensive description of this science see DOE (1994). The surface temperatures and salinities that control the CO_2 solubility can be prescribed or modelled with good accuracy. Given the surface concentration of DIC, the model is then limited by the accuracy and detail of the ocean circulation. Perhaps the most poorly modelled aspect of a simple solubility model is the rate of air-sea gas transfer. In nature this depends in a complex way on parameters such as windspeed and sea-state, but it is usually represented in models as a simple function of average windspeed (Wanninkhof 1992).

The export of biologically generated soft tissue (organic matter) and hard tissue (carbonate) to the deep ocean, collectively known as the *biological pump*, is difficult to model accurately. The HadOCC ecosystem model and its primary production (total uptake of carbon by phytoplankton during growth) are described in Palmer and Totterdell (1998), in which the modelled primary production is shown to be largely consistent with that observed. But it is not total primary production that is the key biological driving field for an ocean carbon cycle model. Nutrients can be cycled through the food web many times before being lost to the deep ocean, and it is the final export of carbon and nutrients to deeper waters, largely as a sinking particle flux, that determines the circulation

of carbon and nutrients on timescales of decades to centuries.

This document describes the physical, chemical and ecosystem components of the HadOCC ocean carbon cycle model, and draws the readers attention to some numerical implementation issues that have arisen during its development. The document is written for HadOCC in version 4.4 of the UKMO Unified Model.

2 Oceanic fugacity of CO_2

Calculation of the fugacity of CO_2 in the surface waters is required for the subsequent calculation of the air-sea flux. The fugacity is dependent on the concentration of dissolved $CO_2(aq)$. Because $CO_2(aq)$ undergoes a series of chemical reactions in sea water, its concentration must be determined by solving equations representing the seawater acid-base system.

Carbon dioxide dissolved in water $CO_2(aq)$ quickly produces carbonic acid, H_2CO_3. It is difficult to distinguish between $CO_2(aq)$ and H_2CO_3 analytically so we consider the two species together as $CO_2^*(aq)$. The reactions which take place when carbon dioxide dissolves in water can then be written as:

$$CO_2^*(aq) \rightleftharpoons H^+ + HCO_3{}^-$$

$$HCO_3{}^- \rightleftharpoons H^+ + CO_3{}^{2-}$$
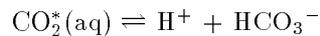
Carbonic acid loses protons H^+ to produce the hydrogen carbonate $HCO_3{}^-$ and then the carbonate $CO_3{}^{2-}$ ion. The three species together are referred to as dissolved inorganic carbon (DIC), which we also write as C_T:

$$C_T = CO_2^* + HCO_3^- + CO_3^{2-}$$

The thermodynamic balance between these three species is governed by the reaction rates, which are dependent on temperature and composition of the water, and on the concentrations of the the species involved. Because the timescales for the reactions are a few minutes or less, the system can be written in terms of chemical equilibria with constants K_0, K_1 and K_2:

$$K_0 = [CO_2^*]/f(CO_2)$$

$$K_1 = [H^+][HCO_3^-]/[CO_2^*]$$

$$K_2 = [H^+][CO_3^{2-}]/[HCO_3^-]$$

In these equations, $f(CO_2)$ is the fugacity of carbon dioxide in the gas phase and brackets represent total stoichiometric concentrations of the chemical species enclosed. The equilibrium constants are functions of temperature, composition (particularly salinity) and pressure of the seawater. Expressions for these constants are given in the appendix. Partial pressure is defined as

the mole fraction multiplied by the total pressure of the gas phase. Fugacity is a 'corrected' partial pressure that accounts for the non-ideal nature of the gas phase. The ratio of fugacity to partial pressure of CO_2 under typical present day oceanic conditions is about 0.995 to 0.997.

To solve for $[CO_2^*]$, and hence the fugacity of CO_2, we need to solve the entire seawater acid-base system to determine H^+. This can be done if the concentrations of all significant weak acid-base pairs and their equilibrium constants are known, as well as the total alkalinity A_T. This is defined as the number of moles of hydrogen ion equivalent to the excess of bases formed from weak acids, under certain constraints (Dickson 1981). It can be measured by titrating seawater against HCl and measuring the pH change, knowing the concentrations of all the acid-base pairs, and is chemically important because it is invariant when CO_2 is added or removed from seawater by air-sea gas exchange. In simple carbon cycle models the alkalinity is prescribed as a constant or as a linear function of salinity (to account for dilution). In the full HadOCC model the plankton uptake of NO_3^- raises the alkalinity through release of OH^-, whereas uptake of CO_3^{2-} for shell building lowers the alkalinity.

The iterative method of Bacastow (1981) is used to calculate $[H^+]$ and hence $[CO_2^*]$. Equilibrium expressions for each acid-base pair are substituted into this simplified alkalinity equation which omits the less important species:

$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+]$$

Equilibrium expressions for the dissociation of CO_2^* and HCO_3^- have been given above. Additionally, the equilibrium expressions for dissocation of boric acid and of water are needed:

$$K_B = [H^+][B(OH)_4^-]/[B(OH)_3]$$

$$K_W = [H^+][OH^-]$$

The equilibrium constants K_B and K_W are calculated using the expressions given in the appendix. The total boron concentration in seawater is principally controlled by freshwater fluxes, so a linear function of salinity is used, taken from Peng (1987):

$$B_T = 4.106 \times 10^{-4} * \frac{S}{35}$$

where the units of boron concentration are moles per kg of seawater and S is the salinity in parts per thousand.

The state variables of the carbonate system in the HadOCC model are total inorganic carbon and total alkalinity. They are stored as oceanic tracers in units of μmoles/litre and μeqs/litre (eqs=equivalents). The units are 'per litre' and not 'per kg' because the ocean model conserves volume but not mass. The chemistry equations were formualted to use C_T and A_T in units of moles or

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equivalents per kg of seawater, so the units of the DIC and alkalinity tracers are changed before use in the above equations using a standard value for the density of seawater of 1026 kg/m^3.

3   Air-sea gas exchange

The air-sea gas transfer of CO$_2$ is usually expressed as a gas transfer coefficient vK_0. The air-sea flux is the gas transfer coefficient multiplied by the air-sea partial pressure difference:

$$F = vK_0(\text{pCO}_{2water} - \text{pCO2}_{air})$$

where K_0 is the solubility and v is a piston velocity that expresses the rate of exposure of the water surface to the overlying air in dimensions of length per unit time. The HadOCC model uses the value K_0 described in the previous section for the solubility. An expression to calculate the solubility given the water temperature and salinity is given in the appendix, but since the expression relates the concentration [CO$_2^*$] to the fugacity and not to the partial pressure it is not clear if this is exactly the correct expression to use. The possible errors, however, are small ($< 1\%$).

The piston velocity v is related to the amount of turbulence and bubble entrainment at the ocean surface. Several studies have tried to construct relationships between wind speed and piston velocity. Two such relationships are available in HadOCC. The first is from Liss and Merlivat (1986) and splits the wind speed range into three domains. A more recent relationship is from Wanninkhof (1992), and uses a Rayleigh wind speed distribution to derive an expression for use with long-term averaged (eg climatological) windspeeds u_{av}:

$$v = 0.39u_{av}^2(S_c/660)^{-0.5}$$

Wanninkhof also supplies a piston velocity expression for use with instantaneous or steady winds, in which the constant is 0.31 instead of 0.39, which would be more appropriate for an ocean carbon model forced with daily wind speeds, for example when coupled to the atmosphere.

Since wind speed is not a parameter available in the ocean model, HadOCC calculates it from the wind mixing energy w using this expression:

$$u_{av} = \frac{\rho_w^{\frac{1}{6}} w^{\frac{1}{3}}}{D^{\frac{1}{2}} \rho_a^{\frac{1}{2}}}$$

where $\rho_w = 1026.0$ kg m^{-3} is a typical density of sea water, $\rho_a = 1.2$ kg m^{-3} is a typical density for air, and $D = 0.0013$ is a typical drag coefficient. The Schmidt number is calculated from the water temperature in Kelvin (T) using the cubic coefficients given in Wanninkhof (1992):

$$S_c = 2073.1 - 125.62T + 3.6276T^2 - 0.043219T^3$$

4 Radiocarbon

The ^{14}C isotope of carbon has been extensively measured in the surface and deep ocean. With a radioactive decay half-life of about 5730 years, ^{14}C is a good tracer for looking at the ventilation of the deep ocean. The ^{14}C content of a sample of seawater is usually expressed as the deviation of the concentration ratio $[^{14}C]/[^{12}C]$ in parts per thousand from a standard ratio, written as Δ^{14}C. In HadOCC, ^{14}C is modelled as a tracer of arbitrary scaling, typically with a value of 100.0 for the preindustrial atmosphere. The model tracer can be converted to Δ^{14}C by subtracting 100.0 and multiplying by 10.0. Seawater values of Δ^{14}C range from typically -50 permil near the surface and in the well ventilated deep North Atlantic to lower than -200 permil in the deep north Pacific, where the oldest oceanic waters are found.

Radiocarbon is modelled by considering air-sea gas exchange, radioactive decay and the advective and mixing processes applied to all ocean tracers. See for example Toggweiler et al. (1989) and Follows and Marshall (1996). The positive influence on Δ^{14}C of the export of young particulate and dissolved organic carbon to depth is not included. Because ^{14}C is modelled as an isotopic ratio, the evasion of CO_2 from the ocean to the atmosphere has no effect on the surface ocean tracer, and the rate of change of ^{14}C in surface waters is written:

$$\frac{d^{14}C}{dt} = \left(^{14}C_{air} - ^{14}C_{ocean}\right)\frac{vK_0 \cdot pCO2_{air}}{C_T} - \alpha \cdot ^{14}C_{ocean}$$

The gas exchange piston velocity v and solubility K_0 for CO_2 are as described in the section on air-sea gas exchange above. C_T is the total inorganic carbon and α is the radioactive decay rate, 3.88915×10^{-12} sec^{-1}.

For a preindustrial experiment the atmospheric $^{14}C_{air}$ is kept fixed. For a historical experiment the atmospheric $^{14}C_{air}$ is varied according to the historical record. Atmospheric Δ^{14}C has been lowered slightly since preindustrial times through dilution by burning of ^{14}C depleted fossil fuels, but raised considerably by atmospheric atomic bomb tests of the 1950's and 1960's. Bomb ^{14}C provides a useful tracer of recent air-sea gas exchange and ocean ventilation because the time history of the atmospheric signal is well known (Broecker et al. 1985). It is often used as a proxy for the oceanic invasion of fossil fuel CO_2 which is difficult to measure directly (Joos et al. 1997).

5 The ecosystem model

The HadOCC ecosystem model calculates the flows of nitrogen between four model compartments; nutrient, phytoplankton, zooplankton and detritus (N, P, Z, D). The flows of carbon within the system are coupled to the flows of nitrogen by fixed carbon:nitrogen ratios C_p, C_z and C_d, but these flows have no effect on the ecosystem because growth is not carbon limited. An average 'Redfield' carbon:nitrogen ratio, C_r, is used in the calculation of biomass equivalents for zooplankton grazing. For a more complete description of the ecosystem

model that justifies the various constants and functional forms see Palmer and Totterdell (1998).

The values of N, P, Z and D are held as extra tracers in the ocean model in units of μmoles of nitrogen per litre.

The cartesian equation for the rate of change of any of the ecosytem components T_i can be written:

$$\frac{dT_i}{dt} = \text{advection} + \text{diffusion} + \text{mixing} + \text{sinking} + \text{biology}$$

The advection, diffusion and mixing terms include all physical transport processes of a tracer in the ocean model. The sinking term is zero except for the detritus which sinks at a speed of $10m/day$. The *biology* terms for each of the four ecosystem compartments are expanded below.

5.1   Phytoplankton

$$\left.\frac{\partial P}{\partial t}\right|_{biology} = RP - G_p - m_0 P^2 - \eta P$$

The specific growth rate of phytoplankton, R, is given by combining Michaelis-Menten light and nutrient limitation terms which saturate at high light and nutrient levels. The light limitation term, L, is calculated using a temperature dependent maximum photosynthesis rate, P_{max}, a maximum photosynthetic efficiency, α, and the average solar irradiance I_{av} within the ocean layer. The temperature dependence of P_{max} allows the growth rate to increase in response to increased local water temperature, T, using a classical $Q10$ parameter raised to a power that increases by 1.0 for every rise of $10°$ Celcius. The average solar irradiance in the ocean layer is calculated using a simple average of irradiances used by the mixed layer model at the top and bottom of the layer. A more complex light model, from Anderson (1993), is also available in the model. This spectrally averaged 'single-band' scheme includes the effects of light absorbtion by phytoplankton on irradiance, and hence on phytoplankton growth and mixed layer physics, but has not been recently tested. Nutrient limitation is controlled by the half-saturation constant N_0.

$$R = L\frac{N}{N + N_0}$$

$$P_{max} = P_{max10}Q10^{\frac{T-10}{10}}$$

$$L = P_{max}\frac{I_{av}}{\frac{P_{mx}}{\alpha} + I_{av}}$$

Loss mechanisms for the phytoplankton population include respiration with a constant specific rate η, grazing by zooplankton G_p and mortality with a rate $m_0 P$ that is quadratic in P to represent stress by overpopulation. Mortality is reduced to zero if the phytoplankton population falls below a concentration of 0.01μmoles/litre. The mortality flow of nitrogen to detritus is limited by the higher carbon content of the detritus. Mortality nitrogen that is left over goes into dissolved nutrient.

5.2   Zooplankton

$$\left.\frac{\partial Z}{\partial t}\right|_{biology} = \beta_p G_p + \beta_z G_z - \mu_1 Z - \mu_2 Z^2$$

Zooplankton grazes on phytoplankton and detritus according to a Holling Type III formulation. The rates of grazing of zooplankton on phytoplankton and detritus are based not on the nitrogen content of P and D, but on the biomass equivalents, $B_p P$ and $B_d D$, where

$$B_p = \frac{14.01 + 12.01 C_p}{14.01 + 12.01 C_r}$$

$$B_d = \frac{14.01 + 12.01 C_d}{14.01 + 12.01 C_r}$$

The total ingestion rate I_{rate} is calculated using a Holling Type III formulation with a threshold below which no grazing takes place. If the available food is $F = B_p P + B_d D$ then:

$$I_{rate} = B_z Z g_{max} \frac{(F - threshold)^2}{(F - threshold)^2 + g_{sat}^2}$$

The loss of phytoplankton and detritus due to grazing in nitrogen units is then G_p and G_z:

$$G_p = \frac{I_{rate}.P}{B_p P + B_d D}$$

$$G_d = \frac{I_{rate}.D}{B_p P + B_d D}$$

The assimilation efficiencies of phytoplankton and detritus β_p and β_d account for 'messy feeding'. As much of the unassimilated material as possible (determined by the carbon:nitrogen ratio of the excess material compared with that of detritus) is egested as detritus. Any surplus carbon immediately becomes dissolved inorganic carbon. Zooplankton mortality represents grazing by higher order predators as well as death by natural causes. It is modelled as the sum of a density independent and dependent terms, with coefficients μ_1 and μ_2. The density dependent term is justified by the observed behaviour of higher grazers, which tend to aggregate where food is plentiful, and increases winter survival rates at high latitudes.

Two thirds of the zooplankton mortality flux is immediately remineralised to nutrient and dissolved organic carbon, representing material travelling up the food chain and being excreted at each stage. The remainder is egested as detritus.

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5.3 Detritus

$$\left.\frac{\partial D}{\partial t}\right|_{biology} = \frac{C_p}{C_d}m_0P + \frac{1}{3}\mu_1 Z + \frac{1}{3}\mu_2 Z^2$$
$$+(1-\beta_p)G_p + (1-\beta_z)G_z - \lambda D - G_z$$

The detritus compartment comprises a combination of dead phytoplankton and zooplankton and egested faecal pellets. It is recycled through zooplankton grazing and remineralisation, which is largely mediated by bacteria (not explicitly included in this model). Remineralisation is specified by a constant rate, λ. At depths down to 240m a remineralisation rate of 0.05 day^{-1} is used. Below the euphotic zone where grazing rates are small, the constant sinking rate of 10 m day^{-1} and constant remineralisation rate of 0.02 day^{-1} imply a detritus density which falls away exponentially with a depth scale of 500m. Ocean circulation subsequently brings this exported nutrient back to the euphotic zone.

5.4 Nutrient

$$\left.\frac{\partial N}{\partial t}\right|_{biology} = -RP + \lambda D + \frac{2}{3}\mu_1 Z + \frac{2}{3}\mu_2 Z^2 + \left\{\frac{C_d - C_p}{C_d}\right\} m_0 P + \eta P$$

The nutrient equation includes sources and sinks deriving from the N, P and Z equations above.

5.5 Carbon and alkalinity

$$\left.\frac{\partial C_T}{\partial t}\right|_{biology} = (mC_p - m_D C_d)P^2 + (C_z - \frac{C_d}{3})(\mu_1 Z + \mu_2 Z^2)$$
$$+(C_p G_p + C_d G_d - C_z G_z - C_d E_D) + \eta C_p P$$
$$+\lambda C_d D - RC_p P - \gamma_c RC_p P + D_{CC}$$

$$\left.\frac{\partial A_T}{\partial t}\right|_{biology} = -\left.\frac{\partial N}{\partial t}\right|_{biology} - 2\gamma_c RC_p P + 2D_{CC}$$

Carbon is not limiting in phytoplankton growth and has no influence on the nitrogen cycling of the ecosystem model. Carbon is carried with nitrogen in the various ecosystem processes according to the C:N ratios of the constituents. Most of the terms in the DIC (C_T) equation are equivalent to terms in the nutrient equation. There are two additional terms which account for the formation of carbonate shells by plankton in surface waters and their subsequent remineralisation at depth. The first is the rate of formation of carbonate, which is assumed to be a fraction γ_c of the total plankton growth. Carbonate is assumed to redissolve evenly throughout the water column below 1500m depth. This modelled sinking flux and remineralisation is instantaneous, unlike the sinking flux of detritus which is modelled explicitly. Carbonate dissolution is

represented by the term D_{CC}:

$$D_{CC} = \begin{cases} 0 & \text{layer-depth} \leq 1500 \text{ m} \\ \frac{\gamma_c C_p}{D_{ocean} - 1500} I(RP) & \text{otherwise} \end{cases}$$

The depth integral of phytoplankton growth is $I(RP)$. The rate of dissolution depends on the depth of the water column D_{ocean}. Where the ocean is shallower than 1500m the carbonate pump is turned off. The precipitation of one mole of carbonate removes two moles of alkalinity from the water because CO_3^{2-} is a divalent base. This alkalinity is released at depth with the associated carbon. Alkalinity is also modified by the uptake of nutrient, as OH^- is observed to be released during nitrate uptake (Goldman and Brewer 1980). Thus the alkalinity equation includes the full negated nutrient time derivative.

Parameter	Symbol	Value
C:N ratio of phytoplankton	C_p	6.625
C:N ratio of zooplankton	C_z	5.625
C:N ratio of detritus	C_d	7.5
Average C:N ratio	C_r	6.625
Max photosynthetic rate at $10^\circ C$	P_{max10}	$0.8 day^{-1}$
Photosynthetic efficiency	α	$0.055(Wm^{-2})^{-1}d^{-1}$
Q10 temp. depend. growth mantissa	$Q10$	1.0
Nutrient limitation half saturation	N_0	$0.1 mMol.m^{-3}$
Phyto respiration, specific rate	η	$0.02 day^{-1}$
Phyto mortality, specific rate	m_0	$0.05 day^{-1}$
Zoo grazing, maximum rate	Zg_{max}	$1.0 day^{-1}$
Zoo grazing, half saturation	g_{sat}	$0.75 mMol.m^{-3}$
Zooplankton grazing threshold	$threshold$	0.1
Assimilation efficiency of phyto	β_p	0.7
Assimilation efficiency of detritus	β_d	0.5
Zoo constant specific mortality	μ_1	$0.05 day^{-1}$
Z-dependent zoo spec. mort. coeff.	μ_2	$0.2 day^{-1}$
Detritus remin. rate, shallow	λ	$0.1 day^{-1}$
Detritus remin. rate, deep	λ	$0.01 day^{-1}$
Detritus sinking velocity		$10 m.day^{-1}$
Carbonate $\div$ primary production	γ_c	0.01

6 Some numerical details

Various problems with the carbon model have been encountered over the years that have complicated the implementation of the scientific equations in this document. Solutions to these problems are described in the subsections below.

6.1 Virtual fluxes of DIC and alkalinity

The ocean model uses fluxes of salt to represent fresh water fluxes. Dilution is a significant factor in correctly modelling alkalinity and must be applied to DIC at the same time to avoid large errors in surface fluxes of CO_2. 'Virtual

fluxes' of alkalinity and DIC are included in the HadOCC model to account for dilution effects. In the Unified Model version 4.4 virtual fluxes from freshwater forcing by the ice model is not included. An additional modset is required if the ice model is being used. The virtual fluxes may be considered as equivalent to transports of tracer within the ocean, and should not be included as part of real air-sea fluxes.

6.2   Plankton growth

The timescale of nutrient uptake by plankton is typically a few hours where conditions are favourable. When growth is nutrient limited, more nutrient may be used in a long explicit timestep than is locally available, leading to numerical problems. To allow ocean model timesteps of 24 hours (actually a 48 hour timestep in the leapfrog timestep scheme) a semi-implicit growth formulation has been implemented in which the nutrient concentration at the end of the timestep is used in the numerator of the Michaelis-Menten nutrient limitation term.

Writing the sum of grazing, mortality, respiration and remineralisation terms from the nutrient equation at time t as:

$$S_t = \lambda D_t + \frac{2}{3}\mu_1 Z_t + \frac{2}{3}\mu_2 Z_t^2 + \left\{ \frac{C_d - C_p}{C_d} \right\} m_0 P_t + \eta P_t$$

the nutrient at time $t + \Delta T$ is written:

$$N_{t+\Delta T} - N_t = -\Delta T L \frac{N_{t+\Delta T}}{N_t + N_0} + \Delta T S_t + N_{supply}$$

where N_{supply} is a nutrient supply term diagnosed from the change in the nutrient tracer during the advection, diffusion and mixing processes on the current timestep. This equation is rearranged to solve for $N_{t+\Delta T}$, which is then used in place of the numerator value of N in the growth terms of the nutrient and phytoplankton equations.

6.3   Post-biology mixing

The biology calculations are performed at the end of the timestep, after the ocean mixed layer routine has been called, to enable the N_{supply} term described above to be evaluated. Plankton growth rates diminish rapidly with depth due to light limitation, and a long timestep leaves the biological tracers far from evenly distributed over the mixed layer when the physical ocean model transports the tracers during the next timestep. This leads to a modest timestep dependence for the ecosystem model. This is largely removed by performing an additional complete mixing of the carbon cycle model tracers within the mixed layer after the biology calculations. By using post-biology mixing and the semi-implicit plankton growth the global export production only varies by a few percent from using a 1 hour to a 24 hour timestep.

6.4 Detrital sinking

The top four layers of the model ocean about are 10m thick. Model detritus sinks at 10m/day. This presents severe numerical problems in explicitly sinking the detritus with a tracer timestep of a day or more. An upwind scheme is used to sink the detritus. To enable longer timesteps to be used the detritus concentration at the end of the timestep is used to determine the advective flux into each box. This is achieved by solving the the detritus balance equation for the top level first. The detritus concentration just calculated for the box above is used to determine the local advective flux divergence. This semi-implicit method yields stable and accurate results for the detrital sinking with timesteps of several days. The small amount of detritus that arrives at the ocean floor is refluxed back into the top ocean level so that carbon and nitrogen are conserved.

6.5 Negative biology tracers

The nutrient, phytoplankton, zooplankton and detritus tracers are physically positive quantities because they represent densities in μmoles/litre. The values of these tracers approach zero in many parts of the ocean, for example in areas of nutrient depletion or very slow growth. Since the ocean model advection and diffusion schemes do not respect the positive definite nature of these tracers the values often fall below zero, for example in areas of strong horizontal divergence. An upwind tracer advection scheme is used to mitigate this problem (see below) but does not eliminate it altogether, and it is important that the carbon cycle model is robust to slightly negative tracer values. This is achieved by setting negative values to zero in the biology model rate calculations (eg growth, grazing rates) with increments added to the original (perhaps negative) tracer values. This scheme results in a stable biology model with slightly negative but not troublesome tracers in a few places close to strong gradients, for example in the nutricline.

6.6 Forward and leapfrog timesteps

The ocean model uses a combination of forward and leapfrog timestepping to maintain numerical stability. Tracer values at time $t - \Delta t$ are used to calculate increments due to advection at time t (leapfrog) whereas values at time t are used for diffusion. Increments are added to the tracers at time t to obtain values at time $t + \Delta t$. The calculations of CO_2 fugacity and air-sea flux, ^{14}C air-sea exchange and radioactive decay and local biological processes are all done using tracers at time t (forward timestepping) because these processes included exponential decay like terms that are unstable if a leapfrog scheme is used. Upwind advection schemes for the tracers and for sinking detritus also use a forward timestep for stability reasons.

6.7 Upwind advection of tracers

The original ocean code used only space centred difference advection requiring a leapfrog timestep to maintain numerical stability. This scheme is difficult to use

with positive defininte tracers that have a large dynamic range often approaching zero, such as nutrient, phytoplankton, zooplankton and detritus, because the tracer values frequently become negative. Pending the implementation of a more sophisticated advection scheme, upwind advection has been implemented in the ocean code and is used to advect the N, P, Z and D tracers. The choice of advection scheme is set in the code using an array of flags. The sinking of detritus is also modelled using an upwind scheme.

7 References

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8 Appendix: Carbon chemistry equilibrium constants

The equilibrium constants for the dissociation of water, boric acid, carbonic acid and of the hydrogen carbonate ion are required for the calculation of the hydrogen ion balance in seawater. An additional equilibrium constant is required to relate the concentration $[CO_2^*]$ to the fugacity of CO_2. The following expressions are taken from DOE(1994). The constants depend on the seawater temperature T (Kelvin) and salinity S (ppt).

8.1 $H_2CO_3 \longleftrightarrow H^+ + HCO_3^-$

$$
\begin{aligned}
ln(K_1) =& \frac{-2307.1266}{T} + 2.83655 - 1.5529413 ln(T) \\
&+ (\frac{-4.0484}{T} - 0.20760841)S^{1/2} + 0.08468345S \\
&- 0.00654208S^{3/2} + ln(1 - 0.001005S)
\end{aligned}
$$

Units of K_1 are moles per kg of seawater, T is the temperature in kelvin and S is the salinity in ppt, typically about 35.

8.2 $HCO_3^- \longleftrightarrow H^+ + CO_3^{2-}$

$$
\begin{aligned}
ln(K_2) =& \frac{-3351.6106}{T} - 9.226508 - 0.2005743 ln(T) \\
&+ (\frac{-23.9722}{T} - 0.10690173)S^{1/2} + 0.01130822S \\
&- 0.00846934S^{3/2} + ln(1 - 0.001005S)
\end{aligned}
$$

Units of K_2 are moles per kg of seawater.

8.3 $B(OH)_3 \longleftrightarrow B(OH)_4^-$

$$
\begin{aligned}
ln(K_B) =& (-8966.90 - 2890.53S^{1/2} - 77.942S + 1.728S^{3/2} - 0.0996S^2)/T \\
&+ (148.0248 + 137.1942S^{1/2} + 1.62142S) \\
&+ (-24.4344 - 25.085S^{1/2} - 0.2474S)ln(T) \\
&+ 0.053105S^{1/2}T
\end{aligned}
$$

Units of K_B are moles per kg of seawater.

8.4 $H_2O \longleftrightarrow H^+ + OH^-$

$$
\begin{aligned}
ln(K_W) \quad &= \quad \frac{-13847.26}{T} + 148.96502 - 23.6521 ln(T) \\
&\quad + (\frac{118.67}{T} - 5.977 + 1.0495 ln(T)) S^{1/2} + 0.01615 S
\end{aligned}
$$

Units of K_W are (moles per kg)^2.

8.5 $fCO_2 \longleftrightarrow CO_2^*(aq)$

$$
\begin{aligned}
ln(K_0) \quad &= \quad 93.4517 \frac{100}{T} - 60.2409 + 23.3585 ln(T/100) \\
&\quad + (0.023517 - 0.023656(T/100) + 0.0047036(T/100)^2) S
\end{aligned}
$$

where the units of K_0 are moles per kg per atmosphere.