GLOBAL MIXED‐LAYER NATURAL AND ANTHROPOGENIC FLUXES

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ABSTRACT

The oceanic surface mixed layer is generally the initial reservoir for materials that enter the ocean from the land and atmosphere. In this paper a number of global biogeochemical cycles of dissolved constituents, gases and particulates are portrayed. Some brief comments are made concerning the role of the mixed layer in the cycling behavior in the ocean of the chemical species H, O, C, N, P, S, Ca, Si, and As, and of particulate materials. It is demonstrated that the open ocean mixed layer can undergo chemical changes induced by perturbations of processes and fluxes on land on a time scale of decades. These perturbations may result from natural causes or may be due to the industrial and agricultural activities of society.

INTRODUCTION

The purpose of this short contribution is to present some information on chemical fluxes across the air‐sea interface, within the oceanic mixed layer, and to the abyssal realm. To accomplish this task, I take the methodological approach that portrays natural system material transport in terms of reservoirs (boxes), transfer paths, that is, processes and mechanisms of transport, and fluxes or rates of transfer. Simply, these types of models are called biogeochemical cycling models.

Obviously not all substances and their interactions with the mixed layer can be considered, but the cases presented are representative of a variety of situations. The biogeochemical cycles shown emphasize the various environments that the oceanic mixed layer interacts with, and the processes affecting the mixed layer. The cycles are derived primarily from publications of Mackenzie and co‐authors (Garrels et al., 1973; Lantzy et al., 1979; Mackenzie et al., 1983; Lantzy and Mackenzie, 1987; Lerman et al., 1987). Reservoir and flux magnitudes are the interpretations of the authors; it should be emphasized that some of these magnitude estimates are the subject of considerable debate.
METHODOLOGICAL APPROACH

Many natural chemical substances circulate through the environment and are important to the chemistry and biology of the earth. The circulation of a particular substance—as defined by its reservoirs, processes affecting it, and fluxes—is termed its biogeochemical cycle. Biogeochemical cycles vary in time and spatial scales. The long-term circulation of earth materials, the exogenic cycle, represents one extreme in which materials are transported through the atmosphere to the land and through the soils to streams that carry materials to the oceans. In the oceans, stream-borne solids, and some originally dissolved substances now part of solids, sink and become sea-floor sediments, and some substances are returned to the atmosphere. Oceanic residence times of dissolved substances vary from less than the mixing time of the ocean (1600 years) to $10^8$ years. Reservoir sizes in the exogenic system can be huge; that of carbonate in sediments is 600 x $10^{20}$ grams.

On the other extreme are the biogeochemical cycles of substances in systems smaller than the global exogenic. In soils, rivers, and estuaries, for example, the circulation of a substance may be described in terms of reservoir sizes of less than tons and turnover times measured in days.

The concepts and principles related to modeling of biogeochemical cycles have been developed extensively elsewhere (e.g., Garrels and Mackenzie, 1971; Lerman et al., 1975; Mackenzie and Wollast, 1977; Holland, 1978; Lerman, 1979; Lasaga, 1981; Wollast, 1986). The mathematical treatment used is briefly discussed below with reference to Figure 1.

Figure 1 represents a system of three reservoirs with two-way fluxes between the reservoirs for substance i. For a closed system at steady state, the mass of substance i in each reservoir ($M_i$), and each flux of i ($F_{ij}$) between reservoirs are constant, and no material enters or departs the system; therefore

$$\sum_{j} F_{ij} = \sum_{j} F_{ji}, \quad (i \neq j) \tag{1}$$

The fluxes are measured in units of mass time$^{-1}$, usually in terms of mols or grams year$^{-1}$, and commonly are taken as proportional to the reservoir mass from which the flux is emanating; that is

$$F_{ij} = k_{ij} M_i, \tag{2}$$

where $k_{ij}$ is a rate constant with dimensions time$^{-1}$ (usually year$^{-1}$). If a flux were second order, its magnitude is a function of both the mass of the source and receiving reservoirs,

$$F_{ij} = k_{ij} M_i M_j. \tag{3}$$
\[
\frac{dM_1}{dt} = F_{21} - F_{31} - (F_{13} + F_{12}) \\
= k_{21}M_2 + k_{31}M_3 - M_1(k_{12} + k_{13})
\]
\[
\frac{dM_2}{dt} = k_{12}M_1 + k_{32}M_3 - M_2(k_{21} + k_{23})
\]
\[
\frac{dM_3}{dt} = k_{13}M_1 + k_{23}M_2 - M_3(k_{31} + k_{32})
\]

Figure 1. Schematic representation of a three-box model of the global biogeochemical cycle of substance $i$. $M_i$ is mass of substance $i$ in reservoirs 1, 2, and 3; $F_{ij}$ are fluxes of $i$ between reservoirs; and $k_{ij}$ are rate constants.

The reciprocal of the rate constant $k$ has been defined as the residence time, and for $J$ fluxes of a substance $i$ for a single reservoir with mass $M_i$,

\[
\lambda_i = 1/k_{ij}.
\]  

(4)

From substitution of eq. (2) into eq. (1), we obtain

\[
\sum_{j} k_{ij}M_j = M_i \sum_{j} k_{ij}.
\]  

(i ≠ j)

(5)

and at steady state

\[
\sum_{j} k_{ji}M_j - M_i \sum_{j} k_{ij} = 0.
\]

(6)

For a system in a transient state (one disturbed by a perturbation for example), the change of the mass of $i$ in a reservoir with time is
\[
dM_i/dt = \sum_j k_{ij}M_j - M_i \sum_j k_{ij},
\]
where \( i \neq j, \) and \( j = 1 \ldots n. \) This equation represents a series of \( n \) differential equations for a system with \( n \) number of reservoirs.

**BIOGEOCHEMICAL CYCLES AND THE OCEANIC MIXED LAYER**

In the following diagrams, the mixed layer of the global ocean is usually taken as the upper 100 m of the ocean. It is recognized that this definition is not necessarily in accord with that used by all oceanographers. The general conclusions drawn, however, are not affected significantly by the nature of the mixed layer, such as its changing depth with season in subtropical regions.

**Oceanic Hydrologic Cycle**

The oceanic hydrologic cycle is shown in Figure 2. In this figure the "mixed layer" is divided into nearshore and open-ocean environments, and fluxes of water are shown in units of \( 10^{16} \) 1 yr\(^{-1}. \) In this model, residence times of \( \text{H}_2\text{O} \) in the nearshore and open-ocean mixed layer are about 11 and 17 years, respectively, whereas that of the deep ocean is 815 years. These residence times are consistent with a global upwelling rate of 4.5 m yr\(^{-1}. \) The annual river input of \( \text{H}_2\text{O} \) to the nearshore realm represents the net imbalance between global oceanic evaporation and precipitation.

Chemical elements are transferred in the water cycle by currents and turbulence as dissolved species in the fluid, or as suspended particles carried by the fluid. If the concentration of an element in a flux involved in the hydrologic cycle is known, then its flux can be calculated as, e.g., concentration of element (g 1\(^{-1}. \)) x \( \text{H}_2\text{O} \) flux (1 yr\(^{-1}. \)) = g yr\(^{-1}. \) This type of calculation forms the basis for estimating many dissolved fluxes in the oceanic system.

**Oceanic Terrigenous And Organic Carbon Cycles**

Particulate materials in the oceanic mixed layer have two principal sources, exogenic and endogenic. Exogenic particulates are derived from the continents and transported to the ocean in the suspended and traction load of rivers, and enter the oceanic mixed layer as dust particles scavenged in oceanic rain or as dry deposition. Endogenic particulates are formed within the mixed layer primarily through biological processes that lead to the generation of inorganic skeletal and organic materials in organisms such as foraminifers, diatoms, pteropods, etc. Figure 3 illustrates the major fluxes associated with the transfer of terrigenous materials and organic matter represented by organic C in the ocean.
Figure 2. The oceanic hydrologic cycle. Fluxes are in units of $10^{16} \text{ l y}^{-1}$. Nearshore surface area and volume are $0.3 \times 10^{14} \text{ m}^2$ and $0.3 \times 10^9 \text{ l}$, respectively. Mixed layer area and volume are $3.31 \times 10^{14} \text{ m}^2$ and $3.31 \times 10^{19} \text{ l}$.

The main flux of terrigenous materials to the oceanic mixed layer is via rivers. Most of this flux, 80–90%, is sedimated in the nearshore environment, but a small amount escapes to the deep ocean. Terrigenously derived dust particles settle on the surface ocean over most of its area. Both of these fluxes are not uniform over the ocean surface, and therefore the effect of these fluxes on the oceanic mixed layer is regional in nature. For example, the rivers of southeast Asia deliver 90% of the solids reaching the ocean annually. Dust storms originating in the Gobi and Saharan Deserts affect different regions of the oceans at different times because of the seasonality of these storms and the wind patterns transporting the dust. Once these terrigenous materials reach the mixed layer they may be chemically unreactive or they may adsorb or desorb chemical species.

In a portion of the mixed layer organic carbon is photosynthesized, and this reaction adds to the particulate burden of this region. These organic particles may be regenerated in the mixed layer by respiration—decay processes or pelletized and transported along with terrigenous
Figure 3. Oceanic terrigenous and organic carbon particulate cycles. Terrigenous fluxes are in units of $10^{14}$ g y$^{-1}$, and organic fluxes in units of $10^{14}$ g C y$^{-1}$. C refers to fluxes of organic carbon.

materials to the deep ocean. If the concentration of an element in terrigenous material reaching the ocean is known, its flux can be calculated as concentration of element (g g$^{-1}$) x terrigenous particulate flux (g y$^{-1}$).

In a similar way, if the organic C:element concentration ratio in marine biota is known then an approximation of the element flux can be made by multiplying the C/element x organic C flux. The important point is that the mixed layer, or part of it, is involved initially in the cycling of elements found in terrigenous materials and involved in the cycling of organic materials.

**Ocean Skeletal Cycle**

The cycling of skeletal CaCO$_3$ and SiO$_2$ in the nearshore and open ocean is shown in Figure 4. In the mixed layer CaCO$_3$ and SiO$_2$ are taken up in the tests and frustules of organisms. As shown for the open ocean mixed layer, these skeletal materials settle out of the mixed layer into
Figure 4. Oceanic cycle of skeletal CaCO₃ and SiO₂. Fluxes are in units of \(10^{14}\) g y⁻¹.

The deep sea where they may dissolve en route to the bottom or at the sediment-water interface. Some CaCO₃ and SiO₂ accumulate in the sediments. The actual site of dissolution of the skeletons of pelagic organisms is very controversial today. Perhaps a significant portion of the skeletal SiO₂ actually is regenerated in the mixed layer and not the deep ocean. Much CaCO₃ may be dissolved at the sediment-water interface after deposition. As with organic matter, upwelling processes return dissolved constituents coming from dissolution of these components to the mixed layer.

C. N. P. S Global Biogeochemical Cycles

The global biogeochemical cycles of the elements that are critical to organic matter synthesis in the mixed layer—carbon, nitrogen, phosphorus
and sulfur—are shown in Figures 5-8. These are reasonably detailed representations of the global aspects of these cycles. Some fluxes between the oceanic reservoir and land via rivers and the atmosphere are emphasized below.

First some comments on organic production. Production in the mixed layer utilizes C derived principally from the atmosphere as CO₂, regenerated N as NH₄ or N biologically fixed from atmospheric N₂, or N transported via streams to the ocean principally as NO₃, regenerated P or phosphorus delivered to the ocean as PO₄ in streams, and sulfur introduced via the atmosphere and streams or regenerated in the ocean. In the global N cycle, the estimated magnitude of the regenerated oceanic N flux is shown as 320 x 10¹² mol N y⁻¹. In the other cycles only the net global fluxes are portrayed. The generalized reaction for phytoplankton synthesis in the ocean is

\[ 106\text{CO}_2 + 16\text{HNO}_3 + \text{H}_3\text{PO}_4 + 138\text{H}_2\text{O} = (\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}\text{H}_3\text{PO}_4 + 1220\text{O}_2. \]

At this ratio of C:N:P, the regenerated C and P fluxes in the ocean would be about 2100 x 10¹² and 20 x 10¹² mol y⁻¹ of C and P, respectively. Leakage of organic carbon out of the euphotic zone with its N, P, and S contents represents the flux that is now known as new production. This flux is probably on the scale of 0.1-1% of total production.

The mixed layer plays an important role in terms of inputs of chemicals to the global environment because of the industrial, agricultural, and other activities of society. Examples of these anthropogenic fluxes are shown in all four global cycles. For example, C, N, and S enter the atmosphere from fossil fuel burning. About 50% of the fossil fuel CO₂ flux dissolves in the ocean leading to an accumulation of C in the ocean reservoir. The initial environment of the ocean affected by this increased C flux is the mixed layer. The ability of the ocean to act as a sink of fossil fuel CO₂ depends on the rate of exchange of mixed layer waters with the deep ocean.

The nearshore mixed layer receives N and P fluxes from agricultural and industrial activities that lead to enhanced organic production in coastal waters. These fluxes are the principal cause of the eutrophication of some coastal marine waters.

Space does not permit further consideration of C, N, P, and S fluxes involving the oceanic mixed layer. Study of Figures 5-8 as an integrated whole can provide the reader with a more complete view of the interactions between the mixed layer and other environments in terms of element processes and fluxes.
Figure 5. Global biogeochemical cycle of carbon. Reservoir masses are in units of mol C, and fluxes in units of $10^{12}$ mol C y⁻¹.

Carbon And Phosphorus Land-Mixed Layer Cycle

In Figures 9 and 10, detailed representations of the coupling between the global land and ocean biogeochemical cycles of C and P are shown. In both cycles the land and ocean reservoirs of Figures 5 and 7 have been subdivided into sub-reservoirs. The open ocean has been separated from the land by a coastal realm, and coastal waters and surface open ocean from the deep ocean. These representations of the C and P cycles are important to an understanding of element transfers from the land to the ocean and of the interactions between the coastal region and the open ocean.
Figure 6. Global biogeochemical cycle of nitrogen. Fluxes are in units of $10^{12}$ mol N yr$^{-1}$.
PHOSPHORUS GLOBAL CYCLE

Figure 7. Global biogeochemical cycle of phosphorus. Reservoir masses are in units of mol P, and fluxes in units of \(10^{10}\) mol P yr\(^{-1}\).

The C and P cycles portrayed are steady state cycles without anthropogenic fluxes. These cycles can be perturbed, and the results of a perturbation calculated using solutions of eq. (7). One of these perturbation scenarios is shown in Figure 11. This figure shows the changes with time in the masses of C and N in the major reservoirs affected, because of changes in weathering rate on land and terrestrial bioproductivity. In this model, the present continental weathering rate has been increased by 1.5 times today's rates given in Figures 9 and 10, and terrestrial productivity reduced by 25 percent.

It can be seen from Figure 11 that the coastal zone and the surface open ocean, plus other shallow-water reservoirs of C and P, gain these elements on a time scale of decades. The ultimate sources of these elements are the land reservoirs of humus and terrestrial biota. Notice that after the initial gain in C and P mass, the atmospheric C reservoir and several of
SULFUR GLOBAL CYCLE

Atmosphere
H₂S: 0.031 x 10⁻²
RT = 3.4 Days

Atmosphere
SO₂: 0.016 x 10⁻²
RT = 1.1 Days

Atmosphere
SO₄²⁻: 0.02 to 0.05 x 10⁻²
RT = 3.4 Days

Biological Decay 1.8

Volcanic Emissions 0.4
Fossil Fuel Burning & Ore Mining 2
Uptake By Plants 0.5
Wet & Dry Fallout 3.4
Biological Decay 1.5

Wet & Dry Fallout 2.1

Land
Biomass: 300 x 10⁻¹²
Soil Humus: 3000 x 10⁻¹²

Ocean
Biomass: 5 x 10⁻¹²
Dissolved SO₄²⁻: 3.9 x 10⁻¹⁸

Rivers 3.6

Reservoir contents: moles
Fluxes in 10⁻¹² moles/yr

Sediments
Oxidized S: 2.0 x 10⁻²⁰ (Mostly CaSO₄)
Reduced S: 2.9 x 10⁻²⁰ (Mostly FeS₂)
RT = 2.6 x 10⁸ Yr

FeS₂ 1.1
Uplift & Erosion
CaSO₄ 0.8

Figure 8. Global biogeochemical cycle of sulfur. Reservoir masses are in units of mol S, and fluxes in units of 10⁻¹² mol S yr⁻¹.

the oceanic C and P reservoir masses decline. This result is due to transfer of these elements to other reservoirs—e.g., C as CO₂ from the atmosphere to the oceanic mixed layer, and C and P from coastal waters to the open ocean. The important point is that the chemistry of the mixed layer is affected on a time scale measured in decades both in the coastal and open ocean setting by changes on land.

This is not an unexpected result, but the modeling of these perturbations emphasizes how intimately connected the mixed layer is to other global reservoirs, and how quickly it may react to environmental changes even as far removed as those obtained on land. Considerations of global oceanic element fluxes must involve an assessment of the interactions between the mixed layer and the land via the coastal realm, as well as the atmosphere and deep ocean.
CARBON: LAND AND OCEAN CYCLE

Figure 9. Global coupled land and ocean cycle of carbon. Reservoir masses are in units of $10^{16}$ mol C, and fluxes in units of $10^{12}$ mol C yr$^{-1}$.

Global Oceanic Arsenic Biogeochemical Cycle

A detailed cycle of the oceanic arsenic cycle is portrayed in Figure 12. This cycle was selected as an example of a trace metal for which the mixed layer plays an important role in its cycling behavior. Arsenic is introduced into the mixed layer by rainfall, dust fallout, and river discharge. Arsenic is removed in the skeletal and organic components of marine biota. Terrigenous particulates may pass through the mixed layer without reaction or they may desorb arsenic.

Arsenic is an element that has been added to the environment by fossil fuel burning, mining, cement manufacturing, and ore smelting activities of
Figure 10. Global coupled land and ocean cycle of phosphorus. Reservoir masses are in units of $10^{12}$ mol P, and fluxes in units of $10^{12}$ mol P yr$^{-1}$.

society. Figure 13 is a model calculation for a scenario in which these anthropogenic fluxes increase at a rate of 2% annually. The calculations are done assuming that the As fluxes change globally, and are consistent with projected growth rates in As utilization. Figure 14 shows the results of calculations demonstrating the importance of the rate of global upwelling to exchange of As between the mixed layer and deep ocean. Calculations of this nature provide some idea of the magnitude of compositional changes that might be anticipated in the mixed layer, and other reservoirs, because of society’s use of trace metals.

CONCLUSIONS

The major purpose of this paper is to provide some idea of the myriad of chemical interactions between the oceanic mixed layer and other
Figure 11. Changes in mass of carbon and phosphorus reservoirs of Figures 9 and 10, because of increased continental weathering and decreased terrigenous organic productivity.
Figure 12. The oceanic biogeochemical cycle of arsenic. All fluxes and reservoir mass changes are in units of $10^8$ As yr$^{-1}$. Notice that the various As reservoirs are presumably gaining this element today, because of increased As fluxes from anthropogenic activities.
Figure 13. Changes in arsenic concentrations in the nearshore, mixed layer, and deep ocean reservoirs of Figure 12, calculated on the basis of a scenario in which As releases to the environment from society's use of this element increase exponentially at a rate of 2% annually.
Figure 14. Effect of global upwelling rate on exchange of arsenic between the mixed layer and deep ocean. Fluxes in units of $10^{16}$ l H$_2$O y$^{-1}$, and $10^8$ g As y$^{-1}$.

environments, and within this important reservoir. The examples presented are only a sampling of the many processes that could be described. An attempt was made to present briefly a methodology employed by chemical oceanographers and geochemists for evaluation of mixed layer chemical changes based on modeling. The physical processes occurring in the mixed layer and responsible for exchange between this reservoir and others exert significant control on mixed layer chemistry, and the overall chemistry of the oceans. There is a strong need to understand these processes and fluxes associated with them before we can hope to answer quantitatively questions concerning global environmental problems, like those related to CO$_2$ and the greenhouse effect.
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