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Interactive comment on “Past and present of sediment and carbon biogeochemical cycling models” *by* F. T. Mackenzie et al.

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The well-thought and very clearly formulated comments of Christoph Heinze and Robert Buddemeier on the paper by Mackenzie et al., go beyond the scope of that paper, making us and, hopefully, the readers think further about the deeper and broader issues of the nutrient biogeochemical cycles within which we as humans are an active part. We are grateful to the two authors and the editorial policy of Biogeosciences for the opportunity to respond to at least some of the important issues raised in the com-ments. Our replies follow.

1. In their comments, both authors address the issues of anthropogenic effects on the global carbon cycle: **(a)** Heinze focuses on the potential CO_2 sequestration in the deep ocean, and **(b)** Buddemeier points out the need to include human-population growth in cycle models.

(a) The geochemical, ecological, and climatic consequences of CO_2 sequestration in the deeper parts of the oceans are a subject of extensive research, without even mentioning numerous engineering and economic feasibility studies (Adams et al., 1997;

Archer et al., 1997, 1998; Bacastow and Dewey, 1996; Bacastow et al., 1995, 1997; Brewer et al., 1998, 1999; Caldeira and Rau, 2000; Caulfield et al., 1997; Dewey et al., 1997; Falkowski, 1997; Hoffert et al., 1979; Murray et al., 1996; Ormerod et al., 1993). From the perspective of the global carbon-balance analysis in our paper, one can compare the magnitude of anthropogenic CO_2 emissions with the mass of dissolved inorganic carbon (DIC) and aqueous CO_2 in the deeper ocean. The potential changes in the ocean would depend, among other factors, on the mass of CO_2 disposed and the volume of ocean water that takes it. Localized disposal, such as in depressions on the ocean floor, is likely to have greater local effects than those of an av-erage disposal over a greater area. In the year 2000, total CO_2 emissions were 6.611 Gt C or 550×10^{12} mol C/yr (Marland et al., 2003). Net CO_2 uptake by the global ocean from the atmosphere near that time is estimated at about one quarter to one-third of the emissions: for example, from measurements, $133\pm20\times10^{12}$ mol/yr (1.6 ± 0.24 Gt C/yr; Tans et al., 1990) and $185\pm37\times10^{12}$ mol/yr (2.22 ± 0.44 Gt C/yr; Takahashi et al., 2002), and from model analysis, 153×10^{12} mol/yr (1.84 Gt C/yr; Ver et al., 1999; Mackenzie et al., 2001).

From the mean chemical composition of deep ocean water (carbonate alkalinity and DIC; Broecker and Peng, 1982), its computed pH is near 7.7 and it is significantly undersaturated with respect to calcite, Ω=0.9. These results, computed from the apparent dissociation constants given in Zeebe and Wolf-Gladrow (2001), are for ocean water of mean salinity of 35 g/kg, temperature of 5°C, pressure of 300 bar that corresponds to a depth of about 3,000 m, and constant total alkalinity of deep ocean water. In the deep ocean, dissolved CO_2 is a fractional 1.6% of total dissolved inorganic carbon. Twenty years of anthropogenic CO_2 emissions at the year-2000 rate would produce 1.1×10^{16} mol C. If this entire amount of CO_2 was added to a deeper one-quarter of the ocean volume (a layer about 950 m thick, of mass 0.35×10^{21} kg), the dissolved CO_2 concentration in the layer would increase by about 30% but the DIC concentra-tion would increase by only 1.5%. The pH of the water layer would decrease from about 7.7 to 7.6 and undersaturation with respect to calcite would deepen from Ω=0.9 to 0.7.

In this case, one would have to consider such changes as a potential return of CO_2 to the atmosphere on a longer-time scale, a possibly faster dissolution rate of $CaCO_3$ in the deeper ocean, CO_2 consumption in carbonate dissolution, and an in-crease in total alkalinity.

The preceding discussion is effectively an outline of a failed CO_2 sequestration case, where carbon dioxide dissolves in ocean water. CO_2 sequestration is concerned not with the disposal of gaseous CO_2 but with its liquid and hydrated phases. Although both CO_2 liquid and CO_2 hydrate can coexist at depths below about 400 m at the lower temperatures in the ocean (Murray et al., 1996), CO_2 hydrate is of primary con-cern at present for disposal purposes (e.g., Ormerod et al., 2002). The hydrate at its density of 1049 to 1100 kg/m^3 (Aya et al., 1997; Teng et al., 1999) is heavier than ocean water of mean salinity of 35 g/kg in a range from 1023 kg/m^3 at a warm surface (25°C) to 1050 kg/m^3 at colder depths (Chapman, 2000; Millero, 2001). Liquid CO_2 has been reported to become heavier than ocean water at depths $\geq$3000 m (e.g., Teng et al., 1999). Because its volume compressibility is greater than that of seawater, its density becomes slightly greater than that of ocean water at $\lesssim$3°C and a pressure near 300 bar (Span and Wagner, 1996; Lemmon et al., 2003; Millero, 2001). However, along the P-T phase boundary of CO_2 gas-liquid equilibrium, the liquid density remains smaller than that of ocean water: it increases from 468 kg/m^3 at its critical point of 31°C and 74 bar to about 940 kg/m^3 at -1.8°C, where the gas-liquid equilibrium pres-sure is about 33 bar, corresponding to a depth of about 330 m (Ambrose, 1994; Grau, 1960; Valentiner, 1960; Span and Wagner, 1996). Uncertainties exist as to the stability and solubility of liquid CO_2 and CO_2 hydrate in contact with ocean water of varying CO_2 concentration. Some published reports indicate that CO_2 hydrate may form a coating on liquid CO_2, reducing its solubility, while others indicate that CO_2 hydrate particles dissolve during settling. Potential dissolution of sequestered CO_2 in the deeper ocean and its return to the atmosphere was estimated by Bacastow and Dewey (1996) as a process at a time scale of centuries. It may be mentioned in passing that the critical temperature and pressure of liquid CO_2 make it stable in some sections of the continental sedimentary lithosphere (Van der Meer, 1993; Lerman et al., 1996; Pruess, 2004): a pressure of about 70 bar may exist between 270 and 700 m depth, depending on whether it is lithostatic pressure or hydrostatic under a column of a saline brine or pure water. At that depth and pressure, a temperature of $\lesssim 30^{\circ}$C would be within the stability field of liquid CO_2.

(b) Anthropogenic perturbations of the carbon and nutrient cycles on land by such processes as fossil fuel burning, land-use changes, chemical fertilization of cropland, and releases of organic sewage and detergents to the continental and coastal waters produce a variety of effects, some of which are mutually competing: for example, increased fertilization of land on a time scale of 300 years of the Industrial Age is driven by the increase in atmospheric CO_2 and greater recycling of the nutrient elements N and P from the soil organic matter (humus), as well as the more recently increased fluxes of chemical fertilizers, organic sewage, and detergents. On the other hand, changes in land-use practices, deforestation, and urbanization are to a variable extent responsible for greater erosion of land and transport of organic carbon and nutrients to the coastal zone. In general, the population density of river drainage basins has been demonstrated to correlate with increased nutrient fluxes, as mentioned by Robert Buddemeier in his comment. Such increases are built into TOTEM, our global dynamic model of interacting C-N-P cycles (Ver et al., 1999; Mackenzie et al., 2001, Lerman et al., 2004), not as an explicit population-size parameter but as time-dependent human forcings mentioned above. As of the year 2000, by far the greatest anthropogenic emissions of C, N, and P were from fossil-fuel burning and land-use practices. The amount of N and P added to the environment from chemical fertilizers and detergents in the 20th century has been much smaller.

The water cycle in TOTEM is in a steady state during the 300 years of model simulation. The following example of nitrogen and phosphorus inputs to the coastal reservoirs demonstrates the possible effects of changes in the river flow. Rivers carry dissolved inorganic nitrogen (DIN) and phosphorus (DIP) to the Coastal Waters reservoir, and dissolved organic (DON, DOP) and reactive particulate forms (50% of PON and POP) to the Coastal Organic reservoir where primary production occurs (Fig. 1). Primary production consuming DIN and DIP from Coastal Waters and their return from remineralization of organic matter in the Coastal Organic reservoir are the largest fluxes in the coastal zone that are responsible for fast turnover in each of the two reservoirs. However, for these two reservoirs combined, the external inputs include rivers, remineralization in coastal sediments, upwelling from the deeper ocean, and N fixation and deposition from the atmosphere. Within these four external fluxes, riverine input accounts for 10% of N and 20% of P. A change in their input rates due to a change in the hydrological cycle would affect the coastal ecological system at a time scale commensurate with the residence times of nitrogen, 25 yr, and phosphorus, 5 yr, within the combined Coastal Waters and Organic reservoirs at an initial pre-industrial steady state. In our continuing work on the model TOTEM, we are addressing river flow changes on a longer time scale, from the Last Glacial Maximum to industrial time.

It should be also noted that increasing environmental perturbations and human forcings are driven not only by the population size and growth alone but also by new technology. The use of fertilizers in agriculture is perhaps a good example of a change in the material source: from the early, pre-scientific reliance on manure, wood ash, potassium nitrate, ground bones, guano, and fish to the industrial production of phosphate and nitrogen fertilizers on a large scale in the 20th century (Aldrich, 1964). As for other transient fertilizer sources, there is an almost anecdotal but not referenced quotation from Justus von Liebig who allegedly accused England of an extensive practice of digging human bones from old battlefields and catacombs for use as fertilizer (Bear, 1962, p. 138; 1986, p. 188). Historical records of population and energy consumption growth show that in industrial time both the population size and energy consumption or production per person had been increasing, making total energy consumption increase faster than the population size: in the U. S., in the years 1850–1970, energy consumption grew at a rate twice as fast as the population growth, at a doubling time of about 25 years as compared to 50 years for the population (Dorf, 1981), and energy

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consumption per person per day in the U. S. in 1970 was three times higher than in the technological society of 1875, at 230,000 as compared to 77,000 kcal/day (Cook, 1971). While world population in the last 50 years of the 20th century increased by a factor of about 2.37 (from about 2.5 to 6 billion), carbon emissions from industrial activities per person increased further by a factor of about 1.8, from 0.63 to 1.12 ton C/yr per person (Mackenzie, 2003). Such differences between the rates of population growth and the rates per person of energy consumption and nutrient releases raise a broader question of whether a cause and effect relationship exists between the population size and human technological innovativeness that produces a variety of byproducts that also lead to environmental perturbations.

2. The question of “error bars to the estimates of carbon net fluxes between shallow seas and the atmosphere" is raised by Christoph Heinze in his comment. In general, sensitivity analysis in deterministic models can show the variation in the results, but it is only as good as the conceptual and mathematical structure of the model and its authors’ choices of the parameter values within some range of testing. In the case of our paper, the large variation both in the direction and magnitude of the CO_2 flux between coastal or near-coastal waters and the atmosphere is reflected in the data in Table 4: about an equal number of observations report flux from the water to the atmosphere as well as in the opposite direction. In Fig. 2A, the uncertainties in the CO_2 transport fluxes between the sections of the shallow ocean and between the coastal and open ocean reflect the uncertainties in the current state of knowledge of these processes. In the inorganic cycle shown in Fig. 2B, the $CaCO_3$ production rates vary by a factor of about two, from a higher value of 94×10^{12} mol/yr given in Fig. 2B to 53×10^{12} mol/yr given by Milliman (1993). The total CO_2 emission rate from the surface ocean to the atmosphere that is a function of $CaCO_3$ production and net storage in sediments is 56×10^{12} mol/yr (Fig. 2B), which is comparable to the flux of 46 to 49×10^{12} mol/yr, calculated for pre-industrial time conditions from net storage of $CaCO_3$ and organic carbon in sediments (Lerman and Mackenzie, 1994).

3. In conclusion, we fully endorse Robert Buddemeier's assertion that there is a need to develop and nurture more extensive working interactions between those who collect data on local and regional scales and those who approach the issues top-down. We are also in complete agreement with Christoph Heinze's views on the limitations of box models as analytical and predictive tools for such complex environments as the global coastal zone. The opinions expressed by the two commenting authors are timely as a guidance for research directions in the near future and we hope that they will be seriously considered by all concerned with the biogeochemical cycles in the combined domains of the land, atmosphere, oceanic coastal zone, and open ocean, both on geologically short and long time scales.

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Figure legend

Fig. 1. Coastal Waters and Coastal Organic Matter reservoirs in model TOTEM at the assumed initial steady state in pre-industrial time, year 1700 (from Ver et al., 1999). Input fluxes of N and P are initially balanced by output fluxes (not shown) of dissolved and particulate N and P from the Coastal Waters and Organic Matter reser-voirs to coastal sediments and open ocean, and gaseous N to the atmosphere. Rapid cycling of N and P by primary production between Coastal Waters and Coastal Organic reservoirs is shown by dashed arrows, leaving the remaining fluxes as inputs to the combined two reservoirs (see http://www.copernicus.org/EGU/bg/bgd/1/27/bgd-2004-0009-Reply-f01.pdf).

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