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BIOLOGICAL CYCLING OF ATMOSPHERIC TRACE GASES

final report prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C. 20546

prepared by

ARTHUR D. LITTLE, INC.
CAMBRIDGE, MASSACHUSETTS 02140

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Dian R. Hitchcock
Alfred E. Wechsler

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I. SUMMARY

A. PURPOSE AND SCOPE

The purpose of this program was to conduct a detailed critical review of present knowledge of the influence of biological processes on the cycling of selected atmospheric gas constituents--methane, carbon monoxide, and gaseous compounds of nitrogen (nitrous oxide, ammonia, nitric oxide, and nitrogen dioxide) and sulfur (hydrogen sulfide and sulfur dioxide). The work included the identification of biological and other sources of each gas, a survey of abundance measurements reported in the literature, and a review of the atmospheric fate of each constituent. The study provided information on which to base conclusions regarding the importance of biological processes on the atmospheric distribution and surface-atmosphere exchange of each constituent, and a basis for estimating the adequacy of present knowledge of these factors. We also conducted a preliminary analysis of the feasibility of monitoring the biologically influenced temporal and spatial variations in abundance of these gases in the atmosphere from satellites.

At the beginning of this project, we hoped to include carbon dioxide within the scope of the study, but limited resources required us to eliminate it as a major topic. Several publications appearing after we began our project (SCEP, 1970; SMIC, 1971; Manabe, 1971; and Bolin, 1970) appear to provide satisfactory coverage of CO_2, and we concluded that we could add little to the published information.

The gases we examined are, in our opinion, the most important trace gases in the atmosphere, including the common reduced gases and the gaseous forms of nitrogen and sulfur. Some of them--CO, SO_2, and NO_x--are common "pollutant" effluents of industrial processes. Because we are concerned with natural cycles of these compounds, we have given little attention to industrial sources, except to note them and to consider the errors that such sources may have introduced into quantitative estimates of global cycles.

In addition to direct gaseous emissions and consequent increases in the amount annually in circulation, human activity can also affect the natural cycles by altering the biological activities which provide sources or sinks for such constitutents. Where information on these effects was available, we have considered and presented it together with other findings.

B. GENERAL CONCLUSIONS

(1) There are large biological sources and/or sinks for CO, CH_4, N_2O, NO, NO_2 and SO_2, and there may be a significant natural source of H_2S. However, available information is in all cases inadequate to estimate accurately the amount of each gas annually cycled through the atmosphere as a consequence of biological activity. The range between the minimum and the maximum probable quantity cycled per year is very large--an order of magnitude for some gases and a factor of two for others. Information regarding the biological cycling of the industrial pollutants CO, SO_2, and NO_x is insufficient to determine reliably whether the anthropogenic emissions represent a large or a small proportion of the total in circulation. The uncertainty is such that these pollutant sources could supply as much as one third to one half the total in circulation, or as little as 5% or less.

(2) The unreliability of the estimates of the natural cycles is due to inadequacies in many kinds of data, but the most outstanding contributors to the present uncertainty are:

(a) Information regarding the ionic content of rivers draining the major continents. Present estimates of the total sulfur and nitrogen in circulation are partly based on analyses of river water collected prior to the recent very large increases in fossil fuel consumption in Europe and North America. In the case of Europe, most of the data were collected prior to 1910 and in a manner now regarded as highly unreliable, due to outmoded technology and statistically inadequate sampling techniques. Data for rivers in the United States are much better than those for Europe, having been collected during the present century. but even these studies are not adequate to the needs of workers wishing to evaluate the effects of recent industrialization and modification of agricultural techniques on continental runoff. Analyses of rivers in Africa, Asia, and South America are scanty and must be broadened if understanding of the natural background cycles is to be improved.

(b) Chemical analyses of precipitation. Many important biologically cycled atmospheric compounds are returned to the surface in precipitation, as gases absorbed from the atmosphere, or as ions derived from particulates washed out of the atmosphere. Most of the analyses now used to estimate global transfer rates were derived from studies of rain collected in regions of Europe and the United States that are almost certainly affected by industry and intensive agriculture. These estimates should be supplemented with analyses of precipitation in remote regions far from pollutant sources. Many of the available analyses of precipitation are of questionable utility insofar as studies of atmospheric nitrogen cycles are concerned; the chemical form of nitrogen compounds may be altered after collection in rain gauges by biological activity, which may oxidize ammonia or organic nitrogen to nitrite or nitrate.

(c) Direct measurements of atmospheric trace gas abundances. In general, the biologically cycled atmospheric constituents are present in the non-urban atmosphere in very low concentrations and show considerable variation in abundance due to variations in the kind and amount of local biological activity. The most abundant compounds studied--methane, carbon monoxide, and nitrous oxide--are present in the range of 0.1 to about 1.5 ppm, while all the remainder--sulfur dioxide, hydrogen sulfide, nitric oxide, ammonia, and nitrogen dioxide--are measured in parts per billion or less. Accurate measurement of such low concentrations in the field presents very difficult problems which have been solved only recently, if at all.

Most atmospheric sampling, like most precipitation analysis, has occurred in relatively densely populated regions of industrially advanced nations, usually in attempts to understand the influence of pollutant sources. These measurements cannot be reliably extrapolated to the entire globe; baseline studies of atmospheric concentrations should be made in diverse, remote, unpolluted environments.

Most existing measurements were made at or very near ground level, so there are few abundance profiles of trace gases for any locations. This information is essential if we are to improve estimates of the total atmospheric load of any biologically cycled gas and understand its atmospheric fate.

(3) Satellite-mounted atmospheric gas sensors appear to have the necessary sensitivity for monitoring biologically influenced variations in atmospheric abundance of trace gases. This potential, combined with the possibility of using such sensors to examine many parts of the globe with the same instrument at nearly the same time, suggests that their use for this purpose may be extremely advantageous.

(4) In addition to adding pollutant emissions to the atmospheric load of gases which are biologically cycled, human activities may increase the biological emissions by establishing and maintaining the conditions for anaerobic production of some gases. Thus, there is some evidence that man-made swamps--rice paddies--may be the major source of atmospheric methane and that methane is emitted into the air near sewage outfalls.

Although this is no cause for immediate concern, since methane is relatively innocuous, more serious questions concern the possibility that the increased biological oxygen demand resulting from nutrient and organic pollution of rivers and coastal regions may greatly increase the atmospheric load of biogenic sulfur dioxide. The available evidence is fragmentary; the mechanisms by which biogenic hydrogen sulfide produced in anoxic water or muds is converted into atmospheric sulfur dioxide are obscure. However, there is some evidence of biogenic sulfur dioxide sources in the open ocean, which implies that the transfer does occur even when the mud in which the sulfide is produced is not exposed to the open air. If this is the case, then increases in the extent of anaerobic activity due to pollution--which seem to occur widely--will be accompanied by increases in the amounts of biogenic sulfur dioxide injected into the atmosphere.

C. SPECIFIC CONCLUSIONS

1. Methane

Methane concentrations in the lower troposphere range between about 1.2 to 1.5 ppm. Its concentration falls off rapidly in the stratosphere, where it is rapidly oxidized by atomic oxygen. The final product of methane oxidation in the upper atmosphere is water and carbon dioxide, and methane is believed to be a major source of water above the tropopause.

Methane is biologically produced by specialized but ubiquitous bacteria in oxygen-free environments where organic matter is abundant. While some methane is produced in swamps and wet soils, some investigators believe rice paddies to be the major natural source. Methane is also biologically oxidized by specialized bacteria found in oxygen-rich environments. These organisms can be isolated from the surface scum in swamps, rice paddies, and canals, and from most soils. Since there have been very few measurements of atmospheric methane near regions of methane production, it is not possible to determine how much of the methane produced in nature is emitted into the atmosphere and how much is biologically consumed before it reaches the atmosphere. Enteric fermentation in large ungulates is also a small but possibly significant source of atmospheric methane. Estimates of biological production of atmospheric methane are very uncertain, but the amount annually produced probably falls in the range 45 to 470 million metric tons.

Anthropogenic sources of methane include gasoline exhausts; natural gas lost during production, transportation, and use; and the natural gas released from coal and lignite mines during mining. Together, these sources contribute between 17 and 68 million tons of methane to the atmosphere each year. As much as 100 million tons of methane may be derived from rice culture in paddies, and this quantity should be considered anthropogenic.

The stratospheric sink for methane has been estimated (on the basis of two vertical abundance profiles) to be approximately 21.4 million tons per year. The discrepancy between this figure and the lowest estimates for biological and anthropogenic emissions implies a tropospheric sink, which may be biological in nature. Very few measurements of methane abundance have been made, and more are needed to determine the strength of natural biological sources and the existence of biological sinks, as well as to refine estimates of the strength of the stratospheric sink.

2. Carbon Monoxide

Biological activity appears to constitute both a source and a sink for atmospheric carbon monoxide. It is produced in marine environments as a direct metabolic product excreted into the water by microorganisms, seaweed, and other organisms, and is also produced as a product of the photolytic decomposition of dissolved organic matter. Seawater is supersaturated with CO, and consequently there must be a transport of CO from water into the air. Estimates of the magnitude of this transport vary from 9 million tons per year for the entire ocean to 330 million tons per year for the northern hemisphere alone. Rain is also supersaturated with CO, and clouds may constitute a source of atmospheric CO. Laboratory studies have demonstrated that carbon monoxide may be both emitted and absorbed by land plants and soils, but present evidence is too fragmentary to support estimates of the total source and/or sink strength of land surfaces.

Anthropogenic sources of CO contribute about 240 million tons per year to the atmosphere, the bulk of which is produced by internal combustion engines. Lesser quantities are contributed by other fossil fuel combustion processes, forest fires, and the burning of agricultural wastes.

Estimates of the residence time of CO range from 0.1 to 9 years. Present knowledge of the exchange of air between the troposphere and the stratosphere and of circulation in the stratosphere is inadequate to determine the effectiveness of the stratospheric sink, or the existence of large biological sinks at the surface. Consequently, there remains some question whether accelerating rates of anthropogenic CO emission will gradually increase the tropospheric load of CO.

Present uncertainties regarding the magnitude of the biological CO cycle and the residence time of CO could be resolved by additional information regarding the ^{14}C activity of CO in well-mixed tropospheric air, field studies of the exchange of CO between plants and soils and the atmosphere, and more measurements of CO abundance in marine air and in the southern hemisphere.

3. Nitrogen Compounds

The major gaseous nitrogen compounds in the atmosphere, other than molecular nitrogen, are nitrous oxide, ammonia, nitrogen dioxide, and nitric oxide. All of these gases are injected into the atmosphere as a result of biological activity, and there is evidence that most of them may be absorbed in gaseous form by soils, as a consequence of soil properties which are the direct or indirect result of microbial activity.

The biological processes which implement the cycling of nitrogen in nature and the emission and uptake of biogenic atmospheric compounds are known only in outline. There is little information regarding the environmental and biological factors that influence the direction and magnitude of the biological transformations of nitrogen. As a result, reliable estimates of the exchange of biogenic nitrogen compounds with the atmosphere are not presently available, nor is it possible to determine the extent to which agricultural practices may have modified these exchanges.

(a) Nitrous Oxide. Nitrous oxide is produced in soils deficient in oxygen as a by-product of the biological reduction of nitrate. This latter compound is used as a source of oxygen. If nitrate levels are low, N_2O may be reduced to N_2 for the oxidation of organic compounds. N_2O is also produced in aerated soils as a product of the biological oxidation of ammonia, and there may also be a marine source of this gas.

Nitrous oxide is the most abundant of the nitrogen trace gases. Its mean tropospheric abundance may be about 0.25 ppm, although reported measurements show ground-level abundance to vary between 0.15 and 0.4 ppm. Nitrous oxide is chemically stable in the troposphere. The only efficient atmospheric sink appears to be photochemical conversion to N_2 and O in the stratosphere, which has been estimated to account for about 15 to 23 million tons of N_2O per year.

Estimates of the residence time of N_2O in the atmosphere, based on vertical abundance in the troposphere, suggest an annual exchange on the order of 144 million tons per year or more; the latter implies the existence of a tropospheric sink, presumably at the surface of the earth. This inference is consistent with the reported variations in ground-level abundance (which suggest a relatively short lifetime) and observations that N_2O can be taken up by soils as a result of biological activity.

(b) Ammonia. Ammonium is biologically produced in soils and aquatic environments as a product of the decomposition of organic matter, and is used as a source of nitrogen by plants. The evolution of gaseous ammonia from soils is not well understood; it appears to depend in a complex way on pH, moisture, organic matter and clay content, and the nature and activity of populations of soil organisms.

Atmospheric ammonia concentrations near the surface show large variations with time and may average between 10 and 30 ppb. Much higher concentrations are encountered in regions characterized by extensive dairy or feedlot operations. The gas may be directly absorbed by soils, but the factors that control this process are not clearly understood. Ammonia is very soluble in acid solutions and is absorbed by cloud and rain droplets. The joint presence of ammonia and sulfur dioxide in the atmosphere leads to the production of ammoniated sulfate aerosols, which may be removed in rain or deposited as dry particulates.

We have found no reliable observations of the abundance profile of ammonia in the atmosphere; however, there are reasons to believe that its abundance drops rapidly with altitude, due to the fact that its removal is greatly influenced by humidity and precipitation. One recent observation suggests that there is less than 0.05 ppb NH_3 above the Pyrenees.

Ammonia exchange with the atmosphere may be estimated on the basis of the ammonium content of precipitation, but measurements of the latter are uncertain because the chemical form of nitrogen compounds in precipitation may be biologically altered in precipitation gauges prior to its collection for analysis. Most of the transfer of ammonia from the atmosphere to the surface may occur by the fallout of particulate ammonia or the direct absorption of gaseous ammonia, but there is very little information on which to base reliable estimates of these rates. Although observations of the ammonia content of marine air imply a marine source of ammonia, most analyses of the ammonia concentration of sea water fail to show the supersaturation that would be expected if large marine sources exist.

Available information suggests that between about 300 and 1200 million tons of NH_3-N cycles through the atmosphere annually. Direct absorption of gaseous ammonia may account for 300 to over 700 million tons.

(c) Nitric Oxide and Nitrogen Dioxide. Observations of the abundance of NO and NO_2 in regions presumed to be remote from pollution imply that both are the direct or indirect consequence of microbial activity in soils, but the mechanisms involved are obscure. NO may be produced by the decomposition of nitrites, which are formed by the biological oxidation of ammonia and the biological reduction of nitrate. Most soil scientists feel that the conditions which lead to the accumulation of nitrite and to its breakdown to NO are rare and unlikely to be of global importance, but the subject has not been thoroughly studied. NO is rapidly oxidized by ozone to NO_2, which undergoes numerous photochemical reactions with biogenic organic compounds to produce a natural smog.

Observations in rural or remote regions show that NO_2 ranges from about 0.1 to nearly 12 ppb and that NO ranges from less than 0.2 to nearly 2 ppb. Since both gases are extremely short-lived, they are probably most abundant near the surface of the earth.

A number of atmospheric reactions of NO and NO_2 with ozone and water vapor lead ultimately to the production of nitric acid vapor; this reacts with aerosols and particulates to form aerosol nitrates, in which form the gases are ultimately returned to the surface. In addition, NO_2 may be directly absorbed by plants or soils. Estimates of the total NO_x in natural circulation in the atmosphere are extremely unreliable, due to the difficulties of estimating the total nitrate removal mechanisms and the NO and NO_2 abundances in remote regions. The natural circulation of NO_x could be as low as 25 million tons per year as N or as high as ten times this quantity. Approximately 16 million tons of NO_x-N is annually emitted as a consequence of fossil fuel combustion.

4. Sulfur Compounds

Sulfur dioxide is the principal gaseous sulfur compound in the atmosphere. In remote, unpolluted environments, its concentration ranges from less than 1 to about 2 ppb. Hydrogen sulfide is believed by many to be the atmospheric precursor to SO_2, but there are no reports of successful attempts to detect it in these regions at the very low concentrations--about 0.5 ppb or less--at which it may be present.

Atmospheric sulfur dioxide is rapidly oxidized to sulfate aerosol (probably ammonium sulfate) in the presence of atmospheric ammonia (NH_3 and NH_4^+ aerosol) at rates which depend on the humidity and the ammonia concentration. The lifetime of sulfur dioxide probably ranges from hours to days. Sulfur as sulfate aerosol is present near the ground in remote regions at concentrations in the range of 2 to 8 mg/m^3. Ammonium sulfate particulates make up the bulk of the stratospheric haze and have been detected at altitudes up to 30 km. The source of this stratospheric sulfate is unknown.

Biogenic sulfur dioxide in the atmosphere is a consequence of the production of H_2S by bacteria that reduce sulfate to oxidize organic matter in aquatic environments in which dissolved O_2 has been consumed by prior biological activity. These environments include wet soils, swamps, the muddy bottoms of lakes, coastal wetlands and estuaries, organic-rich marine muds, and some fjords and ocean deeps where physical barriers prevent flushing with oxygenated water. While there is indirect evidence that biogenic sulfur dioxide does enter the atmosphere, no reliable estimates of the magnitude of the biological cycle can be made at the present time, partly because the mechanisms by which sulfide in anoxic waters or muds is converted into sulfur dioxide in the atmosphere are obscure. It has been proposed that soils and periodically exposed tidal flats are the only sources of biogenic SO_2, but the hypothesis that large quantities of H_2S can be directly emitted from such regions has been challenged. The observation of comparatively high levels of SO_2 in clean ocean air and of large quantities of non-pollutant sulfate in clouds formed at sea imply marine sources of biogenic SO_2. SO_2 of local origin has also been observed in tropical forests at sites remote from pollution sources. The total quantity of biogenic sulfur in atmospheric circulation is probably between 100 and 800 million tons per year.

Volcanoes contribute 7 to 12 million tons of atmospheric sulfur per year as SO_2 or SO_4^{--}. Sea salt particles formed by wave action contribute about 45 to 400 million tons of sulfur as sulfate per year. Industrial sources of atmospheric SO_2 account for about 70 million tons S, and an additional 26 million tons of sulfur is released as industrial sulfuric acid effluents or applied to the land as fertilizer and ultimately removed as sulfate in rivers. About 15 to 43 million tons of sulfate sulfur in rivers is derived from rock weathering, while acid mine drainage contributes about 15 million tons per year.

When all the available uncertainties are taken into consideration, the direct anthropogenic contribution to the total sulfur in circulation is between about 8% and 35% of the total. It may be assumed that the biogenic sulfur circulation has increased as the direct result of organic pollution of coastal waterways and rivers, which promotes anaerobiosis, but it is impossible to say at present how much.

5. Feasibility of Monitoring Biologically Cycled Gases from Satellites

Measurements of the spacial and temporal variations of the concentration of important biologically cycled gases are important to further the understanding of global sources and sinks and atmospheric lifetimes of these gases. Earth based monitoring stations have been proposed; however a large number would be required for monitoring gases with short lifetimes. Monitoring these trace atmospheric gases by satellite has the potential advantage of providing frequent coverage over a large portion of the globe thereby obtaining data on gas circulation patterns, sources and sinks, both in the long and short term. We briefly examined the feasibility of monitoring CH_4, CO, N_2O, NH_3, NO, NO_2, SO_2 and H_2S by infrared absorption spectroscopic techniques from satellites considering two types of measurement concepts--measurement of infrared solar energy reflected by the earth (energy which passes near vertically through the earth's atmosphere) and measurement of infrared solar energy transmitted through the atmosphere nearly parallel to the surface (earth limb occultation). Two criteria for feasibility were considered: (1) the method must have sufficient sensitivity to detect concentration differences (preferably vertical concentration differences as well as total abundances) of about 1/10 the anticipated background concentration levels at the surface and in the upper atmospheric levels and (2) suitable infrared spectral windows must be available for the absorption measurements of the trace gases without extensive interference by the more abundant atmospheric gases. From a review of spectroscopic principals we concluded that most of the trace gases would be detectable at concentrations of 0.01 to 10 ppb depending on the absorption characteristics of the gas, the optical path, and the gas distribution within the path.

Limb measurements will be most useful for determining vertical abundance profiles, whereas direct reflection measurements will provide detailed global coverage. These sensitivities are sufficient for monitoring gases such as CH_4, CO, and N_2O whose normal concentrations near the surface range from 0.1 to 3 ppm and troposphere and stratosphere concentrations are expected to vary from 0.03 to 1.5 ppm. Anticipated instrument sensitivity will probably be adequate for measurements of NH_3, NO, NO_2, SO_2 and H_2S in the lower atmospheric regions but marginal in the upper regions.

From high-resolution atmospheric transmission spectra recorded with ground-based spectrometers using the sun as a source, we conclude that there are suitable spectral regions for measuring all trace gases of interest through the limb, and for measuring all but NO and SO_2 in reflected sunlight. Although much additional work would be required to select the best spectral line or lines for each of the gases of interest, sufficient data have been obtained to demonstrate feasibility in terms of available spectral windows.

These analyses and evaluations indicate that it is probably feasible to make remote measurements from satellites to obtain data on the spatial and temporal distributions of trace gases for the purpose of determining the effects of biosystems on atmospheric composition. A great deal remains to be done, however, before a satellite monitoring program can be implemented. Two critical tasks are discussed below.

(a) Ground-Based Studies. Optimum spectral retions for making trace gas distribution measurements can be selected, and achievable sensitivity can be evaluated through ground-gased measurements. High-resolution infrared spectrometers, such as those now installed at a number of laboratories throughout the world, should be used to record the spectra of trace gases when these are not available and to measure slant-path transmission for both large and small solar zenith angles from representative locations. These spectra can be analyzed to determine the optimum resolving power for a space instrument and optimum spectral regions for its operation. In addition, such data will serve to provide better information on background trace gas levels integrated over long paths than is now available. Such a study is entirely within the state of the art and could be implemented at relatively low cost.

(b) Instrument Development. A study should be undertaken to determine the most effective means of making trace gas concentration measurements from a satellite, both in reflected sunlight and through the limb. It is not evident at this time what the best measurement approach would be. A variety of techniques should be considered, including dispersive spectroscopy, interference spectroscopy with both Michelson and Fabry-Perot instruments, and non-dispersive correlative techniques.

When the systems performance analysis is complete, the most effective approach should be adopted and a prototype instrument developed. The instrument should then be thoroughly tested from the ground using the sun as a source.

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PART I. BACKGROUND

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II. INTRODUCTION

G. E. Hutchinson (1954) pointed out that the most remarkable feature of our planet is the fact that the atmospheric gases, in contact with the liquid and solid materials at the earth's crust, do not represent a mixture in thermodynamic equilibrium, and that this feature is due to the relationship between the atmosphere and the living matter of earth. This observation implies that the biology of earth must constitute a system for actively regulating the composition of the atmosphere and maintaining it in this state of thermodynamic improbability, since most available evidence indicates that the proportions of the major components of the atmosphere have probably not greatly deviated from their present levels in many millions of years.

We have proposed that the maintenance of atmospheric composition is not only a property of terrestrial life, but that it is a function which must be common to the biological systems of every planet on which life is present; consequently, the presence of life on Mars or other planets can be inferred on the basis of observations of chemically anomalous atmospheric mixtures, even though they may bear little resemblance to the oxygen-rich atmosphere of Earth (Hitchcock and Lovelock, 1967). Present knowledge of the biochemistry of the atmosphere supports this proposal, but it is woefully inadequate as a basis for interpreting the biological significance of planetary atmospheres. We do not know enough about the biological and other mechanisms presently supporting the cycling of atmospheric constituents to understand the way in which the composition of the atmosphere is regulated and the degree of control exercised on it by the highly evolved life of Earth. We know still less about the influence of primitive life on the early atmosphere, or the stages through which the atmosphere evolved in parallel with life.

In recent years, the more urgent practical question of the impact of Man on the ecosystem has arisen. It is now apparent that industrial effluents of carbon dioxide are quantitatively significant on a global scale rather than producing merely local effects, and that they are causing the total atmospheric load of this gas to rise at an accelerating rate. Is this buildup evidence that the human capacity for emitting gases into the atmosphere now exceeds the ability of natural processes to regulate their abundance? If this is the case for carbon dioxide, is it also true of other trace gases which are naturally cycled, particularly sulfur dioxide and oxides of nitrogen? What has been the impact of extensive agriculture, deforestation, wetlands clearance, strip mining, and water pollution on the biological mechanisms that cycle atmospheric constituents? These human activities have changed the face of the earth and the distribution of plant and animal life. Can they have failed to have an impact on the global cycling of trace gases of the atmosphere?

There are at present no answers to these questions, because our knowledge of the magnitude and nature of the "natural" cycles of atmospheric constituents is extremely primitive. We can only make educated guesses regarding even the relative magnitudes of the anthropogenic and natural emissions of such important effluents as sulfur dioxide and carbon monoxide.

The first step toward the goal of understanding the biological influences on the atmosphere--whether this knowledge is viewed as essential to an understanding of the atmospheric biochemistry of other planets or the impact of Man on our own life support system--is a critical review of present knowledge in this field, so as to identify information gaps and specify what is needed to fill them. Such a review has been the primary objective of the work reported here, together with a brief analysis of the feasibility of satellite monitoring of biologically caused variations of abundance of important biologically cycled trace atmospheric gases.

Instead of summarizing the most widely accepted theories regarding rates and mechanisms of surface-atmosphere exchange, we have taken care to explain the evidential bases of the conclusions drawn by workers in the field and to reveal--where relevant--the high degree of uncertainty that characterizes practically every aspect of this subject. In doing so, it has not been our intention to establish unreasonably rigorous scientific standards upon which the efforts of many workers will be judged to be inadequate or to criticize specific investigators who have spent much effort on this difficult problem. Instead, our aim has been to document, for the benefit of readers not familiar with the field, how very meager and uncertain this information actually is.

Part I of this document is devoted to introductory material. Chapter III describes the major reservoirs of earth--the atmosphere, hydrosphere, lithosphere, and biosphere--and the manner in which material is exchanged between them. This chapter thus serves as a general introduction to the subject of the biosphere and its interaction with other major reservoirs of earth; it also functions as a reference section that summarizes information presented in other parts of the report. The discussion of the biosphere in Chapter III emphasizes the role of plants in cycling atmospheric oxygen and carbon and describes the important role played by anaerobic microbial metabolism in completing the atmospheric cycles of sulfur and nitrogen, and as sources of the common reduced gases of the atmosphere.

Part II is devoted to a discussion of methane, carbon monoxide, and atmospheric compounds of nitrogen and sulfur. Each compound or family of compounds is considered from the point of view of its atmospheric abundance, sources, atmospheric fate, and probable rate of cycling. Since we are uncertain of the total amount of any trace gas annually cycled in the atmosphere, we have attempted to present the range of estimates reported in the literature (or those which can be inferred from available information), to discuss the evidence on which these estimates are based, and to identify the major uncertainties and most important information gaps. Special attention is given to the range of observed abundances of the various gases in remote unpolluted environments, the effects of pollution on these abundances, and the observed variations in abundance which may be attributed to variations in the rates of biological emission or uptake. Implicit in the latter discussions is a consideration of the availability of abundance information and of its usefulness in improving our knowledge of the nature and effectiveness of biological cycling mechanisms.

Part III reports the results of a preliminary evaluation of the feasibility of monitoring variations in the abundance of these trace gases from satellites. In addition to summarizing the distribution of trace gases in polluted and unpolluted environments, it reviews the kinds of inferences which could be drawn from improved knowledge of biologically caused variations in the abundance of these gases and discusses the accuracy and precision with which these variations should be observed. It concludes by examining the technical feasibility of infrared monitoring of atmospheric trace gas concentrations.

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III. TERRESTRIAL RESERVOIRS

A. INTRODUCTION

This chapter contains a brief introductory description of each of the major reservoirs of earth among which the constituents of the atmosphere may circulate. These are:

- the lithosphere, including soil (the pedosphere);
- the hydrosphere, which includes all the water on earth, but in particular the ocean, which is the major aquatic reservoir of material;
- the atmosphere; and
- the biosphere, including all living creatures on earth as well as organic remains of prior living creatures.

A schematic diagram of these reservoirs and the major exchanges among them is shown in Figure III-1. Table III-1 contrasts the physical dimensions of these reservoirs with those other portions of the earth.

The basic geochemical cycle is that of weathering and erosion of the land, accompanied by transfer of the eroded material to the ocean in streams and by the movement of ground water. Material in the ocean sediments out on the ocean bottoms. In geological time, movements of the crust bring this material above the level of the ocean, and the cycle starts again. Although the rate at which this process transfers material is large in absolute terms (more than 2×10^{16} g per year), it is nevertheless quite small in terms of the total capacity of each reservoir: the mean residence time of material in the lithosphere is appropriately measured in terms of units of 10^8 years, and in the oceans in units of 10^5 to 10^6 years.

The land biosphere and the atmosphere constitute two reservoirs in which the residence times of the components are much shorter--on the order of a hundred years or less for the land biosphere, and from less than one year to about 90,000 years for the atmosphere. The marine biosphere is separated from the other reservoirs and is shown in

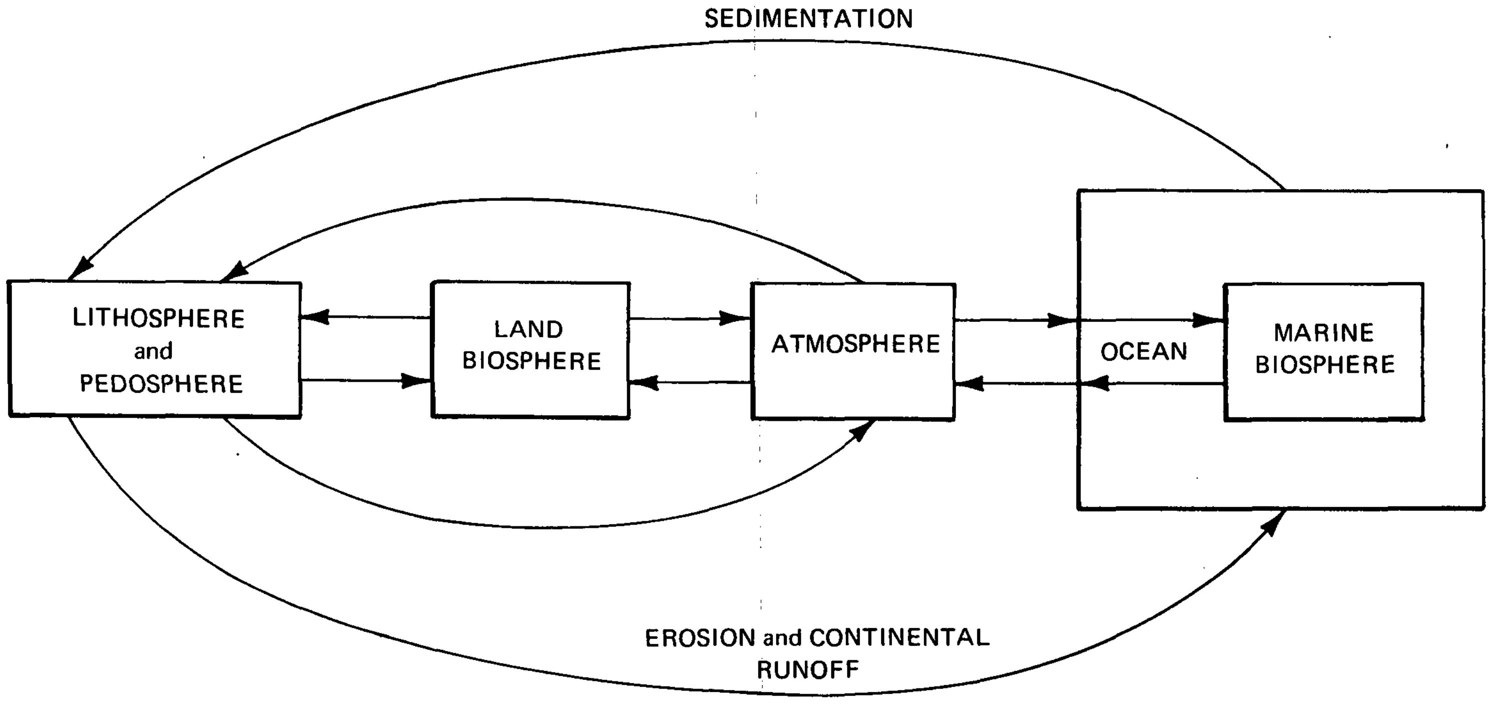

FIGURE III–1 MAJOR PATHWAYS OF RESERVOIR EXCHANGE

TABLE III-1. - TERRESTRIAL RESERVOIRS

	Chemical Characteristics	State	Thickness (km)	Volume (unit of 10^{27} cm^3)	Mean Density (gm/cm^3)	Mass (unit of 10^{27} gm)	Mass Percent
Atmosphere	N_2, O_2, H_2O, CO_2, inert gases	Gas	100 (7.84 at STP)	.005 (.0004 at STP)	0.001 (0.11 at STP)	0.00000514	0.00009
Biosphere	H_2O, C, N, Ca, SiO_2, S and P	Solid and liquid matter, often colloidal					
Hydrosphere	H_2O and dissolved salts	Liquid and solid	3.80 (mean)	0.00172	1.023	0.00176	0.024
Crust	Silicate rocks with an average composition of igneous rock; oceanic crust low in SiO_2; continental crust high in SiO_2	Solid	40 (continental crust) 6 (oceanic crust) 17 (mean)	0.008	2.8	0.024	0.4
Mantle	Silicate materials enriched in Fe and Mg and less siliceous than crustal rock; probably olivine and pyroxene and their high-pressure equivalents	Solid	2,883	0.899	4.5	4.016	67.2
Core	Iron-nickel alloy, perhaps with Si	Outer core, liquid inner core, solid	3,471	0.175	11.0	1.936	32.4
Whole earth			6,371	1.083	5.52	5.975	100.00

SOURCE: Modified from Garrels and Mackensie (1971).

Figure III-1 completely contained in the ocean. Although it exchanges material with the atmosphere, the communication is not direct, in that gases in exchange pass through the ocean.

The major exchanges involving the land biosphere and the atmosphere may be summarized as follows: the land biosphere exchanges water and inorganic nutrients with the soil, cycles all atmospheric gases except the noble gases, and releases a number of complex volatile hydrocarbons and other volatiles together with light particles such as pollen, spores, insect debris, etc. directly into the atmosphere. An important exchange of particulates takes place between the soil and the atmosphere in which the particles are taken up by wind action and returned by ordinary sedimentation or impaction processes or washed out in precipitation. Some gases released from soil or plants react together in the atmosphere to form particles which are returned to the surface by these mechanisms. The atmosphere also exchanges particulate and gaseous material and water with the oceans.

B. LITHOSPHERE AND PEDOSPHERE

The lithosphere is the parent rock of the surface of the crust--including sedimentary rocks--and is the source of the weathered material that is ultimately transported to other reservoirs. Strictly speaking, much of this interaction is with soils rather than parent rock, and for this reason we include soils--the pedosphere--in this reservoir.

Estimates of the distribution, composition, and mass of the various types of rocks on the surface of the earth are necessarily based on theories regarding their mode of formation and on observations that amount to a very imperfectly random sampling of materials on or near the surface. Most of the values cited in this section must be interpreted as rough estimates which may be greatly in error.

Rocks are conventionally divided into igneous rocks, formed by magmatic processes, and sedimentary rocks, which are produced by the more selective secondary process of weathering. Magmatic crystallization produces rocks which are different silicate mixtures (gabbros, diorites, and granites); perhaps 60% of these are feldspars, which are aluminosilicates of calcium, potassium, and sodium with many other minerals as impurities.

Sediments are classified in terms of their manner of derivation and formation from parent igneous rock. Although sediments represent a small proportion of the total crust, they cover about three quarters of the surface and are presently of predominant importance as a source of material weathered in the production of soils and transported to other reservoirs.

Table III-2 compares some characteristics of the four major categories of sediments and "conglomerate," which is a miscellaneous mixture.* The chief categoires are sandstones, lutites (including shales), carbonates (including limestones), and evaporites. Sandstones are defined as rocks composed of sand particules ranging in size from 0.05 mm up to a few millimeters in diameter. Although sandstones show a wide range of chemical compositions, quartz is usually a dominant mineral, with feldspars common.

Lutites are composed of clay particles, which are smaller than sand particles. These commonly represent finer debris carried by ice, running water, and wind, the primary erosional agents. Quartz is common in these materials, but the clay minerals are dominant. In addition to shale (the most common lutite), shist, slate, clay, silt, and muds make up this category.

Carbonate rocks are made up of the carbonate minerals calcite, aragonite, and dolomite. Calcite-or aragonite-rich carbonate rocks are termed limestones; dolomite-rich rocks are called dolomite. Many carbonate rocks have formed as a result of the precipitation of calcite or aragonite by organisms and incorporation of the skeletons of these organisms into sedimentary deposits.

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* This table does not distinguish between the deposited <u>sediments</u> (such as mud and clay) and the <u>sedimentary rocks</u> (such as slate and shists). The latter are formed from the sediments by the lithification process involving heat, pressure, ion exchange, etc.

TABLE III-2. - SOME CHARACTERISTICS OF SEDIMENTARY ROCKS

Rock	Some Sediment Equivalents	Some Metamorphic Equivalents	Origin	Grain Size	Major Minerals	Wt % of Sedimentary Rock Mass
Conglomerate	Pebbles Cobbles Boulders	Conglomerite	Clastic particles (shell fragments)	> 2 mm	Rock fragments	< 1
Sandstone	Sand	Quartzite	Clastic particles	0.05 - 2 mm	Quartz Feldspar Rock fragments	15-20
Lutite	Silt Mud Clay	Slate Schist	Clastic particles	< 0.05 mm	Clay minerals Quartz Feldspar	70-80
Limestone	Reef Lime mud	Marble	Biochemical precipitate, inorganic precipitate clastic particles	Variable, up to cms	Calcite Dolomite Aragonite	≃ 5-15
Evaporite	Salt	None	Precipitate from evaporating water	Variable, up to cms	Halite Gypsum Anhydrite	≃ 5

SOURCE: Garrels and Mackensie (1971).

Evaporites are formed by the evaporation of water, which results in the precipitation of the salts dissolved in it. Although some evaporite deposits are formed from lakes, the most important ones are the result of evaporation of seawater. Calcium sulfate is deposited as gypsum ($CaSO_4 \cdot 2H_2O$) or anhydrite ($CaSO_4$) in evaporite formations.

With rare exceptions, chemical weathering takes place in soils; the manner in which the parent rock is weathered and the products of this weathering are to a certain extent dependent on the nature of the soil, its vegetation, and the local climate, particularly the rainfall. Soil is a very complex mixture of organic and inorganic particles with varying amounts of water in which both organic and inorganic materials are dissolved. Biological activities in the soil produce CO_2 in the soil atmosphere, often at concentrations 10 to 30 times that of the free atmosphere; as a consequence, the water in soil is generally a weak carbonic acid.

Chemical weathering consists of the reaction of this carbonic acid solution with the parent minerals present in the soil. Carbonic acid attacks the parent material to separate it into <u>hydrozolates</u> (clay minerals) and <u>resistates</u> (quartz, Fe_2O_3, and Al_2O_3) by removing such bases as potassium, magnesium, and calcium into the soil mixture as soluble carbonates. This in turn releases oxides of aluminum and silicon that form unstable colloidal particles in the soil and absorb available potassium ions. Proportionately more aluminum than silicon is released in this step.

Clays are extremely small particles (less than 0.002 mm diameter) and in soils are usually strongly bonded to organic materials. The resistates are larger and are termed silt by soil scientists if they are less than 0.05 mm and sand if they are between 0.05 and 1.0 mm. Above this size the material is gravel. The larger the percentage of clay particles in weathered material, the slower is the rate at which water will percolate through it, while very sandy materials will allow water to flow through them rapidly. Soil chemistry and fertility are closely related to the relative amounts of clay and quartz in the inorganic fraction of the soil.

Erosion of the soil in which clays and sands are present usually results in a size sorting of the particles and the selective accumulation and distribution of sands in such locations as the ocean bottoms at the mouths of rivers or on continental shelves. Clays tend to accumulate in swamps and lagoons and on continental shelves in deeper, less agitated regions.

Other sediments are formed of materials precipitated from solution in the oceans. These include carbonates and silicates, which precipitate out in shallow water or deposit as "oozes" in deep water. Both silicates and carbonates appear to be precipitated out of solution in the ocean surface regions largely as a result of the formation of shells and skeletons. Surface water tends to be oversaturated with respect to calcite and other carbonates to a depth of about 10 to 100 meters. In some environments (e.g., some tropic lagoons), calcite precipitates directly from the water, producing a snowlike white deposit which is not redissolved because of the high degree of saturation. More commonly, however, the actual precipitation from solution is a biological reaction resulting in the formation of skeletal material. After death of the organism, the carbonates are deposited as calcareous ooze on the ocean floor. Siliceous oozes are formed in a similar manner from skeletons of diatoms and radiolarians. Upon lithification, these siliceous oozes become cherts.

An important additional category of sediment consists of the fossilized organic materials coal and oil, which are derived from plant remains.

Each major sedimentary category contains materials of very diverse composition. The most practical way to obtain an estimate of the probable elemental composition of the sediments is to generate a "mean" composition for each major sedimentary type. Table III-3, from Bowen (1966), shows the selected elemental composition of a mean igneous rock (granite), shale, sandstone, limestone, and coal. Given such an estimate of elemental composition, the composition of the lithospheric reservoir could be derived from estimates of the relative proportion of each type of sediment and of the total mass of the sedimentary rocks. Table III-4 is a partial list of the composition of the lithosphere. It is based on the estimates of

TABLE III-3. - PROPORTION OF SELECTED ELEMENTS IN THE LITHOSPHERE

(milligrams per kilogram)

	Igneous Rock	Shale	Sandstone	Limestone	Coal
Al	82,300	80,000	25,000	4,200	
B	10	100	35	20	100
Ba	425	580	50	120	1-3,000
C	200	15,300	13,800	113,500	800,000
Ca	41,500	22,100	39,100	302,000	-
Cl	130	180	10	150	3,000
F	625	740	270	330	80
Fe	56,300	47,200	9,800	3,800	-
H	1,400	5,600	1,800	860	50,000
Mg	23,300	15,000	7,000	47,000	-
Mn	950	850	50	1,100	-
N	20	-	-	- -	15,000
Na	23,600	9,600	3,300	400	480
O	464,000	482,600	491,700	496,800	50,000
P	1,050	700	170	400	-
S	260	2,400	240	1,200	10,000
Si	281,500	73,000	368,000	24,000	-

SOURCE: Bowen (1966)

TABLE III-4. - SELECTED CONTENTS OF THE LITHOSPHERE
(Units of 10^{20} grams)

Element	Igneous	Shale	Sandstone	Limestone	Total Lithosphere[a]
Al	19752	1144.0	47.5	4.2	20948
B	2.4	1.4	0.07	0.02	4
Ba	102	8.3	0.10	0.12	111
C	48.0	218.8	26.2	113.5	407
Ca	9960	316.0	74.3	302.0	10652
Cl	31.2	2.6	0.02	0.15	34
F	150.0	10.6	0.51	0.33	161
Fe	13512.0	675.0	18.6	3.8	14209
H	336.0	80.1	3.4	0.86	420
Mg	5592.0	214.5	13.3	47.0	5867
Mn	228.0	12.2	0.10	1.1	241
N	4.8				5
Na	5664.0	137.3	6.3	0.4	5808
O	111360.0	6901.2	934.2	496.8	119692
P	252.0	10.0	0.32	0.4	263
S	62.4	34.3	0.46	1.2	98
Si	67560.0	1043.9	699.2	24.0	69327

[a] Assumes that igneous rocks total 2.4×10^{22} kg, sediments total 1.7 x 10^{21} kg and distribution of shale, sandstone, and limestone is 84:11:6.

Poldervaart(1955) that the total sedimentary mass is 1.7 x 10^{21} kg and that the relative proportion of shale, sandstone, and limestone is 82:12:6. (We consider the total igneous reservoir to be only the top 16 km, on the grounds that this is the largest volume of material which can reasonably be said to be potentially subject to weathering in geologic time.)

The probable validity of the data in Table III-4 can be judged from the data of Tables III-5 and III-6. Table III-5 contains various estimates of the relative proportions of the three main types of sediments--shale, sandstone, and limestone (carbonates). It will be noted that estimates of the proportions of shale based on observations of its distribution range from 42% to 56% of all sediments, while estimates of its proportion based on theoretical considerations range from 70% to 82%. Table III-6 contains some recent estimates of the mass of the sediments, which range from 1.7 to 3.2 x 10^{24}grams. It is clear that the figures presented here are only rough approximations and should be used with care.

1. Soils

The development of soil is generally accompanied by the development of vegetation on that soil. There is evidence that the presence of vegetation greatly accelerates the process of weathering and soil formation. (See, for example, Cawley, Burrus and Holland, 1969, and Jackson and Keller, 1970.) The buildup of products of weathering is accompanied by the buildup of organic material derived from roots of dead plants and from plant litter deposited on the surface and subsequently decomposed by decomposer organisms. In mature soils, the concentration of organic matter may vary from almost 100% (peats) to less than 1% (desert soils). Some of this organic material is in the process of rapid decay and disintegration, while some is very resistant to the attack of decay organisms. This resistant humus also resists laboratory analysis. Organic matter tends to accumulate in acid or waterlogged soils, because decay bacteria and larger members of the soil fauna tend to be much reduced in numbers; decay is more rapid in well drained, less acid soils.

TABLE III-5. - ESTIMATES OF THE PERCENTAGES OF THE THREE MAJOR LITHOLOGIES IN THE SEDIMENTARY LITHOSPHERE

A. Measured

	Leith and Mead (1915)	Schuchert (1931)	Kuenen (1941)	Krynine (1948)
Shale	46	44	56	42
Sandstone	32	37	14	40
Carbonate	22	19	29	18

B. Calculated

	Mead (1907)	Clarke (1924)	Goldschmidt (1933)	Holmes (1937)	Wickman (1954)	Horn (1966)	Garrels and Mackensie (1969)
Shale	82	80	91	70	83	73	74
Sandstone	12	15		16	8	20	11
Carbonate	6	5	9	14	9	7	15

SOURCE: Garrels and Mackensie (1971)

TABLE III-6. - MASS OF THE SEDIMENTS
(units of 10^{20} grams)

Source	Mass
Poldervaart (1955)	17,000
Horn (1966)	20,400
Ronov (1968)	24,000
Garrels and Mackenzie (1971)	32,000

SOURCE: Garrels and Mackenzie (1971)

Humus compounds enter into intimate association with inorganic soil particles to form a clay-humus complex. This complex is chemically active; the individual clay and humus particles are able to effect linkages between one another and are capable of holding ions of hydrogen and nutrient minerals in the soil. The ability to hold these ions is, however, not solely determined by the presence of clay-humus particles in soil. Rainfall percolating through soil can detach (leach) such nutrient ions from the upper layers of the soil and deposit them lower down.

The deposition of organic matter and the weathering of rocks results in zonation of soils from the surface down. On the very top is the recently fallen plant litter. The first zone is the A horizon, which is the zone of greatest humus content and most intense leaching. The second zone or B horizon contains less altered residues and may contain reprecipitated materials carried downward from the leached zone above. The bottom zone or C horizon consists of partially altered parent rock and extends to the parent rock itself.

In regions where precipitation exceeds evaporation, water percolates downward and results in leaching. The soils resulting from this action have ferric oxide and aluminosilicate hydrates as the residues of these processes, and these may be concentrated in the B horizon. Such soils are called pedalfers (pedo(Al) (Fe)r). The process which produces such soils is termed podsolization and usually occurs in temperate humid climates with a forest cover.

Regions where the precipitation is about equal to the evaporation often contain pedocal soils (pedo(Ca) Al). Because the water enters the soils and evaporates out many times, the dissolved materials derived from reaction of soil water with parent mineral are not leached away but concentrate in the A horizon. The less soluble bases, particularly $CaCO_3$, are able to accumulate, so the clay-humus complex remains base-saturated, the soil remains alkaline, and the clay particles have no tendency to dissociate.

The composition of soil and of soil solution shows considerable variability from place to place and may even show some seasonal variation. Tables III-7 and III-8 from Bowen (1966) indicate the extent of such variations. We have used these data in subsequent chapters to estimate the size of the respective reservoirs.

C. THE HYDROSPHERE

1. Introduction

The amount of water contained in various parts of the earth is shown in Table III.-9A. Although most of the water is contained in primary lithosphere and sedimentary rocks, this water exchanges with other reservoirs so slowly that it may be regarded as essentially out of circulation. The basic hydrological cycle consists of the exchange of water in the remaining reservoirs, which is effected essentially by (a) the evaporation of water from the surface and its return as precipitated rain, snow, and condensed dew on land surfaces, (b) the movement of water on land in rivers and as circulating ground water and soil water and its temporary storage in lakes, and (c) the return of water to the ocean in rivers and groundwater discharge. Precipitation processes are important in transferring gaseous and particulate matter from the troposphere to the surface, while fresh water discharging into the oceans carries with it large quantities of suspended and dissolved material from the land surfaces.

Table III-9B also shows the estimated mean residence time of water in the major circulating reservoirs. The distribution of terrestrial waters shown in the table is given in SMIC (1971). This distribution differs from that presented by Hutchinson (1957), who estimates the total circulating ground water as 2.5×10^{20} grams and lake water as 0.25×10^{20} grams.

TABLE III-7. - COMPOSITION OF SOILS

Element	Composition[a] (ppm) Mean	Composition[a] (ppm) Range	Element	Composition[a] (ppm) Mean	Composition[a] (ppm) Range
Ag	0.1	(0.01-5)	Mg	5,000	(600-6,000)
Al	71,000	(10,000-300,000)	Mn	850	(100-4,000)
As	6	(0.1-40)	Mo	2	(0.2-5)
B	10	(2-100)	N	1,000	(200-2,500)
Ba	500	(100-3,000)	Na	6,300	(750-7,500)
Be	6	(0.1-40)	Ni	40	(10-1,000)
Br	5	(1-10)	O	490,000	
C	20,000		P	650	
Ca	13,700	(7,000-500,000)	Pb	10	(2-200)
Cd	0.06	(0.01-0.7)	Ra	8×10^{-7}	($3-20 \times 10^{-7}$)
Ce	50		Rb	100	(20-600)
Cl	100		S	700	(30-900)
Co	8	(1-40)	Sb		(2-10?)
Cr	100	(5-3,000)	Sc	7	(10-25)
Cs	6	(0.3-25)	Se	0.2	(0.01-2)
Cu	20	(2-100)	Si	330,000	(250,000-350,000)
F	200	(30-300)	Sn	10	(2-200)
Fe	38,000	(7,000-550,000)	Sr	300	(50-1,000)
Ga	30	(0.4-300)	Th	5	(0.1-12)
Ge	1	(1-50)	Ti	5,000	(1,000-10,000)
Hf	6		Tl	0.1	
Hg	0.03	(0.01-0.3)	U	1	(0.9-9)
I	5		V	100	(20-500)
K	14,000	(400-30,000)	Y	50	(25-250)
La	30	(1-5,000)	Zn	50	(10-300)
Li	30	(7-200)	Zr	300	(60-2,000)

[a] The figures refer to oven-dried soils. Soils near mineral deposits have been omitted in computing ranges.

SOURCE: Adapted from Bowen (1966)

TABLE III-8. - ELEMENTARY COMPOSITION OF SOIL SOLUTIONS AND RIVER WATERS

	Soil Solution		River Water[a]	
Element	Median	Range	Median	Range
Ag			0.00013	0.00001-0.0035
Al			0.24	0.01-2.5
Ar			0.6	
As			0.0004	<0.0004-0.23
Au			<0.00006	
B		0.03-10	0.013	0.01-1
Ba			0.54	0.009-0.15
Be			0.001	0.0001-0.001
Br		<0.001-0.01	0.021	0.005-140
C(HCO_3-)	4	2-7	11	6-19
Ca	32	1-60 (-1500)	15	4-120
Cd			0.08	
Cl	10	7-50 (-8000)	7.8	5-35
Co			0.0009	<0.006
Cr			0.00018	0.0001-0.08
Cs			0.0002	0.00005-0.0002
Cu		0.01-0.06	0.01	0.0006-0.4
F			0.09	
Fe		0.1-0.25 (-25)	0.67	0.01-1.4
Ga			<0.001	
Hg			0.00008	
I		0.01	0.002	
K	3.5	1-11 (-400)	2.3	1.4-10
Li			0.0011	0.00007-0.04
Mg	25	0.7-100 (-2400)	4.1	1.5-6
Mn		0.02-2 (-800)	0.012	0.00002-0.13
Mo		<0.001	0.000035	<0.007
N (NO_3-)		2-800	0.23	0.01-0.8
Na	15	9-30 (-3500)	6.3	3-25
Ni			0.01	0.0002-0.02
P	0.005	0.001-30	0.005	0.001-0.3 (-12)
Pb			0.005	0.0006-0.12
Ra			3.9×10^{-10}	
Rb			0.0015	<0.008
Rn			1.7×10^{-15}	
S	5	<3-5000	3.7	0.9-30
Se		0.001-3	<0.02	
Si		0.5-12	6.5	2-12
Sn			0.00004	
Sr		<0.1	0.08	0.003-0.8
Th			0.00002	
Ti		<0.07	0.0086	<0.11
U			0.001	0.00002-0.05
V			0.001	<0.007
Zn		0.1-0.3	0.01	0.0002-1
Zr			0.0026	0.00005-0.022

SOURCE: Adapted from Bowen (1966)

TABLE III-9. - THE HYDROSPHERE

A. Non-Circulating Water

	Mass (10^{20} gm)
Primary Lithosphere	
Primary Lithosphere	250,000
Sedimentary Rocks	2,100

B. Circulating Reservoirs

	Mass (10^{20} gm)	Mass (%)[a]	Residence Time
Ocean	13,800	93	3,600 years
Polar Ice	240	2	15,000 years
Terrestrial Water			
Ground water	640	5	up to 10^4 years
Lakes	2.3		10 years
Soil moisture	0.82		2-50 weeks
Rivers	0.012		2 weeks
Atmosphere	0.13		10 days

[a] Of circulating reservoirs

SOURCES: Hutchinson (1957) and SMIC (1971)

2. Water in the Atmosphere

Water enters the atmosphere as water vapor evaporated from warm surfaces and rises with the air to levels where the temperature is low. Here the water vapor condenses to form clouds and may precipitate out of the atmosphere as rain or snow. Over most oceans the amount of water vapor present in the air is a function of temperature, declining with height (by about a third for every 2 km) and with increasing distance from the equator. Most of the water in the atmosphere is present in the equatorial regions.

The total amount of water vapor in a unit column of air is usually expressed as precipitable water vapor. It varies from a maximum of about 50 millimeters in equatorial regions to a minimum of about 5 millimeters over the arctic area and 1.5 millimeters over the antarctic (SMIC 1971). Water vapor near the surface follows the surface temperature distribution and is higher during summer than winter.

Average precipitation, evaporation, and runoff for the major continents and oceans is shown in Table III-10.

The condensation of water vapor in the atmosphere to form clouds requires the presence of a tiny (diameter 10^{-2} to 10^{2} microns) cloud condensation nucleus (CCN), which is removed from the air if the cloud droplet precipitates as rain or snow. Cloud droplets may take up gases directly from the atmosphere, notably sulfur dioxide, carbon dioxide, oxygen, ammonia, methane, and other gases; the quantities absorbed depend upon the solubility and concentration of the gas, and the pH, temperature, and composition of the cloud droplet. The latter is affected by the chemical composition of the particle which acted as a CCN and particles and/or gases which may be dissolved in it after formation.

The process of removing materials present in cloud water that precipitates is termed "rainout." Additional material may be scavenged from the air as the raindrop or snowflake falls, which is termed "washout." Rainout and washout are extremely important processes for removing gases and particles from the atmosphere.

TABLE III-10. - AVERAGE WATER BALANCES

(centimeters per year)

A. Land Areas

	Precipitation	Evaporation	Runoff
Africa	69	43	26
Asia	60	31	29
Australia	47	42	5
Europe	64	39	25
North America	66	32	34
South America	163	70	93
TOTAL LAND AREAS	73	42	31

B. Oceans

	Precipitation	Runoff	Evaporation	Flow
Atlantic	89	23	124	-12
Indian	117	8	132	-7
Pacific	133	7	132	+8
WORLD OCEAN	114	12	126	0

SOURCE: SMIC (1971)

3. Rivers and Streams

The mean estimated global water balance is shown in Table III-11. The amount of precipitation falling on land exceeds the amount of water vapor evaporated from land by about 0.36×10^{20} g per year; the excess is returned to the ocean in rivers (0.32×10^{20} g per year) and as ground water issuing from underground sources (0.04×10^{20} g per year). Differences in the water balance and in the topography and geology of the continents give rise to differences in the amount of runoff and in the concentration of dissolved and suspended solids discharged with river water. Table III-12 gives the estimated runoff from each continent and the load of dissolved and suspended solids, together with estimates of mechanical and chemical denudation (weathering). The chemical composition of the waters draining each continent is given in Table III-13.

Estimates of the global river runoff and ionic composition are derived primarily from Livingstone (1963). He used published analyses of the chemical composition of a large number of the rivers of the world together with estimates of total runoff to arrive at these and related figures. At the time of this compilation, relatively few of the rivers of the world had been adequately sampled and analyzed, and consequently Livingstone urges that the resulting estimates be used with care. In particular, the estimates for Europe were based on a very few analyses, most of which were conducted in the 19th century.

4. The Ocean

The ocean exchanges gases with the atmosphere and may regulate its carbon dioxide level, although the details of this influence are obscure. It is important as the repository of the marine biosphere, and may influence the oxygen content of the atmosphere as well.

Table III-14 contains estimates of the concentration and quantities of selected elements in the ocean. It represents an estimate of the composition at a salinity of 35 o/oo, as confirmed by observations primarily in surface waters. Some constituents are very difficult to measure reliably, and many appear to vary with location and depth (Turekian, 1969; Goldberg, 1965). As a consequence, the values given in Table III-14 may

TABLE III-11. - WATER BALANCE OF OCEANS AND CONTINENTS

	g/cm^2-yr.	10^{20}gm/yr.
Evaporation from Ocean Surfaces	106	3.83
Precipitation on Ocean Surfaces	96	3.47
Evaporation from Land Surfaces	42	0.63
Precipitation on Land Surfaces	67	0.99

SOURCE: Hutchinson (1957)

TABLE III-12. - CONTINENTAL RUNOFF

Continent	Total Discharge (10^{15} liters/yr)	Total Dissolved Solids (10^{14} g/yr)	Total Suspended Solids (10^{14} g/yr)	Average Discharge (10^{6} liters/km^2)	Average Chemical Demdation (metric tons/km^2)	Average Mechanical Demdation (metric tons/km^2)
North America	4.55	7.0	17.8	215	33	86
Europe	2.50	4.6	2.5	229	42	27
Asia	11.05	14.9	145.0	237	32	310
Africa	5.90	7.1	4.9	198	24	17
Australia	0.32	0.2	2.1	42	2	27
South America	8.01	5.5	11.0	513	28	56
Total	32.33	39.3	183.3			

SOURCE: Adapted from Garrels and Mackensie (1971)

TABLE III-13. - MEAN COMPOSITION OF RIVER WATERS OF THE WORLD

(parts per million)

	HCO_3	SO_4	Cl	NO_3	Ca	Mg	Na	K	Fe	SiO_2	Total
North America	68	20	8	1	21	5	9	1.4	0.16	9	142
South America	31	4.8	4.9	0.7	7.2	1.5	4	2	1.4	11.9	69
Europe	95	24	6.9	3.7	31.1	5.6	5.4	1.7	0.8	7.5	182
Asia	79	8.4	8.7	0.7	18.4	5.6	---9.3	---	0.01	11.7	142
Africa	43	13.5	12.1	0.8	12.5	3.8	11	---	1.3	23.2	121
Australia	31.6	2.6	10	0.05	3.9	2.7	2.9	1.4	0.3	3.9	59
World	58.4	11.2	7.8	1	15	4.1	6.3	2.3	0.67	13.1	120
Anions[a]	0.958	0.233	0.220	0.017	---	---	---	---	---	---	1.428
Cations[a]	---	---	---	---	0.750	0.342	0.274	0.059	---	---	1.425

[a] Millequivalents of strongly ionized components.

SOURCE: Livingstone (1963)

TABLE III-14. - ABUNDANCES OF SELECTED ELEMENTS IN THE OCEAN

	Element	Abundance (ppm)	Total (units of 10^{18} g)	Total as Equivalent of Atmospheric Abundance
C	organic C	0.8	1.06	2.0
	$CO_2 + H_2CO_3$	1.0	1.35	2.0
	$HCO_3^- + CO_3^{--}$	28.0	37.8	53.0
N	dissolved N_2	15.5	20.9	0.005
	NO_3^{--}	0.42	0.570	-
	NH_4^+ and NO_2^-	0.08	0.010	-
	organic N	0.67	0.34	-
O	dissolved O_2	6.0	8.1	0.0068
	H_2O	8.83×10^5	11.9×10^5	10^3
	SO_4	1,808.0	2,441	2.06
	PO_4H^-	0.044	0.06	5×10^{-5}
Ca		411	555	
Cl		19,400	26,190	
F		1.3	1.8	
Fe		0.003	0.004	
H	H_2O	1.1×10^5	1.5×10^5	6×10^{10}
	organic CH_2O	0.07	0.09	500
I		0.064	0.086	1.7×10^7
Mg		1,290	1,742	
Na		10,800	14,580	
Mn		0.0004	0.0005	
Si		2.9	3.92	
B		4.45	6.01	
Br		67.3	90.9	

SOURCES: Turekian (1969) Bowen (1966) Hutchinson (1954) incorporate some errors. The importance of the ocean as a reservoir of some atmospheric constituents is indicated in the final column of Table III-14, where the quantities of some atmophile elements present in the ocean are expressed relative to the mean amount of each present in the atmosphere. Thus, there is about 57 times as much CO_2 present in solution in the ocean as there is in the atmosphere, while more than two atmospheres of oxygen are present as SO_4^{--} in the ocean.

The physical circulation of the ocean is extremely complicated and is not understood in detail. Two types of circulation are of interest to us: the horizontal movement of water in surface currents, and the exchange of water between the surface and the intermediate and bottom levels of the deep ocean.

The surface circulation is effected primarily by wind stress on the water and is influenced by the shape of the ocean basins. This general circulation of the surface layer is clockwise in the northern hemisphere and counterclockwise in the southern. In the northern hemisphere the surface currents travel west in the southernmost region near the equator and north along the western boundaries of the ocean basins, turning east at about 40°N and south again on the eastern boundaries. In both hemispheres the western boundary currents tend to be narrow, fast, and relatively deep, with speed decreasing toward the high latitudes. In the eastern part of the ocean the southerly return flow is slower, and the current tends to be diffuse.

This wind-driven circulation extends only to a comparatively small fraction of the total depth of the ocean. It usually does not extend beyond 200-300 meters below the surface, except in the geographically limited western boundary currents, which may be 1,000 meters deep.

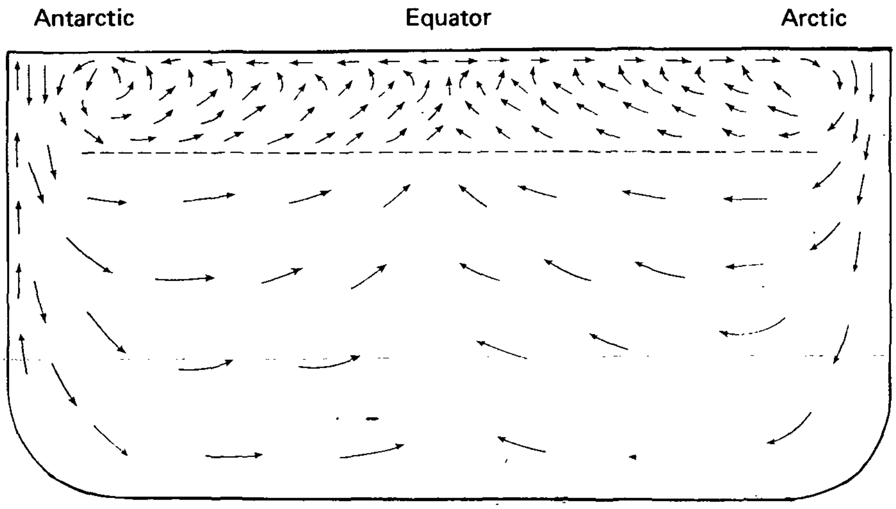
Currents of water exist at all levels in the ocean, but these need not be discussed in detail here, except to point out that deep water horizontal circulation involves the exchanges of vast quantities of water at very slow rates and supports the exchange of water with the surface.

Surface layers of water tend to be isolated from deeper waters by the influence of a stable density gradient, which greatly inhibits vertical mixing. Gross features of the main vertical and horizontal movements of ocean water are depicted in Figure III-2. A thin layer of water from 75 to 100 meters deep extends from about 40^{o}S to 40^{o}N latitude. Warm surface water driven by surface winds travels from the equator poleward to about 40^{o}, where part of it becomes more dense as a result of increase in salinity during evaporation nearer the equator followed by cooling. This water sinks to intermediate levels, providing a return flow, some of which exchanges with the surface. In the Arctic and the Antarctic, cooling of the surface water and increases of density due to the formation of ice cause regular sinking. Bottom water exchanges with sinking water in part of the Antarctic, but most bottom water is believed to return to the surface slowly by mixing with water at intermediate levels, which in turn mixes with layers close to the surface.

The major chemical constituents of sea water--chlorine and sodium--are biologically inactive. Together with other biologically inactive materials, they are transported by the water containing them; variations in their abundance are the result of water movements and the dilution effects of mixing. These biologically inactive materials are termed "conservative" elements. Other components in the ocean--carbon, nitrogen, phosphorus, silicon, and so on--are moved about in this fashion and are in addition subject to modifications of abundance due to biological activity. These constitute the "non-conservative" elements of seawater.

Non-conservative elements are incorporated into particulate plant tissue in the surface zones of the sea, where light for photosynthesis is available. They are then subject to sinking to lower levels, and to consumption by organisms. The vertical movement of organisms returns particulate organic material to the surface. The movement of particulate matter downward through the water column is a faster way for material from the surface to reach bottom than if it traveled as dissolved material with sinking water and bottom currents.

Numerous models of the circulation of water in the oceans have been constructed to provide a basis for estimating the age of surface, bottom, and intermediate water in the various oceans, and the rate of exchange



Source: Eriksson (1962)

FIGURE III–2 SCHEMATIC REPRESENTATION OF THE VERTICAL-MERIDIONAL CIRCULATION OF THE SEA with the surface. Some of the clues which have been used to estimate these properties are the temperature and salinity of the water, which are related to the location where it formed at the surface and sank, and to the other waters with which it has mixed, and the distribution of non-conservative elements, particularly total carbon and ^{14}C activity present in organic matter and in dissolved form. This carbon is derived partly from carbon dioxide absorbed from the atmosphere at the time of sinking and partly from organic material or biogenic calcium carbonate derived from sinking particulate matter.

Observations of the form and distribution of carbon and of the $^{14}C/^{12}C$ ratios, together with estimates of the total amount of carbon which is formed into particulate matter at the surface and the amount reaching the bottom, are used to estimate the probable residence time of bottom waters. Thus, Eriksson (1962) estimates that residence time in bottom waters (i.e., the average time a water molecule remains in the bottom) falls in the range 500 to 2000 years, and Broeker and Li (1970) estimate that the mean deep water residence time is about 1500 years.

The ocean interacts in many important ways with the gases in the atmosphere, most particularly by acting as a reservoir for atmospheric carbon dioxide. The ocean appears to function in part as a buffer of changes in the atmospheric pressure of carbon dioxide. This is due to the existence of the carbonate system of the ocean, which buffers the pH. The system is complicated, and its detailed description is beyond the scope of this report; however, it may briefly be described as a system in which equilibria between dissolved carbon dioxide (CO_2), carbonic acid (H_2CO_3), bicarbonate ion (HCO_3^-), carbonate ion (CO_3^{--}), and hydrogen ion (H^+) provide the principal pH control. The following reactions are involved:

$$H_2O + CO_2 \leftrightarrow H_2CO_3$$

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+$$

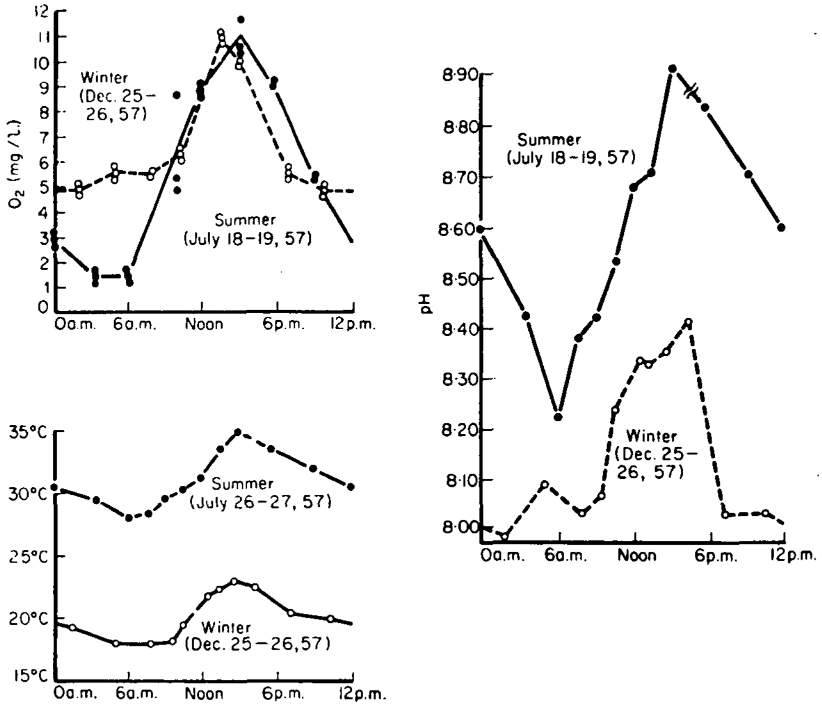
$$HCO_3^- + H^+ \leftrightarrow CO_3^{--} + 2H^+$$

The equilibrium constants for each step in this series are functions of temperature and pressure and of the thermodynamic activities of the participating species. Thus, changes in pressure and temperature resulting from movements of water or changes in salinity resulting from evaporation or freezing may shift the equilibrium positions of the system. Other complications arise from the precipitation of calcium carbonates and the formation of certain ion-pair carbonates, such as $MgCO_3$.

Further variations in the carbonate system are caused by the conversion of dissolved CO_2 into organic matter during photosynthesis (which occurs in surface water that may be simultaneously subject to warming or to changes in salinity resulting from rainfall and/or evaporation). Biological precipitation of calcium carbonate similarly acts to modify the local abundance of species involved in the carbonate equilibria, as does the oxidation of organic matter, which liberates CO_2.

Atmospheric carbon dioxide may enter the ocean (invasion) or be liberated from it (evasion), but the factors which govern the actual transfer are obscure. The relevant reactions determining the rate of release or uptake of atmospheric CO_2 when the atmospheric abundance is not in equilibrium with the amount dissolved in the sea may be the hydration of dissolved carbon dioxide and the dehydration of carbonic acid. These reactions are relatively slow compared with the ionization reactions forming bicarbonate, carbonate, and hydrogen ions, but they may be catalyzed by phosphate, arsenite, borate, nitrogenous bases, and the biological enzyme carbonic anhydrase (Skirrow, 1965).

The mean pH of the ocean at the surface is 8.15. It ranges between about 7.8 and 8.3, primarily in response to local changes in the abundance of dissolved CO_2 due to biological activity and temperature. In regions where photosynthetic activity converts dissolved CO_2 into particulate matter, releasing the O_2 into the water, the decline in pH caused by the reduction in the amount of CO_2 is accompanied by an increase in the amount of O_2 in solution (Figure III-3). In subsurface layers the oxygen level may decline during the day or the season due to the oxidation of organic matter sinking through the water column. The dissolved



Source: Skirrow (1965)

FIGURE III–3 DIURNAL OXYGEN, pH, AND TEMPERATURE VARIATIONS AT REDFISH BAY, TEXAS oxygen in water at levels below the thermocline was obtained from the atmosphere when the water in question was at the surface; hence, it cannot be replenished.

Both oxidation and photosynthesis take place in the lighted zones near the surface. The photosynthesis rate in surface waters usually exceeds the oxidation rate, so the result is an excess of oxygen. Below the depth to which light penetrates, oxidation continues but no photosynthesis can take place, so the net effect is to reduce the level of oxygen present in the water. In regions where the circulation of water is not impeded, the oxygen consumed by oxidation of organic matter is replenished by normal water movements. In some regions water flow is inhibited, for example in the pore waters of sediments, or in basins cut off from adjacent water by the presence of shallow sills that restrict the entry of oxygenated water. These regions are usually oxygen-deficient and may be completely anoxic if the production of organic matter in their surface waters is high; as a consequence, large amounts of organic matter sink to the bottom and are available for biological decomposition. The biological oxidation of this matter can reduce the oxygen level to zero.

Anoxic water occurs in many environments, including fresh water and soils as well as salt water. The best known is the Black Sea, which is permanently anoxic below depths varying from about 150 meters in the center to 250 meters near the coasts. Anoxic basins occur in the tropics--the Cariaco Trench in the Caribbean Sea and Kaoe Bay in Indonesia--and in coastal inlets. Many fjords and inlets in Norway are anoxic, as are basins on the Pacific Coast of British Columbia that are similar to the Norwegian fjords in physiography and circulation. Many fjords are only intermittently anoxic, because they are occasionally flushed by overturns of the water. This is also presently true of some deeps in the Baltic which appear to have become intermittently anoxic as a result of cultural eutrophication (Forsellius, 1970).

Anoxic bottom waters are extremely important sites of anaerobic (biological) processes that reduce sulfate and nitrate, producing H_2S

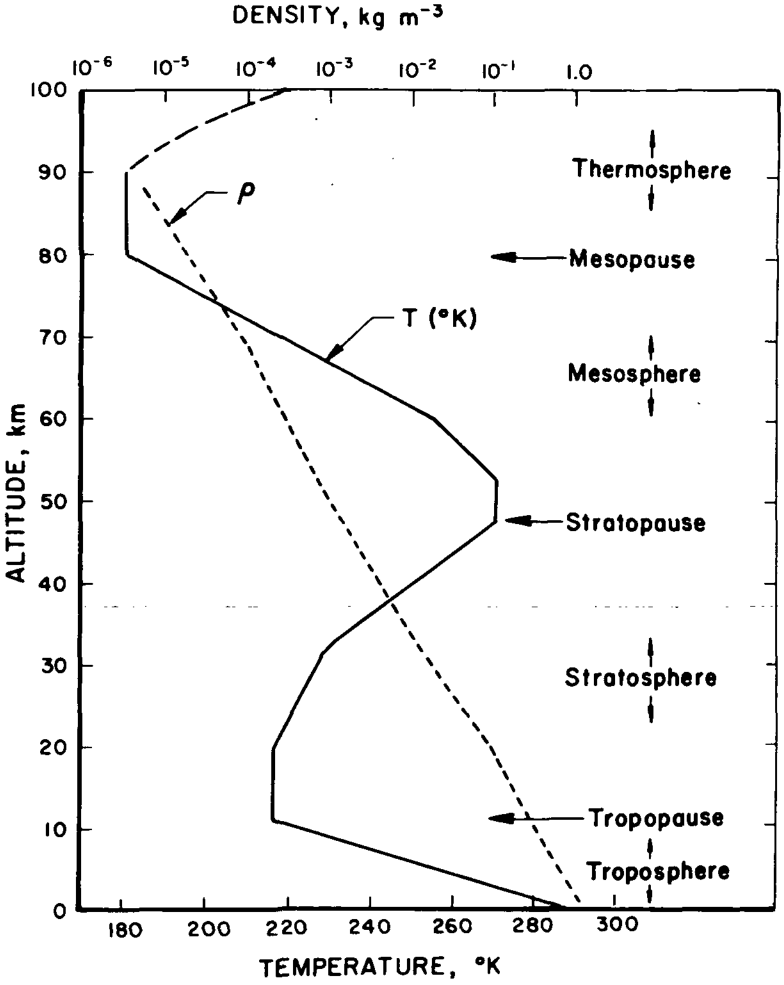
and S^{--} and NH_4^+, N_2 and N_2O. These processes are essential links in the biochemical processing of atmospheric nitrogen and sulfur compounds.

D. THE ATMOSPHERE

The atmosphere is divided into regions in accordance with the change in temperature with altitude, which in turn is due to the interaction of atmospheric constituents with radiation, including relatively short-wavelength radiation from the sun and infrared energy reradiated from the surface of the earth. Figure III-4 is a schematic representation of the atmosphere. Pressure, and consequently density, declines approximately exponentially with increasing altitude. Most of the mass of the atmosphere occurs in the lowest two segments, the troposphere and the stratosphere.

In the troposphere, the lowest region of the atmosphere, infrared radiation originating at the surface of the earth is absorbed by water vapor and carbon dioxide. The absorption of radiation (and the concomitant heating of the atmosphere) diminishes with distance from the surface because (a) absorption attenuates the flux of radiant energy, and (b) as the density of the air decreases, it contains less water vapor and other absorbing gases. Above the troposphere is a region where the temperature ceases to decline with altitude; this is termed the tropopause. It is shown at 10 km in Figure III-4 but actually can occur between about 9 and 15 km; it is higher at the equator than at the poles and is higher in winter than in summer. The temperature at the tropopause is shown to be about 218°K (-55°C), but it also varies; it is colder at the equator, where it is about 193°K (-80°C), and rises to about 218°K to 235°K (-55°C to -40°C) in latitudes greater than 60°.

In the stratosphere, the region above the tropopause, the temperature increases somewhat with altitude (or at least does not decline). The temperature reaches a peak at the upper limit of the stratosphere (about 50 km), and then declines again in the mesosphere up to an altitude of about 80 km. The temperature rise is due to the absorption of ultraviolet light in the solar spectrum by ozone, itself created by



Source: Martell (1971)

FIGURE III–4 TEMPERATURE AND DENSITY PROFILE OF THE U.S. STANDARD ATMOSPHERE reaction of excited oxygen atoms that are photolytically produced when oxygen molecules absorb short-wavelength energy.

In this report we are concerned only with the troposphere and the stratosphere, which contain 99.9% of the mass of the atmosphere, about 5.14×10^{21} grams. Although the portion of this mass that is in the troposphere varies somewhat with time, we assume for the purpose of calculating atmospheric abundances that it represents 82% of the air and that the remainder is in the stratosphere.

Once injected into the atmosphere at the surface, trace gases are distributed and mixed in the troposphere and stratosphere in a manner that depends on the local and large-scale patterns of air movements, which are complex and difficult to predict. In general, unless they are precipitated or otherwise removed, gases emitted at the surface mix upward fairly rapidly, becoming diluted in the large volume of the lower troposphere. Upward movement is often inhibited by the presence of a temporary inversion at altitudes up to two or three kilometers. In the absence of such an inversion, turbulent motions mix gases upward in about a day. Horizontal movements within the troposphere are much faster, and air may become thoroughly mixed in one to two weeks. Separate air masses may retain their compositional identity for several days under some circumstances.

Mixing between the two hemispheres is relatively slow. Nydal (1968) has employed bomb-produced $^{14}CO_2$ to trace the exchange of stratospheric and tropospheric air within and between hemispheres. He gives the mean exchange time of northern and sourthern hemispheric air as 1.0 ± 0.2 years, and the exchange time between the northern and southern stratospheres as 5.0 ± 1.5 years. Mixing between the stratosphere and the troposphere in each hemisphere is also slow: Nydal indicates that every year about 50% of the mass of the stratosphere is exchanged for a like quantity of tropospheric air. (This corresponds to about 10% of the mass of the troposphere.)

Vertical movement within the stratosphere is about one or two orders of magnitude slower than in the troposphere, and there is evidence that vertical mixing is more restricted at higher altitudes within the stratosphere than at lower altitudes. Martell (1971) estimates that contaminants injected into the stratosphere near the tropopause may have a residence time of about one month, but about one to two years at 20 kilometers and about 4 to 20 years at 50 kilometers.

The gaseous constituents of the atmosphere are listed in Table III-15. Three gases--molecular nitrogen, molecular oxygen, and argon--make up more than 99.9% of the entire atmosphere. All the remaining gases are present in very small quantities. Except for the noble gases, all vary in abundance. The relative concentrations of the three main constituents are approximately constant up to about 70 kilometers.

The abundance of a gas may be expressed in units of mass per unit volume of air--usually $\mu g/m^3$ in the case of trace constituents. Such units are not desirable for comparing observations made at different altitudes--and hence different pressures--unless the observations are standardized with respect to pressure and temperature. Alternatively, abundance may be expressed as a volume mixing ratio, or fractional volume abundance with respect to the major gases (nitrogen and oxygen) present. Fractional abundance is usually expressed in terms of volume as parts per million (ppm), parts per hundred million (pphm), or parts per billion (ppb), but it may be expressed simply as a fraction. The abundance of water is often expressed as mass of H_2O per gram or kilogram of air.

Conventionally, aeronomists and meteorologists express quantities of atmospheric constituents in terms of units per square centimeter of earth's surface (centimeter column) or per cubic centimeter of atmosphere. Sometimes the unit used is the number density per centimeter^3. The number density of a molecular component is the number of molecules, that of an atomic constituent is the number of atoms, and so on. Rates of removal or production may be expressed as mass or number density per square centimeter of the earth's surface per second. Table III-16 gives constants and conversion factors for readers unfamiliar with these usages. Except where otherwise specified, the metric system is used throughout this document.

TABLE III-15. - COMPOSITION OF THE DRY ATMOSPHERE

	Mean Fractional Abundance	Total Mass ($x\ 10^6$ tons)
N_2	0.7809	38.65×10^8
O_2	0.2095	11.84×10^8
A	0.0093	0.65×10^8
CO_2	321 ppm	0.0321×10^8
Ne	18 ppm	64×10^3
He	5.2 ppm	3.7×10^3
CH_4*	1.4 ppm	3.27×10^3
Kr	1.0 ppm	14.8×10^3
H_2	0.5 ppm	0.18×10^3
O_3	0.4 ppm	0.35×10^3
N_2O*	0.25 ppm	1.6×10^3
Xe	80 ppb	1.9×10^3
NH_3*	5-15 ppb	12.5-37.4
NO_2*	0.5 ppb	3.4
NO*	≃0.5 ppb	2.3
SO_2*	≃1.5 ppb	14.0
H_2S*	≃0.3 ppb	1.5

*Mean abundance and total atmospheric load calculated only for the troposphere.

TABLE III-16. - UNITS AND CONVERSION FACTORS

Length

0.001 kilometer (km) = 1 meter (m) = 100 centimeters (cm) = 1,000 meters (mm)

1 meter (m) = 1,000,000 microns (μ) = 1,000,000,000 nanometers (nm) = 10,000,000,000 angstrom units (Å)

1 km = 0.6214 statute mile; 1 m - 39.37 inches (in.) = 3.281 feet (ft); 1 cm = 0.3937 in.

1 mile = 1.609 km; 1 ft = 0.3048 m; 1 in. = 2.54 cm

Weight

0.001 kilogram (kg) = 1 gram (g) = 1000 milligrams (mg) = 1,000,000 micrograms (μg)

1 kg = 2.205 pounds (lb); 1 g = 0.035 ounce (oz)

1 lb = 453.6 g = 0.4536 kg

1 metric ton = 2205 lb = 1000 kg

1 short ton = 2000 lb = 907.2 kg

1 megaton = 1,000,000 tons

Volume and Cubic Measure

1 cubic meter (m^3) = 1,000,000 cubic centimeters (cm^3)

1 m^3 = 35.31 cubic feet (ft^3); 1 cm = 0.061 cubic inch (in^3)

1 liter (1) = 1000 cm^3

1 1 = 61.02 in^3 = 0.2642 gallon (gal)

1 ft^3 = 0.02832 m^3 = 28.32 1; 1 gal = 231 in^3 = 3.785 1

TABLE III-16. - Continued

Temperature Scales

	Absolute Zero	Ice Point (water)	Steam Point (water)
Degrees Fahrenheit (°F)	-459.7	32	212
Degrees Celsius or Centigrade (°C)	-273.15	0	100
Degrees Kelvin (°K)	0	273.15	373.15

Area

1 hectare (ha) = 10,000 square meters (m^2) = 10^8 square centimeters (cm^2)

1 hectare = 2.47 acres = 0.003861 square miles

1 square mile - 640 acres = 259 hectares

Time

1 year - 3.15 x 10^7 seconds

Pressure

1 atmosphere pressure = 76 cm mercury = 14.7 lb/in.^{2} = 1013 millibars (mb)

Constants

Area of earth's surface = 5.1 x 10^{18} cm^2 = 5.1 x 10^{10} ha

Area of land surface = 1.48 x 10^{18} cm^2 = 1.48 x 10^{10} ha

Area of ocean surface = 3.61 x 10^{18} cm^2 = 3.61 x 10^{10} ha

Mass of the atmosphere = 5.14 x 10^{21} g

Mass of the troposphere = 4.22 x 10^{21} g

Volume of the atmosphere (STP) = 4 x 10^{18} m^3

Volume of the troposphere (STP) = 3.28 x 10^{18} m^3

TABLE III-16. - Continued

Gases

Name	Formula	Equivalent of 1 ppm in $\mu g/m^3$ (STP)	Equivalent of 1 $\mu g/m^3$ in 10^{-4} ppm (STP)
Water Vapor	H_2O	800	12.50
Ozone	O_3	2,140	4.67
Hydrogen	H_2	89	112.00
Carbon Dioxide	CO_2	1,960	5.10
Carbon Monoxide	CO	1,259	8.10
Methane	CH_4	712	14.05
Formaldehyde	CH_2O	1,340	7.46
Nitrous Oxide	N_2O	1,960	5.10
Nitrogen Dioxide	NO_2	2,050	4.88
Ammonia	NH_3	760	13.15
Nitric Oxide	NO	1,340	7.46
Sulfur Dioxide	SO_2	2,850	3.51
Hydrogen Sulfide	H_2S	1,520	6.58

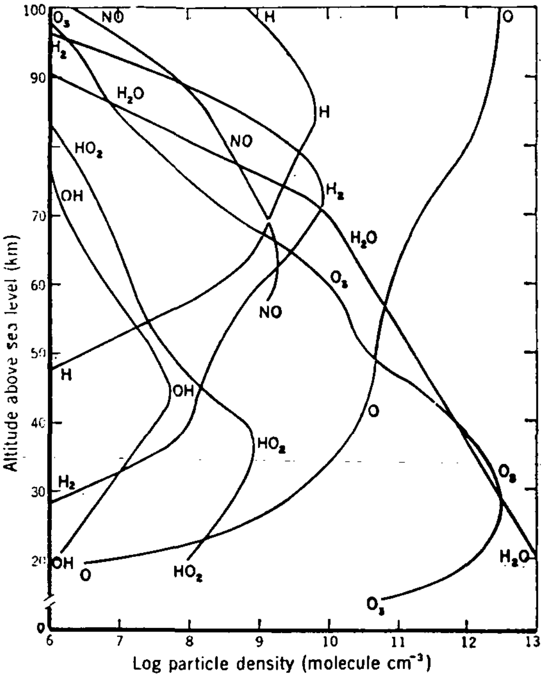
The production and removal of gases in the atmosphere is greatly influenced by the chemical effects of atmospheric interactions between incoming solar radiation and atmospheric constituents. The absorption of radiant energy by molecules or atoms in the atmosphere may produce electronically excited species, photolysis (decomposition), or ionization.

Of the chemical reactions that occur in the troposphere, the most important is the absorption of radiant energy by molecular oxygen, which dissociates to produce oxygen atoms; the latter may further react together, with a third body, and/or with O_2 to produce ozone. (Virtually all ozone is produced in the stratosphere.) The production of ozone and monatomic oxygen has two important effects: ozone absorbs ultraviolet radiation, thus shielding the troposphere and the surface of the ground from potentially harmful radiation, and ozone diffuses downward from the stratosphere to the troposphere, where it is available to enter into reactions with trace constituents. Photochemical reactions in the stratosphere and mesosphere are extremely complicated and poorly understood. Many primary and secondary reactions must be considered in any theoretical treatment, and relatively few good observational data are available.

Figure III-5 from Cadle and Allen (1970) is a plot of the calculated equilibrium distribution of some important species.

In addition to the gases listed in Table III-15, the atmosphere contains a variety of hydrocarbons that are naturally emitted by vegetation or that may be anthropogenic. Except in polluted environments, the concentrations of hydrocarbons other than methane are in the parts per billion range or less, while most organics are even less abundant. Table III-17 shows the concentrations of some organics and hydrocarbons together with that of some fossil fuel combustion products found in polluted environments.

The troposphere and the stratosphere also contain large quantities of particles ranging in size from 10^{-3} to 10^{2} microns. Figure III-6 shows the size and number distribution of particles found in maritime and continental tropospheric air. Particles are introduced into the



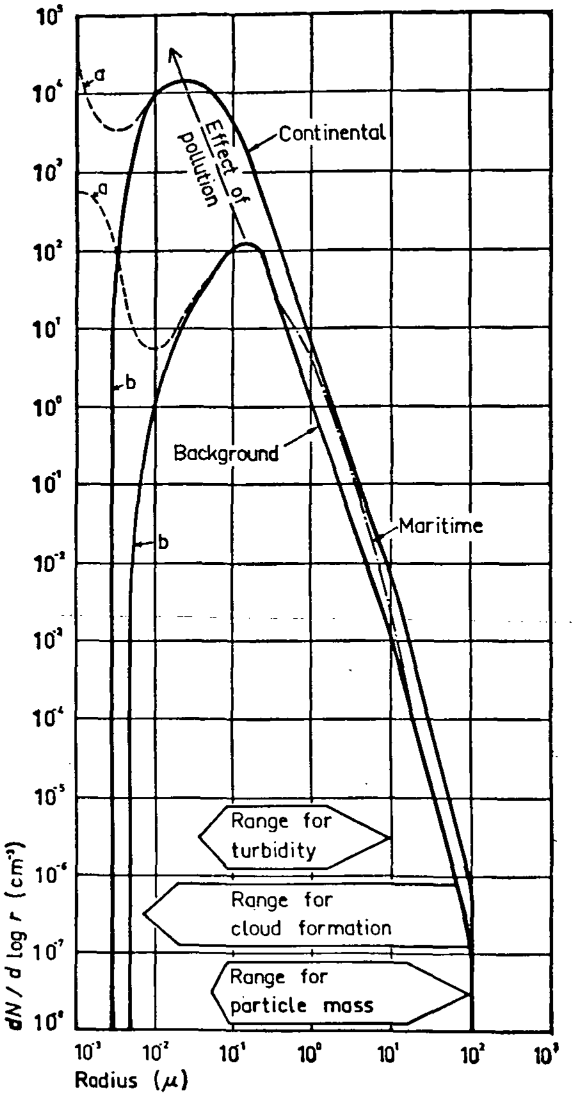
Source: Cadle and Allen (1970)

FIGURE III-5 DAYTIME EQUILIBRIUM PROFILES FOR A HYDROGEN-OXYGEN ATMOSPHERE

TABLE III-17. - TYPICAL CONCENTRATIONS OF TRACE CONSTITUENTS IN PHOTOCHEMICAL SMOG

Constituent	Concentration (pphm)
Oxides of nitrogen	20
NH_3	2
H_2	50
H_2O	2×10^6
CO	4×10^3
CO_2	4×10^4
O_3	50
CH_4	250
Higher paraffins	25
C_2H_4	50
Higher olefins	25
C_2H_2	25
C_6H_6	10
Aldehydes	60
SO_2	20

SOURCE: Cadle and Allen (1970)



Note: Curves a and b refer to possible variation of the size distribution with and without continuous production of very small particles. The arrow indicates the effect of pollution on the location of the maximum of the size distribution.

Source: SMIC (1971)

FIGURE III-6 PARTICLES IN THE TROPOSPHERE atmosphere from a number of sources. Winds lift sand, soil particles, and biological matter such as insect fragments, pollen, bacteria and their spore, and plant debris. Forest fires and volcanoes are sources of ash particles, and small quantities of dust are provided by meteoritic infall. Particles of salt are produced from wave action in the ocean. Some atmospheric particles are produced in the atmosphere as a consequence of reactions between trace gaseous constituents of natural or artificial origin. In polluted atmospheres containing nitric oxide or nitrogen dioxide in addition to organics, solar irradiation produces a complicated series of reactions which result in the formation of organic particles (Cadle 1971). Sulfur dioxide reacts with ammonia in cloud droplets to produce particles composed largely of ammonium persulfate, and NO and NO_2 of industrial or natural origin give rise to nitrate particles (Robinson and Robbins, 1970). Table III-18, taken from Peterson and Junge (1971), lists some sources of particles and estimates the quantities emitted into the air per year.

The concentration of particles in the atmosphere varies with place and time. In general, over land the lower troposphere contains fairly large quantities of particulate matter, while the lower troposphere over the ocean is quite clean, as is the middle and upper troposphere. The number of submicron particles (called Aitken nuclei) present in air is used as an index to total particle count, since the size distributions have been found to be approximately similar except where modified by pollution sources (Figure III-6). Table III-19 contrasts the concentrations of these particles typically found in various environments.

The distribution of water vapor in the troposphere was described in the previous discussion of the hydrosphere (Section C). The stratosphere is extremely dry. Water vapor concentration in the tropical troposphere just below the tropopause (where much exchange with the stratosphere is believed to take place) is about 10^{-7} g/g of air, whereas in the lower stratosphere it is 2 to 3 x 10^{-6} g/g of air (SMIC 1971). The water vapor content of the stratosphere increases with altitude somewhat (Cadle and Allen, 1970); this has been attributed to the oxidation of methane at these altitudes.

TABLE III-18. - ESTIMATES OF PARTICLES SMALLER THAN 20-μ RADIUS EMITTED INTO OR FORMED IN THE ATMOSPHERE MILLION METRIC TONS PER YEAR)

Natural	
Soil and rock debris[a]	100 - 500
Forest fires and slash-burning debris[a]	3 - 150
Sea salt	(300)
Volcanic debris	25 - 150
Particles formed from gaseous emissions:	
Sulfate from H_2S	130 - 200
Ammonium salts from NH_3	80 - 270
Nitrate from NO_x	60 - 430
Hydrocarbons from plant exudations	75 - 200
Subtotal	773 - 2,200
Man-Made	
Particles (direct emissions)	10 - 90
Particles formed from gaseous emissions:	
Sulfate from SO_2	130 - 200
Nitrate from NO_x	30 - 35
Hydrocarbons	15 - 90
Subtotal	185 - 415
Total	958 - 2,615

[a] Includes unknown amounts of indirect man-made contributions

SOURCE: SMIC (1971)

TABLE III-19. - RANGE OF ATMOSPHERIC POLLUTION IN VARIOUS ENVIRONMENTS (NUMBER OF CONDENSATION NUCLEI PER CUBIC CENTIMETER)

Type of Environment	Condensation Nuclei	Degree of Pollution
Oceanic and polar air	<1,000	Clean
Country air	1,000 - 5,000	Light
Suburban air	5,000 -50,000	Medium
Urban and industrial air	>50,000	Heavy

SOURCE: Adapted from Schaefer (1971)

E. THE BIOSPHERE

1. Introduction

As used here, the term biosphere denotes the class of all living things on earth and the organic remains of formerly living systems. As indicated by Table III-1, the biosphere is much smaller than other reservoirs of earth, and its reservoir capacity is very limited. Its importance lies, of course, in the fact that it is very active in the cycling of atmospheric components (particularly carbon dioxide and oxygen) and is the only significant source of virtually all the reduced compounds of the atmosphere--carbon monoxide, methane, hydrogen, hydrogen sulfide, and ammonia.

Biospheric functions may be classified in two groups: (1) those photosynthetic processes which produce organic matter from the components of air and water and a few essential micronutrients found in the lithosphere, and (2) the processes of respiration, decomposition, and mineralization which return the elements contained in the photosynthetic products to the atmosphere, hydrosphere, and lithosphere. In addition, the biosphere is responsible for the conversion of some organic carbon and some carbonates into fossils, which results in the very-long-term removal of some of their constituents from the atmospheric cycles. In our classification we have arbitrarily included incipient fossils as part of the biosphere, whereas reduced carbon in the form of oil and coal is included in the lithospheric reservoir.

Although the biosphere is a very important processor of atmospheric constituents, there are few reliable data regarding the detailed nature of the biospheric transformations, the conditions under which they occur, or the rates at which they take place. These biospheric processes are much less understood than are the chemical transformations that occur in the atmosphere, or the processes of weathering and sedimentation. This is because the biosphere is far more complicated than any of the other systems; it shows greater morphological variety than do other spheres and is organizationally far more complex. Bowen

(1966) has pointed out that while there are about 2000 named minerals in the lithosphere, there are over one million named species of organisms, and the total number of existing species is probably more than three million.

Subsets of these species of organisms occur together in extremely complex associations. An association of organisms together with its local non-living environment is termed an ecosystem. Although ecosystems may be grouped in broad classifications, no two are alike, and no single one is stable in time with regard to such important parameters as the population or biomass distribution.

2. The Carbon Cycle

The primary constituents of organic matter are carbon, hydrogen, oxygen, nitrogen, sulfur, and phosphorus; these elements are organized, together with a large number of other minor elements, into proteins, lipids, carbohydrates, and nucleic acids. The photosynthetic process uses radiant energy, carbon dioxide, and water to produce organic matter in proportions represented by the following reaction:

$$CO_2 + H_2O + \underline{h\nu} \rightarrow CH_2O + O_2$$

Although nitrogen, sulfur, phosphorus, and other elements are also incorporated in organic matter, they are present in much smaller quantities than are carbon, hydrogen, and oxygen. Consequently, these elements are neglected in discussions of quantities of total biomass or total stored energy represented by a given amount of organic matter. The energy stored in organic molecules depends upon the number and types of molecular bonds involved, but averages about 112 kcal per mole of O_2 released in reduction or consumed in oxidation of carbon.

The organic matter represented in an ecosystem and its rates of production and oxidation are conventionally expressed either in terms of the dry weight of the biomass or the mass of the carbon. Since the average oxidation state of organic carbon is approximately that of formaldehyde (CH_2O), the mass of carbon is 40% of the total dry weight.

Many important organizational features of the biosphere and its interaction with other terrestrial reservoirs can be understood in terms of the biospheric cycling of carbon. The carbon cycle of the land biosphere is shown schematically in Figure III-7. Fixation of atmospheric CO_2 transfers carbon from the atmospheric reservoir to the biosphere in the form of organic matter. Respiration of organisms oxidizes this reduced carbon and returns CO_2 to the atmosphere.

In any ecosystem the primary producers are the plants which reduce carbon dioxide to organic matter, and gross primary production is the total amount of material synthesized. Since plants require energy for metabolic processes, some of this production is utilized by them, resulting in the production of respiratory CO_2 released back into the atmosphere. The remainder goes to increase the mass of plant tissue and is termed net primary production. Gross primary production is very difficult to measure in individual plants and correspondingly hard to estimate for whole ecosystems. Net primary production can be measured by painstaking measurements of the increase of plant tissue, corrected for estimates of consumption by animals during the growing season.

Almost all the organic matter formed by primary producers is consumed by grazing animals or microflora that decompose dead plant tissue. Organisms that feed directly on plant tissue are termed herbivores or grazers, which in turn feed carnivores; the latter may be in turn consumed by other carnivores, and so forth. Although these food chains are usually diagrammed as simple pyramids, they are in practice often very complex and include parasites, scavenger, predators that prey on both herbivores and carnivores, organisms that may be herbivorous at one stage of life and carnivorous at another, etc. The major herbivores and carnivores convert some of the organic material they consume into animal tissue, which is referred to as secondary production. They use some directly as an energy source in respiration, releasing CO_2 to the atmosphere, and excrete some as waste material. These wastes, together with dead animal tissue and plant litter (leaves, twigs, dead roots, parts of senescent plants and so forth) are shown in Figure III-7 as entering the soil, where they are subject to

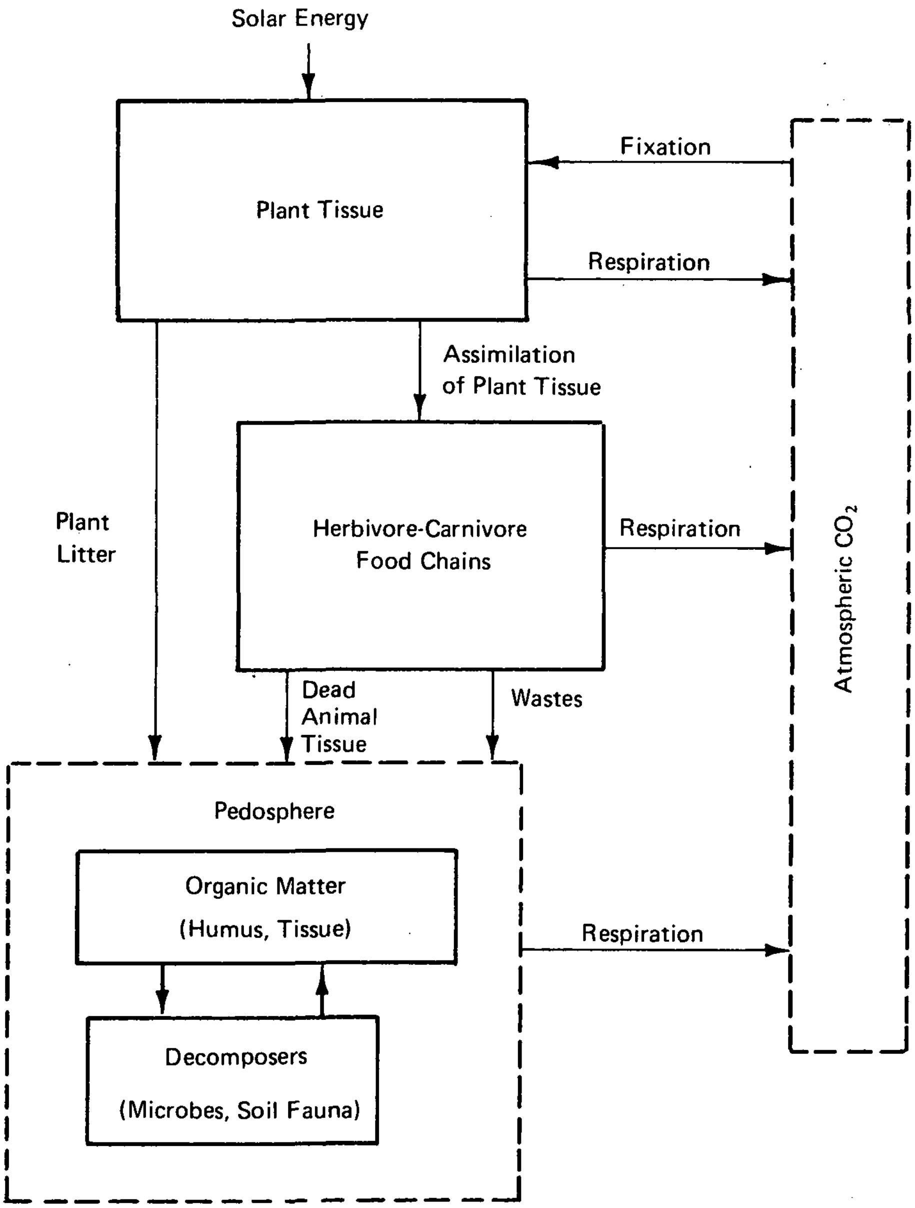


FIGURE III–7 CARBON CYCLE ON LAND

decomposition by animals and microbes in the soil. These include earthworms, mites, snails, termites, and similar relatively large animals as well as extremely large numbers of bacteria, fungi, and other soil microorganisms.

Soil organisms break down the complex organic molecules in the waste and litter, achieving as an end result the transformation of the organic matter into its component elements or inorganic molecules. In Figure III-7 the organic matter in the soil (pedosphere) is represented as being composed of the biomass of the decomposer organisms and the organic matter on which they feed. Some of this is litter which is more or less recognizable as the residue of plants, but the remainder is organic matter, whose origin is obscured by decomposition. Soil scientists distinguish two types of the latter, both of which are called humus. Some is recycleable humus that is in the process of decay and, given enough time, will be ultimately mineralized. Organic matter of this kind accumulates wherever the conditions are unsuitable for rapid decomposition. In general, moisture and high temperatures promote large populations of decomposers and high rates of metabolism; consequently, soil organic matter accumulates slowly in the tropics and rapidly in high latitudes, in spite of the fact that primary productivity is generally very high in the tropics and quite low in high latitudes on account of the short growing season. Because populations of soil animals and bacteria and fungi tend to be inhibited by acid conditions, some acid bogs and swamps accumulate very large quantities of organic matter, some of which may be subsequently converted to fossils--e.g., peat in peat bogs.

In addition to the decomposing organic matter which makes up the recycleable humus, all soils contain some humus that is extremely <u>refractory</u>, both to chemical analysis in the laboratory and to microbial decomposition in the soil. Its resistance to decomposition appears to be a function of the chemical structure of the molecules rather than inhibition of the action of decomposing organisms by the local environment. This refractory humus has been estimated by Waksman (1938) as averaging 2.7 kg/m^2 on a global basis, but this estimate must be regarded as uncertain.

In outline, the carbon cycle in the ocean is similar to that on land. It is discussed in more detail below.

3. Microorganisms in Soils

Microorganisms in soil and in aquatic environments play an extremely important role in the cycling of atmospheric constituents, but one which is difficult to assess quantitatively. This results from the extreme complexity and diversity of microbial communities and the fact that few of the nearly one hundred thousand known species have been studied in detail. Chemical transformations performed by certain bacteria are of considerable importance to the subject of this report and are mentioned in succeeding chapters. This brief discussion of soil microorganisms will serve to familiarize the reader with the terminology employed in other sections and with some of the problems associated with studying these organisms. For a more comprehensive introductory treatment, the reader is referred to Alexander (1961, 1964, 1971), on whose publications this presentation is based.

The microbial population of the soil is made up of five major groups, the bacteria, actinomycetes, fungi, algae, and protozoa. Of these, bacteria are the most abundant group and the most important from the point of view of the chemical transformations discussed in this report.

a. Bacteria

Bacteria are abundant but very small, rarely more than a few microns in length. For this reason, in spite of their numbers, they rarely make up as much as half the mass of total microbiological tissue present in soil. In aerated soils, bacteria and fungi together make up most of the total microbial tissue, but in environments containing little or no O_2, bacteria dominate. Bacteria as a group exhibit a capacity for very rapid growth and vigorous decomposition of a variety of natural substrates. They may be usefully divided into autochthonous and zymogenous species. Autochthonous bacteria derive their nutrient supply from the soil organic fraction; consequently, they are indigenous to a given soil and exhibit relatively few fluctuations in population density. In contrast, zymogenous bacteria are fermentation-producing organisms which are scarce until appropriate nutrient materials are added to the soil; their populations then explode and remain high until the nutrient supply is depleted. The ability of zymogenous organisms to increase their populations in response to the conditions of nutrient supply results in the rapid decomposition of animal waste, dead cells, and the like, and corresponding variations in the local rates at which these materials are mineralized.

An extremely important physiological difference among bacteria concerns their ability to grow in the absence of 0_2. Bacteria are divided into three classes in terms of their need for oxygen. Aerobes require 0_2 in the environment, although some (microaerobes) can survive when 0_2 tension is low. Anaerobes grow only in the absence of 0_2, and facultative anaerobes can develop either in the absence or the presence of the gas, utilizing it for the oxidation of organic matter if it is present and otherwise utilizing other molecules as a source of oxygen.

Although large numbers of bacteria are known to inhabit most soils, species identification and accurate counts of the total numbers of bacteria are not easy to make. Innoculating a plate with a dilute soil solution and counting the number of colonies which have appeared after a delay is the conventional procedure, but a nutritionally adequate growth medium must be supplied. Unfortunately, no single medium is adequate to all bacterial species and the nutritional needs of some are unknown. Moreover, some do not form recognizable colonies and others are very difficult to detach from the clay or humus particles in the soil.

For all these reasons, plate counts of soil bacteria reflect only some fraction of those present, and estimates of bacterial populations vary according to the means of determination. Plate counts usually range from 10^5 to 10^8 bacteria per gram of soil. Estimates by direct microscopy after suitable staining are also employed and typically range from 10^8 to 10^9 bacteria per gram. In most cases there is no correlation between plate and direct microscopic methods of counting, perhaps because the latter may include large numbers of dead cells (Alexander, 1960).

The numbers and types of bacteria are governed to a large extent by soil type and, in agricultural land, by culture. Environmental conditions that affect the density and composition of the bacterial flora include moisture, aeration, temperature, organic matter, acidity, season, and nature and state of the vegetation cover. The maximum bacterial density is found in regions of fairly high moisture content (50% to 75% of soil moisture capacity), where both aerobes and anaerobes can exist; wetter soils may have more anaerobes but fewer total numbers of bacteria (Table III-20). Table III-21 shows the distribution of some microorganisms in various horizons of a soil profile. Horizon A is the region with the most organic matter.

Bacteria as a group exhibit a wide range of nutritional requirements. At one extreme are the autotrophic (self-feeding) bacteria, which require no preformed organic matter; they obtain their energy from sunlight or by the oxidation of inorganic compounds and their carbon by the assimilation of CO_2. Autotrophs are of two kinds: photoautotrophs, whose energy is derived from sunlight, and chemoautotrophs, which obtain the energy needed for growth and biosynthetic reactions from the oxidation of inorganic materials. A few bacterial genera utilize photoautotrophic nutrition, as do all higher plants and algae. Chemoautotrophy is limited to relatively few bacterial species but is very important. Some species of chemoautotrophs are limited exclusively to inorganic oxidations to satisfy their energy needs, and these are considered to be obligate or strict chemoautotrophs; others are facultative autotrophs which may obtain energy either from the oxidation of inorganic material or organic carbon.

The obligate chemoautotrophs are highly specific, and utilize only one of a small group of related compounds. Although nutritionally

TABLE III-20. - THE EFFECT OF WATERLOGGING ON VARIOUS MICROBIOLOGICAL PROCESSING IN SOIL

Days[a]	E_h (volts)	10^3 Bacteria/g		ml Gas/100 g of Soil			
		Aerobes[b]	Anaerobes[b]	O_2	CH_4	H_2	CO_2
0	0.45	34,000	22,000	3.2	0.0	0.0	83
1	0.22	220,000	-	0.3	0.0	0.0	10
2	-0.05	110,000	23,000	0.0	0.0	0.2	172
4.5	-0.23	55,000	50,000	0.0	0.3	0.0	-
6				0.0	2.2	3.6	280
8	-0.25	53,000	170,000	0.0	14.7	2.1	-
10				0.0	21.4	0.0	226
13	-0.25	62,000	130,000				
23				0.0	60.3	13.2	-

[a] Period after waterlogging
[b] Includes facultative anaerobes.

SOURCE: Alexander (1961)

TABLE III-21. - DISTRIBUTION OF MICROORGANISMS IN VARIOUS HORIZONS OF THE SOIL PROFILE

		10^3 Organisms/g of Soil				
Horizon	Depth (cm)	Aerobic Bacteria	Anaerobic Bacteria	Actinomycetes	Fungi	Algae
A_1	3-8	7,800	1,950	2,080	119	25
A_2	20-25	1,800	379	245	50	5
A_2-B_1	35-40	472	98	49	14	0.5
B_1	65-75	10	1	5	6	0.1
B_2	135-145	1	0.4	-	3	-

SOURCE: Alexander (1961)

primitive, in that they fulfill all their needs from a completely inorganic environment, they are physiologically very complex in the sense that they require and can synthesize all the enzymes, vitamins, coenzymes, carbohydrates, and other protoplasmic constituents typical of all cells. Some chemoautotrophs and the oxidations they perform are shown in Table-III-22. Chemoautotrophs form relatively large amounts of product per cell, especially when the energy yield is small, as in ferrous or nitrite oxidation.

Organisms which require preformed organic carbon molecules to support growth are called heterotrophs; most bacteria are of this kind. Some need one or more amino acids in addition to simple inorganic molecules, some need one or more of the water-soluble B vitamins, some require certain of the organic constituents of soil and are therefore classified as requiring a "soil extract," some require a "yeast extract," and some require all of these. That this is not a very discriminating way to classify the nutritional needs of bacteria is demonstrated by Table III-23, which lists some of the common constituents of soil organic matter in "soil extract." Similarly, yeast extract is a complex mixture of organic molecules. However, this classification shows that natural microbial populations in soils are highly interdependent, since many bacteria must depend on other organisms to synthesize and excrete amino acids and vitamins. In fact, the interdependencies are far more complex than this suggests; many microbes are very limited in the number of organic molecules they can decompose and assimilate, and the decomposition and mineralization of organic matter is a process which requires the stepwise participation of different species and groups of organisms.

Most of the geochemically important biological transformations of atmospheric trace constituents appear to be performed by bacteria. These include the conversion of molecular nitrogen in the atmosphere to a form in which it can be utilized by plants and other organisms (nitrogen fixation) and the oxidation of reduced forms of sulfur, nitrogen and carbon, as well as the reduction of oxidized forms of these same

TABLE III-22. - SOME OXIDATION REACTIONS OF CHEMOAUTOTROPHS

Ammonium oxidized to nitrite. *Nitrosomonas*	$NH_4^+ + 1\ 1/2\ O_2 \rightarrow NO_2^- + 2H^+ + H_2O$
Nitrite oxidized to nitrate *Nitrobacter*	$NO_2^- + 1/2\ O_2 \rightarrow NO_3^-$
Inorganic sulfur compounds converted to sulfate. *Thiobacillus*	$S + 1\ 1/2\ O_2 + H_2O \rightarrow H_2SO_4$
Ferrous iron converted to the ferric state. *Ferrobacillus*	
H_2 oxidized. *Hydrogenomonas*, *Methanobacillus*	$2H_2 + O_2 \rightarrow 2H_2O$
CO oxidized to CO_2. *Carboxydomonas*	$CO + 1/2\ O_2 \rightarrow CO_2$

TABLE III-23. - SEVERAL CONSTITUENTS OF THE ORGANIC MOLECULES FOUND IN HUMUS AND SOIL EXTRACT

- I. Amino acids
  - Glutamic acid
  - Alanine
  - Valine
  - Proline
  - Cystine
  - Phenylalanine
- II. Purines
  - Guanine
  - Adenine
- III. Pyrimidines
  - Cystosine
  - Thymine
  - Uracil
- IV. Aromatic molecules
- V. Uronic acids
  - Glucuronic acid
  - Galacturonic acid
- VI. Amino sugars
  - Glucosamine
  - N-acetylglucosamine
- VII. Pentose sugars
  - Xylose
  - Arabinose
  - Ribose
- VIII. Hexose sugars
  - Glucose
  - Galactose
  - Mannose
- IX. Sugar alcohols
  - Inositol
  - Mannitol
- X. Methyl sugars
  - Rhamnose
  - Fucose
  - 2-O-methyl-D-xylose
  - 2-O-methyl-D-arabinose
- XI. Aliphatic acids
  - Acetic acid
  - Formic acid
  - Lactic acid
  - Succinic acid

SOURCE: Alexander (1961)

elements. The latter reactions are performed by anaerobic bacteria in certain aquatic environments or water-logged soils where the level of oxygen has been reduced by the microbial oxidation of organic matter and the replenishment of oxygen from the atmosphere is inhibited.

Table III-20 shows the sequence of events that takes place in water-logged soils. In this case, the coexistence of some aerobic and anaerobic populations during the entire sequence indicates that both aerobic and anaerobic metabolism are taking place. The simultaneous occurrence of these two apparently antagonistic processes in the same small volume of soil illustrates the complexity of the soil environment. Diverse populations and environmental conditions may occur in very close juxtaposition, and even two locations on the same grain of sand may be inhabited by different colonies of bacteria. In aquatic environments, the line separating anoxic from oxygen-rich regions may be very sharp.

Oxidized nitrogen and sulfur are readily reduced wherever organic matter is available in anoxic environments. The reduction of nitrate and nitrite to molecular nitrogen and/or nitrous oxide proceeds first; then sulfate is reduced to sulfide. Anaerobic environments are also the sites of the production of methane by fermentation and the production of carbon monoxide. Anaerobic bacterial metabolic processes appear to be the primary source of ammonia, methane, and sulfur compounds in the atmosphere and may contribute large quantities of carbon monoxide.

b. Other Microbial Inhabitants of Soils

Four other microbial groups--all composed of heterotrophic anaerobes--inhabit soils and, together with bacteria, constitute the total microbial population. These are actinomycetes, fungi, algae, and protozoa.

The actinomycetes include four families of bacteria: Mycobacteriaceae, Actinomycetaceae, Streptomycetaceae, and Actinoplanaceae. They represent in many ways a transitional group between fungi and bacteria. They are characteristically large and filamentous in structure, and may make up from 10% to 50% of the population. Actinomycetes grow slowly and are poor competitors for organic substrates when the nutrient level is high. Many species are able to decompose cellulose, starch, inulin, and chitin, and some metabolize unusual organic molecules such as parafins, phenols, steroids, and pyrimidines. Many members of the order Actinomycetales produce antibiotics, but the function of these antibiotics in natural communities has not been elucidated. Some species of Streptomyces liberate extracellular proteases which lyse bacteria.

The fungi account for the largest part of the total microbial tissue in aerated soils, due to the characteristically large diameter and extensive network of fungus filaments. Fertile land may contain 10 to 100 meters of active fungus filaments per gram of soil, corresponding to 500 to 5000 lb/acre (about 2.7 to 27 metric tons per ha). Fungi are heterotrophic in nutrition, and their distribution depends on the availability of oxidizable carbonaceous substrates. As a group, they exhibit considerable flexibility and can utilize hexoses, pentoses, organic acids, starch, pectin, cellulose, fats, and the lignin molecule as organic substrates. As a result of this flexibility, fungi are very important components of the decomposer populations in forests, where most of the standing crop is in the form of cellulose, and where representatives of all the common classes of fungi can utilize and degrade the major plant constituents. Since fungi can also utilize proteinaceous substances, they are active in the formation of ammonium and simple nitrogen compounds in soil, making these available for uptake by plant roots. Under certain conditions, fungi compete with plant roots for nitrogenous substances.

Algae are single-celled or filamentous plants that contain chlorophyll and are thus capable of photosynthesis in the light. Algae in soils do not appear to be important primary producers, and many falcultatively heterotrophic algae are found at depths where light is absent and photosynthesis impossible. Algae found in soils include green algae, diatoms, and blue-green algae. They are important in colonizing barren rocks and soils, and sometimes are responsible for a surface bloom on on wet virgin soil, producing an algae mat important for binding soil particles. The most important function of algae in waterlogged soils is the fixation of molecular nitrogen, which is performed by some of the genera of blue-green algae. These organisms appear to supply most of the fixed nitrogen in rice paddies and may be significant in other waterlogged soils. Blue-green algae are often prominent in eutrophic lakes and rivers.

The four microbial groups discussed above are microflora; the last is the protozoa, which are classified as part of the soil fauna and constitute the simplest forms of invertebrate animals. Although a few photosynthetic protozoa containing chlorophyll and possessing flagella which enable them to move about are found in soil, they are not particularly important. Most protozoa are predators that feed varaciously on bacteria, and many of them are highly selective in their prey. Therefore, they perform an ecologically important function in regulating bacterial populations, and they also serve to promote the turnover of bacterial tissue.

c. Microbial Decomposition of Soil Organic Matter

The preceding discussions of microbial populations gives some indication of the complexity of the interactions among microbial species present in soils and also serves to indicate the nature of the overall functions performed. Simply, these consist of the breakdown of complex organic molecules present in organized plant and animal tissue into increasingly simple molecules and ultimately into simple inorganic molecules which are available for recycling, including the restoration of N_2 and CO_2 to the atmosphere. All heterotrophs are armed with a battery of enzymes which promote the decomposition of plant and animal tissues and result in the production of microbial tissue and the excretion of some unused decomposition products. Many organisms may share the same enzymes, but the decomposition reactions that any single species can effect are characteristically limited. Many organisms must depend on other members of the community to produce the substrates or essential growth factors they need. This high degree of interdependence is one reason why microbial communities are difficult to describe. Another reason is that many species are extremely versatile and can exhibit a range of reactions when studied in pure cultures in the laboratory which they never or rarely perform in nature, due to the effects of other organisms on substrate availability or other relevant parameters. Demonstration of the occurrence of a reaction in the laboratory is not evidence that it occurs to any significant degree in the natural environment; thus, laboratory data should be extrapolated to the field only with the greatest care.

4. The Terrestrial and Marine Biospheres

For our purposes the overall features of the interaction of the biosphere with other reservoirs can be best understood in terms of the distribution of carbon.

Table III-24 shows the distribution of organic and inorganic carbon on earth. Most of the carbon is present as carbonates in the sediments. At present most inorganic carbonate is being precipitated in the ocean as biogenic carbonate--the shells and skeletons of marine organisms, but in earlier periods much of the carbonates appear to have been precipitated as inorganic deposits (Garrels and MacKensie, 1971). Nevertheless, it is clear that most carbon has been recycled biologically many times.

As shown in Table III-24, the present store of atmospheric carbon dioxide represents a small portion of the total. The ocean contains over fifty times this amount as inorganic carbonates or as free CO_2 (including carbonic acid).

The estimates of organic carbon making up the land and marine biospheres are discussed below.

a. Terrestrial Biosphere

We have pointed out earlier that the land biosphere may be functionally divided into five subgroups comprising (1) the biomass represented by all plants, (2) the herbivores, carnivores, and related consumers,

TABLE III-24. - CARBON RESERVOIRS

	Total Carbon (units of 10^6 metric tons)	Atmospheric CO_2 Equivalents
Lithosphere		
Carbonates in Sediments[a]	35,500 to 99,000 million	53,000 - 147,000
Primary Igneous Rock	4,380 million	6,500
Fossil Organic C[b]	68 million	100
Atmosphere		
CO_2	670,000	1
CH_4	3,270	0.005
CO	213	0.0003
Ocean		
Bicarbonates + Carbonates	35,400,000	53
Free CO_2 (CO_2 + H_2CO_3)[b]	1,350,000	2
Marine Biosphere		
Standing Crop (Plants and Animals)	3,330	0.004
Dissolved Organic Matter	708,000 - 1,400,000	1-2
Biogenic $CaCO_3$	2,000	0.0003
Land Biosphere		
Plant Biomass	1,200,000	1.8
Decomposing Soil Humus	350,000 - 1,500,000	0.5 - 2.2
Resistant Humus	400,000	0.6
Decomposers	2.8	-
Herbivores and Predators	1.6	-

[a] Range of carbon as carbonates in the sediments is defined by the shale: sandstone: limestone ratios 84:.2:6 Ramkama and Sahama, 1950) and 74:11:15 (Garrels and MacKensie, 1969) and the total mass of sediments of 1.7 x 10^{21} kg (Poldevaart, 1955) and 3.2 x 10^{21} kg (Garrels and MacKensie, 1971)

[b] Hutchinson (1954).

(3) the decomposer organisms present in the soil, (4) the soil store of recycling organic matter or humus, and (5) the soil reservoir of resistant humus, which is in fact incipient fossil organic matter. The first four together constitute a reservoir of atmospheric carbon dioxide that is eventually returned to the atmosphere, while the last is a store that is isolated from the atmosphere for a long period of time.

On land the most significant primary producers are trees, which are extremely long lived and massive relative to the animal population. Only about 10% of annual production is consumed by herbivores, and most of this is respired to supply energy to these organisms rather than accumulated as biomass. On the average, the herbivore-carnivore food chain is short, and secondary production by these organisms may be neglected. Most plant biomass is in the form of wood in terrestrial forests, although large areas of other productive systems make important contributions to the total.

The total amount of standing crop is difficult to estimate, because the density of plant cover varies so widely. Tables III-25 and III-26 present two estimates of the total mass of living carbon in the biosphere. Table III-25 (from Olson, 1970) lists estimates of the area and standing crop of several different types of forest and other vegetation areas, and also lists estimates of the annual net primary productivity of each. Table III-26 is a comparable breakdown of types of vegetation and their productivity, but it lists the total recyclable carbon pool (including recycling humus) rather than carbon in living organic matter. Table III-27(from Deevey, 1970) shows estimates of the terrestrial carbon biomass and annual productivity, which we have used extensively in this document. These estimates are larger than those in Table III-26 and imply a total carbon pool somewhat larger than that shown in III-25. The discrepancies illustrate the uncertainty of all methods used to estimate carbon pool size and biospheric CO_2 exchange with the atmosphere.

TABLE III-25. PROVISIONAL GEOGRAPHIC ESTIMATES FOR ECOSYSTEM AREAS, ANNUAL NET PRIMARY CARBON PRODUCTION, AND CARBON BUDGET OF THE WORLD'S LAND MASSES

	Area	Net Primary Production of Carbon		Live Carbon Pool		
	(10^6 km^2	tons/km^2/yr	10^9 tons	tons/km^2	10^9 tons	NPP/pool
Woodland or Forest						
Temperate "cold-deciduous"	8	1,000	8	10,000	80	0.10
Conifer: boreal and mixed	15	600	9	8,000	120	0.075
Rainforest: temperate	1	1,200	1.2	12,000	12	0.10
Rainforest: tropical, subtropical	10	1,500	15	20,000	200	0.075
Dry woodlands (various)	14	200	2.8	5,000	70	0.04
Subtotal	48		36		482	
Nonforest						
Agricultural	15	400	6	1,000	15	0.4
Grassland	26	300	7.8	700	18.2	0.43
Tundra-like	12	100	1.2	600	7.2	0.17
Other "desert"	32	100	3.2	600	19.2	0.17
Glaciers	15		0			
Subtotal	100		18.2		79.6	
Continents	148		54.2		561.6	
Average/continents		366		3,800		
Average/earth surface (continental share)		106		1,100		

SOURCE: Olson (1970)

TABLE III-26. - ORGANIC CARBON AND ITS RATES OF PRODUCTION

(LIVING AND DEAD, EXCLUDING INCIPIENT FOSSIL DEPOSITS)

	Area (10^6 km^2)	Organic Carbon Pool (10^9 metric tons)	Annual Production (10^9 metric tons)
Reservoir			
Forest and woodland	48	1,012	36
Grassland and tundra	38	314	9
Desert and semidesert	32	59	3
Wetlands	2	30	2
Glaciers and barren	15	0	0
Agricultural	15	165	6
Total terrestrial	150	1,580	56
Oceanic	361	703	22
Burning Fossil fuel (1970)			4
Atmospheric pool		683	

SOURCE: SCEP (1970)

TABLE III-27. - LAND BIOMASS, PRIMARY PRODUCTION, AND RESPIRATION

	Biomass/ha (metric tons)	Global Total (10^6 metric tons)
Standing Crop		
Dry Matter	200	3,000,000
As C	80	1,200,000
N	0.1	1,500
Net Primary Production		
Dry Matter	13.4	201,000
As C	5.36	80.000
N	0.162	2,430
Litter Fall[a]		
Dry Matter	11.2	168,000
As C	4.5	67,200
N	0.124	1,860
Accumulation		
Dry Matter	2.15	32,250
As C	0.86	12,900
N	0.038	570

[a] May be considered equivalent to respiration

SOURCE: Deevey (1970)

As a first approximation, the land and marine biospheres are regarded as being in balance; that is, the annual production of biomass is believed to be balanced by an annual oxidation of an equivalent amount of organic matter. The actual balance depends on the individual system under consideration. In young systems, such as fields newly colonized by young trees after a fire, production greatly exceeds consumption by the plants and the associated herbivores and decomposer communities. Consequently, biomass accumulates rapidly. As the community ages, some of the older trees die and are replaced by younger plants, and eventually the community is composed of a variety of individuals of differing species and ages. At some point the death of old plants balances the accumulation of tissue by living ones. The annual addition to the soil reservoir of recycling humus is then equal to consumption by soil flora and fauna. At this point the system is mature, and the production of reduced carbon is balanced by its oxidation.

Until the compilation of Rodin and Bazilevich (1967) made the calculations of Deevey (1970) possible, most workers assumed that the terrestrial biosphere represented such a balanced state, although it is clear that extensive deforestation by humans necessitated by the need for forest products and agricultural land in fact might have put the land biosphere as a whole in an average state of immaturity. Deevey's calculations found this to be the case. On the average, the terrestrial biosphere presently accumulates plant tissue every year. If we assume that the soil organic matter is approximately in balance, so that the annual oxidation of recyclable humus stores is approximately equal to the annual increment in the form of litter fall,* then the total global respiration is seen to be approximately equivalent to the litter fall. (We ignore herbivore grazing, because it is comparatively negligible). Deevey's data then imply that the land biosphere annually withdraws about 80,000 million tons of carbon as carbon dioxide from the atmosphere, but returns only 67,200 million tons, resulting in the temporary reduction of the total CO_2 atmospheric store (under the doubtful assumption that other reservoir exchanges are in balance).

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*This may be questioned on the grounds that some agricultural practices may accelerate the oxidation of stored soil humus.

Table III-28 compares several estimates of the annual net and gross primary productivity in the literature.

Table III-29 contains some estimates of the sizes of the various other carbon reservoirs, expressed both as 10^9 tons of carbon and also in units of years of annual global primary productivity of the land. The uncertainty regarding the size of the reservoir of recycling humus is much greater than indicated in the table; estimates of the humus reservoir are simply guesses. It could be as small as the standing crop of living tissue, or as much as five times this quantity. The figures shown in Tables III-24 and III-29 are used because they have appeared in the literature, or can be derived from figures which have appeared in the literature. The lower estimate is based on Broeker (1970), who estimates a mean soil depth for the world of 10 cm, a density of 1.3 g/cm^3, and a 5% carbon content. Koyama (1964) estimated the amount of soil in world forests and grasslands which are contributing to the production of methane; we have based the larger estimate of total humus on his figures and estimated a 1-5% range of carbon content. To obtain the amount of recycling humus, we merely subtracted Waksman's estimate of the total refractory humus in soils.

The estimates for soil decomposers and herbivores and carnivores were taken from Bowen (1966).

It is clear from this discussion that the mass, composition, and rate of photosynthesis of the land biosphere are very poorly understood. Estimates of the rate of cycling of atmospheric CO_2 based on ^{14}C studies indicate that the most probable rate of removal of carbon from the atmosphere by the land biosphere is 80 x 10^9 tons per year, corresponding to a mean residence time of 8.5 years (Nydal, 1968); however, the analysis is not precise - the implied range is from a maximum of 155 x 10^9 tons per year to a minimum which is essentially negligible - so we may conclude that the ^{14}C method of estimating atmospheric exchange with the biosphere is no more precise than the current methods based on extrapolation of observations of individual vegetation types.

TABLE III-28. - ESTIMATES OF CARBON PRODUCTION IN THE BIOSPHERE
(10^5 Grams per year)

Gross			Net			
Land	Ocean	Total	Land	Ocean	Total	Source
			16.3		16.3	Schroeder (1919)
			15.1	28.6	43.7	Noddack (1937)
20	44-203	64-223				Riley (1944)
	23.5			15		Steeman-Nielson (1958)
24	≤169	≤184	21	32	53	Fogg (1958)
				53		Ryther (1959)
17.2	25	42.2	10.3	25	35.3	Muller (1960)
			106	29	135	Bowen (1966)
			15	12-15	27-30	Lieth (1963)
				19		Ryther (1969)
			56	22	78	MIT SCEP (1970)
			80.3[a]			Deevey (1970)

[a] Annual withdrawal is 80.3; annual respiration is 67.4

SOURCES: Bowen (1966), Lieth (1963), Ryther (1969), SCEP (1970), and Deevey (1970)

TABLE III-29. - CARBON IN THE LAND BIOSPHERE

	Total C (10^9T)	Total C (Yrs global productivity[a])
Living Organic Matter	561 - 1,200	8 - 17
Decomposing Soil Humus	350 - 1,500	5 - 21.4
Refractory Humus	400	6
Decomposers	0.0028	4×10^{-5}
Herbivores and Predators	0.0016	2.3×10^{-5}
Total Recyclable	911 - 2,700	13 - 39
TOTAL	1,311 - 3,100	19 - 44

[a] Assuming annual land fixation rate of 70×10^9 tons of carbon

b. Marine Biosphere

The marine biosphere differs from the terrestrial biosphere as a reservoir for atmospheric elements in several important ways. The primary producers in the sea are single-celled algae, which differ from land plants in containing relatively little cellulose and a larger proportion of protein, and having a very short life. Consequently, although the standing crop is small, the turnover is very large. The extremely small size of these organisms, combined with their relatively large proportion of protein, results in relatively long food chains, so the standing crop of animals--microscopic zooplankton plus larger carnivores--is larger than that of plants.

The overall productivity of the oceans is small compared with their extent or the amount of photosynthetic energy available. This is due to the manner in which nutrient supplies are replenished. As on land, the nutrients are recycled through organic matter, being incorporated in plant tissue at the time of its formation, cycled through consumers and decomposers, and mineralized only as the organic carbon is oxidized. Plants grow in the photic zone, where light is available--usually the top 10 to 100 meters--and increase in size as they accumulate tissue. When these single-celled organisms die, they settle in the water. Some oxidation of organic matter--and release of the nutrient supplies contained in the protoplasm--occurs near the surface where most of the plants are growing, but most of the nutrient regeneration occurs below the levels where sufficient light is available to permit plants to grow and use this nutrient supply.

Some organic matter appears to be oxidized throughout the water column; studies of the changes in concentration of nutrients, oxygen, and carbon near the bottom indicate that some oxidation of organic matter occurs in the very deep water of the oceans (Li, Takahashi, and Broeker, 1969). Consequently, plants growing at the surface are dependent on the natural circulation of the oceans to supply the nutrients they need for growth. Nutrients are available as suspended matter in some coastal waters associated with river outflow or the scouring action of shore currents. In the open ocean there are some regions of upwelling where intermediate water comes to the surface to replace water removed in surface currents; these occur off the western coasts of South America and Africa. The Wedell Sea is a very productive region in summer, due to the direct exchange of surface water with nutrient-rich deep water.

This distribution of upwelling and nutrient availability leads to a very large range of mean productivities in the ocean, and to a corresponding range in the rate at which unicellular plants grow and the size they achieve. In general, rapidly growing organisms become large and can be eaten by larger grazing animals; as a consequence, the food chains tend to be shorter in the more productive areas. The efficiency with which food consumed is converted to animal tissue is a function of the ratio of respiration to food consumption, which also tends to be higher in the productive regions. Tables III-30 and III-31 from Ryther (1969) contain estimates of primary productivity in the various regions of the oceans and the corresponding conversion of this food to animal tissue. We have used these values to derive crude estimates of the standing stock of plants and animals in the ocean, under the assumption that the mean lifetime of plants is 0.1 year and that of animals is 0.5 year.

The data of Ryther (1969) suggest that virtually all the primary production goes to increase plant standing stock. In fact, some of the material photosynthesized by algae is directly excreted into the environment as dissolved organic matter (Duursma, 1965). The proportion of primary production which is so excreted is not known; it may vary with nutrient availability in the environment as well as with the plant species and other factors (Duursma, 1965; Hellebust, 1970; Hoyt, 1970). Some of the excreted organic matter may be used for food, either ingested in dissolved form or after bubbling action in the water has caused it to form complex proteinaceous particulate matter (Baylor and Sutcliffe, 1963; Riley, 1963; Wangersky, 1965), but most remains dissolved.

TABLE III-30. - ESTIMATES OF POTENTIAL YIELDS AT VARIOUS TROPHIC LEVELS (METRIC TONS PER YEAR)

		Ecological Efficiency Factor					
		10%		15%		20%	
	Trophic Level	Carbon	Total Weight	Carbon	Total Weight	Carbon	Total Weight
0.	Phytoplankton (Net particulate production)	1.9×10^{10}		1.9×10^{10}		1.9×10^{10}	
1.	Herbivores	1.9×10^{9}	1.9×10^{10}	2.8×10^{9}	2.8×10^{10}	3.8×10^{9}	3.8×10^{10}
2.	1st Stage Carnivores	1.9×10^{8}	1.9×10^{9}	4.2×10^{8}	4.2×10^{9}	7.6×10^{8}	7.6×10^{9}
3.	2nd Stage Carnivores	1.9×10^{7}	1.9×10^{8}	6.4×10^{7}	6.4×10^{8}	15.2×10^{7}	15.2×10^{8}
4.	3rd Stage Carnivores	1.9×10^{6}	1.9×10^{7}	9.6×10^{6}	9.6×10^{7}	30.4×10^{6}	30.4×10^{7}

SOURCE: Ryther (1969)

TABLE III-31. - PRODUCTIVITY IN THE OCEAN

Province	Percentage of Ocean	Area (10^6 km^2)	Mean Primary Productivity (g C/m^2/yr)	Total Primary Productivity (10^9 T C/yr)	Trophic Level	Efficiency %	Total Secondary Productivity (10^9 T C/yr)
Open Ocean	90	326	50	16.3	5	10	1.811
Coastal Zone[a]	9.9	36	100	3.6	3	15	0.639
Upwelling Areas	0.1	3.6	300	0.1	1.5	20	0.022
Total				20.0			2.572

[a] Includes offshore areas of high productivity

SOURCE: Adapted from Ryther (1969)

As a result of this process, very large quantities of dissolved organic matter are present in the ocean, most of it refractory to further oxidation by biological or abiological means (Wangersky and Gordon, 1965; Menzel, 1970; Menzel and Goering, 1966). This material constitutes a store of "water humus" which is extremely large compared to the probable size of the corresponding store on land or to the annual productivity of the total marine biosphere.

The total quantity of dissolved organic carbon in the ocean is not known. Duursma (1961, as cited in Turekian, 1969) gives 0.5 mg/1 as a mean for the entire ocean, while others suggest that the mean concentration in the top 1000 to 500 meters may be higher. (See, for example, Wangersky, 1965; Menzel and Goering, 1966; and Manzel and Ryther, 1968). The resulting totals are much lower than earlier estimates that have appeared in the literature; Lieth (1963), for example, estimates 3220 x 10^9 tons of dissolved organic carbon in the ocean.

The marine biosphere also processes carbon in the form of carbonate shells and skeletons. Table III-24 gives some estimates of the total quantity of biologically precipitated carbonate present in the ocean, together with estimates of its rate of production. These are based on the work of Li, Takahashi, and Broeker (1969), but should be regarded as uncertain.

Some organic carbon is deposited in the marine sediments every year. Broeker (1970) has estimated this deposition rate as about 2 x 10^{13} grams C per year, which is about 1% of the total estimated annual production. Proportionately much more organic carbon is sedimented in anoxic basins than in oxygen-rich waters. Richards (1965) cites studies showing two to four times as much organic carbon in sediments underlying anoxic regions as in those not exposed to anoxic conditions.

The exchange of carbon dioxide with the ocean has been estimated on the basis of ^{14}C studies to be between 70 and 130 billion tons of carbon per year, based on evidence regarding the exchange during the period after 1963 (Nydal, 1968).

TABLE III-32. - ORGANIC CARBON IN THE OCEAN

	Total C (10^9 T)	Total C (years of global productivity[a])
Green Plants	2.0	0.1
Animals	1.3	0.065
Recycling Dissolved Organic Matter[b]	22.7	1.1
Total in Circulation	26.1	1.3
Refractory Carbon		
Dissolved organic matter[c]	675 - 780	34 - 39
Organic particulates[d]	68 - 78	3 - 4
Total Refractory Carbon	743 - 858	37 - 43
Total Carbon	769 - 884	39 - 44

a. Assumes annual global primary ocean production to be 20 x 10^9 T carbon.

b. Difference between dissolved organic matter in the top 500 meters and that in remainder of water column, assuming data of Menzel and Ryther (1968) are representative for whole ocean.

c. The lower estimate corresponds to a mean concentration of 0.5 mg/l (Duursma, 1961). The higher estimate assumes 0.5 mg/l in deep water and 0.8 mg/l in top 1000 m, and should be regarded as an arbitrary upper limit.

d. Particulates assumed to average 10% of dissolved organic matter.

5. Conclusions

The behavior of the biosphere as a terrestrial reservoir of atmospheric materials is not well understood, because it is such a complicated system. In the following chapters we discuss problems associated with clarifying the role of the biosphere in cycling atmospheric constituents. We will point out the inadequacies of present methods of estimating biospheric exchange rates and mechanisms, and we will suggest methods for improving the bases of these estimates. Better knowledge of biospheric functions in other areas would help clarify its role in these atmospheric exchanges.

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PART II. BIOLOGICAL CYCLING OF SELECTED GASES

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IV. METHANE

A. INTRODUCTION

Methane is odorless, relatively inert chemically, and innocuous in low concentrations. After carbon dioxide, it is the most abundant carbon-containing molecule in the atmosphere. Its concentration is usually reported as 1.5 ppm; however, there have been relatively few studies of its atmospheric abundance, probably because it is uninteresting and because methane pollution seems to represent no particular threat. These observations suggest that the value ranges between 1.2 and 1.5 ppm in the troposphere and lower in the stratosphere.

Methane is the product of anaerobic fermentation by a physiologically specialized group of microorganisms which has not been extensively studied. Although there are good grounds for supposing that methane is produced in large quantities, the fact that it is biologically consumed as well as produced makes it difficult to estimate the annual rate of injection of biogenic methane into the atmosphere. Section B discusses the biological production and consumption of methane.

The chemical reactions of methane in the atmosphere and the relatively few observations of its abundance reported in the literature are discussed in Section C. Although methane is stable in the troposphere, it is rapidly oxidized in the stratosphere; nevertheless, the stratospheric sink for methane may be effectively small, because only small amounts of the gas reach that altitude. Tropospheric abundances of methane are variable, and this variability implies a shorter lifetime than that estimated on the basis of the effectiveness of the stratospheric sink.

The elements of the methane budget are summarized in Section D. There are some uncertainties in the estimates of anthropogenic methane sources associated with coal mining, production and use of natural gas, and automobile hydrocarbon exhausts, but the total involved is modest and falls between 17 and 68 million tons per year. Greater uncertainties regarding biological production of methane and, more important, the proportion of biogenic methane which is injected into the atmosphere lead to estimates ranging from 45 to 494 million tons per year. Together these source estimates imply an atmospheric lifetime of between 6 and 56 years.

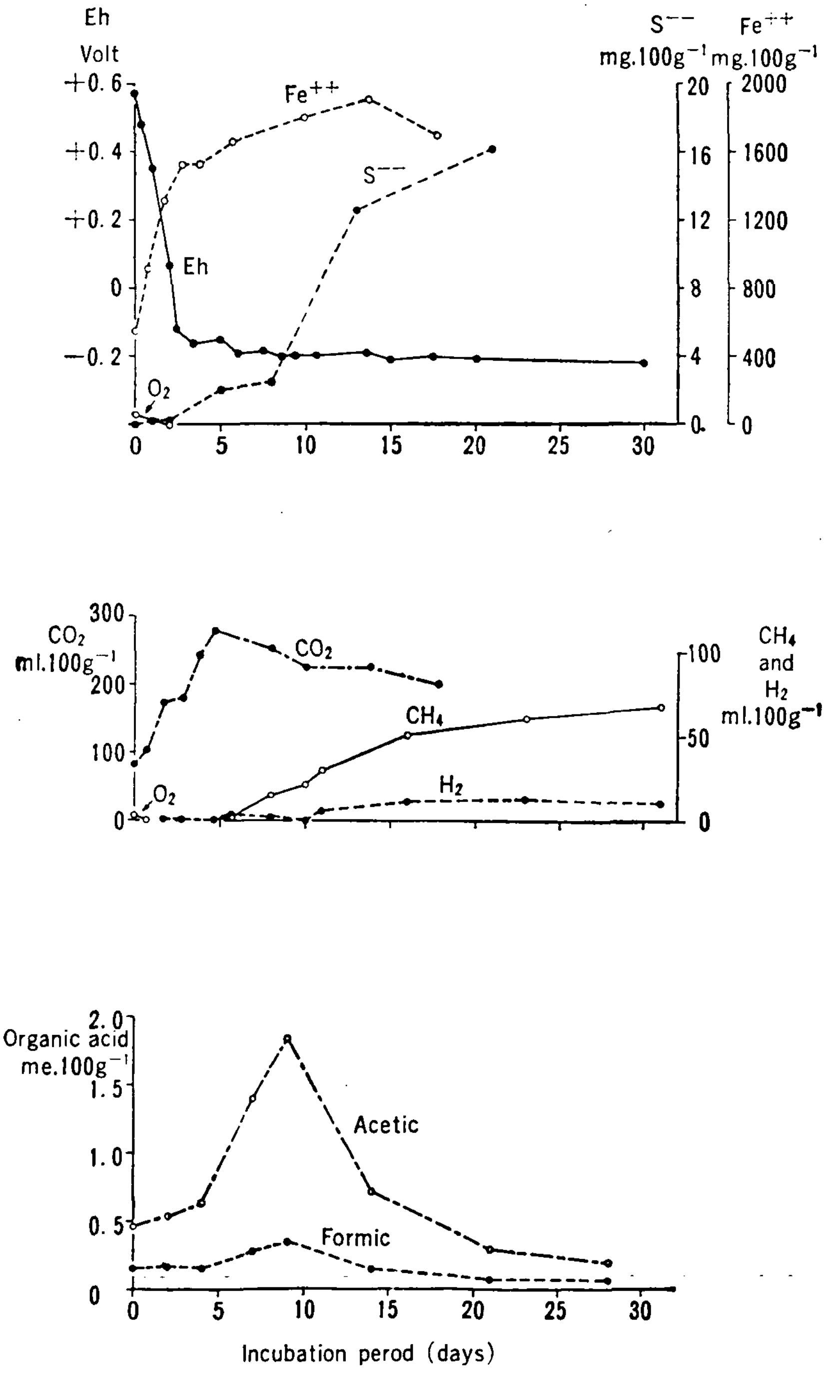
The final brief section discusses some conclusions regarding the nature and utility of additional observations which would improve knowledge of the biological processes involved in the atmospheric cycling of methane.

B. BIOLOGICAL PRODUCTION AND CONSUMPTION OF METHANE

Methane is produced in anoxic environments by a specialized group of bacteria living in waterlogged soils, marshes, swamps, manure piles, the intestines of higher animals, and marine and freshwater sediments. These organisms metabolize simple organic compounds such as short-chain fatty acids and simple alcohols, and can also produce methane from CO_2. Unable to metabolize more complex organic materials, methane producers must associate with other microorganisms that can produce these simple organic substrates from sugars, proteins, cellulose, and hemicelluloses.

In addition to suitable organic substrates, methane producers require an aquatic environment containing no oxygen. This is generally provided by the aerobic respiration of other microorganisms, which removes the available oxygen. If oxygen replacement is limited, or if the demand exceeds the rate at which it can be replaced, the O_2 tension and redox potential E_h fall. Biological action reduces nitrate and nitrite, presumably to N_2 or N_2O, and sulfate reduction and methane and H_2 formation begin. This whole process may take place in 5 to 15 days after flooding of soils or rice paddies (Koyama, 1964) or the initiation of anoxic conditions in the bottoms of thermally stratified lakes.

Koyama (1954, 1963, 1964) studied the production of methane in lakes, flooded soils, and paddy soils. Figure IV-1 shows the changes he observed in one sample of soil incubated under anoxic conditions. The curves illustrate the relationship between the redox potential, the concentration of formic and acetic acid, the production of S^{--}, and methane in a paddy soil incubated at 35°C.



Source: Koyama (1964)

FIGURE IV–1 CHEMICAL CHANGES IN FLOODED PADDY SOIL

Stephenson (1949) lists the following methane-yielding reactions of some methane producers:

$$4HCOOH \rightarrow CH_4 + 3CO_2 + 2H_2O$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

$$HCHO + 2H_2 \rightarrow CH_4 + H_2O$$

$$CH_3OH + H_2 \rightarrow CH_4 + H_2O$$

Koyama (1964) used ^{14}C-labeled acetic acid and carbonate, and observed the following reactions:

$$^{14}CH_3COOH \rightarrow {}^{14}CH_4 + CO_2$$

$$^{14}CO_2 + 4H_2A \rightarrow {}^{14}CH_4 + 2H_2O + 4A$$

$$CH_3{}^{14}COOH \rightarrow CH_4 + {}^{14}CO_2$$

where H_2A is a hydrogen donor.

Methane production is not greatly affected by pressure. Experiments in which productive water-logged soil was incubated under pressure indicate that methane production may continue even at great depths (Table IV-1). Methane produced in such sediments may diffuse into the water, where it may be biologically oxidized if oxygen is available, or it may under some circumstances form bubbles that escape to the atmosphere.

TABLE IV-1. - GASEOUS COMPONENTS PRODUCED IN LAKE SEDIMENTS FROM LAKE KIZAKI-KO, INCUBATED AT 35°C UNDER VARIOUS PRESSURES*

Period of Incubation (days)	Pressure (atm)	CO_2 (ml/100 g)	CH_4 (ml/100 g)	H_2 (ml/100 g)
0	1	17.6	1.08	0.00
4	1	22.6	3.94	0.19
9	1	20.2	7.89	0.51
9	50	19.7	5.05	0.35
9	100	29.0	6.17	0.28
9	150	21.6	6.31	0.52
9	200	20.6	6.39	0.42
9	250	21.2	6.80	0.37
9	360	21.1	6.37	0.09
9	450	24.5	4.95	0.04

*2000 meters depth

SOURCE: Koyama (1964)

Tables IV-2 and IV-3 show the methane concentration of sediments in three Japanese lakes, the pressures of gases in the sediments, and the hydrostatic pressure at the lake bottom. In two cases the total gas pressure exceeds the hydrostatic pressure, indicating that gases must be diffusing out into the water. Measurement of the distribution of gases dissolved in one of the lakes confirms this observation (Table IV-4). Methane is found to be most abundant near the sediment-water interface, where there is no oxygen. Above this level, oxygen concentration increases rapidly and the methane content declines rapidly. There is essentially no methane within 17.5 meters of the surface of this lake.

Hutchinson (1957) points out that methane may reach the surface if production in the depths is sufficient to permit the formation of bubbles. This requires supersaturation of the water and consequently is an inverse function of temperature and a direct function of depth. Hutchinson states that bubble production is possible during summer stratification at depths up to 10 meters, where the critical concentration of methane at which bubble formation is possible is about 29 to 38 mg/l at a temperature of 7°C. He cites evidence that Lake Mendota mud produced approximately this much methane during the entire season when cultured at this temperature.

Hutchinson (1957) also discusses the case of Lake Beloye, which is frozen from November to April and contains a depression about 9 to 13 meters deep. There is a marked and continuous production of methane in this deep; it is most pronounced in summer thaw, when the temperature at the bottom of the lake reaches 10° to 12°, but is considerable in any season. Bubbles produced in the sediments are apparent in the ice cover over the deep.

When formed, the bubbles contain 74.1%-83.5% CH_4 and 5.1-18.4% H_2. During ascent they lose their hydrogen, and the methane content drops to 20%-24%. The oxygen content increases slightly while the nitrogen content increases considerably. Hutchinson concludes that most of the methane and all of the H_2 is oxidized in the water, resulting in locally lowered O_2 concentrations.

TABLE IV-2. - AVERAGE CONTENT OF GASES IN LAKE SEDIMENTS AT THE GREATEST DEPTHS OF THREE LINKED MOUNTAIN LAKES

(In ml/l of Interstitial Water of Sediments)

Location	Depth (m)	CO_2	O_2	N_2	CH_4	H_2
Lake Nakatsuna-ko	12	234	0	12	72	7
Lake Kizaki-ko	29	137	0	17	110	17
Lake Aoki-ko	56	89	0	18	161	24

SOURCE: Koyama, (1964)

TABLE IV-3. - AVERAGE PRESSURES OF GASES IN SEDIMENTS AND THE HYDROSTATIC PRESSURES AT THE BOTTOM

(atmospheres)

Location	Hydrostatic Pressure at the Bottom	Average Total Gas Pressure	Average Partial Pressure			
			CO_2	N_2	CH_4	H_2
Lake Nakatsuna-ko	2.08	2.68	0.18	0.58	1.55	0.37
Lake Kizaki-ko	3.71	4.13	0.10	0.82	2.38	0.83
Lake Aoki-ko	6.32	5.14	0.06	0.82	3.18	1.09

SOURCE: Koyama (1964)

TABLE IV-4. - VERTICAL DISTRIBUTION OF VARIOUS GASES DISSOLVED IN LAKE WATER (Lake Kizaki-ko, November 1, 1962)

Depth (m)	Water Temp. (°C)	pH	O_2 (ml/l)	Total CO_2 (ml/l)	N_2 + A (ml/l)	CH_4 (ml/l)
0	15.10	6.9	6.54	6.43	12.96	0.00
2.5	–	6.8	6.72	7.18	13.20	0.00
5.0	15.00	6.8	6.41	7.34	13.00	0.00
7.5	–	–	6.70	6.43	13.10	0.00
10.0	13.61	6.5	5.35	8.22	14.43	0.00
12.5	9.07	–	3.16	9.73	15.40	0.00
15.0	8.62	6.3	2.93	10.83	15.70	0.00
17.5	–	–	2.50	10.12	15.74	0.006
20.0	7.70	6.3	1.57	11.10	15.70	0.009
22.5	–	6.2	0.16	13.14	15.79	0.024
25.0	7.11	6.3	0.00	14.87	17.27	0.13
27.5[a]	–	6.5	0.00	16.75	18.56	0.29
Above the Bottom Surface (cm)						
50	7.05	6.6	0.00	19.16	19.75	0.36
5	–	6.5	0.00	19.76	20.16	0.54

[a] One meter above bottom

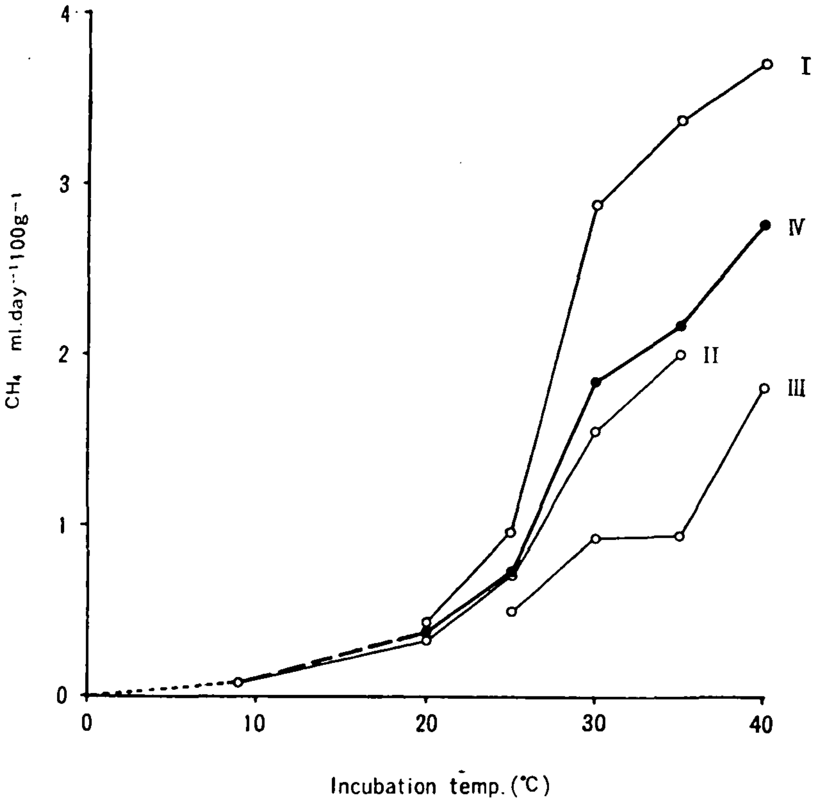
SOURCE: Koyama (1964)

Koyama (1964) infers that methane produced in sediments can be released into the atmosphere only if the water is very shallow. He considers rice paddies, which have an extremely high organic content and are waterlogged for about four months per year. Although these soils are "in contact" with the air through an extremely shallow layer of water, his studies indicate that the redox potential drops rapidly with depth from the soil surface (-0.05 at 0.5 cm depth to -0.22 at 2.0 and 4.0 cm depth), indicating the existence of anoxic conditions necessary for the production of methane and hydrogen. Production of methane in such soils is heavily temperature-dependent and may be very high. Table IV-5 shows the range of observed methane production in nine paddy soils cultured at 30°C. Figure IV-2 shows the dependence of productivity on temperature.

Koyama estimates the average production of Japanese rice paddy soils by considering the range of productivities in numerous samples studied, together with knowledge of the temperature dependence of production. The average production is 2.33 ml/100 gm soil/day, or about 2.3×10^{12} grams CH_4 for the 2.8×10^{14} cm^2 of rice paddy soils in Japan.

To estimate the global production of methane from all sources, Koyama (1964) also studied methane production in cultures of upland grass and forest soils. This was found to be less than 1/200 and 1/1000, respectively, of that in paddy soils, due to the fact that these soils are usually porous and rich in oxygen.

Koyama (1963, 1964) equates the production of methane with its release into the atmosphere. In fact, methane is oxidized by a specialized group of microorganisms that are found in nature and in most environments in which methane is produced. As obligate aerobes, they require O_2 and hence are located near the biological source of methane wherever sufficient oxygen is available. Thus, they may be isolated from a surface film common on paddy soils and swamps; they can also be isolated from most well-drained soils, stream beds, pond muds, sewage, and barnyard manure. These organisms probably subsist on the methane released by



I – Yamoto muck paddy soil
II – Anjo dry paddy soil
III – Yamoto alluvial paddy soil
IV – Average paddy soil

Source: Koyama (1964)

FIGURE IV–2 METHANE PRODUCTION IN PADDY SOILS

TABLE IV-5. - PRODUCTION RATE OF METHANE IN VARIOUS WATERLOGGED PADDY SOILS INCUBATED AT 30°C

(ml/day/100 g of dry soil)

Paddy Soil	CH_4 Produced
Yamoto muck soil	3.91
Nishihata soil	3.75
Yoshida muck soil	3.59
Yashirota soil	2.97
Yoshida good soil	1.72
Anjo soil	1.57
Yoshida sandy soil	1.36
Nagano soil	1.10
Sanage soil	1.04
Average	2.33

SOURCE: Adapted from Koyama (1964)

anaerobic decomposition. In soil they seem to be more abundant in lower layers than near the surface. Their prevalence in the subsoil of areas containing deposits of petroleum or natural gas has led to the suggestion that they be used as a geological tool in prospecting for natural gas (Alexander, 1961).

Some strains of CH_4 oxidizers can also utilize methanol but cannot develop upon more complex hydrocarbons, alcohols, or carbohydrates; other strains metabolize a number of simple hydrocarbons such as propane, ethylene, and hexane (Alexander, 1961). Cell suspensions of CH_4 oxidizers metabolize methanol, formaldehyde, and formic acid in addition to gaseous hydrocarbons. These and other studies indicate that the pathway of CH_4 oxidation proceeds as follows:

$$CH_4 \rightarrow CH_3OH \rightarrow HCOOH \rightarrow CO_2$$

The existence of methane oxidizers clearly implies that production of methane in anoxic environments by fermentation is not equivalent to the injection of methane into the atmosphere, since much of the methane produced may be biologically oxidized before it can reach the atmosphere. Koyama (1964) incubated his soil samples anaerobically and therefore could not observe the effects of aerobic oxidation.

Hutchinson (1954) cites studies implying that the atmospheric release of biogenic methane from swamp environments is low. He discusses methane "production"* data for a freshwater pond 2 m deep draining into Chesapeake Bay, which in late summer produces 0.063 ml CH_4 per cm^2 per day; he considers this rate and this lake exceptionally productive of methane, and states that a mean figure of 3 ml per cm^2 per year is a "probably generous" estimate for this locality and for the small fraction of the 2.5×10^{16} cm^2 of freshwater lakes of the world that actually produce methane. He suggests an upper bound for this fraction of 10^{-3}.

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*The context of this discussion indicates that by "production" Hutchinson means production of atmospheric methane, and probably not total production.

Hutchinson (1954) considers enteric fermentation by domestic and wild ungulates to be the major source of atmospheric methane, and he estimates this source to be about 45 to 90 x 10^{12} gm per year. He also points out that the oxidation of atmospheric methane at the surface of the earth by methane oxidizers seems unlikely once it has escaped to the atmosphere, although he suggests that it is "just possible" that the methane may be oxidized at the surface of the ocean. Recent studies of the uptake of carbon monoxide, oxides of nitrogen, and other atmospheric trace constituents at concentrations less than that of methane suggest that vegetation or soil microflora might provide an effective sink mechanism (Schutz et al., 1970; Hill, 1971; Inman et al., 1971; Arbelles et al., 1971).

C. METHANE IN THE ATMOSPHERE

1. Atmospheric Chemical Reactions of Methane

Methane is extremely stable in the troposphere and does not react appreciably with O_2 there (Bates and Witherspoon, 1952; Cadle and Allen, 1970; Cadle and Powers 1966). Bates and Witherspoon (1951) proposed that the most effective reactions for removing methane in the stratosphere are oxidation by monatomic oxygen and perhydroxyl, but uncertainties regarding the activation energies and concentrations of the reactants below 70 km made estimates of the lifetime of CH_4 in this region unreliable at that time.

Cadle and Powers (1966) report investigations of the reaction of ground-state atomic oxygen with methane, deriving appropriate rate constants under two experimental conditions (with or without large amounts of molecular oxygen). They provide a plot of the rate of loss of methane molecules as a function of altitude (implied by the results of these experiments together with assumed distributions of atomic oxygen taken from the Handbook of Geophysics) and a plot of the number of molecules of methane per cm^3 as a function of altitude corresponding to a constant mixing ratio of 1.4 ppm. From this plot we may infer that the time required to oxidize all of the methane corresponding to this concentration is between about 40 and 500 years at 20 km but drops rapidly to between 4 months and 3 years at 30 km and between 12 days and 4 months at 40 km. The lifetime of methane in the stratosphere before it is oxidized by this reaction therefore depends upon the manner in which it is transported to the altitudes at which oxidation is rapid. The total concentration of methane above 40 km must be extremely small.

Methane may be photolyzed by radiation of wavelengths shorter than about 1600 Å. According to Bates and Witherspoon (1952), photodissociation of methane begins at about 1450 Å and reaches its peak between 1300 and 1200 Å. These authors point out that the amount of solar energy in this region is low, so that the loss rate is slow even at zero optical depth. We may conclude from this work that reaction with ground-state atomic oxygen in the stratosphere is the major atmospheric chemical sink for methane.

Bates and Nicolet (1950) have pointed out that the stratospheric oxidation of methane ultimately produces CO_2 and H_2O and that the transport of methane across the tropopause "cold trap" is in effect a method of bringing water into the stratosphere. The water content of the lower stratosphere is now believed to be about 2 to 3 ppm (SMIC 1971), and the mechanisms responsible for transport of water vapor to the stratosphere are obscure.

2. Distribution of Methane in the Atmosphere

a. Early Observations

Methane in the atmosphere was discovered by Migeotte (1948), using spectroscopic techniques. and its presence was subsequently confirmed by McMath, Mohler, and Goldberg (1948). These and subsequent observations (Table IV-6) indicated a concentration of 1.2 to 1.5 ppm, which appeared to be approximately constant with altitude as far as could be determined within the limits of error of the optical sensing techniques employed.

b. Recent Measurements

Since the middle 1960's methane abundance measurements conducted near the surface of the earth employing gas chromatographic measurement

TABLE IV-6. - ABUNDANCE DETERMINATIONS OF METHANE IN THE ATMOSPHERE

Observer	Year	Place	Lines Used	Abundance cm·atm(STP)
Migeotte (discoverer)	1948	Columbus, Ohio		
McMath, Mohler, and Goldberg	1948	Lake Angelus, Michigan Mount Wilson, California (altitude 1740 m)	15 lines of $2\nu_3$ band	1.0
McMath and Goldberg	1949	Lake Angelus, Michigan Mount Wilson, California (altitude 1740 m)		1.2
Goldberg	1950	Lake Angelus, Michigan Mount Wilson, California (altitude 1740 m)	R(0), R(5), R(10), of $2\nu_3$ band	1.2
Nielsen and Migeotte	1952	Jungfraujoch, Switzerland (altitude 3580 m)	R(0), R(5), R(10), of $2\nu_3$ band	1.2
Bowman and Shaw	1963	Columbus, Ohio (ground level)	3.3 μ	1.4±0.25

SOURCE: Fink, Rank and Wiggins (1964)

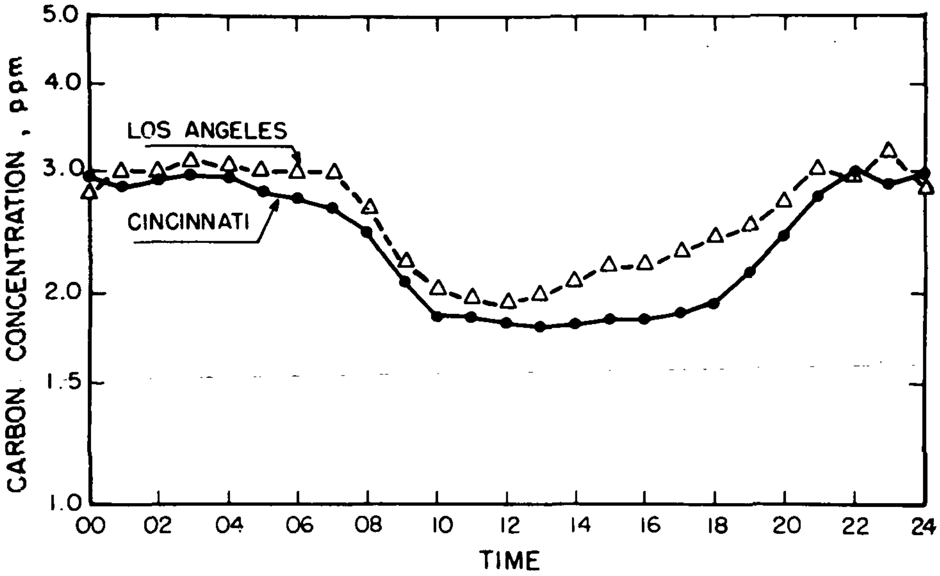
techniques have been reported. These are summarized in Table IV-7.

Although not numerous, these observations, together with a few measurements of the abundance profile of methane, suggest that the concentration of this gas may in fact be quite variable; this would be consistent with the existence of large tropospheric sources and sinks which are almost certainly biological in nature. These observations will be briefly described individually below and then discussed in the following section.

Altshuller, Ortman, Saltzman, and Neligan (1966) report the results of a program of continuous monitoring of methane and "all hydrocarbons" in Los Angeles and Cleveland in the fall of 1964. Although the object of measuring methane was to be able to determine by comparison with "all hydrocarbons" the abundance of non-methane hydrocarbons, the monitoring program provided useful information regarding the concentration of methane and its change with time during the day. Figure IV-3 shows the variation in concentration with time during the day. The average concentration varies with time from a mean of about 1.75 ppm near mid-day to highs near 3 ppm at night, resulting in daily average values of 2.61 ppm in Los Angeles and 2.38 ppm in Cincinnati. Analysis of the data indicated an estimated background biological concentration of 1 ppm, on which was superimposed the effects of an anthropogenic source, which appears to be primarily industries using natural gas (Altshuller, et al. 1966). Methane constitutes about 2% of the unburned hydrocarbons emitted by automobiles.

Methane concentrations in the Arctic were studied by Cavanaugh, Schadt, and Robinson (1969), who also monitored CO and selected non-methane hydrocarbons at Point Barrow, Alaska during August and September 1967. The other hydrocarbons were ethane-ethylene, methanol-ethanol, (measured as composite gas chromatographic peaks), butane, pentane, acetaldehyde, acetone, benzene, n-butanol, and four unknown hydrocarbons.

The observed methane concentration varied between 1.5 and 1.7 ppm and averaged 1.59 ppm during the interval under consideration; the non-methane hydrocarbons were present at concentrations of 1 ppb or less except for n-butanol, which ranged from 34 to 355 ppb. A natural source



Cincinnati, 574 hours during September 1964. Los Angeles, 213 hours during October to November 1964.

Source: Altshuller, et al. (1966)

FIGURE IV-3 DIURNAL PATTERN OF METHANE CONCENTRATION IN POLLUTED AIR

TABLE IV-7. - SUMMARY OF RECENT ATMOSPHERIC METHANE ABUNDANCE OBSERVATIONS

Location	Altitude	Concentration	Observer
Polluted Urban Locations:			
Los Angeles & Cincinnati	Surface Level	1.75-3 (mean 2.68 & 2.31)	Altshuller, Ortman, Saltzman and Neligan (1966)
Arctic (Pt. Barrow)	Surface Level	1.5 - 1.7 (mean 1.59)	Cavanagh, Schadt and Robinson (1969)
Potomac River near pollution sources	Surface Level	up to 3	Swinnerton, Linnenbom and Cheek (1969)
Chesapeake Bay and Atlantic	Surface	1.24 ± 0.03	Swinnerton, Linnenbom and Cheek (1969)
Boulder Colorado	Surface	1.0 to 1.4	Scholz, Ehhalt, Heidt and Martell (1970)
Eastern Texas	Surface	1.6	Bainbridge and Heidt (1966)
	4.5km	1.46	Bainbridge and Heidt (1966)
	24km	1.05	Bainbridge and Heidt (1966)
Western Louisiana	Surface	1.6	Bainbridge and Heidt (1966)
	4.5	1.6	Bainbridge and Heidt (1966)
	24	1.31	Bainbridge and Heidt (1966)

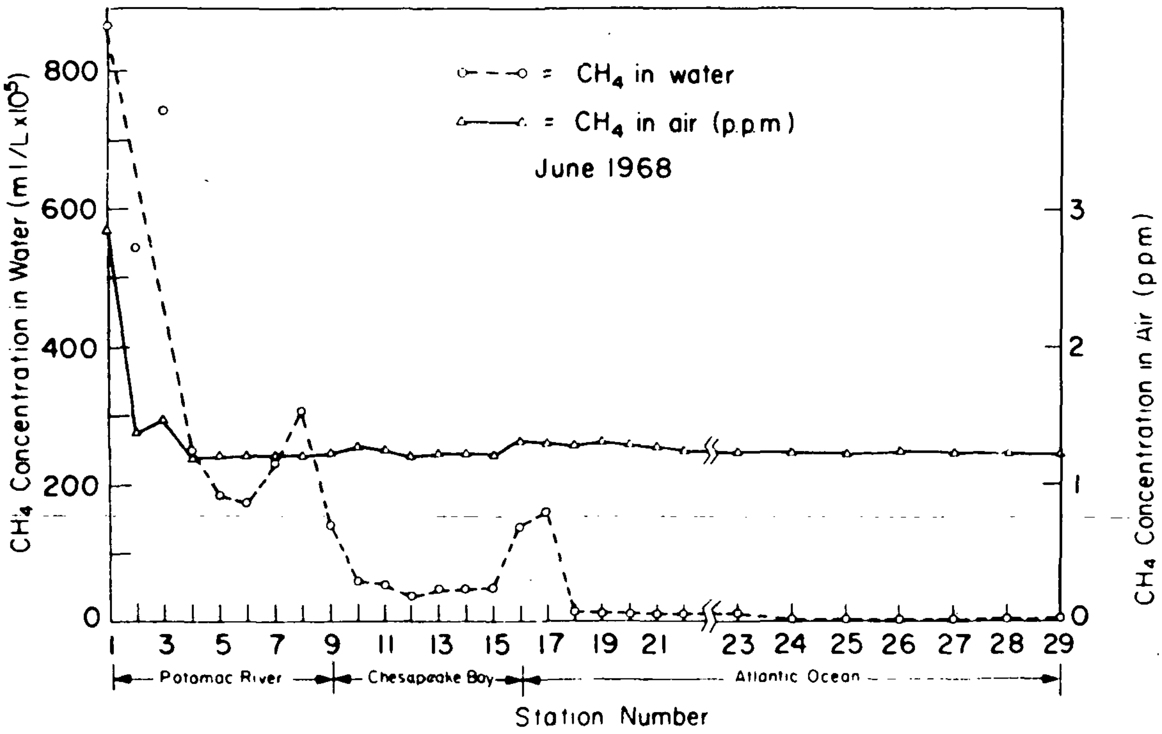
TABLE IV-7. - Continued

Location	Altitude	Concentration	Observer
Scotts Bluff, Nebraska	5000 ft	1.2 - 1.5	Ehhalt (1967)
	10,000 ft	0.8 - 1.5	Ehhalt (1967)
	25,000 ft	0.8 - 1.6	Ehhalt (1967)
	30,000 ft	0.6 - 1.6	Ehhalt (1967)
White Sands, N. Mexico	44-62 km	< .05	Scholz, Ehhalt, Heidt and Martell (1970)

for the very high relative concentration of n-butanol was confirmed when comparable concentrations of these hydrocarbons were detected in flask samples of air collected at more remote Arctic locations. N-butanol, butane, ethane, acetone, and ethanol are all products of fermentation, and the reported plots of their concentrations suggest some tendency to covary. Methane did not exhibit any tendency to covary with these other components, nor did it show a clear relationship to wind speed or temperature. Cavanaugh et al. point out that fermentation may take place in the waterlogged tundra during this period and that on sunny days the temperatures within a few inches of the surface may reach 100°F, which is an optimum for some fermentation reactions. Natural gas wells and pipelines are present in the Point Barrow region, and leaks and seepage could contribute to the observed concentrations (Cavanaugh et al., 1969).

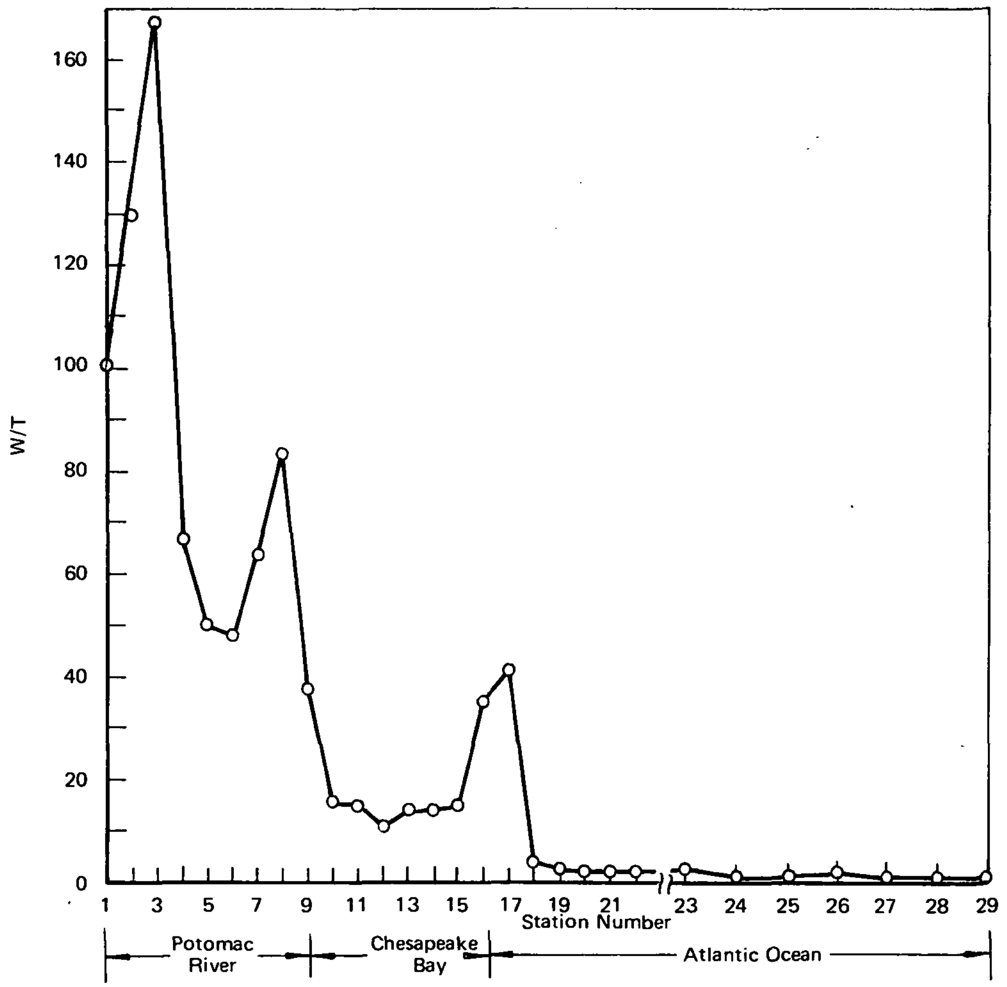
Swinnerton, Linnenbom, and Cheek (1969) studied the distribution of methane between the atmosphere and natural waters on a cruise between Washington,D.C. and Puerto Rico in June 1968. The concentrations of methane in the water and in air sampled on deck are shown in Figure IV-4. High levels of methane in the water correspond to sewage outfalls in the Potomac River between stations 1 and 4 and stations 7 and 8 and to passage through polluted James River water at its mouth in the Chesapeake Bay, at stations 17 and 18. Except at the first three stations, the methane concentration in air was a steady 1.24 ± 0.03 ppm, although there is some suggestion at station 16 of a slight increase in atmospheric methane corresponding to the large increase in methane concentration in the water.

Evidence that the elevated levels of atmospheric methane may be due to biological methane production in the water is provided in Figure IV-5. This figure is a plot of the ratio of W, the observed concentration of methane in water, to T, the concentration in water which would be in equilibrium with the measured concentration in the atmosphere. Values of W/T greater than one correspond to times when the water is supersaturated with respect to the atmosphere and methane can diffuse into the atmosphere.



Source: Swinnerton, Linnenbom, and Cheek (1969).

FIGURE IV–4 METHANE IN SURFACE WATERS AND IN THE ATMOSPHERE



W = Measured Concentration

T = Calculated Concentration Assuming Equilibrium with the Atmosphere

Source: Swinnerton, Linnenbom, and Cheek (1969)

FIGURE IV–5 RATIO OF MEASURED TO CALCULATED METHANE SATURATION

Further evidence of variability of the concentration of methane in the troposphere is provided by the vertical abundance profiles of methane measured by Bainbridge and Heidt (1966) and Ehhalt (1967). Bainbridge and Heidt report two measurements of the abundance of methane as a function of altitude up to 22 km in eastern Texas and western Louisiana. Samples were collected by aircraft below 9 km and by airborne balloon (during descent) from 24 to 9 km.

The analytical data are summarized in Table IV-8. Methane concentration in the region from 4.5 km to the upper troposphere was 1.46 ppm on the first "flight" (upper segment on March 15, lower on April 6 in East Texas) and 1.6 ppm on the second flight (July 20, 1965 in Western Louisiana). The concentration at ground level was 1.6 ppm on both flights, and on both the concentration declined from the tropopause to 24 km by about 0.3 ppm (to 1.05 ppm on the first flight and 1.31 ppm on the second). If this decline is representative of worldwide year-round conditions, the implied annual transfer of methane to the stratosphere is about 4.2×10^{-6} gm cm^{-2} $year^{-1}$ (Bainbridge and Heidt, 1966). This corresponds to about 21.4 million metric tons per year.

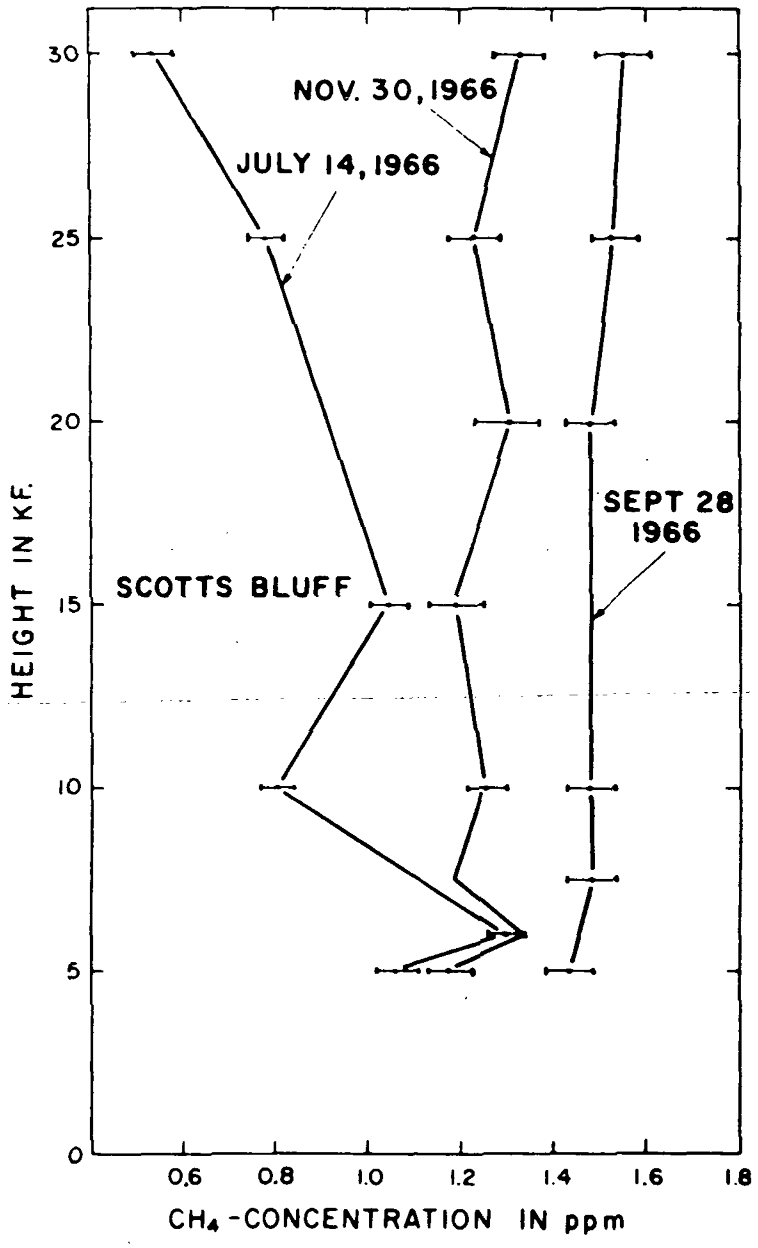
Ehhalt (1967) reports three measurements of the vertical abundance of methane over Scotts Bluff, Nebraska, which are plotted in Figure IV-6. These show a range at 5000 ft of about 1 to 1.5 ppm and differ considerably with each other in the change with altitude. In July the concentration declined somewhat erratically from a high of about 1.2 ppm at about 6000 ft. to a low of about 0.6 ppm at 30,000 feet. In September the abundance was nearly constant with altitude.

In the previous section we have pointed out that consideration of the stratospheric chemical sink for methane implies that the abundance of methane will be low in the stratosphere, especially the upper stratosphere. This is confirmed by the measurements of Kyle, Murcray, Murcray, and Williams (1969), who estimate 1.2 atm-cm of methane per air mass above 10 km, 0.4 above about 22 km, and further declines with altitude to 30 km. These results indicate somewhat more methane than the results of Bainbridge and Heidt show. Kyle et al. suggest that errors of observation and interpretation may yield a systematic overestimate, particularly

TABLE IV-8. - SUMMARY OF ANALYTICAL DATA

Date:	March 15, 1965	April 6, 1965	July 20, 1965
Tropopause level	88 mB	90 mB	130 mB
Concentration (ppm):			
Ground level		1.60 ± 0.03	1.60 ± 0.03
4.5 km		1.46 ± 0.03	1.60 ± 0.03
Upper Troposphere	1.46 ± 0.03		1.60 ± 0.03
24 km	1.05 ± 0.03		1.31 ± 0.03
Stratosphere Vertical Wind			0.75 cm sec^{-1}

SOURCE: Bainbridge and Heidt (1966)



Samples were taken by aircraft and measured later in the laboratory by gas chromatography. The standard deviation (1 σ) is indicated by the bars.

Source: Ehhalt (1967)

FIGURE IV–6 METHANE ABUNDANCE PROFILES

if the concentration in fact declines with altitude. They feel their observations are consistent with a decline in abundance with altitude by a factor of 2 at 30 km.

Scholz, Ehhalt, Heidt, and Martell (1970) analyzed gas samples collected in the interval 44 to 62 km. They found no methane, and inferred a concentration below the 0.05-ppm limit of their technique. They also report a range of concentrations of methane near the ground of 1.0 to 1.4 ppm (Flagstaff Mt., Boulder, Colo. August 1969 to Jan. 1970).

D. ELEMENTS OF A METHANE BUDGET

The first workers to consider the atmospheric budget of methane were Bates and Witherspoon (1952), who concluded that the chemical sink in the stratosphere is the only major methane sink. They obtained a possible range of methane lifetimes from estimates of the probable release of methane into the atmosphere by biological sources and as a consequence of coal and oil mining operations, arriving at the conclusion that the lifetime of methane must be at least 10 years and probably much longer.

Other workers, following Bates and Witherspoon (Koyama, 1963, 1964; Ehhalt, 1967; Robinson and Robbins 1968), derived estimates of the probable lifetime of methane on the basis of the ratio of estimated production sources to that in the atmosphere, on the assumption that methane is in a steady state. These estimates have varied considerably, due primarily to differences in the estimated strength of the biological source of methane.

1. Biological Sources of Methane

Table IV-9 lists some of the estimates of biological methane sources that are in the literature. Bates and Witherspoon (1952), having no available estimates of the rate of biogenic methane production or information on which to estimate the rate at which it is injected into the atmosphere, obtained a maximum possible rate of injection by arguing that at most not more than 1% of total photosynthetic productivity could go toward the production of methane. Using the figure 4 x 10^{20} molecules organic

TABLE IV-9. - GLOBAL BIOLOGICAL METHANE SOURCES

Worker	Source or Basis of Estimate	Quantity (million tons/year)
Bates & Witherspoon (1952)	1% of Total Organic C[a] (upper bound)	540-1250
Hutchinson (1954)	Enteric Fermentation	45-90
	Shallow Lakes (upper bound)	.54
Koyama (1964)	Rice Paddies	190
	Upland Fields	10
	Forests	0.4
Robinson & Robbins (1968)	Swamps	570
	Humid Tropical Areas	610
Estimated Total Biologic Emissions		45-470[b]

[a] Larger figure reflects present estimates of global productivity

[b] See text.

C cm^{-2}/year, they obtained an upper bound of 540 million tons per year of methane. More recent estimates of total photosynthetic productivity are more than twice as large, and these figures would yield an upper bound of about 1250 million tons methane if 1% of organic C were converted to methane and released into the atmosphere.

We have pointed out in Section B that Hutchinson (1954) believed the primary biospheric source of methane to be enteric fermentation, which he estimates at 45 to 90 million tons per year. His upper bound for productive (i.e. rich and shallow) lakes is based on an estimated emission rate of 3 ml cm^{-2} yr^{-1}. He estimated the area of such lakes to be at most 0.1 per cent of all fresh water lakes, whose area he gives as 2.5×10^{16} cm^2.

Koyama (1964) actually cultured rice paddy soils, forest soils, and grassland soils to arrive at a basis for estimating the worldwide production of methane. An examination of his data indicates that he estimates the annual methane production in Japanese paddy fields to be lower than in the paddy fields of the world as a whole, namely 0.8 vs 2.0×10^{-2} gm/cm^2. It would seem that he has used the observed relationship between temperature and productivity in Japanese soils and the known temperature conditions of rice paddies of the world in order to arrive at his global estimate. For upland fields and forests of the world, Koyama employed approximately the same production rates he found in Japanese fields and forests.

Robinson and Robbins (1968) base their estimates on the work of Koyama, but they apparently employ a summary article (Koyama, 1963) in which the experimental work and the basis of the estimates are not clearly explicated. Thus, they assume that all swamps on the globe will be as productive as the average rice paddy and employ an estimate of total swamp area of 10^6 mi^2 together with Koyama's estimated rice paddy productivity to arrive at a very large total for swamp areas. They also assume that hot, humid tropical areas may produce about 10% as much methane as do rice paddies and consequently arrive at a very large total from this source.

Since there is very little information about the emission of methane from rice paddies and swamps--and apparently no measurements of methane in the air in such localities--it is very difficult to evaluate these estimates. In our opinion, Koyama has given an upper bound for the emission of methane from forests, rice paddies, and soils, although he may not have considered natural swamps adequately. The extrapolation of Robinson and Robbins (1968) is almost certainly not warranted, in view of the fact that, unlike world rice paddies, swamps are not exclusively clustered in the warmer regions of the world. However, the data of Cavanagh, Schadt and Robinson (1969) indicate that fermentation occurs in the artic tundra during summer. The large quantities of methane observed by them in the atmosphere may be derived from this source. Alternatively, as they point out, the methane may be natural gas from local oil wells, or from pipelines.

Swinnerton, Linnenbom, and Cheek (1969) provide evidence of atmospheric release of biogenic methane in the polluted reaches of the Potomac. This indicates that under some conditions methane can be emitted into the atmosphere before it is biologically consumed. It further suggests that atmospheric methane injection may be a major consequence of cultural eutrophication.

The problem of the rate of emission of methane into the atmosphere is analogous to that of natural sulfur dioxide, which is discussed in some detail in Chapter VII. Hydrogen sulfide is produced in exactly the same environments as methane, although in freshwater environments its production may be sulfate-limited; it is more soluble in water and oxidizes very rapidly. Thus we might expect that hydrogen sulfide is much less likely than methane to be emitted into the atmosphere. Since, unlike methane, hydrogen sulfide is rapidly oxidized in the atmosphere, we would expect that very little sulfur should be present as H_2S, and in fact little has been found. There is, however, sufficient sulfur dioxide in the atmosphere in remote unpolluted environments for some workers to estimate very large annual cycles of hydrogen sulfide: about 100 to 300 million tons per year as sulfur. If these estimates are valid, then by analogy we must expect a very much larger biological source of atmospheric methane.*

After considering these estimates, we have concluded somewhat arbitrarily that the true global biogenic production of methane (exclusive of that induced by cultural eutrophication) probably lies somewhere between 45 and 470 million tons per year. The first figure is the lower bound for enteric fermentation estimated by Hutchinson (1954). The upper bound is somewhat more difficult to estimate. In our opinion, atmospheric emission of methane from shallow, waterlogged environments is unlikely to exceed 50% of production, and even less will be released from soils. If so, the world production of atmospheric methane in paddy soils and natural swamps will not exceed half of the production estimates given by Koyama (1964) and Robinson and Robbins (1968), or 380 million tons per year. We have neglected other soil sources because emission from them is probably slight and production certainly much less than from rice paddies and swamps. To this total we may add the upper bound for enteric fermentation given by Hutchinson (1954). This estimate does not include methane produced as a result of organic pollution.

2. Annual Methane Cycle

Table IV-10 summarizes other data relevant to the construction of a methane budget. The tropospheric load of methane is estimated on the assumption that it is between 1.5 and 1.24 ppm. The data of Bainbridge and Heidt (1966), Cadle and Powers (1966) and Kyle, Murcray, Murcray, and Williams (1969) imply that the amount in the stratosphere may in fact be very small, and we assume that its mean concentration in the stratosphere is 0.4 ppm.

Bainbridge and Heidt (1966) calculate a possible stratospheric sink for methane on the basis of the tropopause transport implied by their abundance profiles. This is 4.2×10^{-6} g cm^{-2} yr^{-1}.

Anthropogenic sources of methane are chiefly the loss of methane in coal fields during mining operations and the loss of natural gas in

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*This analogy is not valid if biogenic H_2S is oxidized before it is emitted into the atmosphere.

TABLE IV-10. - ELEMENTS OF AN ANNUAL METHANE BUDGET

Annual Sources and Sinks	(million T CH_4 per yr)
Anthropogenic Emissions	
Coal Mining[a]	6.3 - 22
Lignite Mining[a]	1.6 - 5.7
Industrial Losses[b]	7 - 21
Automobile Exhausts[c]	0.5
Volcanic Emissions[d]	0.2
Biological Emissions	45 - 470
Total Sources	60.6 - 519.4
Stratospheric Sink[e]	21.4
Total in Atmosphere	**Million T CH_4**
Troposphere[f]	2,800 - 3,500
Total Atmosphere[f]	3,005 - 3,705

[a] Assuming 5 to 17.7 m^3 CH_4/T coal or coal-equivalent lignite and annual world production of 1750 million T coal and 458 million coal-equivalent T lignite in 1967 (SCEP 1970).

[b] 1 to 3% of all natural gas consumption for 1968.

[c] 2% of estimated world total of 27 million tons of hydrocarbon exhausts.

[d] Koyama (1964).

[e] Bainbridge and Heidt (1966).

[f] Assuming 1.24 to 1.5 ppm in the troposphere and 0.4 ppm in the stratosphere.

industrial processes. Bates and Witherspoon (1952) suggest 5 m^3/ton coal mined as a reasonable methane emission factor for estimating the total methane emitted in coal mining; we use this to obtain our lower bound. Koyama assumes that the total gas emission is 19 m^3/ton coal and that 93% of this is methane, and we use this to obtain the upper bound. Neither cite an estimate for lignite, but we have used the coal equivalent of lignite production figures and the two factors used for coal to obtain an estimate for methane from this source. Solid-fuel production estimates for 1967 are given in SCEP (1970).

Natural gas lost in production, transportation, and consumption may constitute a large natural source of methane in the atmosphere. Ehhalt (1967) cites studies of the ^{14}C content of methane collected in natural gas liquefaction plants, which are usually located in industrialized areas (Table IV-11). These data suggest that even in industrial areas about 25% of the methane is "old" and presumably from this source.

We estimate that these natural gas losses during production, transportation, and consumption (including those at the well head and the emission of methane from oil production operations) are not less than 1% of total natural gas consumption and not more than 3%.

According to Altshuller et al. (1966), approximately 2% of automobile hydrocarbon exhausts are methane. Automobile hydrocarbon exhaust emissions in the United States totaled 13.4 million tons in 1968 (SCEP 1970), which we assume to constitute half the world total.

Volcanic emissions were estimated by Koyama as 1% of total carbon dioxide emissions.

It will be noted from Table IV-10 that our estimated sources are from about 3 to 25 times the stratospheric sink estimate of Bainbridge and Heidt (1966), which in turn is based on only two observations of the abundance profile. If the latter is accurate, then a tropospheric sink for methane is implied. As we have pointed out above, biological processes at the surface may constitute a tropospheric methane sink.

TABLE IV-11. - C-14 CONTENT OF ATMOSPHERIC CH_4 SAMPLES

Sample Origin	Collection Date	^{14}C Content (% Standard Wood)
Tonawanda, New York	October 1950	102 ± 3
Wembley, England	December 1949	75 ± 2
Wembley, England	April 1950	69 ± 2
Gary, Indiana	January 1960	75.2 ± 0.5

SOURCE: Ehhalt (1967)

The implied tropospheric lifetimes corresponding to the minimum and maximum estimates of the tropospheric methane load and the methane sources are 5.4 and 58 years. Ehhalt (1967) and Robinson and Robbins (1968) have observed that the variability in methane abundance observations implies a relatively short lifetime. We are inclined to agree with this observation and with the inference that there are probably very large tropospheric sources and sinks for methane.

E. CONCLUSIONS

The preceding discussion of methane sources, sinks, and atmospheric abundance supports the following conclusions:

(1) Methane sources and sinks are not fully understood. There is considerable inconclusive evidence that biological sources and sinks exist and may be large.

(2) Measurements of methane emission from swamps, rice paddies, and other sites of anaerobic metabolism are necessary to determine the efficiency of injection and consequently the probable magnitude of biological methane sources.

(3) There is evidence that methane injection into the atmosphere is a consequence of cultural eutrophication, and consequently that biological methane emissions may be increasing with time.

(4) Since methane is produced in the same environments as H_2S, greater knowledge of methane sources may lead to improved understanding of the nature of the global circulation of sulfur. In particular, evidence of fermentation in the extensive tundra regions of the arctic suggests that these regions may be large sources of methane and other reduced atmospheric gases.

(5) Estimates of the magnitude of the stratospheric methane sink are based on only two measured abundance profiles and should be confirmed with additional observations.

(6) Systematic observations of the variations in methane abundance that may be related to local biological activity are needed.

(7) Analysis of ^{14}C activity of methane collected from well mixed tropospheric air in regions remote from sources of contamination with natural gas would help in estimating the strength of natural sources.

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V. CARBON MONOXIDE

A. SUMMARY

Carbon monoxide is a permanent but variable constituent of the atmosphere. It is produced at the surface anthropogenically from fossil fuel combustion and by natural biological sources. The CO cycle in the atmosphere is not understood, and hypotheses regarding it have been radically revised as space-time distribution data have become available in the recent past. Before surveys of global concentrations were made, it was believed that no atmospheric sinks existed; CO was thought to be removed from the atmosphere by biological reactions at the surface. Anthropogenic sources of CO are estimated to produce approximately 2.4 x 10^{14} grams yr^{-1}, the major source being gasoline-fueled internal combustion engines. Until recently, natural biological sources were assumed by most workers to be negligible in comparison.

Ambient concentrations on the order of 1 to 3 ppm are frequently observed in polluted city air and not infrequently reach 50 to 100 ppm in heavy traffic.

Surveys of CO concentrations in areas remote from sources of industrial pollution reveal a complicated pattern. Concentrations in marine air have been observed to be higher in the northern hemisphere than south of the equator, although measurements by different groups of workers are somewhat inconsistent on this point. One group of workers found concentrations south of the equator varied from 0.1 to 0.12 ppm in the Atlantic, while another found mean concentrations in the Pacific as low as 0.05 ppm. The first group found values in the Atlantic north of the equator from 0.17 to 0.25 ppm; the second found concentrations in the Pacific to vary greatly, with mean at 50°N of 0.18 ppm.

Upper tropospheric values range from 0.1 to 0.14 ppm, with a mean of about 0.12 ppm, and are relatively constant over the north polar region, the European land mass, Africa, and the North Atlantic. Surface concentrations over land in remote areas of South Africa are similar to those observed in the upper troposphere.

CO concentration shows a very sharp drop between the upper troposphere and the lower stratosphere. Declines of an order of magnitude or more have been observed in the first few kilometers and are attributed to oxidation by OH radicals produced from moist ozone. This reaction may also account for some CO removal in polluted atmospheres.

Surface seawater is supersaturated with CO, indicating that the ocean is a source of atmospheric CO. Contributions from this source have been estimated to be as high as 0.75 to 3.3 x 10^{14} grams yr^{-1} in the northern hemisphere alone.

Present uncertainties regarding the atmospheric abundance of CO, the magnitude of biological sources and sinks, and the rate of stratospheric oxidation of CO make it difficult to estimate the atmospheric residence time of CO or to determine whether the stratospheric sink can account for the removal of the bulk of the CO produced at the surface. Estimates of residence time vary from 0.1 years to about 4 years; recent data support a figure of 1 to 2 years.

Several species of soil microbiota are known to produce or consume CO, and laboratory experiments suggest that higher plants are also capable of producing large quantities of CO. No field evaluations of the significance of these sources have been conducted. Humans and other animals excrete CO as a by-product of heme catabolism, but the total global production from this source appears negligible in comparison to industrial production.

Most of the available evidence regarding atmospheric distribution of CO suggests that its lifetime is long relative to tropospheric mixing. Space-time variations in concentration due to differences in source strength, while large at the surface, may be small relative to the total column abundance of the gas--not exceeding deviations of perhaps ± 25%--except where intensive pollution or forest fires occur. CO concentration may be useful in identifying and tracking air parcels, unless vegetation and soil sinks are very active in removing CO in the lower troposphere.

Information regarding atmospheric concentrations of CO is very scanty. Biological sources may produce much more CO than has been assumed. If so, the residence time must be shorter than a year and space-time variations will be corresponding greater. If, on the other hand, anthropogenic sources are the major ones, the average tropospheric concentration must be increasing.

B. BACKGROUND

Atmospheric CO has been of considerable interest since it was discovered spectroscopically by Migeotte (1949) and by Migeotte and Neven (1950) at the Jungfraujoch. These authors and others (Benesch and Migeotte, 1953 and Locke and Herzberg, 1953) employed spectroscopic data to estimate the mean atmospheric CO concentration as 0.1 to 0.4 ppm.

Bates and Witherspoon (1952), who published the first discussion of sources and sinks of CO, concluded that its major source is fossil fuel combustion, that no significant atmospheric sinks exist, and that the primary sink could be a biological one.

The residence time of any gas may be estimated from its global abundance and its rate of injection or removal, on the assumption that the gas is in a steady state in the atmosphere and that injection is balanced by removal. Bates and Witherspoon used the 0.1 ppm figure provided by Migeotte and Neven (1952) as the mean atmospheric abundance, which corresponds to 3×10^{18} molecules cm^{-2}. They estimated that fossil fuel combustion produced at least 1.8×10^{14} grams yr^{-1}, or 8×10^{17} molecules cm^{-2} sec^{-1}, from which they deduced a residence time of about four years. In exploring sources of CO, these authors considered UV photolysis of CO_2 in the upper atmosphere, but concluded that the yield must be extremely small (less than 10^{16} molecules cm^{-2} yr^{-1}).

Bates and Witherspoon explored chemical reactions in the atmosphere which could account for the removal of CO. Reactions with molecular oxygen and ozone in the troposphere are very slow and were discussed as possible sink mechanisms. Two stratospheric reactions which could remove CO were considered:

$$CO + OH \rightarrow CO_2 + H$$

$$CO + HO_2 \rightarrow CO_2 + OH$$

Bates and Witherspoon concluded that these reactions are also too slow to provide an effective sink, believing that their activation energies must be high. This belief has subsequently been demonstrated to be in error.

Having found no reasonable atmospheric CO sinks, Bates and Witherspoon concluded that biological oxidation near the ground could account for the apparent four-year life of atmospheric CO, commenting that this seemed "rather improbable although not impossible .." In support of this hypothesis, they cited suggestive laboratory observations of the oxidation of CO by *Bacillus oligocarbophilus*, but noted that since the laboratory studies had used artificial atmospheres with CO concentrations far in excess of those found in the lower troposphere, they must be interpreted with care.

These major conclusions--i.e., that the primary CO source is human, that no effective CO sinks exist in the atmosphere, and that all CO must therefore be removed biologically at the surface--now appear to be in error, but they were not seriously questioned until well after systematic observations of space-time variations in the atmospheric abundance of CO began in 1966.

C. COMBUSTION SOURCES

Most discussions of the residence time of CO employ an estimated mean concentration based on observations of the abundance of CO in air and the known rate of production of CO from fossil fuel combustion, since estimates of the latter are reasonably reliable and there are few data on which to base an estimate of the magnitude of "natural" CO sources. The resulting mean residence time is a maximum figure that may have to be revised downward if large natural sources are identified.

Table V-1 lists the most widely quoted figures for probable annual worldwide CO production, which are those compiled by Robinson and Robbins (1968). Most of the CO is produced by internal combustion engines, and a lesser quantity by coal; stationary sources using fuel oil are essentially negligible. Since it is reasonable to suppose that worldwide gasoline

TABLE V-1. - ESTIMATED ANNUAL CO EMISSIONS

Source	Consumption	CO Factor	CO Emission (tons)[a]
Gasoline	379×10^6 T	2.91 lb/gal	193×10^6
Coal (total)	$3{,}074 \times 10^6$ T		12×10^6
Power	$1{,}219 \times 10^6$ T	0.5 lb/T	
Industry	781×10^6 T	3.0 lb/T	
Residential	404×10^6 T	50.0 lb/T	
Coke and Gas Plants, etc.	615×10^6 T	0.11 lb/T	
Wood (fuel)	466×10^6 T	70 lb/T	16.0×10^6
Forest Fires	18.0×10^6 acres	70 lb/T	11.3×10^6
			232.3×10^6 tons
			(2.1×10^{14} grams)

[a] short tons

SOURCE: Robinson and Robbins (1968)

gasoline consumption has increased about 20% since 1966, we may increase the total given by these authors to a present estimate of 2.4×10^{14} grams yr^{-1}.

D. GLOBAL DISTRIBUTION

1. CO In Urban Atmospheres

CO is produced in great quantities by automobiles and is deleterious to human health. As a consequence, its concentration is routinely monitored in most large American cities. Most reliable data on its behavior concern these significantly polluted areas. Jaffe (1968, 1970) has recently reviewed pollution sources and ambient city concentrations of CO; except where otherwise noted, the material in this section is derived from his publications.

The observed concentration of CO in cities shows daily and seasonal variation related to the density of automobile traffic, which is its major source, and to meteorological conditions, which determine the atmospheric ventilation and consequently the degree of dilution of the polluted air. Means of 1.0 to 3.0 ppm are common, although commuters in heavy traffic are typically subjected to concentrations 2 to 7 times larger than those recorded at air monitoring stations located 100 or more feet from the traffic. In major American cities, "in-traffic" concentration averages of 9 to 35 ppm are common during peak commuter traffic, with frequent transient peaks as high as 90 ppm. Concentrations as high as 147 ppm have been observed in New York arterial traffic.

CO in polluted atmospheres characteristically exhibits a diurnal variation in concentration: two peaks corresponding to periods of heavy commuter traffic, and low values corresponding to those times when convection distributes the CO to higher altitudes.

Observations of CO in sites physically remote from pollution sources may often reflect pollution, since CO is an air-mass characteristic which is related to wind direction and other variables defining air parcels. (Robinson and Robbins, 1969).

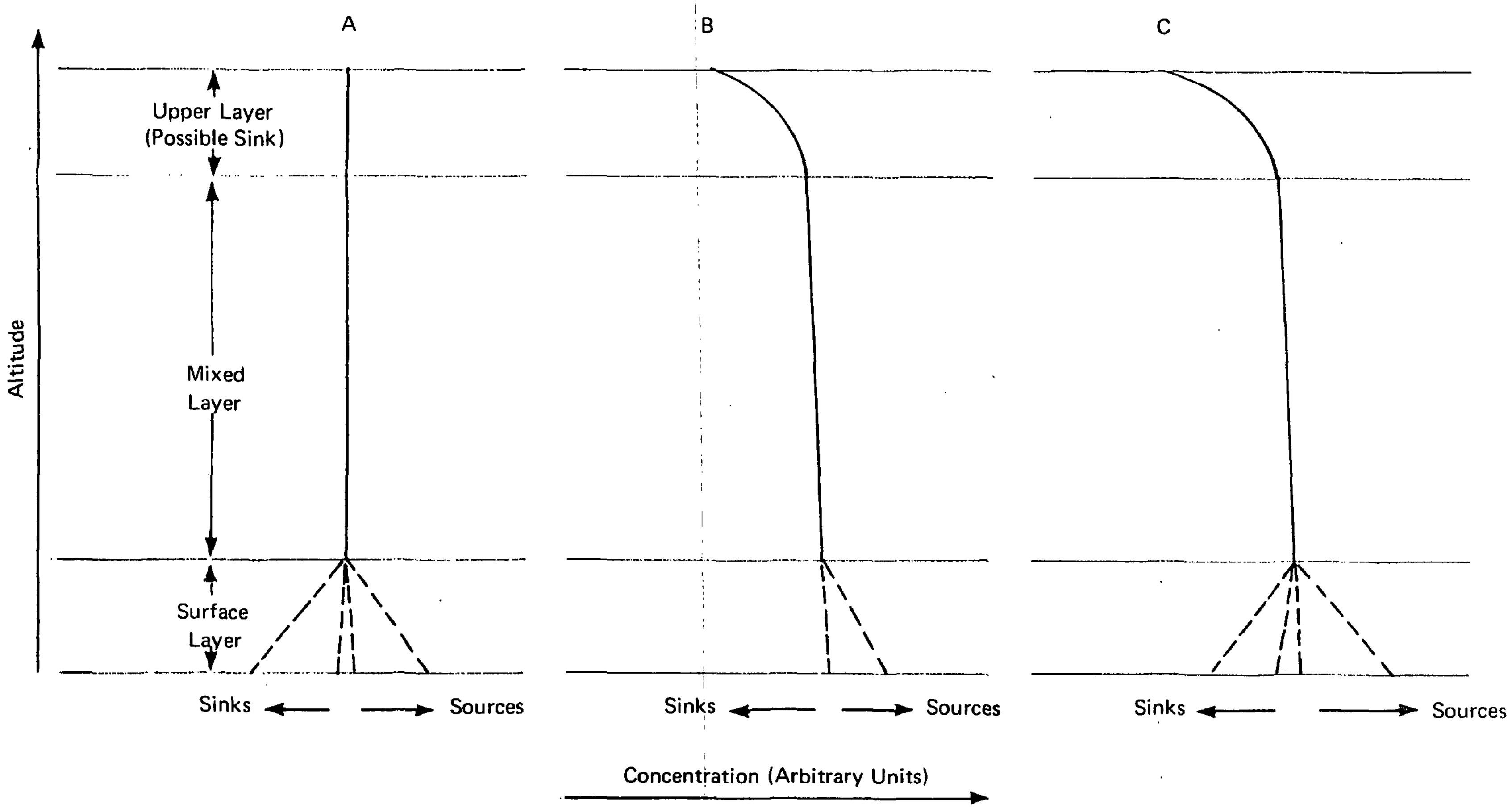
2. Theoretical Distribution

Available information on the global distribution of CO is based on a relatively few series of observations made primarily by three groups of workers. The pattern of distribution is complex. Before discussing the detailed observations, we shall describe the kinds of atmospheric distributions which would be consistent with different hypotheses regarding the sources and sinks of CO.

Information about the abundance profile of CO will provide evidence regarding the location of the sources and sinks. For purposes of simplicity, we shall assume all sources to be at the surface; the important question is whether the sinks are at the surface, in the atmosphere, or in both places.

We may therefore consider the atmosphere divided into (1) a surface layer, where the abundance varies locally with the strength of the surface source or sink, (2) a mixed layer above it, where CO is neither produced nor removed and any variation in concentration with altitude reflects the speed of tropospheric mixing and the transport of CO to higher regions, and (3) an upper layer, where an atmospheric sink could exist.

Figure V-1 shows three schematic diagrams of idealized abundance profiles which would be consistent with different hypotheses regarding the vertical distribution of sources and sinks. In the mixed layer, concentration is constant with altitude if there is no upper atmospheric sink (A), or shows a very slight decline with altitude if there is such a sink (B, C). Concentrations at the surface are larger than those in the mixed layer if there is a local source, the strength of the source being reflected by the amount of the difference. Similarly, local sinks should result in a lower local abundance at the surface than in the mixed layer, but the difference will be small if the sink is weak or widely distributed. The presence of a surface sink may be masked by the effects of a local source that is stronger.



A: surface sources and sinks, no atmospheric sink,
B: source at surface, sink in atmosphere,
C: sink in atmosphere, sources and sinks at surface

FIGURE V-1 IDEALIZED ABUNDANCE PROFILES FOR CO

Thus, observations near the surface and in the mixed layer alone may not suffice to determine the existence and location of surface sinks, especially if they are weak and well distributed. Interpretation of the data is further complicated by local meteorological conditions, which determine the rate at which CO produced at the surface is mixed in the lower troposphere. Consequently, calm weather and the presence of an inversion layer which inhibits mixing will temporarily increase the surface abundance of CO to an extent that varies with the strength and localization of the source, and the height of the inversion.

The nature of the CO surface source can also be partly determined by atmospheric CO concentration, the latter being necessarily affected by source strength and air movements. Tropospheric mixing across the equator is relatively slow. If fossil fuel combustion is the major source of CO, then average northern hemisphere concentrations in well-mixed air should be greater than those observed in the southern hemisphere, since most industry is concentrated north of the equator. Similarly, surface CO concentrations in areas far removed from the influence of industrial sources should be characterized by atmospheric concentrations equal to those in the well-mixed layers of the troposphere; under these conditions, the concentration should be constant throughout the surface layer and well into the troposphere.

If, on the other hand, "natural"--presumably biological--sources of CO exist, then the differences between northern and southern hemisphere tropospheric air would be less than if all CO were anthropogenic, under the assumption that the biological sources in the two hemispheres are not significantly different in strength.

3. Atmospheric Evidence of Sources and Sinks

In this section, we consider first the atmospheric evidence bearing on the relatively simple question of the existence of an atmospheric sink for CO, and then the more complicated question of biological sources and sinks at the surface.

a. Atmospheric Sinks

(1) Stratospheric Sink. Bates and Witherspoon (1952) rejected an atmospheric sink for CO, primarily on the grounds that while the presence of OH and HO_2 in the stratosphere might provide a sink for CO, the reactions must be slow. New interest in the OH reaction was aroused with the discovery that it is, in fact, very fast (Baulch, Drysdale, and Lloyd, 1968; and Westberg, Cohen, and Wilson, 1971).

Direct evidence of an effective stratospheric sink for CO was provided by the first direct observations of upper tropospheric and lower stratospheric CO abundances by Seiler and Junge (1969). They used an aircraft-mounted continuous CO monitoring device on several transpolar flights from Frankfurt to Tokyo. Flight level sections within the troposphere alternated with sections within the stratosphere. The observed CO mixing ratios in the troposphere varied from 0.10 to 0.12 ppm, with occasional transient excursions to levels as high as 0.2 ppm. In the lower stratosphere, the values rapidly dropped below 0.03 ppm and often reached the detection limit (0.003 ppm). The decrease or increase usually occurred within a few minutes of crossing the tropopause.

The publication of these results led to a re-evaluation of the possible role of the OH radical in converting CO to CO_2. Jaffe (1968) had proposed that OH radicals formed from photolysis of aldehydes and subsequent reduction of the perhydroxols in polluted atmospheres might constitute a CO sink. Pressman and Warneck (1970) concluded that this reaction can constitute a significant sink mechanism, and that the supply of OH radicals is sufficient to remove all the CO transported into the stratosphere, under the assumption that its mean concentration in tropospheric air is 0.15 ppm and that the exchange of air between the stratosphere and the troposphere is about 7.8×10^{16} molecules cm^{-2} sec^{-1}. Whether or not this mechanism is the primary sink for CO produced at the surface of the earth depends upon the mean atmospheric concentration and estimates of the sources and sinks.

(2) Tropospheric Sink. The tropospheric sink proposed by Jaffe (1968) for polluted atmospheres, in which the photolysis of aldehydes provides a source of OH and possibly other radicals, has not been extensively investigated, partly because the chemical reactions involving these and other radicals in polluted atmospheres are not well understood. This reaction was investigated by Harteck and Reeves (1967), who irradiated wet CO-N_2O mixtures in the presence of N_2, using a high-intensity light source to simulate a band of natural sunlight. Excited oxygen atoms reacted with water to produce two OH radicals, which in turn oxidized CO. Westberg, Cohen, and Wilson (1971) report the occurrence of this reaction in sample polluted atmospheres where NO is available; the end result is the rapid conversion of NO to NO_2 and subsequent production of ozone by photolysis of the NO_2. The reactions of interest are:

$$OH + CO \rightarrow CO_2 + H$$

$$H + O_2 + M \rightarrow HO_2 + M$$

$$HO_2 + NO \rightarrow OH + NO_2$$

where M represents O_2 or N_2. The net reaction from these steps is:

$$CO + O_2 + NO \rightarrow CO_2 + NO_2$$

These authors described experiments in which mixtures of isobutene (3 ppm), NO or NO_2 (1.5 ppm), and air (relative humidity 70%) with varying amounts of CO (up to 100 ppm) were irradiated with light approximating the intensity and spectral characteristics of sunlight. These concentrations are about an order of magnitude above those found in polluted atmospheres but represent approximately the same relative proportions. When NO was used instead of NO_2, the presence of CO accelerated the appearance of NO_2. The presence of NO_2 leads to the photolytic production of O_3 as follows:

$$NO_2 + \underline{hv} \rightarrow NO + O$$

$$O + O_2 + M \rightarrow O_3 + M$$

The ozone then reacts with NO to produce NO_2 and O_2:

$$O_3 + NO \rightarrow NO_2 + O_2$$

and photolysis of the NO_2 produced results in more NO. The ozone concentration increases in proportion to the amount of NO oxidized to NO_2. However, in the presence of CO, the ozone production decelerates when the ozone concentration reaches about 0.6 ppm (and the NO_2:NO ratio is about 30) as does the conversion of NO to NO_2. Westberg et al. note that the reactions appear to be significantly accelerated if the CO contains iron carbonyl contaminant (0.15%).

These observations strongly suggest that effective CO loss mechanisms may be active in polluted atmospheres. Their significance in rural areas, where the concentrations of the reactants may be about two orders of magnitude less than in heavily polluted atmospheres, remains to be determined.

b. CO in the Troposphere

Observations of atmospheric CO concentration near the surface of the earth in remote "clean air" conditions have been made by three groups of workers: Robinson, Robbins, and co-workers at the Stanford Research Institute in California; Seiler, Junge, and co-workers at the Max Planck Institute for Chemistry in Mainz; and Swinnerton, Linnenbom, and colleagues at the Naval Research Laboratory in Washington. Their findings are not entirely consistent.

(1) SRI Surveys. CO surveys were begun in 1966 by Robbins, Robinson, and co-workers using a newly developed instrument capable of detecting CO concentrations as low as parts per billion (Robinson and Robbins, 1968a, 1969a, 1969b, 1970; Robbins, Borg, and Robinson, 1968; and Cavanagh, Schadt, and Robinson, 1969). Their observations may be summarized as follows:

- Greenland Ice Cap and Pt. Barrow, Alaska -- Robinson and Robbins (1969a) measured the concentration of CO in flask samples gathered at a remote point on the Greenland ice cap about 400 miles northeast of Thule in July and August. Most of the observations were between 0.1 and 0.2 ppm, but concentrations of 0.5 to 1.0 ppm were observed when the air mass had recently traversed a heavily populated area--in this case, the Great Lakes and New England.

- Pt. Barrow, Alaska -- Measurements of CO concentrations at the surface at Pt. Barrow were reported by Cavanagh, Schadt, and Robinson (1969). The sampling site was located at a point remote from combustion sources, and the instruments permitted continuous monitoring of CO, CH_4, and some hydrocarbons. Wind speed and direction were also recorded. The average observed concentration was 0.09 ppm and the range was from 0.055 to 0.260 ppm, with most observations within the range from 0.06 to 0.15 ppm. Daily fluctuations were usually not more than 0.02 ppm. The authors suggest that these may be due to local vegetation sources of CO, but the short sampling period precluded the observation of seasonal variations, which might be expected under these circumstances. The simultaneous monitoring of CH_4 and some hydrocarbons (butane, pentane, acetaldehyde, acetone, methanol/ethanol, benzene) as well as CO_2 and cloud condensation nuclei permitted the authors to look for possible common sources. No obvious correlations were visible between the daily means of CO and any of the other components monitored. Monitoring of cloud condensation nuclei permitted the authors to rule out combustion sources of CO.

TABLE V-2. - GLOBAL DISTRIBUTION OF CARBON MONOXIDE

	Year	CO Mixing Ratio (ppm)
Lower Troposphere		
European surface data		
Mainz	1967-1969	0.11-2.0
Deuselbach	1969	0.15-1.2
Clean-air conditions		
Northern Hemisphere		
Northern Atlantic[a]	1969	0.17-0.21
Tenerife below trade wind inversion	1968	0.17-0.20
Tenerife above trade wind inversion	1968	0.10-0.14
Southern Hemisphere		
Southern Atlantic	1969	0.10-0.12
South Africa	1968	0.10-0.14
Upper Troposphere		
Transpolar flights	1968	0.10-0.15
Transequatorial flight	1968	0.10-0.14
Lower Stratosphere	1968	<0.003
Equilibrium Pressure of CO in Seawater	1969	≈5
Air in Contact with Earth Surface[b]		
Nighttime	1969	≈0.02
Daytime with sunshine	1969	≈0.5

[a] Clean-air conditions

[b] Air in glass container over soil

Source: Seiler and Junge (1970)

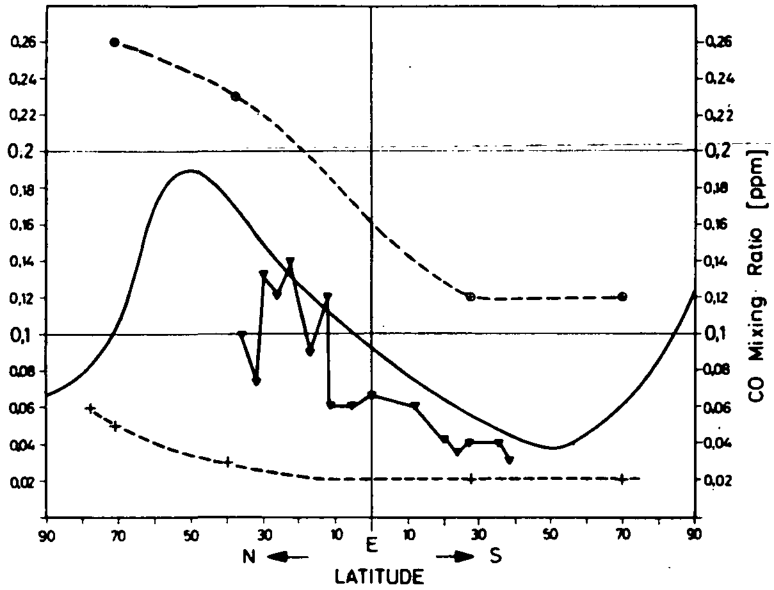
Despite the possibility that the CO observed in Pt. Barrow could be of local biological origin, Robinson and Robbins (1968, 1970) have ruled out major biological sources of CO and argue, like Bates and Witherspoon, that most atmospheric CO is of human origin. This argument is butressed by their data, which show much higher concentrations of CO in the clean surface air in the northern hemisphere than in the southern hemisphere. Robinson and Robbins (1968a) also accepted the arguments of Bates and Witherspoon regarding the non-existence of significant atmospheric sinks for CO and concluded that biological sinks must exist at the surface of the earth. The evidence of the apparent low mean concentration in the South Pacific suggested a major marine sink to these authors.

(2) Max Planck Institute Surveys. The Max Planck Institute group employed the same measurement technique developed at SRI. They developed a continuous analyzer which was used in an extensive survey of the CO concentration in the atmosphere and in seawater. The principal results as reported by Seiler and Junge (1969, 1970) and Junge, Seiler, and Warneck (1971) are summarized in Table V-2.

- CO in Clean Marine Air - Seiler and Junge measured the CO concentration in surface marine air along the 30th meridian west from 10°S to 60°N in 1969. In the southern hemisphere south of the intertropical convergence zone (which separates southern and northern air masses), rather constant CO concentrations of 0.10-0.12 ppm were observed. During passage through the zone, the concentration jumped from 0.14 to 0.21 ppm in a matter of hours and from then on in the northern hemisphere it never dropped below 0.17 ppm nor exceeded 0.25 ppm. Recordings in the North Atlantic were more variable than those in the South Atlantic.

Figure V-3 is a plot of the recordings during the crossing of the ITC. Figure V-4 shows all the results of Seiler and Junge plotted as a function of latitude.

- Pacific Marine Air -- Pacific marine air sampled at the surface was found to be highly variable in CO concentration and showed significant differences in mean concentration as a function of latitude. Figure V-2 shows the mean concentrations and the range of minimum and maximum concentrations observed by Robinson and Robbins (1968b, 1970) as a function of latitude in the Pacific. The estimated mean concentration was low in the north polar region (0.07 ppm), increased to a high of 0.18 ppm at 50°N, declined almost linearly from this point to a low of 0.05 ppm at about 50°S, and then increased slightly as the south polar regions were approached.

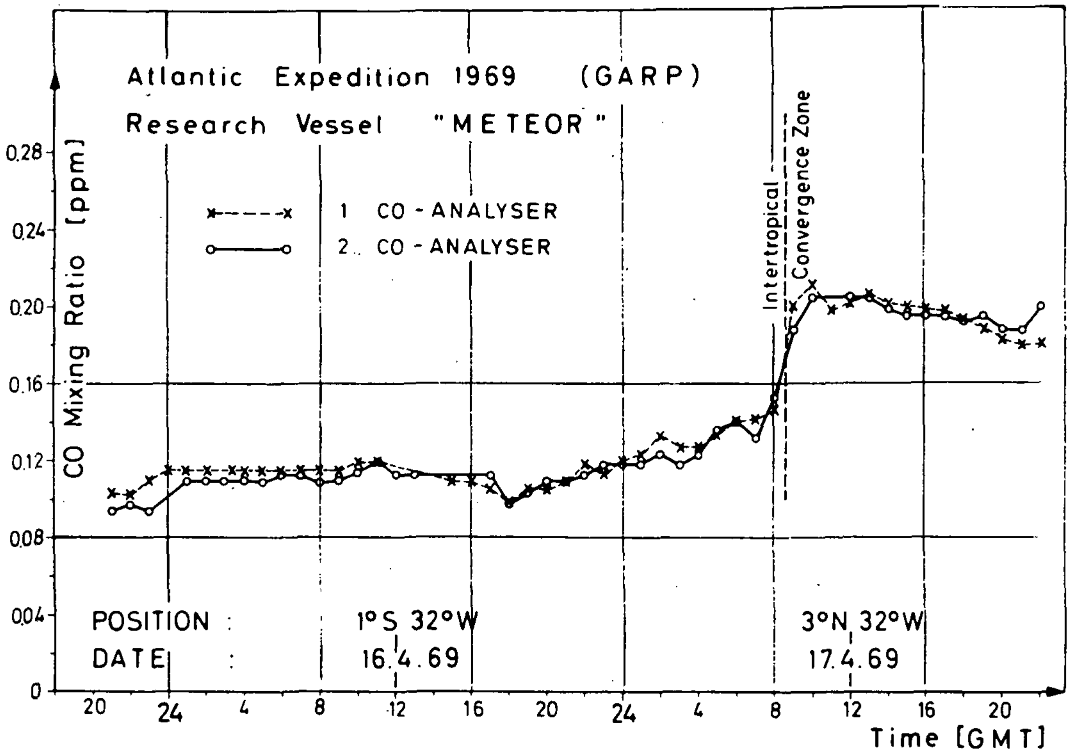


Source: Junge, Seiler and Warneck (1971)

Marine CO concentration measurements made by Robinson and Robbins (1968b)

▼ Cruise from San Francisco to New Zealand in Nov-Dec 1967
+ Lowest CO concentrations at several locations on northern and southern Pacific
● Highest CO concentrations
— Estimated mean distribution of CO as a function of latitude

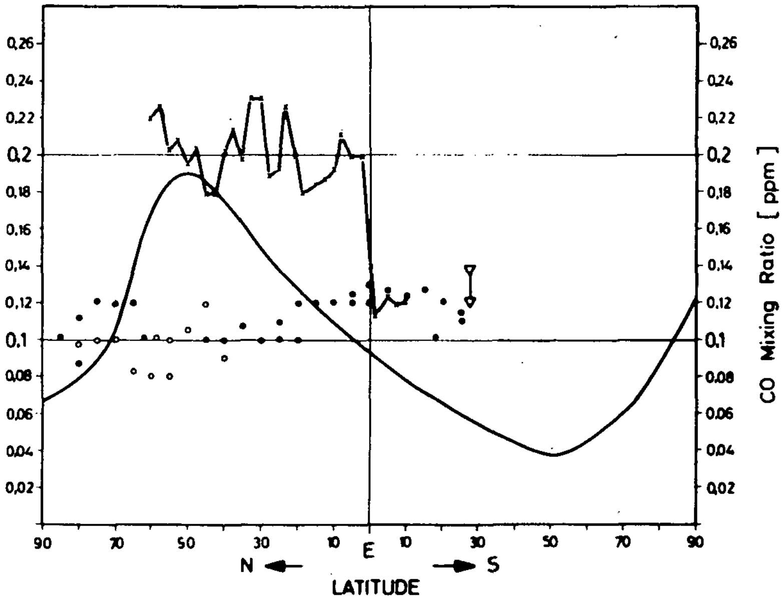
FIGURE V-2 CO CONCENTRATION IN PACIFIC AIR



Source: Seiler and Junge (1969)

CO concentration changes during crossing of the intertropical convergence zone near 3°N along the 30th meridian West, observed in April 1969. Recordings are from two independently operated instruments.

FIGURE V-3 CO CHANGES DURING CROSSING OF THE INTERTROPICAL CONVERGENCE ZONE



Source: Junge, Seiler and Warneck (1971)

X Expedition in southern and northern Atlantic in spring of 1969

∇ Variation of CO concentration at 28°S near Johannesburg over period of 3 weeks

● Concentration in upper troposphere at altitude of 10 km over the Atlantic

○ Concentration in upper troposphere at altitude of 10 km over northern Pacific

— Estimated mean CO distribution as a function of latitude, from Pacific observations of Robinson and Robbins (1968b)

FIGURE V-4 CO MEASUREMENTS BY SEILER AND JUNGE

Clean Atlantic air was also sampled at an intermediate altitude at the observatory of Izana on Tenerife (Canary Islands). The observatory is 2360 meters above sea level and is sometimes below and sometimes above the inversion.

When the observatory is above the inversion, CO concentrations in the range of 0.10 to 0.14 are observed. When the observatory is below the inversion, the concentration rises to 0.18 ppm or more. The concentrations are fairly steady and the prevailing winds are from the North Atlantic. Both these facts tend to rule out contamination sources of CO.

- CO Concentration over Land - Seiler and Junge report observations of the CO concentration at the surface in rural areas in Europe and South Africa and in the upper troposphere on aircraft flights between these two points and over the north pole.

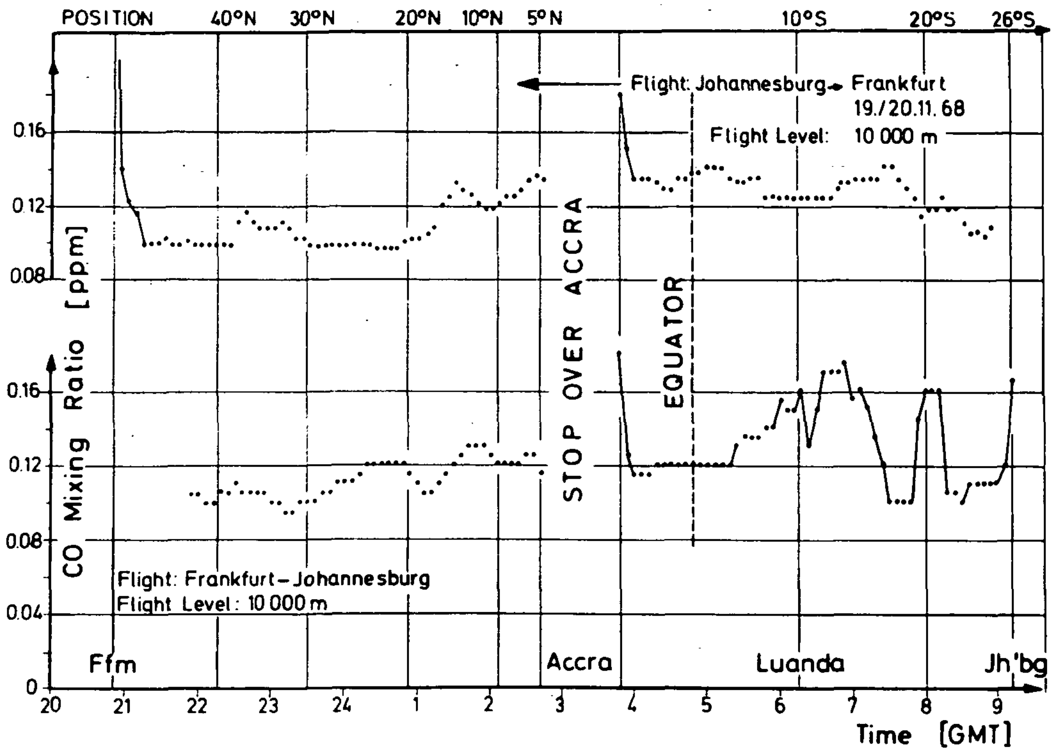
  Observations in a "clean air" rural location at Deuselbach, Germany, in the Hunsruck Mountains at an altitude of 470 meters varied with the weather conditions. The values ranged between 0.6 and 1.2 ppm in calm air and dropped to as low as 0.15 ppm during periods characterized by well-developed westerlies.

  Values observed from aircraft in the upper troposphere over Europe averaged 0.10 to 0.14 ppm, which implies a vertical lapse over land as well as over the ocean.

  Southern hemisphere tropospheric air was analyzed on flights from Frankfurt to Johannesburg and on the surface in South Africa at a point 100 kilometers west of Pretoria, characterized as "entirely unpolluted."

  The aircraft data (Figure V-5) indicate little difference between the two hemispheres at an altitude of 10,000 meters. There is some suggestion that the upper tropospheric CO levels in the southern hemisphere may be somewhat larger than those in the northern hemisphere; for example, little difference in tropospheric and surface level concentrations of CO were detected while landing at Johannesburg, whereas large differences are characteristic of European cities.

  Observations in the South African rural location indicated fairly steady concentrations in the range of 0.10 to 0.14 ppm except when the wind brought air from either Pretoria or Johannesburg, at which times highs of up to 0.25 ppm were observed.



Source: Seiler and Junge (1969)

CO mixing ratio of tropospheric air recorded during transequatorial flights between Frankfurt and Johannesburg.

FIGURE V-5 CO IN THE UPPER TROPOSPHERE

These observations show little detectable vertical decline in CO concentration in the southern hemisphere. However, the fact that southern hemispheric values are about half or more of northern hemispheric values suggests that most of the southern hemisphere CO is of natural origin. This hypothesis is not inconsistent with the apparently constant vertical abundance profile in that hemisphere, as a natural source might be expected to be weak but widely distributed. Alternatively, the southern hemisphere CO may have been brought from the northern hemisphere, which would occur if the lifetime of CO were long relative to the interhemispheric exchange time. Under such conditions, one would expect to see a gradual but definite buildup of atmospheric CO in the northern hemisphere.

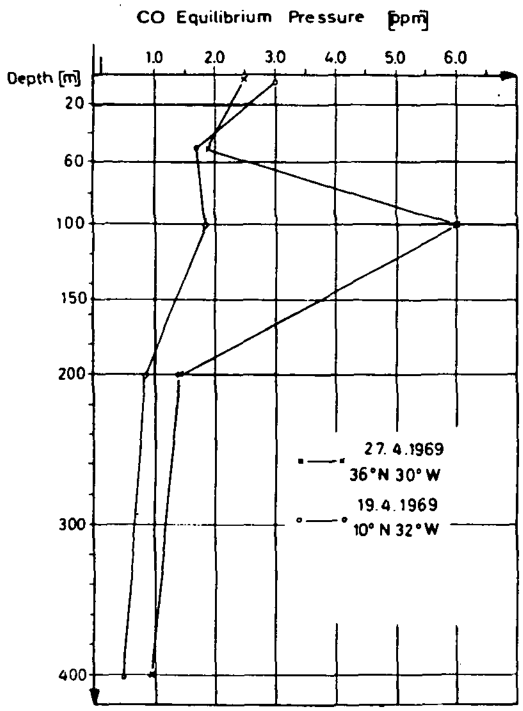
- CO Concentration in Seawater - The observations of Robinson and Robbins suggest a possible oceanic sink for carbon monoxide. CO is not very soluble in seawater. Seawater will be an effective sink only if it is subsaturated with CO.

  However, observations of high values of CO in North Atlantic air in 1968 suggested seawater sources of CO to Seiler and Junge, and they undertook a series of measurements of CO in seawater during the 1969 Meteor expedition. As expected, they found high concentrations in surface seawater, the amount of dissolved CO always being 10 to 40 times greater than the value that would correspond to equilibrium with the atmosphere. Figure V-6 shows two representative profiles of dissolved CO in surface water. The observed peak is at a depth of about 100 meters. In these waters, the thermocline is at about 200 meters. These characteristically high values of seawater CO were observed in both the southern and northern hemispheres. The authors do not state whether the sampled areas were highly productive biologically, but they hypothesize that the CO is a by-product of bacterial decomposition of organic matter.

  Seiler and Junge infer from these data that there are large marine sources of CO.

(3) Naval Research Laboratory Surveys. Swinnerton, Linnenbom, and co-workers began studying the concentration of CO in seawater in 1966 using a gas chromatographic device. (Swinnerton, Linnenbom, and Cheek, 1968, 1969; Swinnerton, Linnenbom, and Lamontagne, 1970a, 1970b.)

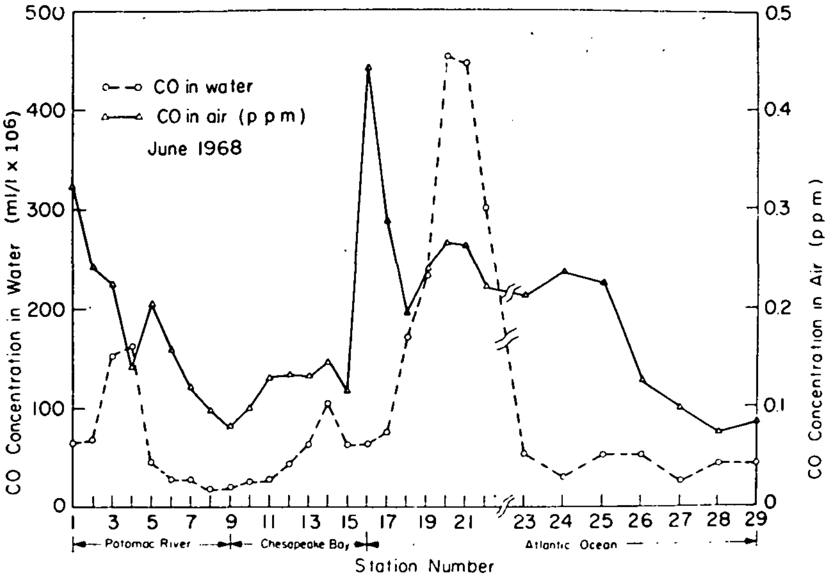
Systematic observations of atmospheric and marine CO concentrations were conducted by Swinnerton and co-workers in June 1968 on an oceanographic cruise between Washington, D.C. and Puerto Rico and again in April 1969. Observations of rain and air concentrations of CO were conducted in Washington D.C., on a cruise from Panama to Hawaii, and in Hawaii in 1969 and 1970.



Source: Seiler and Junge (1969)
Vertical line on upper Abscissa marks simultaneously measured CO mixing ratio of atmospheric air

FIGURE V-6 TYPICAL PROFILES OF DISSOLVED CARBON MONOXIDE IN ATLANTIC OCEAN WATER

- <u>CO Concentrations in Sea Surface Water and Atmosphere</u> - The results of these experiments are shown in Figure V-7. In the Potomac River near Washington and in a channel of extensive shipping traffic off Chesapeake Bay, observed high atmospheric values of CO may be attributed to pollution sources. The Washington peak was about 0.3 ppm and the traffic lane peak was about 0.4 ppm. The atmospheric concentration in the Atlantic ranged between about 0.25 and 0.10 ppm.



Source: Swinnerton, Linnenbom and Lamontagne (1970b)

Measurements of CO in water and air during a cruise from Washington, D.C. to Puerto Rico. Stations 1-9, Potomac River; Stations 10-15, Chesapeake Bay; Stations 16-29, Atlantic Ocean.

FIGURE V-7 CONCENTRATION OF CO IN SURFACE WATERS AND THE ATMOSPHERE

Seawater concentrations also showed considerable variability, but at all times were greatly in excess of what would be expected if marine CO were entirely derived from atmospheric CO, since they varied from 10 to 90 times the amount which would be in equilibrium with the measured atmospheric concentration. CO concentration was highest in the open ocean.

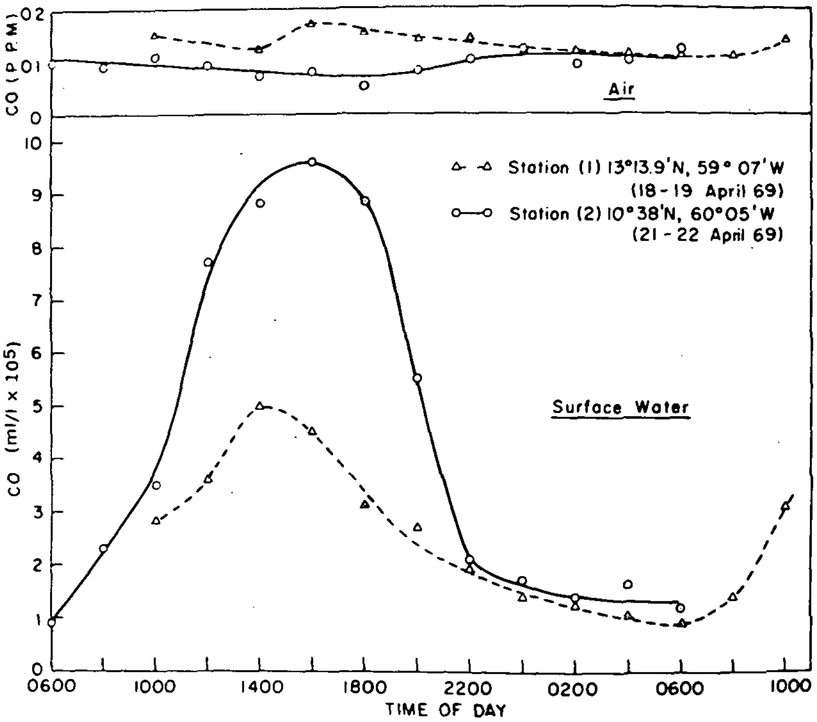
- Temporal Variations in Seawater CO Concentration - Observations during the 1968 cruise indicated that CO concentration in seawater exhibits a diurnal variation, increasing during daylight hours. This phenomenon was further studied in two field experiments. During November 1968, samples of seawater were collected at 1.5-hour intervals during a 24-hour cycle at the Chesapeake lighthouse, located about 15 miles from the entrance to Chesapeake Bay. A threefold increase in CO concentration (1 to 3 x 10^{-5} ml/l) was measured in surface water samples between total darkness and maximum daylight, the maximum occurring at 1400 hours.

In April 1969, these studies were continued at two stations, where both air and surface water samples were taken at two-hour intervals. Station 1, located approximately 17 miles east of Barbados, was relatively low in overall biological productivity compared with Station 2, and skies were somewhat overcast during the sampling period. The second station was located about 70 miles east of Trinidad. At both locations, prevailing easterly tradewinds minimize the likelihood of contamination from man-made sources.

The data (Figure V-8) show a relatively constant level of CO concentration in the atmosphere at both locations and a marked diurnal variation in the surface waters. The average atmospheric concentrations of 0.14 ppm and 0.09 ppm at Stations 1 and 2, respectively, agree with values previously observed by these workers and are consistent with those reported by Seiler and co-workers.

The CO concentration in surface water ranged from a minimum of 1×10^{-5} ml/l at night to high peaks during the afternoon. At the less productive station (Station 1) the peak was about 5×10^{-5} ml/l; at the more productive station the peak was nearly 10×10^{-5} ml/l. Figure V-9 is a plot of R_{CO}, the ratio of measured CO concentration to the concentration that would be expected if there were no marine sources of CO and the seawater were in equilibrium with atmospheric CO. The curves show supersaturation by factors of 5 to 100.

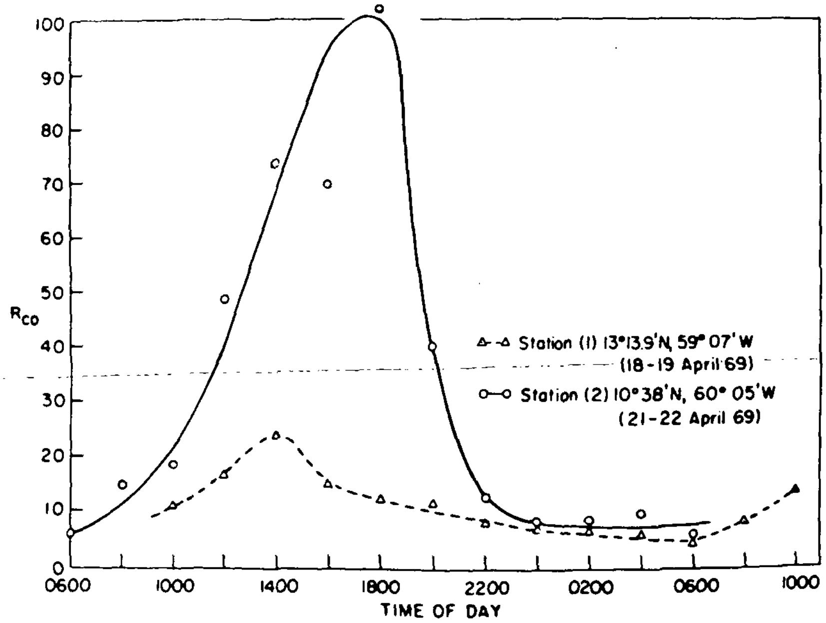
Vertical distributions of CO in seawater were also measured. Plots of the data obtained during darkness and daylight at the second station (Figure V-10) show that the effects of sunlight are observed down to 40 meters.



Source: Swinnerton, Linnenbom and Lamontagne (1970b)

Observed CO concentrations during a 16-hour observation period at two fixed stations. Station (2) is the more biologically productive station.

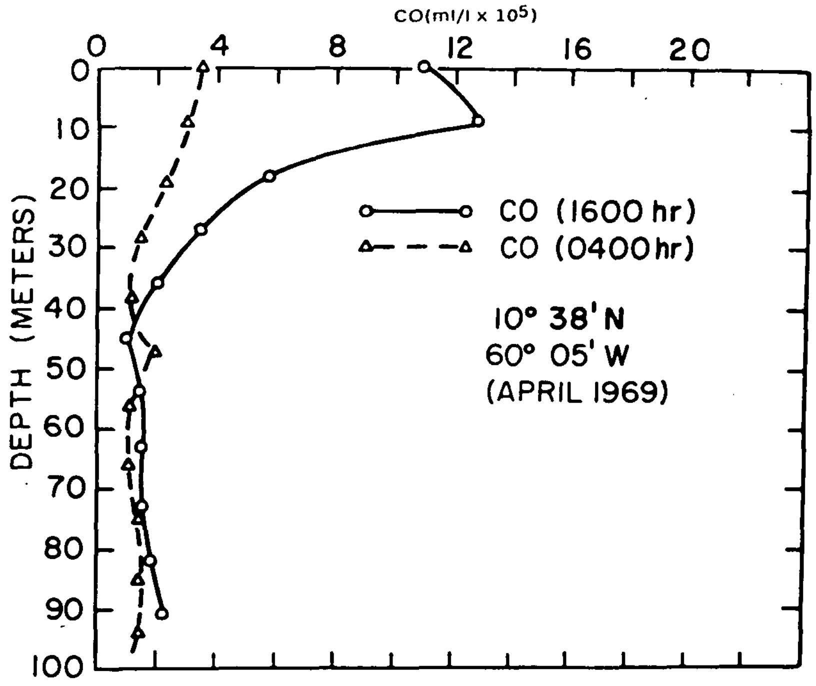
FIGURE V-8 CO CHANGE WITH TIME IN AIR AND WATER



Source: Swinnerton, Linnenbom and Lamontagne (1970b)

Variations during a 24-hour period in the ratio R_{CO} of measured to calculated CO concentrations in surface waters. Calculated concentrations are based on equilibrium distribution of CO between sea and atmosphere, assuming atmosphere to be the sole source of CO.

FIGURE V-9 RATIO OF MEASURED TO CALCULATED CO SATURATION



Source: Swinnerton, Linnenbom and Lamontagne (1970b)

Concentration of CO as a function of depth in seawater in the daytime and at night.

FIGURE V-10 VERTICAL DISTRIBUTION OF CO IN SEAWATER

It is clear from these data that seawater cannot act as a sink for atmospheric carbon monoxide; the observed supersaturation indicates that the net transport of CO across the air-sea interface should be from the water into the atmosphere. Swinnerton, Linnenbom, and Lamontagne (1970c) calculate that if the average concentration of CO in the surface waters of the world is taken to be approximately 10^{-5} ml/l, the oceans could account for an atmospheric injection of about 9×10^{12} grams per year, under the assumption that all the CO in the top two meters is released in every 24-hour period. This corresponds to about 5% of estimated anthropogenic sources.

Figure V-10 indicates that the diurnal difference in CO content is about 2 ml/m^2 at the Trinidad station. If this station is representative of the productive "coastal zones" described by Ryther (1969) in which productivity averages 100 gm C m^{-2} yr^{-1}, then about 10% of the total ocean may be characterized by similar productivity. Assuming this quantity of CO is produced during about half of the year, the annual CO productivity of such zones may be as much as 10^{13} gm yr^{-1}. How much of this may escape to the atmosphere depends upon the rate of transmission through the air-water interface.

- Carbon Monoxide in Rainwater - Swinnerton, Lamontagne, and Linnenbom (1971) investigated the concentrations of carbon monoxide and methane in rain and in air collected simultaneously with the rain in Washington, D.C., Hawaii, and in Pacific marine air. The CO results are shown in Table V-3. The averages of four sets of rain samples collected during the day ranged from 16×10^{-5} ml/l (for four samples taken at different latitudes in the Pacific ocean) to 33×10^{-5} ml/l (for nine samples taken on a little-traveled road in the interior of Hawaii at sites along the windward side of the road facing the trade winds at altitudes ranging from 460 to 1500 meters). Nighttime samples collected at three of the locations varied from 4.1×10^{-5} ml/l (Pacific ocean samples) to 19.0 ml/l (for four samples collected at the Cloud Physics Observatory at Hilo).

Although the ranges in concentration of carbon monoxide in rainwater collected during the day and those collected at night were in general large, the daytime concentrations showed higher mean levels than nighttime concentrations in precipitation collected at the same site. Concentrations of carbon monoxide in air show the effects of pollutant sources: in Washington the average concentration reported is 1.49 ppm, and the Hilo levels are almost twice those of the more remote interior Hawaiian sites.

TABLE V-3. - CARBON MONOXIDE IN RAINWATER AND THE ATMOSPHERE

Location and Number of Samples	Concentration in Rain (10^{-5} ml/l)		Concentration in Air (ppm)		R_{CO}[a]	
	Avg.	Range	Avg.	Range	Avg.	Range
Washington, D.C.(NRL)[b]						
Day (17)	32.0	9.7-140.0	1.49	0.8 -2.7	7.3	1.9- 32
Pacific Ocean[c]						
Day (4)	16.0	14.5- 18.9	0.10	0.08 -0.12	73	56 -110
Night (1)	4.1		0.11		17	
Hawaii (Saddle Road)[d]						
Day (9)	33.0	11.0- 55.0	0.12	0.09 -0.16	123	55 -210
Night (13)	15.0	5.0- 28.0	0.15	0.07 -0.30	52	16 -105
Hawaii (CPO)[e]						
Day (13)	20.0	6.0- 46.0	0.22	0.10 -0.25	41	17 - 86
Night (4)	19.0	13.0- 25.0	0.25	0.19 -0.36	26	21 - 34

[a] Ratio of the measured concentration of CO in rainwater to the calculated concentration based on the partial pressure of CO in the atmosphere (at equilbrium, R=1).

[b] Samples collected at Naval Research Laboratory between December 1969 and April 1970.

[c] Samples collected aboard ship during June 1970 while en route from Panama to Hawaii. Atmospheric concentrations shown refer only to the five samples taken at the time of rainfall.

[d] Samples collected in the interior of the island at altitudes between 1500 and 5000 feet.

[e] Samples collected at the Cloud Physics Observatory, University of Hawaii, Hilo campus (approximately at sea level). Hawaiian samples were collected 16 to 22 June 1970.

Source: Swinnerton, Linnenbom, and Cheek (1971)

All rainwater samples showed supersaturation with respect to the level of carbon monoxide present in the air during the collection of the rain, but the amount of supersaturation varied inversely with the amount of pollution. Thus, in Washington, the most heavily polluted location, the average value of R_{CO} was 7.3, while in the interior of Hawaii during the day, the average value of R_{CO} was 123. The corresponding mean concentrations of CO in rainwater were almost identical: 32 ml/l for Washington and 33 ml/l for interior Hawaii. Swinnerton et al. suggest that the high levels of carbon monoxide in rain may result from the photochemical oxidation of dissolved organic matter in rain and cloud water, or by the dissociation of carbon dioxide caused by electrical discharges within the clouds. The former mechanism is discussed in more detail below.

The mean carbon monoxide concentration for all samples from sites at which day and night collections were reported was 18×10^{-5} ml/l. If this figure is representative of all rain, then the total amount of carbon monoxide produced by this mechanism in rain is not more than about 10^{11} grams per year.

E. THE CARBON MONOXIDE BUDGET

A "budget" for an atmospheric gas is a quantitative description of the exchange of the gas between various reservoirs, derived in accordance with some model of its behavior, and associated measurements of abundance in one or more of the reservoirs. Interest in the CO budget derives primarily from the recognition that future increases in anthropogenic sources will be accompanied by increases in the ambient CO level in the atmosphere if these are the primary sources.

The simplest budgets are merely statements of residence time. The first of these was produced by Bates and Witherspoon (1952), who estimated it to be 4 years or less. Subsequently, Robinson and Robbins (1968a) estimated the residence time as 2.6 years, employing a mean global abundance of 0.05 ppm and an injection rate of 2.1×10^{14} gm yr^{-1}.

More complicated budgets were developed by Pressman and Warneck (1970) and Junge, Seiler, and Warneck (1971), who sought to develop models which permit the available evidence to be interpreted in terms of the relevant questions regarding the existence of large natural sources and sinks.

1. Pressman and Warneck Models

Pressman and Warneck (1970) first consider the OH reaction in the stratosphere as a mechanism for removing CO. Measurements of the rate constants for the reaction became available in 1967, when it was discovered that the reaction is in fact very fast. Pressman and Warneck conclude that it is capable of removing all of the CO transported to it (assuming a tropospheric-stratospheric exchange rate of 7.8×10^{16} molecules cm^{-2} sec^{-1}) and that it could account for a residence time on the order of 3 to 9 years. They then consider the question of the rate at which detectable increases in the concentration of CO will occur, under various assumptions about the lifetime and the speed of interhemispheric mixing of CO relative to the lifetime toward stratospheric oxidation (i.e., the lifetime it would have if stratospheric oxidation were the only sink).

They conclude that doubling of the average global CO concentration will take about 17 to 22 years if anthropogenic sources increase linearly and residence time is 3 to 9 years. If interhemispheric mixing takes about 1 year, which is the most recent estimate provided by Nydal (1968) on the basis of bomb-produced ^{14}C, then a short residence time of 2 or 3 years implies an ultimate ratio of northern to southern hemispheric CO abundance of 1.33, while a 4-year residence time implies a ratio closer to 2. The calculations are only approximate because of uncertainties in the figure for interhemispheric mixing; nevertheless, the results are so close that available abundance data are inadequate to evaluate the model and consequently do not permit any conclusions regarding the possible existence of major sources other than human ones.

2. Models of Junge, Seiler, and Warneck

Junge, Seiler, and Warneck (1971) present a budget for ^{14}CO and ^{12}CO in an attempt to determine whether ^{14}CO can be considered a reliable tracer for ^{12}CO. Pandow, McKay, and Wolfgang (1960) and McKay, Pandow, and Wolfgang (1963) provided the basis for the use of ^{14}CO when they reported that most of the ^{14}C produced by cosmic radiation in the upper atmosphere reacts with oxygen to form ^{14}CO rather than $^{14}CO_2$, as was assumed by Libby (1955). McKay, Pandow, and Wolfgang argued that the lack of atmospheric CO sinks to convert ^{14}CO to $^{14}CO_2$ should result in a significantly higher activity for atmospheric CO than CO_2. They presented measurements of the specific activity of three samples of CO gathered in a polluted atmosphere in South Buffalo, New York. These samples were diluted by non-radioactive CO of industrial origin and showed considerable variation in activity. (Their mean activity relative to 95% NBS oxalic acid standard of zero age in 1955 was reported as +9.3, -39.3, and -27.9%.) The apparent dilution made it impossible to test this hypothesis.

Weinstock (1969) used these data of McKay et al. (1963) as the basis for a crude estimate of the lifetime of atmospheric CO and a demonstration of the possible utility of radioactive CO distribution data in elucidating the CO cycle. He pointed out that the lifetime of CO could be estimated from the atmospheric concentration of ^{14}CO if the following assumptions were accepted: (1) cosmic radiation in the upper atmosphere is the only significant source of ^{14}CO; (2) the residence times of ^{14}CO and ^{12}CO in the atmosphere are identical; (3) ^{14}CO is uniformly distributed about the globe; and (4) ^{14}CO is in a steady state. Weinstock calculated that the mean lifetime of CO is about 0.1 year, based upon a ^{14}CO concentration of 4×10^{-13} ppm (equivalent to a global abundance of about 1 kg of ^{14}C as CO) and a ^{14}C rate of formation 1.3×10^{19} atoms sec^{-1}. Weinstock points out that this estimate is probably too low, because ^{14}CO may be oxidized in the atmosphere by means of the OH reaction, so that ^{12}CO and ^{14}CO are not subject to the same removal processes.

The mean sample activity on which Weinstock based his estimate of the global abundance of ^{14}CO is a poor estimator of the probable mean concentration of ^{14}CO. The mean of the samples is +28.7 and the best estimate of the standard deviation of the population is 27.9.

The ^{14}CO and ^{12}CO budgets developed by Junge, Seiler, and Warneck (1971) are elaborations of Weinstock's model, modified by somewhat more realistic assumptions made possible by the observations of the Max Planck Institute group. (Junge et al. confine their consideration to the northern hemisphere, for which they have collected many data.)

Instead of considering the entire atmosphere as a single ^{14}C reservoir with an injection rate corresponding to the production rate, Junge et al. distinguish the tropospheric from the stratospheric reservoir and ask whether the tropospheric residence time of ^{14}CO is the same as that of ^{12}CO.

In place of the assumption that ^{14}CO production is 1.3×10^{19} atoms sec^{-1}, they use a figure of 1.9 atoms cm^{-2} sec^{-1} for the whole atmosphere and consider only the 44% of these which are produced in the troposphere. They then consider how much, if any, of the stratospheric production survives OH oxidation long enough to support a net downward flux of ^{14}CO through the tropopause. This will occur only if the concentration just above the tropopause is greater than that just below, and this in turn depends on the chemical lifetime of CO in the stratosphere and vertical differences in the production of ^{14}C. Although the latter can be modeled with reasonable accuracy, neither the coefficient of chemical loss in the stratosphere nor the vertical eddy diffusion are known within an order of magnitude. Evaluating the model for the range of values of these parameters now believed to be the most probable shows that the stratosphere could either be a net source or a net sink for ^{14}CO. But even if there is some ^{14}CO flux from the stratosphere to the troposphere--and, as a consequence, tropospheric lifetimes of ^{14}CO and ^{12}CO are not identical--the differences in tropospheric lifetimes are small, and Junge et al. conclude that ^{14}CO is therefore a good tracer for ^{12}CO.

The lifetime of ^{14}CO in the troposphere is 0.2 years, if the mean activity of the three samples of MacKay et al. is representative of tropospheric abundance of ^{14}CO. This figure seems too low to Junge et al., as they have detected no major sources of CO which would yield such a lifetime, and because this figure implies major tropospheric sinks which have not yet been detected. These authors favor instead a mean residence time in the northern hemisphere on the order of 1 year, basing their conclusion on estimates of the anthropogenic source and on their own evidence that the northern hemispheric marine source is of the same order of magnitude as the anthropogenic source, so that the total northern hemispheric production is about 5×10^{14} grams yr^{-1}.

Junge et al. use two approaches to develop an estimate of marine production of CO in the northern hemisphere. The first procedure employs their data on the supersaturation of CO in seawater. The transfer of CO from the ocean to the atmosphere is a function of the pressure difference--assumed to average 3.3×10^{-6} atmospheres, corresponding to supersaturation by a factor of about 20--and an exchange coefficient, which is a function of the physico-chemical properties of the CO. No direct measurements of the exchange coefficient exist, but these authors adopt the figure for O_2 used by Bolin and Keeling (1963) on the grounds that the solubilities of the two are similar. This rate coefficient is 15 grams cm^{-2} yr^{-1} atm^{-1}, and the resulting marine injection estimate for the northern hemisphere is 0.75×10^{14} gm CO yr^{-1} for the whole 1.5×10^{18} cm^2 of ocean. This corresponds to about 29% of anthropogenic production, the total of which is taken as 2.6×10^{14} grams.

The second procedure for estimating marine sources employs data on the vertical gradient of CO mixing ratio over the oceans, together with estimates of the vertical eddy diffusion coefficient for the troposphere, which is taken to be 2×10^5 cm^2 sec^{-1}. Using their own data (Figure V-2), Junge et al. conclude that the mean vertical gradient over the Atlantic is from 0.2 ppm at the surface to 0.12 ppm at the tropopause (10 km). The corresponding figures for the Pacific are 0.15 ppm at the surface to 0.12 ppm at the tropopause. These estimates yield vertical gradients of 8 and 3 x 10^{-14} cm^{-1}, respectively; an average figure of 5 x 10^{-14} cm^{-1} is employed in the calculations, which yield an estimated total flux across the tropopause above these oceans of 3.3 x 10^{14} gm CO yr^{-1}, or 130% of the estimated production of anthropogenic sources on land.

Junge et al. conclude on the basis of these two estimates that natural marine production in the northern hemisphere is of the same order of magnitude as northern hemisphere anthropogenic sources (since most anthropogenic CO is released in the northern hemisphere). They argue that most of the CO in the marine atmosphere is of natural marine origin, on the grounds that the relative lack of variability observed in their measurements implies few pollutant sources.

The estimated 2.6 to 3.3 x 10^{14} gm CO yr^{-1} emitted from the northern hemisphere oceans to the atmosphere corresponds to 1.2 to 1.5 x 10^{11} molecules cm^{-2} sec^{-1} when averaged over the whole ocean, or 0.7 to 0.8 x 10^{11} molecules cm^{-2} sec^{-1} when averaged over the whole northern hemisphere.

These estimates of biological CO production correspond to a relatively insignificant ^{14}CO production from this source compared with that produced by cosmic bombardment in the troposphere. If the ratio of ^{14}C to ^{12}C is the same in biogenic carbon monoxide as it is in other biological material (1.24 x 10^{-12}), then this source can supply only about 350 gm ^{14}CO per year, or about 0.88 x 10^{-1} molecule cm^{-2} sec^{-1} (averaged over the whole hemisphere). In contrast, the tropospheric ^{14}CO production is about 8.4 x 10^{-1} molecule cm^{-2} sec^{-1}.

F. BIOLOGICAL SOURCES

Although slight quantities of CO may be emitted by volcanoes, "natural" sources at the surface of the earth are almost certainly biological in origin. Biological production of CO in the pneumatocysts (float bladders) of kelp and siphonophores has been known for some time, and numerous studies have shown that a number of higher plant species form and oxidize CO. Few data on actual production and utilization rates under field conditions are available, and at present it is not possible to make estimates of the probable global production from these sources.

Delwiche (1970) and Loewus and Delwiche (1963) report laboratory studies of the production of CO by various species of higher plants. Work with intact tissue of seaweeds, alfalfa, and other plants revealed high rates of production in both intact tissues and in macerated tissue, and a strong light-dependency of the reaction. Table V-4 shows production rates of excised tissues incubated in phosphate buffer for 5 hours. Medicago sativa, a species of alfalfa, showed the highest CO productivity, followed by three species of seaweed. Extrapolation of these laboratory rates to field conditions suggests that a 100-hectare field of alfalfa could produce approximately 2000 liters of CO in a 10-hour period. This corresponds to a mean productivity of about 7×10^{-11} gm cm^{-2} sec^{-1} for this period, or 1.5×10^{12} molecules cm^{-2} sec^{-1}.

Extracts of mascerated tissue also showed a capacity to produce CO in light; even in extracts that had been heated, the yields were up to 50% of that of the intact tissue. Delwiche (1970) attributes this production to the photodecomposition of various polyphenolic compounds in the tissue extracts.

Other workers who have observed CO production in plants include Wilks (1959), who reports CO production from cut, dried, or injured vegetation stimulated by UV radiation, and production of CO during photosynthesis; and Siegal, Renwick, and Roxen (1962), who observed CO production during seedling germination.

Evidence of Swinnerton, Linnenbom, and Lamontagne (1970b) and Seiler and Junge (1969) regarding possible large marine sources of CO has resulted in renewed interest in the marine production by known sources. One of these is the siphonophore population of the deep scattering layer, whose matabolism and behavior have been reported by Pickwell (1970).

TABLE V-4. - CARBON MONOXIDE PRODUCTION BY EXCISED TISSUES OF SEVERAL SPECIES

Tissue[a]	CO (moles x 10^{-9} per g/hr)
Egregia menzies	5.0
Zostera marina	7.0
Nereocystis luetkeana	5.6
Catiara thron sp.	4.0
Laminaria sp.	2.5
Rhodomela larix	1.6
Marcrocystis sp.	1.8
Iridia flaccum	0.4
Medicago sativa	8.5

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[a] Tissues were incubated in phosphate buffer at pH 7.0 for five hours.

SOURCE: Delwiche (1970).

Although these organisms emit CO from their floats while migrating vertically in quantities that are enormous relative to their metabolic requirements (the ratio of energy consumed in CO production to that used in metabolism is about 200:1), the total production from these sources probably does not exceed 10^8 or 10^9 grams per day.*

A larger source of CO that might account for the observed light-dependency of marine CO concentration was reported by Wilson, Swinnerton, and Lamontagne (1970). They studied the production of CO by bacteria-free cultures of the ultradiatom Chaetoceros galvestonensis and found, to their surprise, that sterile controls incubated in the light showed a production of CO as well as unsaturated hydrocarbons, although at rates much lower than those characterizing the ultradiatom cultures, in which the concentration of CO and of ethylene and propylene increased markedly with time. Experiments in which the amount of light and the initial quantity of dissolved organic matter (DOM) were systematically varied revealed that productivity in illuminated samples was 5 to 10 times that in samples maintained in the dark. In the light, CO production in natural seawater containing DOM was positively correlated with DOM content; the reverse was true in the dark. Distilled water to which DOM was added also produced CO, but in small quantities. In this case, as with natural seawater, much more CO was produced in the light than in the dark, and light production was positively correlated with DOM content.

Bacterial contamination of the cultures of C. galvestonensis sometimes had serious effects on the concentrations of the gases. In one case, one strain of bacteria caused the CO concentration to go to zero and produced CH_4.

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*Basis for this estimate: 10% of the ocean is productive coastal of the sort inhabited by siphonophora, and the population density is 1 to 10 per square meter. Of these, only about 25% migrate each night, releasing 21 micrograms of C, or about 50 micrograms of CO, per migration. There are 3.6×10^{13} m^2 of productive coastal waters.

Seiler and Junge (1969) report the early results of an experiment designed to determine whether soil functions as a source or a sink for CO. They studied the CO concentration in a 20-liter glass vessel that covered the soil surface. Initially the jar was filled with ambient air containing 0.2 ppm CO. The concentration of CO exhibited pronounced daily variations, with maxima of about 0.5 ppm around noon and broad minima of 0.02 and lower during the cold part of the day. Temperature dependence was very marked. For loam and humus, artificial temperature control showed that the concentration increased if the temperature was above and decreased if it was below 25°C, suggesting that there is a temperature at which CO concentration is in balance.

It is difficult to interpret the significance of this experiment, as too few details are supplied. However, the rate of production or assimilation could be as high as 3 to 12 x 10^{-12} grams cm^{-2} sec^{-1} (6 to 26 x 10^{12} molecules cm^{-2} sec^{-1}).*

Other minor biological sources of CO have been described. CO is a by-product of catabolism of hemeoproteins--primarily blood cells and myoglobin--in humans and, presumably, all other higher animals. Although some of this CO is probably oxidized, slight quantities are secreted in respired air, and higher animals constitute a net source of CO (Fenn 1970, Sjostrand 1970, Coburn 1970). In normal humans, the degradation of senescent red cells at the end of their normal life span accounts for approximately 75% of the total endogenous CO production. Production of CO varies with the physical condition of the patient, and the excretion rate depends in part on the concentration in inspired air, but mean endogenous CO production and excretion rates of about 19 micromoles per hour in normal humans have been observed (Coburn 1970).

If we assume that this rate of production is a useful average for all warm-blooded terrestrial animals, the annual human production of 0.176 mole per human per year implies a production rate of 3.5 x 10^{-3}

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*The volume of the jar is 20 liters, the area covered by the mouth could be 60 to 100 cm^2 and the time required to shift from minimum to maximum or back again could be 5 to 12 hours.

moles per kg per year, on the assumption that the average human weighs 50 kg. Since there are about 2.6×10^{11} kg of mammals and aves in the world (Bowen, 1966), we may arrive at a crude estimate of 2×10^{10} grams per year from this source, which is clearly negligible on a global basis.

G. BIOLOGICAL SINKS

It has been known for some time that some chemoautotropic bacteria (*carboxydomonas*) oxidize carbon monoxide as an energy source. Alexander (1961) describes the anaerobic conversion performed by *Methanosarcina barkeri* as follows:

$$4\,CO + 4\,H_2O \rightarrow 4\,CO_2 + 4\,H_2$$

$$CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O$$

Bacillus oligocarbophilus uses oxygen to oxidize CO to CO_2 and this organism has been cited by both Bates and Witherspoon (1952) and Robinson and Robbins (1968a) as a possible converter of atmospheric CO to CO_2.

Delwiche (1970) cites numerous experiments which show that CO has visible effects--often analogous to those of ethylene--on some plants. He reports CO fixation by barley leaves and other plants; ^{14}C tracer studies showed that the CO was incorporated in plant tissue. These assimilatory reactions are light-dependent. Table V-5 shows rates of uptake of different 1-carbon compounds by barley leaves.

These studies of the uptake of CO by plants have employed partial pressures of CO from 10^3 to 10^6 times atmospheric levels, or more. If, as seems likely, uptake is concentration-dependent, then production of CO by plants may exceed assimilation. Field studies are necessary, as are additional comparative laboratory data for a greater variety of species.

TABLE V-5. - RATE OF UPTAKE OF DIFFERENT 1-CARBON COMPOUNDS BY EXCISED BARLEY LEAVES

Compounds	Experimental Conditions	Light, (foot candles)	Uptake (moles x 10^{-9} per gm/hr)[a]
CO_2	0.05% in air	2,000	13.0
CO_2	2.0% in air	2,000	760.0
CO	12°C	2,000	0.018
CO	28°C	2,000	0.038
HCOOH	Air, 29°C	2,000	1.05
HCOOH	Air, 23°C	Dark	0.105
H_2CO	Air, 23°C	2,000	0.168
H_2CO	Air, 23°C	Dark	0.0011
CO	Air, 12°C	Dark	0.00065

[a] Comparisons are not completely valid because of wide ranges in partial pressures of gases (CO was 65%), differences in the manner in which substrate was provided, and varietal differences.

SOURCE: Delwiche (1970)

Robinson and Robbins (1968a) suggest that CO and other trace constituents in the air are absorbed through the stomata together with CO_2 in quantities proportional to their concentrations, so that all of these constituents have essentially the same residence times.

Hill (1971) studied the removal of pollutant gases by vegetation canopies inside test chambers, in which air was recycled at rates of 3 to 5 miles per hour over alfalfa and oat canopies. No evidence of CO uptake could be measured with a test atmosphere containing 0.05 ppm.

Inman, Ingersoll, and Levy (1971) report an extensive series of tests of the ability of soils to remove carbon monoxide from the atmosphere. Soils were exposed to test atmospheres containing 80 to 130 ppm CO, and the concentration of CO in the test chamber was monitored until "CO depletion stopped". The rate of CO uptake at the end of the test period was determined from the last two or three determinations.

The ability of the soil to remove CO was shown to vary with temperature (Table V-6) and with organic content and acidity (Table V-7). Although there were some exceptions, acidic soils and those with a high organic content were generally the most active in removing CO from the test atmospheres.

Autoclaving the soils completely eliminated their ability to remove CO under the test conditions used. After autoclaving, soils released CO. This release of CO is reported as being temperature dependent in the dark: at 20°C approximately 3.5 mg of CO per hour per kilogram of soil was evolved; at 40°, 36 mg of CO per hour per kilogram of soil; and at 55°, 136 mg of CO per hour per kilogram. CO evolution by autoclaved soil is reported as being about 30% greater in the light at 40° than in the dark.

No CO evolution by non-autoclaved soils was observed. Innoculation of autoclaved soil with non-sterile soil caused CO removal activity to increase gradually with time, returning to normal after 36 days.

TABLE V-6. - RATE OF CO REMOVAL OVER 100 GRAMS OF POTTING SOIL AT DIFFERENT TEMPERATURES

Temperature (°C)	CO Uptake Rate[a] (mg/hr per square meter of soil)	Test Period Duration (hr)
10	0.30	24
15	0.38	6
20	1.25	5
25	2.38	3
30	3.46	2
35	2.44	2.3
40	1.89	4
45	1.17	4.5
50	0.20	19

[a] Average rate at end of test period

SOURCE: Inman, Ingersoll and Levy (1971)

TABLE V-7. - RATE OF REMOVAL OF CO FROM TEST ATMOSPHERE AT 25°C BY VARIOUS

Location of Soil[a]	Vegetation	pH	Sand: Silt:Clay (%)	Organic Matter (%)	CO Uptake[b] (mg/hr per square meter of soil)
Eureka-Arcata	Coast redwoods	5.7	53:34:13	25.1	16.99
H. Cowell State Park	Oak	5.3	73:12:15	11.2	15.92
H. Cowell State Park	Coast redwoods	5.7	57:26:17	13.6	14.39
Lake Arrowhead [c]	Ponderosa pine	6.2	65:24:11	17.4	13.89
Redding	Grass-legume pasture	5.1	53:32:15	21.0	11.94
Riverside[c]	Grapefruit[d]	6.6	75:14:11	4.3	11.48
Yosemite Valley	Grass meadow	5.05	49:42:9	20.6	10.52
Kauai, Hawaii	Forest	4.74	58:18:24	22.8	9.90
San Bernardino Freeway[c]	None	7.2	55:30:15	2.2	6.89
Mojave Desert	Chaparral	7.9	79:6:15	2.4	6.46
Woodland	Oak Stubble[d]	6.6	33:32:35	2.1	6.23
Riverside (desert)[c]	Chaparral	7.35	85:4:11	1.0	4.31
Yosemite wall	White fir	5.1	65:18:17	5.7	3.48
Corcoran	Cotton (fallow)[d]	7.1	57:22:21	2.8	3.48
Hanford	Almond[d]	6.95	53:26:21	3.5	2.82
Boynton Beach, Florida	Weeds (fallow)[d]	6.0	86:0:14	1.4	2.65
Oahu, Hawaii		4.93	40:26:34	15.3	2.16

[a] All soils were collected in California unless otherwise noted.

[b] Average rate at the end of the test period; two to three determinations.

[c] Locations where high levels of air pollution occur as a result of the combustion of fossil fuels and photochemical smog.

[d] Land under cultivation or with recent history of cultivation.

SOURCE: Inman, Ingersoll and Levy (1971)

Addition of antibiotics or saline solution prevented carbon monoxide uptake. In one series of tests, soil was cultured in an N_2 atmosphere and then tested with CO in N_2. No CO removal was observed under these conditions. It is concluded on the basis of this evidence that aerobic micro-organisms alone are responsible for CO removal and that organisms commonly present in soil do not produce CO.

Inman, Ingersoll, and Levy report no observations of a dependence of removal capacity on CO concentration, and their experiments were apparently not designed to determine whether these high rates of removal of CO could continue at concentrations characteristic of urban or rural atmospheres (that is, 0.1 to 3 ppm). They point out that if the removal capacities listed in Table V-7 are representative of the average capacity of soils in temperate regions, the removal rate is equivalent to 191.1 metric tons per year per square mile, or 569×10^6 metric tons per year for the whole United States. This estimate ignores the temperature dependency effects they report, since it is the average of removal rates observed at 25°C, and year-round mean temperatures for the United States are about 9°C. The nonlinear temperature response suggests that such estimates of the possible magnitude of the CO sink should be viewed as approximate upper bounds.

These findings are not consistent with the observations of Seiler and Junge (1970) reported above, who observed both CO evolution and CO removal by soil. The concentration of carbon monoxide in a 20-liter glass vessel covering an area of soil surface varied diurnally with temperature, exhibiting a peak of about 0.5 ppm at noon to a minimum of 0.02 ppm.

More studies of the interaction of soil microflora and vegetation with the atmosphere will obviously be required before the existence and magnitude of a biotic sink can be determined.

H. CONCLUSIONS

It is clear from the foregoing sections that the carbon monoxide cycle of the atmosphere is not understood, and that radical revisions of hypotheses regarding it have occurred as space-time distribution data have become available in the recent past. At present, these data are too scanty to provide answers to the crucial questions regarding the atmospheric lifetime of CO and the existence of large tropospheric sinks and natural sources. More information is necessary, principally the following:

(1) Better estimates of the tropospheric and stratospheric concentrations of CO, particularly those in the southern hemisphere. If the lifetime of CO is short, than there must be large natural sources, and the possible temporal and regional variations in the total air column may be larger than those which can be estimated from the presently available data. These would appear to be on the order of ± 25% at most, and part of these differences may be due to movement of air parcels.

(2) Reliable information regarding the vertical abundance profile in diverse locations. In particular, variations in the region of the tropopause might provide a basis for a better estimate of CO flux into the stratosphere than is now possible.

(3) Measurements of the distribution of radioactive CO. Such measurements would aid in identifying the mean residence time of CO and in resolving the question of the existence of tropospheric sinks.

(4) Field studies. Monitoring CO concentration in the field will help to determine whether terrestrial plants and/or soils constitute significant sources and sinks of atmospheric CO. Since tropospheric reactions with OH radicals may constitute a sink, every effort should also be made to monitor other constituents which might throw light on the interaction of diverse gases of biological origin.

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VI. NITROGEN COMPOUNDS

A. SUMMARY

Nitrogen is an essential biological element present in all living matter, as a constituent of protein, urea, porphyrins, and numerous important organic molecules. The nitrogen cycle in nature is extremely complex, however, and is known only qualitatively. The major reservoir for nitrogen is the atmosphere, where it is present as molecular nitrogen and in numerous trace constituents that are all directly or indirectly of natural biological or human industrial origin.

In addition to N_2, the atmosphere contains nitrogen as nitrous oxide, ammonia, nitric oxide, and nitrogen dioxide. It also contains ammonia and nitrate in solution in aerosols and cloud droplets. The tropospheric abundances and annual rates at which these compounds are exchanged with the surface are not known, and available estimates differ by an order of magnitude.

Atmospheric processes are extremely important in the circulation of nutrient nitrogen. The delivery of nitrogen as ammonia and nitrate in rain has long been recognized as an important source of fixed nitrogen. Recent evidence suggests that the direct absorption of gaseous ammonia and nitrous oxide and the dry deposition of ammoniated sulfate particles may constitute a quantitatively more significant exchange mechanism than the washout of nitrogen compounds in rain.

There is evidence that nitric oxide (NO) is released from many soils and that it is of biological origin, in the sense that it is a product of the decomposition of biogenic nitrite. The rapid oxidation of this NO by ozone produces NO_2. The presence of these two compounds in nature results in the production of natural photochemical smog. These compounds are also released as a byproduct of fossil fuel combustion. Presently available information about the abundance, distribution, and tropospheric lifetime of natural NO and NO_2 is insufficient to determine whether the anthropogenic contribution to the tropospheric load is major or minor. At high concentrations, NO_2 is directly absorbed by vegetation and soils.

Ammonium is an important atmospheric cation which is involved in particle-forming gas reactions in the atmosphere. Ammonia is known to be released from some soils, and although terrestrial emission rates are not known, it is clear that the quantity annually released is large. There is some evidence that the ocean is also a source of atmospheric ammonia, but the mechanisms of production are very obscure. As there is no information regarding the abundance profile of ammonia in the troposphere, the tropospheric load cannot be estimated with accuracy.

Nitrous oxide varies considerably in local abundance with location, altitude, and season. It is slowly removed by photolysis in the stratosphere and upper atmosphere. Taken together, these two facts imply a tropospheric sink for N_2O which may involve direct uptake by soil and/or vegetation.

B. NITROGEN RESERVOIRS

Nitrogen is found in large quantities in the crust of the earth in primary or igneous rock, in the atmosphere, and, in lesser quantities, as N_2 in the ocean and in sediments in association with fossil reduced carbon. The major reservoirs are shown in Table VI-1.

Land reservoirs of nitrogen include soil, where it is present in small quantities as NH_4^+ and in larger quantities as organic nitrogen in the humus fraction. Bowen (1966) gives a range of 200 to 2500 ppm as the nitrogen content of dry soil; we have used his mean of 1000 for this estimate. Plant biomass nitrogen content was taken from Deevey (1970), who based his estimate on surveys of the production and mineral cycling in various terrestrial communities. The animal biomass figures reflect the relatively small quantities of animal biomass estimated by Bowen (1966) and the relatively high proportion of nitrogen found in animal tissue.

Primary rock in the lithosphere contains large quantities of nitrogen, but the figure here includes much crustal material which may never

TABLE VI-1. - NITROGEN RESERVOIRS

	Quantity (million tons N)	See Note
Land		
Soil (Organic and Inorganic)	45,000	(a)
Plant Biomass	12,000-15,000	(b)
Animal Biomass	200-400	(c)
Lakes and Streams (as NO_3^-)	7	(d)
Ground Water (as NO_3^-)	66	(d)
Marine		
Dissolved N_2	21,000,000	(e)
NO_3^-	570,000	(e)
NH_4^+ and NO_2^-	10,000	(e)
Ocean Biomass	120	(f)
Dead Organic Matter	246,000-900,000	(g)
Lithosphere		
Igneous Rock	430,000,000	(h)
Fossil N	355,000,000-550,000,000	(i)
Nitrate Deposits	100	(i)
Atmosphere		
N_2	3,668,000,000	(i)
N_2O	1,150	(j)
NH_3	10-30	(k)
NH_4^+ in Aerosols	2.5-10	(l)
NO_2	0.35-1	(m)
NO	0.35-1	(n)

NOTE:

(a) Assumes a mean soil composition of 1000 ppm (Bowen 1966) and an average worldwide soil depth of 30 cm.
(b) From Deevey (1970) and Delwiche (1970)
(c) Based on data of Bowen (1966) and Delwiche (1970)
(d) Assumes ground- and lake-water composition identical to that of average river runoff given by Livingstone (1963)
(e) Turekian (1969)
(f) Assumes an ocean standing crop of 700 million tons C (SCEP 1970) and a C:N ratio of 1:0.17 by weight (Redfield et al., 1963).
(g) The lower estimate based on C:N ratio of 3.5:1 for nonliving particulate and dissolved organic matter (Riley, Wangersky and van Hemert, 1964). Higher estimate from Delwiche (1970).
(h) From Bowen (1966)

TABLE VI-1. - Continued

NOTE:

(i) Hutchinson (1954)

(j) N_2O mean abundance of 0.26 ppm in troposphere only.

(k) NH_3 mean abundance of 5 to 15 ppb in troposphere only.

(l) Particulate NH_4^+ concentration of 1 to 4 micrograms/m^3 in troposphere only.

(m) NO_2 mean abundance of 0.17 to 0.5 ppb in troposphere only.

(n) NO mean abundance of 0.17 to 0.5 ppb in troposphere only.

erode and consequently is actually out of circulation. A similar amount of nitrogen occurs in the sediments as reduced nitrogen found in association with fossil carbon. Nitrate accumulates in superficial deposits wherever conditions prevent either its biological transformation into a gaseous form or its transfer to the ocean via continental runoff. Nitrates are found in the North Chilean desert and the Ross ice shelf. (Mueller, 1968; Claridge and Campbell, 1968).

Nitrogen comprises approximately 78% of the terrestrial atmosphere, and this is by far the largest mobile terrestrial reservoir. The atmosphere also contains trace quantities of other nitrogen compounds, virtually all of which are of biological origin.

The next two sections discuss the biological mechanisms which cycle nitrogenous compounds through the atmosphere and the evidence regarding the abundance of these compounds in the atmosphere. This is followed by a summary of information relating to the annual budget of nitrogen compounds in the atmosphere.

C. BIOLOGICAL TRANSFORMATION OF NITROGEN

1. Introduction

Next to oxygen, carbon, and hydrogen, nitrogen is the most abundant constituent of plant and animal tissue, where it is found primarily in protein. Most of the nitrogen utilized in the natural biospheric cycle is biologically fixed from the molecular nitrogen of the atmosphere, although very small quantities of juvenile nitrogen are released from volcanoes and negligible amounts are fixed by electrical processes in the atmosphere. Significant quantities of atmospheric nitrogen are industrially fixed in the production of nitrogen fertilizers and in the combustion of fossil fuels.

The fixation of nitrogen requires a large amount of energy for the splitting of the N_2 molecule--160 kcal/mole--and all subsequent chemical transformations of nitrogen yield energy to the organisms involved. This investment of energy accounts for the fact that in most natural environments fixed nitrogen is rapidly taken up by organisms, and a lack of fixed nitrogen often limits biological productivity. The major biological transformations of nitrogen are shown in Table VI-2.

Once nitrogen is fixed, a variety of biological mechanisms mediate its subsequent chemical transformations in the biosphere. These are illustrated in Figure VI-1.

These transformations include ammonification, whereby nitrogen incorporated in plant and animal tissue and in animal waste products is converted to ammonium ion, which may be held on soil colloidal particles or released as ammonia gas. Nitrification is the process whereby ammonia is converted to nitrate, generally by means of a two-step process which produces nitrite which is subsequently oxidized to nitrate.

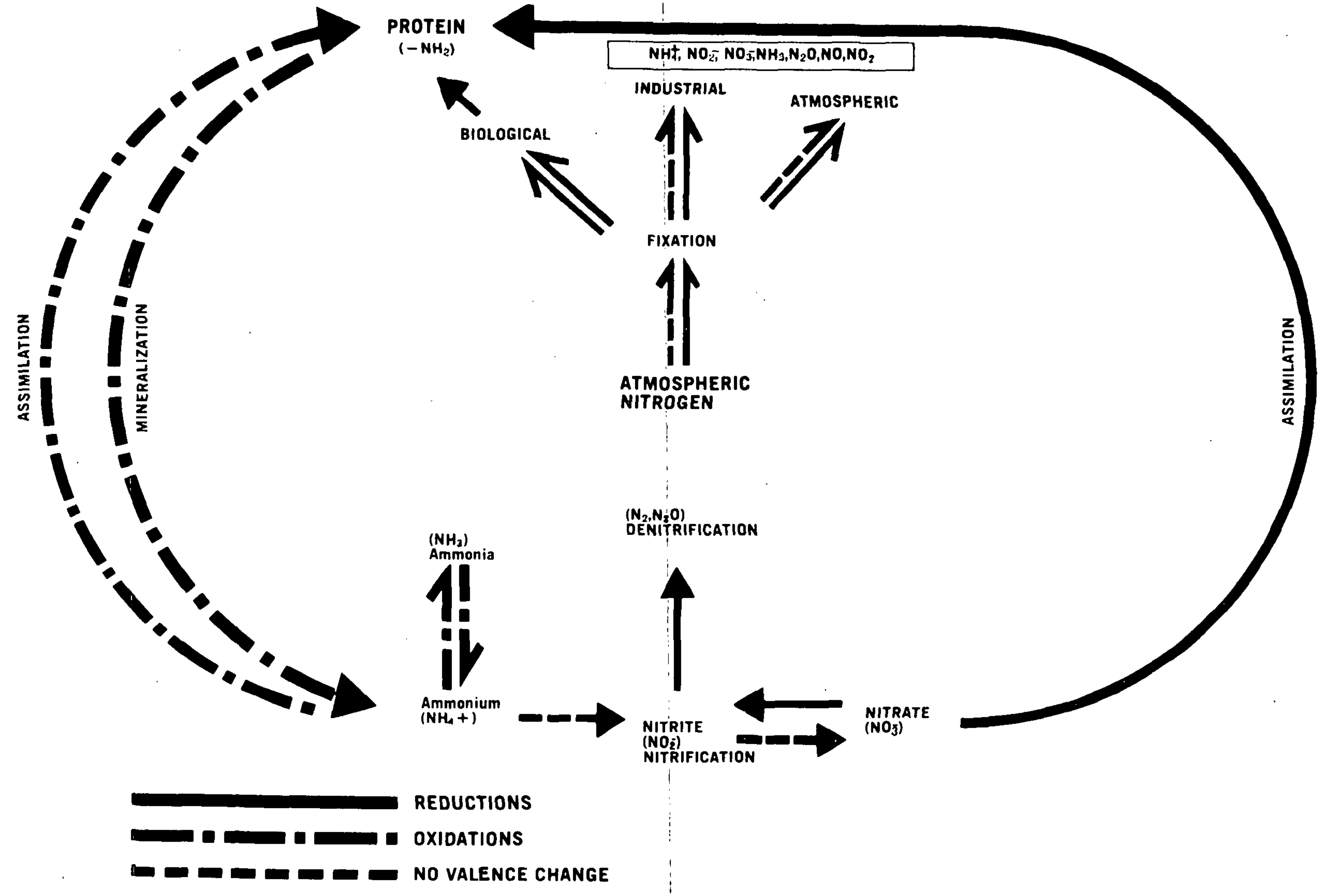
Plants take up nitrogen both as ammonia and nitrate, thereby recycling soil nitrogen through the plant and animal cycle. Nitrogen is returned to the N_2 atmospheric store by denitrifiers, which convert nitrate to N_2 in the absence of oxygen. In addition, denitrifiers produce nitrous oxide. Small quantities of nitric oxide are released from soil and possibly some nitrogen dioxide as well. Although certain organisms responsible for these transformations have been extensively studied, the organisms are so numerous and their habitats and mechanisms are so varied that the details of most nitrogen cycles are still unknown. In particular, the processes which return nitrogen to the atmosphere are poorly understood. The main routes of these biological transformations are discussed in the subsequent sections.

2. Nitrogen Fixation

The conversion of atmospheric molecular nitrogen to atomic nitrogen requires 160 kcal per mole of nitrogen, and all organisms which effect this conversion utilize energy derived directly or indirectly from photosynthesis. The quantitatively most important nitrogen fixers appear to be those which live in symbiotic association in root nodules of plants from which they derive their energy. These include bacteria living in leguminous plants, which are widely cultivated and also occur

TABLE VI-2. - REPRESENTATIVE BIOLOGICAL TRANSFORMATIONS OF NITROGEN

Reaction	Energy Yield	
	Kcal	Kcal/Mole N
Nitrogen Fixation		
$N_2 \rightarrow 2N$	- 160	- 80
$2N \rightarrow 2NH_3$	12.8	6.4
Ammonification		
$CH_2NH_2COOH + 1\ 1/2\ O_2 \rightarrow 2\ CO_2 + H_2O + NH_3$	176	176
Nitrification		
$NH_3 + 1\ 1/2\ O_2 \rightarrow HNO_2 + H_2O$	66	66
$KNO_2 + 1/2\ O_2 \rightarrow KNO_3$	17.5	17.5
Denitrification		
$C_6H_{12}O_6 + 6\ KNO_3 \rightarrow 6\ CO_2 + 3H_2O + 6\ KOH + 3\ N_2O$	545	91
$5C_6H_{12}O_6 + 24\ KNO_3 \rightarrow 30\ CO_2 + 18\ H_2O + 24\ KOH + 12\ N_2$	570 (per mole of $C_6H_{12}O_6$)	109
$5S + 6\ KNO_3 + 2\ CaCO_3 \rightarrow 3\ K_2SO_4 + 2\ CaSO_4 + 2\ CO_2 + 3\ N_2$	132 (per mole S)	110



Source: GEP (1971)

FIGURE VI–1 THE NITROGEN CYCLE

naturally, particularly in the tropics. Non-leguminous plants containing symbiotic nitrogen fixers include woody angiosperms such as alders, buckthorn, and the ginko. That such symbiotic associations can be extremely effective in fixing nitrogen may be inferred from Table VI-3, which contrasts nitrogen fixation rates of some species. No estimates of global rates of fixation of nitrogen by non-cultivated nodulated plants are available, but Delwiche (1970) estimates that cultivated legumes--which include clover, alfalfa, soybeans, and peanuts--annually fix 14 million tons of N_2 per year.

Blue-green algae are probably next in importance in fixing nitrogen. Although not all species of blue-green algae fix nitrogen, those which do are numerous and widely distributed, and some live in association with higher plants or with fungi, which they presumably supply with fixed nitrogen (Alexander, 1971).* Independence of sources of fixed nitrogen gives some blue-green algae a competitive advantage in environments in which nitrogen is limiting but other nutrients are available. This fact accounts in part for the explosive growth of some blue-green algae in waters polluted with phosphorus-rich wastes. Blue-green algae are important in flooded paddy fields and are believed to supply nitrogen for rice growth. Numerous species of marine blue-green algae exist and have been reported to fix nitrogen.

Some free-living heterotophic bacteria can also fix nitrogen in soils, using respiratory energy. These include Azotobacter, which inhabits alkaline soils and is aerobic, as well as Clostridium, which is anaerobic and inhabits acid soils. Such free-living heterotrophs have been found in association with roots of higher plants (Postgate, 1970). Nitrogen fixation by free-living bacteria in the aphotic anoxic zone of fresh-water lakes has been reported (Brezonik and Harper, 1969).

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*Nostoc, a nitrogen-fixing genera of blue-green algae, is a common sybiont of lichens, and both Nostoc and Anabaena species have been observed to inhabit cavities in the fern Azolla and the liverwort Blasia, which have been demonstrated to fix nitrogen (Alexander, 1971).

TABLE VI-3. - QUANTITIES OF NITROGEN FIXED BY FREE-LIVING MICROORGANISMS AND SYMBIOTIC ASSOCIATIONS

Group	Species or Habitat	N_2 Fixed (lb/acre/yr)
Nodulated legumes	Alfalfa: *Medicago sativa*	113-297
	Red clover: *Trifolium pratense*	75-171
	Soybean: *Glycine max*	57-105
	Black locust trees: *Robinia pseudoacacia*	600
Nodulated nonlegumes	*Alnus glutinosa*	200
	Casuarina equisetifolia	52
	Hippophae rhamnoides	62
	Myrica gale	8
Blue-green algae	Arid soil in Australia	3
	Paddy field in India	30
	Aulosira in paddy field	48
	Cylindrospermum in paddy field	80
Free-living heterotrophs	Soil under wheat	14
	Soil under grass	22
	Soil and litter under pine	32
	Rain forest in Nigeria	65

SOURCE: Alexander (1971)

3. Ammonia Production and Oxidation

The nitrogen incorporated in the tissues of the original nitrogen fixers or their hosts is converted to mineral form by soil bacteria and fungi which process dead plant material, humus, and organic wastes by breaking them down into simple inorganic compounds. In the case of nitrogen, the end product of this process is the ammonium ion. This process is fairly rapid for all substrates except humus, which is only very slowly mineralized, and constitutes the main nitrogen reservoir in most soils.

The NH_4^+ produced may be bound by clay particles in the soil, in which case it is relatively unavailable for plant uptake or microbial oxidation. NH_4^+ not so bound does not survive long in most soils. Some of it is assimilated by the populations of mineralizing microbes, and ammonia is readily taken up by plant roots and incorporated in new plant material. If oxygen is available, the NH_4^+ will be converted into nitrate by means of a two-step process performed sequentially by two distinct forms of organisms; the ammonium is first converted to nitrite by the chemoautotroph Nitrosomonas and physiologically related bacteria that are common in soils, ocean bottoms, marine muds, and freshwater habitates. The nitrite is then oxidized to nitrate by Nitrobacter and related species.

Although the ammonia-oxidizing nitrifiers are commonly thought to produce nitrite as the primary product of nitrification, Yoshida and Alexander (1970) found that Nitrosomonas europea oxidizes ammonia to nitrous oxide, a reaction which may be of global biogeochemical significance.

Nitrite is the sole energy source for Nitrobacter and related forms, which produce nitrate from nitrite made available by ammonia oxidizers. These forms are almost as ubiquitous as Nitrosomonas and are believed to constitute the dominant populations responsible for nitrification. Nitrobacter is somewhat sensitive and can be inhibited by small quantities of ammonium in a manner which shifts with pH, the effect being more pronounced with increasing pH (Alexander, 1971).

Ecological relationships between nitrifying microorganisms and the plants in soils they inhabit are complex. Some tropical grasses secrete a material from their roots which is toxic both to ammonia oxidizers and to nitrite oxidizers (Munro, 1966a, 1966b; Meiklejohn, 1968). The number of nitrifiers in the soil in association with the roots of these plants is low and increases as the pasture is improved by the substitution of more nutritious plants (Meiklejohn, 1968). Likens, Bormann, and Johnson (1969) found that the nitrate content of a stream draining a forested watershed increased greatly from 0.9 ppm to 53 ppm after clear cutting of the watershed; this was attributed to an increase in microbial nitrification. Larger populations of nitrifiers were found to inhabit soils of the cutover watershed than those of control watersheds (Smith, Bormann, and Likens, 1968). Likens, Bormann, and Johnson (1969) hypothesize that prior to clearing, the vegetation had inhibited populations of nitrifiers.

Nitrate is not strongly held by soils, and loss of nitrate from fertilized fields contributes to the pollution of surface and ground waters (Feth, 1966).

4. Denitrification

Textbooks typically attribute the return of nitrogen to the atmosphere to nitrate reducers, which utilize nitrate as an electron acceptor in the oxidation of organic matter in environments characterized by low O_2. The primary product of this reaction is N_2, but some N_2O may also be evolved. The latter evolution is attributed to the fact that N_2O is a precursor of N_2, and some may be lost in the conversion process. (This conclusion is supported by the fact that N_2O is utilized as an electron acceptor in the absence of NO_3 by the same organisms.) Soil nitrate reduction by this process is dependent upon the water level and organic matter content in soils (Meek, Grass, and MacKenzie, 1969) and on the O_2 level in marine and freshwater environments.

This relatively simple view of denitrification is complicated by the fact that nitrite--which is produced by ammonia oxidizers--is also an interim product of nitrate reduction and is capable of undergoing numerous chemical reactions with other soil constituents, some of which may result in the evolution of gaseous forms of nitrogen. Thus, Allison (1963) and others have pointed out that nitrite may react with ammonia to produce ammonium nitrite, which is unstable and may decompose to produce ammonium, N_2, and water. In acid environments nitrite itself may decompose to produce NO, nitrate, and water, or N_2 and N_2O (Allison, 1963; Bulla, Gilmour, and Bollen, 1970).

Experimental evidence of the production of N_2, N_2O and NO from nitrate at a wide range of pH values has been reported. Steen and Stojanovic (1971) report that NO was volatilized from an aerobically incubated soil to which ammonium sulfate or urea was added. They attributed this reaction to the biological formation of nitrite from some of the added ammonia (or that biologically produced from urea), which then reacted with the ammonia remaining in the soil and with other soil components (organic matter and iron) to form NO. The reaction was dependent on large concentrations of both reactants and consequently is believed to be unimportant in nature, in spite of the fact that it proceeds at soil pH values in the range 6.5 to 8.0, which are common.

In a series of experiments, Bulla, Gilmour, and Bollen (1970) demonstrated the evolution of large amounts of NO and somewhat lesser amounts of N_2 from sterile soils containing varying proportions of clay and organic matter at a wide range of pH values. N_2O was also evolved from some of the soils tested. Soil organic matter content and clay content appeared to influence the stability of nitrite in these experiments.

As the preceding discussions have indicated, nitrite is unstable under many soil conditions and may give rise to gaseous NO or NO_2. It is therefore important to understand the conditions which lead to the accumulation of nitrite and which may be responsible for the evolution of natural oxides of nitrogen. Bollag, Orcutt, and Bollag (1970) report a series of experiments in which denitrifiers isolated from soil were studied under a variety of experimental conditions. They stress that the effects of variations in soil nitrate and nitrite, temperature, and pH on individual cultures of four soil isolates or combinations of them are so complex as to preclude generalizations regarding nitrification behavior in soil for applied uses. Among the interesting observations reported is the fact that the nitrite reducing systems of the organisms studied appeared to be more stnsitive to environmental variables than the nitrate reducing systems, in that accumulations of nitrite occurred under some unfavorable conditions. In general, the higher the level of nitrate present initially, the larger the amount of nitrite present after three days of anaerobic growth.

Gaseous nitrogen compounds may also be produced by microorganisms that do not reduce nitrate. Yoshida and Alexander (1970) report the production of N_2O by the ammonia-oxidizing nitrifier Nitrosomonas europaea. These authors also report the discovery that numerous organisms not previously known to reduce nitrite or nitrate can do so, and that they produce N_2O rather than N_2. These organisms include Bacillus subtilis, Escherichia coli, Aerobacter aerogenes (which reduce both nitrate and nitrite), and Aspergillus flavus and Penicillium atrovenetum (which reduce only nitrite).

In summary, molecular nitrogen and nitrous oxide are biologically produced from the anaerobic reduction of nitrite or nitrate by numerous species of organisms; nitrous oxide is aerobically produced by nitrifiers which oxidize ammonia; and both these gases plus NO may be produced from biologically generated nitrite under a variety of conditions of soil pH and clay and organic matter content. The global significance of the latter reactions has not been determined.

5. Biological Cycle of Nitrogen in Marine and Freshwater Environments

The biological transformations of nitrogen in freshwater environments are analogous in many respects to those occurring on land, but there are important differences. As on land, the location and nature of the process depends on the presence or absence of oxygen and light as well as on the occurrence of the requisite substrate. Nutrient nitrate may be supplied by runoff from land sources, or it may be fixed by algae and free-living bacteria from molecular nitrogen dissolved in the water. Ammonia is produced from decomposing organic matter in virtually all zones where it is present and is rapidly attacked by nitrifying bacteria in oxygenated regions to product nitrite and nitrate. Ammonia may be directly assimilated by aquatic plants. In anoxic regions, nitrate reduction gives rise to nitrite and ultimately N_2, and sulfate reduction may be accompanied by the release of ammonia.

In marine environments the situation is complex and not well understood. Large quantities of molecular nitrogen are present in the ocean, but very little seems to be fixed by marine nitrogen fixers, although marine species of blue-green algae and of free-living bacteria capable of fixing molecular nitrogen exist (Vaccaro, 1965; Ryther and Dunstan, 1971). Dissolved organic matter is rich in organic nitrogen, but it is refractory to biological degradation, and organic N does not appear to be an important source of nutrient nitrogen (Thomas, Renger, and Dodson, 1971).

As on land, ammonia in the marine environment is produced by the bacterial decomposition of plant and animal tissue and animal wastes. This ammonia may be reassimilated by phytoplankton, or it may be oxidized by nitrifiers to nitrite and nitrate (nitrification). Nitrate reduction in anoxic regions leads to the production of nitrite and N_2.

The major elements of the biological nitrogen cycle in the ocean are nitrate, ammonia, and nitrite, all of which show wide fluctuations in local abundance due to variations in biological activity and in the factors that determine vertical mixing. Nitrate concentrations decrease as a result of phytoplankton growth and are replenished by in situ decomposition of organic matter and upwelling of nutrient-rich bottom water. Nitrate nitrogen concentrations may vary from less than 1 µg-atoms NO_3^--N/liter in regions of low productivity or during seasonal minima to 200 to 300 µg-atoms NO_3^--N/liter or more (Vaccaro, 1965; Thomas et al., 1971). Ammonia is often present at less than 3 µg-atoms NH_4^+-N/liter, but concentrations up to 28 µg-atoms NH_4^+-N/liter have been observed in association with large increases in the local zooplankton populations (Vaccaro, 1965). Nitrite is produced in oxygen-rich water by the bacterial oxidation of ammonia, and in anoxic waters by the anaerobic reduction of nitrate. Near the surface it is generally present in quantities that are low relative to ammonia. The end product of denitrification in the sea appears to be N_2 rather than N_2O. Barbaree and Payne (1967) studied the marine denitfier Psuedomonas perfectomarinus and found that it produced N_2 but no N_2O during nitrite reduction, although this organism could metabolize N_2O in the absence of nitrate. Craig and Gordon (1963) report that in very deep ocean water (2.5 km or more), N_2O is in equilibrium with an atmospheric composition of about 0.12 ppm, whereas shallower water is essentially in equilibrium with atmospheric levels of N_2O found at the surface (0.3 ± 0.1 ppm). These results tend to confirm the hypothesis that there is little biogenic nitrous oxide production in the ocean; but Schutz, Junge, Beck, and Albrecht (1970) mention that simultaneous measurements of N_2O in surface water and in the air above it indicated a marine source of atmospheric N_2O (see Section D.1 below).

Richards and Benson (1961) concluded that N_2 is produced in nitrate reduction in the anaerobic waters of the Cariaco Trench in the Caribbean and in the Dransfjord in Norway, and that ammonia is a byproduct of sulfate reduction. They found the ammonia content much greater in the anoxic zones characterized by high concentrations of sulfides than in the oxygenated waters near the surface, but the ammonia concentrations were nowhere very high. Thus, in the Caribbean, surface water contained 3 μg-atoms NH_4^+-N per liter while the maximum concentration in the sulfate-reducing zone was 11.3 μg-atoms NH_4^+-N/liter. The figures for Dramsfjord are 0.2 and 8.8 μg-atoms NH_4^+-N/liter. Upwelling of oxygen-poor waters to the surface provides ammonia, which may be biologically or abiologically oxidized to nitrate and nitrite.

Nitrate in surface waters may be photolytically converted to nitrite (Hamilton, 1964), but the significance of this reaction for the nutrient cycle in the sea remains to be determined. It has been reported that ammonia may also be photooxidized, but Hamilton found no evidence of this reaction.

D. NITROGEN COMPOUNDS IN THE ATMOSPHERE

The atmosphere contains, in addition to N_2, nitrous oxide (N_2O), ammonia (NH_3), nitrogen dioxide (NO_2) and nitric oxide (NO) as gases. In addition, aerosols may contain ammonium sulfate, ammonium nitrate, and nitric acid as well as trace amounts of nitrogen in amino acids.

1. Nitrous Oxide

a. Atmospheric Reactions of Nitrous Oxide

Nitrous oxide is not produced anthropogenically; all nitrous oxide in the troposphere has a natural biological source. The gas is believed to be chemically quite stable in the troposphere.

Three photochemical loss reactions have been studied by Bates and Hays (1967):

$$N_2O + \underline{hv} \rightarrow N_2 + O(^1D)\lambda < 3370\ \mathring{A} \quad (1)$$

$$\rightarrow N_2 + O(^1S)\lambda < 2100\ \mathring{A} \quad (2)$$

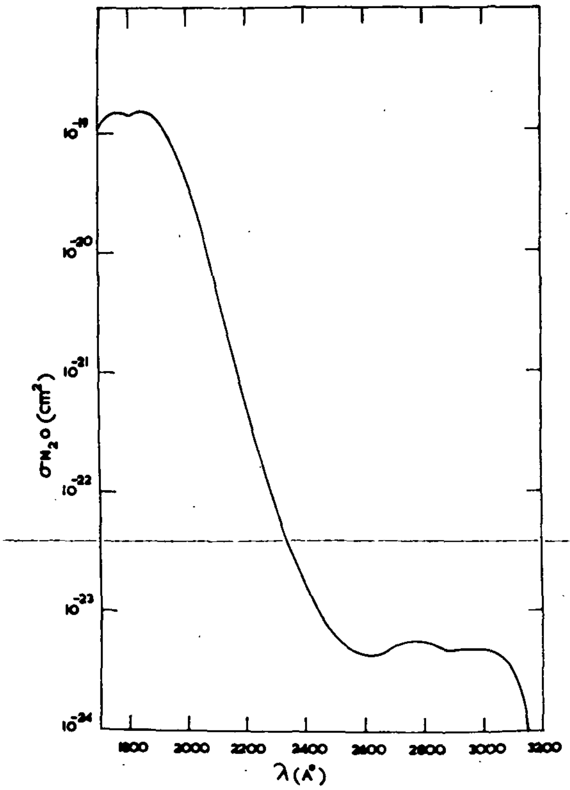
$$\rightarrow NO + N\lambda \quad < 2500\ \mathring{A} \quad (3)$$

Using the photodissociation cross-section of N_2O shown in Figure VI-2, Bates and Hays calculated the rate of photodissociation of nitrous oxide as a function of altitude and of incoming radiation. The results of these calculations are shown in Figure VI-3. The calculated temporal and latitudinal rate average for the whole earth corresponds to a loss of 2 to 3×10^9 molecules of N_2O cm^{-2} sec^{-1}, or 24 to 35 million tons N_2O per year; this corresponds to 15 to 23 million tons as nitrogen.

N_2O can also be destroyed by reaction with $O(^1D)$ produced by photolysis of ozone, producing NO (McElroy and McConnel, 1971):

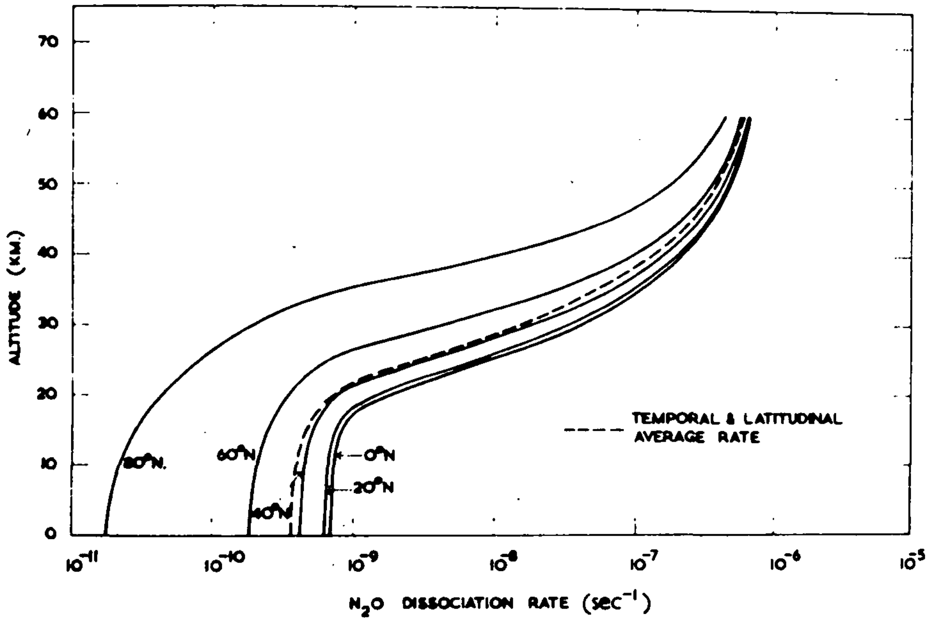
$$O(^1D) + N_2) \rightarrow NO + NO$$

$$\rightarrow N_2 + O_2 \quad (4)$$



Source: Bates and Hays (1967)

FIGURE VI-2 PHOTODISSOCIATION CROSS SECTION OF NITROUS OXIDE



The full curves refer to the latitudes indicated; the dashed curve is the mean.

Source: Bates and Hays (1967)

FIGURE VI-3 DISSOCIATION RATE OF NITROUS OXIDE IN THE ATMOSPHERE

This reaction has been studied by McElroy and McConnel (1971), who conclude that while it constitutes the main source of stratospheric NO (on the grounds that reaction (3) is not as effective as Bates and Hays believed), it constitutes a negligible stratospheric sink for N_2O in comparison with the photodissociation reactions (1) through (3).

N_2O may be produced in the stratosphere by reaction of ozone with molecular nitrogen:

$$N_2 + O_3 \rightarrow N_2O + O_2 \tag{5}$$

This reaction was explored by Goody and Walshaw (1953), who conducted some inconclusive experiments, one of which suggested that reaction (5) might be able to produce about 2×10^9 molecules cm^{-2} sec^{-1}. Goody and Walshaw discounted this as a significant source of N_2O, because they had calculated the atmospheric sink to be approximately 8×10^{10} molecules cm^{-2} sec^{-1}, using a photodissociation rate corresponding to the equatorial noon sun.

The abundance profile of N_2O that may be expected to result from the photodissociation reactions studied by Bates and Hays depends upon the efficiency with which tropospheric air is transported to the stratospheric regions where photodissociation takes place. Assuming a constant mixing ratio of 0.25 ppm in the troposphere and a tropospheric vertical exchange coefficient of 10^5 cm^2 sec^{-1}, Bates and Hays calculated the abundance profiles corresponding to a variety of assumed stratospheric vertical exchange coefficients, which are shown in Figure VI-4. These calculations did not take into consideration the possibility of stratospheric production of N_2O by means of reaction (5) with ozone.

b. Atmospheric Abundance of Nitrous Oxide

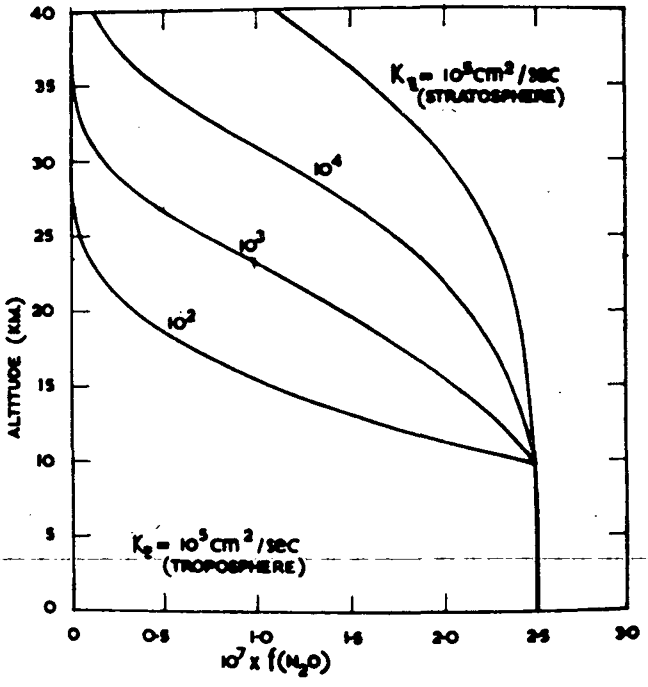
Nitrous oxide is the most abundant of the nitrogen trace gases. It is presently believed to average about 0.26 ppm in the troposphere, although reported measurements vary from 1.25 to 0.12 ppm (Bates and Hays, 1967; Schutz, Junge, Beck, and Albrecht, 1970; Junge, 1963). Some of these are tabulated in Table VI-4. This range of values is

TABLE VI-4. - REPORTED MEASUREMENTS OF N_2O ABUNDANCE

Reference	Method	Abundance (ppm)	Comments
Goody (1954)	Solar Spectrum	0.27 ± 0.8	3 - 10 km
Seeley and Houghton (1961)	Solar Spectrum	0.12	From aircraft (300 mb or less)
Rank, Slomba, Gardner, and Wiggins (1962)	Solar Spectrum	0.25 ± 0.4	
Birkeland and Shaw (1959)	706 m Absorption Path	0.27 ± 0.5	
Slobod and Krogh (1950)	Mass Spectrometer	0.5 ± 0.1	Ground level
Craig and Gordon (1963)	Gas Chromatograph	0.3 ± 0.1	Ocean air
Goody (1969)	Solar Spectrum	0.25 - 0.30	From 205 m observatory
Goldman, Murcray, Murcray, Williams, Kyle and Brooks (1970)	Solar Spectrum	0.14 ± 0.4	4.5 to 13.5 km

SOURCE: Data taken from Bates and Hays (1967), Goody (1969), and Goldman et al. (1970)

quite large, and although some disagreement is to be expected due to differences in measurement techniques, the discrepancies seem unusually high. These discrepancies are important because, in general, evidence of large variations in abundance implies a short atmospheric lifetime.

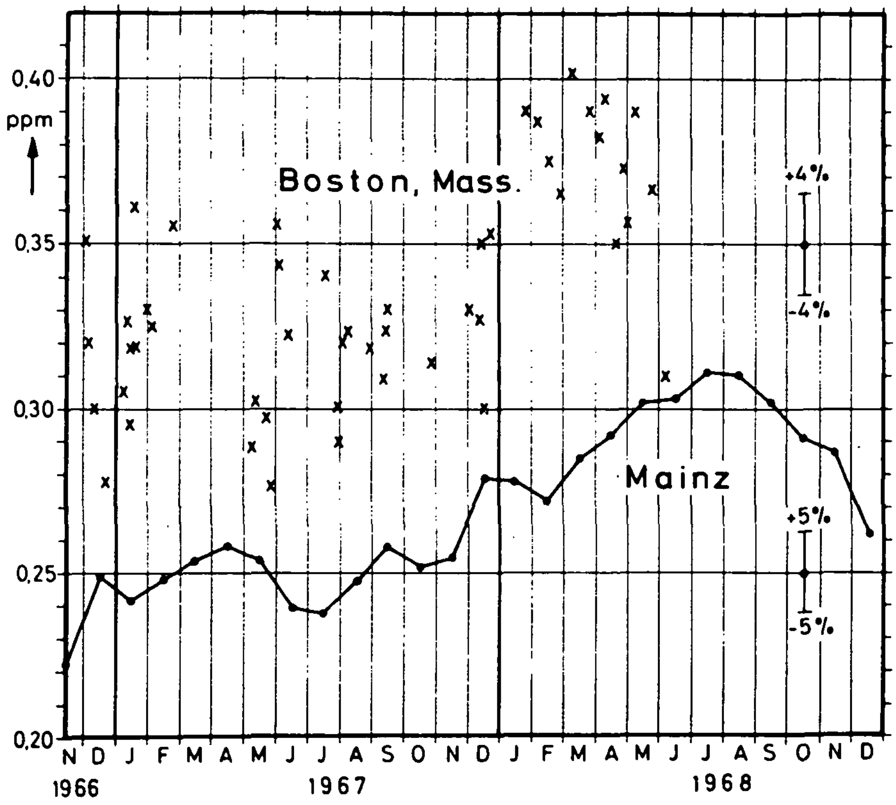


Source: Bates and Hays (1967)

FIGURE VI-4 FRACTIONAL VOLUME ABUNDANCE OF ATMOSPHERIC NITROUS OXIDE f(N_2O), FOR SELECTED VALUES OF THE VERTICAL EXCHANGE COEFFICIENT K_Z

Reports of measurements published since 1969 show the same discrepancies as those characterizing earlier reports. Goody (1969) reported a series of weekly N_2O measurements taken from the ground with a cross correlating spectrometer near Boston for a period of nearly two years (Figure VI-5). The values ranged from a low of about 0.28 ppm to over 0.4 ppm, and the observed scatter greatly exceeded the estimated measurement error. The highest values (mean 0.3) were observed in winter and spring, with lower values (mean 0.25) during the summer and fall.

Schutz, et al. (1970) reported an extensive series of observations of N_2O levels made with a specially designed gas chromatograph, which



Source: Schutz, et al. (1970)

N_2O measurements made in Boston by Goody (1969) plotted with N_2O measurements made in Mainz. The vertical bars indicate the standard error of individual values for the two methods.

FIGURE VI-5 COMPARISON OF N_2O CONCENTRATIONS IN BOSTON AND MAINZ showed values on the average significantly lower than those reported by Goody. They also reveal an apparent two-year increase in concentration at ground level.

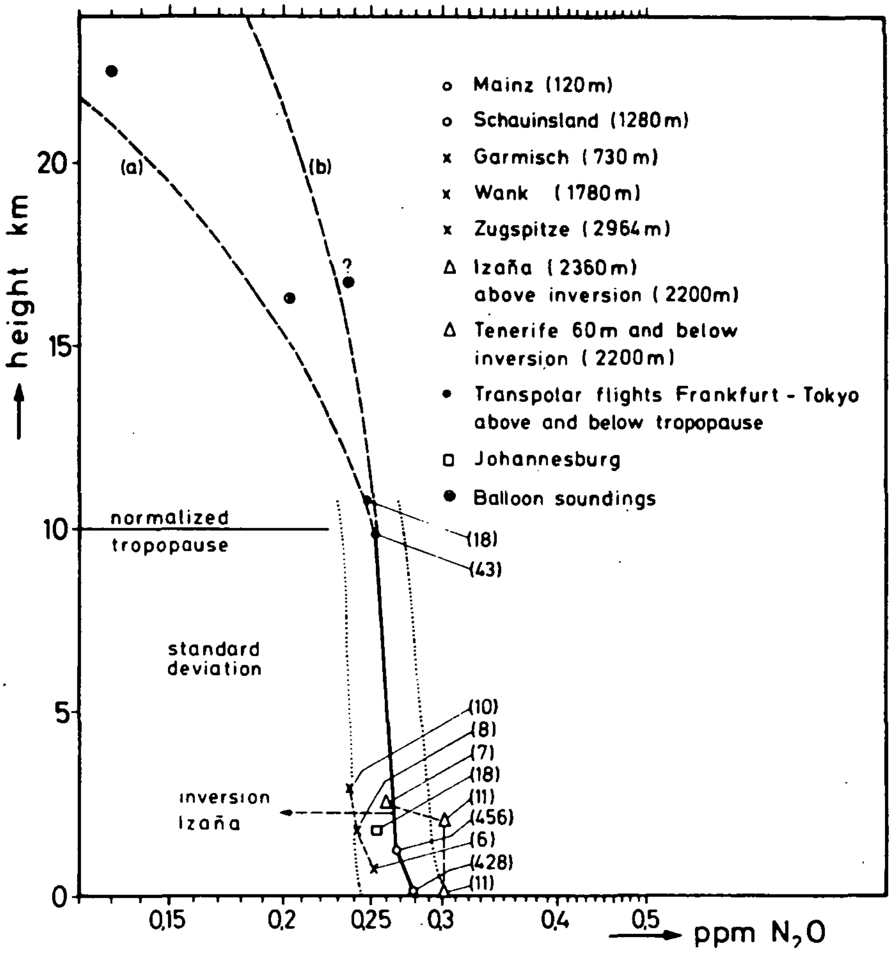
Goldman, et al.(1970) reported a series of N_2O measurements made with a balloon-borne grating spectrometer taken at altitudes of from 4.5 to 13.5 km. These showed evidence of a mixing ratio that was constant with altitude and averaged 0.14 ppm in this altitude range.

The lack of agreement among observations may be due in part to the differences in techniques used by the various investigators, but the evidence of temporal variations at a given locality provided by Goody (1969) and by Schutz et al. (1970) suggest that some of the discrepancies may reflect differences in the concentrations of N_2O.

The most extensive observations of N_2O are those of Schutz et al. (1970) which are summarized in Figure VI-6 and discussed below.

(1) Tropospheric Concentrations Over Land. Schutz, et al. made a series of daily measurements of N_2O over a period of 2.5 years from November 1966 to May 1969 at Mainz on the campus of the Max Planck Institut fur Chemie (altitude 120 m) and from June 1967 to November 1968 simultaneously made observations at Schauinsland, a 1280-meter mountain peak at Black Forest, to obtain information about possible regional as well as altitudinal differences. In addition, for a very short period during July 1968, simultaneous measurements were made at three mountain peaks in the Alps at locations which were close to one another but which differed in altitude (Garmisch-Partenkirchen, 780 m; Wank mountain, 1780 m; and Zugspitze mountain, 2964 m). Southern-hemisphere air was briefly sampled at a location near Johannesburg during the southern winter on a dry plateau characterized by little vegetation at an altitude of 1800 m.

The results of these observations may be summarized as follows: Mean abundance consistently declined with increases in altitude, but there was large variation in day-to-day means and little correlation between monthly or seasonal measurements at the Mainz-Schauinsland



Tropopause level was assumed to be 10 km. Dotted lines give standard deviation of tropospheric series of measurements with sufficiently numerous values. Dashed lines a and b are calculated profiles of Bates and Hays (1967) for stratospheric eddy diffusion coefficients of 10^3 and 10^4 cm^2/sec, respectively. Number of measurements is given in parentheses.

Source: Schutz, Junge, Beck, and Albrecht (1970)

FIGURE VI-6 COMPILATION OF ALL N_2O MEASUREMENTS REPORTED BY SCHUTZ, ET AL. (1970) AS A FUNCTION OF ALTITUDE locations. Observations at the other locations confirmed this trend, but the variations were so great and the observations so few than the differences in the means were not always significant. Monthly means of the Mainz-Schauinsland observations are plotted in Figure VI-7; these show a slight indication of a seasonal trend, with winter months averaging concentrations about 10% lower than in summer.

A trend toward increased concentrations was observed in the Mainz data, the average mixing ratios for the individual years being

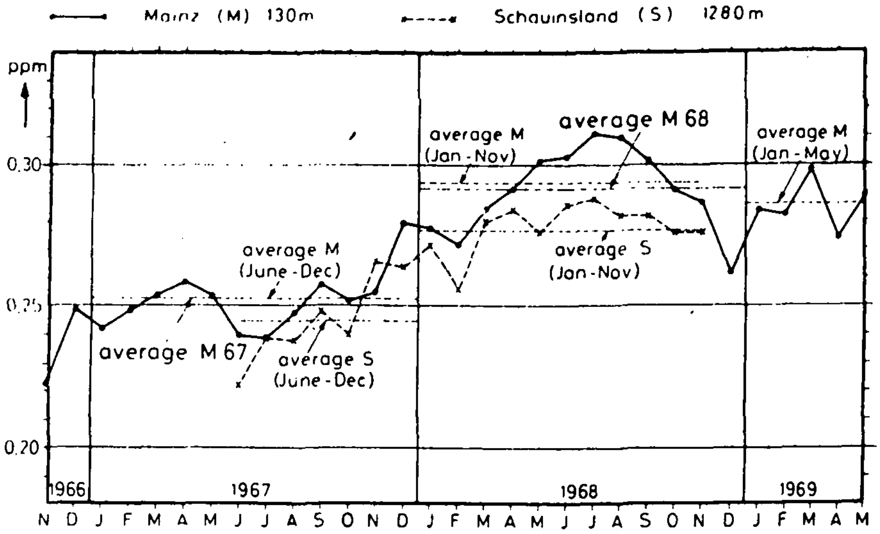
1967	0.249 ppm
1968	0.292 ppm
1969	0.286 ppm

The Schauinsland data also indicated such a trend, but the duration of the observations was too short to confirm this.

Although the observations in the Alps were too limited to support generalizations regarding altitudinal influences, they, too, indicated a decline with altitude. Figure VI-8 is a plot of these observations. The investigators were unable to detect clear relationships between N_2O concentrations and meteorological parameters in the data from the Alps or that from Mainz or Schauinsland.

<u>(2) Upper Tropopause and Stratosphere</u>. N_2O concentrations just above and below the tropopause were sampled on a series of transpolar flights between Tokyo and Frankfurt. These observations indicated a slight decrease in mixing ratio between Schauinsland and the region estimated to be just below the tropopause, and a larger decrease between this region and that just above the tropopause. Regions farther above the tropopause were sampled by means of three balloon-borne samplers, which indicated a further decrease in N_2O mixing ratio with altitude. These tropospheric and stratospheric results are shown in Tables VI-5 and VI-6.

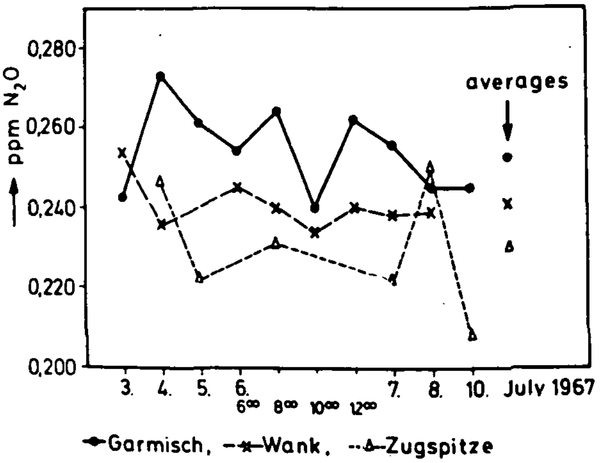
<u>(3) Atlantic Ocean</u>. Clean air from the Atlantic Ocean was sampled on the island of Tenerife, at 28°N about 300 km off the west coast of Africa. Air was sampled at the Observatory of Izana (2300 meters) above the inversion layer and simultaneously below the inversion layer



Source: Schutz, Junge, Beck and Albrecht (1970)

Dashed horizontal lines give average values for indicated periods.

FIGURE VI-7 MONTHLY AVERAGE VALUES OF N_2O FOR MAINZ AND SCHAUINSLAND



Source: Schutz, Junge, Beck, and Albrecht (1970)

FIGURE VI-8 VERTICAL DISTRIBUTION OF N_2O AT THREE STATIONS ON THE NORTHERN SLOPES OF THE ALPS

TABLE VI-5. - COMPARISON OF TROPOSPHERIC N_2O MEASUREMENTS FOR VARIOUS ALTITUDES

Location	Number of Data	Average (ppm)	Standard Deviation of Individual Measurement (%)	Standard Error of Average Value (%)	Range of Average Values within Standard Error
Mainz	573	0.271	10.8	0.45	0.2698-0.2722
Schauinsland	456	0.266	10.2	0.48	0.2647-0.2673
Below Tropopause	43	0.252	7.9	1.2	0.2490-0.2550
Above Tropopause	18	0.246	7.9	1.9	0.2413-0.2507

SOURCE: Schutz, Junge, Breck, and Albrecht (1970)

TABLE VI-6. - STRATOSPHERIC N_2O DATA

Balloon Launch Site	Date	Sampling Altitude (km) Above Sea Level	Sampling Altitude (km) Above Tropopause	N_2O Mixing Ratio (ppm)
Meppen	27 June 1967	17.3	6.3	0.229
Ravensburg	2 July 1968	18.0	6.3	0.204
Ravensburg	24 October 1968	23.0	12.5	0.103

SOURCE: Schutz, Junge, Breck, and Albrecht (1970) at 2200 meters and at sea level (60 m) during a period when the inversion was well developed and the winds both above and below the inversion were from the northwest sector, indicating air masses that had traveled long distances across the Atlantic. Below the inversion the concentration was constant with altitude and averaged 0.302 ppm; above the inversion it was 0.260. These results indicate a marine source of N_2O in this region.

c. Exchange of N_2O Between the Atmosphere and the Surface

The flux of N_2O from the surface can be estimated on the basis of the observed decline in abundance with altitude, on the basis of known atmospheric and/or surface sinks, or on the basis of estimates of the rate of emission and/or uptake from soil or water surfaces. Given the inadequacies of available data, none of these methods is suitable for evaluating the current exchange of N_2O with the surface.

Schutz et al. (1970) have used the mean concentration differences with altitude which they have measured to estimate the upward flux of N_2O. The differences between Schauinsland and the lower troposphere have been interpreted to imply a flux corresponding to a mean lifetime of 8.0 years for the tropopause (assuming a mean tropopause concentration of 0.26 ppm). The larger differences between Mainz and Schauinsland implied a flux on the order of 3×10^{-4} gm cm^{-2} sec^{-1}, or an average lifetime of 0.3 year. If, as may be the case, the agricultural and forest land of Central Europe constitutes an especially strong source area, the mean flux implied by these data can be estimated on the basis of the proportion of such land in the whole hemisphere, which is 0.17. This gives an adjusted lifetime of 0.3/0.17 = 1.8 years.

Estimates of total possible soil emission of N_2O have been prepared by Arnold (1954) as possibly equivalent to the chemical loss rate estimated by Goody and Walshaw (1953), which is 8×10^{10} molecules cm^{-2} sec^{-1} (9600×10^{12} gm N_2 per year for the whole earth). Since the denitrification reaction depends on a number of soil properties which are difficult to evaluate, this must be regarded as an order of magnitude estimate.

Some authors have proposed that the N_2O release rate cannot exceed the rate at which nitrogen is fixed in the biosphere (Hutchinson, 1954; Bates and Hays, 1967). It will be noted that this argument is valid only if all nitrous oxide which is released is lost to the biosphere. Nitrous oxide can act as a source of fixed nitrogen to organisms, and it is possible that atmospheric N_2O is absorbed by the soil. Schutz et al. (1970) suggest that the heated arid soils of the Sahara may act as a sink for nitrous oxide, having observed very low concentrations of N_2O in air masses which have passed over this area. The discrepancies in the lifetime of N_2O as estimated from the vertical flux at the ground and the estimated atmospheric chemical sink clearly imply the existence of tropospheric sinks, but identifying their location and efficiency requires additional information regarding space-time variations in abundance. Better vertical abundance information would help to identify tropospheric sinks and provide a basis for better estimates of the mean abundance and vertical flux.

2. Ammonia

Ammonia is present as a gas in the atmosphere in quantities ranging from 5 or less to 75 ppb (Hanawalt, 1969a, 1969b). Junge (1963) gives the tropospheric average near the surface as 10 ppb on the basis of measurements made mostly in the temperate zone; Pate, Lodge et al. (1970) propose 15 ppb as a tentative tropospheric average, based in part on their measurements in tropical rain forests and Atlantic air. However, recent solar spectra taken at Mont-Louis Observatory in the French Pyrenees indicate that the upper limit for NH_3 in the atmosphere above the site is 0.05 ppb, which is inconsistent with a tropospheric mean of 15 ppb (Dionne, 1971).

Although small amounts of ammonia are introduced into the atmosphere from the burning of coal and from other industrial sources (Junge, 1963; Georgii, 1963; Robinson and Robbins, 1968), the biosphere is the major source of what appears to be a large quantity of ammonia annually in circulation between the surface and the atmosphere. Biological mechanisms for the production of ammonia were discussed in Section B of this chapter.

a. Atmospheric Reactions of Ammonia

According to Cadle and Allen (1970) and Cadle (1971), ammonia is removed from the atmosphere by reaction with acids, which results in the formation of aerosols, but otherwise is stable. Evidence of aerosol formation in the stratosphere is provided by the existence of the sulfate aerosol layer there, which could be produced by reaction of ammonia and sulfate or SO_2 introduced from the troposphere. (See Chapter VII-E-7.)

Junge (1963) describes the mechanisms by which ammonia is removed from the atmosphere, namely, washout, which involves the solution of gaseous ammonia in cloud droplets as they form, and rainout, by which is meant the scavenging of gaseous and particulate ammonia from regions below the clouds by precipitation falling from them.

The removal of gaseous ammonia in washout is heavily dependent on the pH of the droplet and is very effective in the pH range of 5 to 6 which is characteristic of rain. If no anions such as SO_2 or NO_2 are present in the atmosphere, the absorption of ammonia will result in increasing the pH of the rain. As Junge (1963) points out, however, the pH of rain is in the range 5 to 6, which implies that such anions control it, and that washout is an effective way of removing gaseous ammonia from the atmosphere. Simultaneous measurements of ammonia in rainwater and air during rain suggest that rainout may not be effective in removing gaseous ammonia, although particulate ammonia (NH_4^+) present in large or giant particles found in the lower troposphere is effectively scavenged by precipitation (Junge, 1963).

Ammonia does not absorb visible or ultraviolet radiation of wavelengths exceeding 2200 Å and consequently does not undergo excitation or photolysis below the ionosphere (Cadle and Allen, 1970).

Georgii (1963) suggested that ammonia may be oxidized in the troposphere to NO_2, particularly in the tropics, but he cites no experimental confirmation of the occurrence of this reaction. Although a strong correlation between ammonia and nitrate in rain samples has been noted by several authors (Junge, 1963; Georgii and Weber, 1960; Syers, 1966), it provides only indirect evidence for the occurrence of such a reaction, and this correlation could be explained as resulting from nitrification processes acting after the deposition of the rain in the collecting vessel (Feth, 1966; Junge, 1963).

b. Atmospheric Distribution of Ammonia

Conclusions regarding the atmospheric distribution of ammonia are based on direct measurements of NH_3, which are scanty and restricted to levels near the ground, and the analysis of the NH_4^+ content of rainwater.

Interest in the atmospheric cycle of ammonia and other nitrogen compounds began in the late 1800's, when it was recognized that nitrogen delivered in rain is an important source of plant nutrients. Direct measurements of gaseous ammonia at that time seem rather high in comparison with present results, the lowest values being about 20 $\mu g/m^3$. In 1880 the values at Pic du Midi fluctuated between 7 and 30 $\mu g/m^3$. Recent measurements of atmospheric NH_3 are summarized in Table VI-7.

In the middle 1950's, Egner and Eriksson (1955) established an air sampling network data from Scandanavia which revealed a general NH_3 level between 5 and 20 $\mu g/m^3$ (7 to 26 ppb). Monthly average values for four stations are shown in Table VI-8 (Junge, 1963). Stations are arranged in order from north to south.

Georgii (1963) reports studies of the concentration of NH_3 and NO_2 in continental and marine air. These showed ammonia concentrations much higher at continental stations than at coastal stations where marine air is sampled, which is consistent with the belief that land sources predominate. Some of these values are plotted in Figure VI-9. The Frankfurt concentrations of 18-20 $\mu g/m^3$ (24 to 26 ppb) probably reflect some pollution from coal combustion.

Junge (1963) reports that marine air concentrations are in general low, but that the mean of 4 nighttime measurements above the tradewind inversion at Mauna Kea (3200 meters) was 1.4 ppb, which was lower than the mean of 14 measurements taken at sea level on the east coast of the

TABLE VI-7. - SUMMARY OF NH_3 OBSERVATIONS

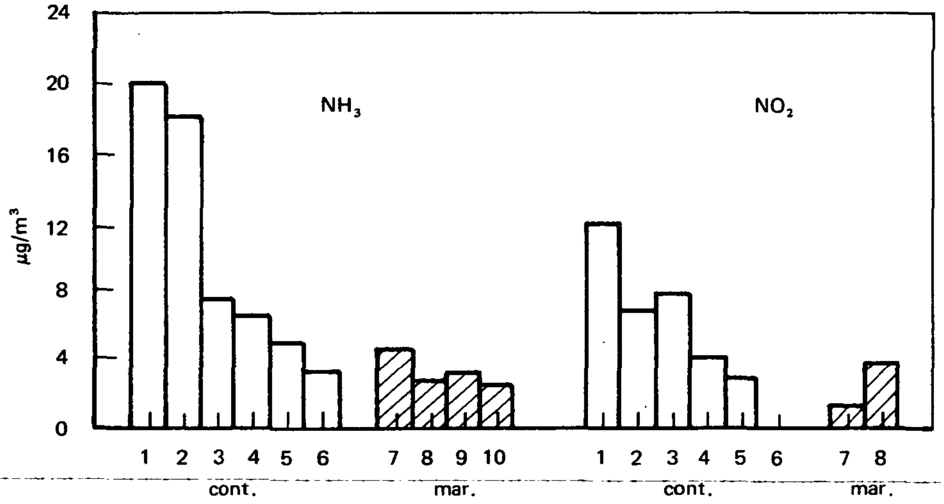
Location	Concentration (ppb)	Source
Scandinavian network	7-26	Egner & Eriksson (1955)
Frankfurt on Main (winter)	$\sim$ 26	Georgii (1963)
Frankfurt on Main (summer)	$\sim$ 24	Georgii (1963)
Kleiner, Feldberg (winter)	$\sim$ 9	Georgii (1963)
Zugspitze	$\sim$ 9	Georgii (1963)
St. Moritz	$\sim$ 7	Georgii (1963)
Hohenpeissenberg	$\sim$ 5	Georgii (1963)
Albrook Forest, Pan.	2-40 (mean 14-17)	Pate, Lodge, Sheesley and Wartburg (1970) and Wartburg, Pitombo, Pate, Sheesley, LaHue, and Lodge (1970)
Caribbean air	27	Pate, Lodge, Sheesley and Wartburg (1970) and Wartburg, Pitombo, Pate, Sheesley, LaHue, and Lodge (1970)
Amazon forest	7	
Atlantic air	15	
Florida	2.9-10.6 (mean 6.7)	Junge (1963)
Hawaii-coast	1.5- 5.2 (mean 3.3)	Junge (1963)
Hawaii-3200 m	1-1.7	Junge (1963)
Ipswich, Mass.	4.4-18.4 (mean 8.1)	
United Kingdom	5	Healy, McKay, Pilbeam and Scargill (1970)
Mont-Louis	<0.05	Dionne (1971)

TABLE VI-8. - MONTHLY AVERAGE VALUES OF TOTAL NH_3 FROM SOME STATIONS OF THE SWEDISH NETWORK (PARTS PER BILLION)

	Nov. 1954	Dec. 1954	Jan. 1955	Feb. 1955	Mar. 1955	Apr. 1955	May 1955	June 1955	July 1955	Aug. 1955	Sept. 1955	Oct. 1955
Offer	1.8	2.6	3.4	2.9	4.0	5.5	5.3	5.4	7.8	6.5	5.5	2.8
Erken	0.8	4.2	1.5	2.9	1.9	1.6	1.7	1.3	2.9	2.9	0.1	4.0
Falsterbobruk	2.9	1.3	1.7	5.0	1.7	2.9	2.4	2.5	3.8	5.3	3.8	4.5
Alnarp	5.0	2.9	4.5	4.5	5.3	5.9	4.6	7.9	12.4	12.4	6.6	6.3
Average	2.6	2.5	2.8	3.8	3.2	4.0	3.4	4.2	6.7	6.7	4.0	4.6

SOURCE: Junge (1963)

island of Hawaii, which was 3.3 ppb (Table VI-9). Simultaneous measurements of the pH and NH_4^+ concentration in sea water near Hawaii indicate that the equilibrium concentration of NH_3 in the air was at that time lower than the measured concentration, implying that the sea could not have been the source of the ammonia. Junge suggests that the marine NH_3 source may not be the ocean itself but a film of organic matter on the surface.



1 Frankfurt on Main (winter)
2 Frankfurt on Main (summer)
3 Kleiner Feldberg, Taunus (winter)
4 Zugspitze (summer)
5 St. Moritz (summer)
6 Hohenpeissenberg
7 Florida
8 Hawaii
9 Vesima, Italy
10 Westerland, North Sea

Source: Georgii (1963)

FIGURE VI–9 CONCENTRATION OF NH_3 AND NO_2 IN AIR AT DIFFERENT CONTINENTAL AND MARITIME LOCATIONS

Goering and Menzel (1965) explored this suggestion by comparing the chemistry of sea water collected in the top 3 mm with that collected at a depth of 1 meter. Their analyses of water collected in the tropical Atlantic confirmed Junge's conjecture that the surface chemistry may be very different from that at depths of 1 meter or more. They found significantly greater concentrations of ammonia at the surface than at 1 meter, but the difference averaged only 0.311 µg/liter. The surface concentrations at these stations averaged between 0.3 and 0.4

TABLE VI-9. - CONCENTRATION OF NO_2 AND NH_3 IN UNPOLLUTED ATMOSPHERES

(PARTS PER BILLION)

Location	Remarks	NO_2		NH_3	
		Range	Average	Range	Average
Florida	Trade winds, southeast coast, 13 values, July-August 1954	0.5-1.8	0.9	2.9-10.6	6.7
Hawaii	East coast Island of Hawaii, 14 values, November 1954	0.7-1.6	1.3	1.5-5.2	3.3
Hawaii	Mauna Kea, 3200 meters(above the trade-wind inversion), 4 night values, November 1954	0.8-1.1	0.9	1.0-1.7	1.4
Ipswich, Mass.	9 values, December-January 1954-55	0.3-1.9	1.3	4.4-18.4	8.1

SOURCE: Junge (1956)

μg/liter, which is insufficient to account for the concentrations observed by Junge in pure maritime air. Slightly greater concentrations of nitrite were also found at the surface, and were attributed to oxidation of ammonia.

Ammonia concentrations in the tropics were reported by Pate, Lodge, Sheesley, and Wartburg (1970), who studied the concentrations of selected trace gases in a forest at two heights during wet and dry seasons, and the concentrations in Caribbean air samples at a shore station. Wartburg, Pitombo, et al. (1970) reported the measurements on a few selected days of the same constituents in the Amazon rain forest at a site within the forest and in the air over a river (Rio Tarumã). These results are shown in Tables VI-10 and VI-11. The NH_3 mean of Caribbean air sampled at the Panama coast was 27 ppb (21 $\mu g/m^3$) while that of Atlantic air sampled at the island of Barbados was 15 ppb (11 $\mu g/m^3$); this is interpreted as evidence for a Caribbean marine source but no significant Atlantic source. The Panama forest showed a mean of 14 ppb, and the differences between above-canopy and below-canopy measurements do not appear to be great, nor do those between wet and dry seasons. In Amazonia the forest values averaged 7 ppb (5 $\mu g/m^3$), while air sampled over the river averaged 35 ppb (27 $\mu g/m^3$). The authors believe the high values associated with water are real and indicate NH_3 sources in the Caribbean and the river. The lower values over the forest may indicate that oxidizing conditions are generally characteristic of tropic forests. Healy, McKay, Pilbeam, and Scargill (1970) report that NH_3 concentrations over the United Kingdom average 4 $\mu g/m^3$ (about 5 ppb).

c. Ammonia in Rain

Several workers have studied the distribution of ammonia (NH_4^+) in rain in an effort to identify its sources and its fate. Angstrom and Hogberg (1952a,b) analyzed the distribution of ammonia in rain collected by means of the Scandinavian network. Their results are summarized by Junge (1963) and Feth (1966). In general, the concentration near the coasts was found to be less than that over land, and the amount of

TABLE VI-10. - SEASONAL MEANS OF DAILY MEDIANS IN PANAMA--AMMONIA AND SULFUR DIOXIDE

	NH_3 (ppb)		SO_2 (ppb)	
	Dry	Wet	Dry	Wet
Albrook - 2 m	14	14	1.1	1.6
Albrook - 46 m	17	15	0.8	1.0
Ft. Sherman	27	29	1.9	0.8

SOURCE: Pate, Lodge, Sheesley and Wartburg (1970)

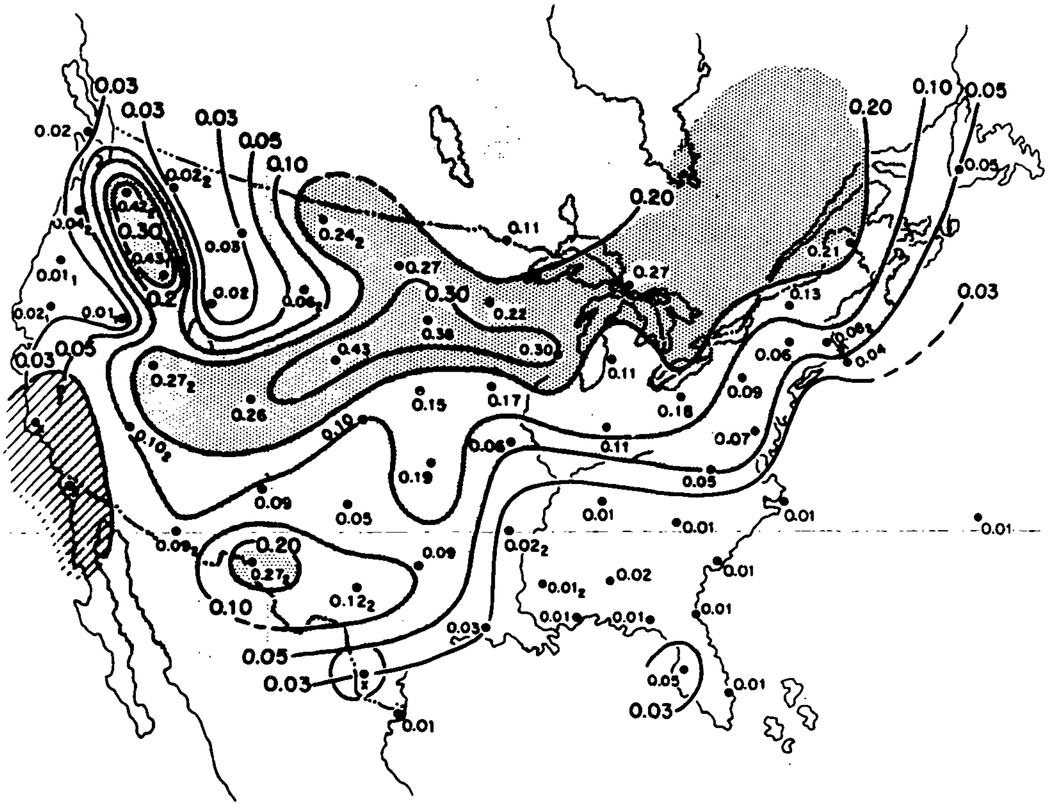
TABLE VI-11. - COMPARISON OF ATMOSPHERIC TRACE GASES IN BRAZIL AND PANAMA

	Concentration (ppb by volume)					
	NH_3	N_2O	NO	NO_2	RCHO	SO_2
Brazil						
Ducke Forest Preserve	7		0.1	0.2	1.0	0.2
Rio Tarumã	35		0.3	0.4	4.7	0.1
Panama						
Albrook Forest	14	237	0.4	0.6	3.7	1.6
Darien	14	269	0.3	0.4	---	0.4
Maritime						
Caribbean Coast-Panama	27	270	0.4	0.4	4.4	0.8
Barbados	15	266	0.5	0.2	---	0.4

SOURCE: Wartburg, Pitombo, Pate, Sheesley, LaHue, and Lodge (1970) ammonia decreased with increasing latitude. The nitrate N concentrations were about half those of the ammonia N, which varied from 0.17 to 1.5 ppm. Junge (1958) reported a nationwide survey of ammonium and nitrate in rain over the United States during July, August, and September 1955; the ammonium data are plotted in Figure VI-10. There were pronounced seasonal and geographic variations but little evidence of a significant industrial source. Rains near the coast were characterized by very low NH_4^+ concentrations, as were those in the Southeast. The latter was attributed by Junge to the low pH characteristic of the prevailing laterite soils in that region, which may result in very low rates of release of ammonia. He infers that the area north and west of this region is a large source of NH_3, and interprets the sharpness of the border as implying a concentration of NH_3 near the surface, which permits air from this region to be rapidly depleted of NH_3 as a result of absorption and rainout when it approaches the region of high-laterite soils. Seasonal variations in the United States indicate peak NH_3 concentrations in rain from April to June, decreasing somewhat until September and with a broad minimum during the winter (Junge, 1958, 1963). The Swedish data of Angstrom and Hogberg show a pronounced maximum in spring and a minimum in the fall.

Junge (1963) reports that while NH_4^+ concentrations in rain vary from 0.1 to 1.0 mg/liter, most values of precipitation over land fall in the range 0.1 to 0.2 mg/liter, while those over the ocean are about half this. Feth (1966) points out that coastal stations do not always receive less ammonia than inland stations, and he presents in evidence data collected from the Northern European Sampling Network for July 1955 to June 1956 (the same period during which Junge studied the ammonia and nitrate content of rain in the United States). These are shown in Table VI-12. It will be seen that the measured ammonia and nitrate concentrations are in general higher for the rural coastal stations than for the rural inland stations.

Feth cautions that under the sampling conditions used in this network, the oxidation state of the nitrogen compound when analyzed may have only a



Source: Junge (1963)

Figures represent milligrams NH_4^+ per liter.

Data originally recorded by Junge (1958)

FIGURE VI–10 AVERAGE NH_4^+ CONCENTRATION IN RAIN OVER THE UNITED STATES, JULY-SEPTEMBER 1955

TABLE VI-12. - OCCURRENCE OF NH_3-N AND NO_3-N IN SAMPLES OF PRECIPITATION FROM SELECTED STATIONS IN THE NORTHERN EUROPEAN SAMPLING NETWORK, JULY 1955-JUNE 1956

Station	NH_3-N calculated to equivalent NO_3^{-1} ($mg/m^2/yr$)	NO_3-N calculated to equivalent NO_3^{-1} ($mg/m^2/yr$)	NH_3-N ($mg/m^2/yr$)	NO_3-N ($mg/m^2/yr$)	Total N ($mg/m^2/yr$)
		Rural Inland Stations			
Riksgransen	176	88	40	20	60
Kiruna	260	100	59	23	82
Jyvaskyla	292	228	66	51	117
Kvarntorp 7	636	320	143	72	215
Feldberg	1480	972	333	219	552
		Rural Coastal Stations			
Robacksdalen	284	188	64	42	106
Amot	348	236	78	53	131
Strangsnas	308	244	70	55	125
Brakne Hoby	548	516	123	116	239
Newton Abbot[a]	4876	716	1097	161	1258

SOURCE: Modified from Feth (1966)

[a] The very high NH_3-N value for this station depends on a single month's sample, November 1955, and may be an analytical error or the result of contamination of the sample. If that value is deleted, the station is still one of the highest, about equivalent to Feldberg.

coincidental relationship to the state of the compounds falling in precipitation, due to the fact that the sampling device is continuously exposed for a month while the sample accumulates. This provides occasion for bacterial reduction of nitrate, fixation of nitrogen, and other changes. Nitrogen is present in the organic matter in rain, and the quantities may be large compared to the soluble nitrogen. Junge (1963) reports long-term averages in milligrams per liter for several locations: Mt. Vernon, Iowa, 0.4; Ottawa, Canada, 1.1; Dehra Dun, India, 2.6; and Rothamstedt, England, 2.0. Soluble ammonia may be produced from the decomposition of this organic nitrogen.

Ammonia is also present in the atmosphere in aerosols as ammonium sulfate or ammonium nitrate, in all size ranges. Ammonium in particulates in urban areas was reported by Lee and Patterson (1969) to range from 4 to 9.45 $\mu g/m^3$, while nitrate concentrations were about 3 $\mu g/m^3$. Most of the ammonium was believed to be in the form of ammonium sulfate. Robinson and Robbins (1968, 1970b) report average tropospheric concentractions of particulate ammonium N to be 1 $\mu g/m^3$. Heard and Wiffen (1969) studied sub-micron particulates in rural air, reporting a mass of 3.9 $\mu g/m^3$ of ammonium sulfate in one sample and 7.5 $\mu g/m^3$ in another. Pate, Pitombo et al. (1971) suggest that the ambient world-wide concentration of ammonia compounds in particulate form may be about 4 $\mu g/m^3$ and believe that it may be approximately equal to the gaseous NH_3-N concentration. They further speculate that the residence time of gaseous ammonia may be hours rather than days. If the residence time of gaseous ammonia is very short, then most of that present in the atmosphere may be concentrated at levels below about 3 or 4 km, which is consistent with the Mont-Louis observations mentioned above, but inconsistent with the observation of a mean of 1.4 ppb NH_3 at Mauna Kea, Hawaii (altitude 3200 meters) unless there are local biological sources of ammonia near the ground in this region.

d. Exchange of Ammonia Between the Surface and the Atmosphere

Although it is generally agreed that the biosphere is the primary source of ammonia, there are few data on which to base an estimate of the rate of release of ammonia from the soil or from bodies of water. Allison (1955) studied ammonia loss and concluded that it is governed by the availability of ammonia and by the pH of the soil, being high for alkaline soils. Stewart (1970) discusses the evolution of ammonia from urea nitrogen in feedlots and finds that the release of gaseous ammonia is dependent on the moisture content of the two types of soil studied. He found that up to 90% of added urea nitrogen was volatilized as ammonia if the soil is dry, whereas wet soil results in a proportionately greater conversion to nitrate, very wet soil showing volatilization of 25% of ammonia and conversion of 65% of urea nitrogen to nitrate. Loewenstein, Engelbert, Attoe, and Allan (1957) reported that large quantities of added ammonia nitrogen fertilizer may be volatilized within 6 weeks of fertilizer application, although they did not determine whether the gas was evolved as nitrogen or in some other gaseous form.

Small quantities of gaseous ammonia are injected into the atmosphere from anthropogenic sources. Robinson and Robbins (1968) estimated the total ammonia from these sources as 4 million tons per year, most of it from coal combustion. This quantity is negligible from the point of view of a global nitrogen budget.

Eriksson (1952) concluded that considerable quantities of gaseous atmospheric ammonia may be absorbed by soil on the basis of measurements of the amount of atmospheric ammonia taken up by acid solutions exposed to the air. Allison (1955) indicated that low pH values of soils enhances their ability to absorb atmospheric ammonia.

Nyborg (1969) studied the fixation of gaseous ammonia by soil organic matter, which he reported to increase with decreases in pH. He studied the reaction between small quantities of soil and large quantities of gaseous NH_3 (100 gm soil and 161 meg gaseous NH_3).

Hanawalt (1969a, 1969b) studied the influence of atmospheric and soil factors on the uptake rate. He reports that 20 to 70 kg NH_3-N/ha/yr may be absorbed by soils in New Jersey where the NH_3 concentration is about 57 $\mu g/m^3$ (74 ppb) due to local pollution. He concluded that at concentrations of gaseous ammonia characteristic of ambient atmospheres (as opposed to the much higher concentrations of ammonium ion in fertilizers) the most important parameters are temperature and those factors which govern the delivery of the gas to the soil surface. Absorption was positively related to ammonia concentration in air, temperature, air velocity, and the moisture content and air permeability of the soil. Absorption was found to vary relatively little with soil properties that relate to number and strength of bonding sites. Although changes in organic matter content of the soil affected the absorption, the differences were not great under the conditions studied. Similarly, soil acidity had relatively little effect.

3. Nitric Oxide and Nitrogen Dioxide

Nitric oxide is produced in soils from the decomposition of nitrates and can be thought of as a biological product, in view of the fact that its precursor is biogenic. Nitrogen dioxide is produced from nitric oxide in the atmosphere; for this reason, and because their subsequent atmospheric fates are interconnected, the two gases will be considered together.

a. Atmospheric Reactions of Nitric Oxide and Nitrogen Dioxide

The atmospheric chemistry of NO and NO_2 is extremely complicated and has been extensively studied, because NO and NO_2 and the products of their reactions with other constituents are prominent components of photochemical smog. It is not important for our purposes to review this literature, except to point out that the ultimate fate of tropospheric NO and NO_2 is the production of HNO_3 and HNO_2. NO is rapidly oxidized to NO_2 by oxidation with ozone:

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (6)$$

When nitrogen dioxide is irradiated with near-ultraviolet radiation, NO and monatomic oxygen are formed.

$$NO_2 + \underline{hv} \rightarrow NO + O \qquad (7)$$

The oxygen may then react with O_2 to form ozone, which can react with the NO to form more NO_2, establishing a chain reaction. Ozone may also react with NO_2:

$$O_3 + NO_2 \rightarrow NO_3 + O_2 \qquad (8)$$

This reaction is rapidly followed by:

$$NO_3 + NO_2 + M \rightarrow N_2O_5 + M \qquad (9)$$

The N_2O_5 reacts very rapidly with water vapor to form nitric acid vapor. Nitric acid vapor is also produced by reaction of nitrogen dioxide with water:

$$NO_2 + H_2O \rightarrow HNO_3 + HNO_2 \text{ or } NO \qquad (10)$$

About 5% of the NO_2 is converted into nitric acid by this reaction at concentrations characteristic of air.

Nitric acid vapor may be absorbed on salt particles or dissolved droplets containing NaCl to produce sodium nitrate and HCl gas. Nitric acid vapor may be dissolved directly in cloud droplets or scavenged by rain and, in the presence of gaseous ammonia, aerosols containing ammonium nitrate are formed. Photolytic decomposition of the latter may produce ammonium nitrite (Petriconi and Papee, 1970).

Although some nitrate in rain may be due to the fixation of N_2 as NO_2 by electrical discharge phenomena in clouds, the quantities formed in this way are generally agreed to be negligible in comparison with the total amount of NO_3 found in rain (Reiter, 1970; Georgii, 1963; Junge, 1963).

Another source of NO and NO_2 is the stratospheric photolysis of N_2O, or its reaction with $O(^1D)$. (See Section D.1.a.) Bates and Hays (1967) considered the tropospheric abundances of NO + NO_2 resulting from the photodissociation of nitrous oxide. Assuming that the vertical exchange coefficients in the troposphere and stratosphere are 10^5 and 10^4 cm^2 sec^{-1} respectively, they concluded that the resulting ground-level abundance would be about 0.001 ppb if the tropospheric lifetime were as long as 50 days.

In drawing these conclusions, Bates and Hays assumed that about 20% of photodissociation reactions to the short-wavelength side of 2500 Å entail the production of NO. According to McElroy and McConnel (1971), more recent evidence suggests that only 1% of such reactions produce NO, and that NO is produced in the stratosphere from N_2O primarily by reaction with $O(^1D)$ produced by photolysis of ozone. (See Equation 4.) These authors conclude that the production of NO from this source is between about 3 and 6.6×10^7 molecules cm^{-2} sec^{-1}. Since this is much less than the production assumed by Bates and Hays, we may infer that stratospheric production of NO has a negligible effect on the tropospheric concentrations of this constituent.

Nitric oxide is also produced in the ionosphere, but there is little information regarding the effect of this production on stratospheric values.

b. Atmospheric Abundance of NO and NO_2

Both NO and NO_2 are products of the combustion of fossil fuels, which results in an emission of about 18 million tons per year as N. High levels may be temporarily attained in polluted environments. Typical concentrations in polluted environments range from 100 to 300 ppb (Junge, 1963) and may reach 500 or more in some circumstances (Pate, Sheesley, et al., 1971). Although most of this pollutant NO_x emission presently occurs at ground level, Johnston (1971) has pointed out that a fleet of SST's operating in the stratosphere 7 hours per day would provide a stratospheric pollutant source averaging 1.2×10^7 molecules of NO cm^{-2} sec^{-1}. Because the lifetime of NO and NO_2 is short, we will not consider pollutant sources of these gases further, except to consider the total emission in discussions of nitrogen budgets.

Measurements of NO_2 and NO concentrations are summarized in Table VI-13. Most of the evidence regarding the distribution of NO and NO_2 in nonpolluted environments consists of measurements of the NO_3^- content of precipitation, but in recent years some direct measurements of NO and NO_2 concentrations have been reported. Fischer, Lodge, Wartburg, and Pate (1968) reported measurements of NO_2 at several locations in the Antarctic during the southern summer in 1966. They found it to be sporadically present, but rarely in quantities greater than 0.6 ppb; on one occasion, however, it reached 4.3 ppb, and on several occasions quantities in the range 0.7 to 2.3 ppb were observed. Figure VI-11 shows the levels of NO and NO_2 measured above and below the forest canopy in Panama during 1967 and 1968, reported by Wartburg, Pitombo, et al. (1970). There was usually more NO than NO_2 present, and there was considerable variation in the monthly means of daily medians. (Tables VI-10 and VI-11 summarize data from Panama and Brazil.) The levels observed an Atlantic air in Barbados show more than NO than NO_2, whereas at other locations NO_2 showed a slight predominance. Pate, Pitombo et al. (1971) recommend that 0.5 ppb be adopted as a tentative tropospheric mean for both of these gases, on the grounds that the measurement technique used in Panama and Brazil results in a slight underestimate of the concentration.

Ripperton, Kornreich, and Worth (1970) measured concentrations of NO, NO_2, and ozone at two locations in North Carolina and found concentrations from 1 to 10 ppb. At one of these, a point about 12 miles from Chapel Hill, air was continuously sampled at two heights above the ground. Simultaneous measurements of ozone and NO_2 are plotted in Figure VI-12. A clear inverse relationship between ozone and NO_2 may be interpreted as evidence of the oxidation of NO_2 by O_3; it is also consistent with the apparent decline with height of the NO_2, since O_3 is more plentiful at higher altitudes. The latter is derived from photochemical reactions at greater altitudes and brought near the surface by turbulent processes. Both NO_2 and O_3 may be seen to decrease during the night, which is attributed to reactions between the two, combined with lowered vertical transport (which may tend to dilute NO_2 during the day). The morning peaks are attributed to increases in the

TABLE VI-13. - SUMMARY OF OBSERVATIONS OF NO AND NO_2 CONCENTRATIONS

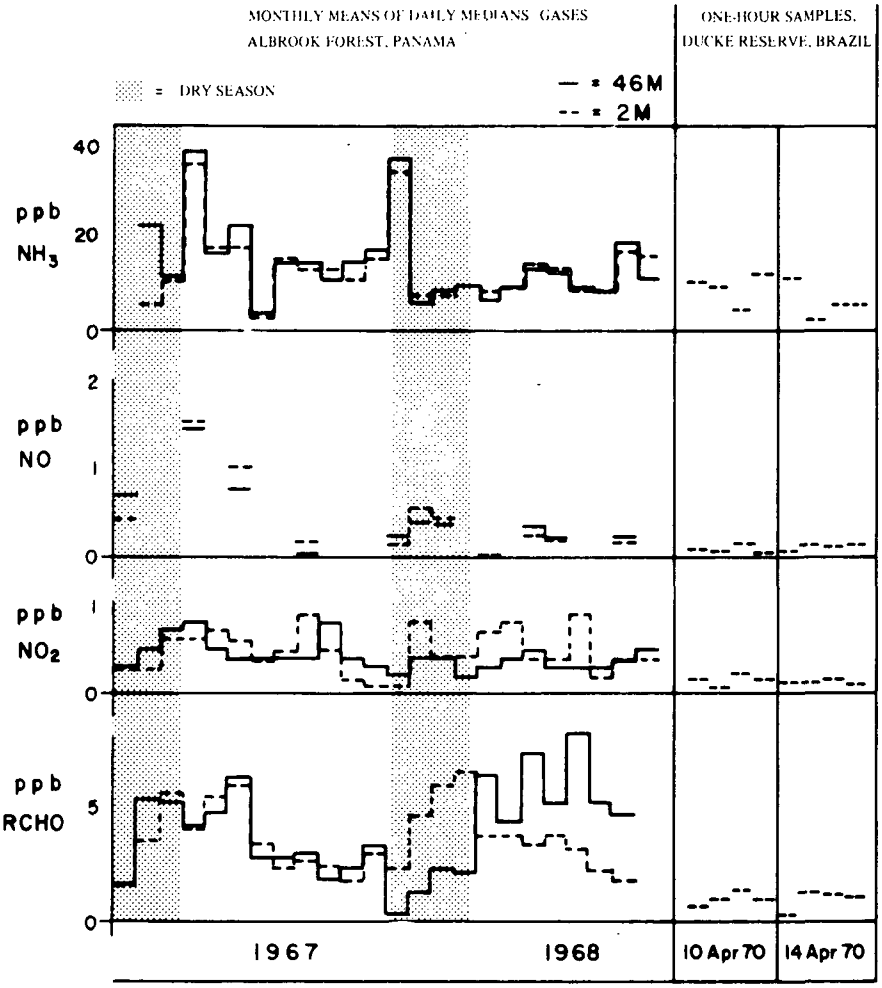
(PARTS PER BILLION)

	NO_2		NO	
	Range	Mean	(Mean)	Measured by
Florida	0.5-1.8	0.9		Junge 1963
Hawaii (east coast)	0.7-1.6	1.3		
Hawaii (3200 m)	0.8-1.1	0.9		
Ipswich, Mass.	0.3-1.9	1.3		
Ducke Forest, Brazil[a]		0.2	0.1	Wartburg, Pitombo, Pate, Sheesley, LaHue, and Lodge (1970)
Rio Taruma Brazil[a]		0.4	0.3	
Albrook Forest, Panama[a]		0.6	0.4	
Darien, Panama[a]		0.4	0.3	
Caribbean Coast, Panama[a]		0.4	0.4	
Barbados [a]		0.2	0.5	
Antarctic	0 -4.3	∿0.5		Fischer, Lodge, Wartburg and Pate (1968)
Frankfurt on Main (winter)[b]		5.9		Georgii (1963)
Frankfurt on Main (summar)[b]		3.4		
Kleiner Feldberg, Taunus (winter)[b]		4		
Zugspitze (summer)[b]		2.4		
St. Moritz (summer)[b]		2		
Piedmont, North Carolina[c]		∿5.8	1.9	Ripperton, Kornreich, and Worth (1970)
Green Knob, North Carolina		4	2.6	

[a] Means of daily medians

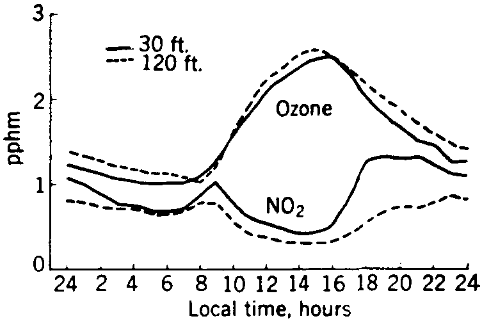
[b] See Figure VI-9.

[c] Range of averages for different observation periods and heights above the ground.



Source: Wartburg, Pitombo, Pate, Sheesley, La Hue and Lodge (1970)

FIGURE VI-11 COMPARISON OF PANAMA AND BRAZIL GAS DATA rate of production, combined with the persistence of a nocturnal radiation inversion that permits concentrations to build up. The extreme vertical gradient of concentrations, combined with the large variations during the day, imply a high rate of local production of NO_2 and, by inference, of NO.



Average hourly readings over period from
Sept. 1966 to Jan. 1967 near Chapel Hill, N.C.

Source: Ripperton, Kornreich and Worth (1970)

FIGURE VI-12 HOURLY VARIATION OF OZONE AND NITROGEN DIOXIDE CONCENTRATION

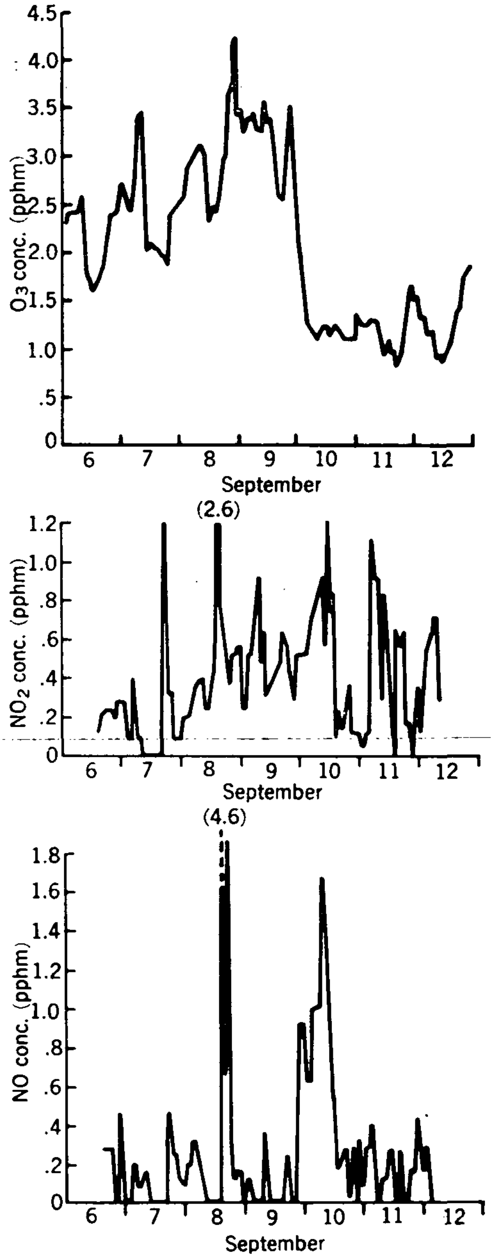
Table VI-14 (Ripperton, Kornreich, and Worth, 1970) shows the means of concentration of NO and NO_2 observed at Piedmont and at Green Knob at a field sampling site on a mountain in the southern Appalachians. Extreme variability of the concentrations of both these substances was observed. Diurnal averages for NO, NO_2, and O_3 are plotted in Figure VI-13.

Georgii (1963) summarizes earlier measurements of NO_2, plotted in Figure VI-9. Studies of the nitrate content of rain were reviewed by Junge (1963), Georgii (1963), and Feth (1966). Some of these have been discussed in the preceding section on ammonia. Junge (1963) summarizes findings on the nitrate content of rain up to 1962. He reports the range of NO_3^- concentrations in precipitation over land to be about 1.0 to 2.5 mg/liter in Europe and somewhat lower--i.e., 0.3 to 2.0 mg/liter--in other areas; over sea or in coastal regions, NO_3^- concentrations range from 0.15 to 0.5 mg/liter. Angstrom and Hogberg (1952a)

TABLE VI-14. - NO & NO_2 VALUES, NORTH CAROLINA

Site	Type Sampling	NO_2 Average (pphm)	NO_2 Average ($\mu g/m^3$)	NO Average (pphm)	NO Average ($\mu g/m^3$)
Piedmont					
- September 1966-January 1967					
30 ft	Continuous	0.76	14.3		
120 ft	Continuous	0.61	11.5		
- November 1965-January 1966					
4 ft	Discrete 2-hr Samples	0.56	10.6	0.19	2.34
Green Knob September 1965	Discrete 1 and 2 hr Samples	0.40	6.4	0.26	2.72

SOURCE: Ripperton, Kornreich, and Worth (1970)

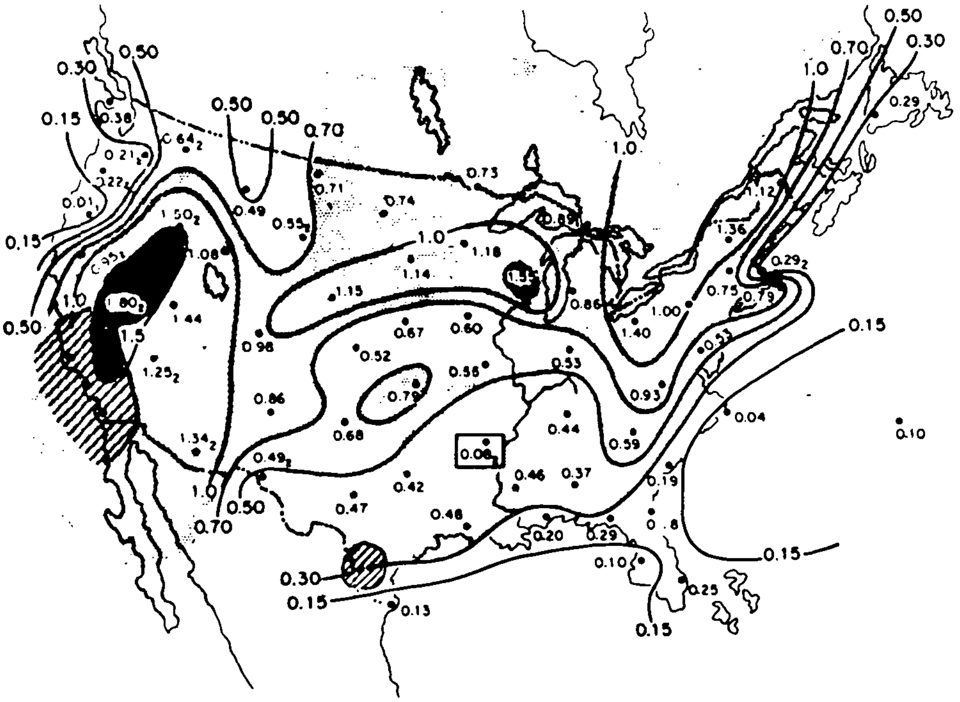


Source: Ripperton, Kornreich, and Worth (1970)

Measurements made at Green Knob, N.C., in Sept. 1965.

FIGURE VI-13 DIURNAL AVERAGES FOR NITRIC OXIDE, NITROGEN DIOXIDE, AND OZONE

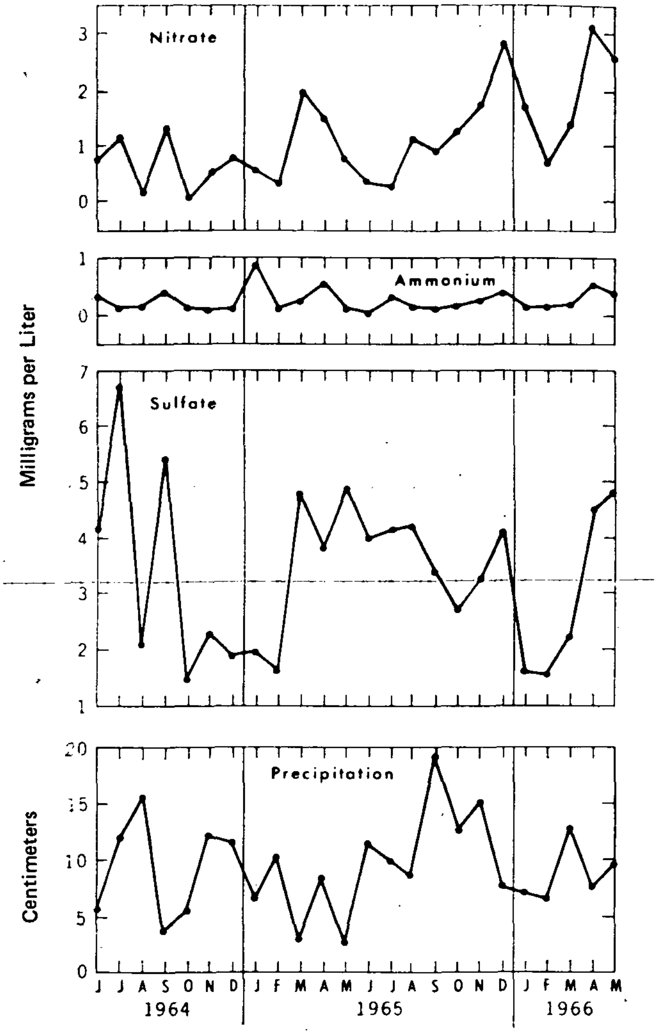
found a strong correlation between NH_4^+ and NO_3^-, with an average weight ratio of about 1:2. (Note that this corresponds to a NH_4^+-N to NO_3^--N ratio of about 2:1.) Syers (1966) found the ratio of NH_4-N to NO_3-N to be approximately 1:0.42. Figure VI-14 shows average concentrations of nitrate (as NO_3 in mg/l) over the United States in June-September 1955. Figure VI-15 (from Fisher, Gambrell, Likens, and Bormann, 1968) is a plot of the concentration of ammonia and nitrate nitrogen in precipitation in an experimental forest in New Hampshire. Some concentrations of nitrite, nitrate, and ammonia reported by Feth (1966) are shown in Tables VI-15 and VI-16. The nitrite concentration is uniformly low, and the relationship between ammonia and nitrate is seen to be variable.



Source: Junge (1963)

Readings are in milligrams NO_3^- per liter.

FIGURE VI-14 AVERAGE CONCENTRATION OF NO_3^- IN RAIN OVER THE UNITED STATES, JULY-SEPTEMBER 1955



Source: Fisher, Gambell, Likens, and Bormann (1968)

FIGURE VI-15 PRECIPITATION AND CONCENTRATIONS OF SULFATE, AMMONIUM, AND NITRATE IN PRECIPITATION

TABLE VI-15. - AVERAGE CONCENTRATIONS OF NITROGEN COMPOUNDS IN PRECIPITATION SAMPLED AT MENLO PARK, CALIFORNIA

(PARTS PER MILLION)

Compounds	Rain 1957-1958	Rain 1958-1959	Bulk Precipitation
NH_4^+	- - - not determined - - -		
NO_2^-	0.01	0.05	0.03
NO_3^-	0.15	0.16	2.56

SOURCE: Feth (1966)

TABLE VI-16. - AVERAGE CONCENTRATIONS OF NITROGEN COMPOUNDS IN SNOW SAMPLED IN THE WESTERN UNITED STATES

Compounds	Average Concentration (ppm)	Number of Samples	Number of Samples in which Concentration was below Limit of Detection
NH_4^+	0.2	21	18
NO_2^-	0.03	52	28
NO_3^-	0.1	68	32

SOURCE: Feth (1966)

If accurate information regarding the nitrate content of rain were available, this would provide a basis for estimating the annual cycle of NO, under the assumption that all NO is converted to NO_2 and is ultimately returned to the surface in precipitation as nitrate. Unfortunately, precipitation samples may be subjected to bacterial action, which converts organic nitrogen to ammonia and soluble ammonia to nitrate before collection. Therefore analyses of the nitrate content of rain provide only a very crude basis for estimating total exchange of NO.

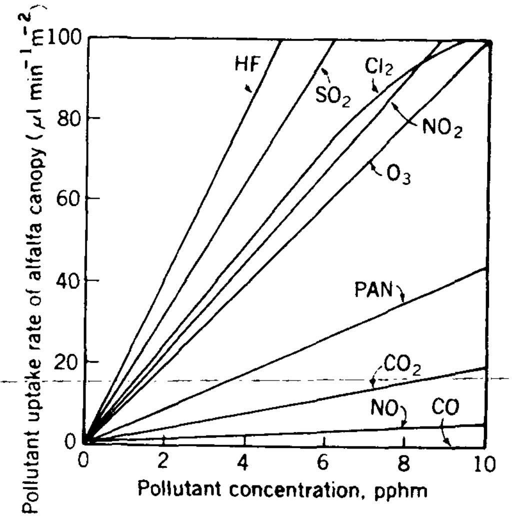
c. Exchange of NO_2 Between the Surface and the Atmosphere

The removal of NO_2 as nitrate in rain has been discussed in the preceding section. NO_2 may be removed from the atmosphere by means of direct uptake by soil and/or vegetation. Several recent studies have demonstrated that soil and vegetation have a capacity to remove large quantities of NO_2 from a controlled atmosphere, and evidence of NO_2 damage to vegetation suggests that atmospheric NO_2 is in fact removed by reaction with vegetation.

Hill (1971) studied pollutant uptake as a function of concentration by an alfalfa canopy. The concentrations used were higher than those reported for rural areas--50 to 100 ppb--and at these high levels uptake was linear with concentration during the one- and two-hour experimental periods used in the study. Both NO_2 and NO were among the numerous pollutants absorbed by the vegetation during this series of experiments, NO_2 at a much higher rate than NO. Absorption rate versus concentration results are plotted in Figure VI-16.

Arbeles, Craker, Forrence, and Leather (1971) studied the ability of soils to remove NO_2, SO_2, and ethylene, as measured by the decline of the gas in question in the atmosphere inside a desiccator containing the soil in question in a petri dish. NO_2 concentration was reduced from 100 to 3 ppm in 24 hours. Autoclaving the soil "reduced the uptake to 13 ppm after 24 hours" (Arbeles et al. 1971), and this is interpreted by the authors as indicating a chemical rather than a microbial removal process. The authors extrapolate from these results to the conclusion that soil can provide a sink for 600 million tons of NO_2 per year. This would seem to correspond to about 75 gm NO_2/m^2/year, which is an extremely large value; we question the validity of extrapolating an annual rate based on the observation of a 24-hour rate.

Neither Hill nor Arbeles et al. have discussed the question of extrapolating their results obtained with extremely high values of pollutant concentrations to the lower concentrations characteristic of rural areas. Neither discusses the soil or vegetation variables that may determine uptake rates.



Source: Hill (1971)

FIGURE VI-16 UPTAKE RATES OF DIFFERENT POLLUTANTS BY AN ALFALFA CANOPY

E. ELEMENTS OF AN ANNUAL BUDGET OF NITROGEN

The nitrogen cycles in the atmosphere are complex. Information presently available regarding strengths of sinks and sources or even vertical abundance profiles is not adequate to the requirements of budget construction.

Therefore we shall not attempt to construct a balanced budget, but will confine our attention to a presentation of the ranges of values for the relevant abundances and exchange rates that have been presented in the literature or which might be inferred from available information. These are summarized in Table VI-17.

TABLE VI-17. - ELEMENTS OF AN ANNUAL BUDGET OF ATMOSPHERIC NITROGEN

	Nitrogen (Million Tons/yr)
N_2 ASSIMILATION	
Land Plants	1,600 - 2,400
Marine Plants	3,400 - 3,700
Land Bacteria and Fungi	1,700
Marine Animals and Bacteria	642
Total Land Assimilation	3,300 - 4,100
Total Marine Assimulation	4,042 - 4,342
N_2 FIXATION	
LOWER BOUND (Land Only)	
Combined Nitrogen Runoff	
Nitrate N (0.23 ppm)	7.4
Ammonia N (0.1 ppm)	3.2
Organic N (0.39 ppm)	12.6
Biogenic Emission	
As N_2	?
N_2O Stratospheric Sink	15 - 23
Total	38 - 46
UPPER BOUND (Land and Marine)	210
DELWICHE'S ESTIMATES	
Leguminous Crops	14
Fertilizer	30
Other Land	30
Marine	10
Total	84
N_2O EXCHANGE	
Stratospheric Sink	15 - 23
1.8-Year Lifetime	639
8-Year Lifetime	144

TABLE VI-17. - Continued

AMMONIA EXCHANGE	
Precipitation	
Land (0.1 - 0.2 ppm)	8 - 16
Ocean (0.05 - 0.1 ppm)	14 - 27
Robinson and Robbins (1970b)	150
Particulate Deposition	5 - 37.5
Gaseous Uptake	300 - 738
Total	327 - 1,253
NO_X EXCHANGE	
Fossil Fuel Combustion	16.1
Nitrate in Precipitation	
Land (0.05 - 0.1 ppm)	1.1 - 2.3
Ocean (0.025 - 0.05 ppm)	2 - 4
Robinson and Robbins (1970b)	75
Particulate Nitrate Fallout	0.5 - 19
NO_2 Dry Fallout (1 cm sec^{-1}, 0.5 - 1 ppb)	53 - 105
NO_2 Dry Fallout (1 cm sec^{-1}, 0.2 ppb)	20
Total	40 - 262

SOURCE: Discussed in text.

1. Nitrogen Assimilation

The annual biological turnover of nitrogen is a useful figure from which the gross dimensions of the biospheric transformation of nitrogen can be conceptualized. This consists of the nitrogen assimilated in primary (plant) production, and that assimilated in the production of animal and bacterial tissue of consumer organisms. Plant nitrogen assimilation on land has been estimated by Deevey (1970) as 162 kg/ha/yr for the 1.5 x 10^{10} ha of land surface. This corresponds to a total of 2430 million tons of nitrogen per year for land plants. A somewhat smaller amount--1600 million tons per year--has been estimated by a committee of scientists (GEP, 1971) on the basis of smaller values for land productivity than those used by Deevey. (See Table VI-18.) Ryther (1969) estimates the annual marine plant production to be 20 x 19^9 million tons of carbon. Using a mean phytoplankton nitrogen/carbon ratio of 0.17 (Redfield, Ketchum, and Richards, 1963), we may infer a marine plant nitrogen assimilation rate of 3400 million tons per year.

On land, relatively little of the organic carbon is consumed by grazing animals. Most of the plant production consists of wood produced in temperate and tropic forests, which is consumed by decomposer bacteria and fungi. According to Table VI-18, 1700 million tons of nitrogen per year is annually assimilated in microbial tissue production on land; we use this as the total, because production in the herbivore-carnivore food chain is low.

We have estimated the total marine productivity of herbivores and carnivores as 2570 million tons of carbon per year (Chapter III). This implies nitrogen assimilation of about 442 million tons per year, to which must be added the production of marine bacterial tissue, given as about 200 million tons per year in Table VI-18.

2. Nitrogen Fixation

A basic datum in any consideration of the biological influence on the composition of the atmosphere is the annual rate at which molecular nitrogen of atmospheric origin is biologically fixed. The preceding

TABLE VI-18. - ESTIMATE OF NITROGEN AND CARVON PRODUCTIVITY

(BILLION TONS PER YEAR)

	N	C	Bacteria and Fungi	Total	
				N	C
Land	1.6	56	1.7	3.3	56
Ocean	3.7	22	0.2	3.9	22
TOTAL	5.3	78	1.9	7.2	78

SOURCE: GEP (1971)

sections of this chapter have indicated how few data there are on which to base an estimate of N_2 fixation, since so many sources of fixed nitrogen are available to plants. We may approach the problem of generating such an estimate by considering bases for reasonable lower and upper bounds for global nitrogen fixation rates.

Hutchinson (1954) points out that the annual rate of weathering of nitrogen from the lithosphere is negligible, and that if the nitrogen in soils and in ground water is in balance--with nitrogen losses from the land compensated by biological atmospheric nitrogen fixation--then the annual rate of nitrogen fixation on land may be estimated from knowledge of the rate at which nitrogen is lost from it. He argues that under these assumptions, the annual rate of nitrogen fixation cannot be less than the annual rate at which combined nitrogen is transferred from the land to the ocean in continental runoff, which he estimates as 12 million tons per year as nitrate, ammonia, and organic N.

More recent information provides a basis for a new estimate of the runoff of combined nitrogen. Thus, Livingstone (1963) gives 1 ppm as the mean nitrate content of river water and 32.33×10^{15} liters per year as the annual total runoff, of which 120 ppm is the total dissolved solid content (excluding organic matter). Livingstone does not give the total ammonia content of rivers, but Feth (1966) points out that it may be high in some circumstances. We may employ Hutchinson's estimate of 0.1 mg/liter as the ammonia N content of rivers, and similarly follow him in estimating the organic N content as 3% of the total dissolved organic matter, which he gives as equal to 10% of the total dissolved salts, or about 12 ppm.

Nitrogen may be lost from the land in the form of molecular nitrogen of biological origin, or as N_2O and other gaseous nitrogen compounds. Some of these gaseous emissions are returned to the biosphere as combined nitrogen and consequently cannot be considered as "lost" for the purposes of estimating a minimum annual N_2 fixation rate. It is clear, however, that N_2O which reaches the stratosphere and is converted ultimately to N_2 is lost in this sense, and we therefore include the estimated 15 to 23 million tons of N per year which is removed by the stratospheric nitrous oxide sink. Totaling these figures, we arrive at a lower bound of N_2 fixation of about 38 to 46 million tons per year.

However, it should be pointed out that this lower bound assumes that soil and ground-water nitrogen is in a steady state; this assumption may be questioned. Thus, Feth (1966) points out that cultivation techniques appear to enhance the rate at which nitrogen bound in soil organic matter is released, and that a reduction in soil organic matter is a characteristic result of virtually all cultivation techniques. The nitrogen anthropogenically fixed in fertilizer almost certainly contributes to the nitrogen lost in continental runoff; however, the minimum annual rate of biogenic N_2 fixation presently occurring cannot be estimated by subtracting the present rate of fertilizer N fixation from the lower bound estimated here, since the latter is based on runoff data collected when different and largely unknown quantities of fertilizer were being used.

An upper bound for N_2 fixation may be derived from an estimate of the annual probable rate of fixation of N_2 in productive agricultural land. This has been estimated by Moore (1966) as 10^{11} molecules cm^{-2} sec^{-1}, corresponding to 200 million tons per year if averaged over the entire land surface. Since natural fixation rates are certainly less than those of productive agricultural land--especially in deserts and the arctic--this figure may be taken as a conservative upper bound for the land. To arrive at an upper bound for the globe as a whole, we must consider nitrogen fixation in the oceans. Although this is believed to occur, many authors argue that it is quantitatively negligible, on the ground that marine productivity has often been observed to be limited by the availability of nitrate, nitrite, or ammonia. (See, for example, Ryther and Dunstan, 1971.) Delwiche (1970) has estimated marine fixation at 10 million tons per year, and it would seem that the total global fixation rate does not exceed 210 million tons per year even though Delwiche's estimate is not an upper bound.

We may conclude on the basis of these arguments that the annual rate of N_2 fixation is probably somewhere between the lower bound of about 38 million tons and the upper bound of about 210 million tons, of which fertilizer production and combustion fixation of nitrogen constitute an unknown proportion. This range compares well with the global N_2 fixation rates estimated by Delwiche (1970), which are also listed in Table VI-17. Delwiche estimates the total natural fixation rate as 30 million tons on land and 10 million tons in the ocean. The former figure includes cultivated non-leguminous crops as well as uncultivated regions of the land surface. Anthropogenic activity has increased this rate of annual fixation by the growing of leguminous crops, which contribute an additional 14 million tons per year, and by the use of industrially fixed nitrogen in the form of fertilizers. Atmospheric nitrogen is also "fixed" in numerous combustion processes which produce NO and NO_2; Table VI-19 contains estimates of the annual rate of fixation of atmospheric nitrogen in these processes, which contribute a total of 16.3 million tons of fixed nitrogen per year.

3. Nitrous Oxide Cycling

Estimates of the annual exchange of nitrous oxide between the surface and the atmosphere may be based on the apparent lifetime of N_2O and the assumed tropospheric mass. If we assume that the mean concentration of N_2O is 0.26 ppm, the total tropospheric mass of N_2O-N is about 1150 million tons. Schutz et al. (1970) used evidence of declines in mixing ratio with altitude to infer vertical fluxes of N_2O and corresponding residence times, all of which turned out to be very high when compared with the estimated 50- to 77-year lifetime to be expected if the photochemical destruction of N_2O were its only sink. Thus, lifetimes based on vertical fluxes varied from 1.8 to 8 years. The observed variations in N_2O concentration are analogous to those of CO_2, and on this basis Schutz et al. speculated that its lifetime may be on the same order, and that under certain circumstances the soil may act as a sink for N_2O. A 10-year lifetime implies an annual exchange with the surface of about 115 million tons of N_2O-N.

TABLE VI-19. - WORLDWIDE URBAN EMISSIONS OF NITROGEN OXIDES

(T = SHORT TONS)

Fuel	Source	Fuel Usage	Emission Factor	NO_2 Emission ($T \times 10^{-6}$)	NO_2-N ($T \times 10^{-6}$)	NO_2-N (Metric Tons)
Coal	Power Generation	$1{,}219 \times 10^6$ T	20 lb/T	12.2	4.1	3.7
	Industrial	$1{,}369 \times 10^6$ T	20 lb/T	13.7	4.6	4.2
	Domestic/Commercial	404×10^6 T	5 lb/T	1.0	0.3	0.3
Petroleum	Refinery Production	$11{,}317 \times 10^6$ bbl	6 T/10^5 bbl	0.7	0.2	0.2
	Gasoline	379×10^6 T	0.113 lb/gal	7.5	2.5	2.3
	Kerosene	100×10^6 T	0.072 lb/gal	1.3	0.4	0.4
	Fuel Oil	287×10^6 T	0.072 lb/gal	3.6	1.2	1.1
	Residual Oil	507×10^6 T	0.104 lb/gal	9.2	3.1	2.8
Natural Gas	Power Generation	2.98×10^{12} ft^3	390 lb/10^6 ft^3	0.6	0.2	0.2
	Industrial	10.72×10^{12} ft^3	214 lb/10^6 ft^3	1.1	0.4	0.4
	Domestic/Commercial	6.86×10^{12} ft^3	116 lb/10^6 ft^3	0.4	0.1	0.1
Others	Incineration	500×10^6 T	2 lb/T	0.5	0.2	0.2
	Wood	466×10^6 T	1.5 lb/T	0.3	0.1	0.1
	Forest Fires	324×10^6 T	5 lb/T	0.8	0.3	0.3
				52.9	17.7	16.3

SOURCE: Adapated from Robinson and Robbins (1968)

4. Ammonia Exchange with the Surface

Space time variations in abundance of ammonia and the large variations in the quantities of ammonia which are apparently returned from the atmosphere to the surface in precipitation imply a relatively short lifetime and consequently large annual rates of atmospheric cycling of ammonia. We have found no estimates of the vertical abundance of ammonia, although Junge (1963) argues persuasively that it may decline rapidly with altitude. Recent observations at Mont-Louis Observatory in the French Pyrenees indicate that the maximum abundance above this site cannot exceed 0.05 ppb (Dionne, 1971). We have somewhat arbitrarily estimated the tropospheric load of NH_3-N as between 10 and 30 million tons; this corresponds to mean NH_3 concentrations ranging from 5 ppb (which might result from a surface level concentration of 10 ppb and a rapid decrease with altitude) to a mean concentration throughout the entire troposphere of 15 ppb, as suggested by Pate, Pitombo et al. (1971). The corresponding range is 12 to 36 million tons of NH_3. Ammonium is also present in the atmosphere in aerosols, estimated at 1 to 4 micrograms/m^3, which corresponds to 2.5 to 10 million tons NH_4^+-N, for a total of 12.5 to 40 million tons of N as NH_3 or NH_4^+.

Ammonia deposition in rain may be crudely estimated on the basis of the ranges cited by Junge (1963). These are 0.1 to 0.2 mg/liter in precipitation on land and half this amount in precipitation over oceans. The resulting totals for the globe are 27 to 54 million tons per year as NH_4^+ or 21 to 42 million tons as N. Much larger estimates of the total ammonium content of rain have been published by Robinson and Robbins (1968, 1970a), who cite Eriksson (1952) as the source of the data on which they base estimates of 2800 million short tons of ammonium in precipitation. This estimate is apparently based on an error; in a subsequent publication, Robinson and Robbins (1970b) give the total content of ammonium in precipitation as 213 short tons per year, which by our calculations is equivalent to 150 million metric tons N per year. This corresponds to a mean ammonium content in precipitation of 0.43 mg/liter.

Ammonia is also returned to the surface by means of particulate (aerosol) deposition and by direct gaseous uptake by vegetation and soil surfaces. Robinson and Robbins (1968, 1970a, 1970b) have estimated the latter as totaling about 25% of the deposition in precipitation, but the basis for this estimate is obscure. This corresponds to 37.5 million tons of N if we employ the revised precipitation estimates of Robinson and Robbins (1970b), or about 5 to 10 million tons if we employ the lower precipitation deposition estimates cited above.

Vegetation and soil uptake of ammonia has been estimated by Robinson and Robbins (1968, 1970a, 1970b) as corresponding to 900 million short tons of NH_3 per year, assuming a mean deposition velocity of 1 cm sec^{-1} and a mean concentration of 6 ppb. This corresponds to 738 million tons per year as nitrogen, which we consider rather high. One study of the uptake of NH_3-N by soils showed that in a highly polluted atmosphere which averaged 75 ppb NH_3, the soil gained 20 to 70 kg/ha/year, which corresponds to a deposition velocity of 0.13 to 0.4 cm sec^{-1}. Hanawalt (1969a, 1969b) studied the influence of soil properties and temperature and air movement on the uptake of gaseous ammonia by various soils. The maximum rate of uptake observed by him corresponds to a deposition velocity of about 1.3 cm sec^{-1}, but the velocities most commonly encountered were in the range 0.1 to 0.5 cm sec^{-1}. This evidence suggests that the mean deposition velocity employed by Robinson and Robbins may be unrealistically high. On the other hand, their estimates of the mean concentration of gaseous ammonia near the ground may be too low. A mean concentration near the ground of 10 ppb and a deposition velocity of 0.3 cm sec^{-1} would yield an annual global uptake of about 300 million tons of NH_3-N.

According to the above estimates, a total of 327 to 1253 million tons of nitrogen is exchanged annually as NH_3, assuming that none of the atmospheric ammonia is returned to the surface in any other form of nitrogen. The corresponding lifetimes of tropospheric NH_3 and NH_4^+ are 4 to 44 days.

5. NO, NO_2 and Nitrate in Atmospheric Circulation

We assume that the primary pathway for the circulation of biogenic NO involves conversion in the atmosphere to NO_2, which may then be directly absorbed by the soil or converted to nitrate and returned in precipitation or by means of nitrate particulate fallout. We may also assume that anthropogenic NO_x has the same fate in the atmosphere. Table VI-19 lists major sources of pollutant NO_x (listed there as equivalent to NO_2). These total about 16 million tons of N per year.

Pate, Pitombo, et al. (1971) have suggested a tentative tropospheric mean abundance of NO and NO_2 of about 0.5 ppb, based on their measurements of these gases at ground level. Because both of these gases are very short-lived and may be expected to be concentrated near the surface, the total atmospheric load may be only about one third of the ground-level concentration. The resulting tropospheric loads of NO_2-N and NO-N are 0.35 to 1 million tons each.

The nitrate content of precipitation varies widely. Junge (1963) suggests that precipitation nitrate concentrations average about half the ammonium concentration, or 0.05 to 0.1 mg/liter for precipitation over the land and half this amount for precipitation over the oceans. The result is a modest total of 3.1 to 6.3 million tons per year as nitrogen, which contrasts sharply with an estimate of 1130 million tons nitrate-N in precipitation published by Robinson and Robbins (1968, 1970a), cited as being based on Eriksson's (1952) estimate of 9 $mg/m^2/yr$ as the global mean nitrate content of precipitation. This estimate was revised in Robinson and Robbins (1970b) to 75 million tons nitrate-N.

Robinson and Robbins (1968, 1970a, 1970b) estimate nitrate particulate fallout at 25% of the nitrate precipitation deposition, which corresponds to 0.5 to 19 million tons N per year, depending on which precipitation nitrate estimate is employed.

Dry deposition of gaseous NO_2 has been estimated by Robinson and Robbins by using a deposition velocity of 1 cm sec^{-1} and a concentration of 1 ppb, which corresponds to 350 million tons per year of NO_2 or

105 million tons per year as N. Lower mean concentrations suggested by Pate, Pitombo, et al. (1971) imply a deposition of half this amount.

If the only route for the removal of NO is the removal of the NO_2 formed from it in the atmosphere, and the latter occurs only through dry deposition as NO_2 and precipitation and dry fallout of nitrate, then the total NO_x circulation appears to be between 40 and 262 million tons per year. The corresponding lifetime is between 0.5 and about 6 days.

Alternative estimates of the circulation of NO and NO_2 can be based on the mean atmospheric load of NO and an assumed average lifetime. The diurnal variations observed by Ripperton, Kornreich, and Worth (1970) indicate a lifetime on the order of 1 day, or an annual circulation of NO-N on the order of 128 to 365 million tons per year. However, the frequent failure to detect any NO_2 at ground level in locations remote from combustion sources or temperate zone agricultures --the Antarctic and tropical forests* --suggests that ground-level means may be about 0.2 ppb or less. If this is the case, the fact that both NO and NO_2 have very short lifetimes would imply that our estimates of the mean tropospheric load are generous and the total annual circulation is less than calculated. Thus, the quantitatively most effective mechanism for atmosphere-surface transfer appears to be dry deposition of NO_2, estimated on the basis of a mean ground-level concentration in the range of 0.5 to 1 ppb and a deposition velocity of 1 cm sec^{-1}. A ground-level concentration of 0.2 ppb would reduce the minimum estimate of the total natural circulation of biogenic NO_x to less than 25 million tons N per year.

F. CONCLUSIONS

(1) All the important nitrogen-containing trace gases in the atmosphere are biologically cycled, but estimates of the quantities of molecular nitrogen, nitrous oxide, ammonia,

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*See Wartburg, Pitombo, Pate, et al. (1970); Fisher, Lodge, Wartburg, and Pate (1968); and Pate, Pitombo, Wartburg, et al. (1971).

nitric oxide, and nitrogen dioxide in circulation are extremely uncertain. The ranges of the available estimates, in million tons N per year, are: N_2, 38 to 210; N_2O, 20 to 640; NH_3, 327-1253; NO_x, 56 to 200.

(2) The biological processes which implement the cycling of nitrogen in nature are understood only in outline. Few quantitative data regarding the magnitude of the various nitrogen cycles are available, and there is little information regarding the environmental and biological factors which influence the direction and magnitude of the biological transformation of nitrogen.

(3) Most nitrogenous constituents in the atmosphere appear to vary in concentration widely in space and time, but observations of their concentrations are scanty. In particular, lack of information regarding the vertical abundance of all the trace constituents precludes reliable estimates of the lifetimes and annual exchange rates.

(4) All the gaseous and particulate nitrogen compounds are present in the atmosphere in very small quantities, except for N_2O, which is difficult to measure reliably. Extremely sensitive and reliable measurement techniques are therefore needed to gather the information on which accurate budgets must be based.

(5) Some of the uncertainties regarding the nature and magnitude of biological cycling of atmospheric nitrogen compounds could be resolved with better information regarding the quantity and chemical form of nitrogen in precipitation and continental runoff, and by an improved understanding of the manner in which gaseous ammonia, nitrous oxide, and nitrogen dioxide are removed from the atmosphere by vegetation and soils.

(6) At present, the most interesting questions regarding the sources and sinks of these compounds appear to be:

- Is there a marine source for NH_3 and, if so, what is its strength?
- What is the lifetime and abundance profile of NH_3 in the atmosphere?
- Under what conditions is NO (and possibly NO_2) released from the soil? What is its annual rate of release and atmospheric lifetime, and is the background biogenic cycle of NO large compared with the anthropogenic injection of NO_x?
- Is there a tropospheric sink for N_2O?
- What is the role of biogenic nitrogen compounds in the removal of pollutants from the atmosphere?

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VII. SULFUR COMPOUNDS

A. OVERVIEW

Sulfur is present in the atmosphere as H_2S and SO_2 in gas form and as SO_4^{--} and "ammoniated sulfate" in liquid or dry aerosols. H_2S has apparently been undetected in unpolluted environments but is presumed to occur in the atmosphere as a biogenic precursor to sulfur dioxide and sulfates. Measurements of SO_2 are scanty and indicate very low natural background levels near the ground of 1 ppb or less. Sulfur as sulfate in aerosols has been reported in concentrations of 2 to 8 $\mu g/m^3$ in the lower troposphere. Neither the abundance profiles nor the tropospheric lifetimes of H_2S and SO_2 are well known, but recent evidence suggests that both compounds may be short-lived. The lifetime of SO_2 depends on the concentration of ammonia (NH_3 and NH_4^+ in aerosols) and the humidity.

The biogeochemical cycle of sulfur is simple in outline. The largest mobile reservoir is the ocean, which contains about 1220 x 10^{14} tons of sulfur as sulfate. In the lithosphere, sulfur is present in both primary and sedimentary rocks. It is concentrated in the sedimentary rocks, having been deposited from the ocean as sulfides partly through the action of anerobic processes, and as evaporites produced when seawater evaporated and its salts were precipitated. In the basic geochemical cycle, sulfur is weathered from the crust, carried to the ocean as sulfate in continental runoff, and then deposited in marine sediments as sulfides or evaporites. In addition, some sulfur is cycled from the ocean to the land as sea salt particles formed by the action of breaking waves and then carried inland by winds.

Studies of these sulfur sources indicate that the amounts of sulfur carried as sulfate from the land to the ocean are too large to be the result of weathering and the precipitation of sea salt particles, even when the sulfur anthropologically injected into the cycle--industrial sulfuric acid, products of the combustion of fossil fuel, and other industrial processes--are taken into consideration. The origin of this "excess" sulfate is not known with certainty, although biological sources are implicated by available indirect evidence.

In certain anoxic environments sulfate may be reduced to H_2S by sulfur-reducing bacteria in the oxidation of organic matter. If this H_2S reaches the atmosphere, it will be oxidized to SO_2. This mechanism is offered to explain the presence of "excess sulfate" in rain and continental runoff, as well as the presence of sulfur dioxide in remote, unpolluted regions. Biological sulfate reduction results in fractionation of the sulfur isotopes, producing hydrogen sulfide with a higher proportion of ^{32}S than the sulfate substrate. Studies of the isotopic composition of sulfate in rainwater have indicated that not all of the sulfate is derived from sea salts; fossil fuel combustion is not ruled out as a contributing source. Sulfur in fossil fuels shows a broad range of isotopic distributions and often is nearly as light as biogenic H_2S. Further studies of the isotopic distribution of rain collected in circumstances which eliminate pollutant sources should clarify the role of biological sulfate reduction in the cycling of atmospheric sulfate.

Even if biological sulfate reduction is the source of excess sulfur cycled in the atmosphere, much of this may be the indirect result of organic pollution of estuaries and coastal regions, or enhanced organic production caused by cultural euthrophication. Both types of pollution can produce the anoxic conditions necessary for the initiation of biological sulfate reduction and a supply of organic material to be metabolized by the sulfate-reducing bacteria. If the H_2S produced reaches the atmosphere, it could be carried back over land and ultimately removed as excess sulfate in precipitation.

One study of the composition of rivers draining the continents shows that about two-thirds of the sulfate sulfur (15 out of 21 million tons per year) in European rivers sampled between 1848 and 1906 was excess sulfate. In contrast, analyses of Asiatic, South American, and African runoff conducted in this century show no excess sulfate in the runoff from these non-industrialized continents. This suggests that the excess sulfate is a consequence of the industrialization prevalent in Europe at the time;

but since fossil fuel consumption was low and chemical fertilizers essentially unknown, the excess sulfate cannot have been derived from these sources. The inference is that organic or nutrient pollution is responsible for promoting biological sulfate reduction in near-shore marine environments.

Sulfur has been detected in rain at sea and in cloud water from clouds originating at sea in quantities which are too large to be derived from sea salt, where the latter is estimated on the basis of the measured chlorine content of the water and the known ratio of sulfate to chlorine in the sea. This implies either that (1) sea salt particles are enriched in sulfur with respect to chlorine by a natural mechanism acting during their formation, or (2) the excess sulfur is from biogenic marine sources present in the open sea. Both alternatives have been advocated, and there is at present insufficient evidence to choose between them. H_2S is rapidly oxidized in oxygenated water, and the likelihood that H_2S produced below the surface of the ocean can survive even a short transit of oxygenated water to be injected into the atmosphere seems remote. Better information regarding the spatial and temporal distributions of H_2S or SO_2 over the ocean would be extremely useful in clarifying this question of marine sources of sulfur dioxide, as would isotopic studies of rain and cloud water collected from unpolluted marine air masses.

Several estimates of the annual total sulfur in circulation have been made. These are of questionable value, since they are all based on very partial information, and the abundances and lifetimes of sulfur compounds in the atmosphere are not well known. Present information suggests that the H_2S level does not exceed 0.5 ppb in unpolluted environments and that it is very short-lived, producing SO_2 by oxidation with O_2 or being absorbed directly by vegetation, soil, or water surfaces. Recent estimates for the tropospheric abundance of SO_2 vary from 0.5 to 2 ppb. SO_2 may be converted into aerosols by particle-forming reactions with ammonia in the atmosphere or by reaction with aerosols or dry particles to produce ammoniated sulfate particles. Aerosols may be removed from the air by rain or may sediment out of the air if they are large enough, or may impact on vegetation. Sulfur dioxide may be taken up by soils or by vegetation, either by reaction with damp surfaces of leaves or by uptake through the stomata of respiring leaves. This diversity of estimates of composition and of mechanisms for the transfer of sulfur compounds from the atmosphere to the surface makes it very difficult to estimate the magnitude of the annual cycle; on the basis of present information, the amount is somewhere between 200 and 800 million tons per year. Anthropogenic sources of atmospheric SO_2 are about 68 million tons S per year, and sea salt injection could account for an additional 44 to 400 million tons.

B. TERRESTRIAL RESERVOIRS

The distribution of sulfur in terrestrial reservoirs is shown in Table VII-1. The ocean represents a very large reservoir of sulfur as sulfate, but most of the sulfur is in the lithosphere. Only very minor amounts are present in the biosphere or atmosphere at any one time.

Table VII-2 shows the distribution of sulfur in the lithosphere and its isotopic composition in terms of the distribution of ^{34}S and ^{32}S. This is expressed as the value of $\delta\ ^{34}S$, which is the difference between the $^{34}S/^{32}S$ ratio of the sample and that of a standard (troilite from Canyon Diablo Meteorite), normalized and expressed as parts per mil (o/oo). Thus,

$$\delta\ ^{34}S\ (o/oo) = \frac{^{34}S/^{32}S\ \text{sample} - ^{34}S/^{32}S\ \text{std}}{^{34}S/^{32}S\ \text{std}} \times 1000$$

The isotopic composition of various terrestrial reservoirs is shown in Figure VII-1.

The major geochemical cycle of sulfur is evident from these two tables: sulfur weathered from rocks is transported to the sea, where it is deposited either in shale-forming sediments in the ocean bottom or as evaporites precipitated from evaporating ocean brines. The sharp difference between the mean $\delta\ ^{34}S$ of these two kinds of sedimentary rock indicates that processes with significantly different isotopic fractionation characteristics are involved. The precipitation of sulfur as iron

TABLE VII-1. - SULFUR RESERVOIRS

	Million Metric Tons S	
Lithosphere		
Sedimentary rocks, including connate water	8,800,000,000	(a)
Continental igneous and metamorphic rock	6,700,000,000	(a)
Deep ocean mafic rocks	2,332,000,000	(a)
Land		
Soil (organic and inorganic)	28,000	(b)
Plant biomass	2,100	(c)
Animal biomass	30-60	(d)
Lakes and streams (as SO_4^{--})	83	(e)
Groundwater (as SO_4^{--})	825	(e)
Marine		
Sulfate	1,220,000,000	(f)
Ocean biomass	23	(g)
Dead organic matter	35,000 to 130,000	(h)
Atmosphere (troposphere)		
H_2S	Less than 2.4	(i)
SO_2	1.6 to 6.2	(i)
Sulfate aerosols	5.6 to 26	(i)

[a] Hosler and Kaplan (1966).

[b] We assume an average soil depth of 30 cm for the entire earth and a mean concentration of 700 ppm, as given by Bowen (1966).

[c] The dry biomass of the land is 3×10^6 million tons, and the proportion of S is 7×10^{-4}, as given by Deevey (1970).

[d] Derived from the nitrogen estimates in Chapter VI and the assumption that the ratio of nitrogen to sulfur is 7:1 by weight.

[e] Assumes mean composition of lakes and streams given by Livingstone (1963).

[f] From data of Turekian (1969).

[g] GEP (1971).

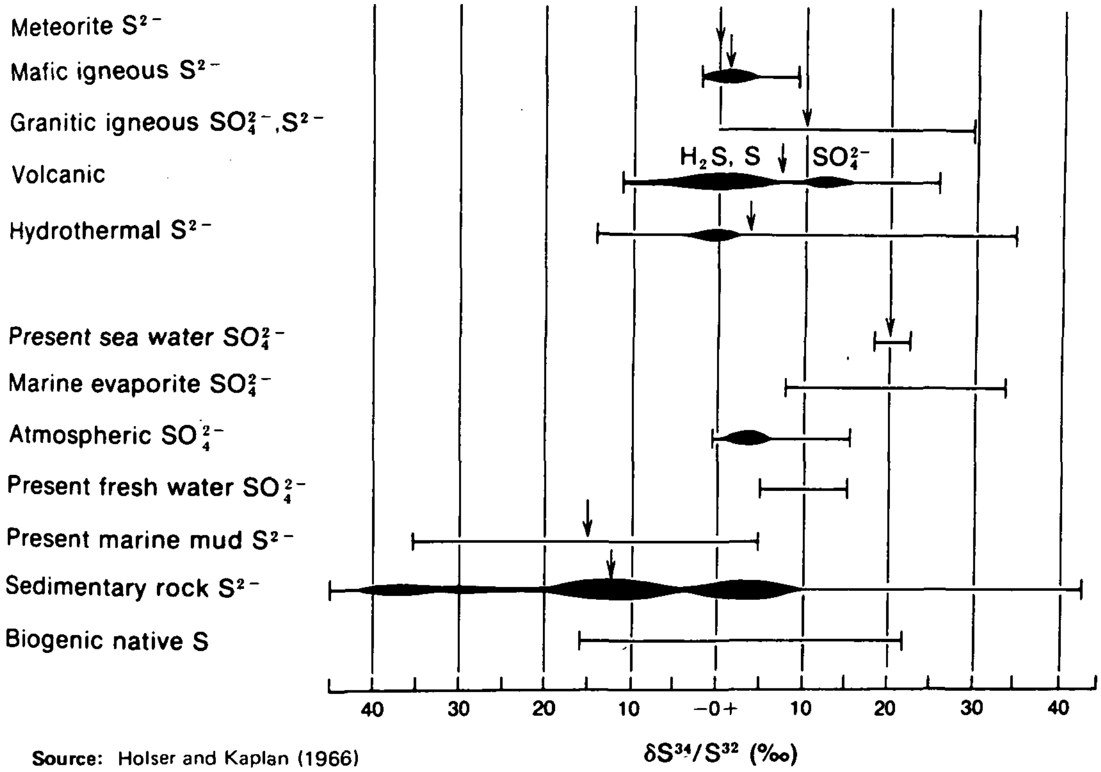
[h] Very uncertain; derived from figure for nitrogen in dead organic matter, using nitrogen:sulfur ratio of 7:1.

[i] Atmospheric abundances calculated as follows: $H_2S < 0.5$ ppb; SO_2, 0.5-2 ppb; aerosols 1.6 to 8 μg S/m^3.

TABLE VII-2. - SULFUR INVENTORY IN LITHOSPHERE

ROCK TYPE	MASS OF ROCK $(10^{15}T)$	S CONTENT (%)	MASS OF S $(10^{12}T)$	$\delta^{34}S$ (o/oo)	EXCESS ^{34}S (o/oo)
Deep Ocean					
Sediments	300	.025	75	+20 ± 1	+1.5
Mafic (to Moho)	4,400 ± 1,100	.053 ± .013	2,332 ± 800	+1 ± 2	+2.3 ± 5
Sedimentary Rocks					
Sandstone	280 ± 70	.090 ± .01	252 ± 60	-12 ± 5	-3.0 ± 1.5
Shale	750 ± 190	.27 ± .04	2,025 ± 580	-12 ± 5	-24 ± 13
Limestone	290 ± 80	.13 ± .01	380 ± 110	-12 ± 5	-4.6 ± 2.3
Evaporites	30 ± 12	17.0 ± 4	5,100 ± 1,600	+17 ± 2	+87 ± 30
Volcanics	120 ± 30	.4 ± .01	50 ± 18	+5 ± 5	+.2 ± 0.2
Connate Water	140 ± 30	.019 ± .02	27 ± 5	+ 17 ± 2	+.5 ± 0.1
Total Sedimentary	1,600 ± 220	.49 ± .13	8,800 ± 1,700	+7.1 ± 4.5	+55 ± 33
Continental Igneous and Metamorphic Rocks					
Granitic	10,500 ± 2,600	.021 ± .003	2,205 ± 600	+10 ± 1	+22 ± 12
Mafic	8,700 ± 2,200	.053 ± .013	4,600 ± 1,600	+1 ± 2	+4.6 ± 9
TOTAL	21,000 ± 3,000	.032 ± .005	6,720 ± 2,500	+4 ± 3	

Source: Adapted from Hosler and Kaplan (1966)



Source: Holser and Kaplan (1966)

Arrows indicate the mean values.

FIGURE VII-1 ISOTOPIC GEOCHEMISTRY OF SULFUR pyrites entails the biological reduction of marine sulfate, which in turn results in a large fractionation favoring the lighter isotope in the sulfide. In contrast, the precipitation of $CaSO_4$ (gypsum and anhydrite) involves virtually no fractionation (Ault and Kulp, 1959; Thode, Monster, and Dunford, 1961; Holser and Kaplan, 1966). Therefore, the isotopic ratio of sulfur in evaporites reflects the isotopic distribution of the ocean from which they precipitated, whereas that of precipitated iron pyrites (FeS_2) and related iron-sulfur compounds reflects biological fractionation effects as well as the isotopic composition of the sulfate substrate involved.

Although sedimentary rock is the largest reservoir of sulfur, sedimentary sulfur is exchanged with other reservoirs very slowly. Estimates of the mean rate of weathering of sulfur at the present time and during "representative" periods in geologic history are difficult to determine, since human activity may have accelerated the rate of weathering (Gregor, 1970), and accurate estimates of the distribution of sulfur-containing rocks subjected to weathering are not available. The most recent estimate of the present rate of weathering of sulfur is that of Berner (1971b), who concludes that about one-third of the sulfate in river water (43 million tons per year as S) is derived from the weathering of rocks. Of this, pyrite weathering accounts for one third and the weathering of calcium sulfate minerals the remainder. This estimate assumes that the ratio of pyrite to calcium sulfate in the crust is 1:2 and that the measured Ca^{++} in river runoff reflects the amount of Ca^{++} weathered. Berner employs Livingstone's compilation of chemical analyses of rivers of the world (Livingstone, 1963) in making this estimate. For the most part, these analyses were conducted prior to the great increase in industrial fossil fuel consumption which occurred in the last two decades.

Inorganic soil reservoirs of sulfur consist of sulfate in soil water; organic soil sulfate is primarily in the form of resistant humus (Bowen, 1966). The plant biomass contains relatively little sulfur--averaging only 0.07% of the dry weight (Deevey, 1970)--because it is made up largely of cellulose. The estimate for sulfur content of animal biomass is derived from that for nitrogen, on the assumption of a ratio of 7:1 nitrogen to sulfur by weight, which is approximately that of protein. (Most of the nitrogen and sulfur in animal tissue is in the protein.)

The estimate of the sulfur content of dissolved organic matter is very uncertain. We have found no analyses of sulfur in dissolved organic matter, but we assume it is present in the resistant fraction at a fairly constant ratio in proportion to the nitrogen. We have arbitrarily used the 7:1 ratio and applied it to the figures given for nitrogen in Chapter VI.

The sources of the estimates of the atmospheric loads of sulfur compounds are given in later sections of this chapter.

C. BIOLOGICAL PROCESSING

1. Use and Distribution

Sulfur is present in the biosphere in relatively minor quantities although it is essential to all living organisms. Sulfur is an element in some amino acids and hence essential for the production of proteins. It is also present in a number of small organic molecules.

The concentration of sulfur in organisms depends largely on their protein content. The average concentration in the land biomass is small, because most of this mass is composed of cellulose in the trunks and branches of trees. In Table VII-1 we have assumed the weight of sulfur relative to the dry biomass to be 0.07% for land plants (Deevey, 1970) and 0.7% for marine organisms (Bowen, 1966). Dead organic matter in the oceans contains large quantities of organic nitrogen and probably also some sulfur, although we have found no analyses of the sulfur content of this material. We have estimated a range of organic sulfur in marine detritus by employing the figures given for nitrogen and an assumed nitrogen/sulfur ratio of 7:1. In marine plants this ratio is about 1.3:1, while in marine animals it may be as high as 8:1 (Bowen, 1966).

Sulfur is present in soils, both as sulfate in soil water and as organic sulfur (largely amino acids and various sulfate esters). Plants normally use sulfate as a source of sulfur for growth, but can also assimilate amino acids, whereas higher animals (with the exception of ruminants) require organic sources of sulfur. Many microorganisms can assimilate sulfur as sulfide, sulfite, thiosulfate, elemental sulfur, or in other forms.

2. Assimilatory and Respiratory Metabolism

In considering the biological transformations of sulfur compounds, it is conceptually useful to distinguish assimilatory from respiratory sulfur metabolism.

Assimilatory metabolism entails the incorporation of sulfur into tissue by reducing the sulfate to an -SH group, which is then used in forming various essential compounds. The reverse of assimilation is mineralization or decomposition, in which tissues are transformed into simpler compounds and ultimately into minerals. This process results in the formation of sulfate if it is carried through to completion, or the production of relatively simple organic sulfur compounds which are then reassimilated by plants or animals. Assimilatory metabolism of sulfur is not particularly relevant to the present study, because relatively little of the sulfur assimilated is exchanged with the atmosphere. The amount of sulfur cycled annually (estimated on the basis of the carbon/sulfur ratios in terrestrial and marine plants and annual productivity) is about 100 million tons per year for the land and 380 million tons per year for the ocean.

More interesting sulfur transformations are involved in respiratory metabolism of the sulfur bacteria, where the oxidation state of sulfur is changed in the process of providing metabolic energy. Sulfur-reducing bacteria utilize sulfate as a source of oxygen for oxidation of metabolizable organic compounds and produce H_2S as a by-product. Some of the sulfur may be assimilated by the organism, but most is excreted into the environment in the form of H_2S. Other sulfur bacteria oxidize reduced compounds--usually H_2S and S, although other relatively reduced forms of sulfur are utilized by some organisms--producing sulfate as a by-product. While sulfur reduction occurs in anaerobic environments and sulfur oxidation generally occurs in aerobic environments, one subset of sulfur bacteria (the green and purple photosynthetic sulfur bacteria) oxidizes sulfur compounds anaerobically, using H_2S or S as an electron acceptor in the presence of light to reduce CO_2. The primary interest in these transformations is the fact that they utilize inorganic sulfur and require anoxic environments, in that they either entail or depend on the anaerobic production of H_2S. These processes are of considerable geochemical importance and are intimately involved in the atmospheric cycle of sulfur compounds. They may also have a significant role in the regulation of atmospheric oxygen and, perhaps, of atmospheric carbon dioxide.

3. Geochemically Important Biological Sulfur Transformation

a. Sulfate Reduction

Sulfate reduction occurs only in anaerobic environments, where it is carried on by the action of sulfate-reducing bacteria of the genus *Desulfovibrio*. It occurs in waterlogged soils and in freshwater and marine environments where oxygen levels can be reduced to zero and the circulation is inhibited so that anoxic conditions can be maintained. Given water with an initially high oxygen tension and adequate supplies of organic matter, the process is as follows:

(1) Aerobic metabolism reduces the oxygen tension to zero, and ferric iron is simultaneously reduced to ferrous iron. This requires that the system be isolated from additional sources of oxygen. This process occurs in freshwater lakes in summer during thermal stratification, when the temperature structure inhibits mixing of oxygen-rich surface waters with bottom waters. It also occurs in both marine and freshwater muds if the grain of the sediments is very fine, since the exchange of "interstitial" water in the muds with the water column above it is slow, and oxygen enters only by diffusion. In some marine and freshwater environments, the shape of the basin may also tend to reduce the mixing with surface waters. The oxidation of organic matter is as follows:

$$CH_2O + O_2 \rightarrow CO_2 + H_2O;$$

$$NH_3 + 2\ O_2 \rightarrow HNO_3 + H_2O$$

(2) After the oxygen level has been reduced to zero, biological nitrate reduction proceeds, removing nitrate:

$$5\ CH_2O + 4\ HNO_3 \rightarrow 5\ CO_2 + 2\ N_2 + 7\ H_2O$$

$$5\ NH_3 + 3\ HNO_3 \rightarrow 4\ N_2 + 9\ H_2O$$

(3) If metabolizable organic material remains, sulfate-reducing bacteria utilize SO_4^{--} to oxidize organic matter according to the following overall reactions:

For carbohydrates--

$$2\ CH_2O + H_2SO_4 \rightarrow 2\ CO_2 + H_2S + 2\ H_2O$$

For amino acids--

$$4\ CH_2NH_2COOH + 3\ H_2SO_4 \rightarrow 3\ H_2S + 4\ NH_3 + 4\ H_2O + 8\ CO_2$$

The NH_3 is not oxidized.

Sulfate reduction continues until the organic matter supply or the sulfate supply is exhausted, or until modification of the circulation pattern restores oxygen. The H_2S produced will rapidly react with available ferrous iron, producing ferrous sulfide (FeS), which precipitates. The production of ferrous sulfide is limited by the availability of reactive iron. The H_2S may diffuse upward in the water column until it encounters oxygenated water; where it is rapidly reoxidized, first to sulfite and ultimately to sulfate; alternatively, oxidation to sulfate may be performed by sulfur-oxidizing bacteria. If light is available, anaerobic oxidation of H_2S by photosynthetic sulfur bacteria may produce free sulfur, which is either excreted into the environment or stored intracellularly as granules (see below).

With the exception of lakes that are polluted with industrial sulfuric acid, freshwater and soil water tend to be relatively low in sulfate

(3.7 and 5 ppm); thus, freshwater sulfate reduction is usually sulfate-limited (Hutchinson, 1957; Stuiver, 1967). In contrast, marine environments contain a virtually unlimited supply of sulfate (905 ppm) that is constantly resupplied by the diffusion of seawater from the overlying water column. Any oxygen that may diffuse downward with the sulfate reacts with the H_2S to produce more sulfate, which in turn can be recycled. Sulfate reduction ceases when usable organic matter supplies are exhausted. (Holser and Kaplan, 1966; Berner, 1964, 1971a.)

H_2S is highly toxic to most benthic organisms. If the conditions of stagnation and/or the supply of organic matter are sufficient to permit sulfur reduction in the bottom waters (as opposed to the mud-water interface) extensive kills of benthic organisms may result. This provides additional organic matter to support continued sulfate reduction. Fonselius (1970) has pointed out that once sulfate reduction begins in the bottom waters, natural conditions are very difficult to restore; the volume of anaerobiosis may increase for some time before turnover restores oxygenated conditions. This restoration may be only temporary, as the turnover, in addition to supplying oxygen to the bottom, mixes the bottom waters with the surface. This causes H_2S poisoning of marine life until the H_2S is oxidized. It also brings nutrients to the surface, which in turn support a bloom of organic matter. The organic matter produced during the bloom eventually settles to the bottom, and the cycle begins again. Areas in the Baltic Sea are now in the process of cycling in this fashion (Fonselius, 1970).

b. Isotopic Fractionation During Sulfate Reduction

Bacterial sulfate reduction is accompanied by a relatively large isotopic fractionation whereby the sulfide is considerably enriched in ^{32}S. In the laboratory the reduction of $^{32}SO_4^{--}$ to hydrogen sulfide has been found to be about 2% faster than the reduction of $^{34}SO_4^{--}$ at 32°C (Nakai and Jensen, 1964); the fractionation effect varies with temperature, being faster at lower temperatures (Kemp and Thode, 1968).

In nature the amount of fractionation will depend upon the availability of additional supplies of sulfate. In a closed system, the ^{32}S

in the substrate will be preferentially transformed to H_2S, a process which results in depletion of light sulfur in the substrate and its preferential incorporation in the product. With time, the difference between the substrate and the product increases, although the product may become somewhat heavier as supplies of light sulfur in the substrate are depleted.

This prediction was experimentally confirmed by Nakai and Jensen (1964), who observed biological reduction in a closed system with a limited supply of substrate. Fractionation factors increased from 1.043 during the early phase of the experiment to 1.062 after 70 days. During this period the sulfate content decreased from 300 mg/l of medium to 10; the $\delta^{34}S$ values of the sulfate were +30.7 o/oo and +56.6 o/oo, while the sulfide $\delta^{34}S$ values were -12.0 and -5.3, respectively. If the available sulfate substrate were constantly replenished and the ^{32}S:^{34}S ratio of this sulfate is constant, then the fractionation will not vary with time.

A wide range of fractionation factors have been observed between sulfides and associated sulfates in natural environments. Sulfides in Gulf Coast salt domes were observed to be enriched from 24 to 56 o/oo, while marine waters and sediments have yielded enrichments of 15 to 62 o/oo (Kemp and Thode, 1968).

Recently, Smejkal, Cook, and Krouse (1971) summarized studies demonstrating that the fractionation effects are species-dependent and that the overall fractionation effect may consequently be due to factors which determine the local abundances of species performing the reduction. In experiments with microorganisms isolated from thermal springs in western Canada, they found that the fractionation effect was essentially negligible, while in other experiments the reduction of $^{32}SO_4^{--}$ was up to 4% faster than the reduction of $^{34}SO_4^{--}$.

c. Sulfur Oxidation

A number of species of bacteria are known to oxidize reduced sulfur compounds in the presence of free oxygen, in many cases at rates which are dependent on the oxygen concentration. Some of these oxidize H_2S to S^0, which may then be stored intracellularly as sulfur granules until the supply of H_2S is depleted, at which time the S^0 is oxidized to H_2SO_4.

Some strains also oxidize other reduced forms of sulfur such as thiosulfate. Although most sulfur-oxidizing strains are aerobic, at least one species--Thiobacilli denitrificans--can oxidize sulfur anaerobically in the presence of nitrate. The reaction, as delineated by Stephenson (1949), is:

$$6\ KNO_3 + 5\ S + 2\ CaCO_3 \rightarrow 3\ K_2SO_4 + 2\ CaSO_4 + 2\ CO_2 + 3\ N_2$$

H_2S is also oxidized by purple and green photosynthetic sulfur bacteria.

An additional reaction which appears to be of some geochemical importance is the oxidation of pyrite (FeS_2) to sulfuric acid. Nakai and Jensen (1964) studied the oxidation of both pyrite and native sulfur to sulfate by Thiobacillus thiooxidans. They found that the oxidation of native sulfur was very fast relative to the abiological oxidation rate, but that the oxidation of pyrite was much slower than the oxidation of sulfur. A very slight biochemical fractionation was observed in both reactions.

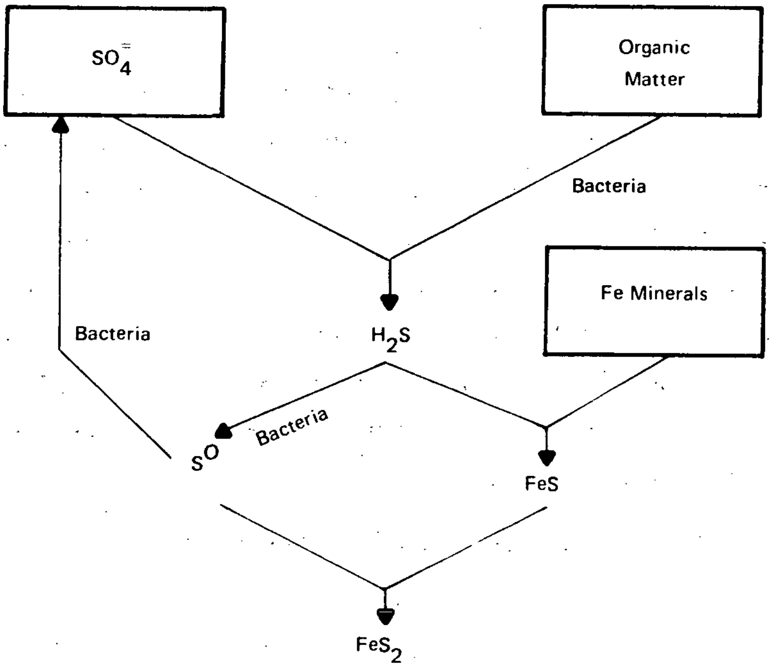
D. GEOCHEMICAL EFFECTS OF BACTERIAL TRANSFORMATIONS

1. Pyrite Formation and Deposition

Virtually all the sulfur in the sediments has undergone biological transformation at some point in time, and much of it has been through numerous biochemical processes. This statement is supported by the fact that the majority of the sedimentary sulfur deposits show strong fractionation of sulfur of a kind which can be explained only as the result of biochemical processes that favor the light isotope. In general, deposits of reduced sulfur are lighter and deposits of oxidized sulfur are heavier than the mean, and therefore also heavier than primordial homogeneous sulfur may be presumed to have been.

This fractionation is attributed to the action of sulfate-reducing bacteria. The latter produce isotopically light H_2S and S^0, which abiogenically converted to FeS_2 (pyrite). As a consequence, deposits of reduced sulfur in shale, limestone, and sandstone are light (mean $\delta\,^{34}S =$ -12), while those of calcium sulfate (gypsum and anhydrite) in evaporites tend to be heavy (mean $\delta\ ^{34}S = +17$). (See Figure VII-1 and Table VII-2.)

Figure VII-2 shows the process by which iron pyrite (FeS_2), the major sedimentary sulfide, is produced. The preliminary sulfate reduction step occurs in anoxygenic environments where organic matter is plentiful. If reactive iron is present, the first step is the production of black iron monosulfides, chiefly mackinawite (FeS) and greigite (Fe_3S_4). Pyrite formation may be limited by the presence of reactive iron, i.e., the adsorbed coatings of colloidal ferric oxides such as hematite and goethite on detrital clays and silt grains. Many forms of iron present in sediments--large grains of hematite, goethite, magnetite, and ferruginous silicates--are nonreactive (Berner 1970, 1971a). Terrigenous sediments are rich in these "rusty" coatings, while carbonate and other biogenic sediments, which are low in detrital matter, have few iron-oxide-coated grains. The pyrite content of such sediments tends to be low; in some cases, however, the biogenic sediments may have large quantities of pyrite in spite of low reactive iron concentrations because the iron present is, relatively speaking, more reactive (Berner, 1971a).



Source: Adapted from Berner (1971a)

FIGURE VII-2 FORMATION OF PYRITES

Some of the H_2S remaining after the precipitation of iron monosulfides is oxidized to elemental sulfur by aerobic or anaerobic bacteria. After compaction of the sediments, part of this elemental sulfur then reacts with the iron monosulfides, by way of solution-reprecipitation reactions, to form pyrite, while the remaining elemental sulfur is reoxidized bacteriologically to sulfate and does not accumulate.

Sulfate reduction and pyrite formation sometimes takes place in freshwater environments (Vallentyne, 1964), but the marine sediments are the usual environment, primarily because freshwater environments are usually limited in sulfate content.

2. Biological Influence on Marine Sulfate Concentrations

Although the ocean may be assumed to be an infinite reservoir of sulfate with an isotopic ratio constant over short time periods, it is in fact finite, and continued sulfur fractionation over long periods of time combined with variations in the rate of inflow and outflow of sulfur may be able to change the isotopic composition as well as the total concentration of sulfate (Holser and Kaplan, 1966).

The ocean exchanges sulfur with the environment in two ways. Weathered sulfur from the crust enters the ocean in continental runoff, contributing ^{32}S and ^{34}S in a manner characteristic of their abundances in the material weathered, and in quantities that may have varied over geological time. Simultaneously, the ocean is constantly losing sulfur by the two processes of evaporite formation and sulfate reduction. Sulfate reduction results in isotope fractionation favoring the lighter isotopes; in contrast, the precipitation of $CaSO_4$ entails no fractionation, and its isotope ratio reflects the abundances of these isotopes in the ocean at the time of deposition.

Several authors have pointed out that the isotope abundance in evaporite sulfate deposits shows variations through geological history (Ault and Kulp, 1959; Thode and Monster, 1965; Nielsen and Ricke, 1964; and Holser and Kaplan, 1966). (See Figure VII-1.) Holser and Kaplan have argued that these correspond to variations in the concentration of sulfate in seawater. These arguments are summarized below.

The ratio of $^{32}S/^{34}S$ is regulated by the influx of weathered sulfur, derived from isotopically light shales and heavy evaporites, and the bacterial production of H_2S accompanied by precipitation of the sulfide. The critical issue is that of the balance of input of light sulfur into the ocean from weathered shales and its removal in sulfide precipitation.

Although the actual isotopic composition of sulfate in river water and that formed in sulfides varies with time, a very simplified model of the changes in isotopic distribution in the ocean developed by Holser and Kaplan views them as being the result of addition to or subtraction from a reservoir of shale sulfur of constant isotopic ratio equal to the mean $\delta^{34}S$ value of sedimentary sulfides (-12.0 o/oo). According to this model, increases in the proportion of ^{34}S in the ocean occur at times when the deposition of ^{32}S in the sediment occurs at a greater rate than the introduction of light sulfur from the sediments as a result of weathering. The total ocean reservoir is therefore being depleted in ^{32}S, and the result is a higher mean $\delta^{34}S$ for the sulfate in the ocean. If the volume of the ocean is constant, the result of this process is a lower concentration of sulfate. Decreases in the proportion of ^{34}S and the value of $\delta^{34}S$ occur when the deposition of ^{32}S in the formation of sulfide sediments is slow compared with the weathering of sulfides from the crust, so that more light sulfur enters the ocean than leaves it. At these times, the sulfate concentration increases. The total quantity of sulfate sulfur in the ocean corresponding to different values of $\delta^{34}S$ can be calculated from the present sulfate content and $\delta^{34}S$ value of the oceans.*

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*The difference d between the present sulfate content of the ocean S_p (expressed in units of 10^{14} tons sulfur) and S_t at some time t can be calculated knowing the value V_p of $\delta^{34}S$ of the present ocean and the value V_t of the ocean at time t, since

$$V_t S_t = V_p S_p + V_r d$$

and

$$S_t = S_p + d$$

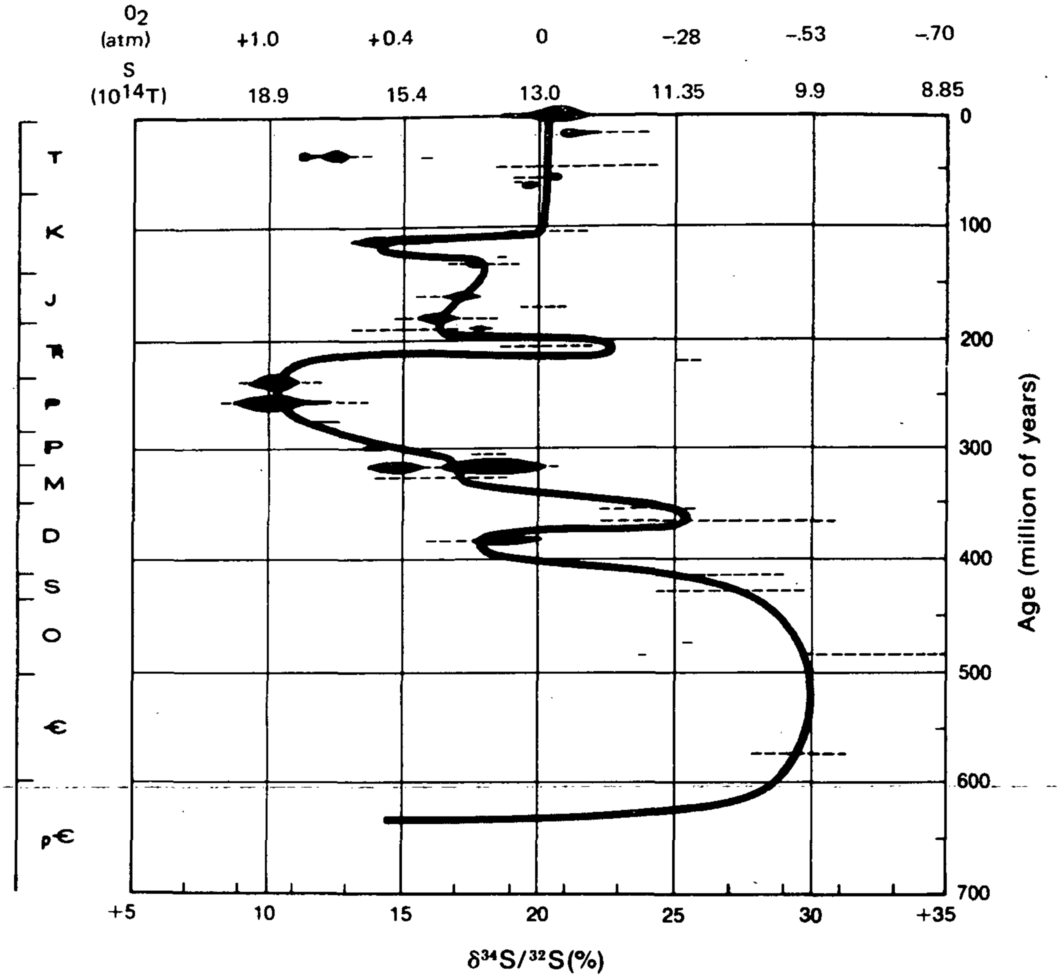
where V_r, the $\delta^{34}S$ value of the sulfide reservoir, is -12.0, V_p is 20 and S_p is 13. Thus, the value of the difference is $(260 - 13 V_t)/(12 + V_t)$.

The total quantity of sulfur in the ocean corresponding to various $\delta^{34}S$ values is indicated at the top of Figure VII-3. If we assume that the exchange of reduced sulfur with the sediments also corresponds to the exchange of the associated oxygen in the sulfate with the atmosphere, then deviations in the sulfate content of the ocean may be viewed as variations in its capacity as a reservoir of atmospheric oxygen. The atmosphere presently contains 11.84×10^{14} tons of oxygen, and the deposition of about 6×10^{14} tons of sulfur in the sediments as sulfide corresponds to the release of about one atmosphere of oxygen into the atmosphere or other terrestrial reservoir. The increase of sulfate in the ocean by a similar amount corresponds to the transfer of one atmosphere of oxygen from the atmosphere (or from other available reservoirs) into the ocean.

Holser and Kaplan (1966) ignore the influence of the deposition of evaporite sulfur on the isotopic composition of the ocean sulfate on the grounds that there is virtually no fractionation of sulfur during the deposition of $CaSO_4$, whereas the production of sulfides entails considerable fractionation.

Rees (1970) challenges these conclusions. He points out that the influence of evaporite formation and weathering is important and argues that the isotopic composition of the ocean will be controlled by the balance of these processes and the deposition and weathering of sulfide sulfur. Rees suggests that evaporite deposition may have a regulating effect on the salt content and consequently the sulfate content of the ocean, since evaporite formations will in general be formed faster if the concentration of salt is high. The ratio of evaporite to sulfide sulfur in the sediments is 2:1, which suggests that the effects of evaporite formation may be important if Rees's model is valid.

Regardless of the relevance of Rees's comments, it would seem that the Holser-Kaplan model is a crude one, and that it might be usefully elaborated by considering the variations in ratios of evaporite deposition and weathering relative to sulfide deposition and weathering which yield the observed isotopic composition of the evaporites and also



Source: Redrawn from Holser and Kaplan (1966)

Plot of evaporite sulfur isotope ratio as a function of the estimated age of the sample. Thickness of the line indicates the number of analyses, and dashed lines indicate ranges where only a few analyses or insufficient data have been published. Heavy line is the estimate of Holser and Kaplan (1966) of the sulfur isotope ratio of marine sulfate. Corresponding total mass of sulfur in the ocean and deviations from the present marine store of oxygen in sulfate indicated at top.

FIGURE VII-3 MARINE SULFATE ISOTOPE AGE CURVE

satisfy the condition that the ratio of evaporite to sulfide weathered in the sediments be 2:1. This would yield estimates of the total flux of both forms.

3. Biological Regulation of Atmospheric Composition

Redfield (1958) and Redfield, Ketchum, and Richards (1963) have proposed that sulfate reduction in the ocean may be a means of regulating the atmospheric concentration of oxygen, since the sulfate reduction is determined by the overall level of oxygenation of ocean waters, which in turn is a function of atmospheric O_2 pressure. Thus, if the pressure declines, the system will respond by releasing CO_2 into the water and ultimately (given sufficient ocean productivity) O_2, which in turn will be released into the atmosphere. If the atmospheric O_2 pressure increases, the level of ocean oxygenation will increase and the deposition of sulfide will cease. Meanwhile, continued weathering of crustal sulfide deposits will result in their oxidation with atmospheric oxygen, and the release of the resulting sulfate into the ocean, for a net transfer of atmospheric oxygen into the ocean sulfate reservoir.

This suggestion is extremely interesting and merits further consideration. It implies a fairly massive sulfide reduction system in the ocean. Evidence of the existence of such a system has been reported by Lloyd (1968), who calculated that the sulfate oxygen in the ocean is not in isotopic equilibrium with the oxygen in the water, and that the only effective mechanism which could account for the observed fractionation is biological production of H_2S which is subsequently oxidized by O_2 dissolved in the ocean. He estimates that about one third of the sulfate in the ocean must have been bacterially reduced to H_2S and then reoxidized within the last 50,000 years (or, more likely, a shorter period) in order to explain the discrepancy. This corresponds to an annual marine sulfate reduction of not less than 8,600 million tons of sulfur per year, which seems high.

Although sulfate reduction is presently going on in the ocean, and pyrite formation is depositing about 7 million tons of sulfur per year (Berner, 1971a), the sulfate content of the ocean is increasing. Berner estimates that of the 368 million tons of sulfate in river runoff earlier in the century, approximately 12% was derived from weathering of sulfides. This corresponds to about 15 million tons of sulfur, which implies (together with estimates of sulfide deposition) that there is presently a net transfer of oxygen from the atmosphere into the ocean sulfate reservoir. This figure does not include the "weathering" of sulfides in fossil fuels that results from their combustion. At the present time about 58 million tons of sulfur is annually injected into the atmosphere as SO_2 from sulfides in fossil fuels; this is further oxidized to sulfate and transported to the ocean. Since all of the oxygen consumed in these oxidation processes is derived from the atmosphere, the result is an annual transfer of about 175 million tons of oxygen to the ocean sulfate reservoir. An additional 26 million tons of sulfuric acid sulfur is consumed in industrial processes and transferred to the ocean reservoir by a variety of routes. Assuming that this industrial sulfuric acid is manufactured from sulfides or native sulfur, its production consumes an additional 80 million tons of atmospheric oxygen. The result is an annual transfer of about 260 million tons of atmospheric oxygen to the sulfate reservoir as a direct result of human activity. These quantities are negligible compared to the total atmospheric reservoir of oxygen or that of marine sulfate.

Many factors should be considered in evaluating the possible long-term effectiveness of bacterial reduction as a means for controlling the atmospheric concentration of oxygen. An obvious one is the effect of temperature on the system. Increases in the surface temperature of the ocean tend to decrease the amount of oxygen in the surface waters. If the increase is uniform, the net result would be an increase in the amount of sulfate reduction. If this were accompanied by an increase in the amount of sulfide deposition, there would be a net transfer of oxygen into the atmosphere, assuming the photosynthetic conversion of the CO_2 into O_2 and subsequent escape of the O_2 to the atmosphere. Thus we would expect that periods of high temperature correspond to periods of withdrawal of sulfate from the oceanic sulfate reservoir, and may also correspond to increases in the oxygen concentration in the atmosphere and enhanced rates of deposition of organic carbon in marine sediments.

Alternatively, the oxygen withdrawn from the oceanic sulfate reservoir may have gone somewhere else. (Possibilities include the atmospheric CO_2 and carbonate or other oxidized sediments.) A crucial question is that regarding the form in which the released oxygen enters the atmosphere (as O_2 or CO_2) and the conditions which determine this.

Studies of the oxygen isotope ratios in evaporite sulfates might shed light on this question, as would a careful review of other evidence bearing on the temperature history of the earth during the periods of variations in the sulfur isotope ratio of the evaporite sulfate. The geologic history of factors influencing the rates at which sedimentary sulfur is transferred from the continent to the ocean is also relevant, as is information bearing on the oxygen content of the atmosphere.

4. Other Geochemical Effects

Sulfur or iron bacteria play an important geochemical role in the modification of sulfide ores and the production of sulfuric acid. The H_2S in thermal springs (produced by reaction of ground water with sulfides accumulated by the magmatic process) is converted to sulfuric acid by sulfur-oxidizing bacteria (Erlich and Schoen, 1967; Schoen and Rye, 1970; Zajic, 1969). Deposits of volcanic iron sulfides (pyrites and marcasite) may also be weathered with the aid of sulfur-oxidizing bacteria, which convert them to sulfuric acid (Ivanov, 1971). Sulfuric acid present in the runoff of abandoned coal and copper mines is attributed to the action of iron and sulfur bacteria (Thiobacillus thiooxidans, Ferrobacillus ferrooxidans, Ferrobacillus sulfooxidans); these are believed to catalyze the abiological oxidation of pyrite by ferric iron, primarily by reoxygenation of the Fe^{++} produced (Baker and Wilshire, 1970; Singer and Stumm, 1970). The latter authors report that the presence of microbes accelerates the pyrite oxidation rate by more than 10^6.

The overall weathering rate is determined largely by the acidity of soil water in contact with the rocks. Any mechanism that affects the pH of rain has an indirect effect on the rate of weathering. Recent increases in the sulfate content of rain in the Northeast United States have been reported to accelerate measurably the weathering of granite in at least one location in New Hampshire (N. Johnson, personal communication). Although the present increase in acid content of rain is a human artifact and thus not biological in exactly the same sense that term is used throughout most of this report, we may infer that any non-human biological action which increases the sulfate content of rain or of ground water will enhance weathering.

The native sulfur accumulated in salt domes appears to be the direct result of the action of sulfur-oxidizing bacteria acting in conjunction with sulfate-reducing bacteria (Ault and Kulp, 1959; Zajic, 1969).

E. ATMOSPHERIC CYCLES OF SULFUR

1. Introduction

Although the basic elements of the atmospheric cycle of sulfur are known, the source of some of the sulfur in circulation remains obscure, and there is considerable uncertainty regarding the magnitudes of some of the reservoir exchanges. Table VII-3 summarizes the major reservoir exchanges and indicates the ranges of the estimates that have been given in the literature.

There appears to be more sulfur in circulation through the atmosphere than can be accounted for by such sources as volcanic and thermal hot springs emissions, industrial sources of sulfur dioxide, and the injection of sulfur into the atmosphere in the form of sea salt particles produced by the action of winds and waves. The sulfur transferred from the atmosphere to the surface consists of sea salt sulfur and "excess" sulfate in precipitation, so designated because estimates of the concomitant chloride content of the precipitation indicate that the sulfur probably was not derived together with chlorine from the ocean. The total excess sulfate in precipitation is estimated (on the basis of rainfall collected in 1955) to be about 130 million tons sulfur per year. At that time, industrial sulfur dioxide contributed only about 40 million tons of sulfur while volcanic and thermal hot springs contributed around 10 million tons, leaving about 80 million tons of excess sulfate in

TABLE VII-3. - ESTIMATED ANNUAL RESERVOIR EXCHANGES OF SULFUR

	Million Metric Tons S	
To Atmosphere		
Sea salt	45 to 400	(a)
Industrial SO_2	68.5	(b)
Volcanoes and hot springs	7 to 12	(c)
Biogenic H_2S	98 to 800	(d)
To Freshwater		
Industrial SO_4^{--}	26.3	(e)
Acid mine drainage	15	(f)
Rock weathering	15 to 43	(g)
Atmosphere to Land Surface		
Excess sulfate in precipitation	58	(h)
Sea salt sulfate	5	(h)
Dry deposition of aerosols and gases	46 to 100	(i)
Atmosphere to Ocean		
Excess sulfate in precipitation	73	(h)
Sea salt sulfate	40	(h)
Dry deposition of aerosols and gases	29 to 100	(i)
Sedimentation in Ocean Floor	7	(j)

[a] From Eriksson (1959) and Blanchard (1963).

[b] From GEP (1971). This includes 11.3 million tons from refinery operations and 57.2 million tons from fossil fuel combustion.

[c] From Koyama, Nakai, and Kamata (1965) and Holser and Kaplan (1966).

[d] The range of estimates found in the sulfur budgets of Eriksson (1963), Junge (1963), and Robinson and Robbins (1968, 1970) is 98 to 280 million tons per year. The data of Pate, Pitombo et al (1971) imply a flux between 200 and 800 million tons per year.

[e] GEP (1971). This includes chemical fertilizers and other industrial sulfuric acid consumption.

[f] Extrapolated from U.S. coal production and acid mine drainage estimates.

[g] From Eriksson (1963) and Berner (1971a).

[h] Based on Junge's estimate (1963) of 2.2 mg/liter of excess sulfate in precipitation over land and 0.5 mg/liter over the ocean. The sea salt figures are derived from Eriksson's estimate (1963, 1959) that 10% of sea salt production is deposited over the land and the remainder returns to the sea, and includes dry fallout as well as washout by rain. This assumes that the sea salt production is 45 million tons per year.

[i] Range of estimates of Eriksson (1963), Junge (1963) and Robinson and Robbins (1968, 1970).

[j] Berner (1971a).

precipitation unaccounted for by these sources.

Additional evidence of the existence of excess sulfur comes from analyses of the salt content of water in rivers draining the continents. Analyses of individual rivers performed during the interval from 1848 to 1960 were used to generate an estimate of the total sulfate, chloride, and other salts annually transported from the land to the sea. Sulfur in river water comes from rock weathering, sea salt sulfur precipitated over the land, freshwater industrial sulfuric acid emissions, chemical fertilizers applied to the land, and volcanic and industrial sulfur dioxide emissions that are precipitated out on land in rain and snow. Comparisons of the total sulfur contents of rivers with appropriate estimates of these sources also indicate the presence of excess sulfur.

The primary mechanism which has been invoked to account for this excess sulfur is the injection of biogenic H_2S into the atmosphere from soils and aquatic environments depleted in oxygen. There is very little direct evidence regarding the existence of such a transfer, and there are some grounds for supposing that the transfer of large quantities of sulfur by this means is unlikely.

This section reviews the question of excess sulfur in circulation and discusses evidence bearing on the existence of such a circulation as well as some possible sources of excess sulfur. The section begins with a brief discussion of industrial sources of atmospheric sulfur and other sulfur that appears in runoff, followed by a section on the volcanic emission of sulfur compounds. Mechanisms for the production of sea salt are then discussed, including a theory which holds that sulfur in sea salt is enriched with respect to chlorine by variable amounts. Next we review available indirect evidence which supports the conclusion that excess sulfate is from biogenic H_2S.

The forms of sulfur in the atmosphere and the chemical reactions which they undergo are then examined, including evidence bearing on the question of the lifetime of sulfur dioxide, the factors that influence the rate at which it is converted to aerosol sulfates in the atmosphere, the mechanisms for the removal of aerosols, and the direct removal of SO_2 by vegetation.

Finally, we review the measurements of concentrations of sulfur compounds in the atmosphere, including direct measurements of sulfur dioxide and sulfate as well as indirect measurements in the form of observations of sulfate in rain.

2. Industrial Sources of Sulfur

Industrial sources of atmospheric sulfur are fossil fuel combustion--mainly coal--and certain smelting operations (primarily the refining of copper, lead, and zinc). Worldwide totals shown in Table VII-3 are based on estimates of the total coal and oil consumed in the world and rough extrapolations of other industrial sources on the basis of the U.S. production figures. In 1968 it was estimated that combustion sources accounted for 57.2 million tons per year while other industrial sources contributed 11.3, for a world total of 68.5 million tons (GEP, 1971). The injections are increasing annually at a rate of about 4% or 5% a year. (As recently as 1955, fossil fuel sources were estimated at only 40 million tons per year.) In addition, worldwide production of sulfuric acid for industrial purposes was about 26.3 million tons as sulfur in 1968; a little over 12 million tons of this was used to produce fertilizer, which was then spread on the land, to appear shortly in rivers and ground water and return to the sea. The remaining sulfuric acid may also be regarded as almost immediately recycled to the sea, as most of it is discharged in coastal or inland waterways after use.

Acid mine drainage is another minor source of sulfur in surface and ground water that may be regarded as industrial pollution. The U.S., which produces 20% of the coal mined in the world, contributes an estimated 8 million tons of SO_4, or nearly 3 million tons of S. Extrapolation on the basis of production figures suggests that the world supply of sulfate from this source may total about 15 million tons of S.

3. Volcanic Sulfur Sources

Since magmatic processes tend to collect sulfur in the crustal rock, sulfur is a prominent component of volcanic effluents and is emitted from hot springs. The concentration and form of sulfur in volcanic effluents varies with the volcano, the vent from which the sample is collected, and the eruption (Koyama, Nakai, and Kamata, 1965; Cadle, Wartburg, and Grahek, 1971). This is illustrated in Table VII-4, which shows the atomic composition of effluent gases of four Japanese volcanoes, and in Table VII-5, which shows the differing concentrations of sulfates and sulfur dioxide in gases collected from different vents or at different times from Kilauea volcano in Hawaii, as reported by Cadle, Wartburg, and Grahek (1971). Particles collected from this volcano were largely dilute sulfuric acid droplets containing dissolved sulfates of markedly varying concentration. Large variations in the proportion of sulfate to SO_2 were observed. Cadle et al. point out that this phenomenon can be explained as due to varying degrees of oxidation of H_2S, S, and SO_2 at high temperatures by atmospheric oxygen. They also observe that if such oxidation occurs during very explosive eruptions, such as that characterizing Gannung Agung in Bali in 1963, large amounts of sulfuric acid droplets containing various sulfates may be injected directly into the stratosphere. These droplets are in the micron and submicron size range and therefore would remain in the stratosphere for a long time.

Average annual injections of sulfur from volcanoes and hot springs have been estimated by Koyama, Nakai, and Kamata (1965) as 7 million tons per year, and by Holser and Kaplan (1966) as 12 million tons per year. We do not know how accurate these figures may be, nor by how much such emissions may vary from year to year.

4. Sea Salt Particles

Significant quantities of sulfur are transferred from the ocean to the atmosphere in the form of sea salt particles. Estimates of the total production of these particles vary, and the mechanisms of their formation are not clearly known. As sea salt particles are efficient rain drop nucleators, they are returned to earth chiefly in precipitation. Analyses of rainwater have provided much of the information about sea salts, in particular the fact that some fractionation of seawater constituents occurs during the process of the formation of sea salt particles, since the ratio of the various ions in seawater and that in sea salt particles are not the same. Specifically, there is more flourine, iodine, and phosphate in particles, and there may be more sulfate relative to

TABLE VII-4. - ATOMIC COMPOSITION OF VOLCANIC GASES FROM SOME VOLCANOES

	Element			
Volcano	H(%)	O(%)	C(% x 10^{-2})	S(% x 10^{-2})
Nasudake	66.49	33.30	5.3	14.5
Showashinzan	66.45	33.41	10.7	0.47
Satsuma Iwojima	65.73	33.73	12.8	40.6
Kilauea	65.79	33.73	42.3	5.5

Source: Kusakabe (1969).

TABLE VII-5. - AMOUNTS OF SO_2 AND SO_4 COLLECTED FROM KILAUEA FUME

Location and Date	SO_2 (μg)		SO_4^{--} (μg)
	West and Gaeke	Fluorescence	
East rift fumarole (August, 1969)	53	-	< 4
Halemaumau (August, 1969)	115	-	< 4
Halemaumau (August, 1969)	87	-	< 4
Crevasse near Aloi (May, 1970)	324	567	5000
Halemaumau (May, 1970)	2700	2400	140
Crack in erupting spatter cone (May, 1970)	11,000	11,600	130
Crevasse near Aloi (May, 1970)	2200	2000	1500

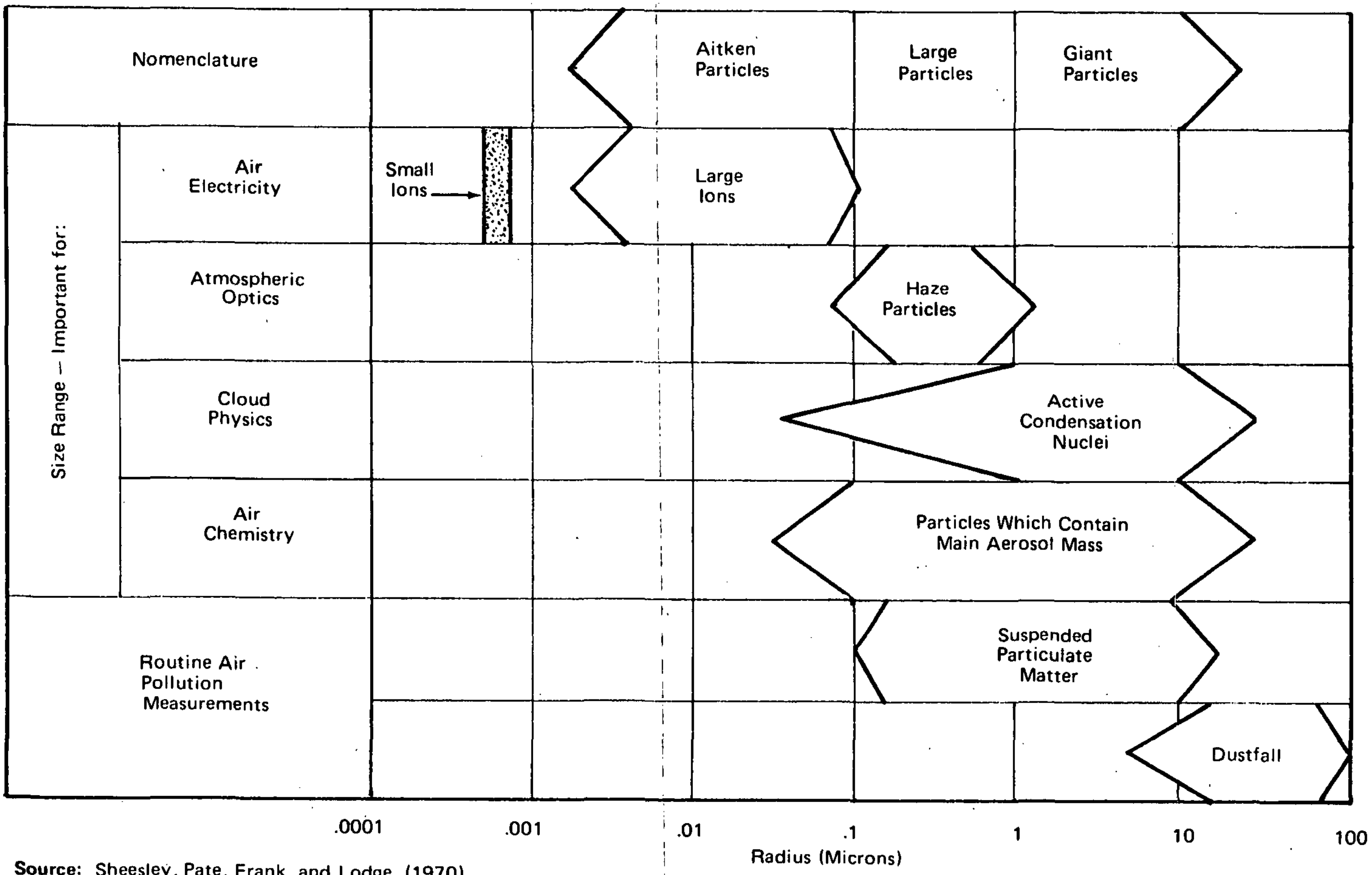
Source: Cadle, Wartburg, and Grahek (1971).

chlorine (Rossby, 1959; MacIntyre, 1970; and Miyake and Tsunogai, 1963).

The mechanisms involved in the production of sea salts and the various fractionation mechanisms that account for the composition of raindrops produced are complicated by the fact that the marine air contains many classes of particles not originating from the sea. Figure VII-4 shows the major size classification of atmospheric particles. Aerosols, dusts, and biological material of continental origin are common constituents of maritime air (Cadle, 1966; Folger, 1970; and Junge, 1963). Furthermore, after introduction into the atmosphere, particles of diverse origin may coagulate or be scavenged by cloud or rainwater. Changes in humidity may force particles to go through several sequences of condensation and evaporation of water and other vapor present in the atmosphere.

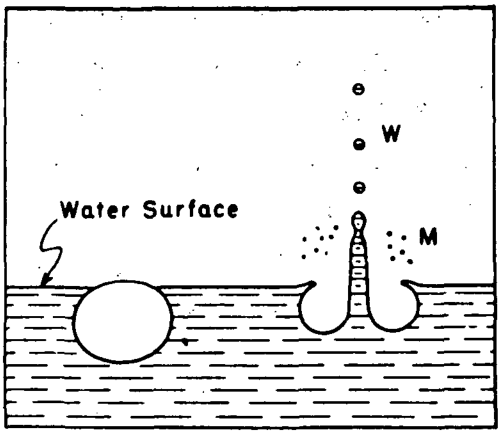
The basic mechanism involved in the production of sea salt particles is the bursting of bubbles of air captured below the surface by wave action or by the impact of raindrops. As the bubble bursts, a small jet rises from the bottom of the bubble and quickly breaks into 2-10 droplets (see Figure VII-5). These droplets, marked W in Figure VII-5, are all about the same size and about one-tenth the size of the bubble (Cadle, 1966; Junge, 1963). The size distribution is dependent on the size of the bubble, which in turn depends upon how the bubbles are formed. The smallest bubbles formed from small waves are about 100 microns in diameter. Evaporation of the seawater in the droplets produces particles about 2.5 microns in diameter (ocean water is about 3.3 to 3.6% sodium chloride in composition). These particles constitute the "giant" sea salt particles. In addition, a very large number of particles about one-tenth the diameter of the giant particles is also produced by the bursting of the thin film of the bubble. These are all about the same size (diameter about 0.3 micron or less) and give rise to "large" particles (see Figure VII-4). Mason (1962) observed 100 to 200 small droplets produced from the bursting of each bubble.

Numerous authors have proposed that the monomolecular layer of insoluable organic matter at the surface of the ocean is involved in the formation of sea salt particles (Eriksson, 1960; Blanchard, 1964; Pueschel, Charlson, and Ahlquist, 1969; Garrett, 1968; Barger and Garrett, 1970).



Source: Sheesley, Pate, Frank, and Lodge (1970)

FIGURE VII-4 CLASSIFICATION OF ATMOSPHERIC PARTICLES



Source: *Mason (1962)*

The large particles (w) originate upon disintegration of the jet formed when bubbles burst. More numerous and smaller particles (M) can form from the bursting of the bubble film.

FIGURE VII-5 FORMATION OF SEA SALT PARTICLES

MacIntyre (1970) proposes that this layer is responsible for the enrichment of phosphate in sea salt particles which occurs during the process of bubble bursting. He also proposes that a similar mechanism is responsible for an enrichment of sulfate and sodium with respect to chloride, but that the amount of the enrichment varies with factors that are difficult to predict. MacIntyre cites the work of Bruyevich and Kulik (1967), who observed enrichment of sulfate relative to chlorine in rain collected at sea from clouds formed at sea. In the mid-Indian Ocean, they observed sulfate enrichment relative to chlorine by a factor of 1.7; in the mid-Pacific, sulfate was enriched by a factor of 4.6.

The possibility that bubble bursting may concentrate sulfate is extremely interesting, since some of the evidence for the existence of excess sulfate is the observation that the ratio of sulfate to chlorine in sea salt particles is higher than 0.14 (which is characteristic of the ocean); consequently, the sulfate in question is inferred to be derived from sources other than sea salts. Junge and Werby (1958) and

Eriksson (1959, 1960) distinguish between sea salt sulfate and excess sulfate on the basis of the measured concentration of chlorine in precipitation. Lazrus, Baynton, and Lodge (1970) distinguish between components in cloud water collected off Puerto Rico derived from sea salts and those from other sources on the basis of whether or not variations in their concentrations correlate with those of chlorine. They found that while the chlorine concentration varied by almost an order of magnitude, the excess sulfate concentration was nearly constant and averaged 2.1 ppm. The $\delta^{34}S$ value of seawater sulfate averages about +20.2, while biological H_2S is usually enriched in ^{32}S by about 20 to 35 o/oo. Sulfides in coal occupy a broad range from +12 to +23 (Koyama, Nakai, and Kamata, 1965), while oil sulfides are much lighter. Studies of the isotopic distribution of rain collected at sea would clarify the source of the sulfate. Seawater sulfate concentrated in sea salts by the mechanism proposed by MacIntyre (1970) should be identical in isotope distribution to sulfate in the sea. The presence of lighter sulfate would indicate another origin.

Mizutani and Rafter (1969) report a study of the isotope distribution of rainwater sulfate sulfur collected in Gracechurch, New Zealand. They found that the $\delta^{34}S$ value varied inversely with the amount of excess sulfate, where the latter was defined in the conventional fashion, which supports the conclusion that excess sulfate is too light to be marine sulfate. No evidence is presented to indicate the source of this sulfate, and we may infer from the location, which is not far from Wellington, that combustion pollutant sources cannot be definitely ruled out.

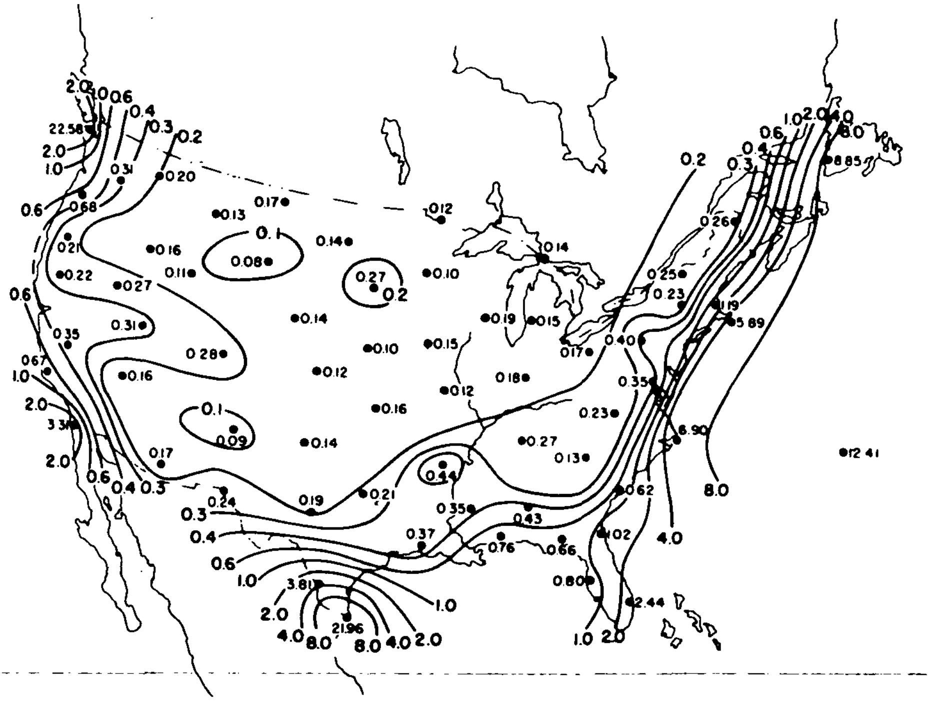
Cortecci and Longinelli (1970) obtained essentially the same results when they examined the isotope distribution of sulfur in precipitation sulfate collected in Pisa. They attributed the isotopically light excess sulfur to industrial sources of SO_2, on the grounds that there are extensive sources in the region in question and there are no intertidal flats (which presumably constitute the most effective sources of biogenic H_2S).

The mechanism by which sea salt particles are removed from the atmosphere depends on their size. Giant particles are heavy enough to fall out by themselves and large enough to be effectively scavenged by falling rain (Junge, 1963; Cadle, 1966). Large particles are less effectively scavenged by rain and almost too light to sediment out under normal conditions. Vertical air movements may carry them to high altitudes, and they may ultimately be removed by means of impaction or other forms of dry deposition. Consequently, precipitation near coastal regions shows high concentrations of sea salt chlorine and sulfate, believed to be derived from giant sea salt particles. These decline rapidly with distance from the coast, as all the giant particles are rapidly removed from the air. This effect is seen in Figure VII-6, which shows the chlorine content in precipitation in the United States.

Distinguishing between sea salt and excess sulfate in precipitation on the basis of the amount of chloride present is somewhat complicated by the fact that there are other sources of atmospheric chloride. Thus, Figure VII-6 shows high concentrations of chloride in the southwest near the eastern border with Mexico and in adjacent arid areas, attributed to sources in salt flats in those regions (Junge and Werby, 1958). Chloride is a constituent of coal and is emitted in coal combustion effluents; excess chloride in precipitation near centers of industrial activity is attributed to this source (Junge, 1963).

The production of sea salt depends upon wind speed. Eriksson (1959) estimated the total annual production to be approximately 1100 million tons, which corresponds to about 44 million tons of sulfate sulfur. Eriksson estimates that about 10% of this is carried inland, the rest returning to the ocean in precipitation or by means of dry deposition. Blanchard (1963) estimated the annual sea salt production to be 10 billion tons. The corresponding injection of sulfur would be about 400 million tons if the ratios of sodium, chlorine, and sulfate are about the same as in seawater.

This discussion of sea salt sulfate indicates that the quantity of sulfur injected into the atmosphere in the production of sea salt is not known. If the ratio of chlorine to sulfate in sea salts is the same



Source: Junge and Werby (1958)
Average Cl⁻concentration (milligrams per liter) in rain over the United States from July 1955 to June 1956.

FIGURE VII-6 CHLORIDE IN PRECIPITATION OVER THE UNITED STATES as that in seawater, then the annual injection of sea salt sulfur may be between 44 and 400 million tons per year, and of this about 10% may be returned to the surface over land. The proposal that the mechanisms which produce sea salts may enrich the sulfate with respect to chlorine by a variable factor has not been supported experimentally.

5. Biological Sources of Atmospheric Sulfur

Many authors have proposed that biogenic sulfur in the form of H_2S may be released into the atmosphere in appreciable quantities (Eriksson, 1960, 1963; Junge, 1963; Conway, 1943; Robinson and Robbins, 1968, 1970; Koyama, Nakai, and Kamata, 1965; Jensen and Nakai, 1961; and Berner, 1971a). No measurements of H_2S concentrations in swamps, estuaries, or near tidal flats have been reported in the literature to confirm this, although the presence of H_2S can sometimes be detected by its odor in such environments.

There are grounds for doubting whether biogenic H_2S can be emitted into the atmosphere in quantities sufficient to account for the quantities of excess sulfate estimated to be in circulation. As we have pointed out above, most sulfate reduction takes place in the marine environment at or near the mud-water interface, where anoxic conditions can be maintained and where the high sulfate concentration of the sea provides large supplies of sulfate substrate. Under such conditions, gas bubbles of H_2S form in the mud. These bubbles may be released from intertidal mud flats that are exposed twice daily and crack in the process of drying (Ostlund and Alexander, 1963). However, intertidal mud flats are negligible in extent and are unlikely to supply H_2S in the quantities presumably required to support the apparent excess sulfur cycle. H_2S could be released from the water surface if it were able to survive long enough as H_2S to diffuse upward from the site of production at the bottom to the surface. Whether or not this occurs depends on the oxygen content of the intervening water, its depth, and the rate of diffusion. Ostlund and Alexander (1963) found no detectable sulfide in the water overlying a tidal flat at high tide or in the water in a mangrove swamp, both of which were believed to be sites of sulfide production. They report experimental data indicating that H_2S and dissolved O_2 combine very rapidly, the half life of H_2S in water containing 5 ml oxygen per liter being 17 minutes. Well-oxygenated ocean water contains about this much oxygen or more. On the bases of these experiments, Ostlund and Alexander conclude that normal sea water, deep or shallow, cannot release H_2S to the atmosphere, and that oxygenated sea water is more likely to be a sink than a source of H_2S.

Pate, Sheesley, Wartburg, Pitombo, and Lodge (1971) also express skepticism that H_2S is injected into the atmosphere in significant quantities. They cite studies by Brinkman and Menenez dos Santos of the overturn of a eutrophic lake which resulted in the mixing of H_2S-rich bottom layers. The concentration of H_2S in the surface waters never become significant, although the oxygen content dropped sharply as the oxygen was used in rapid oxidation of the sulfide, and diffusion of oxygen from the surface was not rapid enough to establish viable concentrations in the upper layers.*

Indirect evidence, interpreted as implying that large quantities of sulfur are annually injected into the atmosphere from anoxic aquatic environments in which it is produced as H_2S, has been presented by Jensen and Nakai (1961), Nakai and Jensen (1967), Koyama, Nakai, and Kamata (1965), and Berner (1971a). We find none of this evidence wholly persuasive. Because of the importance of this issue, we will discuss the arguments and evidence in some detail.

a. Evidence of Isotopic Ratios in Sulfate in Precipitation

We have pointed out above that biological reduction of sulfate usually entails an enrichment of ^{32}S by 20 o/oo or more in the sulfide relative to the sulfate substrate. If sulfate in precipitation is enriched in ^{32}S relative to seawater, at least some of the sulfate must

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*Pate, Sheesley, et al. suggest that biogenic H_2S is produced in soils and rapidly oxidized to SO_2 in the soil atmosphere, to be released as SO_2 into the atmosphere. They suggest that under some circumstances, the H_2S may be oxidized rapidly to aerosol sulfate.

have been derived from sulfur that is isotopically lighter than seawater sulfate, and some of it may have been derived from biogenic H_2S.

Ostlund (1959) presented evidence that the sulfate in precipitation is isotopically lighter than seawater sulfate and therefore cannot all be derived from seawater. He measured the isotopic ratios of sulfur in rainwater gathered in four locations in or near Stockholm, one location on the coast of Washington, and one location on the coast of Texas. In all locations the sulfate in precipitation was much lighter than that in seawater, exhibiting $\delta\ ^{34}S$ values of +3.2 to +8.2 (Table VII-6). Ostlund points out that while this light sulfur cannot have been derived from seawater, it is not possible to determine whether its source is biological or industrial, since industrial sulfur is also isotopically light.

Jensen and Nakai (1961) and Nakai and Jensen (1967) studied the isotopic distribution of sulfate in rain collected in several locations in Japan, one group of locations designated "industrial" and the other "non-industrial." In addition, studies of coal in Japan were undertaken to provide information on which the origin of the sulfur in precipitation could be based. Figure VII-7 relates the sites of collection locations of intense industrial activity. Figure VII-8 is a plot of the sulfur isotope distributions observed in the Japanese rain samples, together with precipitation from two locations in New England, and the values found in Japanese coal and a sample of seawater. The authors infer from these data that there are two types of precipitation in Japan: (1) rain or snow that falls in heavily industrialized areas and is greatly depleted in ^{34}S relative to seawater ($\delta\ ^{34}S$ range about +3 to +8) and (2) rain or snow from "non-industrialized" locations which is only moderately depleted in ^{34}S ($\delta\ ^{34}S$ range of about +12 to +16). They conclude that the first type of precipitation contains excess sulfur derived from fossil fuels, in spite of the fact that the coal samples they examined show a range of $\delta\ ^{34}S$ values of +12 to about +24. They attribute the discrepancy between observed fuel sulfur isotopic distributions and those of the rain believed to be contaminated with fossil fuel sulfur to sampling error in the coal

TABLE VII-6. - ISOTOPIC COMPOSITION OF SULFUR IN INDUSTRIAL COAL AND SEA, LAKE, AND ATMOSPHERIC SULFATE

Sample Location	Sample	Sample Content (mg SO_4^{--} per liter)	Isotopic Data	
			δ S^{34} (o/oo)	S^{32}/S^{34}
	Ostlund Samples[a]			
Stockholm, Sweden	Snow	1.5	+ 5.4	22.09
Stockholm, Sweden	Snow	4.0	+ 6.8	22.06
Koping, Sweden[b]	Rain	3.2	+ 8.2	22.03
Stockholm, Sweden	Rain	7.9	+ 3.2	22.14
Stockholm, Sweden	Rain	18.8	+ 5.0	22.10
Stockholm, Sweden	Rain	7.2	+ 4.5	22.11
Stockholm, Sweden	Rain	5.1	+ 3.6	22.13
Stockholm, Sweden	Rain	6.1	+ 6.8	22.06
Stockholm, Sweden	Rain	9.5	+ 6.8	22.06
Huddinge, Sweden	Rain	5.3	+ 6.8	22.06
Huddinge, Sweden	Rain	2.8	+ 6.3	22.07
Flahult, Sweden	Rain	7.6	+ 7.3	22.05
Port Aransas, Texas[c]	Rain		+ 6.3	22.07
Nahcotta, Washington[c]	Rain		+ 5.4	22.09
Arctic Sea	Seawater	2740.	+20.2	21.77
North Sea	Seawater	2170.	+19.7	21.78
Gulf of Bothnia, Baltic Sea	Seawater	450.	+20.7	21.76
Lake Malaren	Lake water	47.	+ 2.7	22.15

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[a] Ostlund's isotopic data have been corrected by subtracting 0.12 from ratio values.

[b] Koping is located near Lake Malaren.

[c] Coastal locations, U. S.

TABLE VII-6. - (Continued)

Sample Location	Sample	Sample Content (mg SO_4^{--}) per liter)	Isotopic Data δS^{34} (per mil)	 S^{32}/S^{34}
	Sugawara Samples			
Tokyo(A), Japan[d]	Rain	8.9	+ 7.3	22.05
Tokyo(B), Japan[d]	Rain	8.6	+ 7.3	22.05
Tokyo(C), Japan[d]	Rain		+ 5.0	22.10
Nagoya(B), Japan[d]	Rain	2.3	+ 5.9	22.08
Nagoya(C), Japan[d]	Rain		+ 3.2	22.14
Wakayama, Japan[c]	Rain	3.5	+ 7.3	22.05
Nara, Japan[e]	Rain	1.3	+ 6.3	22.07
Kurume(A), Japan[f]	Rain	3.0	+15.6	21.88
Kurume(B), Japan[f]	Rain	2.1	+12.8	21.93
Kurume(C), Japan[f]	Rain		+15.6	21.88
Tottori(A), Japan[f]	Snow	2.7	+13.2	21.92
Tottori(B), Japan[f]	Rain	2.3	+15.1	21.88
Matsumoto, Japan	Rain		+12.3	21.94
Wakayama, Japan	Seawater		+20.7	21.76
East China Sea	Seawater		+20.7	21.76
	Nakai Samples			
Long Island Sound, Conn. (surface)	Seawater	2170.	+20.2	21.77
Long Island Sound, Conn. (7-m depth)	Seawater	2170.	+20.2	21.77

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[d] Industrial sites
[e] Near industrial sites
[f] Nonindustrial sites

TABLE VII-6. - (Continued)

Sample Location	Sample	Sample Content (mg SO_4^{--} per liter)	Sample Content (percent by weight)[g]	δS^{34} (per mil)	S^{32}/S^{34}
	Nakai Samples				
Linsley Pond, Conn. (surface)	Lake water	10.2		+ 7.7	22.04
Linsley Pond, Conn. (13.5-m depth)	Lake water	9.6		+ 7.3	22.05
Queechy Lake, Conn. (12-m depth)	Lake water	13.8		+ 7.3	22.05
Kyushu, Japan	Coal		1.54	+23.5	21.70
Kyushu, Japan			1.44	+23.9	21.69
Kyushu, Japan	Coal		3.05	+11.9	21.95
Kyushu, Japan			3.14	+11.9	21.95
Kyushu, Japan	Coal		1.49	+22.1	21.73
Hokkaido, Japan	Coal		0.33	+18.3	21.81
Hokkaido, Japan	Coal		0.35	+15.1	21.88

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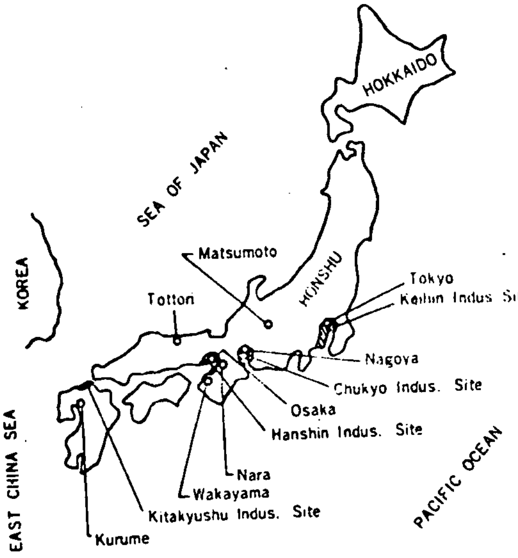
[g] Determined by Parr Bomb method

Source: Jensen & Nakai (1961)



Source: Nakai and Jensen (1967)

Sulfur isotope values of precipitation samples collected in industrial and nonindustrial sites were related to distance from sites of industrial activity. Hatched areas identify regions of intense industrial activity.

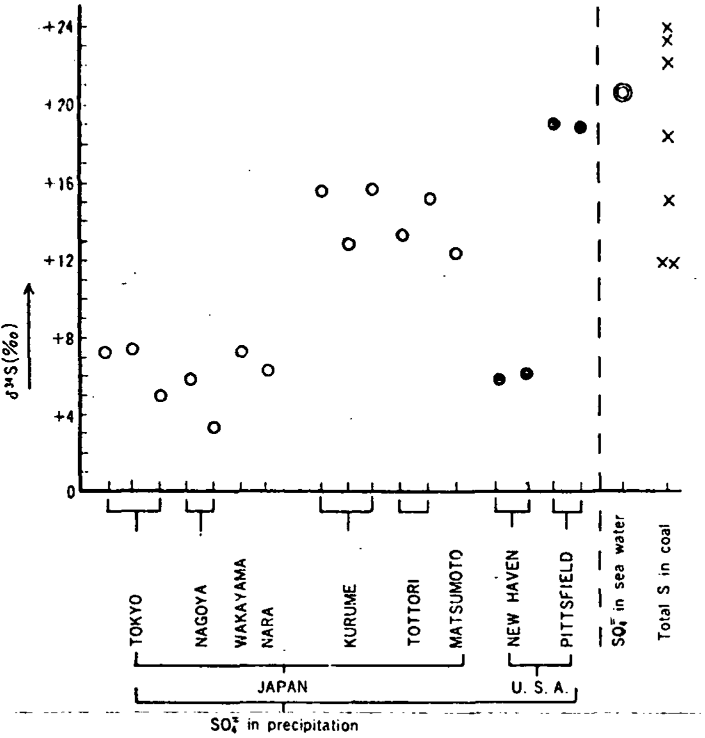
FIGURE VII-7 LOCATION MAP OF RAIN AND SNOW SAMPLES

series. They also conclude that the moderately light sulfur in precipitation collected in "non-industrialized" locations is due to an admixture of biogenic H_2S which may be enriched in ^{32}S by about 20 o/oo.

These conclusions are puzzling to us. The "non-industrialized" locations are in fact not far distant from the industralized sites, and atmospheric movements could easily transport atmospheric sulfates and perhaps even SO_2 such distances. If light sulfur from fossil fuels is responsible for the ^{34}S depletion in industrialized sites, then it could also be responsible for that observed in "non-industrialized" sites. The isotopic data presented in these reports do not support the conclusion that two sources of light sulfur are responsible for the observed $\delta\ ^{34}S$ depletion with respect to marine sulfate, although they do imply a non-marine source of some of the sulfate in precipitation.

b. Evidence of Total Sulfur in Circulation, Based on "Dry Deposition" Estimates

Koyama, Nakai, and Kamata (1965) demonstrate the occurrence of extensive biological sources of atmospheric sulfur on the evidence that:



Source: Nakai and Jensen (1967)

Lightest sulfate sulfur was found in precipitation near industrial sites.

FIGURE VII-8 SULFUR ISOTOPES IN PRECIPITATION AND SEAWATER SULFATE AND COAL SULFUR

(1) more sulfur is transferred from the atmosphere to the surface in Japan than can be accounted for by the known or estimated industrial, sea salt, and volcanic sources, and (2) isotopic balance considerations imply that the sulfur from this unknown source must be relatively light ($\delta^{34}S = + 9.1$) and hence almost certainly biogenic.

Tables VII-7 and VII-8 list the data on which these conclusions were based. Precipitation quantity and sulfate content was estimated on the basis of samples collected at 200 unspecified sites in Japan and the known mean precipitation during the years in question. The isotopic ratios of 1959 sulfate in precipitation were obtained by averaging the analyses of Japanese rain reported in Jensen and Nakai (1961). The estimates of volcanic sources of sulfur were derived from estimates of mean world volcanic activity and the assumption that activity in Japan is one tenth of this. Estimates of sea salt sources of sulfate were derived from analyses of chloride in precipitation and dry fallout. The ratio of chloride in precipitation to chloride in dry fallout was based on river water chloride corrected for known non-precipitation sources, which has an excess chlorine content totaling 2.3 times the precipitation chlorine. The sea salt contribution of sulfate was estimated from total chloride on the assumption that sulfate is present in sea salt at the same concentration as in seawater.

Sulfur from fossil fuel sources was estimated in conventional fashion, and the isotopic ratios were derived from analyses of samples of coal in use in Japan (Table VII-9).

The total amount of sulfur transferred from the atmosphere to the surface is assumed to consist of sulfur in precipitation plus that in "dry fallout." As described by Eriksson (1960), dry fallout comprises particles impacted on vegetation and other surfaces, gases absorbed on the same surfaces, and particles which sediment out. Koyama et al. estimated dry fallout by comparing the chemistry of rainwater collected in the open with that collected under bushes and trees, and attributed all differences to material filtered or absorbed from the air, i.e., to dry fallout. Table VII-10 shows the mean chemical composition of

TABLE VII-7. - COMPARISON BETWEEN ESTIMATES OF ATMOSPHERIC SULFUR BUDGET FOR ISLANDS OF JAPAN IN 1946 and 1959

	1946	1959
Average concentration of SO_4^{--} in precipitation	1.34 mg/1	4.5 mg/1
Average concentration of Cl^- in precipitation	0.80 mg/1	1.1 mg/1
Amount of SO_4^{--} brought down by precipitation and dry fallout	2.6×10^6 T/yr	8.7×10^6 T/yr
Amount of SO_4^{--} from sea origin through precipitation and dry fallout	0.2×10^6 T/yr	0.3×10^6 T/yr
Amount of sulfur from volcanoes as SO_4^{--}	0.1×10^6 T/yr	0.1×10^6 T/yr
Amount of sulfur emitted by fuel, as SO_4^{--}	0.4×10^6 T/yr	1.8×10^6 T/yr
Total amount of SO_4^{--} from sea spray, volcanoes and fuel	0.7×10^6 T/yr	2.2×10^6 T/yr
Amount of SO_4^{--} from sources other than sea spray, fuel and volcanoes	1.9×10^6 T/yr	6.5×10^6 T/yr
Total sulfate brought down by precipitation	0.87 T/yr	2.9 T/yr

Source: Koyama, Nakai, and Kamata (1965)

TABLE VII-8. - ATMOSPHERIC SULFUR ORIGINATED FROM VARIOUS SOURCES IN JAPAN FOR 1959 AND ITS ISOTOPIC COMPOSITION

	SO_4^{--} (T/yr)	SO_4^{--} (T/km^2/yr)	%	S^{32}/S^{34}	δS^{34}
Sea Spray	0.3×10^6	0.8	3.4	21.77	+20.2
Volcano	0.1×10^5	0.3	1.1	22.13	+ 3.8
Fuel	1.8×10^5	5.0	20.7	22.00	+ 9.1
Other sources	6.5×10^6	18.1	74.8	22.00	+ 9.1
Total	8.7×10^6	24.2	100	21.99	+10.0

Source: Koyama, Nakai, and Kamata (1965)

TABLE VII-9. - ISOTOPIC COMPOSITION OF SULFUR IN INDUSTRIAL COAL AND OIL

Sample Location	Sample	S^{32}/S^{34}	δS^{34}
Japan	Coal	Range 21.95-21.70	Range +12.0 - +23.6
		Average 21.78	Average +19.6
U.S.A.	Coal	Range 21.81-21.76	Range +18.0 - +23.6
		Average 21.78	Average +19.6
U.S.A.	Oil	Range 22.32-21.88	Range - 4.6 - +15.3
		Average 22.11	Average + 4.6

Source: Koyama, Nakai, and Kamata (1965)

TABLE VII-10. - ESTIMATED AMOUNTS OF VARIOUS ELEMENTS IN PRECIPITATION AND DRY FALLOUT

(sampling location near campus of Nagoya University, Japan)

	Average Composition of Precipitation Excluding Dry Fallout (mg/l)	Average Composition of Precipitation Including Dry Fallout (mg/l)	Composition of a Spring Water (mg/l)
Na^+	0.44	2.05	3.24
Ca^{++}	0.13	1.07	0.72
Mg^{++}	0.08	0.35	0.54
Cl^-	0.76	3.67	5.48
SO_4^{--}	1.13	3.37	0.51

	(A) Amounts of Various Elements From Precipitation (mg/m^2/year)	(B) Amounts of Various Elements From Dry Fallout (mg/m^2/year)	B/A
Na^-	700	2580	3.7
Ca^{++}	210	1500	7.1
Mg^{++}	130	430	3.3
Cl^-	1220	4650	3.8
SO_4^{--}	1810	3580	2.0

Source: Koyama, Nakai, and Kamata (1965)

precipitation samples collected in this fashion; the composition is quite different from that of samples collected in the open, and the sulfate in dry fallout is approximately twice that found in precipitation. The total amount of sulfate transferred from the atmosphere to the surface was assumed to be three times that observed in precipitation for both of the periods under study.

The question of the existence and efficacy of impaction and direct gaseous absorption as a means of transferring material from the atmosphere to the surface is complex and will not be discussed here in detail. Briefly, we may note that the method employed by Koyama et al. to estimate dry fallout confounds two completely different mechanisms: dry fallout, as defined by Eriksson and others, and nutrient leaching or nutrient fall-through, which is the cycling of nutrients taken up from soil solution by plants through leaves and back again to the ground. In the latter process, which has been confirmed in laboratory work with labeled tracers, the plant absorbs nutrients together with soil water and transports them vertically to the leaves during transpiration. The nutrients remain in the leaves until rain leaches the material from the leaf surfaces and returns it to the soil. The composition of the leachate varies with the plant, the nutrient status, and the soil. This process is presently under investigation, but it is known that extremely large quantities of nutrients are cycled in this manner.

Atmospheric particulates may be actively filtered from the air by vegetation, or they may be sedimented from the air due to the effect of vegetation on air movements. Dry deposition caused by these factors will tend to concentrate in the region of the vegetation, and much of it will be collected on the plant surfaces, to be washed off during subsequent rains. There is evidence that SO_2 is directly taken up by vegetation, partly through stomata and partly by absorption on wet surfaces at night. (See below.)

All of these considerations suggest that the method used by Koyama et al. for estimating the sulfur contribution of dry fallout may be inaccurate, and that it may overestimate the effectiveness of this mechanism of transferring sulfur from the atmosphere.

The sources of atmospheric sulfur calculated by Koyama et al. total less than the amount estimated to be in circulation on the basis of the precipitation and dry fallout data. Therefore, an unknown other source must be inferred for 1.9 million tons in 1946 and 6.5 million tons in 1959. This corresponds to about twice the sulfur in precipitation in 1946 and three times this quantity in 1959. Koyama et al. identify this source as biological, on the grounds that the isotopic balance of output and input requires a source which is relatively light - i.e., $\delta\ ^{34}S$ = +9.1. (See Table VII-8.) Such a source is heavy compared with biogenic H_2S, which usually shows a fractionation factor of about 20 to 35 o/oo relative to seawater, and consequently should have a $\delta\ ^{34}S$ value of about -10. The quantity of sulfur from unknown "other" sources estimated by Koyama et al. is a minimum, because they assume that essentially all fuel sulfur is precipitated on the island itself. By contrast, Junge and Werby (1958) estimate that only one half the sulfur of fuel origin in the United States is precipitated over the country, the remainder being transported out to sea. If half of the industrial sulfur dioxide produced in Japan is transported out to sea, the quantity of "other" sulfur needed to balance the circulation becomes greater, but not by very much. The new estimates would be 1.95 million tons for 1946 and 7.4 million tons for 1959, increases of about 2% and 15% respectively. Although the resulting "other" sulfur source could be isotopically lighter than the $\delta\ ^{34}S$ value given by Koyama et al., it would still not indicate a fractionation of marine sulfate of 20 to 35 o/oo relative to seawater that would be expected from biogenic H_2S.

Our main reservations regarding the conclusion that very large amounts of sulfur from "other" sources are needed to balance the total circulation are based on doubts about the accuracy of the method by which sulfate in dry fallout is estimated. Dry fallout could be overestimated if some of the sulfate collected under bushes and trees contains sulfate in leachate derived from the soil, or if it contains sulfate from particles or absorbed gases concentrated out of the atmosphere by the selective action of the vegetation itself. We do not know whether or how the sulfur that may be absorbed through stomata is eliminated by the plant, but it is possible that some may be leached out by rainwater.

These criticisms of the work of Koyama et al. suggest that their conclusions cannot be accepted without further confirmation, perhaps in the form of observations of coastal marine sources of isotopically light sulfur dioxide as well as better estimates of the total sulfur in circulation.

c. Evidence of Excess Sulfur in Continental Runoff

Berner (1971b) infers the existence of very large biological sources of sulfur by means of two arguments which compare the amount of sulfur contained in river runoff with known sources.

The first argument considers anthropogenic sources in Europe and North America, and concludes that the quantity of sulfur released into the environment as a consequence of industrial activity must be greater than the quantity of sulfur injected into the air as a byproduct of fossil fuel combustion plus that directly injected into rivers or applied in fertilizer to the soil. To arrive at this conclusion, Berner contrasts the ratio of sulfate and chlorine in river runoff in North America and Europe with that in Asia, Africa, and South America. (See Table VII-11.) The ratio is about one in the three nonindustrialized continents and much larger in Europe and North America. Berner argues that if the runoff in the three nonindustrialized continents can be interpreted as the unpolluted "norm," then we may infer considerable excess sulfate due to industrialization in the first two continents, corresponding to 45 million tons of sulfate from Europe and 55 million tons from North America. This corresponds to about 27% of the total world sulfate runoff and about two thirds of the total for the continents in question. Since the river water data are not contemporary--most of the European data were collected before 1900, and most of those for North America were collected before

TABLE VII-11. - FLUX OF SULFATE FROM NATURAL AND POLLUTION SOURCES TO THE OCEANS FOR EACH OF THE MAJOR CONTINENTS

Continent	Concentration (mg/l)[a]			Flux to Ocean (10^6 tons/yr)[a]		
	Total Cl^-	Total SO_4^{--}	Pollutant SO_4^{--}	H_2O	SO_4^{--} (Nature)	SO_4^{--} (Pollution)
Europe	6.9	24	17	2.5×10^6	17	45
N. America	8.0	20	12	4.6×10^6	37	55
S. America	4.9	4.8	0	8.2×10^6	39	0
Africa	12.1	13.5	0	6.0×10^6	81	0
Asia	8.7	8.4	0	11.2×10^6	94	0
			TOTAL	32.5×10^6	268	100

[a] Data for average Cl^- and SO_4^{--} concentrations and water flux from Livingstone (1963)

Source: Berner (1971b)

1950--the fact that present industrial sulfur dioxide and sulfuric acid emissions are quantitatively almost sufficient to account for this excess does not explain the apparent discrepancy, especially for Europe. Both these industrial sources were negligible at the time that the European river water analyses were performed, although organic pollution of estuaries and coastal waters may have been extensive in some areas and may have accounted for some sulfate reduction.

Berner's second argument is also based on apparent excess of sulfate in river runoff, but for this argument he estimates the sulfur sources for the entire world and compares these with the total estimated runoff (Table VII-12).

A major source of sulfate in runoff is the weathering of sulfide and sulfate in sedimentary rocks. Berner employs the measured concentration of calcium in river water as an index to the amounts of pyrites and $CaSO_4$ weathered, and arrives at an estimate of 45 million tons sulfur per year, or 35% of the total river sulfate. Volcanic activity and sea spray are estimated to account for 13% of the total sulfate, leaving 52% to be accounted for by biological and marine sources and pollution. This totals 188 million tons of sulfate, or about 63 million tons as sulfur. Berner assigns 88 million tons, or almost half of the total to biological sources of H_2S returned to the land in precipitation, but does not give the basis for his estimate. The remainder is attributed to pollution sources. Although contemporary industrial sources of sulfur emissions could account for this, Berner points out that the age of the river water data preclude the use of contemporary values. Consequently, most of this is attributed to the effects of organic pollution, which promotes the anoxygenic conditions and provides the organic substrates necessary for bacterial production of H_2S.

The only serious reservations which may be voiced regarding these conclusions concern the utility of <u>any</u> interpretation of the European river water data presented by Livingstone (1963), who was careful to enumerate their inadequacies. Outmoded analytical techniques and the

TABLE VII-12. - ESTIMATED SOURCES OF SULFATE IN WORLD AVERAGE RIVER WATER

Source	ppm SO_4	% of Total	Total SO_4 (10^6 tons)	Total S (10^6 tons)
Rock Weathering				
Pyrite	1.3	12	45	15
$CaSO_4$	2.6	23	90	30
Volcanic Activity	0.8	7	25	8.3
Sea Spray	0.7	6	22	7.3
Marine H_2S	2.7	24	88	29.3
Total	8.1	72	268[a]	89.3
Pollution	3.1	28	100	33.3

[a] From Livingstone (1963)

Source: Berner (1971b)

failure to sample the water during an entire year to compensate for seasonal variations characterize much of the old data on which the European averages are based. The seriousness of the problem is indicated by the fact that the ion content of one third of the European runoff is estimated on the basis of chemical analyses of three Swedish rivers performed respectively in June, July, and October, 1905, while that of the remaining two thirds is based partly on analyses performed in 1848.

6. Atmospheric Chemical Reactions and Other Removal Mechanisms

Sulfur is present in the atmosphere in gaseous form as H_2S and SO_2 and in aerosol form as sulfuric acid and a variety of sulfates. (Junge, 1963; Robinson and Robbins, 1968, 1970; Georgii, 1970; Eriksson, 1963; and others.) The main removal mechanisms that are considered important in the atmosphere are briefly discussed below.

a. Oxidation of H_2S

Hydrogen sulfide undergoes a number of oxidation reactions in the troposphere. Hydrogen sulfide reacts with ozone, which is produced in photochemical smog and also mixes into the troposphere from the stratosphere, where it is a natural constituent. The product of this reaction is mainly sulfur dioxide and water, but the reaction is slow and consequently believed to be unimportant (Cadle and Allen, 1970).

H_2S does not appreciably absorb radiation of wavelength greater than about 2700 Å. Since the hydrogen bond energy of 81.1 kcal per mole per S-H bond corresponds to a wavelength of 3510 Å, H_2S does not undergo photolysis or react photochemically with molecular oxygen (Cadle and Allen, 1970). Hydrogen sulfide is soluble in water, as are ozone and molecular oxygen, but its rate of oxidation in solution in fog or cloud droplets has not been studied (Junge, 1963; Cadle, 1971).

H_2S reacts rapidly with atomic oxygen

$$H_2S + O \rightarrow OH + HS$$

A subsequent chain of reactions leads to the production of SO_2, SO_3, H_2SO_4, H_2, and H_2O. These reactions must occur to some extent wherever photochemical smog reactions produce atomic oxygen, and any H_2S that reaches the stratosphere should be rapidly removed by stratospheric O (Cadle and Allen, 1970).

b. Oxidation of SO_2

Sulfur dioxide reacts with atomic oxygen in a three-body reaction:

$$SO_2 + O + M \rightarrow SO_3 + M$$

This reaction must occur in smog. Experimental evidence suggests that the loss of SO_2 and the reduction of oxidants occurs in synthetic smog mixtures containing SO_2, NO or NO_2, and a suitable organic (Cox and Penkett, 1971; Wilson and Levy, 1970; and others). Thus, Wilson and Levy show that the rate of decay of SO_2 is greatly increased in the presence of photochemical smog and the production of oxidants is reduced significantly. However, they experimented with concentrations characteristic of heavily polluted cities: 0.75 ppm SO_2 and 1 ppm NO. Relative humidity also influenced the smog reaction and the effect of SO_2.

The reaction between SO_2 and O may be very important in the stratosphere and may aid in the production of the stratospheric sulfate aerosol, which is described in more detail below. The sulfur trioxide formed never persists in the open atmosphere; it reacts very rapidly with water vapor to form sulfuric acid.

SO_2 absorbs near-ultraviolet radiation and the excited molecule may react with O_2; according to Cadle (1971), however, the quantum yield is low. SO_2 may also react with O_3 while excited, but this reaction has not been studied. SO_2 dissolves in atmospheric water, forming sulfurous acid (H_2SO_3) or bisulfite (HSO_3), which is then oxidized by dissolved oxygen from the air. The oxidation of the dissolved SO_2 depends on the acidity of the water and the presence of certain catalysts, such as iron and manganese salts (Junge and Ryan, 1958; Johnstone and Coughanowr, 1958). The reaction slows if the droplet becomes highly acid, so the accumulation of sulfuric acid by this means is self-limiting.

If ammonia is present in the atmosphere, it increases the rate of reaction, since it is highly soluble and is capable of maintaining a favorable pH. The effect of NH_4^+ on the conversion of SO_2 to H_2SO_4 and to $(NH_4)_2SO_4$ has been studied by several workers (Junge and Ryan, 1958; Van den Heuvel and Mason, 1963; Scott and Hobbs, 1967; and McKay, 1971). McKay reports studies of the kinetics of the reactions involved in the conversion of SO_2 and NH_3 to ammonium sulfate. He found that the reaction is an order of magnitude faster than had been estimated by previous workers. The reaction is dependent on ammonia concentration and temperature as well as on the phase volume ratio of droplets to air. In a cloud or a thick mist, appreciable quantities of sulfur dioxide and ammonia may be fixed quite rapidly, but the reaction will slow down as the reactants are depleted and will stop when one or the other has been exhausted. The reaction rate increases as the temperature declines. Table VII-13 shows some characteristic times required for the fixing of one or two $\mu g/m^3$ of NH_3 as ammonium sulfate as a function of temperature, phase volume ratio, and initial concentration of NH_3 and SO_2. His results indicate that significant quantities of NH_3 and SO_2 may be converted to ammoniated sulfate in a matter of hours under the proper humidity and temperature conditions. This work provides a possible explanation for observed differences in the concentrations of SO_2 and SO_4^{--} in different environments. (See discussion of the results of Georgii (1970) in section 7b below.)

c. Aerosol Removal Mechanisms

SO_2 that is converted to sulfate and/or ammonium sulfate aerosols will eventually be removed by precipitation, but the lifetime of the aerosol is a function of many factors. The size and mass of the particle determines its sedimentation rate; below a certain size range (0.1 micron diameter), the particle is effectively too light to sediment out, although it may be brought down to the surface by vertical air movements (Junge, 1963; Eriksson, 1959; Cadle, 1966). The size of an individual aerosol may vary, becoming smaller and more concentrated if moisture is evaporated under drying conditions, or larger if it acts as a cloud

TABLE VII-13. - TIME REQUIRED TO FIX AMMONIA AS AMMONIUM SULFATE
(minutes)

Temp. (°C)	Vol. ratio	NH_3 µg/m^3 :	2.7	5.3	10.6	5.3	5.3	5.3	5.3
		SO_2 µg/m^3 :	20	20	20	20	40	100	200
25	10^{-7}	Time for fixing of 1µg/m^3 NH_3	17	6	3	6	5	4	2
	$3x10^{-8}$		270	70	24	70	39	22	12
15	10^{-7}		6	4	2	4	3	2	1
	$3x10^{-8}$		53	17	7	17	11	8	5
25	10^{-7}	Time for fixing of 2µg/m^3 NH_3	210	30	9	30	16	10	6
	$3x10^{-8}$		>300	>300	145	>300	265	131	57
15	10^{-7}		40	9	3	9	6	4	3
	$3x10^{-8}$		>300	200	30	100	61	30	16

Source: Adapted from MacKay (1971)

condensation nucleus when humidity increases. Particles and other trace constituents are scavenged by rainfall, but the effectiveness of washout by rain depends on a number of factors such as intensity and duration of the rain and size of the rain droplet. In general, small particles are less effectively removed than large ones (Cadle, 1966).

d. Lifetime of SO_2

There is considerable evidence from experiments in the field that anthropogenic SO_2 does not survive long and that its removal rate is dependent on humidity. Rodhe (1970) concluded that the lifetime of sulfur from the city of Upsala in winter is about 5 hours. Meetham (1950) estimated a residence time of roughly 10 hours for anthropogenic SO_2 in England and concluded that most of it was removed by reaction with wet surfaces, particularly vegetation. Gartell, Thomas, and Carpenter (1964) report a loss of 50% of the SO_2 in the smoke plume from a power plant within 20 minutes to 3 hours. Weber (1970) estimates that under neutral or stable conditions in the highly polluted atmosphere of Frankfurt-am-Main, 50% of the anthropogenic SO_2 is converted to sulfate within 20 minutes to 1 hour.

The role of ammonia in the conversion of anthropogenic sulfur dioxide to sulfate has not been extensively studied. Healy, McKay, Pilbeam, and Scargill (1970) reported that a large fraction of the NH_3 entering polluted atmospheres is converted to ammonium sulfate in a matter of hours, and that the reaction occurs in the dark. Heard and Wiffen (1969) report that 99% of the mass of particles below 0.1 micron diameter (collected in a rural region about 50 miles from London) are ammonium sulfate. They estimate an average ammonium sulfate content of 15.5 $\mu g/m^3$ at ground level, while the NH_3 concentration was 5.5 $\mu g/m^3$. Healy, McKay, Pilbeam, and Scargill (1970) report that reactions between sulfuric acid droplets (produced, for example, in the smoke plume of power plants) and gaseous ammonia are important only at levels of 70% relative humidity or more, and that gas-phase reactions between NH_3 and SO_2 are unlikely to account for the production of ammonium sulfate. At relative humidities below 70%, reacting atmospheric droplets would have to be stabilized by dissolved solids, which might act as catalysts for the oxidation of dissolved SO_2.

e. Removal of SO_2 by Vegetation

Gaseous SO_2 is also removed from the atmosphere by reactions with vegetation, although the mechanism involved is not known in detail. Meetham (1950) attributed much of the removal of atmospheric SO_2 to reaction with wet surfaces, particularly vegetation. Spedding (1969) studied the uptake of SO_2 by barley leaves at SO_2 concentrations ranging from 10 to 20 $\mu g/m^3$ (which is characteristic of ground-level air in rural regions of England) to the 100 - 150 $\mu g/m^3$ found in industrial districts. Using ^{35}S at carefully controlled concentrations, temperature, and relative humidity, he measured the deposition velocity v_g per unit area of leaf surface.

$$v_g = \frac{SO_2 \text{ absorbed per cm}^2 \text{ of leaf surface per second}}{SO_2 \text{ per cm}^3 \text{ in air}}$$

V_g has the dimensions of velocity and is expressed in cm per second.

Spedding measured the uptake of SO_2 as a function of relative humidity. At low relative humidities the stomata are closed and the deposition velocity is low--0.0028 to 0.011 cm/sec for relative humidities of 10 to 85%. At high humidities the stomata are open, and the deposition velocity increases to 0.066 to 0.18 cm/sec for relative humidities of 80 to 95%. Table VII-14 shows the results of experiments with other surfaces, using relatively high concentrations of SO_2.

Extrapolation of these results to field conditions requires that the actual leaf area be taken into consideration. The leaf area index (ratio of area of leaves to that of the ground) varies with the species and its age; it may be 4 or 5 for grasses, meadow plants and crops, and as high as 10 or more for mature deciduous temperate forests in the summer. The effectiveness of leaves for removing SO_2, CO_2, or other trace gases varies with position in the canopy and ventilation. After converting by appropriate factors, Spedding estimates a deposition velocity for barley to be 1.5 cm/sec.

TABLE VII-14. - DEPOSITION VELOCITIES FOR SO_2 ONTO A VARIETY OF SURFACES AT LOW AND HIGH HUMIDITIES AT 18°C

(centimeters per second)

	High Humidity[a]	Low Humidity[b]
Oolitic limestone	0.062	0.032
Lead foil	0.054	0.035
Mild steel	0.20	0.0017
Copper sheet	0.40	0.002
Aluminum foil	0.035	0.0012
Filter paper	0.31	0.010

---

[a] Humidity 81%, SO_2 concentration 372 μg/m^3, exposure time 10 minutes.

[b] Humidity 11%, SO_2 concentration 365 μg/m^3, exposure time 21 minutes.

Source: Spedding (1969)

Eriksson (1960) employed the data of Johansson (1959) to estimate a deposition velocity of 2.0 cm/sec. Meetham (1950) estimated that of the 5 million tons of SO_2 emitted each year in Britain during the 1940's, 3.9 million tons was deposited on land, but that of this only 0.7 million tons was collected in deposit gauges, leaving 3.2 million tons to be deposited on land in other ways. This implies a mean deposition velocity of 1.8 cm/sec when averaged over the entire land area of Britain (Spedding, 1969).

In laboratory experiments, Hill (1971) studied the uptake of several common gaseous pollutants by an alfalfa canopy. He found that appreciable quantities of SO_2 were removed, but he did not calculate deposition velocity nor provide data from which it could be readily estimated. Except for O_3, uptake rate is approximately related to solubility of the gas studied.

The effectiveness of vegetation in reducing SO_2 levels was confirmed in the field by Martin and Barber (1971), who measured the SO_2 level in air collected at two points above a large hawthorn hedge. Air was sampled by means of collectors in two positions--one was located 0.15 to 0.5 meter above the hedge, while the other was located 1.5 meters above it. Most of the time, lower concentrations were observed in air collected by the sampling instrument nearer the hedge. Whenever the concentration detected by means of the more distant instrument was 200 ppb or more, the difference between the two sampling locations was always at least 200 ppb. Concentrations near the hedge were never larger than those farther away. Martin and Barber counted the number of times lower concentrations were detected near the hedge. These occurred most frequently at high temperatures and high humidities, which suggests that they were related to stomata opening. However, differences were also recorded at night, when the stomata are closed, and this suggests that absorption by thin films of water may be important.

These experiments indicate that vegetation plays a role in the removal of sulfur dioxide from the atmosphere, but they do not provide useful information regarding the mechanisms involved or the fate of the absorbed sulfur dioxide. The effectiveness of vegetation sinks may vary with humidity and atmospheric concentration. The global effectiveness of vegetation sinks is difficult to estimate on the basis of present information, and the subject needs more thorough study.

7. Atmospheric Abundances of Sulfur Compounds

Information regarding sulfur compounds in the air comes from direct recording of concentrations, usually of gaseous and particulate compounds separately, and indirect evidence in the form of chemical analyses of precipitation. Networks established in Sweden, Europe, and the U.S. provide the best available data, but they are limited for the most part to relatively polluted environments in the north temperate zone. In general, precipitation data are more readily available than direct measurements of atmospheric concentrations, and information on gas concentrations usually provide measurements only of SO_2. H_2S presents special collection and measurement problems, and appears often to be present only at very low concentrations. Routine air pollution monitoring stations usually monitor the particulate content of the air but do not normally conduct chemical analyses of the particulates. Thus, the relative concentrations of SO_2 and SO_4^{--} usually cannot be inferred.

In the 1950's and early 1960's, interest in the natural background circulation and geochemistry of sulfur and other atmospheric constituents led to attempts to determine the background concentrations in environments believed unaffected by industrial pollutant sources. As a result, many useful measurements were made in suburban and rural locations. More recently, measurements made in isolated locations such as the Arctic, the Antarctic, and remote tropical forests have become available. The latter show such low concentrations of all trace constituents that many of the rural and suburban locations, previously thought to be unpolluted, are now recognized as strongly affected by anthropogenic emissions.

a. Ground Level Concentrations

Concentrations of sulfur compounds observed at ground level in cities and in surburban or rural locations are given in Table VII-15. These data are collected from a variety of sources and represent a diversity

TABLE VII-15. - CONCENTRATION OF SULFUR COMPOUNDS IN THE LOWER TROPOSPHERE IN VARIOUS LOCATIONS

Location	SO_2 (ppb)	H_2S (ppb)	SO_4 Particulates (μg/m^3)	Source
Bedford, Mass.[b]	23.5	5-6		Junge (1963)
Frankfurt-am-Main[a] (winter)	151			Georgii (1960), cited in Junge (1963)
Frankfurt-am-Main[a] (summer)	30			Georgii (1960)
Hawaii[d,e]	0.4			Georgii (1960)
Alnarp (southern Sweden)[f]	2.3 to 14.4			Junge (1963)
Offer (northern Sweden)[d,f]	0.0 to 4.2			Junge (1963)
Central Germany[c]	5-10			Georgii (1970)
Boulder, Colorado	0.8			Georgii (1970)
Antarctic[d],	0.0 to 2			Fisccher, Lodge et al. (1970)
Panama[d,g]	0.8 to 5			Pate, Lodge et al. (1970)
U.S. Urban[a]	10 to 180		10	Ludwig, Morgan & McMullen (1970)
U.S. Intermediate, rural[d]			2-5	Ludwig, Morgan & McMullen (1970)
England, rural[b]	20-70			Martin & Barber (1971)
England, cities[a]	more than 100			Martin & Barber (1971)
Harwell, England[b]			11.2	Heard & Wiffen (1969)

---

[a] Cities or locations near industrial sites

[b] Suburban areas or small cities

[c] Rural locations within a few hundred miles of cities

[d] Very remote locations

[e] Maritime air from Pacific samples on coast

[f] These are the maximum and minimum monthly means detected during a year of sampling in 1954-55.

[g] SO_2 measurements are from various locations representing Caribbean air and inland forest air. (See text.)

of measurement techniques, locales, and time periods.

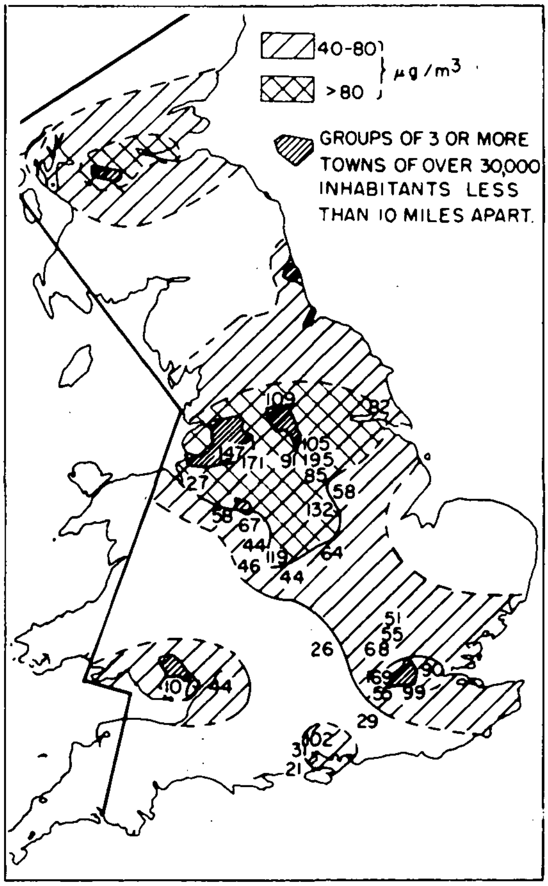
Figure VII-9 is a map of England showing the mean concentrations of atmospheric SO_2. It shows the clear influence of industrial sources. Sulfur dioxide concentrations in selected U.S. cities are shown as a function of time in Figure VII-10.

A long-term study of atmospheric chemistry in remote locations--particularly polar and tropical regions--has been recently initiated by the National Center for Atmospheric Research. Some of the findings with respect to the sulfur cycle are reported in Pate, Lodge, Sheesley and Wartburg (1970), Pate, Pitombo, Wartburg, et al. (1971), Pate, Sheesley, Wartburg, et al. (1971), Wartburg, Pitombo, Pate, et al.(1970), and Fisher, Lodge, Wartburg and Pate (1968). These may be summarized in part as follows:

(1) SO_2 is present at extremely low concentrations in the tropical forest of both Panama and Brazil (Table VII-16). Its concentration varies with humidity. If the lifetime is short--as the humidity and NH_3 concentrations would indicate--the evidence suggests the presence of weak sources of atmospheric sulfur compounds in the forest floor. Thus, in Albrook forest (a mixed deciduous forest near the Pacific side of the Ithmus which receives prevailing winds from the Caribbean coast), there was more SO_2 under canopy than above it.

(2) Sulfuric acid aerosols were detected in the interior of Panama, while ammonium sulfate aerosols were found closer to the coast. Since oceanic NH_3 sources are also indicated by the data, the inference is that at least some of the sulfuric acid is of local origin.

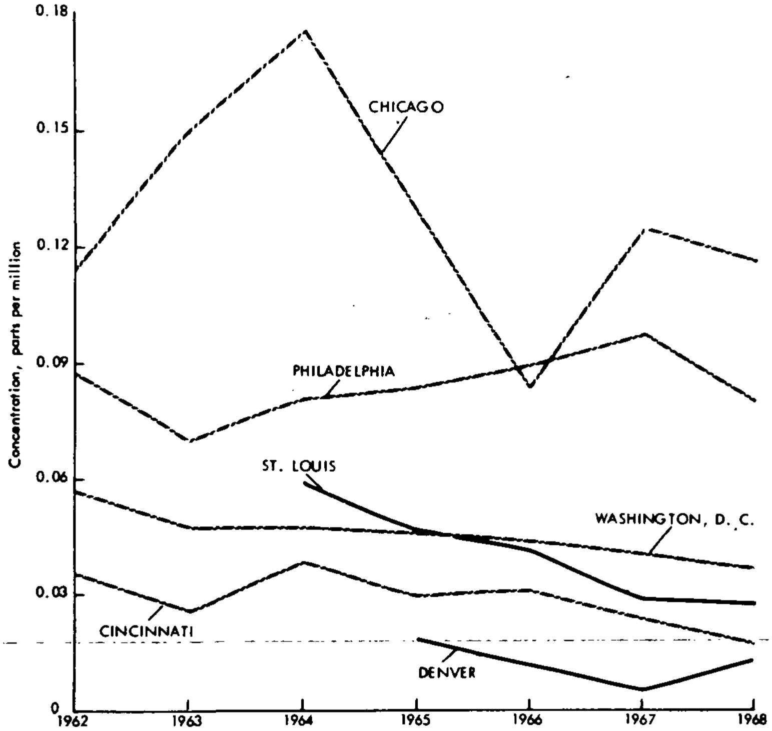
(3) Amazon data indicate that the natural tropospheric background concentration is not more than 0.5 ppb, and that this SO_2 is of local, presumably biological origin. Under conditions of high humidity, concentrations may be as low



Source: Meetham (1959)

Distribution of SO_2 in air over England in winter. Units are μg/m^3.

FIGURE VII-9 SO_2 OVER ENGLAND IN WINTER



Source: Ludwig, Morgan, and McMullen (1970)

VII-10 TRENDS IN ANNUAL AVERAGE SO_2 CONCENTRATIONS IN U.S. CITIES

TABLE VII-16. - SEASONAL MEANS OF SULFUR DIOXIDE CONCENTRATIONS IN THE TROPICS

(parts per billion by volume)

	Wet Season[a]		Dry Season[b]
Forest			
Ducke Forest Res. (Brazil) under canopy	0.2		0.3
Albrook Forest (Panama) under canopy[c]	1.1		1.6
Albrook Forest (Panama) above canopy[c]	0.8		1.0
Interior River			
Rio Taruma/Solimoes (Brazil)	0.1		0.5
Chagres River (Panama)			0.3
Maritime			
Barbados (Atlantic air)		0.4	
Ft. Sherman (Panama) (Caribbean air)	1.9		0.8

[a] Wet season samples: Brazil, September/October; Panama, April/ December
[b] Dry season samples: Brazil, April; Panama, January/March
[c] Seasonal mean of daily medians

Source: Pate, Lodge, Sheesley, and Wartburg (1970) as 0.1 ppb under the canopy; drier conditions lead to larger concentrations of SO_2, up to perhaps 2 ppb.

(4) No reportable H_2S was detected, which suggests that the upper bound for this gas in the troposphere is 0.5 ppb.

(5) SO_2 was detected in wind from the Caribbean (Ft. Sherman) at twice the concentration observed in wind from the Atlantic, which suggests a Caribbean source that is stronger than any Atlantic source.

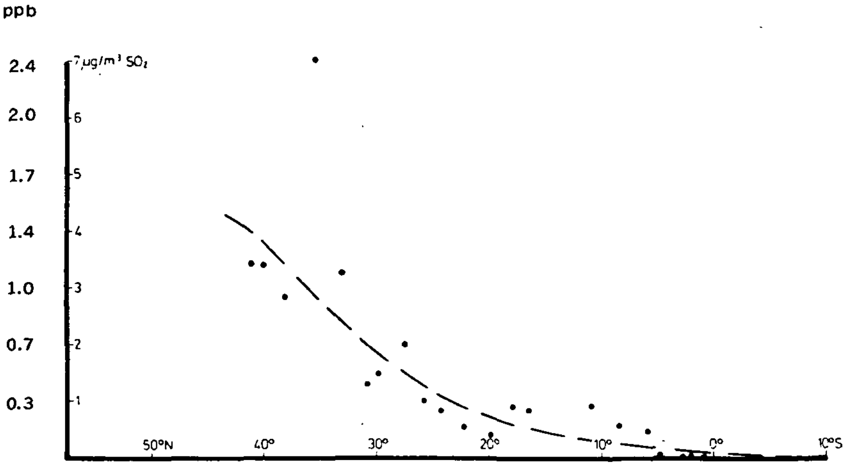
(6) SO_2 concentrations in the Antarctic are comparable to those observed in the tropical forests. (Fischer, Lodge, Pate and Cadle, 1969.)

We have found only one report of SO_2 concentrations over the ocean. Georgii (1970) reports measurements of SO_2 during a voyage of the Meteor from south to north along 30° W longitude in the middle of the Atlantic, January-March 1969. The results are shown in Figure VII-11. No SO_2 was detected south of the equator, and a gradual increase north of the equator was observed to about 4 $\mu g/m^3$. This SO_2 is attributed to European pollution sources. Sulfate concentration of aerosols is shown in Figure VII-12.

b. Abundance Profiles in the Troposphere

Georgii (1970) reports a series of abundance profiles in which he measured both SO_2 and sulfate concentration as a function of altitude over many locations in rural Germany and also over Boulder, Colorado. Under inversions the SO_2 concentration was relatively constant or declined slowly with altitude. (See Figures VII-13 and VII-14.) Above the inversion layer SO_2 declined rapidly with altitude and usually reached half its ground level concentration at 3 km or lower, but above 3 km relatively little decline with altitude was observed. Georgii does not give the quantity of the background concentration present above 3 km but his plots suggest it may be about 0.5 $\mu g/m^3$.

The sulfate concentration showed less variability and slower decline with altitude than SO_2. The ratio of sulfate to sulfur dioxide increases with altitude, which suggests that (at least over rural Germany) SO_2 is being gradually and continuously converted to sulfate within an extended layer of the atmosphere. In the much dryer air of Boulder, Georgii found much less sulfate and SO_2 than over Germany, and a characteristically lower ratio of sulfate to SO_2, which may be attributed to the fact that drier conditions do not promote sulfate formation (Figure VII-13).



Source: Georgii (1970)

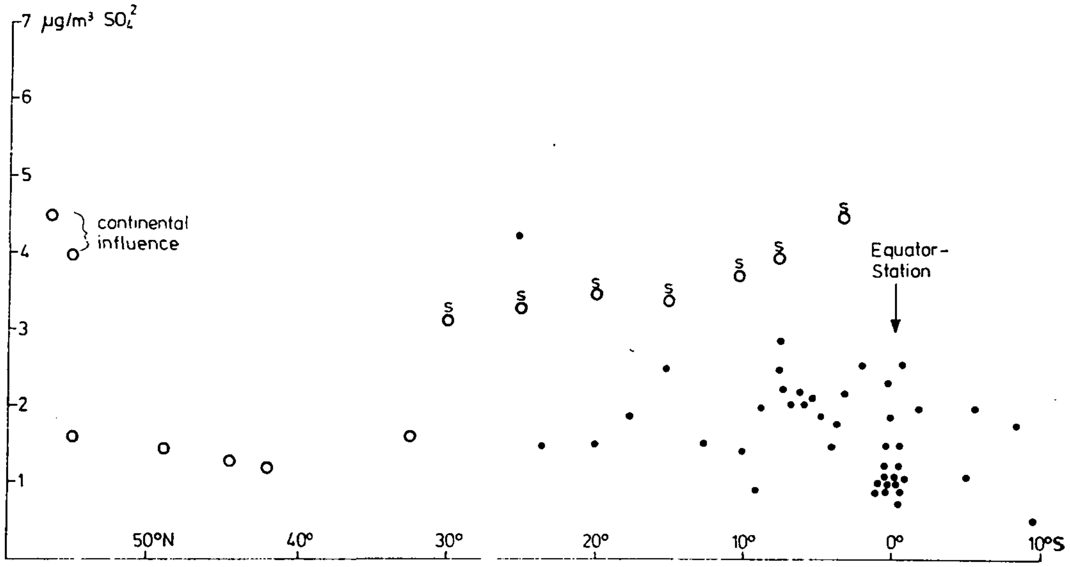
SO_2 measured in surface air over the Atlantic Ocean, January-March 1969.

FIGURE VII-11 SO_2 OVER THE ATLANTIC OCEAN

c. Sulfur in the Stratosphere

The gas composition of the stratosphere is not known, but numerous speculations regarding the presence of sulfur and nitrogen compounds in gaseous form have been based on the observations of the stratospheric large-particle layer, which is mainly composed of ammonium sulfate.

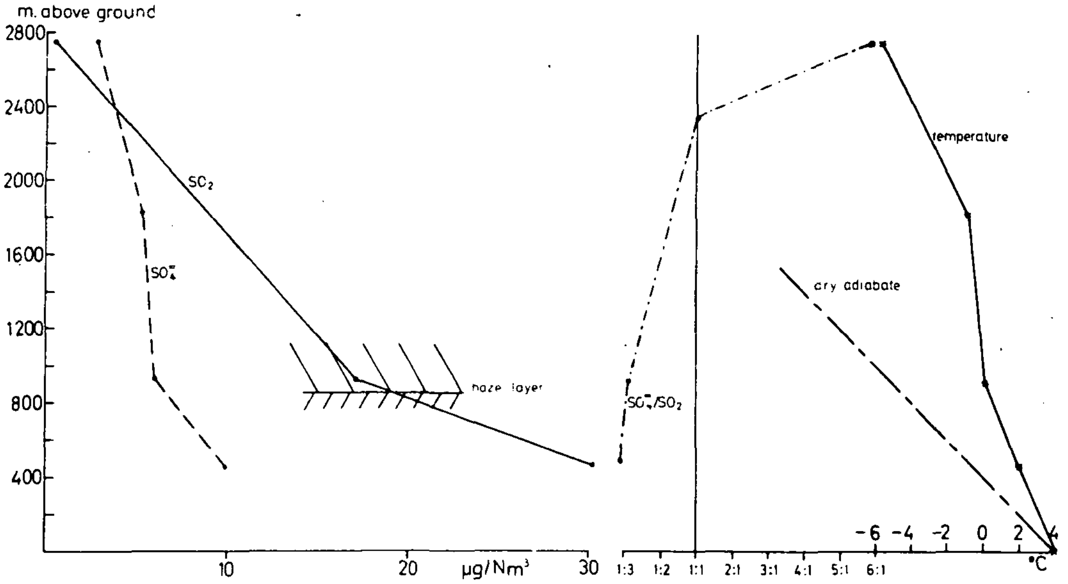
The stratosphere contains both Aitken particles, which are less than 0.1 micron in diameter, and large particles in the range 0.1 to 1 micron (see Figure VII-4). The latter appear to reach maximum concentration at about 20 km, as reported by Junge, Chagnon, and Manson (1961) and



Source: Georgii (1970)

● First section (1/19/69 - 2/27/69) and equator station
○ Third section (4/12/69 - 5/8/69)
s Advection of dust from the Sahara Desert

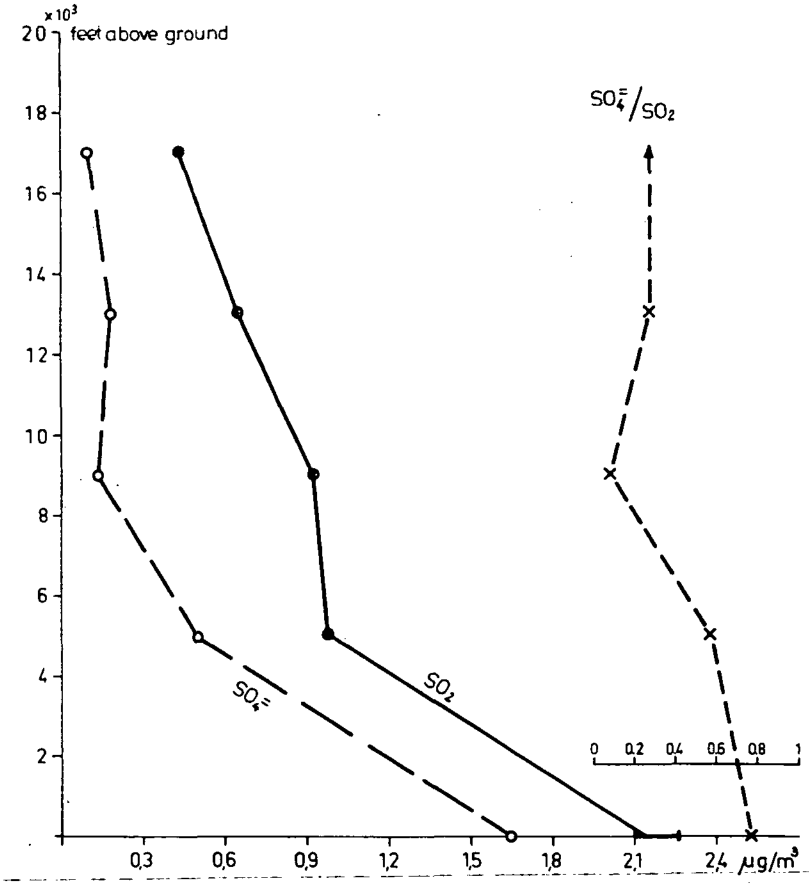
FIGURE VII-12 SULFATE CONCENTRATION IN AEROSOLS OVER THE ATLANTIC



Source: Georgii (1970)

Vertical distribution of SO_2 and SO_4^{--} in aerosols in unpolluted air over central Germany, February 25, 1967.

FIGURE VII-13 SO_2 AND SO_4^{--} OVER CENTRAL GERMANY



Source: Georgii (1970)

Vertical distribution of SO_2 and SO_4^{--} in aerosols in the region of Boulder, Colorado, September 14, 1967.

FIGURE VII-14 SO_2 AND SO_4^{--} OVER BOULDER, COLORADO

Chagnon and Junge (1961); but Bigg, Ono, and Thompson (1970) reported apparent increases in particle concentrations to about 27 km. Accurate estimates are difficult, because techniques for collection have different collection efficiencies which usually vary with altitude and particle size range. In addition, there is evidence that concentrations vary by an order of magnitude or more.

Aitken particles found in the stratosphere decline in concentration with altitude (Junge, 1963; Martell, 1966) and have been attributed to sources in the troposphere. The origin of the stratospheric large particles is unknown.

Friend (1966) states that the large particles are almost entirely made up of ammonium sulfate or ammonium persulfate; Mossop (1963, 1965) reports that most contain a small, insoluble nucleus. Bigg, Ono, and Thompson (1970) report that the chemical composition changes with altitude, with more ammonia in aerosols collected at higher altitudes. Martell (1966) proposed that large particles are formed by coagulation of Aitken nuclei transported from the tropopause, but the observation of large particles at altitudes up to 36 km similar to those found at 20 km is interpreted by Bigg, Ono, and Thompson as evidence against this origin.

Junge, Chagnon, and Manson (1961) suggested that stratospheric oxidation of H_2S or SO_2 diffusing upward from the ground forms sulfur trioxide, which could attach to Aitken nuclei to form sulfates. At that time, it was not known that the sulfate layer contains appreciable amounts of NH_4^+, and relatively high levels of SO_2 in the upper troposphere (about 8 $\mu g/m^3$) were not considered unreasonable. Bigg, Ono, and Thompson (1970) suggest that the presence of the stratospheric ammonium sulfate layer at 36 km implies that at some levels the stratosphere should be saturated with sulfuric acid vapor, and that a relatively complicated chemistry is to be expected in the middle and upper stratosphere.

The ammonium sulfate layer changed after the Gannung Agung volcanic eruption in 1963; Mossop (1965) found liquid aerosols and liquid coatings on particulate aerosols that had not been seen before. Many observers reported increases in the overall turbidity of the atmosphere beginning about this time. Cadle and Frank (1968) have suggested that explosive eruptions of volcanoes would transport considerable sulfate into the stratosphere, which may contribute to the stratospheric particulate load.

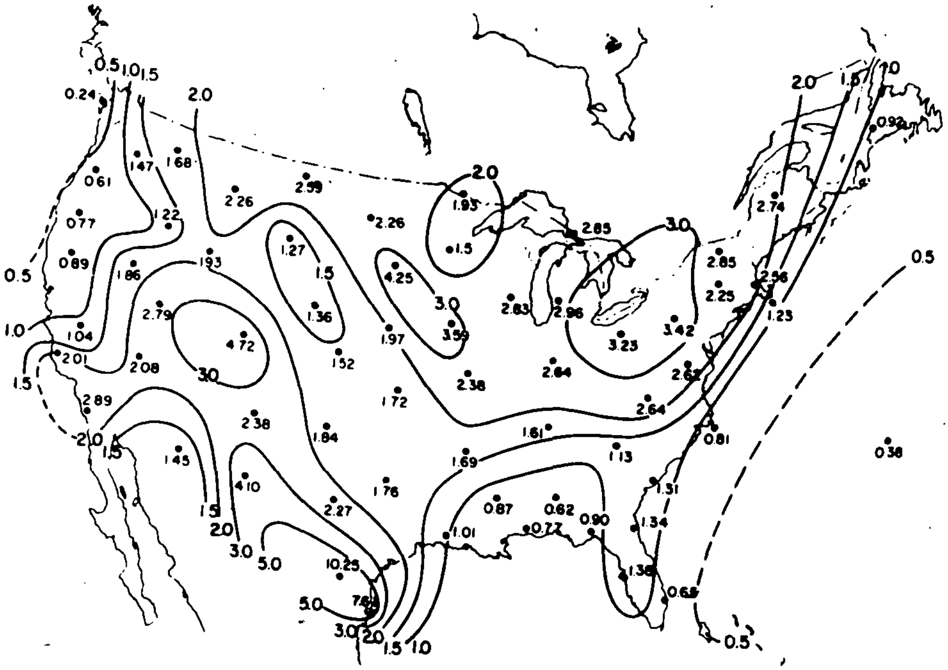
From a quantitative point of view, the sulfur in the stratosphere is unimportant. At most (making a generous interpretation of the observations of the highest concentrations), the mean burden would not seem to total more than 0.1 million tons S. This corresponds to 1 particle per cm^3 of pure $(NH_4)_2 SO_4$ for the whole stratosphere. The significance of this stratospheric sulfate layer lies in the fact that it may have a disproportionate effect on the radiation balance of the earth and that human activities may be contributing to an increase in the load. (See, for example, Rasool and Schneider, 1971; Landsberg, 1970; and SCEP, 1970 for discussions of this controversial position.)

d. Sulfate in Precipitation

Sulfur is transferred from the atmosphere to the surface in the rain and snow. The most widely used estimate of the annual removal of sulfate by precipitation is that provided by Junge and Werby (1958), who analyzed precipitation for an entire year for the whole continental United States.

The removal of particulate and gaseous sulfur by rain is a complex phenomenon which depends on the concentration in the atmosphere and a number of rainfall variables (see Georgii and Wotzel, 1970; Junge, 1963; Munn and Bolin, 1971; and Beilke and Georgii, 1968) as well as year-to-year fluctuations in the atmospheric circulation (Eriksson, 1970; Munn and Rodhe, 1971). Therefore, it is desirable to estimate the mean sulfur content of rain on the basis of measurements averaged for a long time over a large region such as the continental United States.

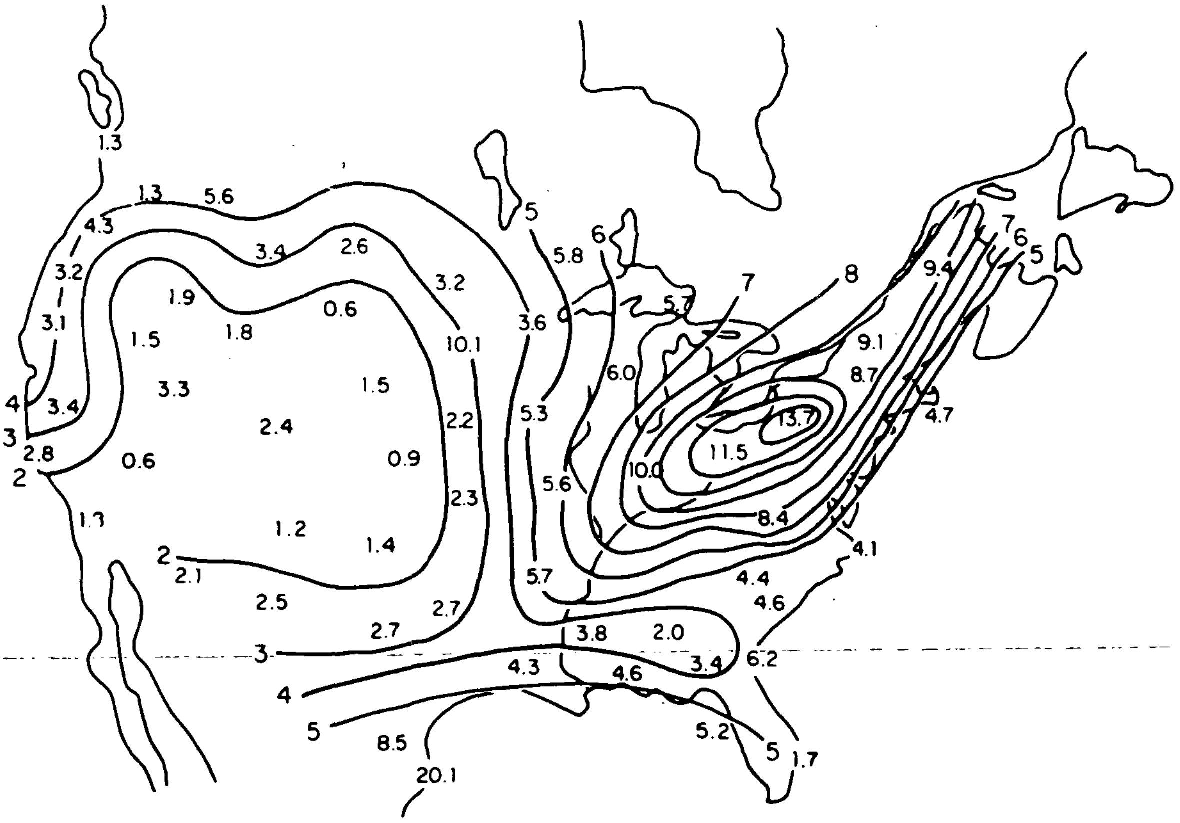
Figure VII-15, from Junge and Werby (1958), shows excess sulfate in rain in mg/liter; "excess" is determined on the basis of the observed chlorine content, under the assumption that some of the sulfate and chlorine is derived from sea salt particles in ratios characteristic of their concentrations in the ocean. Figure VII-16 shows excess sulfate in units of grams per m^2 of land, calculated by considering the total



Source: Junge and Werby (1958)

Average excess SO_4^{--} concentration in precipitation over the United States, July 1955 to June 1956, in milligrams per liter.

FIGURE VII-15 EXCESS SO_4^{--} IN PRECIPITATION OVER THE UNITED STATES



Source: Eriksson (1960)

Data from Figure VII-15 are plotted in units of gm/m^2/yr sulfur to emphasize the effects due to local pollution sources.

FIGURE VII-16 EXCESS SULFUR IN PRECIPITATION OVER THE UNITED STATES rainfall at various points in the country. (Chlorine concentrations in the rain were shown in Figure VII-6.) This map clearly shows the influence of industrial sources of sulfur on the eastern coast, in the Northeast, and in the Great Lakes region. High concentrations of excess sulfate along the Mexican border are attributed to the presence of windblown soil material from deserts of relatively high salt content, but the "local disturbances" over Brownsville and Laredo are not explained.

Table VII-17 contains estimates of sources of sulfur for the United States for the year in which the rainwater was collected. The total excess sulfur detected in precipitation was only 9.2 million tons calculated as sulfate, while estimated United States atmospheric sulfur emissions correspond to nearly 26 million tons sulfate. This implies that, at a minimum, about two thirds of the industrial sulfur emitted to the atmosphere was transported to other parts of the northern hemisphere or removed by means other than precipitation. There is no need to invoke biogenic H_2S to account for sulfur in circulation.

European precipitation data are shown in Figure VII-17. Here sulfur is expressed as grams sulfur/m^2. The concentration of high values in the eastern and southern portions of the area studied seems to reflect the effects of industry.

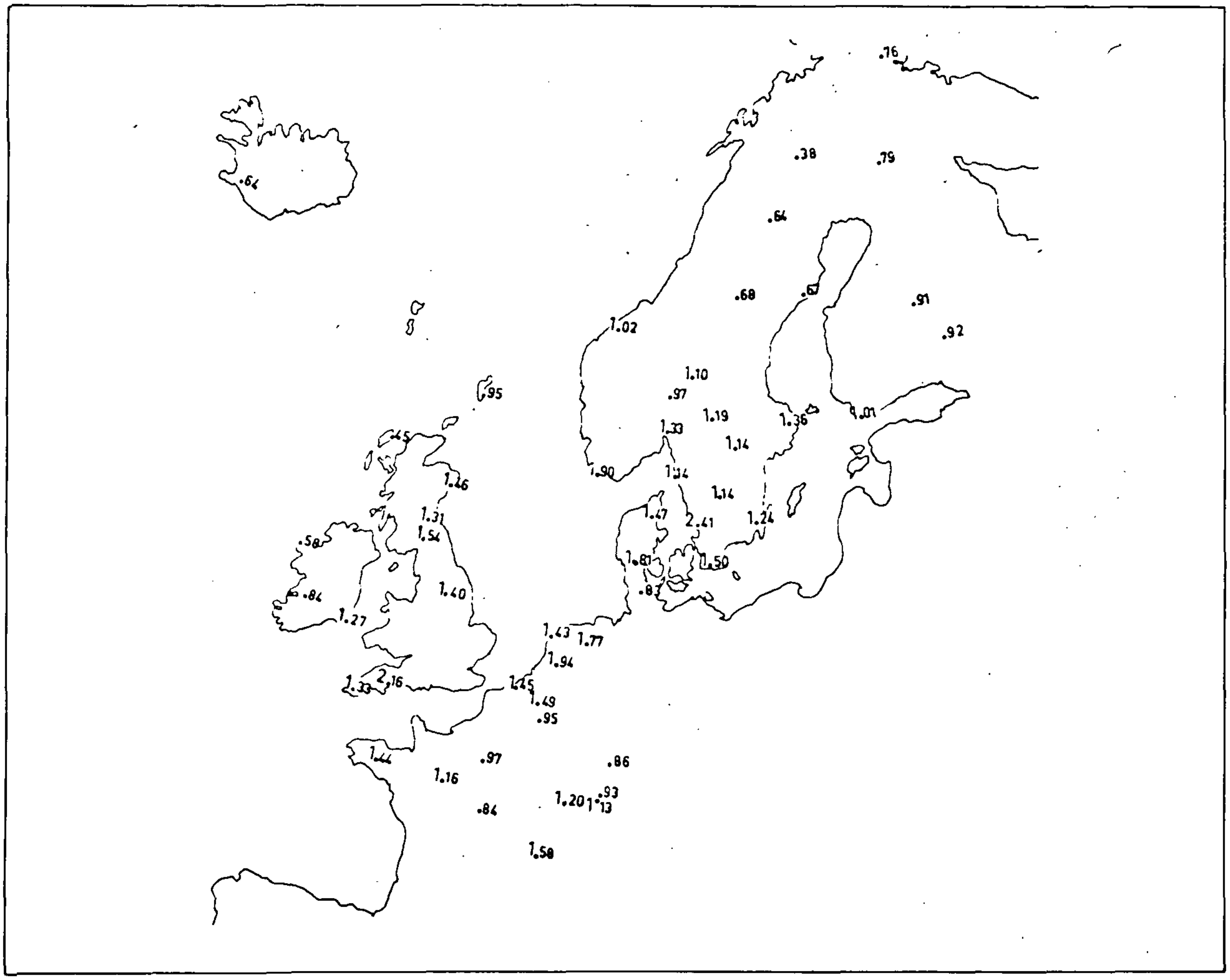
Sulfur in precipitation collected at a single point varies with the general features of the circulation, in a way that sometimes masks trends (Eriksson, 1970).

This discussion indicates that accurate estimates of the average concentration of sulfur or any other constituent in rainfall must be based on careful sampling over a large geographical area for a relatively long time period. The first estimates to satisfy these requirements were those published by Junge and Werby (1958) for the United States. Excess sulfate averaged 2.2 mg/liter of rain over land and 0.5 mg/liter over oceans. These figures have been used extensively by subsequent investigators, who extrapolate these concentrations to the entire world for the purposes of calculating the total annual transfer of sulfur from the atmosphere to the surface in precipitation.

TABLE VII-17. - SOURCES OF SULFUR FOR THE UNITED STATES, CALCULATED AS $SO_4^=$

Average concentration of excess $SO_4^=$ in rain	2.2 mg/l
Total amount of $SO_4^=$ brought down by rain, including sea spray	1.06×10^7 T/yr
Total amount of excess $SO_4^=$ brought down by rain	0.92×10^7 T/yr
Total U.S. estimated sulfur emission, 1957, calculated as $SO_4^=$	2.59×10^7 T/yr
Total U.S. sulfur consumption, 1957, calculated as $SO_4^=$	1.45×10^7 T/yr
Total U.S. sulfur production, 1957, calculated as $SO_4^=$	1.88×10^7 T/yr

Source: Junge (1963)



Source: Eriksson (1970)

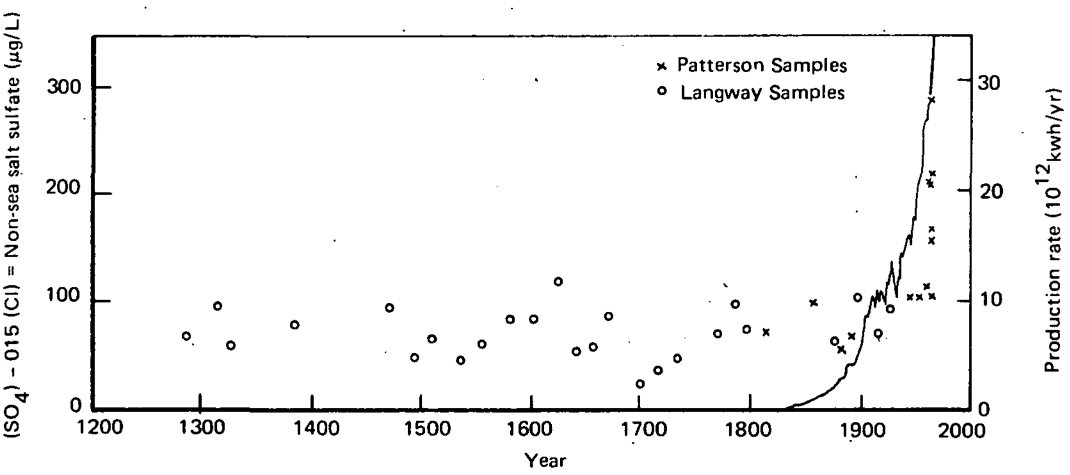
Mean concentration of sulfate in precipitation in the west European area during 1963, expressed as gm S/ m^2.

FIGURE VII-17 SULFATE IN PRECIPITATION IN WEST EUROPE

Examination of Table VII-17 indicates that more sulfur was emitted from industrial sources in 1957 than was returned in precipitation. Figure VII-16 clearly shows the profound effect of concentrations of industry on the distribution of the returned sulfur. It is difficult to avoid the conclusion that precipitation on this continent is significantly affected by pollution; thus, these data provide a very poor basis for estimating the worldwide content of sulfur in precipitation.

A long history of excess sulfate in Arctic precipitation has been preserved in the Greenland ice sheet. Junge (1960) studied the sulfate/sodium ratios in snow from the interval 1915 to 1957, during which fossil fuel consumption rose sharply, but could find no evidence of an increase in sulfate concentrations. He found sulfate/sodium ratios clustering around 7, which indicates considerable excess sulfate. The mean sulfate concentration for the entire interval is 250 μg/liter and that of chlorine is 37 μg/liter. Murozumi, Chow, and Patterson (1969) examined Greenland ice and ice from the Antarctic for evidence of lead pollution, and found pollutant lead in Greenland from about 1720 and in Antarctica from about 1940. Both these findings are consistent with the increase in industrial uses of lead in the northern and southern hemispheres. The failure to find sulfate in Greenland snows may be interpreted as due either to the fact that the anthropogenic injection of sulfur is low compared to the natural sulfur cycle, or that the atmospheric lifetime of sulfur is so short that too little survives transport to Greenland to be observable above the local levels. The magnitude of natural sources closer to Greenland is not known.

Koide and Goldberg (1971) studied sulfate and chloride concentrations in Greenland snows for the interval 1300 to 1965. Although they found significantly lower concentrations of sulfate than Junge (1960) or previous workers reported, they confirmed the general finding that no increase in sulfate concentration attributable to human activity can be discerned in these samples prior to 1960. Between 1300 and 1960 the sulfate/chloride ratio varied from 0.4 to 3.0, with a mean of about 2. Post-1960 samples show a mean of 200 μg/liter. Figure VII-18 is a plot



Source: Koide and Goldberg (1971)

Sulfate concentration in the Greenland glacier is plotted on a salt-free basis as a function of the year in which precipitation occurred. Solid curve shows world production of energy from coal, lignite, and crude oil.

FIGURE VII-18 SULFATE IN GREENLAND ICE

of the excess sulfate found by Koide and Goldberg, on which is superimposed a plot of the world consumption of thermal energy from coal, lignite, and crude oil. The last decade, during which excess sulfate in Greenland snow increased dramatically, was characterized by an explosive growth in the consumption of fossil fuel. Koide and Goldberg found that the seasonal variations in sulfate deposition correlated well with seasonal variations in pollutant lead deposition in 1965, which provides further confirmation of the attribution of the sulfate to relatively distant pollutant sources rather than local sources.

F. SULFUR BUDGETS

Three sulfur budgets have been constructed to describe the circulation of sulfur in nature. The best known of these was produced by Eriksson (1963) and was based on his examination of the circulation of chlorine and sulfur in nature (Eriksson 1959, 1960). Junge (1963) also produced a sulfur budget, largely based on the same information used and in many cases developed by Eriksson.

In 1968 Robinson and Robbins produced a new sulfur budget which has been subsequently quoted widely (Robinson and Robbins, 1970, SCEP, 1970). This one relied on several measurements and estimates developed by Eriksson, but it employed new data on the mean abundances of sulfur compounds in the atmosphere to estimate critical transfer rates.

In our opinion, all of these budgets are deficient in that they employ the method of balances to estimate some of the exchanges among some of the reservoirs, under the steady-state assumption that inputs balance outputs in all reservoirs except the one to which material injected anthropogenically eventually goes (traditionally the oceans). All three budgets use biological emission of H_2S into the atmosphere as a balancing mechanism to make the inputs balance the outputs with respect to the atmosphere and the biota (or soil). As a result, estimates of a natural background cycling of biogenic H_2S are necessarily inflated and misleading if other exchanges with the atmosphere are overestimated.

A critical examination of these budgets and of the information and assumptions on which they are based will help to summarize the problems that remain to be solved and the information that must be gathered before the atmospheric cycle of sulfur can be understood.

The three budgets are shown in Table VII-18 and in Figures VII-19 and VII-20.

Table VII-19 compares the estimates for several important exchanges which are contained in these budgets and describes the methods employed by the authors to arrive at their estimates.

Table VII-20 summarizes the atmospheric portions of the three budgets.

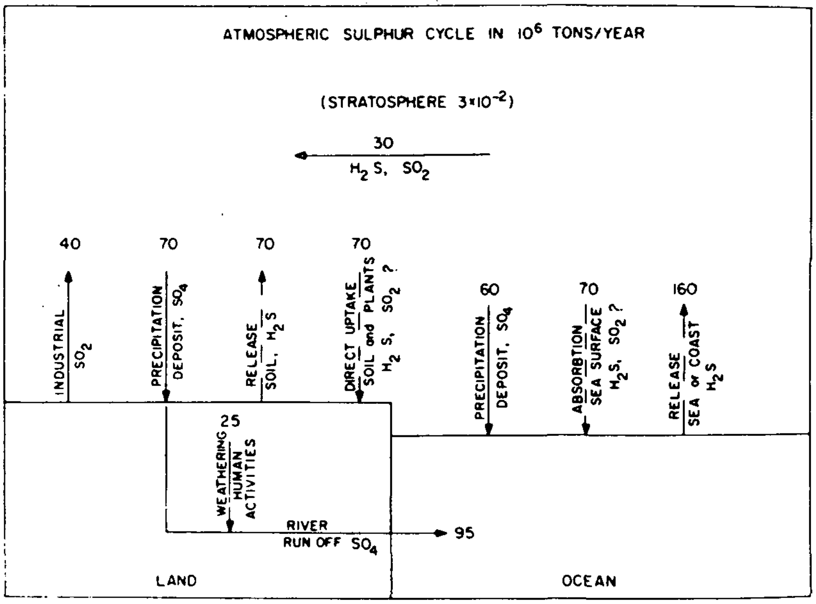
Although it is difficult to reconstruct the reasoning behind specific sulfur budgets, examination of Tables VII-19 and VII-20 suggest that the variations in the estimated transfer from atmosphere to land and sea are due primarily to different estimates of the mean concentrations of gases in the atmosphere. In 1960 (when most of the estimates on which

TABLE VII-18. - YEARLY BUDGET OF SULFUR IN NATURE
(millions of tons)

Item	Atmosphere		Lithosphere (Sediment Rocks)		Pedosphere		Hydrosphere (Oceans)	
	To	From	To	From	To	From	To	From
River discharge						80	80	
Weathering				15	15			
Fertilizers				10	10			
Precipitation		165			65		100	
Sea Spray	45							45
Dry deposition		200			100		100	
Sedimentation			15					15
Industrial	40			40				
Increase in sea			50[a]					50
Balance								
Soils-atmosphere	110					110		
Oceans-atmosphere	170							170
Sum	365	365	65	65	190	190	280	280
Specification								
As SO_4 sulfur	45	165			90	80	180	95
As SO_2 sulfur	40	200			100		100	
As H_2S sulfur	280					110		170
As other forms of sulfur				65	65			15

[a] For the balance, this must be treated as borrowed by the ocean from the lithosphere.

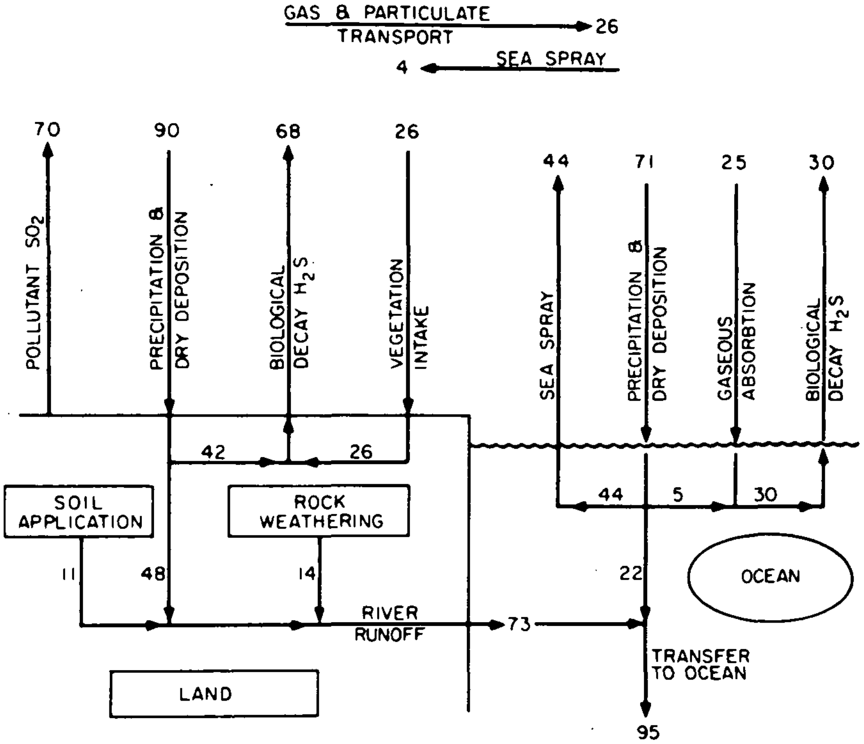
Source: Eriksson (1963)



Source: Junge (1963)

Tentative global budget of excess sulfur in circulation, prepared by Junge. Sea salt sulfur is excluded. Dashed arrows represent the most uncertain estimates.

FIGURE VII-19 JUNGE'S SULFUR BUDGET



Source: Robinson and Robbins (1968)

Global sulfur circulation as estimated by Robinson and Robbins. Units are 10^6 metric tons S per year.

FIGURE VII-20 ROBINSON AND ROBBINS' SULFUR BUDGET

TABLE VII-19. - COMPARISON OF SELECTED ITEMS IN SULFUR BUDGETS
(units are millions of tons S)

<u>River Discharge</u>		
Eriksson	80	Based on Swedish river runoff at turn of century derived in Eriksson (1959)
Junge	95	Summed rock weathering and sulfur in precipitation on land
Robinson & Robbins	73	Followed Eriksson (1959, 1960)
New estimate	123	Livingstone (1963)
<u>Precipitation Over Land</u>		
Eriksson	65	Extrapolation of Junge and Werby's results for the U.S. (1958)
Junge	70	Same as above
Robinson & Robbins	70	Same as above
<u>Rock Weathering</u>		
Eriksson	15	Estimate given in Eriksson (1950, 1960) uses mean of sulfur concentration in sedimentary rock and estimated rock weathering
Junge	14	Follows Eriksson
Robinson & Robbins	14	Follows Eriksson
New estimate	43	Berner (1971a)

TABLE VII-19. - (Continued)

Anthropogenic SO_2 Emission		
Eriksson	40	Uses estimates of worldwide emissions for 1955-56 (date of U.S. precipitation data collection)
Junge	40	Same as above
Robinson & Robbins	70	Use data for 1966 collected by themselves (Robbins & Robinson 1968)
Sulfate Application on Land		
Eriksson	11	Considered only sulfate in fertilizer
Junge	11	Followed Eriksson (1960)
Robinson & Robbins	11	Same as above
New Data	27	This includes most recent estimates of total sulfuric acid consumption by industry. Part of this goes to produce fertilizer, but all may be assumed to enter rivers.
Dry Deposition Over Land		
Eriksson	100	Assumes an average S concentration (presumably as SO_2 or H_2S) of 1 $\mu g/m^3$ and a vertical deposition velocity of 2 cm sec^{-1}
Junge	70	This estimate is not explained and is described as very uncertain.
Robinson & Robbins	46	26 as uptake by vegetation, estimated by assuming 0.5 ppb and a deposition velocity of 1 cm/sec. 20 estimated from sedimentation of particulate matter (method not described)

TABLE VII-19. - (Continued)

Dry Deposition and Gaseous Absorption Over Sea		
Eriksson	100	Assumes vertical transport velocity of 0.9 cm sec^{-1}, which would seem to imply an assumed concentration of 0.4 ppb as sulfur.
Junge	70	Does not specify. Indicates that estimate is very uncertain.
Robinson & Robbins	29	14 is dust (basis for estimate not specified); 25 is gaseous absorption, estimated by assuming vertical deposition velocity of 0.9 cm sec^{-1} and concentration of SO_2 of 0.2 ppb.
H_2S Emissions from Land		
Eriksson	110	Assumed 6 $\mu g/m^3$ S as H_2S in the atmosphere (based on measurements at Bedford and New York). Needed large injections to balance large removals from the atmosphere.
Junge	70	Assumed that vegetation release balances vegetation intake.
Robinson & Robbins	68	Uses for balancing the vegetation intake and land deposition not assumed to be transferred to the sea in river runoff.
H_2S Emissions from Sea		
Eriksson	170	Needed to balance removal from the atmosphere
Junge	160	Needed to balance the excess sulfate in precipitation over the sea and to transfer 30 to the atmosphere to make up the difference between fossil fuel injection and sulfate deposited in the rain.
Robinson & Robbins	30	Needed to balance the transfer from marine atmosphere to sea surface and the transfer from marine atmosphere to land atmosphere.

TABLE VII-20. COMPARISON OF ATMOSPHERIC CYCLES OF THREE SULFUR BUDGETS (millions of tons)

	Total In Atmospheric Circulation	Total H_2S Emission	Total Fossil Fuel SO_2
Eriksson	365	280	40
Junge	270[a]	230	40
Robinson & Robbins	212	98	70

[a] Does not consider sea salt

the budgets of Junge and Eriksson are based were made), mean tropospheric concentrations of SO_2 and H_2S were believed to be high, probably because most measurements had been made in relatively polluted air (see Table VII-21). Since dry deposition (specifically, vegetation and soil uptake) is dependent on the concentration of gas in the troposphere, large annual transfers result from the use of these generous estimates of tropospheric concentrations.

These removals from the atmosphere must be balanced by correspondingly large injections, and the only known source is biogenic H_2S. Thus, all of the 280 million tons of sulfur Eriksson assumes is emitted from biological sources is required to balance estimated removal. Robinson and Robbins need 68 million tons of S as H_2S from land sources; this figure results from combining the river runoff Eriksson estimated for the turn of the century in Europe with pollutant emission of SO_2 from the 1960's and sulfate precipitation data based on United States measurements of Junge and Werby (1958), which are almost certainly greatly inflated with pollutant sulfate. These land applications total 116 million tons, or a total of 141 million tons when 25 million tons of sulfur in rock weathering and fertilizer applications are added. But since only 73 million tons of sulfur is assumed to be transferred to the sea each year, the remaining 69 million tons is transferred to the atmosphere via H_2S production.

This example illustrates the manner in which mixing of contemporary estimates of pollution emission and old estimates of river runoff can lead to dubious conclusions. It would seem that any further developments of budgets for sulfur should await better information about contemporary rates of river discharge of sulfur, as well as estimates of the abundance and, hopefully, the mean lifetimes of tropospheric sulfur in all its forms.

While estimates of H_2S injection based on assumed high atmospheric concentrations of sulfur compounds need not be considered seriously, very short lifetimes of atmospheric SO_2 in remote locations might require

TABLE VII-21. ESTIMATES OF TRACE GASES IN THE ATMOSPHERE
(parts per billion)

		Background		
	Polluted	Published Means (after Junge, 1963)	Recent	Most Recent[b]
Oxygen		209,000,000		
Carbon Dioxide		300,000	320,000[a]	
Methane		1,400	1,250	
Hydrogen		700	500	
Nitrous Oxide	2,000	420	240	
Hydrogen Sulfide	500	10	2	<0.5
Sulfur Dioxide	2,000	10	1	0.5
Ammonia	2,000	10	15	
Formaldehyde	1,000	5	4	
Nitrogen Dioxide	2,000	2	0.5	<0.5
Nitric Oxide			0.5	

[a] After Robinson (1967)

[b] Personal communication, R. C. Cadle, NCAR

Source: (First three columns) Pate, Lodge, Sheesley & Wartburg (1970) considerable rates of biogenic production to maintain the implied flux. For example, if the background level of SO_2 is in fact about 0.5 ppb throughout the entire troposphere, as suggested by Pate, Pitombo, et al. (1971), then the mean atmospheric load is only 2.3 million tons of S; but if the effective lifetime of SO_2 in the atmosphere is one to four days, the annual flux would have to be about 200 to 800 million tons per year.

G. CONCLUSIONS

The discussions in this chapter have focused on questions regarding the magnitude of the role of biological processes in the cycling of atmospheric sulfur, and on problems of estimating this and of determining the quantities of sulfur in annual circulation. Implicit in these discussions is the further question regarding the significance of the fact that anthropogenic sources are presently responsible for the direct release of about 95 million tons of sulfur into the environment per year and may be responsible for much more as the consequence of organic pollution of coastal waters. At present we do not know whether this direct emission is a very large or a very small proportion of the total in circulation, and the annual flux of sulfur through the atmosphere may be as little as about 300 million tons or as much as 800 million tons. Some of the critical gaps in available evidence may be summarized as follows:

(1) Measurements of the tropospheric abundances of sulfur compounds are inadequate for determinations of the total average atmospheric load. Measurements presently available are concentrated near the ground and in urban and rural areas that are contaminated with pollutant sources. It is necessary that abundance profiles of these compounds be determined, and that surveys of their concentrations at points remote from pollution sources be continued.

(2) Information regarding the lifetime of sulfur dioxide and other sulfur compounds in the atmosphere is inadequate. More information regarding declines in sulfur dioxide concentration as a

function of distance from source, source strength, and other relevant parameters could greatly improve estimates of the lifetime of SO_2 as well as the location of its sources. It would seem that satellite monitoring is well suited to this task, since it permits nearly simultaneous collection of concentration information from a large number of points on the surface of the earth. Knowledge of ammonia concentration, relative humidity, and (if possible) abundance, size distribution, and composition of aerosols would also be of great value in determining the fate of sulfur dioxide and aerosol sulfates.

Useful studies could also be performed by satellite-mounted instruments that were unable to detect the very low concentrations characteristic of remote unpolluted environments (about 0.2 ppb near the ground) or to distinguish differences in concentration on the order of 0.1 or 0.2 ppb. Instruments capable of detecting concentrations on the order of 10 ppb and of distinguishing concentrations differing by the same magnitude could provide much useful information regarding the fate of pollutant SO_2 and the possible existence of large natural SO_2 sources such as tidal flats and polluted estuaries. These less-sensitive instruments might also be of some use in providing information regarding the natural cycle of sulfur in the atmosphere, but delineating their utility would require further study. Of course, instruments capable of providing surveillance of sulfur compounds at the very low concentrations characteristic of remote environments would be of great value.

(3) Estimates of the amount of sulfur in circulation are based in part on observed concentrations of sulfate in rainwater in the continental United States and adjacent coastal areas. Precipitation in this region and in Europe, where long-term precipitation studies have been carried out, is almost certainly heavily contaminated with pollution sulfate; consequently, these data

provide a poor basis for estimating the sulfate content of rain over the whole globe. Better precipitation data for remote regions are essential.

(4) There remains some uncertainty regarding the quantities of marine sulfate transferred to the atmosphere in sea salts. Analyses of precipitation from clouds formed in clean ocean air, combined with isotopic studies of the sulfate sulfur and oxygen, would provide a better basis for estimating the quantities of marine sulfur in circulation and for identifying excess sulfate resulting from biological sulfate reduction.

(5) Berner (1971a) concludes that very large quantities of excess sulfate present in European river water during the 19th century must be attributed to the activity of the industrialized society present at that time, even though sulfate fertilizers were not in wide use and sulfur dioxide and sulfuric acid emissions were negligible. He attributes this excess sulfate to bacterial sulfate reduction induced by organic pollution of inland and coastal waters. If Berner is correct, then the present sources of pollution-induced excess sulfate must be much larger than those of a century ago.

Berner's conclusion is based on evidence of European river water composition which is very out of date, and which may be erroneous. Better data on the composition of river water are essential, and they should be combined with studies of possible contemporary sources of pollution-induced biological sulfate reduction in this region. Comparable studies in the United States would be desirable. Isotopic studies of sulfur in rivers, rain, and industrial wastes would help to interpret the impact of human activities, but they would present problems because of the need to know the isotopic distribution of industrial sulfur sources or effluents.

(6) There is considerable evidence that vegetation (and possibly soils) can remove sulfur dioxide from the atmosphere at concentrations exceeding about 200 ppb, and also that trees and plants influence the removal of particulates from the atmosphere. However, many questions remain regarding the efficacy of this "dry deposition" as a mechanism for transferring sulfur compounds (and other compounds) from the atmosphere. One problem is that experimental techniques in use do not clearly distinguish between the effects of dry deposition and nutrient leaching. The topic is sufficiently important to warrant further study.

(7) Redfield's proposal that biological sulfate reduction in the sea regulates the atmospheric concentration of oxygen (Redfield, 1958; Redfield, Ketchum and Richards, 1963) deserves careful exploration, especially in view of the evidence of Lloyd (1968) that biological sulfate reduction is extremely active in the ocean, and the fact that the sulfate concentration of the ocean has apparently exhibited wide fluctuations in the past. A study of the relationships between these fluctuations and other geological evidence bearing on the exchange of oxygen with other terrestrial reservoirs is indicated, as well as a study of the effects of changes in temperature, atmospheric composition, and altered sea levels and/or circulation patterns cn marine sulfate reduction.

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VIII. FEASIBILITY OF SATELLITE MONITORING OF TRACE ATMOSPHERIC CONSTITUENTS

A. INTRODUCTION

As discussed in earlier sections of this report, there is considerable uncertainty concerning the concentrations and distribution of many trace atmospheric constituents. To provide a better understanding of the global sinks and sources of these gases, to evaluate their lifetimes in the atmosphere, and to determine any changes or trends in their abundance or distribution, a global monitoring system seems needed. Several earth-based global networks have been proposed for monitoring gases such as CO_2, CO, SO_2, NO_x, and hydrocarbons; a review of the network density and number of stations required is given in SCEP (1970).

Basically, a good network must be sufficiently dense to obtain representative data both regionally and globally (being more dense for short-lived gases than others); however, a compromise between density and cost is usually necessary. For gases such as CO_2, the SCEP study recommends a minimum of 10 stations; for monitoring short-lived gases, 100 stations would be desirable. It is recommended not only that surface samples be obtained, but that aircraft- and balloon-borne monitoring in the troposphere and stratosphere be conducted with regularity to collect information on sources, sinks, and circulation patterns.

While these monitoring stations will provide useful data and may resolve some of the current uncertainties, it seems logical that remote sensing of gas distribution by orbiting satellite has several advantages when combined with an earth-based network--namely, the ability to obtain a broad global coverage and sufficient frequency to determine both short-term (daily), intermediate (monthly or seasonably), and long-term changes. As indicated below, satellite monitoring could potentially measure both spatial and temporal distribution of gases in the atmosphere; this is particularly important for gases with short lifetimes, since many specially equipped earth-based monitoring stations would be required to obtain sufficient resolution in time and space to evaluate the cycling of these constituents. As satellite monitoring cannot be used to fully evaluate gas distribution at or near the surface, a combination of earth-based and remote techniques will be required.

Although we have also stressed the importance of obtaining data on the distribution of particulates in the atmosphere, in this section we will concentrate on a brief evaluation of the feasibility of using satellites to make remote measurements of atmospheric trace gas concentration and distribution. First, we will review the types and distribution of biologically cycled trace atmospheric constituents and indicate the range of concentrations which must be monitored. Next, we will discuss the fundamentals of spectroscopic measurement methods, concentrating on the infrared portion of the spectrum. We will examine the sensitivity and limitations of infrared techniques and then consider several trace gases to determine if a suitable spectral region for measurement is available. The combination of sensitivity sufficient to measure gases in the low concentrations which exist in the atmosphere and an unobscured spectral region for measurements is indicative of the feasibility of the satellite measurement approach.

B. DISTRIBUTION OF BIOLOGICALLY CYCLED TRACE CONSTITUENTS

In this section we relate the space-time distribution of selected trace constituents discussed in earlier chapters to our evaluation of the utility of satellite monitoring systems. Essentially, we wish to determine whether the spatial and temporal concentration gradients of interest can be detected from satellites.

Table VIII-1 summarizes the observed abundances of each of the major gases of interest. The second column lists the concentration differences observed at ground level which might be associated with important differences in biological reactions involving these gases. There is little information about the lifetime and abundance profile of any of these gases. Comments regarding the distribution of the individual gases are given below.

TABLE VIII-1. - ABUNDANCE OF TRACE GASES

	Concentration at Surface				Upper Troposphere	Stratosphere
Gas	Differences[a]	Polluted	Rural	Remote		
CH_4	1×10^{-7}	1 - 3 ppm	1 - 1.6 ppm	1 - 1.7 ppm	0.8 to 1.6 ppm	0.6 to 1.6 ppm in lower stratosphere <50 ppm at stratopause
CO	1×10^{-8}	0.6 - 3 ppm ($\leq$150 ppm in traffic)	0.15-0.25 ppm	0.1-0.21 ppm	0.10 - 0.15 ppm	$\leq$0.03 ppm in lower stratosphere
N_2O	1×10^{-8}	not a pollutant	0.22-0.40 ppm	-	0.14-0.255 ppm	0.25 ppm above tropopause; 0.12 ppm at ≃ 22 km
NH_3	1×10^{-10}	20-30 ppb in cities 75 ppb near feed lots	5-26 ppb	1-15 ppb	may be <0.05 ppb	may be <0.05 ppb
NO	1×10^{-10}	100-500 ppb	2-3 ppb	0.1-0.5 ppb	< 0.5 ppb	small amount in upper stratosphere due to N_2O photolysis
NO_2	1×10^{-10}	2 ppm	1-8 ppb	0.2-0.6 ppb	< 0.5 ppb	-
SO_2	1×10^{-10}	2 ppm	10-30 ppb	0.5-2 ppb	≃ 0.5 ppb	-
H_2S	1×10^{-10}	500 ppb	2-8 ppb	-	< 0.5 ppb	-

[a] Differences in surface contentration that should be measured to assess biological effects accurately.

1. Methane (CH_4)

There is some evidence for a vertical decline in abundance of methane in the troposphere and considerable evidence of variability in abundance at the surface, which implies that the residence time may be short. A chemical sink for this gas exists in the stratosphere, and theoretical considerations indicate that its concentration should decline to zero below the stratopause. More observations of the abundance in the upper troposphere and lower stratosphere are required before the effectiveness of the chemical sink can be estimated. Localized terrestrial sources of methane--swamps and rice paddies--may be very large, and methane may be a significant product of cultural eutrophication of waterways.

2. Carbon Monoxide (CO)

Large quantities of carbon monoxide are produced in industrialized areas, largely by internal combustion engines; mean concentrations in cities are about 2 to 3 ppm, but temporary peaks of 50 to 150 ppm are observed in heavy traffic. In rural and remote locations, concentrations vary from 0.1 to 0.25 ppm. There is evidence of a decline in carbon monoxide with altitude in the troposphere of the northern hemisphere and of generally high levels over the Atlantic. Concentrations in well mixed tropospheric air seem to be lower in the southern hemisphere than in the northern hemisphere, and upper tropospheric values seem to be about the same in both hemispheres (0.10 to 0.12 ppm). There are large natural sources of carbon monoxide, but available evidence is insufficient to show whether the anthropogenic emission is large in comparison with the natural background cycle.

The ocean produces large amounts of CO, partly from photolytic decomposition of dissolved organic matter and partly as a byproduct of the metabolism of some organisms. The strength of the marine source may therefore vary with season and location, but it is not at present possible to say whether these variations in source would give rise to observable space-time gradients in the atmospheric abundance of CO near the ground or in the entire atmospheric column. There is evidence that vegetation and soils may remove CO from the atmosphere, together with other trace constituents. Its concentration may be a characteristic of air masses that can be used to track their movements.

3. Nitrous Oxide (N_2O)

The reported concentrations of N_2O in the lower troposphere near the surface are quite variable, with weekly means ranging from 0.2 to 0.4 ppm. All N_2O is biogenic. Its concentration shows a general tendancy to decline with altitude in the troposphere and to decline quite rapidly in the stratosphere. There is a large stratospheric sink for N_2O whose effectiveness depends upon the speed of vertical mixing in the stratosphere. Concentrations of N_2O near the tropopause have been measured by a gas-liquid chromatographic technique and found to be about 0.25 ppm, while spectroscopic measurements indicate a mean of 0.14 ppm above 4.5 km. N_2O can be removed from air by contact with soils; this fact, together with the variability of its concentration near the surface, suggests a large natural tropospheric sink for N_2O.

4. Ammonia (NH_3)

Although there are some industrial sources of ammonia, most of the ammonia in the atmosphere is biogenic. Some of the latter comes from feed lot wastes. The concentration of ammonia near the surface appears to be extremely variable, and there is some evidence that it decreases very rapidly with altitude. Observations in polluted locations suggest means of about 20 to 30 ppb in cities partly due to emissions from coal burning, and partly from wastes or industry. Some rural areas may exhibit very high atmospheric concentrations due to fertilizer and farmyard waste pollution.

Low abundances have been reported in some marine air (Hawaii), but other observations indicate that marine and freshwater aquatic environments may be significant sources of atmospheric NH_3. Some of the variation in observed abundance may be due to variations in the strength of the biological source, or to variations in humidity and concentration of SO_2, which influence the lifetime of HN_3. (Ammonia may react in the atmosphere with SO_2 or with cloud or rain droplets containing sulfate ions.)

Although some have argued that ammonia is well mixed in the troposphere and consequently there is some background concentration present in the upper troposphere (perhaps 10 to 15 ppb). Recent spectroscopic observations indicate that all ammonia may be concentrated near the ground (see below).

5. Nitric Oxide (NO)

The few measurements of nitric oxide that have been made suggest that it is very short lived and concentrated near the ground. It is a major industrial pollutant; concentrations in cities may be high as 500 ppb. Under some circumstances, NO can be produced naturally, but there are few data on which to base an estimate of the probable rate of biogenic production. Observations in one rural location indicated extremely variable concentrations of NO, with means of 2 to 3 ppb. Its production may be influenced by agricultural techniques. Recent observations in very remote regions have shown concentrations of 0.1 to 0.5 ppb.

If NO is present in the upper troposphere--which seems unlikely--its concentration almost certainly does not exceed 0.5 ppb. Small quantities of NO are produced in the upper troposphere as a consequence of N_2O photolysis, but this product may be short lived.

6. Nitrogen Dioxide (NO_2)

Nitrogen dioxide is a product of fossil fuel combustion and is also formed by reaction of ozone with biogenic NO. Its concentration in cities may be as high as 2 ppm, while 1 to 8 ppb has been measured in rural locations. Recent measurements in very remote areas indicate lower concentrations--0.1 to 2 ppb. If NO_2 is present in the upper troposphere, its concentration probably does not exceed 0.5 ppb. Little is known about its stratospheric concentration.

7. Sulfur Dioxide (SO_2)

Sulfur dioxide is a major product of fossil fuel combustion. High levels have been observed near the ground in heavily polluted environments, and rural locations often show the effects of industrial pollution. In remote locations unaffected by pollutant (fossil fuel) sources, concentrations are very low, ranging from 0.5 or less to 2 ppb. Upper tropospheric concentrations may be about 0.5 ppb, and little is known about the concentration in the stratosphere. There may be major biological sources of SO_2, especially in coastal marine locations, but they have not been confirmed. The atmospheric emission of biogenic SO_2 may be promoted by cultural eutrophication. The conversion of SO_2 to particulate sulfate is governed by humidity and ammonia concentration.

8. Hydrogen Sulfide (H_2S)

Hydrogen sulfide is a pollutant product of some industrial processes, and it may be present in relatively large quantities in some heavily industrialized regions. Very few direct measurements of H_2S in the atmosphere have been made, but indirect evidence suggests that its concentration is almost certainly less than 0.5 ppb at the surface in remote locations, and that much of it may be concentrated near the ground.

One theory of the biogenic cycling of SO_2 holds that its precursor is biogenic H_2S emitted from anoxic water enriched in organic matter, but observations of atmospheric H_2S near such environments are required to verify this theory.

9. Other Gases

A satellite monitoring system should be able to observe the concentrations of other gases that are important biological products or that influence the concentrations of other biogenic trace constituents. These include carbon dioxide, ozone, water vapor, nitric acid and sulfuric acid vapor, OH and O.

C. MEASUREMENT OF CONCENTRATION AND SPATIAL DISTRIBUTION

1. Spectroscopic Methods

We have considered the monitoring of atmospheric trace constituents from unmanned orbiting satellites (non-synchronous) using only infrared absorption as the measurement method.* Two basic types of such measurements are discussed here: (1) direct, near-vertical viewing of the infrared energy from the sun reflected by the earth, and (2) direct viewing of the sun through the earth-limb (occultation).

In the earth reflection method, the energy passes twice through the atmospheric column in a near-vertical direction; energy is absorbed by the atmospheric gases, and the resulting absorption spectrum is detected by an infrared sensing system on the satellite. This technique directly gives the total energy absorption in the optical path--a quantity related to the total number of molecules of the trace gas in the atmospheric column or the mean gas density for a given column thickness. Methods are available for relating the details of the absorptive spectra to the vertical gas density distribution, provided the vertical temperature distribution is known (or can be measured from gases of known density distribution) and the instrument has sufficient sensitivity and resolution. This method permits a large portion of the globe to be viewed fairly frequently, as the satellite orbits the earth; but since the sun is the source, measurement can be made only during the day.

In the earth-limb measurement, sensors on the satellite measure the absorption of infrared energy from the sun by trace gases when the sun is on the horizon, so that the energy passes through essentially horizontal layers of the atmosphere. Thus, the earth-limb measurement has the potential for directly measuring the vertical abundance profiles; as the sun is occulted by the earth, the absorption spectra through different layers are measured, indicating the effective concentration of each layer.

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* A more extensive review of satellite monitoring systems and a comparison of measurements by ultraviolet, infrared, microwave, and Raman spectral techniques have been made by Edelburg (1971) and Hanst et al. (1971).

The earth-limb measurement has greater spatial resolution in the vertical direction than the earth reflection method and is not affected by clouds at upper atmospheric levels, but it has less frequent and extensive global coverage, because it can be used only at the several "sunrises" and "sunsets" seen by the satellite each day. Both methods are subject to interference from the absorption of infrared energy, principally by water and carbon dioxide, and absorption and scattering by particulates and aerosols.

A number of different experimental (sensor) approaches to measuring the absorption spectra are possible--gas filter correlation (Ludwig, Bartle, and Griggs, 1969), correlation interferometry (Davies, 1970) gas filter correlation interferometry (Lorah et al, 1971), and other adaptations of basic spectroscopic principles. However, in the discussion which follows, we will consider the general subject of instrument sensitivity without regard to specific instruments.

2. Mathematical Considerations

Most of the gases of interest to the study of biologic cycling have strong bands in the infrared specturm. Each band consists of many separate lines whose spectral locations provide generally unambiguous fingerprints to identify the molecules and whose strengths permit quantitative analysis. In the troposphere and lower and middle stratosphere, the shapes of the lines are due to collision broadening. The absorption coefficient of an individual line under these conditions is given by:

$$k_{\tilde{\nu}} = \frac{S_i}{\pi} \frac{\alpha_i}{(\tilde{\nu} - \tilde{\nu}_i)^2 + \alpha_i^2} \tag{1}$$

where the line intensity (i.e., the total integrated absorption coefficient is:

$$S_i = \int_{\text{line}} k_{\tilde{\nu}} \, d(\tilde{\nu} - \tilde{\nu}_i) \tag{2}$$

α_i is the half-width, defined as the spectral distance from the line center, and $\tilde{\nu}_i$ is the spectral position of the line center. $\tilde{\nu}$ is the frequency divided by the velocity of light, or the number of waves per centimeter; its units and those of α_i are cm^{-1}.

The monochromatic fractional transmission is

$$T_\nu = \exp\left(\int_c -k_\nu \, dc\right) \tag{3}$$

or, where the concentration is uniform and the absorption coefficient is constant,

$$T_\nu = \exp(-k_\nu c) \tag{3a}$$

where c is the path length, generally expressed in units proportional to the numbers of molecules of the specific gas. We use here the dimension cm-atm, defined as the path lengths reduced to 1 atm and 0°C. $k_{\tilde{\nu}}$ has, of course, the inverse dimension.

The line intensities S_i, which are different from line to line, are functions of temperature; but for the strongest lines, which are most useful for detecting and measuring trace constituents, this temperature dependence is weak. The strongest lines of the bands of the molecules in which we are interested have intensities that are generally of the order of 10 cm^{-1} per cm-atm, within a factor of two or three.

The half-width α_i is directly proportional to the pressure and generally inversely proportional to a fractional power of the temperature. At standard temperature and pressure, a typical value of α_i for the strongest lines is 0.07 cm^{-1}.

The integrated fractional absorption by a line whose absorption coefficient follows equation (1) usually called the equivalent width, has the value

$$W_i = \int_{\text{line}} (1-T_{\tilde{\nu}})\,d\tilde{\nu} = S_i c \exp(-X)\,[I_o(X) + I_1(X)] \tag{4}$$

where

$$X = S_i c/2\pi\alpha_i \qquad (5)$$

and I_o and I_1 are Bessel functions of imaginary arguments. The asymptotic limits of equation (4) are:

$$W_i \xrightarrow[X\to 0]{} S_i c \qquad (6)$$

and

$$W_i \xrightarrow[X\to\infty]{} 2\sqrt{S_i c\alpha_i} \qquad (7)$$

The regime governed by equation (6) is appropriate for determining minimum detectability. If the bandpass used by the spectrometer is $\Delta\tilde{\nu}$, the fractional absorption FA in this pass band is approximately

$$FA \simeq Sc/\Delta\tilde{\nu} \qquad (8)$$

A more exact formula for a rectangular bandpass $\Delta\tilde{\nu}$ is:

$$FA = c\int_{\Delta\tilde{\nu}} k_{\tilde{\nu}}\, d\tilde{\nu}/\Delta\tilde{\nu} = \frac{S_i c}{\pi\Delta\tilde{\nu}}\int_{\Delta\tilde{\nu}} \frac{\alpha_i}{(\nu-\nu_i)^2+\alpha^2} = \frac{Sc}{\Delta\tilde{\nu}}\,\frac{2}{\pi}\arctan\left(\frac{\Delta\tilde{\nu}}{2\alpha_i}\right) \qquad (9)$$

$\Delta\tilde{\nu}/2\alpha_i$ is the number of half-widths on each side of the line included in the bandpass. We will define this by

$$V = \Delta\tilde{\nu}/2\alpha_i \qquad (10)$$

and

$$f(V) = \frac{2}{\pi}\arctan\left(\frac{\Delta\tilde{\nu}}{2\alpha_i}\right) \qquad (11)$$

so that equation (9) becomes

$$FA = \frac{Sc}{\Delta\tilde{\nu}} f(V) \qquad (9a)$$

Values of f(V) are tabulated in Table VIII-2, as are $\Delta\tilde{\nu}$ and $f(v)/\Delta\tilde{\nu}$ for $\alpha = 0.07$. The limiting value for a very narrow bandpass is $\lim_{\Delta\tilde{\nu}\to 0} f(V)/\Delta\tilde{\nu} = 4.55$.

With a wider bandpass, contrast would be diminished; it would disappear altogether if the bandpass were equal to or greater than the line spacing. With a narrower bandpass, more would be lost by the decrease in signal-to-noise ratio (which would be at least linearly proportional to the bandpass width for measurements at this high resolution) than is gained by the increase in fractional absorption. This can be seen from Table VIII-2; if the bandpass is reduced by a factor of 1.5 in going from 0.42 cm^{-1} to 0.28 cm^{-1}, the fractional absorption is increased by a factor of only 1.31.

3. Measurement Sensitivity

Of the trace gases considered for monitoring, N_2O has the most closely spaced principal features, with typical line spacing of about 0.8 cm^{-1}. Although the average line spacing is smallest for SO_2, the most useful band, at 9μ, corresponds to a vibrational change in dipole moment perpendicular to the axis of the smallest moment of inertia, so that the spectra tends to consist principally of clusters separated from each other by 1-1/2 to 2 cm^{-1}. Thus 0.4 cm^{-1} would seem to be a good value for the bandpass of a measuring instrument. For $\Delta\tilde{\nu} = 0.4$, $f(V)/\Delta\tilde{\nu} = 2$.

Let us now use this value of $f(V)/\Delta\tilde{\nu} = FA/Sc$ and consider a strong line in a strong fundamental, say with $S = 30\ cm^{-1}/cm\text{-}atm$. For the earth-reflection experiment, we will assume that the earth is viewed in the vertical and the solar zenith angle is 60°. The sum of the secants along the viewing angle is thus 3. If we assume the gas is uniformly distributed and limited to the lowest one-kilometer layer and the units

TABLE VIII-2. - TYPICAL VALUES OF f(V)

V	f(V)	$\Delta\tilde{\nu}$ for α = .07	FA/Sc = $f(V)/\Delta\tilde{\nu}$
1	0.50	0.14	3.6
2	0.70	0.28	2.5
3	0.80	0.42	1.9
4	0.84	0.56	1.5
5	0.87	0.70	1.24
6	0.90	0.84	1.07
7	0.91	0.98	0.93
8	0.92	1.12	0.82
9	0.93	1.26	0.74
10	0.94	1.40	0.67

of c are cm-atm, the concentration is 10^{-5}c. Two percent absorption (FA = .02) is a reasonable detection threshold; then, from equation (9a) the threshold concentration is $0.02 \times 10^{-5} \div (30 \times 3 \times 2) \approx 10^{-9}$ (one part per billion). For a strong line in a weak fundamental, say with S = 3 cm^{-1} per cm-atm, to obtain 2% absorption the contentration would have to be about 10 parts per billion.

The precision with which small concentrations can be measured is the same as the minimum detectable sensitivity, so long as lines are chosen for which the absorption is approximately a linear function of the gas concentration. Thus, for a strong fundamental considerdred above, the concentration can be measured with a precision of about 1 part per billion in the range from 1 to 25 parts per billion, and to about 4% about 25 parts per billion. For a weak fundamental, the precision will be about 10 parts per billion in the range from 10 to 250 parts per billion and about 4% above 250 parts per billion. If the gases were uniformly distributed throughout the atmosphere instead of being only in the lowest kilometer, they would be detectable with concentrations of about 0.15 part per billion and 1.5 parts per billion respectively for strong and weak absorbers, almost an order of magnitude improvement from that given above.

A further order-of-magnitude improvement of the detectability or measurability of small concentrations can be obtained from the spectrum of sunlight directly transmitted by the atmosphere through the limb, rather than in reflection. As mentioned earlier, such measurements have the further important advantage of allowing more direct determination of vertical distributions (which should be obtainable with 1- or 2-km resolution) by observations at successively lower tangent heights together with relaxation inversion techniques. Although the presence of clouds will usually prevent such determinations for the lower and perhaps even the upper troposphere, limb measurements will be valuable for obtaining background concentrations and upper atmospheric distributions.

For gases which have strong bands accessible to reflection spectroscopy, such as the 3.3- and 3.4- micron bands of methane, the general trend of the height distribution can be obtained from the different pressure and temperature dependences of the weak and strong lines.

The feasibility of these measurements presumes that window regions can be found in the atmospheric spectrum, through which appropriate lines can be measured. This depends on the locations of the bands and is discussed for the separate gases later.

We will illustrate the use of the method of measurement described above by determining an upper limit to the background concentration of NH_3 away from surface sources. Recent solar spectra taken at Mont-Louis Observatory in the French Pyrenees at better than 0.1 cm^{-1} resolution and with signal-to-noise ratio decidedly better than 50 to 1 indicated complete absence of extremely strong Q-branch lines of NH_3 from 960 to 968 cm^{-1} (Dionne, 1971). Our intensity analysis of these lines in spectra by Garing, Nielsen, and Rao (1959) indicates that the strongest lines (actually coincidences of four separate, strong lines) have intensities greater than 100 cm^{-1} per cm-atm. With $\Delta\tilde{\nu} = 0.1\ cm^{-1}$, FA = 4 Sc. Thus, the upper limit for the amount of NH_3 is $C < .02/(4 \times 100) < 5 \times 10^{-5}$ atm-cm. Since we are interested in the permanent background component, we will take the total atmospheric path equal to 10 km. The upper limit to the concentration is therefore $5 \times 10^{-5} \div 10^{6}$ = 0.05 ppb, much less than the quoted background concentration. Even with the larger bandpass that would be used in a satellite, the increase obtainable from limb measurements can bring the detectability limit down to perhaps ten parts per trillion.

Although these detection limits seem quite low, they are comparable with those of Ludwig (Edelberg, 1971), who estimated a sensitivity for CO of 0.1 to 10 ppb at altitudes of 20 and 70 km (limb experiment). An interferometer now being developed for satellite use by General Electric Company and Barringer Associates will have a sensitivity in the range of 10 ppb to 10 ppm (Hanst et al, 1971).

Referring again to Table VIII-1, we see that expected sensitivities of about 0.1 to 1 ppb will be sufficient for monitoring gases such as CH_4, CO and N_2O, even in the upper troposphere and stratosphere. For the other gases, this sensitivity will be marginal at upper atmospheric levels but adequate at lower levels. The comparison between predicted sensitivity and anticipated concentrations suggest that very sophisticated instruments combined with the largest possible pathlengths will be required for maximum benefit from satellite monitoring.

D. CHOICE OF SPECTRAL REGION

Successful remote sensing of trace gas distributions, either in reflected sunlight or through the limb, hinges on finding a spectral region where the earth's atmosphere is relatively transparent and contains one or more strong lines of the component of interest not significantly overlapped by lines of other infrared-active species (water vapor, carbon dioxide, ozone, etc.) For measurements through the limb, suitable spectral regions will be limited by atmospheric absorption due principally to water vapor, carbon dioxide, and ozone. Measurements in reflected sunlight are further restricted to wavelengths shorter than about 4 microns, since atmospheric emission effects will dominate at longer wavelengths.

Suitable regions for making measurements in reflected sunlight can be determined from study of the laboratory spectra of the trace atmospheric gases of interest and study of high-resolution atmospheric transmission spectra recorded by using ground-based spectrometers with the sun as a source. In view of the very low background concentrations of many of the trace gases, only the strongest lines in fundamental bands seem to be suitable. The preliminary analysis given below indicates that there are suitable spectral regions for studying all gases of interest except NO and SO_2 in reflected sunlight.

Prospects for limb measurements are more difficult to evaluate. For small tangent heights, the optical path through the limb is very long upwards of 50 air masses. For such long paths, the available spectral windows are further reduced and narrowed. Since we do not have high-resolution transmission spectra for solar zenith angles near 90°, our evaluations for limb measurements are somewhat more tentative; however, we believe that there are suitable spectral regions for studying all gases of interest. Our analysis of limb measurements is confined to fundamental vibration rotation bands, but there are many combination and overtone bands for each of these molecules that could also be considered. These bands are somewhat weaker, so sensitivity would be reduced; however, since many of them fall in spectral regions where the atmosphere is more transparent, they may be useful.

1. Methane

The four fundamental bands of methane are centered at 3.4, 6.6, 3.3, and 7.65 microns. The 3.3- micron band is an excellent choice for measurements either in reflected sunlight or through the limb.

2. Carbon Monoxide

The fundamental for carbon monoxide falls at 4.65 microns and the first overtone at 2.3 microns. Both bands can be used in remote sensing. Only the overtone band can be used for measurements in reflected sunlight because of atmospheric emission in the fundamental.

3. Nitrous Oxide

The fundamentals of nitrous oxide are at 7.8, 17 and 4.5 microns. In addition, there is a strong overtone due to $2\ \nu_1$ at 3.8 microns, which is probably the best choice for both reflected sunlight and limb measurements.

4. Ammonia

The four fundamental bands of ammonia fall at 3.0, 10.5, 2.94 and 6.15 microns. The first of these is suitable for measurements in reflected sunlight, but the band in the 10.5- micron region may be a better choice for limb measurements.

5. Nitric Oxide

The fundamental band for this molecule is centered at 5.45 microns and the first overtone at about 2.7 microns. Both of these bands are badly overlapped by water vapor or water vapor and CO_2, so neither is suitable for use in remote sensing. The fundamental may be suitable for limb measurements at higher altitudes, where the concentration of water is small.

6. Nitrogen Dioxide

The fundamental bands of NO_2 are centered at 7.6, 15.4, and 6.16 microns, respectively. In addition, there is a strong overtone band near 3.35 microns. Serious interference is encountered with all of the fundamental bands, but the overtone band is probably strong enough to be used for remote sensing, both in reflected sunlight and through the limb. A better spectral region for measurements is probably in the electronic bands, where the absorption coefficients are stronger.

7. Sulfur Dioxide

The fundamental vibration rotation bands for sulfur dioxide ν_1, ν_2, and ν_3 are centered at 8.7, 19.2, and 7.34 microns, respectively. Neither the 7.34- nor 19.2- micron band is suitable for use in remote sensing. The 8.7- micron fundamental, although overlapped by the ν_2 band of H_2O, is suitable for use in limb measurement. No SO_2 band is suitable for use in reflected sunlight.

8. Hydrogen Sulfide

The centers of the fundamental rotation band of hydrogen sulfide ν_1, ν_2, and ν_3 fall at 3.83, 7.75 and 3.73 microns. Only the 3.83- and 3.73- micron bands are suitable for this application, since the 7.75- micron band is badly overlapped by both water vapor and N_2O. There is some interference with methane for the short-wavelength bands. However, the problem is certainly not serious for measurements in reflected sunlight and is probably not serious for limb measurements.

9. Carbon Dioxide

Carbon dioxide has two infrared-active bands, centered at 15 and 4.3 microns. It also has many overtone bands. The ones at 1.6 microns are ideal for both reflected sunlight and limb measurements.

E. SUMMARY AND CONCLUSIONS

Two criteria for feasibility were examined--measurement sensitivity and available spectral windows:

- Infrared absorption measurements of solar energy reflected from the earth (direct reflection) or transmitted through the earth's atmosphere (limb) should result in sensitivities in the range of 0.01 to 10 ppb for most trace gases. Limb measurements will be most useful for determining vertical abundance profiles, whereas direct reflection measurements will provide detailed global coverage. These sensitivities are sufficient for monitoring gases such as CH_4, CO, and N_2O, whose normal concentrations near the surface range from 0.1 to 3 ppm and whose tropospheric and stratospheric concentrations are expected to vary from 0.03 to 1.5 ppm. Instrument sensitivity will probably be adequate for measurements of NH_3, NO, NO_2, SO_2, and H_2S in the lower atmosphere but marginal in the upper regions.
- From high-resolution atmospheric transmission spectra recorded with ground-based spectrometers using the sun as a source, we conclude that there are suitable spectral regions for measuring all trace gases of interest through the limb, and for measuring all but NO and SO_2 in reflected sunlight. Although much additional work would be required to select the best spectral line or lines for each of the gases of interest, sufficient data have been obtained to demonstrate feasibility in terms of available spectral windows.

These analyses and evaluations indicate that it is probably feasible to make remote measurements from satellites to obtain data on the spatial and temporal distributions of trace gases for the purpose of determining the effects of biosystems on atmospheric composition. A great deal remains to be done, however, before a satellite monitoring program can be implemented. Two critical tasks are discussed below.

1. Ground-Based Studies

Optimum spectral regions for making trace gas distribution measurements can be selected and achievable sensitivity can be evaluated through ground-based measurements. High-resolution infrared spectrometers, such as those now installed at a number of laboratories throughout the world, should be used to record the spectra of trace gases when these are not available and to measure slant-path transmission for both large and small solar zenith angles from representative locations. These spectra can be analyzed to determine the optimum resolving power of a space instrument and optimum spectral regions for its operation. In addition, such data will serve to provide better information on background trace gas levels integrated over long paths than is now available. Such a study is entirely within the state of the art and could be implemented at relatively low cost.

2. Instrument Development

A study should be undertaken to determine the most effective means of making trace gas concentration measurements from a satellite, both in reflected sunlight and through the limb. It is not evident at this time what the best measurement approach would be. A variety of techniques should be considered, including dispersive spectroscopy, interference spectroscopy with both Michelson and Fabry-Perot instruments, and non-dispersive correlative techniques.

When the systems performance analysis is complete, the most effective approach should be adopted and a prototype instrument developed. The instrument should then be thoroughly tested from the ground using the sun as a source.

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