Some Perspectives of the Major Biogeochemical Cycles
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CHAPTER 8

Interactions Between Major Biogeochemical Cycles in Marine Ecosystems

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ABSTRACT

The geochemical cycle of the elements in a marine system is strongly dependent on or influenced by biological activity. The production of organic matter acts as a major process of transfer of elements from the dissolved to the particulate state as soft or hard tissues. On the other hand, respiration or biological degradation may lead to the redissolution of particulate species.

As primary productivity is strictly limited to the photic zone and decay of organic matter is pursued in the deeper water masses of the oceanic system, the distribution of many elements exhibits a strong vertical gradient.

The biological activity also strongly affects master variables of seawater: pH, oxydo-reduction potential, and alkalinity. These changes may in turn induce chemical dissolution or precipitation reactions and influence the distribution of biologically inactive elements.

A general model of the cycle of various elements based on biological productivity and regeneration in a water column divided into a photic zone and a deep-water layer is presented here. It is based on the cycle of organic matter in the ocean acting as the driving force.

The vertical fluxes between the two water reservoirs are due to the settling of particulate organic and inorganic matter and to the transfer of dissolved species related to vertical advection and turbulent diffusion.

It is possible in this way, to build coherent global models describing the fluxes of organic carbon, phosphorus, nitrogen, silica and calcium carbonate in the ocean, and interrelations between the dynamics of the marine biota and the cycle of other minor elements may be expected.

8.1 INTRODUCTION

The first and necessary approach to modelling of chemical cycles in the ocean is to establish a mass balance model where the ocean is considered as a black box. It is generally assumed that a steady state is realized on the time scale considered, that is the composition of the system is independent of time. This model describes transport paths and fluxes among a limited number of physically well-defined portions of the earth like the continents, the atmosphere, the marine sediments.

The quality of such a model is controlled by the mass balance between the input and the output fluxes, which is equal to zero if no accumulation or removal in the reservoir is assumed (steady state). These models already permit an estimation of the importance of the modifications to natural chemical cycles owing to perturbations introduced by human activities. They are, however, insufficient to predict the effect of these perturbations, which requires furthermore that we also understand the mechanism responsible for the various fluxes involved in the model.

In the case of the geochemical cycles in the ocean, a first improvement was introduced by Sillen (1961) who considered that seawater could be viewed on a geologic time scale as an aqueous solution nearly in equilibrium with typical minerals (clays, carbonates, . . .). The thermodynamic model of seawater has serious limitations when short-term controls of chemical composition are considered. Also it is obvious that for many elements showing vertical concentration gradients in the ocean, which is the case for the elements vital to life, an equilibrium model is not applicable. Moreover, organic matter itself is thermodynamically unstable in the physicochemical conditions prevailing in the oceans.

The trend today is away from thermodynamic modelling and towards kinetic models, particularly those involving biological processes as kinetic controls on element cycles. Many elements are directly involved to a certain extent in biological processes, or their behaviour is indirectly affected by the physicochemical changes induced by the biological activity. Conversely, the biological activity itself is dependent on the available concentration of certain well defined chemical species in the marine environment, and the domain of potential activity of living organisms is in turn determined by thermodynamic factors. The interrelations between the cycles of the elements are for these reasons extremely intricate and difficult to handle without drastic simplifications.

I have chosen to present some tentative cycles for various elements based on the cycle of organic matter in the ocean considered as the driving force. The fluxes in the marine ecosystem of other elements vital to life will then be computed on the basis of the carbon cycle.

I shall first describe the model of organic carbon in the ocean as a driving parameter and show how the biological activity affects the distribution and behaviour of other elements. The relative importance of the biological processes in the cycle of these elements may further be compared with the global geochemical cycle restricted for the oceans to the continental input and the sedimentary output.

8.2 THE BIOGEOCHEMICAL CYCLE OF ORGANIC CARBON

The production of organic matter by photosynthesis is limited by the penetration of light and is thus restricted to the surface layer of the ocean (maximum depth of

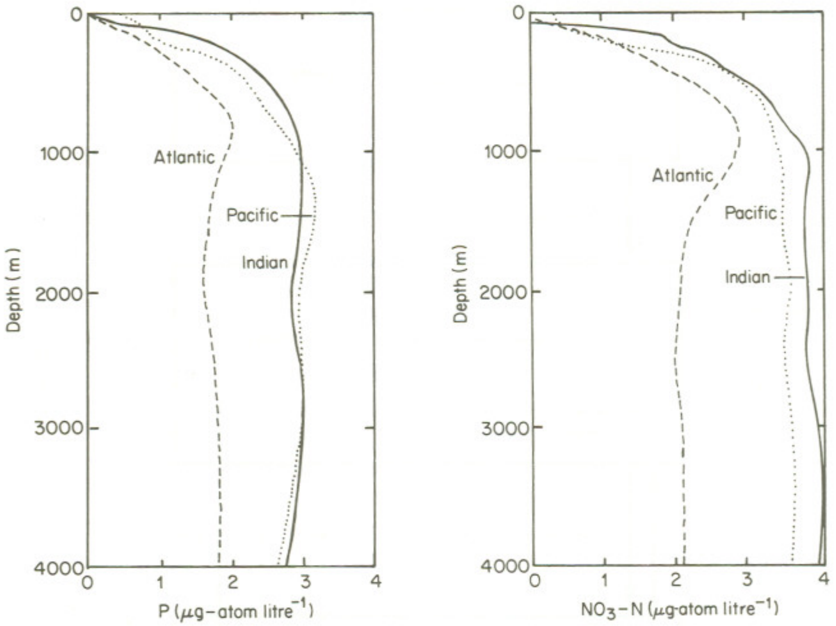

Figure 8.1 Mean vertical distribution of phosphate and nitrate in the oceans (from Svedrup *et al.*, 1942)

200 metres). In addition to light, the rate of photosynthesis is also limited by the supply of nutrients, particularly nitrogen and phosphorus.

These nutrients are virtually exhausted (Figure 8.1) from the photic zone by incorporation in phytoplankton. The phytoplankton is consumed by marine animals and the excreta and dead bodies are bacterially degraded with regeneration of the nutrients either in the surface waters or in the deeper water masses, as the organic debris sinks. As a consequence the deeper waters are enriched in nutrients which may be restored to the photic zone by upwelling or by vertical turbulent mixing.

Finally, a fraction of the biogenic material reaches the sediment–water interface. Further degradation of the organic matter or dissolution of the skeleton proceeds until the reactive material has been either exhausted or covered by a sufficient layer of accumulating sediment.

A general model of the cycle of biological productivity and regeneration shows (Figure 8.2) a water column divided into a photic zone and a deep-water layer. The fluxes between these two reservoirs are due to the settling of particulate organic and inorganic matter from the surface waters to the intermediate and deep waters and to the transfer of matter related to advection and turbulent diffusion.

The model limited to the water column must also take into account the fluxes at the boundaries including river input, exchanges with the atmosphere, sedimen-

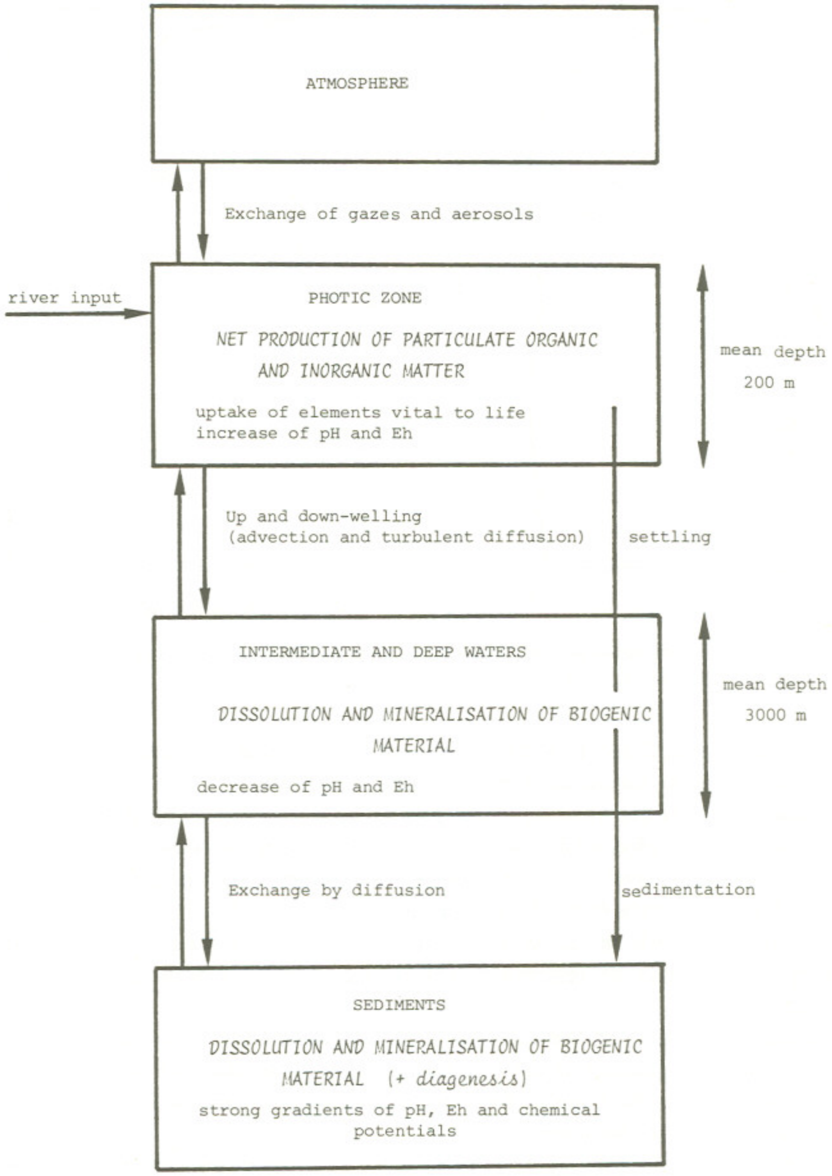

Figure 8.2 Major reservoirs and fluxes of the biogeochemical cycle of elements related to the biological activity in the ocean

tation of particulate matter at the bottom, and exchanges of dissolved species with the pore waters of the sediments by diffusion.

The transfer of compounds from the continents and from the atmosphere to the photic layer may be estimated from the global river discharge and the annual rainfall over the oceans multiplied by the mean concentration of the compounds in rivers and rain water. A total river discharge of 0.32×10^{20} g yr^{-1} and yearly precipitation on the oceans equal to 3.47×10^{20} g were used in the following calculations.

Besides the role played by the living organisms in the transfer of chemical species between reservoirs, it is also important to remember that the biological activity affects some master chemical variables such as the pH, the redox potential, and the total inorganic carbon content. Thus in the surface layer where photosynthesis exceeds respiration, the water exhibits a higher pH and a higher oxydo-reduction potential whereas in the deeper water only respiration occurs which lowers the pH and the Eh.

The influence of photosynthesis and respiration on these two variables is well demonstrated if one considers the following reversible reaction:

$$CO_2 + 4H^+ + 4e^- \rightleftharpoons CH_2O + H_2O$$

Eventually the deep water may become anoxic if the flux of detrital organic matter and its subsequent decomposition exceeds the available quantity of dissolved oxygen. However, the anoxic conditions are mainly realized in the sediments where oxygen is generally depleted at a depth of a few centimetres.

These changes may indirectly affect the behaviour of some elements particularly those sensitive to changes of the oxydo-reduction potential like N, Fe, Mn, Cu, I, and so forth.

Quantitatively there are now rather coherent values for the carbon cycle in the ocean. de Vooys (in press) has critically reviewed the various recent estimates of the primary production in the marine environment and has concluded that 43.5×10^{15} g C yr^{-1} is the best approximation of primary production in seas and oceans now available.

The same author also collected some estimates from the literature concerning the per cent of total primary production which sinks to deeper levels and to the bottom. Some six per cent sinks from the photic zone, based mainly on the vertical distribution of particulate organic matter in the water column. A value of 0.6 per cent was chosen for the transfer of particulate organic matter to the sediments on the basis of the organic content of surficial sediments.

It must be pointed out that this organic matter is further subjected to biological degradation and according to Garrels and Perry (1974) only one third of the deposited organic material is finally preserved in the sediments.

There are quite large uncertainties concerning the concentration of particulate and dissolved organic matter in river and rain waters but their contribution is very small compared to the primary productivity.

I have adopted here the values of Garrels *et al.* for the river discharge which are respectively equal to 0.13×10^{15} g C yr^{-1} for dissolved organic carbon and 0.07×10^{15} g C yr^{-1} for particulate organic carbon.

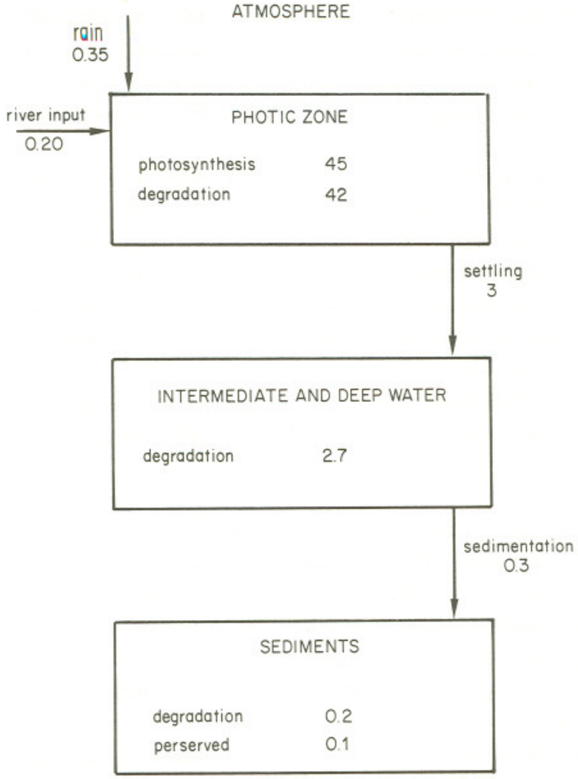

Figure 8.3 Tentative global cycle of organic matter in the ocean. Organic matter values times 10^{15} g C yr^{-1}

Maier and Swain (1978) have estimated from a range of data collected in the literature that a value of 1 mg C $litre^{-1}$ in rain water may be used as representative of unpolluted atmospheric conditions. The corresponding flux over the ocean is then 0.35×10^{15} g C yr^{-1} for dissolved and particulate organic carbon.

A tentative global cycle of organic carbon in the ocean based on the data presented here is given in Figure 8.3. For convenience, the values used in this figure have been rounded but are well within the range of the existing uncertainties.

The biological activity characterized by the carbon cycle will be used in the next section as the driving force which controls the fluxes of various other biogenic elements in the oceanic system. The mean composition of the phytoplankton and of the suspended detrital organic matter in the various water layers and in the sedimentary column permits an evaluation of the fluxes of the particulate species between the reservoirs. The steady-state assumption applied to each reservoir then allows me to compute by difference the compensating fluxes of the dissolved species required to satisfy the mass balance.

I shall discuss successively the case of the classical nutrients N and P, of the biogenic portions of SiO_2 and $CaCO_3$ and finally of some trace elements vital to life.

8.3 THE PHOSPHORUS AND NITROGEN CYCLES

I have adopted the well-known Redfield ratio 106C:16N:1P (Redfield *et al.,* 1963) for the mean composition of the marine plankton. This ratio allows me to compute from the carbon cycle the amount of nutrients consumed and mineralized in the photic zone and the amount of particulate P and N transferred to the deep waters as organic detrital matter.

The mineralization of the organic N and P compounds in the intermediate and deep water has been slightly increased with respect to the organic carbon. This increase is justified by the fact that many N and P compounds are more rapidly degraded and that, as a consequence, the C:P and C:N ratios in the suspended matter tend to increase with depth in the water column.

8.3.1 The Phosphorus Cycle

The results for the phosphorus cycle are presented in Figure 8.4. The amount of phosphorus preserved in the sediments has been taken from Lerman *et al.* (1975) and is based on the mean composition of marine sediments. It should be noted that these authors have computed a more detailed model including the terrestrial cycle. The fluxes calculated here are in good agreement with their previous estimations, shown in parentheses in Figure 8.4.

The validity of this model was tested further from independent evaluations of the fluxes of nutrients between the intermediate water and the photic zone due to upwelling and turbulent diffusion.

The rate of vertical mixing in the ocean has been estimated mainly from the vertical distribution of natural isotopes like ^{14}C, ^{32}Si, and ^{226}Ra or man-made isotopes like ^{3}H, ^{90}Sr, ^{137}Cs (Broecker, 1974).

A rather consistent mean of 3 ± 1 m yr^{-1} may be deduced from the collected data (Lerman, 1979) for the rate of mixing of deep and intermediate water with surface water. If this value is multiplied by the mean concentration of dissolved phosphate in the deep water (70×10^{-3} g P m^{-3}) taken from Figure 8.1, I obtain a vertical flux of 75×10^{12} g P yr^{-1}. This value is in remarkable agreement with the evaluation based on the carbon cycle discussed above (71×10^{12} g P yr^{-1}).

It is also possible to evaluate the relative importance of upwelling and turbulent diffusion to the vertical mixing. The turbulent diffusion across the thermocline is a very slow process which may be considered as a limiting step. Lerman (1979) has reviewed the available data for the oceans and lakes and from his work I have selected a mean value of 1500 m^2 yr^{-1} (0.5 cm^2 s^{-1}) for the eddy diffusion coefficient.

From Figure 8.1, the mean concentration gradient of dissolved phosphate is approximately 60×10^{-6} g P m^{-3} m^{-1} which gives over the total area of the ocean a vertical flux by diffusion of 35×10^{12} g P yr^{-1}.

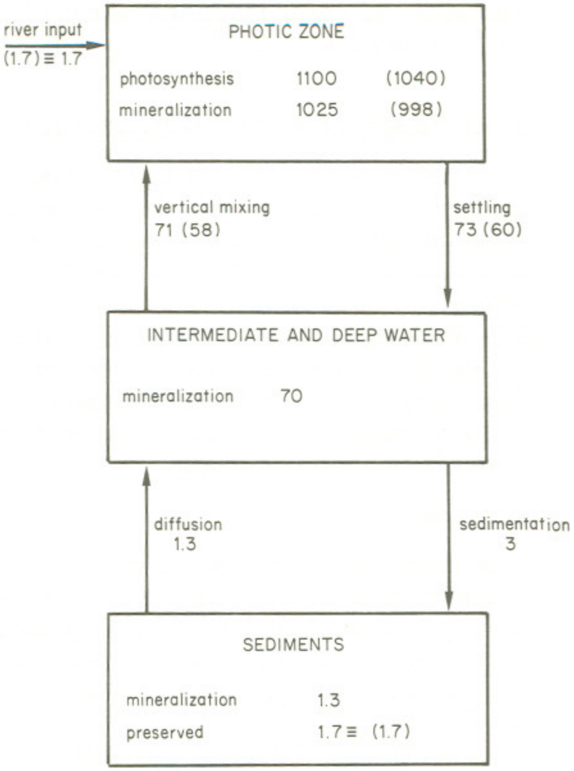

Figure 8.4 Tentative cycle of phosphorus in the ocean. The figures in brackets are independent estimates from Lerman *et al.* (1975) (≡) indicates values adopted here from these authors. Phosphorus values times 10^{12} g P yr^{-1}

Thus approximately one half of the vertical flux of phosphate is due to turbulent diffusion and the other half to advection (upwelling). However, upwelling is mainly restricted to coastal zones whereas turbulent diffusion prevails in the open ocean. The differences in the surface areas of these two zones explain well the drastic differences of primary productivity observed between coastal regions and the open sea.

8.3.2 The Nitrogen Cycle

The nitrogen cycle is more complicated due to the various species of inorganic N (NH_4^+, N_2, N_2O, NO_2^-, NO_3^-) involved in the biological cycle and to the influence of the local oxydo-reduction conditions on the thermodynamic stability of these species. The energetic implications related to the thermodynamic properties of the nitrogen species control in turn the possible pathways of the bacteriological activity.

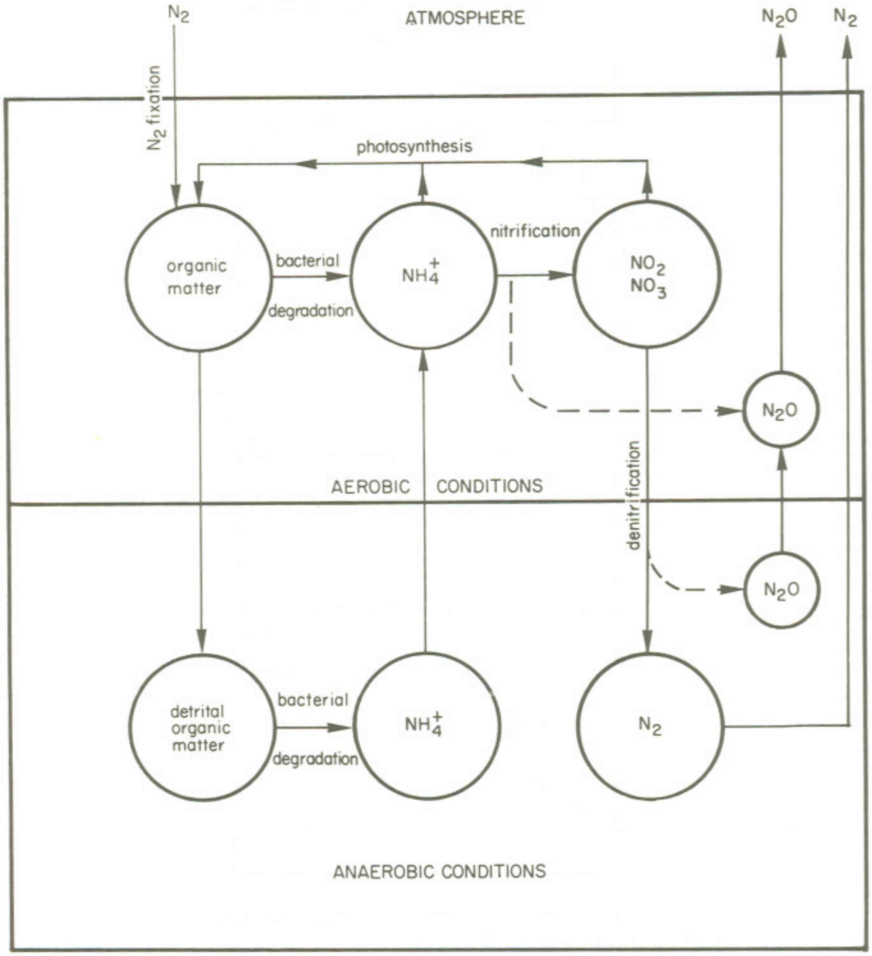

Figure 8.5 Schematic biological pathways of nitrogen in aerobic and anaerobic environments

I have considered here a rather simplified scheme (Figure 8.5) where a distinction is made between aerobic and anaerobic environments.

A tentative cycle for nitrogen is presented in Figure 8.6. The oceanic waters are generally sufficiently oxygenated that nitrate is usually the final more stable compound in solution. I do not have sufficient data on the restricted cases of anaerobic conditions to evaluate the amount of denitrification which may occur in the intermediate and deep waters. On the other hand, oxygen is rapidly depleted in the pore water of marine sediments and the anaerobic conditions prevailing there are favourable to the denitrification process. The tentative figures given for the cycle of nitrogen in the sediments are based on an extended study of North Sea sediments (Billen, 1978).

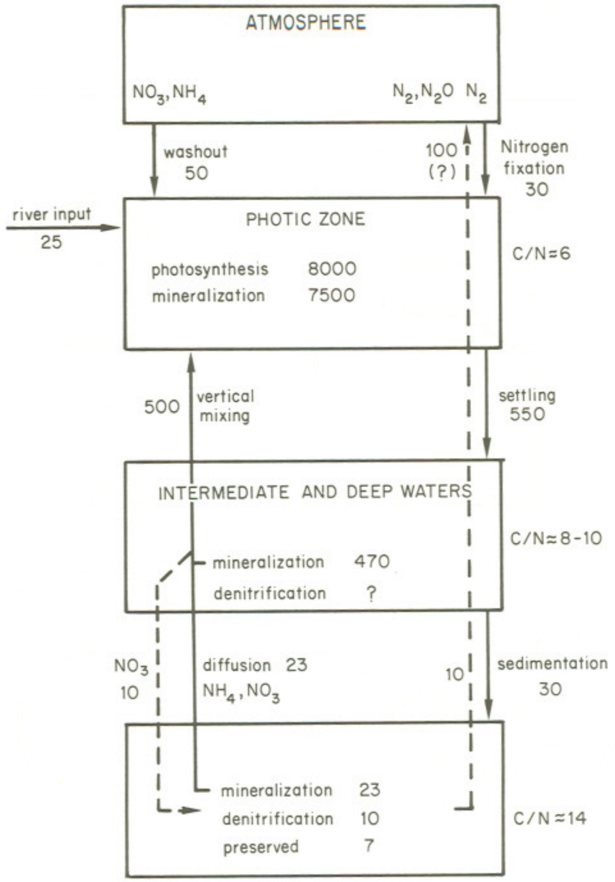

Figure 8.6 Tentative cycle of nitrogen in the ocean. Nitrogen values times 10^{12} g N yr^{-1}

According to Söderlund and Svensson (1976) the total nitrogen flux due to river runoff to the ocean is between 13 and 24 × 10^{12} g N yr^{-1}. However, more recent estimates are slightly higher: 20 × 10^{12} g N yr^{-1} (McElroy, 1976), 30 × 10^{12} g N yr^{-1} (Sweeney *et al.*, 1977) and 35 × 10^{12} g N yr^{-1} (Delwiche and Likens, 1977). An intermediate value of 25 × 10^{12} g N yr^{-1} is adopted here.

For the rainout, fallout, and washout of nitrogen species over the ocean, again the range of the various estimates is broad: 30 to 80 × 10^{12} g N yr^{-1} (Söderlund and Svensson, 1976) and a mean value of 50 × 10^{12} g N yr^{-1} has been selected here.

In the photic zone, upwelling and vertical mixing remain the dominant sources of nitrogen but the river input and the atmospheric washout are relatively more important sources than in the case of phosphorus.

The extent to which nitrogen fixation occurs in the marine system is not accurately known and was estimated to be 20–120 × 10^{12} g N yr^{-1} (Söderlund and Svensson, 1976). I have selected here an estimate of 30 × 10^{12} g N yr^{-1}, as the best approximation.

It should be noted that the total mass balance for nitrogen in the system would require that approximately 100 × 10^{12} g N yr^{-1} are restored to the atmosphere as N_2 and N_2O). Here again there are not sufficient data about this flux and my value is subject to great uncertainties. The total nitrogen flux due to oceanic denitrification was estimated to vary between 25 and 179 × 10^{12} g N yr^{-1} by Söderlund and Svensson (1976).

As for phosphorus, it is possible to test the validity of the vertical flux due to vertical mixing. If I apply the same values as previously for the vertical mixing to the mean dissolved nitrogen concentration of the deep waters I obtain a vertical flux of 450 × 10^{12} g N yr^{-1}, which is again in good agreement with the computed value from the carbon cycle (500 × 10^{12} g N yr^{-1}).

The contribution of vertical turbulent diffusion to this flux, calculated on the basis of a mean concentration gradient of dissolved nitrogen of 280 × 10^{-6} g N m^{-3} m^{-1}, is equal to 160 × 10^{12} g N yr^{-1}. The relative importance of advection and turbulent diffusion is very similar to what I have observed for phosphorus and the same conclusions as earlier may be drawn here concerning the distribution of the productivity in the oceans.

8.4 THE CYCLES OF OPAL AND CALCIUM CARBONATE

The skeletons of the organisms produced in the photic zone represent an important weight fraction of the biogenic material. They are mainly composed of opal, an amorphous variety of silica and calcium carbonate, either as calcite or aragonite. After death of the organisms, the organic coating of the skeleton is rapidly removed and the mineral phase may dissolve during sinking if the water masses are undersaturated with respect to this phase. The cycles of silica and calcium carbonate are thus also intimately related to biological activity.

8.4.1 The Silica Cycle

More than 80 per cent of the silica is consumed by photoactive organisms (diatoms and silicoflagellates) in the surface waters. It is thus possible to connect the rate of uptake of dissolved silica directly to the primary productivity if the ratio of amorphous silica to organic carbon is known for the plankton.

There are large discrepancies for this ratio in the literature ranging from 2.3 for pure diatom blooms (Lisitzin, 1972) to 0.35 for a mean composition of the marine phytoplankton (Martin and Knauer, 1973). Considering the seasonal and geographical variations in the activity of the diatoms, I have selected a mean ratio of 0.6.

The annual production of opal in the photic zone is then estimated to be 25×10^{15} g SiO_2 yr^{-1}.

Seawater is always strongly undersaturated with respect to opal which constitutes the skeleton of these organisms and their frustules are thus submitted to rapid dissolution, especially in the surface waters where dissolved silica is virtually exhausted. Only three per cent of the biogenic opal reaches the sediment where dissolution continues. Finally only 1.5 per cent of the initial production is accumulated in the sedimentary column, mainly combined with clay minerals (Wollast, 1974; Berger, 1976). This accumulation is, however, balanced exactly by the river input.

The various steps of the behaviour of silica have been discussed previously and remain valid (Wollast, 1974) but the cycle presented here has been slightly modified to take into account more recent values for the vertical mixing in the oceans. The upward flux of dissolved silica, for a vertical mixing rate of 3 m yr^{-1} and a mean concentration of 8.4 g SiO_2 m^{-3} is equal to 9.1×10^{15} g SiO_2 yr^{-1}.

From the mass balance, it may be assumed that 60 per cent of the opal skeletons are thus redissolved in the photic layer. This value is well within the range of the rapid decrease of siliceous frustules with depth observed within the ocean (Kozlova, 1964; Lisitzin, 1972; Berger, 1976).

This cycle presented in Figure 8.7 shows again the considerable importance of the biological activity on the dynamics controlling the behaviour of a typical mineral compound in the ocean.

8.4.2 The Calcium Carbonate Cycle

Calcium carbonate is mainly produced in the water column by coccolithophores, foraminifera (both as calcite) and pteropods (as aragonite). The ratio method used earlier for silica is not applicable to carbonates because of the abundance of foraminifera and pteropods which are not primary producers. However, it is still possible to find some mean empirical factor to relate carbonate fixation to primary production (Berger, 1976).

Broecker (1974) estimates that particulate matter falling from the surface into the deep sea contains approximately 0.5 moles of silica and 0.5 moles of calcium carbonate per mole of organic matter. In more recent measurements of the composition of the particulate matter in the surface waters of the ocean, Lal (1977) found a mean weight content of 60 per cent of organic matter. Although considerable geographical differences occur, the mineral phase (40 per cent) contains on the average equal amounts of silica and calcium carbonate.

In a production-regeneration model in oceans based on the vertical fluxes in the water column and mass balances for the various reservoirs, Lerman (1979) has evaluated the fluxes of organic carbon, silica, and calcium carbon that leave a one kilometre thick surface layer, and found respectively 3.5×10^{15} g C yr^{-1}, (or 8.8×10^{15} as CH_2O yr^{-1}), 10×10^{15} g SiO_2 yr^{-1}, and 12.2×10^{15} g $CaCO_3$ yr^{-1}.

Thus I conclude that the flux of $CaCO_3$ leaving the photic zone must be nearly

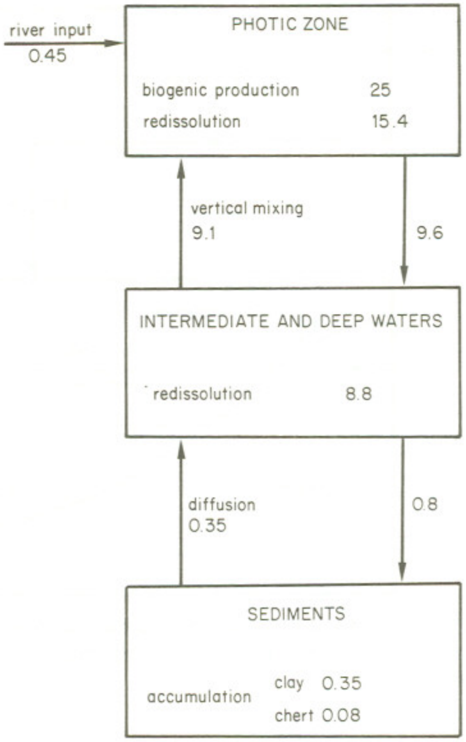

Figure 8.7 Tentative cycle of silica in the ocean. Silica values times 10^{15} g SiO_2 yr^{-1}

equal to the flux of organic matter (7.5×10^{15} g yr^{-1}) and of opal (9.6×10^{15} g SiO_2 yr^{-1}) computed in our previous cycles.

The surface waters are always oversaturated with respect to calcite and aragonite and thus the carbonate skeletons should be entirely preserved in the photic zone. It then may be concluded that the biological production of $CaCO_3$ which is equal to the flux of particulate inorganic carbonate would probably be close to 8.5×10^{15} g $CaCO_3$ yr^{-1}.

From the vertical distribution of calcareous shells, Berger (1976) concluded that only about one sixth of the biological production is finally preserved in the sediments. In fact, the water of the ocean becomes with depth, successively undersaturated with respect to aragonite and calcite. Further dissolution occurs in the sediments during early diagenesis. The amount of calcium carbonate accumulated yearly in the sedimentary record is rather well documented and may be estimated at 1.5×10^{15} g $CaCO_3$ yr^{-1} (Turekian, 1965; Garrels and Mackenzie, 1972).

Taking into account the preservation ratio of Berger cited above, an initial production of 9×10^{15} g $CaCO_3$ yr^{-1} may be calculated which is in good agreement

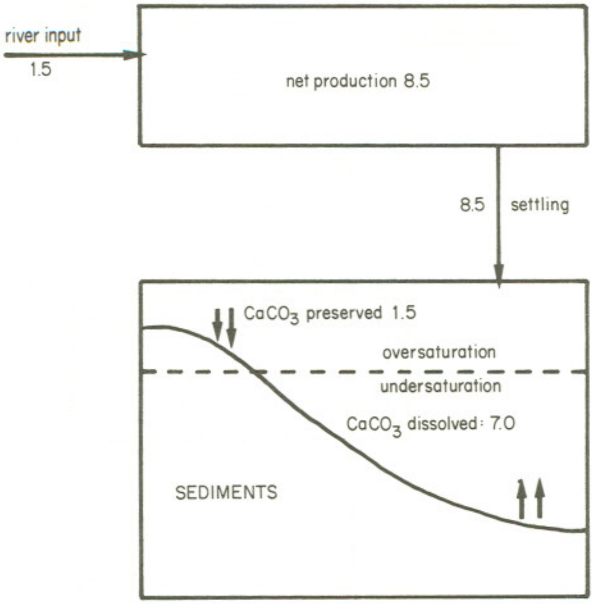

Figure 8.8 Tentative cycle of calcium carbonate in the ocean. Calcium carbonate values times 10^{15} g $CaCO_3$ yr^{-1}

with the previous estimate. The tentative cycle for calcium carbonate is given in Figure 8.8.

8.5 THE CYCLE OF MINOR ELEMENTS

Besides the major nutrients N and P, and the skeleton materials SiO_2 and $CaCO_3$, several minor elements are vital to life and their cycle may be controlled in the same way, that is by the biological activity in the ocean. Many trace elements exhibit a minimum of their concentration in the surface waters which corresponds to the hypothesis of a depletion in the surface waters by biological uptake and an increase of concentration in the intermediate and the deep water due to remineralization and dissolution of the biogenic material. However, a similar distribution may be obtained in some cases if the main source of one element for the open ocean is constituted by the atmospheric input of particulate matter which is submitted to dissolution during settling.

It is possible to obtain a better proof of the validity of this hypothesis by checking the eventual correlations existing between the vertical distribution of the element considered and the concentration of major nutrients like N, P, SiO_2. At the present time, the data concerning the mean elemental composition of the marine plankton are extremely scattered and vary often by several orders of magnitude partly due to the difficulties encountered in isolating the planktonic material in

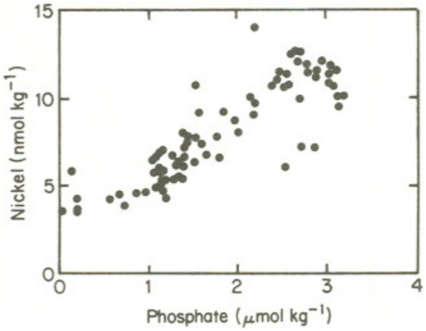

Figure 8.9 Relation between dissolved nickel and phosphate in the ocean (from Sclater *et al.*, 1976)

the sea without contamination, and also probably to large geographical and climatological changes. It is thus difficult to evaluate quantitatively the importance of the biological activity on the cycle of minor elements in the ocean.

To demonstrate the possible importance of the biological processes on the distribution of trace elements in the oceans, I have selected four examples where the concentration of the element is strongly depleted in the surface waters and where there is a strong correlation with the concentration of another element whose distribution is known to be controlled by biological activity.

The first case is related to the distribution of nickel in the Atlantic and Pacific. Sclater *et al.* (1975) showed that the vertical distribution of dissolved nickel is actively controlled by the biological cycle and is closely related to the distribution of both phosphate and silicate (Figure 8.9).

Boyle *et al.* (1976) have demonstrated that cadmium profiles in the Pacific resemble those of phosphate and that the covariance with phosphate (Figure 8.10) suggests that cadmium is regenerated in shallow waters like the labile nutrients, rather than deeper in the ocean as for silicates.

On the other hand Bruland *et al.* (1978) reported a stronger correlation between zinc and silicon (Figure 8.11) than between zinc and phosphorus and nitrogen. The marked surface depletion of Zn and the fact that phytoplankton concentrates large amounts of this element all suggest that diatoms play an important role in the biogeochemical cycling of this element.

A similar correlation was found for aluminium (Figure 8.12) in the Mediterranean by Mackenzie *et al.* (1978) but a more critical analysis of other similar results indicates that aluminium is probably not only consumed by diatoms but also by a larger spectrum of the plankton (Caschetto and Wollast, 1979).

8.6 CONCLUSIONS

I have shown that it is possible to build coherent global models describing the fluxes of organic carbon, nitrogen, phosphorus, silica, and calcium carbonate in

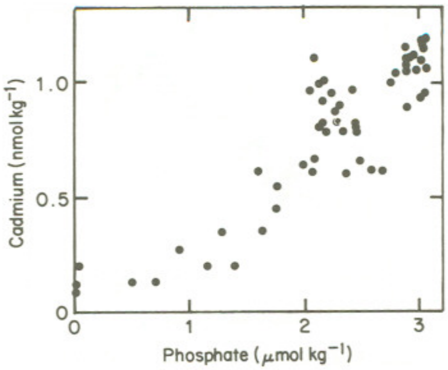

Figure 8.10 Cadmium concentration against phosphate for three Pacific profiles (from Boyle *et al.*, 1976)

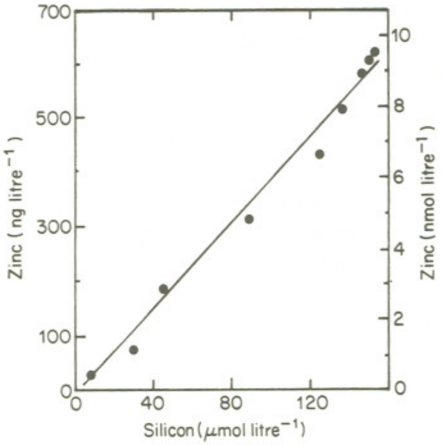

Figure 8.11 Zinc versus dissolved silica in the northeast Pacific (from Bruland *et al.*, 1978)

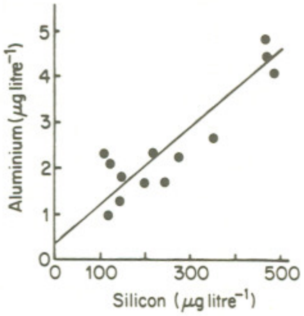

Figure 8.12 Covariation of dissolved aluminium and silicon (from Mackenzie *et al.*, 1978)

the ocean, by considering the existing interrelations between these compounds in the dynamics of the marine biota. It may be expected that similar interrelations apply for many trace elements vital to life.

The study of these cycles is not only important for a better understanding of the phenomena controlling the various steps of the biological activity of marine organisms. It is becoming more and more evident that these biological processes are important kinetic controls on the concentration and distribution of elements within the ocean.

8.7 REFERENCES

Berger, W. H. (1976) Biogenous deep sea sediments, in Riley, J. P. and Chester, (eds), *Chemical Oceanography,* London, Academic Press, volume 5, 265–388.

Billen, G. (1978) A budget of nitrogen recycling in North Sea sediments of the Belgian coast, *Estuarine and Coastal Marine Science,* **7**, 127–146.

Boyle, E. A., Sclater, F. and Edmond, J. D. (1976) On the marine geochemistry of cadmium, *Nature,* **263**, 42–44.

Broecker, W. S. (1974) *Chemical Oceanography,* New York, Harcourt Brace Jovanovich.

Bruland, K. W., Knauer, G. A. and Martin, J. H. (1978) Zinc in the north-east Pacific water, *Nature,* **271**, 741–743.

Caschetto, S. and Wollast, R. (1979) Vertical distribution of dissolved aluminum in the Mediterranean sea, *Marine Chemsitry,* **7**, 151–155.

Delwiche, C. C. and Likens, G. E. (1977) Biological response to fossil fuel, in Stumm, W. (ed.), *Global Chemical Cycles and their Alteration by Man,* Berlin, Dalhem Conference, 73–88.

de Vooys, C. G. N. (1979) Primary production in aquatic environments, in *SCOPE Workshop on Biogeochemical Cycling of Carbon,* in press.

Garrels, R. M. and Mackenzie, F. T. (1972) A quantitative model for the sedimentary rock cycle, *Marine Chemistry,* **1**, 27–41.

Garrels, R. M. and Perry, E. A., Jr. (1974) Cycling of carbon, sulfur and oxygen through geologic time, in Goldberg, E. D. (ed.), *The Sea,* New York, Wiley, volume 5, 303–306.

Kozlova, O. G. (1964) *Diatoms of the Indian and Pacific Sectors of the Pacific,* Moscow, Akad. Nauk.

Lal, D. (1977) The oceanic microcosm of particles, *Science*, **198**, 997–1009.

Lerman, A., Mackenzie, F. T. and Garrels, R. M. (1975) Modelling of geochemical cycles: Phosphorus as an example, *Geol. Soc. Amer. Mem.,* **142**, 205–218.

Lerman, A. (1979) *Geochemical Processes: Water and Sediment Environments,* New York, Wiley.

Lisitzin, A. P. (1972) *Sedimentation in the World Ocean,* Society of Economic Paleontologists and Mineralogists, Special Publication No. 17.

Mackenzie, F. T., Stoffyn, M. and Wollast, R. (1978) Aluminium in sea-water: control by biological activity, *Science,* **199**, 680–682.

Maier, W. J. and Swain, W. R. (1978) Lake Superior organic carbon budget, *Water Res.,* **12**, 403–412.

Martin, J. H. and Knauer, G. A. (1973) The elemental composition of plankton, *Geochim. Cosmochim. Acta,* **37**, 1639–1653.

McElroy, M. B. (1976) Chemical process in the solar system: a kinetic perspective, in Herschbach, D. (ed.) *MTP International Review of Science,* London, Butterworth, 127–211.

Redfield, A. C., Ketchum, B. H. and Richards, F. A. (1963) The influence of organisms on the composition of sea-water, in M. N. Hill (ed.), *The Sea,* New York, Wiley-Interscience, volume 2, 26–77.

Sclater, F. R., Boyle, E. and Edmond, J. M. (1976) On the marine geochemistry of nickel, *Earth and Planetary Sci. Letters,* **31**, 119–128.

Sillen, L. G. (1961) The physical chemistry of sea-water, in Sears, M. (ed.), *Oceanography*, Washington, D.C., AAAS, 549–581.

Söderlund, R. and Svensson, B. H. (1976) The global nitrogen cycle, in Svensson, B. H. and Söderlund, R. (eds), *Nitrogen, Phosphorus and Sulphur–Global Cycles,* SCOPE Report 7, *Ecol. Bull. (Stockholm),* **22**.

Svedrup, H. U., Johnson, M. W. and Fleming, R. H. (1942) *The Oceans*, New York, Prentice Hall.

Sweeney, R. E., Liu, K. K. and Kaplan, I. R. (1977) Oceanic nitrogen isotopes and their uses in determining the source of sedimentary nitrogen, in *Proc. International Symposium on Stable Isotope Chemistry*, New Zealand.

Turekian, K. K. (1965) Some aspects of the geochemistry of marine sediments, in Riley, J. P. and Skirrow (eds), *Chemical Oceanography*, New York, Academic Press, volume 2, 81–126.

Wollast, R. (1974) The silica problem, in Goldberg, E. D. (ed.), *The Sea*, New York, Wiley-Interscience, volume 5, 359–392.