Exchange of Materials Between Terrestrial Ecosystems and the Atmosphere

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Many biogenic trace gases are increasing in concentration or flux or both in the atmosphere as a consequence of human activities. Most of these gases have demonstrated or potential effects on atmospheric chemistry, climate, and the functioning of terrestrial ecosystems. Focused studies of the interactions between the atmosphere and the biosphere that regulate trace gases can improve both our understanding of terrestrial ecosystems and our ability to predict regional- and global-scale changes in atmospheric chemistry.

THE STEADILY INCREASING CONTENT OF CARBON DIOXIDE in the atmosphere (1.5 ± 0.2 ppm/year) has provided an unequivocal signal of the global impact of human activities (*1*). Moreover, a number of other gases of biotic or industrial origin, or both, are increasing in concentration in the troposphere, as well as having direct and indirect effects on terrestrial biota. The sources, sinks, and dynamics of these trace gases are important for several reasons. First, many gases affect the chemistry and physics of the atmosphere and thus alter characteristics as diverse as the energy budget of the earth, the concentration of oxidants in the troposphere, and the absorption of ultraviolet radiation in the stratosphere. Attempts to predict the future evolution of the atmosphere must account for biological processes that regulate these gases. Second, trace gases or their reaction products affect terrestrial biota directly in ways that can be more or less species-specific and that range from enhancing productivity or competitive ability to causing substantial mortality. Finally, the production and consumption of trace gases in terrestrial ecosystems indicate the presence and magnitude of particular physiological processes or ecosystem fluxes or both (Fig. 1). Measurement and understanding of trace gas fluxes will thus be useful for understanding terrestrial ecosystem dynamics as well as the atmosphere.

In this article we examine the biotic interactions of trace gases and note the mechanisms that produce them, their local and regional patterns of production, and their potential effects on the biota. We also discuss how human perturbations modify the extent and patterns of gaseous emissions from natural systems. In most cases there are substantial uncertainties in our knowledge of the sources, sinks, or effects of particular gases. Nonetheless, advances in information, concepts, and techniques place the ability to understand the global fluxes and effects of trace gases increasingly within our grasp.

Relatively Stable Gases

Trace gases in the atmosphere vary from highly reactive species with lifetimes in seconds to hours to stable compounds with atmospheric lifetimes of years to centuries. Concentrations of the more stable gases are generally higher (except for the wholly anthropogenic chlorofluorocarbons), their distribution and seasonal patterns are better characterized, and their increasing concentrations in the atmosphere are often documented by direct measurements and by analyses of air bubbles trapped in Antarctic ice (*2, 3*). We first summarize information on carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O), three relatively stable biogenic gases that are increasing globally. We then discuss biotic sources and interactions of water vapor and of more reactive trace gases.

Carbon dioxide. The extent, causes, and consequences of increasing CO_2 concentrations in the atmosphere have been discussed thoroughly elsewhere (*1, 4*). The complexities of this analysis have been formidable. At first, even the sources and sinks of CO_2 were controversial, although now alternative estimates are increasingly convergent. The effect of increasing CO_2 on climate has been more difficult to demonstrate or to predict (*5*), but overall the most difficult problem has been predicting biotic responses to the direct effects of increasing CO_2 as well as to indirect effects of a changing climate.

Terrestrial sources and sinks of CO_2. Ecosystems produce CO_2 through respiration. Respiration is positively related to temperature for a given organism, but different kinds of organisms differ in their rate of respiration at a given temperature. For example, cold climate plants may respire as rapidly at a cold temperature as do warm climate plants at a higher temperature.

Overall, approximately 100×10^{15} g of carbon (gC) are released into the atmosphere per year through respiration. Fire is another source of CO_2; it can be considered a form of rapid decomposition since it quickly releases chemically bound carbon that decomposers

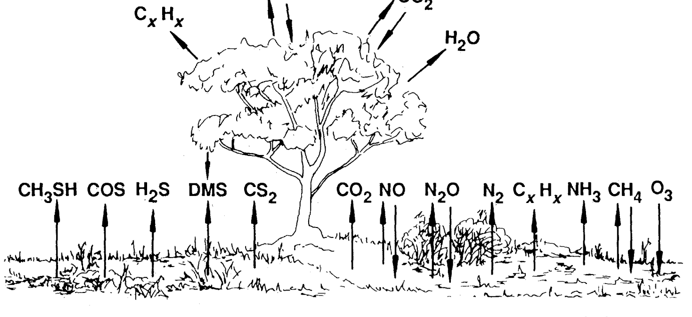

Fig. 1. Exchange of gases between ecosystem components and the atmosphere.

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would otherwise release over a period of time. Estimates of global CO_2 release through biomass burning range from 2×10^{15} to 5×10^{15} gC year^{-1} (*6, 7*); fossil fuel combustion releases 5×10^{15} gC year^{-1}. The earth's terrestrial ecosystems also serve as enormous sinks for CO_2 and take up through photosynthesis almost the same amount as is released in respiration and fires.

Regional variation. The terrestrial ecosystems of the earth's surface vary in their productive capacity and their rates of CO_2 exchange and carbon storage depending on temperature and the availability of water and nutrients. For example, nutrient-rich tropical swamps and marshes have less than a quarter of the areal extent of boreal forests and yet have a greater total CO_2 exchange. Humid tropical forests constitute only 6.6% of the earth's terrestrial surface area but have over 17% of the total net primary production (*8*).

The CO_2 released from fires also varies regionally. Moist tropical forests have estimated mean annual carbon release rates through fire of 30 g m^{-2} year^{-1}, in contrast to 150 g m^{-2} year^{-1} for seasonally dry tropical savannas and scrubland. Fires in closed tropical and subtropical forests contribute 0.5×10^{15} gC year^{-1}, whereas temperate broadleaf forests contribute only 0.1×10^{15} gC year^{-1}; tropical woodlands and savannas contribute the greatest amounts at 1.5×10^{15} gC year^{-1} (*7*).

Seasonality. The seasonality of CO_2 production and use by biota was first clearly demonstrated on a hemispheric scale by atmospheric measurements on Mauna Loa in Hawaii (*9*). Winter versus summer concentrations in the atmosphere in this region vary from 5 to 8 ppm; seasonal cycles are even greater at higher latitudes (Fig. 2) (*10*). Large areas of the earth's surface are covered by ecosystems that fix CO_2 only during warm seasons (temperate deciduous forests and grasslands) or moist seasons (tropical dry forests and savannas). The seasonality of activity of these systems is easily seen and directly quantified by remote sensing from satellites, and the amplitude of seasonal variation in active photosynthetic tissue correlates well with seasonal cycles in CO_2 (*10, 11*).

Human influence. As much as 30% of CO_2 fixation on land occurs in human-dominated ecosystems (*12*), and global patterns of CO_2 exchange have been greatly modified by human activities. Changes have come about principally from the altering of carbon storage patterns, particularly the release through harvesting, burning, and plowing of carbon stored in old growth forests and in grassland soils. However, biotic substitutions and plant resource changes have simultaneously modified the intensity of gas exchange. Irrigation and fertilization have enhanced the productive capacity of many regions (as desertification has decreased it in others), and high-productivity crop plants have been substituted for low-productivity native species.

At present, our best estimates are that human modifications in the distribution and amount of the earth's biota in the past decade, mostly in the tropics, have resulted in a net annual release of CO_2 to the atmosphere of $1.6\ (\pm 1.0) \times 10^{15}$ gC (*13*), which is much lower than the 5.0×10^{15} gC released by the burning of fossil fuels.

Effects on biota. The increasing concentration of CO_2 in the atmosphere is likely to have large effects on terrestrial biota, both directly and through its effects on climate. However, the exact nature of these effects is difficult to predict. Even the widely anticipated climatic warming resulting from elevated CO_2 concentrations cannot be analyzed in detail; its effects on cloudiness and the distribution of precipitation remain speculative.

Terrestrial plants can be divided into two principal photosynthetic types, those that show a linear increase in photosynthesis with increasing CO_2 concentration (C_3 plants, such as soybeans), and those which are saturated at ambient concentrations (C_4 plants, such as corn). However, this information alone is insufficient to predict responses to CO_2 enrichment, because additional species-specific physiological interactions within plants also affect growth and reproduction. Moreover, it is uncertain whether any increase in carbon fixation that results from CO_2 enrichment will also cause increased decomposition. This point is crucial, because it is the change in net carbon storage, not photosynthesis, that controls feedback from CO_2 absorption by plants to further alter atmospheric concentrations. Decomposition could simply increase with increasing productivity. However, where nutrients (especially nitrogen) are limiting to growth, plants produce tissue with higher ratios of carbon to nutrients when CO_2 levels are elevated (*14*). This altered tissue chemistry could reduce the rate of decomposition and attendant nutrient release and possibly feed back to decrease productivity in the long term.

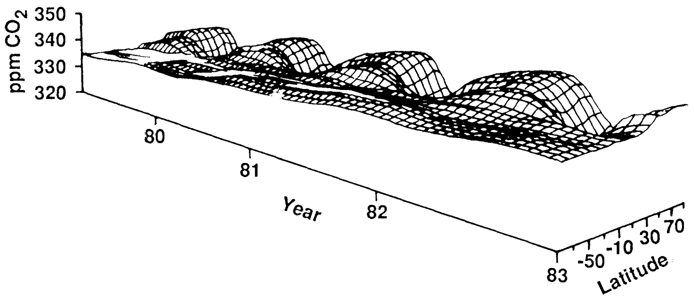

Fig. 2. Seasonal and latitudinal variation in atmospheric CO_2 concentrations (*10*).

Methane. Measurements of atmospheric methane concentrations since 1965 demonstrate that tropospheric methane is increasing at about 1.1% per year, which is a substantially greater percentage increase than for CO_2 (*15, 16*). Analyses of ice cores also indicate that methane concentrations have more than doubled over the past 200 to 300 years to a level between 1.6 and 1.7 ppm after having remained relatively stable for thousands of years (*2, 3, 17*). Increased concentrations could be caused by increases in the sources of methane or decreases in the sinks; current evidence suggests that human-caused changes in land use contribute substantially to the observed increase.

Methane is produced by specialized anaerobic bacteria that couple the oxidation of reduced compounds (principally hydrogen and acetate) to the reduction of carbon dioxide to methane. These bacteria are found in anaerobic environments within natural wetland ecosystems and rice paddies, in the anoxic rumen of cattle, and in the gut of termites and other wood-consuming insects. Estimates of the magnitude of methane production from particular biogenic and anthropogenic sources are variable, but the total annual flux to the atmosphere is probably between 400×10^{12} and 650×10^{12} g year^{-1} (*18, 19*). Differences in flux estimates are based on disagreements in the magnitude and duration of emission as well as the extent of particular source areas (*20*).

Natural wetland ecosystems represent a large source of methane; the estimated annual fluxes range from 11×10^{12} to 300×10^{12} g year^{-1}, with many recent estimates between 100×10^{12} and 150×10^{12} g year^{-1} (*20–22*). Methane emissions from wetlands vary depending on soil and air temperature, soil moisture, the amount and composition of organic substrate, and vegetation. Plants themselves are important conduits for methane transport from axonic sediments to the atmosphere. Recent analyses suggest that the extensive, organic-rich arctic and boreal wetlands are especially important sources of methane (*23*); they account for about half of total emissions from natural wetlands worldwide (*20, 24*). The large seasonal cycle in atmospheric methane concentrations in high northern latitudes may be caused by fluxes from wet tundra (*25*).

Although emissions of methane are positively related to temperature over a broad range, freshwater swamps at lower latitudes apparently have lower emission rates than northern peatlands (*26*), which is possibly caused by differences in organic matter content. Recent measurements in the Amazon floodplain found relatively high emissions in macrophyte beds; Devol *et al.* (*27*) estimated annual emissions of 7.8×10^{12} to 13.2×10^{12} g for the Amazon basin as a whole. Human activity that alters wetlands (for example, draining or flooding) alters methane emission.

Rice paddies also produce methane, with estimates ranging from 35×10^{12} to 170×10^{12} g year^{-1} (*28, 29*). Most emission data have been obtained in areas with relatively intensive agricultural practices and thus may not represent worldwide rates. The dominant form of transport of methane to the atmosphere appears to be through plants. Activities that alter the productivity of rice paddies (for example, continuous inundation or multiple cropping) or extend their areal extent will increase methane emission. Seiler and Conrad (*30*) estimate that methane emissions may have increased from 75×10^{12} g year^{-1} in 1950 to 115×10^{12} g year^{-1} in 1980 because of increases in the areal extent of rice paddies.

Estimates of methane produced by microorganisms in the rumen of cattle, goats, and sheep range from 60×10^{12} to 200×10^{12} g year^{-1} (*21, 22, 31*). A recent review (*32*) calculated production by all animals as a function of animal diet, nutrition, and species; it was estimated that domestic animals produce 74×10^{12} g year^{-1}. Increased populations of grazing animals have caused a fourfold increase in methane production by this source since 1890, and further land-use changes that convert forest to pasture-grazing systems will lead to further increases in methane production.

Termites are an additional natural source of methane. Based on laboratory studies, Zimmerman *et al.* (*33*) estimated that this source contributes 150×10^{12} g year^{-1}. Some subsequent studies (*29, 34, 35*) suggest that methane emissions from termite nests are considerably less, perhaps as low as 15×10^{12} g year^{-1}, but the issue is not fully resolved. If land clearing from forest to pasture increases termite populations, this source could become more important. Mining of fossil fuels and emissions from solid-waste disposal sites also appear to be relatively important sources of methane (*36*).

Effects on terrestrial ecosystems. Increased methane in the atmosphere affects terrestrial ecosystems through its effects on climate and atmospheric chemistry. Methane acts as a strong greenhouse-effect gas by absorbing outgoing infrared radiation within the troposphere 20 times more effectively per molecule than CO_2. Moreover, because it is temperature-dependent, methane production itself may increase with atmospheric warming in the mid- to high-northern latitudes. Finally, methane strongly reacts with the atmospheric hydroxyl radical (OH) and can be involved in the production of tropospheric carbon monoxide and ozone (O_3).

The direct effects of increased methane concentrations are much less certain. Dryland soils represent a sink for methane (*37, 38*), but their uptake is small compared to reaction with hydroxyl radical. The extent to which uptake by soils increases with increased atmospheric concentrations is unknown, as is the effect of any increased uptake on populations of methane-oxidizing soil microorganisms.

Nitrous oxide. Nitrogen is the most abundant element in the atmosphere, but it is also the element that most limits photosynthesis and primary production in most agricultural and many natural terrestrial ecosystems. This apparent paradox arises because the enormous pool of dinitrogen [3.9×10^{21} g of dinitrogen (N_2)] in the atmosphere can be converted to biologically available forms of nitrogen by only relatively few species of prokaryotes, and because biological nitrogen fixation itself is energetically expensive.

Considerable effort has gone into understanding nitrogen cycling at scales ranging from local to global (*39*). Biological nitrogen fixation in natural ecosystems has been estimated at about 90×10^{12} g globally; human-caused nitrogen fixation (by industrial fixation for fertilizers, by legume crops, and as a by-product of internal combustion) is about the same magnitude (*40*). Our current understanding of fluxes of nitrogen gases from terrestrial ecosystems to the atmosphere is less certain (*41*). Dinitrogen is the most abundant form emitted; it is produced by microbiological denitrification of nitrate. However, dinitrogen is inert and for all practical purposes invariant in the atmosphere (atmospheric lifetime is estimated at $>10^7$ years). Nitrous oxide (N_2O) is a relatively stable gas that is present in the atmosphere at concentrations around 300 ppbv; its concentrations are now increasing at ~0.2% per year globally (*3, 16, 34*).

Nitrous oxide is produced as an intermediate in the process of denitrification; under some conditions, it can even be the major product (*41*). Denitrification is most rapid in anaerobic soils with an abundant supply of nitrate and oxidizable carbon, but it can also occur in anaerobic microsites within generally aerobic soils (*42*). Nitrous oxide can also be produced by biomass burning or fossil fuels (*43, 44*), by nitrifying bacteria (*45*), and apparently in small amounts by a wide range of soil microorganisms (*46*).

The major sink for N_2O is reaction with activated oxygen in the stratosphere. Approximately 10×10^{12} g of N_2O are consumed annually by this pathway. The existence or importance of other sinks is uncertain, although denitrifying organisms can use nitrous oxide as a substrate. The annual increase in nitrous oxide concentrations in the atmosphere amounts to approximately an additional 3×10^{12} g. To balance these sinks, the oceans are a minor source, whereas tropical forest soils appear to be a major source (*38, 47*) and account for perhaps as much as 6×10^{12} to 8×10^{12} g year^{-1}. Most tropical forests circulate much more nitrogen annually than do most temperate or boreal forests (*48*), and even within the tropics, N_2O fluxes are significantly larger from nitrogen-rich than nitrogen-poor forests (*49*). Fertilized agricultural ecosystems also emit more nitrous oxide than do most natural ecosystems (*50, 51*). The global increase in nitrous oxide concentrations can be explained primarily by combustion sources (*44*); it is uncertain whether the increased use of nitrogen fertilizers in agriculture or increases in deforestation and other land use changes (*47, 52*) contribute significantly.

Effects on terrestrial ecosystems. Nitrous oxide is a greenhouse gas, and its increasing concentrations are expected to contribute a small amount towards global warming in the next 50 years (*53*). Additionally, nitrous oxide oxidizes to nitric oxide in the stratosphere, and stratospheric nitric oxide reacts with ozone there. Increasing concentrations of nitrous oxide may thus make a small contribution toward the breakdown of the stratospheric ozone layer (*54*), although the wholly anthropogenic chlorofluorocarbons now exert a much greater effect.

The Water Cycle

Water vapor is a relatively unreactive gas, in that the physical processes of evaporation and precipitation are quantitatively much more important than chemical reactions in controlling its concentrations in the atmosphere; it differs from other unreactive gases in that its atmospheric lifetime is short (~10 days). Vast quantities of water vapor move from the earth's surface through evaporation into the atmosphere and then back again through precipitation annually. The amount involved in this cycle is estimated at 973 mm per year averaged over the earth's surface, for a total evaporated volume of about 500,000 km^3 (500×10^{18} g of water) (*55*).

Most of the earth's water is stored in the oceans (97.4%) or polar ice (2%). Here we focus on the less than 1% of the water contained in the atmosphere, soil, lakes, and rivers. The atmosphere contains only 0.001% of the earth's water (13,000 km^3 or 13×10^{18} g H_2O versus 720×10^{15} gC), which would amount to an average depth over the earth's surface of 20 to 30 mm. There is great spatial and temporal variation in atmospheric water content, from 50 mm in the atmosphere of some tropical regions to as low as 5 and 1.5 mm over arctic and antarctic regions, respectively (*56*). Despite these small quantities, water vapor is the prime controller of tropospheric temperature structure through its effects on both solar and terrestrial radiation.

Vegetation interacts with the hydrological cycle both directly and indirectly. First, it influences the amount of precipitation that enters the soil. Some of the incoming precipitation is intercepted by vegetation and evaporates before reaching the ground, the amount of which depends both on the nature of the vegetation and on characteristics of precipitation. Annually as much as a third of the incoming precipitation may be intercepted by a wide variety of forest communities ranging from tropical to boreal types (*57*). Second, vegetation influences the amount of water that enters the soil profile; vegetation-free surfaces have much greater runoff and erosion rates than vegetated areas (*58*). Third, the presence of vegetation alters the amount of intercepted radiation (*59*), boundary-layer characteristics, and the amount of water available for evaporation. Water in the soil below a depth of about 10 to 20 mm (*60*) is not subject to evaporation unless an area is vegetated, but the penetrating roots of plants transport water from deep in the soil profile and bring it to leaf surfaces. There it is in direct contact with the atmosphere whenever leaf stomatal pores are open (which they generally are during the day, as long as there is a supply of soil moisture and the atmosphere is not unusually dry).

The influence of vegetation on the hydrological cycle has been most clearly demonstrated where all of the vegetation on a watershed has been removed. Streamflow in such watersheds generally increases in direct proportion to the amount of vegetation removed; the recovery period is approximately related to the logarithm of time subsequent to felling (*61*).

Influences of vegetation type on the hydrological cycle have been experimentally demonstrated for evergreen conifers versus deciduous hardwoods. Water loss to the atmosphere is greater for pines than hardwoods, which is caused in part by the greater leaf and branch surface area per unit of ground surface of pines and in part by their year-round maintenance of leaves (*62*). Even species-specific effects have been documented. For example, biological invasions of salt-cedar (*Tamarix spp.*), which are exotic species with unusually deep roots, significantly increase evapotranspiration from semiarid regions of the southwestern United States (*63*).

Regional effects. Almost 70% of the total evaporation on land as well as over water takes place within the tropical latitudes of 30°N to 30°S, although the fractions of land and water within the tropics constitute only 44 and 52%, respectively, of the total global surface areas (*55*). The water balance of different regions also varies considerably. Of the 2000 mm of total incoming annual precipitation in the Amazon Basin, 48.5% is returned to the atmosphere through transpiration by the vegetation, 25.6% is returned by evaporation from intercepted water, and about 26% is lost through runoff (*64*). In contrast to the 1500 mm annual evapotranspiration over tropical forests in general, annual water loss over boreal coniferous forests is only 240 mm per year. The total evapotransportation from tundra and boreal forest accounts for only 0.7% of the global evapotranspiration, although these areas cover 8% of the earth's land area (*65*).

Effects of vegetation on water balance and climate. Because of the necessity of integrating over large areas, most analyses of the effects of vegetation on regional atmospheric composition and dynamics are based on simulations that use global circulation models. Mintz (*66*) reviewed the many simulations in which surface albedo or soil moisture or both were altered, and noted that whenever soil moisture or albedo was changed regionally, so was precipitation, temperature, and the movement of the atmosphere. These simulations are important and suggestive, but the global circulation models in use have very limited land surface inputs. For example, the rate of evapotranspiration used for these models is that for open pans rather than for vegetated surfaces. The simulations often use unrealistic inputs, such as a total lack of soil moisture or vegetation over large regions. Models with finer levels of resolution are being developed and include biophysical models that fully account for the influence of vegetation on the transfer of radiation, moisture, and momentum (*67*). In these models the properties of the vegetation determine land surface interactions with the atmosphere and thus provide for atmosphere-biosphere interactions. Additionally, measurements of stable isotope ratios in precipitation and the atmosphere (*64*) can be used to integrate rates of evapotranspiration over large areas and to validate models of evaporation and water transport.

The further development of techniques for estimating the water balance is crucial to our ability to predict atmosphere-biosphere interactions. The amount and distribution of water vapor control both atmospheric and ecosystem dynamics directly, and enormous regional changes in water budgets are forecast as the earth's energy balance is altered by the increasing concentrations of carbon dioxide, methane, nitrous oxide, and other greenhouse gases.

Reactive Gases

A large number of highly reactive gases are produced biologically or by biomass combustion, and the concentrations of many of these gases are currently increasing in the atmosphere. These reactive gases pose a very different problem from more stable gases; their concentrations are generally low and often ephemeral, so it is more difficult to identify their sources, sinks, and effects with certainty. Moreover, many of these gases interact in ways that cause the production or destruction of other gases. Globally averaged concentrations or atmospheric lifetimes of the reactive gases are thus not only difficult to obtain but also not very informative, because the occasional coincidence of high concentrations of two or more gases regionally or locally can have a great effect on atmospheric chemistry as well as the terrestrial biota.

Carbon. The major reactive carbon gases are a suite of hydrocarbons (non-methane hydrocarbons or NMHC) and carbon monoxide (CO). These two are linked in that oxidation of NMHC is a major source of atmospheric CO.

Non-methane hydrocarbons. Two major biogenic classes of NMHC are isoprene (C_5H_8) and terpenes. Zimmerman *et al.* (*68*) estimated annual global emission rates of 350×10^{12} g and 480×10^{12} g for isoprene and terpenes, respectively, and calculated that the oxidation of these hydrocarbons could account for 39% of global CO production. Similarly, Logan *et al.* (*69*) suggested that biogenic hydrocarbons contribute significantly to the production of atmospheric CO.

Terpene production by plants has been studied for many years in relation to resistance to and attraction of insects (*70*), and emissions of volatile terpenes were first suggested to affect atmospheric chemistry by Went (*71*). Terpene emissions from vegetation are controlled by the chemical potential gradient between leaf and surrounding air (*72, 73*), a gradient that is controlled by the vapor pressure of the individual monoterpenes.

Isoprene is also produced and emitted by many plant species (*74,* *75*). Its biosynthesis is associated with photorespiration and intermediates of the glycolate pathway (*76*), and thus its emission is closely related to light levels and biosynthetic rates. Like terpenes, isoprene emissions increase exponentially with temperature, but they are more strongly stimulated by light (*73, 77*).

A number of studies have measured isoprene and terpene emissions from individual species and in the atmosphere above vegetation canopies. From these studies, Zimmerman (*75*) concluded that the highest emissions (especially of terpenes) in the United States occur in the northern tier of states, which includes temperate deciduous and coniferous forest regions. More recent studies of emissions in tropical areas suggest that rates of production (especially of isoprene) are higher than in cool temperate species (*78*), and Gregory *et al.* (*79*) reported elevated concentrations of isoprene in the planetary boundary layer over forests in Guyana. Greenberg and Zimmerman (*80*) suggested that the Amazon may be a globally important source of biogenic hydrocarbons; ambient levels of isoprene are similar to northern coniferous forests, but its average atmospheric lifetime is shorter in the tropics.

Global estimates of isoprene and terpene emission have been based on the assumption of a constant relation between foliar biomass and emission rate for classes of vegetation. Given this assumption, permanent conversion of forest to pasture or agriculture use would reduce biogenic NMHC emission (but perhaps increase anthropogenic hydrocarbon emissions through biomass burning and subsequent human activities). However, little information is available on relations between soil fertility and NMHC emissions or on emissions from successional vegetation; the species planted in short-rotation tree plantations are often prodigious sources of NMHC (*81*).

Because of their high reactivity and short atmospheric lifetimes, biogenic NMHC do not directly affect climate. They do interact with other atmospheric compounds, however, in that their reaction with ozone can be a significant sink for ozone and a source for carbon monoxide. Although emissions of terpene and isoprene represent a loss of fixed carbon to plants on the order of 0.5 to 1% of photosynthetic uptakes, there is no evidence that atmospheric concentrations directly affect physiological or biochemical characteristics of vegetation.

Carbon monoxide. Carbon monoxide is a relatively short-lived gas (with an atmospheric lifetime of less than half a year) that appears to be increasing in the troposphere (*19*). About 1000×10^{12} g of carbon enters the atmosphere annually as CO, about half of which results from oxidation of methane and NMHC. Fossil fuel combustion, agricultural burning, and land-clearing fires account for most of the remainder (*43, 69*).

Approximately 10% of the CO that is destroyed annually is consumed in soils; most of the remainder is oxidized by OH radicals. No direct biological effects of current atmospheric levels of CO are known, but it interacts with nitrogen oxides and OH to produce tropospheric ozone, which clearly does affect organisms, as discussed below.

Nitrogen. The major reactive nitrogen gases are oxides of nitrogen, collectively referred to as NO_x. Combustion is a major source of NO_x; it is both oxidized from fuel nitrogen and fixed from atmospheric N_2 during combustion (*44*). Lightning also fixes NO_x (*82*), and NO in particular is produced by the abiotic reduction of nitrite in acid soils and by biological processes related to nitrification and denitrification (*83*). The limited and rather difficult measurements of NO_x fluxes from soils show that they generally correlate with N_2O fluxes on an annual basis (*51*), although NO fluxes are relatively greater when the soil surface is dry. Thus seasonal tropical forests and fertilized agriculture probably represent significant sources of NO_x.

NO_x plays a complex role in atmospheric chemistry. At low concentrations (as in the stratosphere), it catalyzes the breakdown of ozone. At higher concentrations (which are often realized in industrially affected air), however, it can interact with CO, OH, and hydrocarbons to produce ozone (*84*). Moreover, atmospheric NO_x is converted within days (more rapidly in solution) to nitric acid that represents a substantial contribution (30 to 50%) to the acidity of precipitation within and downwind of industrial regions. Increased deposition of fixed nitrogen fertilizes natural and managed ecosystems and alters pathways of nitrogen cycling in apparently natural forests (*85*). Although this probably increases terrestrial productivity at moderate levels of deposition, high levels of nitrogen deposited into normally nitrogen-deficient forest ecosystems could cause increased herbivory (*86*), undesirable patterns of root-shoot allocation (*87*), growth limitation by other nutrients, and possibly increased mortality (*88*).

In the longer term, increased nitrogen-deposition is likely to alter decomposition as well as production by increasing the nitrogen content and carbon quality of plant litter (*89*). Moreover, increased nitrogen will probably affect the outcome of competition among plant species (*90*), and alter population and community dynamics in even the best protected nature reserves. The large amounts of nitrogen deposited on natural and managed ecosystems of northern Europe and eastern North America probably cause many of these effects now.

Ammonia. Ammonia is also present at low and variable concentrations in the atmosphere, and our knowledge of ammonia fluxes has been limited by analytical difficulties. Ammonia is in *p*H-dependent equilibrium with nonvolatile ammonium in soils and solutions; its major natural sources appear to be volatilization from alkaline soils, animal excreta, and senescing leaves (*91*). These sources are probably increased by intensive agriculture and animal husbandry practices.

Once in the atmosphere, ammonia can be dissolved or adsorbed by aerosols and water droplets or taken up directly by vegetation. Most of the ammonia that enters the free troposphere is returned as ammonium in bulk precipitation or captured aerosols. Ammonia in aerosols or dissolved in cloud droplets can accept a proton to form ammonium, thereby reducing the acid intensity of precipitation. However, where deposited ammonium is retained within terrestrial biota or lost as nitrate (true of most sites), it can contribute substantially to soil acidification (*92*).

Ammonia can contribute significantly to the overall deposition of nitrogen downwind of seabird rookeries (*93*), feedlots, and agricultural regions where anhydrous ammonia or urea are used heavily. In such areas it causes effects on nitrogen cycling identical to those of nitrate derived from NO_x.

Sulfur. An even wider variety of trace sulfur gases than nitrogen gases are emitted from natural terrestrial ecosystems, and most are relatively reactive. The most important are hydrogen sulfide (H_2S), dimethyl sulfide (DMS), methyl mercaptan (CH_3SH), carbon disulfide (CS_2), and carbonyl sulfide (COS); all except COS are short-lived. These gases are produced by a variety of pathways in soils and within higher organisms (*94, 95*); estimates of their fluxes have been limited by sparse sampling and insufficiently validated analytical procedures, so that these gases will be discussed only briefly.

Most of the trace sulfur gases are produced most rapidly in wholly anaerobic environments, and hence marshes and other wetlands have been considered relatively active sources of sulfur gas emissions. In upland sites, current evidence suggests that at least the flux of H_2S is much greater in tropical than temperate forests (*96*). However, our knowledge of sulfur gas fluxes remains in a state of flux itself; successive refinements in technique, sampling area, or sampling frequency often alter flux estimates substantially (*95*).

Table 1. The regions and land uses for which emissions of the listed trace gases are believed to be at a maximum. Annual flux is to the atmosphere.

Species	Natural system or geographic area of maximum flux	Land use for maximum flux	Approximate annual flux (log g)	Atmospheric lifetime (days)
CO_2	Wet tropical forest	Forest, biomass burning	17	~2500
H_2O	Wet tropical forest	Forest	20.5	10
CH_4	Wetlands	Rice paddies, pasture (animal husbandry), biomass burning	14.5	~3600
N_2O	(Fertile) tropical forest	Fertilized agriculture, biomass burning	13	~60,000
C_5H_8	Tropical forest	Forest	14.5	<1
$C_{10}H_{16}$	Temperate forest, shrublands	Forest	14.5	<1
CO	Produced from C_xH_x in atmosphere	Biomass burning	15	75
NO_x	Tropical forest	Fertilized agriculture, biomass burning	14	4
NH_3	Temperate grasslands	Pasture (animal husbandry), fertilized agriculture, biomass burning	14	9
COS	Wetlands	Biomass burning	12.5	~900
Sulfur gases*	Wetlands, wet tropical forest, oceans	Fertilized agriculture, biomass burning	13	2

*Includes other reduced sulfur gases such as hydrogen sulfide (H_2S), dimethyl sulfide (DMS), methyl mercaptan (CH_3SH), and carbon disulfide (CS_2).

In addition to biogenic sulfur gases, sulfur enters the atmosphere as aerosols from sea salt, gas from volcanoes, through deflation of sulfate-containing dust in arid regions, and as a result of biomass and fossil fuel combustion. Fossil fuel combustion is the major perturbation to the global sulfur cycle, but human activities can also change fluxes of sulfur to the atmosphere through the formation or drainage of wetlands and through desertification.

Effects of additional atmospheric sulfur on terrestrial ecosystems include well-documented biotic changes attendant upon lake and stream acidification (*97*), and alterations in nutrient cycling within forest ecosystems (*85*). Another major effect of sulfur gas emissions could be an increase in the background (at times of low volcanic activity) stratospheric sulfate aerosol layer caused by increasing concentrations (not yet documented) of the relatively stable gas COS (*98*).

Interactions with tropospheric ozone. Ozone is unique in that it absorbs short-wave ultraviolet in the stratosphere and thereby serves to protect living organisms, whereas in the troposphere it is a strong oxidant that can damage organisms (*54*). Hence both its breakdown in the stratosphere and its increasing concentrations in the troposphere represent serious environmental problems (*19*). Occasional episodes of elevated ozone concentrations are currently observed in industrial and developed agricultural regions, and tropospheric ozone is demonstrably reducing productivity and yield in agriculture (*99*) and most likely in natural ecosystems in much of the developed world.

Many of the reactive gases interact with ozone (and its daughter product the hydroxyl radical) in complex ways. Hydroxyl radical and ozone are major oxidants in the breakdown of CO, CH_4, isoprene, and terpenes. At low concentrations of NO, CO oxidation represents a sink for O_3. At elevated NO concentrations, however, O_3 concentrations can actually be increased during CO oxidation (*84*). This interaction may be partially responsible for increasing tropospheric ozone concentrations in developed regions (*100*). Further increases in NO concentrations due to fossil fuel combustion, biomass burning, or agricultural fields could cause more widespread increases in tropospheric ozone.

Conclusions

The interactive nature of the biota and the atmosphere has become increasingly understood in recent years. Large amounts of many biologically produced trace gases are exchanged annually between the atmosphere and biosphere (Table 1), and many of these are now increasing in flux or concentration or both as a consequence of human activities. Although trace gases are often considered in terms of globally averaged fluxes, many are highly variable in space and time. Tropical forests and wetlands are particularly active sources (Table 1); and these systems are further subject to rapid alteration through land clearing and drainage. Human activities that generate trace gases are also concentrated into particular ecosystems—fossil fuel combustion is concentrated into the north temperate zone, and biomass burning is most active in areas formerly covered by dry tropical forest and savanna (which are now mostly agricultural and pasture land).

An understanding of atmosphere-biosphere interactions and their effects is a problem vast in scope, one that encompasses the entire planetary ecosystem. Unfortunately, the information available is still insufficient to make reasonable projections on the effects of changes that now occur. What is needed? First, the considerable uncertainty that surrounds estimates of the various gas fluxes between the land and the atmosphere must be reduced. This will involve a more adequate network for global environmental measurements, one which emphasizes the control of spatial and temporal variation as well as new ways for accurately determining land use changes and associated changes in gas fluxes. Second, methods for measuring and integrating gas fluxes on regional scales comparable to those used in global circulation models must be developed and refined. Finally, experiments must be performed at the level of whole ecosystems to develop the capacity to predict the consequences of a changing atmosphere and climate.

New research initiatives are under way that propose such global studies (*101*). These initiatives build upon the emerging technology of laser-based measurements of atmospheric chemistry, planetary boundary-layer sampling, and means for viewing continuously not only the state of the earth's terrestrial ecosystems but also of their exchange processes. A concerted effort in this area should yield the ability to analyze and predict how biologically driven fluxes of trace gases either cause or could cause changes in atmospheric chemistry, radiation budget and climate, and the functioning of terrestrial ecosystems.

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