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The Sulfur Cycle

Man's contributions are compared to natural sources of sulfur compounds in the atmosphere and oceans.

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There is a growing awareness of the fact that the earth's atmosphere is finite and a concern lest it be overloaded with man-made contaminants. This is one aspect of our more general concern with the preservation of our environment.

Sulfur in its various forms has long been identified as a major component of air pollution in some of the industrialized parts of the world. There are also a number of significant natural sources of sulfur that were producing sulfur long before civilized man learned to unlock the element from its resting place in beds of coal and pools of petroleum.

We believe that it is important at this time to try to put the man-made contribution of sulfur compounds to the atmosphere (and oceans) into perspective by comparing it with the contribution of the natural sources, because this will give us a better idea of how seriously we may be affecting the normal balance of nature. The key questions that we will try to answer are:

1) What are the sources (natural and man-made), sinks, and lifetimes of sulfur compounds in the atmosphere-ocean system?

And from this:

2) How do man's activities compare with nature's in determining the overall budget of atmospheric sulfur compounds?

When we can provide reasonably satisfactory answers to these questions, we can begin to think about the matter of regional and global air pollution caused by sulfur compounds on a more rational basis.

We can no longer study the sulfur cycle in its natural state, since man has already become so active in modifying it, but we have the tools to analyze the major parts of this cycle separately and to recombine them into a model of the global system. Although the emphasis in this article is on the global and long-term picture, some of the facets of the study, as will be seen, have important implications for regional and even local air pollution problems.

Chemistry of Sulfur

The element sulfur (S) occurs in a variety of stable compounds in which it can have either a positive or negative oxidation state. It can be reduced to hydrogen sulfide (H_2S) or oxidized to sulfur dioxide (SO_2) and sulfur trioxide (SO_3). All of these compounds, and their derivatives, take part in the sulfur cycle. Thus, it is necessary to keep track of all the various forms of sulfur as it moves through the cycle, and to understand how the conversions from one form to another occur.

Hydrogen sulfide, which is added to the atmosphere in uncertain and possibly great quantities, is oxidized to SO_2, but the rate at which this oxidation takes place depends on a number of factors. Hydrogen sulfide can undergo a number of oxidation reactions involving atomic oxygen (O), ordinary molecular oxygen (O_2), and ozone (O_3) (*1*). Ozone is a natural constituent of the stratosphere, where it is formed, and some mixes down into the troposphere. It is also produced in photochemical smog. Hydrogen sulfide and O_3 react to form mainly SO_2 and H_2O but only very slowly, except possibly in the presence of aerosol particles that can provide surfaces on which the reaction can take place (*2*). Hydrogen sulfide does not absorb solar radiation reaching the troposphere, that is, wavelengths greater than about 2900 angstroms. It does not, therefore, undergo photolysis or react photochemically with O_2. Hydrogen sulfide, O_2, and O_3 are soluble in H_2O, and the rate of oxidation of H_2S by these oxidants in solution, for example, in fog or cloud droplets, may be very fast. However, little is known concerning such reactions in the atmosphere.

Atomic oxygen is produced in small amounts in the troposphere, especially in highly polluted air, by the photolysis of O_3 and of nitrogen dioxide (NO_2). In the stratosphere and mesosphere it is produced in much larger amounts by the photolysis of O_3 and O_2. The oxidation of H_2S by atomic oxygen probably occurs to an appreciable extent in photochemical smog, and H_2S reaching the stratosphere will also be oxidized in this manner. The first, and rate-controlling, step (*3*) of this reaction can be represented by the equation

$$H_2S + O \rightarrow OH + HS \qquad (1)$$

This reaction is followed by reaction chains producing SO_2, SO_3, and sulfuric acid (H_2SO_4).

Sulfur dioxide is not only a product of the oxidation of H_2S, but also con-

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stitutes about 95 percent of the sulfur compounds resulting from the burning of fossil fuels that contain sulfur (*4*). It is reduced to H_2S by bacterial action, and in air it is further oxidized to SO_3, but the rate at which this oxidation takes place depends on the presence of ultraviolet radiation and other reactants or catalysts. Sulfur dioxide in its electronic ground state does not react at an appreciable rate with O_3 in the gas phase (*5*). It does, however, absorb near-ultraviolet solar radiation to form electronically excited SO_2, which may then react with O_3. This possible reaction has not been investigated. Ground-state SO_2 does not react with O_2 except in the presence of a catalyst, such as certain finely divided solids (*6*). However, excited SO_2 does react with O_2 to form SO_3, although the rate is probably too slow for this to be an important atmospheric reaction. Recent results in our laboratory are in support of an oxidation rate for SO_2 at midday in the troposphere by this mechanism of about five molecules per 1000 molecules of SO_2 per hour (a half-life of more than 12 days, considering that the reaction proceeds only in sunlight).

When SO_2 is dissolved in fog or cloud droplets, it becomes sulfurous acid (H_2SO_3), which is rapidly oxidized by dissolved O_2 to H_2SO_4. This is probably a much more important process in the lower atmosphere than the gas-phase photochemical reactions described above, especially when certain metal salts, which serve as catalysts, are also dissolved in the droplets. Such salts may be part of the airborne particles which serve as condensation nuclei on which the cloud droplets form.

Sulfur dioxide can undergo a three-body reaction with atomic oxygen:

$$SO_2 + O + M \rightarrow SO_3 + M \qquad (2)$$

where M is a molecule of O_2 or N_2. The third body, M, carries off the excess energy of the reaction, thus preventing the prompt reversal of the reaction.

The SO_3 formed this way reacts almost immediately with H_2O vapor to form H_2SO_4, and these molecules combine with H_2O to form droplets of H_2SO_4 solution. Any ammonia present in the atmosphere will rapidly react with these droplets to form ammonium sulfate or ammonium bisulfate (*7*); if the H_2SO_4 condenses on or coalesces with sodium chloride (NaCl) particles, hydrogen chloride gas (HCl) will be released and the residue will be sodium sulfate. The formation of sulfates or sulfuric acid (XSO_4) by the oxidation of SO_2 (by Eq. 2) is of great importance in the stratosphere, where it is probably largely responsible for the layer of H_2SO_4 or sulfate particles found at an altitude of about 18 kilometers.

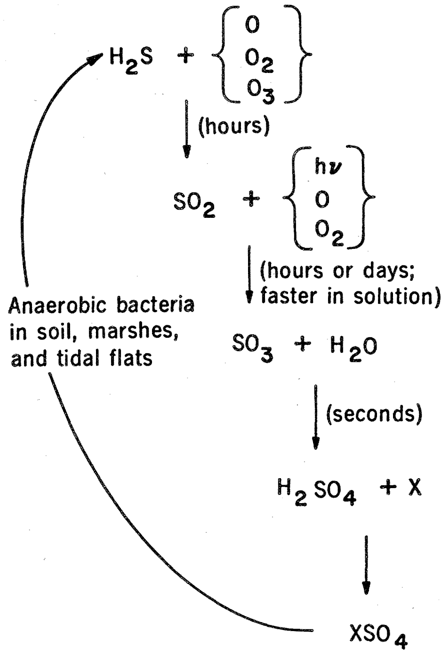

Fig. 1. Schematic representation of the chemical processes involving environmental sulfur, with indications of the mean lifetime of each compound in the lower atmosphere.

Laboratory experiments have demonstrated that in photochemcial smog SO_2 is oxidized at rates that are much too rapid to be explained by any of the above mechanisms. This enhanced rate of oxidation occurs when mixtures in air of SO_2, olefins such as those occurring in automobile exhaust gases, and oxides of nitrogen (NO or NO_2), all at concentrations comparable to those found in photochemical smog, are irradiated with sunlight. The exact mechanism of this oxidation is unknown, but it must involve several steps, one of which may be the oxidation of the SO_2 by organic peroxy free radicals. We should not overlook the possibility that this oxidation mechanism may still occur in the ambient "unpolluted" atmosphere where the concentrations of these substances are much lower.

In the surface layer of the ocean, dissolved SO_2 (sulfurous acid) and H_2S may be slowly oxidized to the sulfate anion (SO_4^{2-}) by the combined presence of dissolved O_2 and trace amounts of transition metal salts as catalysts. In the depths of the ocean, however, the dispersed sulfate may be reduced to SO_2, S, and H_2S by the action of oceanic bacteria. Sulfide ions and H_2S gas are found locally in seawater and may be widespread in stagnant bottom waters.

Sulfates and H_2SO_4 deposited in freshwater lakes may also be reduced by the bacteria present. However, it is likely that absorbed SO_2 will be less rapidly oxidized in freshwater than in seawater because of the much lower salt content of freshwater. Furthermore, this lack of metals and their oxides means that acids added to the water will not be neutralized. Accordingly, the *p*H of the surface layer of freshwater areas would be lowered by the accumulation of SO_2 and H_2SO_4 from rain and surface runoff. This effect has, in fact, been observed in parts of the world where man-made SO_2 has polluted the atmosphere, for example, in Sweden (*8, 9*).

Anaerobic bacteria in soils and marshy areas can reduce sulfate to S and H_2S, and the H_2S may escape to the atmosphere. However, H_2S diffusing upward through the soil may undergo a number of reactions, including deposition as sulfide, or oxidation variously to S, SO_2, or SO_4^{2-}.

Figure 1 is a summary of the sulfur reactions and the approximate mean lifetimes of the various compounds, introduced here to provide an easy reference for the discussions in the succeeding sections.

Atmospheric Concentrations of Sulfur Compounds

Information concerning the concentrations of sulfur compounds in relatively clean air over remote parts of the continents and oceans is quite limited, but here, in summary, is much of the available information.

Hydrogen sulfide. Junge (*10*) has suggested concentrations at ground level of 2 to 20 micrograms per cubic meter of air (*11*), and Lodge and Pate (*12*) have obtained values of <1 to 4 $\mu g/m^3$ for Panama, and latter figure having been obtained on the Caribbean coast. However, unpublished work at the National Center for Atmospheric Research (NCAR) has shown that all these results are unreliable. Liquid scrubbers were used, and so far no way has been found to prevent the oxidation and loss of significant amounts of H_2S.

Sulfur dioxide. Many of the early measurements of SO_2 concentrations, including his own, have been reviewed by Junge (*10*), who reported worldwide concentrations at ground level of 0 to 20 $\mu g/m^3$. However, many of these measurements were made over Europe where the air is quite contaminated. Recent measurements in tropical air in Panama (*12*) yielded values of <1 to 5 $\mu g/m^3$. Georgii (*13*) has obtained values of <1 to 4 $\mu g/m^3$ over the Atlantic Ocean and from 0.5 to 2 $\mu g/m^3$ over Colorado in measurements made with NCAR sampling aircraft. Cadle *et al.* (*14*) found SO_2 concentrations in Antarctic air of <1.0 to 3.2 $\mu g/m^3$.

Sulfates. Junge (*10*) also reviewed the early measurements of sulfate concentrations. Concentrations of 1.1 $\mu g/m^3$ in Hawaii, 0.6 $\mu g/m^3$ in Florida, 5.0 $\mu g/m^3$ along the east coast of the United States, and 20 $\mu g/m^3$ in Frankfurt, Germany, were typical. Recent studies by Georgii (*13*) indicated concentrations over the Atlantic of 2 to 5 $\mu g/m^3$ and about 1.7 $\mu g/m^3$ near Boulder, Colorado. Junge *et al.* (*15*) analyzed airborne particles collected along the Oregon coast, obtaining concentrations of SO_4^{2-} between 1.4 and 3.3 $\mu g/m^3$. Robinson and Robbins (*16*) suggested that, of the total mass of sulfur compounds in the atmosphere, 70 percent is in the form of sulfate aerosol. This is not borne out by Georgii's results (*13*). He found SO_4^{2-}/SO_2 mass concentration ratios in various parts of the world indicating that, even in air far from SO_2 sources, the concentration of sulfate is about the same as that of SO_2; but, using aircraft, he found an increase in this ratio with altitude, which he attributed to the oxidation of SO_2.

The stratosphere contains a layer of particles with maximum concentrations at altitudes of about 16 to 18 kilometers which Junge and Manson (*17*) found to be predominantly sulfate. The nature of this layer has been reviewed by Rosen (*18*). Recently Cadle *et al.* (*19*) analyzed particles collected on filters carried on Air Weather Service aircraft from the tropical and midlatitude stratosphere at an altitude of about 18 kilometers during the period from 1968 through 1969. Ambient sulfate concentrations above Central America were 0.1 to 0.3 $\mu g/m^3$, whereas those over the central United States were 0.2 to 0.4 $\mu g/m^3$. These values are more than ten times larger than the values obtained by Junge for 1960 through 1961, thus suggesting a change due to volcanic activity (see next section). This thesis is strengthened by the fact that preliminary results from NCAR/Air Weather Service stratospheric flights in late 1970 and early 1971, following a prolonged period of low volcanic activity, showed a return toward the values measured by Junge before the 1963 eruption of the Agung volcano in Bali (*10*).

Sources of Atmospheric Sulfur Compounds

The atmosphere receives most of its sulfur compounds from burning fossil fuels, from decomposition and combustion of organic matter, from sea salt over the oceans, and from volcanoes. These sulfur compounds are then transported and mixed in the atmosphere by winds and turbulence, and, after some period of time (which we will estimate), they are redeposited on the ground or in the oceans. The atmosphere can therefore be thought of as the main vehicle for the transport of sulfur from various sources to one or the other of its resting places, or "sinks," the land surfaces and the oceans.

Man-made SO_2 and SO_3. Most of man's emissions of sulfur to the atmosphere (about 95 percent) are in the form of SO_2. Numerous estimates have been made of the worldwide SO_2 emissions resulting from man's activities. Perhaps the earliest was that of Katz (*20*) who made estimates for each year during the period from 1937 through 1947. Eriksson (*21, 22*) and Junge (*10*) used calculations of Katz in their evaluation of the sulfur cycle. For example, Katz estimated that in 1943 the total amount of sulfur emitted, calculated as SO_2, was 77 × 10^6 metric tons. About 67 percent of these emissions resulted from the burning of coal. Robinson and Robbins (*16*) estimated that in the mid-1960's the total annual SO_2 emission was 146 × 10^6 tons; they estimated that 70 percent resulted from coal combustion, 16 percent from the combustion of petroleum products, and the remaining emissions from petroleum refining and nonferrous smelting. These estimates were based mainly on 1965 world figures from coal production, petroleum refining activity and production, and smelter production, each combined with an estimate of an SO_2 "emission factor" per unit of production.

The most recent and exhaustive review of the production of SO_2 (and many other contaminants as well) is contained in the report of the Study of Critical Environmental Problems (SCEP) (*23*). Drawing on U.S. and United Nations statistics for 1967 and 1968, it was concluded that worldwide production of SO_2 from the burning of fossil fuels (mostly for electrical power generation) amounted to 66 × 10^6 tons, and that another 27 × 10^6 tons was produced by major industrial sources (excluding power). This amounts to a total of 93 × 10^6 tons of SO_2 per year. The fact that this SCEP estimate is considerably less than that of Robinson and Robbins is partly due to the fact that in the SCEP report "emission factors" that were based on U.S. statistics were used, and these may be low relative to the values for the rest of the world, because the United States is ahead of most of the other nations of the world in reducing SO_2 emissions by resorting to low-sulfur fuel (petroleum and natural gas) wherever possible. Thus, although the United States generates 35 percent of the world's power and consumes a corresponding fraction of the fossil fuel, its production of SO_2 may be less than 35 percent of the world's production from energy sources. We will adopt the figure of 100 × 10^6 tons of SO_2 per year for the total man-made contribution to the atmosphere, and this corresponds to 150 × 10^6 tons per year of SO_4^{2-} into which most of the SO_2 is converted. Although this is a worldwide figure, it is significant that about 93.5 percent was produced in the Northern Hemisphere, and only 6.5 percent in the Southern Hemisphere (*23*).

An attempt was made in the SCEP report to predict future rates of use of fossil fuels, and, if we use the factors employed in the SCEP table 1.2 (4 percent annual growth rate until 1980, and 3.5 percent growth rate thereafter) and assume that SO_2 production will remain roughly proportional to carbon dioxide (CO_2) production, then the SO_2 production by the year A.D. 2000 will be about 275 × 10^6 tons per year. (We need hardly remind the reader that any 30-year forecast of world economic trends is fraught with uncertainty.)

All of these values can be assumed

to hold for both SO_2 and SO_3 (which is quickly converted to H_2SO_4), since, when first emitted, about 95 percent of the sulfur is in the form of SO_2, and this is converted to H_2SO_4 before being removed from the atmosphere.

Volcanic production of sulfur compounds. The sulfur compounds emitted by volcanoes are predominantly SO_2 and H_2S, along with smaller amounts of SO_3 and various sulfates. Relatively small amounts of elemental sulfur are also emitted. Considerable oxidation of the more reduced sulfur compounds to SO_3 may occur as the hot eruption clouds mix with atmospheric oxygen (*24*). As the hot gases cool, the SO_3 reacts almost immediately with H_2O vapor to produce H_2SO_4 droplets, and vapor-phase sulfates of ammonium ion, alkali metals, and alkaline-earth metals also occur in the eruption cloud.

The percentages of these various forms of sulfur in the fume from an erupting volcano vary greatly from volcano to volcano, and even from one eruption to another of the same volcano. For obvious reasons very little is known concerning the composition of the gases liberated directly during very explosive eruptions such as those of Mount Agung in Bali in 1963, or the eruption of Krakatoa in the East Indies in 1883. The little that is known concerning the composition of the gases from such volcanoes has been obtained by the analyses of gases emitted by fumaroles. Probably the most dependable analyses were those made by Shepherd (*25*) of gases collected from the tops of small lava fountains at the milder volcano Kilauea, in Hawaii, during the early part of this century. Krauskopf (*26*) also summarizes results of the analyses obtained in several other volcanic regions. The particles in the fume from Kilauea and other volcanoes consist largely of various sulfates and any finely divided lava that may be emitted in the form of pumice and "ash." The nature of the fume particles from Kilauea and other volcanoes has been discussed by Cadle and his co-workers (*24, 27*).

We can estimate the mean annual emission of sulfur compounds by volcanoes over the last few hundred years, but the assumptions required to make the evaluation may be grossly incorrect. Rittmann (*28*) has quoted Sapper on the production of volcanic materials between the years 1500 and 1914. The total amount of lava extruded (including pyroclastic material) was estimated to be 3.9×10^{17} cubic centimeters. If we assume a density of 3 grams per cubic centimeter, this corresponds to 1.2×10^{18} grams. MacDonald (*29*) estimated that the weight of gas evolved during fairly recent Hawaiian eruptions was in the vicinity of 0.5 percent by weight of the lava evolved; if, as Shepherd's analyses indicate, about 10 percent by weight of the gas is SO_2 [and this apparently was the major form of sulfur (*30*)], the total weight of SO_2 evolved over the approximately 400 years must have been about 6×10^{14} grams, or 1.5×10^6 tons per year.

This can be compared with a total annual SO_2 liberation to the atmosphere as pollution of 100×10^6 tons. Thus, if this evaluation for the average yearly emission of SO_2 is correct, volcanoes contribute about two orders of magnitude less sulfur and its compounds to the atmosphere than man's activities do.

Unfortunately, the uncertainties in the above estimate are very large indeed. The ratios of the weight of gases to the weight of lava emitted from explosive eruptions may exceed unity, as indicated by Rittmann (*28*). On the other hand, the analyses of the gases from fumaroles of volcanoes, where such explosive eruptions occur, indicate that often more than 99 percent of the gases are H_2O vapor. If this composition also applies to the actual eruption fume, the large difference in the ratio of the weight of gas to the weight of lava may result from differences in the amounts of H_2O vapor alone. If this is the situation, the above estimate may be essentially correct; however, if the composition of the gases in the explosive type eruptions is similar to those from Kilauea, which is unlikely, the average annual emission of SO_2 by all volcanoes may be considerably larger than we have estimated, and could approach the values from fossil fuel sources.

Although the rate of emission of SO_2 from volcanoes averaged over the earth's surface and over time is probably several orders of magnitude less than that from man-made sources, the huge local emission by a volcano of sulfur compounds over periods of a few days or weeks may have a marked effect on the atmosphere. Particularly striking is the great enhancement by such an eruption of the layer of particles at an altitude of 18 to 20 kilometers in the stratosphere. This enhancement results from the injection of particles into the stratosphere and the reaction in the stratosphere of SO_2 and H_2S with atomic oxygen to form SO_3, followed by hydration to form H_2SO_4 droplets (*31*). This increased particle loading of the high atmosphere produces brilliant sunsets for 2 to 3 years and may affect the heat balance of the stratosphere (*32*).

The oceans as sources of atmospheric sulfur compounds. Seawater contains about 2.65 milligrams of SO_4^{2-} per gram of H_2O, and the particles of sea salt formed by the breaking of myriads of bubbles are an important source of atmospheric sulfate, especially over the oceans. Eriksson (*21, 22*) has estimated that the annual production of SO_4^{2-} is 130×10^6 tons, of which 10 percent passes over the continents. The remainder is precipitated back into the oceans.

The oceans have been suggested as a source of H_2S. This hypothesis has usually arisen from a theoretical need for a source of atmospheric sulfur to balance a suggested sulfur cycle. Thus Eriksson (*21, 22*) speculated that the annual H_2S emission from the oceans is 202×10^6 tons, and Robinson and Robbins (*16*) suggested that it is 30×10^6 tons. Undoubtedly some H_2S is liberated from tidal flats, but probably very little is emitted from continental surface H_2O, or the open oceans, the rate of oxidation by dissolved oxygen being too rapid as the H_2S is transported up from the depths (*33*). This conclusion is borne out by the fact that, with certain exceptions, such as the deep and stagnant layers of the Black Sea, the concentrations of H_2S in ocean H_2O are too small for detection with presently available techniques.

Sulfur dioxide is very soluble in H_2O, and the oceans are generally considered to be a sink for SO_2. However, from a physicochemical viewpoint, the oceans could equally well be a source of SO_2 if the equilibrium vapor pressure of SO_2 in surface H_2O exceeds the partial pressure of SO_2 in the air immediately above it. Some recent measurements of Pate *et al.* (*34*) at Panama and Barbados Island indicated that, when there was a breeze off the oceans, the SO_2 concentrations decreased with increasing distance inland. This result suggests that the oceans or coastal areas in those regions may be a source of SO_2, but much additional information is needed. The *p*H of ocean H_2O is about 8.1 ± 0.2, and this alkalinity will increase the rate of oxidation of SO_2 by dissolved oxygen to sulfate. However, whether this oxidation is fast enough to prevent the escape of SO_2 from ocean H_2O is unknown.

Hydrogen sulfide from biological processes on land. Hydrogen sulfide is produced in swamps and other land areas by the decay of vegetation, but little more is known about the annual rate of release of H_2S to the atmosphere from this source than about that from the oceans. Eriksson (*21, 22*) estimated that decaying organic matter on land would liberate annually about 82×10^6 tons of H_2S to the air and revised this later (*35*) to 112×10^6 tons. Robinson and Robbins (*16*) suggested a land area emission of about 70×10^6 tons to achieve a balance in their proposed sulfur cycle. In a subsequent section we will follow somewhat the same procedure in order to obtain a "balanced budget" of sulfur compounds (see Table 3). A significant portion of the natural sulfate that comes from the land areas of the globe and is then removed by rain may originate as H_2S, but we cannot say what fraction this is.

Evidence from studies of stable isotopes. Variations in the stable isotope ratios of sulfur and oxygen in atmospheric sulfur compounds afford a means of distinguishing between various natural and pollutant sources. Some preliminary investigations of this nature have been carried out by Östlund (*36*), Ault and Kulp (*37*), Jensen and Nakai (*38*), Thode *et al.* (*39*), Rafter (*40*), Nakai and Jensen (*41*), Mizutani and Rafter (*42*), and Manowitz and Tucker (*43*). Reported variations in the sulfur isotope content of sources of atmospheric sulfur are summarized in Table 1.

Only meteoritic sulfur, which is used as the reference standard for sulfur isotope measurements, and sea salt sulfur have very specific values of the $^{32}S/^{34}S$ ratio. However, the spread and overlap in the values for this ratio (Table 1) do not eliminate the usefulness of the isotopic method as a means of discriminating among sulfur sources. The sea salt contribution can also be determined by measurement of the ratio of chloride to sulfate in aerosol or precipitation samples. The use of oxygen isotope as well as sulfur isotope measurements to distinguish between biological sulfur and fossil fuel sulfur has been discussed by Mizutani and Rafter (*42*). Volcanic sources are unimportant except locally in regions and periods of volcanic activity, and in the stratosphere after major volcanic explosions. Furthermore, the spread of $^{32}S/^{34}S$ ratios will be much narrower for individual pollutant sources and within each industrial area.

Table 1. Isotopic composition of sources of atmospheric sulfur.

Source	$^{32}S/^{34}S$	$\delta_{^{34}S}$*	Reference
Meteoritic sulfur (standard)	22.225	± 0.2	(*39*)
Sea salt sulfate	21.79	$+20.1 \pm 0.3$	(*39*)
Biogenic H_2S	22.08 to 22.71	-23 to $+6$	(*37*)
Volcanic SO_2	21.8 to 22.4	-8 to $+18$	(*37*)
Volcanic H_2S	22.27 to 22.42	-9 to -2	(*37*)
Petroleum	21.9 to 22.45	-9.8 to $+16$	(*43*)
Coal (Japan)	21.69 to 21.95	$+11.9$ to 23.9	(*38*)

$$* \ \delta_{^{34}S} = \left(\frac{22.225}{^{32}S/^{34}S \text{ (sample)}} - 1 \right) \times 10^3 \text{ parts per mil.}$$

Except for the evaluation of source ratios, isotopic measurements of atmospheric sulfur compounds published up to the present time have been limited to studies of sulfate in precipitation (*36, 38, 40–42*). If we compare results for industrial and remote areas (*38, 40*), precipitation samples with the lowest SO_4^{2-} concentration (and presumably less pollution) have higher $\delta_{^{34}S}$ values, an indication of a proportionally greater contribution to unpolluted air from sea salts and other sources with characteristically high $\delta_{^{34}S}$ values, and not from biogenic H_2S with its lower value. The results for Gracefield, New Zealand, rains also indicate fossil fuels and sea salts as the two major sources of atmospheric sulfate in that region, with only minor contribution from the biosphere. It has been speculated, as mentioned above, that some 50 percent or more of the total atmospheric sulfur budget is contributed by biogenic H_2S (*16, 22, 44, 45*); we will come to a similar estimate in Table 3. Since the isotopic evidence suggests that H_2S from the biosphere may not be an important source of atmospheric sulfur (except in the vicinity of tidal flats and coastal belts), we seem to have two conclusions that are inconsistent with each other. These results emphasize the need to resolve this question of biogenic sulfur sources.

Removal from the Atmosphere

Rainout and washout. The removal of trace constituents such as sulfates from the atmosphere by means of precipitation can be considered to occur by two general processes: rainout and washout. Rainout can be defined as all processes within the clouds that result in removal, and washout as the processes of removal by precipitation below the clouds.

Sulfate ion in precipitation H_2O originates from both dissolution of particulate sulfate and absorption of SO_2 with subsequent oxidation. The relative contributions of these processes have been estimated theoretically by Beilke and Georgii (*46*), who concluded that 70 percent of the sulfate in rainwater comes from the washout of SO_2, and 20 percent from the rainout of sulfate aerosols. These results apply for rains in Frankfurt, Germany, and in similar regions where the SO_2 concentration below the average cloud base is significantly greater than at higher levels, implying strong sources at the surface. In uncontaminated air, rainout of particulate sulfate becomes a relatively more important source of sulfate in rainwater.

These computed estimates have recently been confirmed in Russian field experiments by Petrenchuk and Selezneva (*47*). In the southern regions of the European portion of Russia, where there is considerable pollution of the atmospheric boundary layer, rainout processes contributed only 20 to 25 percent to the sulfate content of rainwater. However, in the uncontaminated northern region the rainout contribution was 55 percent.

The amount of sulfate in precipitation H_2O depends to some extent on the contribution from sea salt aerosols in the air. The SO_4^{2-} in a sample of precipitation H_2O that originated as sea salt may be calculated, to a first approximation, from the equation:

$$(SO_4^{2-})_{\text{sea salt}} = (SO_4^{2-}/Cl^-)_{\text{sea salt}} \times (Cl^-)_{\text{obs}} \qquad (3)$$

Equation 3 is not strictly valid, since it disregards any change in the atmospheric Cl^- content due to additions from the land surface or removal by the conversion of NaCl to HCl. The former effect is unimportant, and the latter effect causes little change because

Table 2. Annual deposition of "excess sulfate" (see text for definition) in precipitation over the Northern Hemisphere.

Location	Deposition (ton/km^2)	Deposition by region ($\times 10^6$ tons)
United States	2.7	26
Europe (excluding Russia)	2.2	11
European portion of Russia	4.0	19
Asia	1.8	79
Remaining land areas of the Northern Hemisphere	1.5*	54
Ocean areas of the Northern Hemisphere	0.5	75
Total		264

* Assumed value.

HCl is highly soluble in water and the Cl^- will still be removed by rain along with SO_4^{2-}.

Even though the concentration of excess sulfate in precipitation is variable, by the nature of the process it represents an integration over time and space. (The expression "excess sulfate" refers to total sulfate from all sources other than sea salt.) The excess sulfate in rainwater is a direct measure of the main removal mechanism and therefore a key to any budget estimate for atmospheric sulfur.

Estimates for excess sulfate deposition over the Northern Hemisphere by precipitation (Table 2) are based upon data of Lodge *et al.* (*48*), DeBary and Junge (*49*), and Selezneva and Drozdova (*50*). The values given are the products of the measured concentration of excess sulfate, the mean annual rainfall, and the area involved. Some of the major uncertainties in these estimates are as follows: (i) the data tend to be too sparse geographically for accurate averaging over large areas; (ii) the sampling networks were not operated concurrently and involved the use of different sampling and analytical techniques; and (iii) the periods of observation were too short for an accurate determination of the long-term averages and trends in concentrations.

Because there are very few data on the sulfate content of rainwater in the Southern Hemisphere, it is difficult to make reliable estimates of the sulfur budget in the Southern Hemisphere. However, using estimates of the total excess sulfate deposition over the Northern Hemisphere, and assuming a predominantly continental origin for the biogenic component, one can make rough estimates of the contributions from the Southern Hemisphere, which we do below in the section entitled "Model of the Sulfur Cycle."

Removal of SO_2 by diffusion to soil and vegetation. An estimate of the rate of uptake of SO_2 by soil and vegetation can be made by assuming that all SO_2 reaching the earth's surface is removed in this way. Eriksson (*21*) made such a calculation based on turbulent diffusion throughout most of the atmosphere and molecular diffusion in the laminar boundary layer. He concluded that the "deposition velocity" is 1 to 2 centimeters per second, a measure of the rate of diffusive transport from some reference level to the surface. Robinson and Robbins (*16*) used a rate of 1 centimeter per second and a concentration of SO_2 over land of 1 $\mu g/m^3$, obtaining an estimated uptake of 52×10^6 tons of SO_2 per year.

Swinbank (*51*) made a similar calculation based on relations he had derived by dimensional arguments which connect the vertical fluxes of heat and horizontal momentum in the "constant flux" layer with other relevant variables (*52*). He showed that the downward flux of SO_2 in a steady-state situation, which is constant with height in the boundary layer, can be estimated by the relation

$$F_s = \frac{\rho\, s_z\, k u_*}{\ln\left(\dfrac{k u_*\, z + \nu}{\nu}\right)} \cong \frac{\rho\, s_z\, k u_*}{\ln\left(\dfrac{k u_*\, z}{\nu}\right)} \qquad (4)$$

where ρ is the air density, s_z is the mixing ratio of SO_2 by mass at a height z, k is von Karman's constant (0.4), ν is the molecular diffusivity of SO_2 in air (about 0.2 square centimeter per second), and the friction velocity u_* can be evaluated from

$$u_* = 0.2\ u_z^{7/8}\ f^{1/8}\ z_0^{1/8} \cong 8 \text{ cm sec}^{-1} \qquad (5)$$

where u_z, the surface geostrophic wind, can be taken to be about 2 meters per second as a mid-latitude annual mean; f is the Coriolis parameter (about 10^{-4} per second at 40° latitude); and z_0, the roughness length, can be taken to be 5 centimeters (neither of the last two factors is critical, since they appear in the equation to the ⅛ th power). This value of u_* corresponds to a "diffusion velocity" of about 0.4 centimeter per second at a height of 2 meters. Substituting all these values in Eq. 4, with a mean concentration of SO_2 at 2 meters above the ground taken to be 2 parts per billion in the Northern Hemisphere and 1 part per billion in the Southern Hemisphere, $F_s \cong 0.96 \times 10^{-12}$ gram per square centimeter per second in the Northern Hemisphere, and half this value in the Southern Hemisphere. We will make use of this rate of diffusion in our model of the global sulfur budget.

Dry removal of sulfate particles. It was noted above that rainout and washout are important processes for the removal of sulfate particles from the atmosphere. In addition, sulfate particles, rapidly mixed by eddy diffusion in the lower atmosphere, are continuously removed by various deposition mechanisms which operate at or near the earth's surface. Observed high concentrations of radioactive particles on trees and plants indicate that deposition of atmospheric particles on vegetation must be an efficient process. Published data (*10, 12, 21, 22, 35*) indicate that the mass concentration of sulfate particles in the lower troposphere over continental areas is about equal to that of SO_2. On the assumption that SO_2 and sulfate are removed with comparably high efficiency by reaction with or attachment to the surfaces of trees and plants, the mass of annual dry deposition of sea salt plus excess sulfate particles over continents is about the same as for SO_2, derived in the preceding section.

Eriksson (*21, 22*) estimated that a global total of about 130×10^6 tons of sea salt sulfate is cycled through the atmosphere each year. He also concluded that only about 10 percent of the total, 13×10^6 tons, is deposited over land areas. We are assuming that this comes down in rain rather than as dry material since sea salt particles tend to be larger than sulfate particles of continental origin.

Two additional mechanisms for the removal of dry sulfate particles, gravitational sedimentation and scavenging of sulfate particles by sea spray and fog droplets over ocean areas, are considered to play only a minor role in sulfate particle deposition. Gravitational sedimentation has negligible influence on the deposition of the very small sulfate particles produced by the oxidation of atmospheric SO_2, but undoubtedly has some influence on the deposition of the much larger sea salt particles.

Residence Times

Published estimates of the average lifetime of sulfur compounds in the atmosphere (*10, 16, 53, 54*) reflect our limited knowledge of the atmospheric distribution of these compounds as well as the rate of each competing chemical reaction and deposition mechanism. The average lifetime, τ, is the reciprocal of the "exponential removal rate," which is defined as the fraction of a constituent removed per unit time. Residence times based on estimates of source inventories and mean air concentrations are unreliable because of the very large uncertainties in such estimates. Perhaps the best that can be done at present is to estimate an upper limit for the residence time of each compound on the basis of known rates of reaction or removal.

The fraction of H_2S that enters the atmosphere reacts rapidly with O_2 to form SO_2 and H_2O or is dissolved in fog and cloud droplets where it is hydrolyzed and rapidly oxidized by dissolved O_2. Junge (*10*) pointed out that the mean lifetime of atmospheric H_2S due to its reaction with tropospheric O_3 alone would be only 1.7 days. Considering other reactions of H_2S in the lower atmosphere, its actual residence time must be appreciably shorter than 1 day.

Atmospheric SO_2 is removed by several competing processes: diffusion to plant surfaces where it is adsorbed and reacts chemically; incorporation into fog and cloud droplets where it is oxidized catalytically and photochemically to sulfate; or direct removal by deposition as bisulfate in precipitation. Estimates of SO_2 residence times range from $\tau = 12$ hours to 6 days (*10, 16, 53, 54*). With one exception (*54*), these estimates did not take into account the important role of precipitation in the removal of SO_2 and must be revised downward accordingly. On this basis the average lifetime of SO_2 in the atmosphere is only several days, or less, but with wide variations which depend on meteorological and other environmental factors.

The small amount of SO_2 that mixes up into the stratosphere will react rapidly with atomic oxygen in its ground state (*31*) followed by hydration to form H_2SO_4, with lifetimes of about 14 and 2.4 days at altitudes of 15 and 20 kilometers, respectively.

The residence time of sulfate particles in the lower atmosphere is perhaps best determined from the radioactivity ratios of the atmospheric radon (Rn) daughters ^{210}Pb and ^{210}Bi, which are created by the decay of atmospheric Rn and quickly attach themselves to airborne particles. The apparent residence time of aerosols based on $^{210}Bi/^{210}Pb$ ratios is about 6 days at cloud level (*55*) and usually less in surface air (*56*). However, recent studies (*56, 57*) make it clear that the ^{210}Bi and ^{210}Pb present in the atmosphere include a contribution of aerosol from soil and plant surfaces in which the ^{210}Bi and ^{210}Pb are in secular equilibrium before becoming airborne. This finding indicates that the actual residence times of particles in the lower atmosphere are shorter than the apparent lifetimes based on a simple application of $^{210}Bi/^{210}Pb$ ratios. Therefore, it appears that sulfate particles in surface air over land and at cloud level have average residence times of several days and about 1 week, respectively. The residence time will increase markedly at higher levels in the troposphere.

Thus, the best present estimates of the residence times of H_2S, SO_2, and sulfate particles in the lower atmosphere are shorter than has generally been assumed. Because sulfur com-

Table 3. Basis for the model of the sulfur cycle shown in Fig. 2 (units are 10^6 tons calculated as sulfate per year).

Component	Land	Oceans	Totals
Deposition in the Northern Hemisphere			
Sea salt SO_4^{2-} in precipitation (130 × 10^6 tons global total, 10 percent of global total deposited on all land)	8	53	61
Diffusion of SO_2 to surface (theoretically derived flux)	36	0	36
Diffusion of SO_4^{2-} to surface (mass equivalent to SO_2 diffusion)	24	0	24
Excess SO_4^{2-} in precipitation (from Table 2)	185	75	260
Totals	253	128	381
Sources of sulfate deposited in the Northern Hemisphere			
Man-made excess SO_4^{2-} (93 percent of worldwide production, and assume 80 percent deposited on land)	112	28	140
Sea salt SO_4^{2-}	8	53	61
Natural excess SO_4^{2-} (total calculated to make a balance, assumed 80 percent deposited on land)	144	36	180
Totals	264	117	381
Sources of sulfate deposited in the Southern Hemisphere			
Man-made excess SO_4^{2-} (7 percent of worldwide production, and 80 percent deposited on land)	8	2	10
Sea salt SO_4^{2-} (130 × 10^6 tons global total, 10 percent of global total deposited on land)	4	65	69
Natural excess SO_4^{2-} (assumed same source as Northern Hemisphere, proportional to land area, 80 percent deposited on land)	72	18	90
Totals	84	85	169
Deposition in the Southern Hemisphere			
Sea salt SO_4^{2-} in precipitation	4	65	69
Diffusion of SO_2 to surface (theoretically derived flux, half the concentration in surface air of the Northern Hemisphere, and half the land area)	9	0	9
Diffusion of SO_4^{2-} to surface (mass equivalent to SO_2 diffusion)	6	0	6
Excess SO_4^{2-} in precipitation (total calculated to make a balance, same proportion of precipitation deposition over land as in the Northern Hemisphere)	61	24	85
Totals	80	89	169

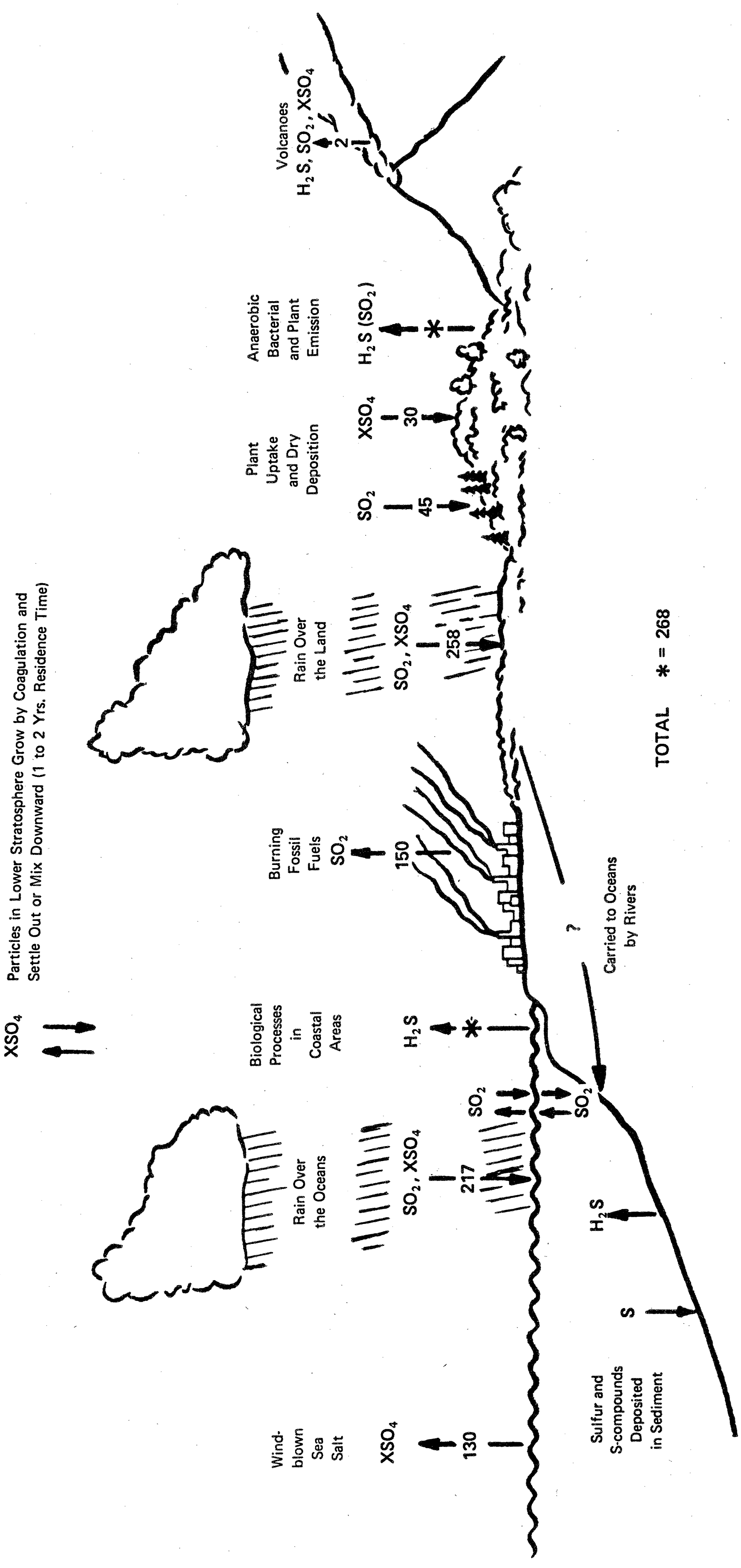

Fig. 2. Sources and sinks of atmospheric sulfur compounds. Units are 10^6 tons calculated as sulfate per year (see text and Table 3 for the derivation of these rates).

pounds will be chemically modified or removed from the lower troposphere to a large extent within hundreds to a few thousands of miles from their sources, their spatial distribution will exhibit large variations.

Experience with the dispersal and removal of radioactive debris from the stratosphere indicates a much longer mean residence time for stratospheric aerosols and trace gases (*58*). The residence time applicable to particles in the sulfate aerosol layer in the lower stratosphere is about 1 to 2 years. As a result of the long residence time, the distribution of sulfate aerosol in the stratosphere is usually fairly uniform horizontally, although it does show marked variations with altitude and latitude after large volcanic eruptions.

Transport by Rivers

Rivers transport sulfur compounds from three major sources to the oceans: rocks, fertilizers, and the atmosphere. The largest amount of sulfur transported is that produced by precipitation and dry deposition. Eriksson (*35*) estimated that, for the period around 1960, the total annual amount of sulfate carried to the sea by rivers was 240×10^6 tons; this figure includes 45×10^6 tons from rock weathering, 30×10^6 tons applied to the soil as fertilizer, and 165×10^6 tons from precipitation or dry deposition.

Eriksson's data were based on measurements made about 1900 showing that about 12 percent of the inorganic matter in river waters was made up of sulfate and that the total yearly runoff of sulfate at that time amounted to about 200×10^6 tons. Although the river flow must remain relatively constant, the ever-increasing use of sulfate fertilizers in many parts of the world plus the growth in the production of sulfate from fossil fuels must result in a steadily increasing amount of sulfate being carried to the oceans. Any estimate of this part of the sulfur cycle must also take account of the holdup time on the land of the freshly deposited sulfate, since it can hardly be considered as a steady-state situation. We have not attempted to bring Eriksson's estimate for river transport up to date, although it should be done. This part of the cycle is therefore not closed here, nor can it be without several additional considerations that are beyond the scope of this study.

Model of the Sulfur Cycle

Taking the uncertainties of our estimates into account, and recognizing that over a year's time there must be an approximate balance between inputs and removal for the atmosphere as a whole, we can construct a diagram similar to that of Robinson and Robbins (*16, 45*) and of Junge (*10*). The "model" of the sulfur cycle shown in Fig. 2 is, in effect, a summary of most of the information that we have presented piecemeal, combined into a coherent whole with the help of a few additional assumptions. Since the calculation is a bit complicated, we have summarized it in Table 3. To the clues in the text should be added the following useful, although approximate, numbers: area of earth, 5.1×10^{18} square centimeters; area of land, 1.4×10^{18} square centimeters; there is about twice as much land area in the Northern Hemisphere as in the Southern Hemisphere.

The line of reasoning used in constructuring Table 3 can be outlined as follows: (i) the deposition of sulfur in the Northern Hemisphere is estimated from measured concentrations in precipitation and theoretically derived fluxes to the ground, to which is added a proper proportion of the total sea salt sulfate that is rained out; then (ii) the total natural excess sulfate produced in the Northern Hemisphere can be calculated to achieve an overall balance, there being no other way to estimate it (assume no atmospheric transport of sulfate or SO_2 between hemispheres); then (iii) the total sulfate and SO_2 deposition in the Southern Hemisphere can be calculated, if we may assume that the same natural processes operate there and if we know the man-made contribution; and finally (iv) a balance can be invoked again to calculate the excess sulfate in Southern Hemisphere precipitation. This "bookkeeping approach" allows us to estimate the unknown (unmeasured) parts of the cycle and to achieve a balanced budget.

Others have used the same general method, notably Robinson and Robbins (*16*), but our approach differs in a number of ways from theirs, and also takes advantage of more recently obtained data. Major differences between our estimates and those of Robinson and Robbins are the smaller contributions of man (based on estimates from 1967 through 1968) and the greater amount of sulfur removed from the atmosphere by precipitation. Furthermore, the oceans are not considered to be either sources of H_2S or sinks for SO_2 for reasons discussed above. Hydrogen sulfide probably does not escape from the open oceans, and we do not know whether the oceans are sources or sinks for SO_2. There must be, however, a net transfer of sulfur to the oceans from rain and runoff, probably originating largely from man-made emissions to the atmosphere; thus the cycle is not closed in all respects.

Conclusions

Even granting our uncertainties about parts of our model of the sulfur cycle, we can draw some conclusions from it:

1) Man is now contributing about one half as much as nature to the total atmospheric burden of sulfur compounds, but by A.D. 2000 he will be contributing about as much, and in the Northern Hemisphere alone he will be more than matching nature.

2) In industrialized regions he is overwhelming natural processes, and the removal processes are slow enough (several days, at least) so that the increased concentration is marked for hundreds to thousands of kilometers downwind.

3) Our main areas of uncertainty, and ones that demand immediate attention because of their importance to the regional air pollution question, are: (i) the rates of conversion of H_2S and SO_2 to sulfate particles in polluted as well as unpolluted atmospheres; (ii) the efficiency of removal of sulfur compounds by precipitation in polluted air. And for a better understanding of the global model we need to know: (i) the amount of biogenic H_2S that enters the atmosphere over the continents and coastal areas; (ii) means of distinguishing man-made and biogenic contributions to excess sulfate in air and precipitation; (iii) the volcanic production of sulfur compounds, and their influence on the particle concentration in the stratosphere; (iv) the large-scale atmospheric circulation patterns that exchange air between stratosphere and troposphere (although absolute amounts of sulfate particles involved are small relative to the lower tropospheric burden); (v) the role of the oceans as sources or sinks for SO_2.

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Golgi Apparatus: Influence on Cell Surfaces

A role in the assembly of macromolecules makes the organelle a determinant of cell function.

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There is a growing awareness that many cellular functions are directly influenced or "controlled" by macromolecules "outside" the cell, either as components of the plasma membrane, or as cell surface–associated materials, or as components of intercellular matrices (*1*). Many of these macromolecules have now been shown to have carbohydrate moieties (for example, glycoproteins, mucopolysaccharides, proteoglycans, and some glycolipids are involved). The Golgi apparatus functions both in the synthesis or assembly of some of these carbohydrate-containing materials and in their transport to the cell surface as part of the secretory process. The apparatus thus provides a focal point to which we may relate many of the findings regarding cell surface–mediated phenomena that come from numerous separate fields.

Much attention has been directed to the specificity of proteins and the manner in which this specificity is genetically determined by nucleic acid coding of amino acid sequences. Nonetheless, the fact that there is a high degree of genetically controlled specificity in certain carbohydrate groups has also been known for many years from various studies with microorganisms, from blood group studies, and from immunochemical studies (*2*). Carbohydrate-containing materials found generally at the surface of cells (*3, 4*) have now been implicated in fundamental aspects of cellular function such as recognition, motility, and association (*4–6*). For example, specific carbohydrate groups are responsible for recognition and adhesion between mating types in many unicellular organisms (*7*) and may be responsible for recognition by gametes of higher organisms (*8*). They are also involved in recognition and cell-specific adhesion in the structuring of multicellular forms, for example, in the species-specific aggregation of sponge cells, in the histiotypic association of embryonic cells, and in the formation of cell contacts in *Dictyostelium* (*9*). Alteration of carbohydrate-containing surface materials brought about by virally induced cell transformation may explain several characteristics of virus transformed cells such a cell fusion, selective agglutination, and the release of cells from contact inhibition (*4, 5, 10*), and may relate to the development of malignancy in general (*4, 5, 11*). Antigenic specificity characteristics of glycoproteins with blood group activity are determined by particular sugar groups added sequentially to a polypeptide moiety (*12*). In many instances, the particular characteristics of surface materials can be correlated with sugar sequences that include galactose, fucose, and sialic acid.

The surface specificity of cells provides selectivity for materials taken into the cell both by passage through the membrane and by endocytic phenomena. In instances of the intake of materials by endocytosis, surface specificities may determine the fate of the engulfed material, for example, whether and to what extent it is degraded in the lysosomal system (*13*). Removal of segments of plasma membrane with associated material during endocytosis can be compensated for by incorporation of secretory vesicle membranes. Such "new" membrane segments may carry different specificities into the plasma membrane (*14, 15*). The cycling and recycling of surface materials may provide for the changing specificities in informational content essential for the control of differentiation and development.

Both at the cellular and supracellular levels various developmental phenomena may be guided by cell-to-cell and cell-to-environment interactions in which carbohydrate-containing materials act as determinants. It has been proposed that "informational potential" of such materials located at the cell surface could explain characteristics of cell movement, morphogenesis, and adaptability to environmental stimuli during embryogenesis (*16*). Similar materials have been implicated in various mor-

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