Chapter 2
Atmospheric Biogeochemistry

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Glossary

Aerosol	A solid or liquid suspended in the atmosphere. The definition usually does not include cloud droplets, although many aerosols have water vapor on their surfaces.
Dry deposition	Removal process for gas and aerosol species in which the species are deposited onto the lower surface due to either turbulent fluxes (overturning air) forcing the constituent to hit and stick to the surface, or from gravitational settling of aerosols. Gravitational settling is the dominant mechanism for removal for larger aerosols.
Lifetime	The atmospheric lifetime of a constituent describes how long the constituent will remain in the atmosphere. It is typically calculated by dividing the total amount of the constituent in the atmosphere by the total flux out of or into the atmosphere. The flux can be due to atmospheric chemical reactions, and/or exchanges between other reservoirs in the earth system (e.g., land or ocean). This lifetime is an e-folding lifetime; if one starts with an initial perturbation of the constituent, the amount of the perturbation remaining after a length of time equal to the lifetime is equal to 1/e of the original value of the perturbation.

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Wet deposition	Process by which an atmospheric constituent is removed by precipitation. This is especially important for water-soluble and aerosol species.

Definition of the Subject and Its Importance

Biogeochemistry represents the interaction of biology, chemistry, and geology in the Earth system. For many processes, an understanding of biological uptake and emission, chemical processing, and geological sequestration is necessary to resolve the sources and sinks of a particular constituent. For example, to discover the sources and sinks of atmospheric carbon dioxide, it is important to understand how biota take up carbon dioxide and chemically convert the carbon to organic carbon, and then how this organic carbon is used either to produce energy by biota or is deposited to the land or ocean surface and can become sequestered in geological formations. Often when biogeochemistry is referred to, one refers to the nutrient cycling of important nutrients. Atmospheric biogeochemistry, as defined in its narrowest sense, is the flux of nutrients and pollutants important for biogeochemistry through the atmosphere. In its broadest sense, atmospheric biogeochemistry is the interaction of the atmosphere and atmospheric processes with the biogeochemistry of the earth system. This broader definition is used here. The hydrologic cycle is one of the most important biogeochemistry cycles, and is a worthy topic of its own. It is discussed in several other sections of this encyclopedia (e.g., Climate Change and Global Water Sustainability, Water Resource and Quality Management for Adaptation to Climate Change, Water Availability and Quality, Sustainable).

Introduction

Atmospheric biogeochemistry is increasingly relevant for today's society, as evidenced by the changing composition of the atmosphere. Atmospheric biogeochemistry views these changes in the composition as part of a collection of changes to the earth system occurring during the anthropocene. One very serious sustainability issue at the core of atmospheric biogeochemistry is the accumulation of carbon dioxide in the atmosphere. This is a result of human emissions of carbon dioxide both directly from fossil fuel burning, and from land use change, especially tropical deforestation [1]. Interestingly, only about ½ of the carbon dioxide emitted into the atmosphere remains there: The rest is taken up by the land and ocean. This important negative feedback on human emissions of carbon dioxide is a result of biogeochemical cycling of carbon in the system. As human emissions of carbon dioxide grow, it is not clear that the land and the ocean will be able to keep up, and thus more of the carbon dioxide is likely to stay in the atmosphere [2]. Some studies suggest that warming itself leads to less carbon dioxide being taken up by the land and ocean [2], although this also depends on the cycling of other nutrients such as nitrogen as well [3]. Thus understanding the biogeochemistry of carbon is required to understand how much carbon can be emitted in the future.

The atmospheric transport and subsequent deposition of trace gases and aerosols can provide an important mechanism for circulation of different constituents. Whether this deposition serves as a nutrient or a pollutant usually depends on the deposition level, as well as the ability of the biota to process these compounds. Some compounds can be nutrients at low levels, but pollutants at high levels. Thus, referring to the atmospheric transport of nutrients and pollutants as "atmospheric biogeochemistry" allows for these changes in impacts depending on amount. For transport from the land to ocean, many constituents can also be carried by rivers; in the sections below, the relative importance of atmospheric versus riverine inputs is discussed. The atmosphere tends to be able to transport species more quickly and farther distances; however the mass of the atmosphere is much less that of water, providing a constraint on the amount of constituent the atmosphere can transport. For the cases of constituent transport from the oceans to land, or upstream on land, atmospheric transport on short timescales is often the most important, as the only other mechanism would be geological changes in orography.

The final important aspect of atmospheric biogeochemistry is that it allows us to understand the composition of the atmosphere, and the fluctuation in this composition, in an earth system context. Thus understanding atmospheric biogeochemistry represents an integrative approach to understanding the atmosphere and its relationship with the land, ocean, and crysophere.

Cycling in the Atmosphere

Since most nutrients cycle through the atmosphere, the atmospheric portion of their biogeochemistry is important. The most important nutrients to sustain life are carbon, nitrogen, and phosphorus, but many other nutrients are required. Here some of the most important nutrient cycles for the earth system are discussed, and cycles that are being perturbed due to human activities have to be focused upon.

Carbon Cycle

The carbon cycle receives substantial interest today because of the anthropogenic perturbation of the carbon cycle and the documentation of global warming. The carbon cycle represents the most important of the nutrient cycles, with the exception of water, for living organisms because living tissue is primarily composed of carbon. The dominant form of carbon in the atmosphere is carbon dioxide, a chemically inactive, but radiatively important species in the atmosphere. The riverine flux of carbon is 0.8 Tg/year, while the gross land and ocean fluxes with the atmosphere

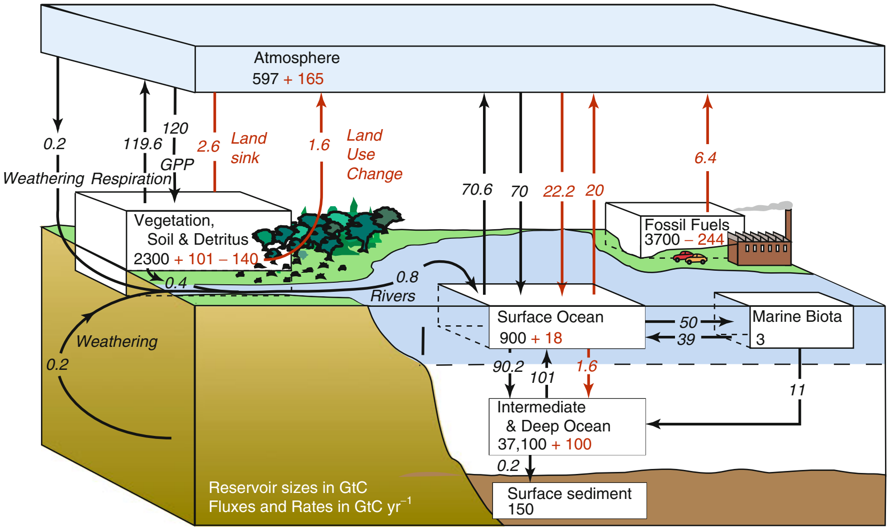

Fig. 2.1 The global carbon cycle for the 1990s, showing the main annual fluxes in PgC/year: preindustrial "natural" fluxes in black and "anthropogenic" fluxes in red. Gross fluxes generally have uncertainties of more than ±20% but fractional amounts have been retained to achieve overall balance when including estimates in fractions of PgC/year for riverine transport, weathering, deep ocean burial, etc. "GPP" is annual gross (terrestrial) primary production. Atmospheric carbon content and all cumulative fluxes since 1750 are as of end 1994 (Figure from [4])

are closer to 120 and 70 Tg/year (the net fluxes are closer to zero). This suggests that changes in the land or ocean carbon balance will be communicated rapidly through the atmosphere.

Carbon dioxide is removed from the atmosphere, not through chemical reactions, but through huge fluxes into the land or oceans, with an atmospheric lifetime of several years (Fig. 2.1 from [4]). In reality, however, the land and ocean fluxes are reasonably well balanced and it is difficult for all the extra carbon to be taken up, suggesting that the lifetime of the additional carbon dioxide emitted by humans is on the order of a few hundred years [4, 5]. However, there will be some carbon (perhaps 20–35%) that stays in the atmosphere for 3–7 kyr, thus the lifetime for atmospheric carbon dioxide is ambiguous [5].

Carbon dioxide shifts between glacial and interglacial climates are one of the most robust signals from the ice core records [6], and carbon dioxide tends to be about 80–100 ppm smaller during glacial periods than during interglacial periods (like today). These changes in carbon dioxide have not yet been explained, but are likely to be caused by a combination of colder temperatures, changes in ocean circulation, and changes in ocean productivity [7]. Indeed these changes in carbon dioxide are important forcing agents for maintaining the cold temperatures in the glacial periods [8], and thus must be an integral part of explaining the glacial/interglacial cycles over the past several hundred thousand years.

Currently, carbon dioxide emissions are increasing, and while preindustrial values of carbon dioxide were about 280 ppm, current values are over 380 ppm [4]. The reason for these changes in carbon dioxide values are due to human emissions of carbon dioxide release from combustion of fossil fuels and deforestation or other land-use change process. Carbon dioxide emissions currently (2008) are estimated to be about 8.7 +/− 0.5 PgC/year from fossil fuels, and another 1.5 +/− 0.7 PgC/year from land-use change (e.g., deforestation) [1]. Recent studies suggest that about 43% of anthropogenic carbon dioxide, from fossil fuel burning or deforestation, remains in the atmosphere, while the remainder is taken up by the land or the ocean, with more than half going into the ocean [1]. In the future, it is likely that less of the carbon dioxide that is emitted will be taken up by the land and ocean, due to both a saturation of the sinks of carbon dioxide, as well as the impact of climate change on the carbon cycle [2].

This increasing carbon dioxide in the atmosphere may increase land productivity and change land biogeochemistry. Higher carbon dioxide levels may allow plants to better adapt to water stress and can enhance productivity, a process called the carbon dioxide fertilization effect [9]. It is unclear how strong this fertilization effect is on land, because of limitation by other nutrients or water [10, 11]; however, available ecosystem studies support the hypothesis that increased carbon dioxide will result in higher productivity [9].

Higher carbon dioxide levels will tend to cause the ocean to take up more carbon, since the atmosphere will be supersaturated with respect to the oceans, especially in colder regions. This additional carbon dioxide is likely to lead to lower pH values in the oceans, called ocean acidification [12], and reduce the ability of calcifying organisms to create skeletons [13, 14]. This has potentially huge repercussions on ocean biogeochemistry and biodiversity [13, 15].

Carbon also exists in the atmosphere in other forms. The next most important constituent in terms of atmospheric mass is methane. Methane is formed by the decay of reduced organic species under anerobic conditions, occurring in wetlands, in geologic formations, or in the intestines of animals. Methane sources are estimated to be about 580 Tg/year, with anthropogenic sources (such as fossil fuel extraction or agriculture) representing 55–70% of the total emissions [4]. Methane is oxidized in the atmosphere by the OH radical with a lifetime of about 9 years, as well as smaller sinks of removal at the surface and photolysis in the stratosphere [4]. Methane is even more radiatively important than carbon dioxide on a per molecule basis, and thus its accumulation in the atmosphere is of concern for global warming. Methane concentrations have increased from ~650–1,770 ppb over the past couple hundred years, largely due to human activity [16]. Methane oxidation converts the methane into carbon dioxide.

Other important carbon-containing gases include carbon monoxide and non-methane hydrocarbons. Carbon monoxide is a product of incomplete combustion, and after carbon dioxide is the largest form of emission of carbon into the atmosphere (1,800–2,700 Tg CO/year) [17]. Carbon monoxide chemically reacts with the OH radical in the atmosphere, and has a lifetime of about 2 months [17]. The oxidation of carbon monoxide to form carbon dioxide represents an important sink of oxidants in the atmosphere [17]. Non-methane hydrocarbons refer to a large collection of carbon-containing compounds that are important for tropospheric photochemistry and the generation of ozone and oxidizing compounds. Non-methane hydrocarbons undergo oxidation via many mechanisms. The complete oxidation results in one mole of carbon dioxide for each carbon atom in the original molecule [17]. The lifetime of non-methane hydrocarbons vary considerably, but are usually less than the lifetime of methane. They are important for air quality, since they are precursors to ozone, and may themselves be toxic, but are not sufficiently abundant to have radiative impacts [17].

Carbon is also a component of atmospheric aerosols, but at much lower concentrations than the gases described above. These aerosols can, however, be important for radiation and chemistry, because they exist as a solid in a gas phase. Sources of carbonaceous aerosols include by-products from combustion processes, compounds emitted from vegetation, and in situ product from the condensation of non-methane hydrocarbons.

Nitrogen Cycle

The dominant form of nitrogen in the atmosphere is molecular nitrogen (N_2), which represents over 70% of the air. However, this form is chemically inert and not biologically available. Thus, the nitrogen cycle usually refers to the cycle of reactive nitrogen compounds. The dominant form of reactive nitrogen in the atmosphere is nitrous oxide, a long-lived gas (>70 years), which is destroyed predominately in the stratosphere by photolysis. The sources of nitrous oxide are in the soils, as by-products of nitrogen fixation and denitrification processes, which convert molecular nitrogen to reactive nitrogen and back. Humans have increased nitrous oxide from 270 to 319 ppb, largely due to an increase in nitrogen fertilizer application [4]. Emissions of nitrous oxide are estimated to be 11 Tg/year. Nitrous oxide is a potent green house, and represents the third largest radiative forcing gas (after carbon dioxide and methane) [4].

Potentially even more important than nitrous oxide are the nitrogen oxides (NO and NO_2), which currently have emissions of more than 140 Tg/year, while preindustrial emissions were thought to be closer to 30 Tg/year [18]. Nitrogen oxides are emitted during combustion process, with smaller contributions from soils and lightning. Nitrogen oxides have a short lifetime in the atmosphere (a few days), and are important for atmospheric photochemistry and air quality because of their role in producing ozone [17]. In addition, nitrogen oxides deposit onto the earth's surface as they are removed from the atmosphere, and thus move nitrogen from one region to another in large quantities (e.g., [19]).

Since preindustrial times, emissions and concentrations of ammonia have increased with current emissions of 52 Tg/year compared with an estimated 22 Tg/year in preindustrial times [18]. Ammonia is emitted predominately from natural soils and agriculture, with small contributions from oceans and energy use. Ammonia has a short lifetime in the atmosphere (a few days) and is removed through wet or dry deposition onto the surface.

Similar to carbon species, nitrogen is also contained in organic gas species and to a smaller extent in inorganic and organic aerosols. These species can act as reservoirs of reactive nitrogen (e.g., [17], and thus be important for atmospheric chemistry. The fraction of nitrogen species that are in aerosols is dependent on chemical equilibrium with other aerosols, especially the strong acid sulfate [20]. In the future, as sulfate emissions decrease, nitrogen aerosols may become more important in terms of the radiative forcing of the climate as the fraction of nitrogen in aerosol form increases [20].

Riverine inputs to oceans are thought to be 55–80 Tg/year [21], which is of the same magnitude as the fluxes of many nitrogen compounds discussed above, suggesting that the atmosphere plays an important role in the cycling of nitrogen between the land and ocean.

Because many terrestrial ecosystems are nitrogen limited, the impact of nitrogen deposition, especially from nitrogen oxides and ammonia, is thought to be large for land ecosystems [3, 22–25]. Nitrogen is also a limiting nutrient for ocean systems, and there have been large increases in nitrogen deposition to ocean systems [21]; however, because of the large reservoir of reactive nitrogen in the oceans, deposition to the oceans is not thought to substantially modify the ocean nitrogen budget [26].

Phosphorus Cycle

Unlike carbon or nitrogen, most of the phosphorus in the atmosphere is in the aerosol form, with little phosphorus in the gas phase (e.g., [27]. As phosphorus is approximately 700 ppm in crustal material, and mineral aerosols (soil particles suspended in the atmosphere) represent a major source of aerosols, most of the phosphorus in the atmosphere is in mineral aerosols [28] at about 1.15 TgP/year. The next largest source is thought to be primary biogenic particles (0.16 TgP/year), but these aerosols are very poorly understood [28]. Combustion sources from fossil fuels, biomass burning, and biofuels represent a small source (0.0.7 TgP/year), while volcanoes and sea salts are thought to provide small amounts as well [28]. Thus, continental regions, especially deserts are the dominant source of atmospheric phosphorus [28].

Aerosols deposited to ocean have a limited residence time in the ocean mixed layer, before they sink to the ocean floor and become incorporated into the sediment. Only the fraction of phosphorus which is soluble or bioavailable can contribute to the phosphorus cycle of the ocean [28, 29]. The bioavailable fraction is often considered phosphate or soluble-reactive phosphorus [28], and the fraction of phosphorus in aerosols that is soluble varies from 7% to 100% [28, 29]. Transects of the North Atlantic suggest that desert dust aerosols average about 10% solubility [30, 31]; however a gradient in solubility is observed as the particles move away from the desert dust source area, suggesting that atmospheric processing may make the phosphorus in aerosols more soluble [30]. Studies in Mediterranean suggest that acidification, partly due to anthropogenic emissions of sulfur and nitrogen species, can make the phosphorus in desert dust more soluble [32]. Non-dust phosphorus is thought to be much more soluble ($\sim$50%), based on studies of European-derived aerosols in the Mediterranean [28, 33–36].

Phosphine gas (PH_3) has been measured in limited studies, with concentrations of between 0.39 and 2.45 ng/m^3 in remote regions and up to 178 ng/m^3 in urban locations or near paddy fields [37–39]. While traditionally, the gas phase transfer of phosphorus has been considered negligible [28, 40], some of the values listed here are similar in magnitude as those found for phosphorus in aerosols [28]. This suggests that phosphine could be an important mechanism for transferring phosphorus, yet is not well understood. Small amounts of phosphine could be generated in soils, agricultural and industrial processes, and lightning, but phosphine in the presence of sunlight is converted to phosphoric acid [37, 38].

Because phosphorus limitation is thought to be widespread in tropical forests and savannahs [41, 42], atmospheric deposition of desert dust may play a role in the long-term viability of tropical soils. For example, it has been suggested that the atmospheric deposition of desert dust from North Africa is responsible for the maintenance of the Amazon forest [43], and that deposition from Asia is important source of phosphorus to the tropical forests in Hawaii on long timescales [44]. The atmospheric deposition of phosphorus is likely to be important in many land ecosystems on geological timescales [45]. Forest and grassland ecosystems can also lose phosphorus through the atmosphere, as primary biogenic particles or biomass burning particles contain a large proportion of the phosphorus in tropical forests [46, 47].

The ocean tends to be a net sink of phosphorus from the atmosphere [28], and since productivity in the ocean is thought to be phosphorus limited on long timescales [48] and in some regions [49, 50], the atmospheric deposition of phosphorus could be an important source. Riverine inputs of phosphorus to the oceans are much larger than the atmospheric fluxes described here (11 Tg/year) [51]; however this phosphorus is input to the oceans in the coastal regions, and it is unclear how much of this phosphorus is advected into the open oceans [52]. However, on short timescales, large increases (25%) in phosphorus deposition to oceans which could be due to human activity [28] is not thought to substantially impact ocean biogeochemistry, because of the large reservoir of phosphorus already in the oceans [26].

Sulfur Cycle

Sulfur is an important trace compound in the earth system, used by some microorganisms for energy. It is commonly found in rocks with smaller quantities measured in the atmosphere [27]. The atmospheric portion of the sulfur cycle is important because of the climate interactions of the sulfur species, especially in the sulfate aerosol form. The sulfur compound with the longest lifetime (5 years) and most common by mass is carbonyl sulfide (OCS) [27]. The dominant sources (10 GgS/year) of carbonyl sulfide are the oceans and soils, with small contributions from combustion processes and the chemical oxidation of CS_2 [27]. Carbonyl sulfide is destroyed by oxidation in the atmosphere, as well as by stratospheric phytolysis and uptake by vegetation at the surface [27, 53]. Carbonyl sulfide is thought to contribute about half of the sulfur that forms the stratospheric aerosol layer, the other half coming from volcanic emissions [54].

Sulfur dioxide is a naturally occurring compound released from volcanoes and biomass burning ($<10\%$ total) as well as oxidation of the naturally emitted dimethyl sulfide ($\sim 20\%$), but the dominant source currently are human combustion activities with a total emission of about 91–125 TgS/year [16, 18]. Once released into the atmosphere, sulfur dioxide is oxidized within a few days to form sulfate aerosols. Because sulfate is highly hydrophilic, sulfate aerosols take up water and make a larger contribution to aerosol-radiation interactions than their mass would suggest [16]. In addition these aerosols readily interact with cloud droplets to modify cloud optical properties (aerosol indirect effect on clouds) [16]. Sulfur dioxide from human emissions is responsible for a large portion of the anthropogenic radiation forcing of aerosols [16].

Dimethyl sulfide is a natural source of sulfur gas to the atmosphere from the ocean, with a magnitude of about 15 TgS/year, which is readily oxidized to sulfur dioxide and then to sulfate aerosol (lifetime about 1.5 days). This is the dominant gas phase species of sulfur released from the ocean to the atmosphere. Because of sulfate aerosol interactions with clouds, it was hypothesized that biota could modulate their temperature by modifying emissions of dimethyl sulfide [55]; however, recent studies suggest this mechanism is not a dominant mechanism, for example, under anthropogenic climate change [56].

Sea salts are 7.7% sulfate by weight [57], and represents the largest source of sulfur to the atmosphere. Approximately 10,000 Tg/year of sea salt aerosols [58] is emitted into the atmosphere, which translates to 770 Tg SO_4/year or 250 TgS/year. Sea salt aerosols reside in the atmosphere from hours to days, and tend to redeposit back onto oceans [58], and are important as cloud condensation nuclei [59].

Sulfur moves from the land to the ocean at a rate of approximately 130 TgS/year [27], which is similar in magnitude to many of the atmospheric fluxes, suggesting that atmospheric sulfur is an important part of the global biogeochemical cycle.

Iron Cycle

Iron is required in small quantities by almost all organisms (e.g., [48, 60]), and is often considered a micronutrient. Because some regions of the oceans are iron limited [61], atmospheric deposition of iron is important for providing new iron to ocean biota [62]. Riverine inputs of iron are large, but are largely removed in coastal regions [63]. There is some evidence that the nitrogen-fixing organisms have larger iron requirements

Similar to the phosphorus cycle, iron resides almost entirely in atmospheric aerosols, predominately in desert dust. Combustion and other sources of iron are

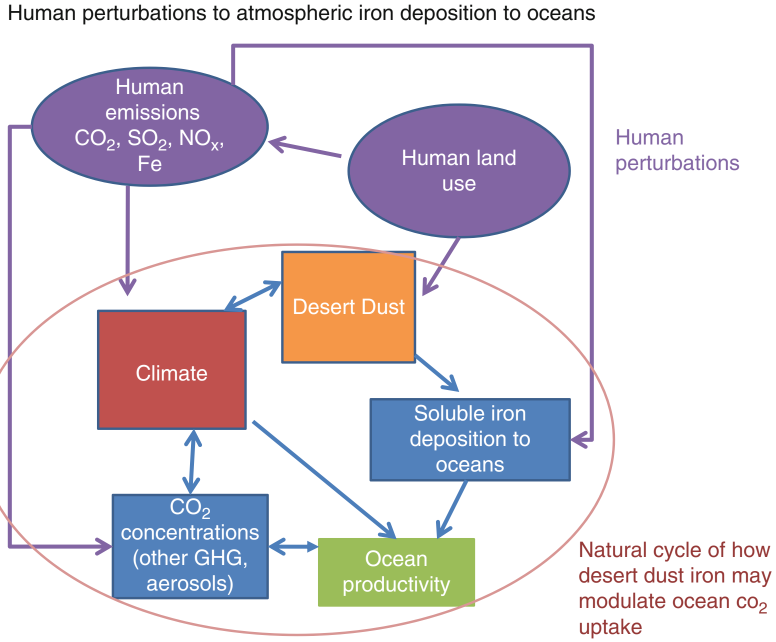

Fig. 2.2 Skematic representing feedbacks between natural ocean carbon cycle, carbon dioxide concentrations, and iron inputs also shows humans could be perturbing the iron deposition (Figure from [65])

estimated to be less than 5% of the total iron in aerosols [64, 65]. Crustal material is on average about 3.5% iron [66], with some minerals having substantially higher or lower concentrations [67, 68]. However, estimates and observations suggest that desert dust aerosols vary in their iron content by only a factor of 2, suggesting that the high heterogeneity in the soils is mixed in the atmosphere [65, 69]. There are also small sources of atmospheric iron from volcanoes [70, 71], cosmic dust [72], and combustion [64].

Because atmospherically deposited dust only resides in the mixed layer of the ocean for a short time, many researchers consider the soluble fraction of the iron the most relevant for ocean iota [73]. However, which fraction of the iron is really bioavailable is not well understood, but is likely to be a small fraction of the total iron in aerosols (1–80%) (see reviews in [65, 73]). Because the soluble fraction of iron in soils is much smaller than what is observed in the atmosphere, it is thought that atmospheric processing of iron is important [73, 74]. It is likely that the acidity and insolation play a role in processing of iron [73–75]. Some iron-containing minerals are more easily solubilized than others and iron in combustions is significantly more soluble than iron in mineral aerosols; these factors complicate our understanding of iron solubility [68, 76–78] (Fig. 2.2 from [65]).

Some regions of the ocean are iron deficient and additions of iron can result in phytoplankton blooms [79, 80]; however, there is limited evidence showing conclusively that a case of deposition of atmospheric iron results in a bloom [81, 82]. Additional atmospheric iron deposition could also lead to increases in ocean nitrogen, because of the potential for higher iron requirements for nitrogen-fixing organisms [48, 83]. There is some evidence for this effect [84–86], although some of these effects may be due to the isotopic signature of direct anthropogenic nitrogen deposition [87]. It is likely that human changes in iron deposition are more important than the large increase in direct nitrogen deposition to the ocean, in terms of both the nitrogen budget of the ocean, as well as carbon dioxide changes [26, 88].

Estimated changes in soluble iron due to increases in desert dust sources as well as the increase in atmospheric acidification (associated with more sulfate and nitrate aerosols) could be as large as a factor of 2–4 globally averaged [65, 89]. Model results suggest this would lead to an increase in the nitrogen fixation in the oceans, and a small sink of carbon dioxide [89, 90].

Oxygen Cycle

The atmospheric concentrations of oxygen are one of the clearest indications that life exists on this planet [27, 91]. The bulk of the atmospheric oxygen is in the gaseous state, in the form of molecular oxygen (O_2), which represents 21% of the atmosphere. Atmospheric oxygen is changing slightly due to human activity. For every molecule of CO_2 formed through combustion, one molecule of O_2 is lost from the atmosphere, and while small, these changes can be detected and provide important information about the carbon cycle [92, 93]. This molecular oxygen is also important as it absorbs high-energy uv light from the sun [94].

The oxygen species that exist in very small quantities in the atmosphere are extremely important for atmospheric composition, and control the oxidation of reduced species such as methane or nitrogen oxides. Ozone is produced in the stratosphere in the presence of high-energy uv light, and this ozone, as well as the process which generates the ozone, protects life from uv light at very short wavelengths [17, 94]. This also changes the thermal structure of the atmosphere, contributing to the increasing temperatures in the stratosphere [94]. Stratospheric ozone has been impacted by the release of chlorofluorocarbons, which are inert enough to reach the upper atmosphere, where they are photolyzed [95]. The largest impact has been in the polar regions, where an "ozone hole" has appeared during the hemispheric spring, although midlatitude reductions in ozone have also been observed [96]. In the troposphere, human emissions of nitrogen oxides, carbon monoxide, and non-methane hydrocarbons have led to an increase in ozone [17]. While the bulk of the ozone remains in the stratosphere, ozone is a highly oxidizing substance, so that increases in tropospheric ozone impacts human health and materials [17]. Ozone acts as a greenhouse gas, and the observed changes in ozone, both in the troposphere and stratosphere, have impacted the radiative budget [16].

Oxidation of organic and reduced species in the troposphere is the sink for many important greenhouse gases (e.g., methane), and other important trace species in the atmosphere (e.g., sulfur dioxides, nitrogen oxides) [17]. Much of this oxidation does not occur directly by ozone, but rather by the hydroxyl radical, a by-product of ozone photochemistry in the troposphere [17]. Because this constituent reacts so quickly, it is difficult to determine its concentration directly, but it can be deduced from changes in concentrations in some of the compounds it reacts with [97]. It is unclear whether humans are increasing or decreasing the hydroxyl radical, and will continue to do so, because of the complex nonlinear chemistry [16].

Other Cycles

Most elements are cycled in the atmosphere, and because long-range transport is much faster in the atmosphere than on land or oceans, this transport can be important for many elements. Here the focus is on a few critical elements for global biogeochemistry. However, some elements are important for their negative impacts, especially heavy metals. For example, mercury emissions from humans impacts human and ecosystem health [98]. Some studies have suggested that atmospheric deposition of heavy metals far from source areas can adversely impact ocean biogeochemistry [99]. In addition, atmospheric deposition of acid is thought to reduce the ability of some ecosystems to retain some nutrients and to negatively impact land and aquatic ecosystems [101–103], and to enhance ocean acidification [100].

Anthropogenic Modifications to Atmospheric Biogeochemical Cycles

Direct human emissions of carbon dioxide, sulfur dioxide, and nitrous oxides gases, as well carbonaceous aerosols, through the increase in combustion that humans use to generate energy, has substantially increased the sources and atmospheric concentrations of these compounds [16] (Fig. 2.3). In addition, changes in land use have increased carbon dioxide, methane, nitrous oxide, and ammonia emissions [16] (Fig. 2.3). These modifications are likely to continue into the future, with some decrease in emissions of combustion-sourced compounds estimated (Fig. 2.3) [101–107]. A combination of climate change and land-use change seems to have resulted in an increase in mineral aerosol over the past 100 years [89], which increases the flux of phosphorus and iron. In addition, bioavailable iron and phosphorus are likely to be even more susceptible to acidity and combustion sources; thus these compounds have changed more than simply from mineral aerosol changes over the past 100 years (Fig. 2.3). All of these factors have accelerated the atmospheric biogeochemical cycling of these compounds.

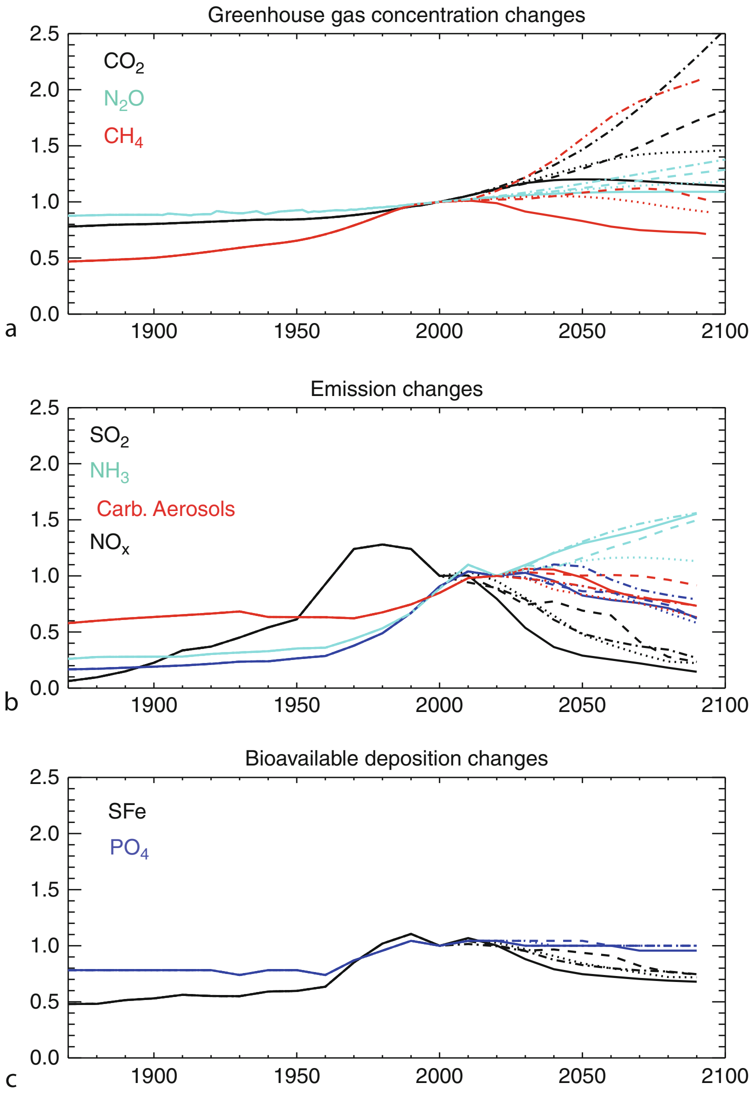

Fig. 2.3 Relative changes in green house gas concentrations (**a**), for carbon dioxide (*black*), nitrous oxide (*cyan*), and methane (*red*), relative to concentrations in 2000, based on atmospheric and ice core measurements for the past time period [127–130]. For the future, estimates are based on the representative concentration pathways estimates for four different scenarios [101–107], represented by the four lines into the future. Emission changes for important species, all normalized to 2000 values (**b**) for sulfur dioxide (*black*), ammonia (*cyan*), carbonaceous aerosols (*red*), and nitrogen oxides (*blue*) based on historical estimates [18], and for future estimates, the representative concentration pathways [101–107]. Deposition changes for bioavailable iron (*black*) and phosphorus (*blue*) are shown relatively to 2000 estimates (**c**), based on historical estimates and future estimates, using estimates of desert dust changes from [89], assuming in the future the model mean for no carbon dioxide fertilization changes in source area from [131], with iron solubility estimates from [64, 65], scaled by the sulfur dioxide emissions changes shown in (**b**), and for combustion soluble iron sources from [64] scaled by the black carbon emission changes included in (**b**). For soluble phosphorus (phosphates), desert dust estimate changes are the same as described for iron, and combustion sources of phosphorus come from [28], and are scaled by black carbon emissions, included in (**b**)

Atmospheric Modification to Other Biogeochemical Components

Atmospheric Biota

Atmospheric aerosols are likely to be composed in part by primary biogenic particles, or particles derived from the biota, for example, plant or insect bits, pollen, bacteria, or viruses [108]. Recent estimates suggest less than 5% of the aerosols are primary biogenic particles [109]. Some small fraction of these biogenic aerosols may contain viable living cells. While estimates of culturable bacteria are dependent on the methods used, estimates suggest that some bacteria do remain viable in the atmosphere, and can perhaps grow again if deposited onto the ground [110, 111]. Clearly, plants depend on pollen, and fungi on spores, to move genetic material from one place to another, and some fraction of this pollen and spores can be carried far from the source [112]. The amount of viable biota moving through the atmosphere and the importance of this process for global biogeochemical cycling is not well understood, but deserves future study.

Climate Modification of Biogeochemical Cycles

Changes in atmospheric biogeochemistry can modify climate, which in turn can also modify land and ocean biogeochemistry. This feedback has been used as a mechanism for understanding how carbon dioxide can be modulated on long timescales. For example, it is hypothesized that there are higher temperatures and more precipitation on land during higher carbon dioxide levels, thus increasing weathering [113]. This will reduce the atmospheric concentrations of carbon dioxide levels, acting as a feedback to prevent a runaway green house effect [113].

In the anthropocene, modeling studies have suggested that changes in anthropogenic aerosols and mineral aerosol particles can modify precipitation, incoming solar radiation, and temperature, and therefore modify land and ocean biogeochemistry enough to be seen at the global level [89, 90, 114, 115].

The Atmosphere as an Integrator

The atmosphere is the one part of the earth system that is transparent in many wavelengths of light, and thus can be readily observed using remote sensing methods. In addition, we live at the interface of the atmosphere and land surface, and thus have easy access to the lower layers of the atmosphere. This means that we have much better observations of the state of many biogeochemical cycles in the atmosphere, than in the land or ocean [16]. Thus understanding atmospheric biogeochemistry provides important information for understanding global biogeochemical cycles.

Transport in Atmosphere

The distance a chemical travels from its source region is highly dependent on its atmospheric lifetime. Many of the biogeochemically relevant gases discussed above are long-lived gases, which will reside in the atmosphere for several months to hundreds of years (e.g., CO_2, CH_4, N_2O). Other, reactive species (such as the hydroxyl radical OH), can have very short lifetimes (<1 day), and thus will not travel far from the sources. Aerosol species tend to have lifetimes between 1 day and a few weeks, and this lifetime is dependent on the size of the particle as well as whether precipitation has occurred, as this will remove particles.

For chemical species that have a relatively long lifetime ($>$ a few days), long-range transport can occur. Once emitted into the atmosphere, constituents mix quickly into the atmospheric boundary layer (the lowest 1–3 km of the atmosphere, where mixing is strongest), and can be transported long distances. Air parcels stay on a constant buoyancy surface (called isentropes), unless they are heated or cooled [116]. These surfaces of constant buoyancy tilt upward between the tropics and the high latitudes, because the high latitudes are colder (Fig. 2.4a from [109]). An air parcel emitted in the tropical boundary layer can reach the stratosphere (>10 km high) in the high latitudes without being heated by moving along an isentropic surface. On average, most of the atmosphere is radiatively cooling slightly during non-stormy conditions, so, over time, parcels of air will become heavier and move downward. If the parcel encounters a storm system with clouds and precipitation, the parcel can experience large heating or cooling and move vertically very quickly, perhaps traveling from the boundary layer up to 10 km in less than 1 h [117]. At the same time, the precipitation within the storm system can cause wet deposition of soluble gases or aerosols. Based on atmospheric heating rates, the residence time for a parcel on a given isentropic surface varies between <1 day for the tropics to 3–6 days in midlatitudes (based on 75 percentile heating rates) (Fig. 2.4a). If a parcel moves away from the pole, the tilting of the neutral buoyant surfaces will direct the parcel downward vertically and vice versa.

Geographically, there tend to be particular regions in midlatitudes that have more storms (Fig. 2.4b), called the storm tracks. Winds in the midlatitudes (30–60°) tend to be from the west, while winds in the tropics and highlatitudes ($>60°$) are less uniform. Tropical aerosols are more likely to encounter storms, resulting in vertical mixing or quick removal (Fig. 2.4b). Transport across latitudes tends to occur less often than transport along a latitude [118]. Thus, in the midand high latitudes, one can think of a parcel containing a constituent moving along isentropes, following the local winds, slowly cooling, and moving to a lower isentropic surface until it encounters a storm system, at which time it can be quickly removed or vertically transported.

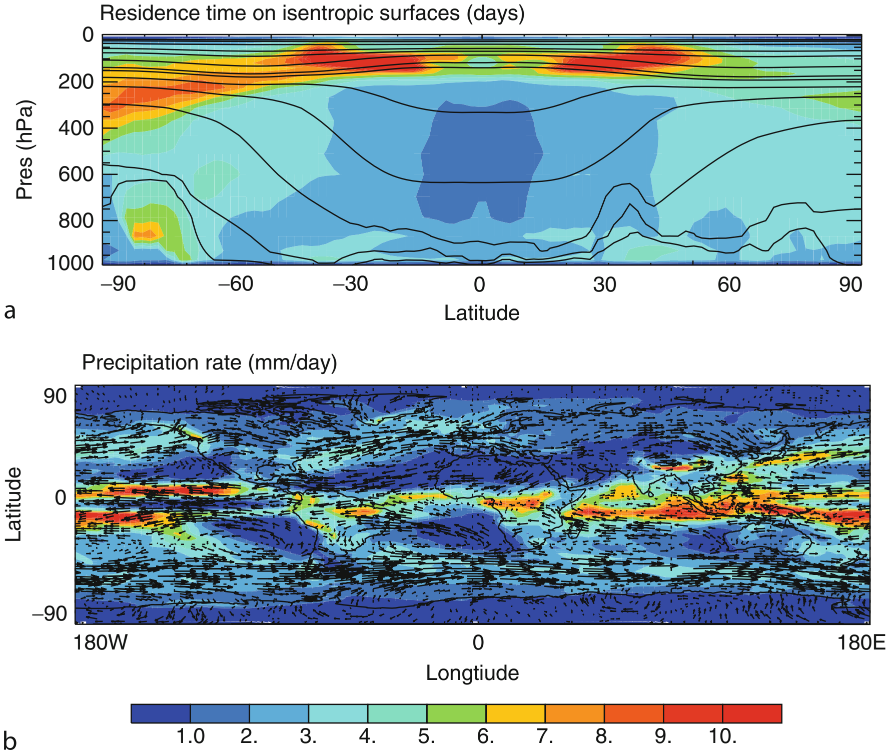

Fig. 2.4 Transport pathways of atmospheric constituents. Vertical distribution with latitude of the residence time of aerosols along a neutrally buoyant layer (isentrope), considering only vertical motion by heating in colors (**a**), with *black lines* marking surfaces of constant buoyancy (isentropes). These results are based on the 75% heating rates (warming or cooling) of the six hourly instantaneous results. Annually averaged precipitation rate (mm/day) in color, with annual mean wind vectors for 850 hPa (just above the boundary layer) (**b**) (Figure from [109])

Inverse Modeling

Inverse modeling is the practice of using atmospheric concentrations to deduce the sources and sinks of various important compounds [119]. Because many biogeochemically relevant species have natural sources and sinks, they have sources of uncertain magnitude. Inverse modeling has become quite common for these constituents. The initial studies used simple models to best match available data [120, 121]. With time, studies focused on regional budgets but used higher temporal and spatially resolved datasets and models to resolve regional and time-varying sources as well as sophisticated statistical techniques [122–124]. These studies (called top-down studies, because they use atmospheric concentrations to constrain sources and sinks) provide important information about the sources and can provide alternative views from upscaling flux measurements or inventories (called bottom-up approaches) [125]. Current approaches often estimate parameters based on available data, instead of resolving budgets, allowing models to be tuned to best match observations at a site, before applying that model to other regions to extrapolate to regional and global budgets [126]. Thus understanding atmospheric biogeochemistry of important compounds can facilitate a better understanding of the land and ocean biogeochemistry, using inverse modeling approaches.

Future Directions

The study of atmospheric biogeochemistry as a field is just beginning, although some of the most important elements, such as the carbon cycle, have been studied for many years. Our knowledge, however, of even the carbon cycle is insufficient to understand how global carbon dioxide levels will respond in the future, even assuming that human emissions can be predicted [2]. Important nutrient cycles highlighted here include the carbon, nitrogen, phosphorus, sulfur, iron, and oxygen cycles. All of these cycles in some way are heavily impacted by human activities, and in addition, feedback onto our climate and environment in important ways. Many of the important innovations over the last few years have involved understanding how the different cycles interact. Thus atmospheric biogeochemistry remains an important field for continued research and innovations.

The atmosphere is unique with respect to the other components of the earth system in our ability to easily observe many layers using remote sensing. This means that the atmosphere provides a location where biogeochemistry as a whole can be better understood. Inverse methods and modeling, in addition to the many observations, may allow us to improve our understanding of not just atmospheric biogeochemical cycles, but land and ocean biogeochemical cycles.

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