Phosphorus and Sulfur

The Important Nutrient Phosphorus

Phosphorus is a key nutrient, fueling organic productivity on land and in water. A portion of its cycle is shown in Figure 18. The P cycle is considered here both because it is closely coupled with those of carbon and nitrogen and for completeness.

Controversy still exists, particularly between marine biologists and geochemists, as to whether phosphorus or nitrogen is the limiting nutrient in the marine environment. Globally and on a long time scale, phosphorus is probably the limiting nutrient, if for no other reason than that the atmosphere contains essentially an unlimited supply of nitrogen for fixation in aquatic systems.

The major difference between the phosphorus cycle and the carbon, nitrogen, and sulfur cycles is that no biological process generates an important gas flux of phosphorus from the earth’s surface to the atmosphere (Figure 18). A phosphorus gas known as phosphine or swamp gas (PH$_3$ gas) causes a small flux, but the amount is insignificant compared to other fluxes of phosphorus. As with nitrogen, fluxes of phosphorus between the

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**Figure 18.** Part of the modern global biogeochemical cycle of phosphorus, emphasizing the exchange of P among the land, atmosphere, and ocean. Units and symbols are as in Figure 9. Notice, as with nitrogen (Figure 12), that the internal recycling fluxes in the ocean and land reservoirs by organic production and decay are much larger than the exchanges. Also as with nitrogen, the land is gaining P because of its mining, its use in the manufacture of fertilizers and detergents, and sewage inputs. “Wet-dry fallout” is the precipitation of phosphorus on the ocean as particles and in rain. DP is dissolved phosphorus, and “pollutant” is excess phosphorus from human activities (modified from Mackenzie, 1995).
land, ocean, and atmosphere are small compared to the amounts that cycle within the land and ocean systems.

**Sinks and sources**

Unlike nitrogen, phosphorus accumulates in both organic and inorganic sediments. Because of the direct tie between N and P in organic matter, the only organic sink shown in Figure 16 is the important phosphorus flux to sediments as P incorporated in dead organic matter (bottom right-hand corner of the figure). The inorganic sinks, which are not shown in the figure, involve the precipitation of the mineral carbonate fluoroapatite $\text{Ca}_5(\text{PO}_4)_3(\text{OH,F})$, scavenging by iron oxy-hydroxides, and incorporation in oxidized iron coatings on the surfaces of calcium carbonate.

Phosphorus mining is the largest source of P to the land surface. Much of the mined phosphorite rock is used to make commercial fertilizers. The major impact of humankind on the phosphorus cycle results from the application of both commercial and organic fertilizers to croplands and the disposal of sewage. Phosphorus from these sources is introduced to streams via direct sewage discharge or by leaching. The increased amount of phosphorus in rivers, lakes, and coastal marine waters results in increased rates of eutrophication of these systems in cases where phosphorus is the limiting nutrient.

**Feedbacks**

Two major biological feedbacks in the phosphorus cycle may be of importance in global climate change. One involves the enhanced eutrophication of aquatic systems as a result of human activities, as just mentioned. The global dissolved phosphorus flux, carried by rivers to the coasts, has doubled since preindustrial times because of these activities (Figure 18). The resulting eutrophication of the coastal regions has led to a potential accumulation of organic carbon in these systems of about 140 million tons of carbon per year (Figure 18, top right). This enhanced flux is a negative feedback on the accumulation of anthropogenic $\text{CO}_2$ in the atmosphere today and, as with nitrogen, could become more important in the future.

The second biological feedback has to do with the land reservoir of phosphorus. Notice in Figure 18 that phosphorus is accumulating on land because of mining, fertilizer use, and sewage discharges. Because most chemical weathering and biological decomposition rates increase with increasing temperature, a climate warming would mean that phosphorus in this reservoir may be more easily leached into aquatic systems. This additional phosphorus could increase eutrophication in these systems and lead to increased accumulation of organic matter. This flux is a negative feedback on $\text{CO}_2$ accumulation in the atmosphere and hence on global warming. However, the effect is quite small. If all the phosphorus now stored on land were leached and transported by rivers to coastal systems, and all the other nutrients in coastal marine systems could be used for plant growth (which may not be the case), the increase in organic carbon storage would be 800 million tons. This is equivalent to only 13% of one year’s flux of carbon to the atmosphere because of the burning of fossil fuels.

**Reduced and Oxidized Sulfur Gases**

The reduced and oxidized sulfur cycles (Figures 19 and 20) are closely tied, because the reduced sulfur gases that dominate the earth’s biological sulfur emissions are oxidized in the atmosphere. These reduced gases are dimethylsulfide or DMS $[(\text{CH}_3)_2\text{S}]$ and carbonyl sulfide (OCS), which are emitted by the ocean surface, and hydrogen sulfide (H$_2$S), emitted by decaying terrestrial vegetation. Oxidation converts these gases to sulfur dioxide ($\text{SO}_2$) gas and sulfate aerosol, that is, microscopic sulfur-containing particles. Sulfur enters the atmosphere as the earth emits the reduced sulfur gases and leaves the atmosphere as sulfate aerosol floats or is washed to the earth.

The chemistry of DMS and OCS has two major connections with climate, by way of cloud condensation nuclei and stratospheric sulfate.

**Cloud condensation nuclei**

DMS is produced by bacteria in phytoplankton. Its concentration in the oceans is very low, but it is found nearly everywhere at the sea surface,
where it may escape into the troposphere. Once airborne, it is oxidized by OH* to sulfate within a few days. Along with other chemical species in the atmosphere, it condenses into small (micron-sized) aerosol particles. These atmospheric sulfate aerosols act as cloud condensation nuclei (CCN)—the centers on which water droplets may form, facilitating cloud formation. In the remote marine atmosphere, DMS emissions are likely the main source of the aerosols that act as CCN.

One hypothesis argues that a warming of earth’s climate could lead to enhanced phytoplankton growth and thus greater emission of DMS from the sea surface. The increased DMS flux could result in increased production of sulfate aerosols and CCN in the remote marine atmosphere, creating more and denser clouds. Besides leading to more rain, clouds also reflect incoming solar radiation and have a cooling effect on the lower atmosphere and surface of the earth. Thus an increase in cloud cover would give rise to a cooling of the troposphere, a negative biotic feedback on global warming. To counteract a warming owing to a doubling of atmospheric CO2 would require a 25% increase in the number of cloud condensation nuclei.

The validity of this hypothesis is not yet confirmed by real-world evidence. For example, in ice cores collected by drilling at Vostok Station in Antarctica, a record of methane-sulfonic acid (MSA) has been obtained from the ice. MSA is a product of DMS oxidation. If this theory were correct, one would expect to find more MSA in ice that dates from warmer periods, since increased
levels of the compound would wash out of the atmosphere. However, the record shows just the opposite: higher levels of MSA in the ice from the last ice age, which culminated 18,000 years ago, than in this and past interglacial stages.

**Stratospheric sulfate**

OCS is produced mainly by the photolysis of organic sulfur in the surface waters of the ocean and by photochemical oxidation of the biogenic gas carbon disulfide (CS₂) in the atmosphere. It is the most abundant reduced sulfur species in the remote marine atmosphere. Because it is chemically inert, it has a long residence time in the troposphere and can enter the stratosphere. Once in the stratosphere, OCS is destroyed by reacting with ultraviolet light and atomic oxygen. It is converted to SO₂ and then on to sulfate aerosol. This reduced sulfur gas supplies about half of the mass of sulfate aerosol found in the lower stratosphere (the so-called Junge layer).

If global warming causes any change in the flux of OCS to the stratosphere, it will have an effect on climate through change in the Junge layer. An increased stratospheric sulfate burden would give rise to cooling of the atmosphere; a decreased burden would lead to warming. The likely feedback effect on an initial warming is difficult to predict.

Figure 20. Part of the global biogeochemical cycle of oxidized sulfur. See Figure 9 for an explanation of the units and symbols used. Notice that the flux of oxidized sulfur from land as SO₂ is dominated by the combustion of fossil fuels and biomass burning. This sulfur reacts with OH⁺ to produce sulfate aerosols of ammonium and hydrogen. About 40% of the sulfur falling back on the earth's surface is derived from these sources. Volcanism can add sulfate aerosols to the stratosphere and produce a temporary cooling of the planet, as after the eruption of Mt. Pinatubo in 1991. Sulfate aerosols derived from combustion of fossil fuels and biomass burning exert a strong cooling effect, but only in the regions where they are produced (modified from Mackenzie, 1995).
Oxidized sulfur

To complete the picture of the global cycle of sulfur gas species, the earth surface–atmosphere oxidized sulfur cycle is shown in Figure 20. Natural sources of oxidized sulfur in the atmosphere include oxidation of reduced sulfur gases as mentioned above, volcanism, and aerosols from the sea. The oxidized sulfur is removed from the atmosphere by deposition of aerosols.

One of the most dramatic demonstrations of the connection between volcanism, sulfate aerosols, and climate was the eruption of Mt. Pinatubo in the Philippines in 1991. The eruption plume rose high into the stratosphere, where sulfate aerosol was generated and distributed over much of the globe. The aerosol scattered and reflected solar energy back to space. This event led to a cooling of the planet of about 0.5°C during 1991–93. At its maximum in 1993, the cooling reached –3–4 watts per square meter. This is considerably more than the enhanced greenhouse forcing of +2.5 watts per square meter.

Human activities have strongly interfered with the global biogeochemical cycle of oxidized sulfur. This disturbance in the cycle has led to the acidification of land and freshwater systems—the problem of acid precipitation. Of the total global deposition of oxidized sulfur today, approximately 40% is derived from the human activities of combustion of fossil fuels, biomass burning, and smelting of sulfide ores. The deposits from these activities vary enormously spatially.

Recently a new hypothesis has emerged linking our sulfur emissions with climate. In the Northern Hemisphere, emissions of SO₂ have led to an increased mass of sulfate aerosol. Because of the aerosol’s short lifetime in the atmosphere, it remains concentrated over the eastern half of the continent and the western Atlantic Ocean. This regional enhancement could be cooling the atmosphere enough to explain the discrepancy between the observed temperature record of the past 100 years and the higher temperatures predicted by climate models that include only the effects of increased greenhouse gases and not increased aerosols. On the other hand, when climate modelers attempt to introduce the cooling effect of sulfate aerosols into their models, the modeled temperatures are generally lower than those observed in the recent past. This difficulty implies that sulfate aerosols are an important component of the temperature record, but that the amount by which they cool the planet is not yet known.