CHAPTER 2

The Atmospheric Sulfur Cycle in the Tropics

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2.1 Introduction

Sulfur is ubiquitous in nature: it exists in soils mainly as organic compounds, but also as sulfate or sulfide (0.5 mg S/g); in sea water as sulfate (2.65 mg
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S/g); in plants as sulfate, sulfide, or organic compounds (0.1 to 2 mg/g of dry matter); and in the atmosphere in gaseous and solid states (0.3 μg to 1 μg/kg). The exchange of sulfur between these different media generally takes place in the atmosphere. Sulfur is emitted into the atmosphere in a more or less reduced state as hydrogen sulfide, organic sulfides, or as sulfur dioxide. Much of it is then oxidized into sulfuric acid or its salts and removed mainly by precipitation.

In the absence of major climatic changes this natural sulfur cycle is stable, disturbed mainly by volcanic eruptions. A recent perturbation is the result of industrialization, mainly as a consequence of increasing energy demand. Based on evidence from Arctic polar ice samples (Herron, 1982; Murozumi et al., 1969), this perturbation became significant around 1900 and is mainly confined to the Northern Hemisphere. Assessments of sulfur fluxes from both natural and anthropogenic sources vary (Kellogg et al., 1972; Friend, 1973; Robinson and Robbins, 1975; Granat et al., 1976; Cullis and Hirschler, 1980; Sze and Ko, 1980; Müller, 1984a, b). In these studies the natural emissions were poorly known owing to the small number of reliable measurements. Natural processes have become better understood during the past decade thanks to data obtained by Aneja et al. (1979a, b), Adams et al. (1979, 1980), Delmas et al. (1980a), Delmas and Servant (1983). These studies, carried out in the eastern US and in equatorial Africa, showed that a positive gradient of the S-flux is to be expected with decreasing latitudes and that the maximum occurs in equatorial regions.

The global natural and anthropogenic emissions based on the most recent estimations are presented in Table 2.1. The production of sulfur by sea-spray has been omitted. The natural emissions emanating from land and sea

<table>
<thead>
<tr>
<th>Source</th>
<th>Intensity</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Marine</td>
<td>40-48</td>
<td>Andreae and Raemdonck, 1983 (revised by Savoie, 1984)</td>
</tr>
<tr>
<td>Continental</td>
<td>35-50</td>
<td>Möller, 1984a</td>
</tr>
<tr>
<td>Volcanic</td>
<td>2-12</td>
<td>Möller, 1984a; Cadle, 1980</td>
</tr>
<tr>
<td>Anthropogenic in 1975</td>
<td>69-104</td>
<td>Möller, 1984b; Cullis and Hirschler, 1980</td>
</tr>
</tbody>
</table>
are approximately equal, and man-made emissions are of the same order of magnitude.

Sulfur compounds in the atmosphere are rapidly removed or oxidized, except for carbonyl sulfide (COS). According to Granat et al. (1976), the production of submicron particles is considered the most important reason for the elaboration of a global sulfur budget. These submicron particles consist partly of sulfuric acid and sulfates. Sulfuric acid is probably the main agent of rainwater acidification even in the presence of other strong (e.g. nitric) or weak (e.g. formic and acetic) acids. However, in the ionic state of sulfate, sulfur is a natural fertilizer in air and in some soils (Tamm, 1976).

This chapter describes the sulfur cycle in tropical regions in order to provide data on the state of acidification of air and rainwater in a tropical environment before further industrialization.

### 2.2 THE ATMOSPHERIC SULFUR CYCLE IN EQUATORIAL REGIONS

In order to describe the effects of the atmospheric sulfur cycle on a particular ecosystem, three components should be considered: (i) the external or internal sources, (ii) the chemical and physical transformations of the different compounds emitted to the atmosphere, and (iii) the sinks that include deposits and transport outside the ecosystem.

Different sources of atmospheric sulfur are found in equatorial regions. The main source is associated with the biological transformations of sulfur in soil and in the biosphere. The reduction of sulfates to sulfides by the mineralization of organic matter under special conditions supplies the atmosphere with gaseous sulfur compounds. These compounds are emitted in reduced forms such as hydrogen sulfide (H$_2$S) and different methyl and carbon sulfides.

The complexity of the cycle and of the processes concerned are illustrated in Figure 2.1. In the total sulfur cycle, reactions in the soils are bidirectional. In the strongly oxidizing environment of the earth's atmosphere, however, natural conversion from reduced to oxidized forms is the rule; there is no important reverse reaction from a higher oxidation state to a lower one. While the direction of the reaction does not vary during the day, reaction rates do. The processes in the soils are continuous, but their intensity is modulated by the type of soil and vegetation, and by climatic variations.

Biomass burning is the other source linked to the biosphere; it includes bushfires in dry savannas, and fires used in agriculture or for deforestation. This source is mainly of anthropogenic origin and is sporadic, occurring only during the dry season.
Figure 2.1  Simplified sulfur cycle in the tropics
In the equatorial regions, atmosphere-biosphere exchanges are the main sources of atmospheric sulfur, although other sources exist. The main sources are:

(a) The oceans: all the continental zones in the intertropical regions are influenced by oceanic air in the lower layers of the atmosphere, either permanently (South America, equatorial Africa, Oceania), or sporadically, according to the latitudinal position of the meteorological equator (West Africa, tropical Asia) (Riehl, 1954).

(b) The soils: important quantities of dust, moved into the air by strong winds, are a source of particulate sulfur. This phenomenon is particularly important in the Asian and African desert zones.

Other sources are industrial and domestic activities and volcanic emissions. Some compounds introduced into the atmosphere are stable, such as particulate sulfates (oceanic, soil-derived); others are unstable. The unstable compounds can be reduced gases such as H₂S (biosphere), methyl sulfides (ocean, biosphere), or carbonyl sulfides (biosphere, fires); oxidized gases such as sulfur dioxide (SO₂), emitted during combustion or derived from the oxidation of reduced gases; and some other species with short lifetimes.

Sulfur compounds are eliminated from the atmospheric reservoir by dry and wet deposition, with different speeds at different steps in the oxidation chain. Wet deposition arises from in-cloud scavenging and below-cloud scavenging. Rain acidity is due to the incorporation of acidic compounds (SO₂, H₂SO₄). Vertical and long-range horizontal transports could also be considered as sinks, particularly for carbonyl sulfide (COS).

2.2.1 The Tropical Environment

The previous discussion described how the natural environment influences the atmospheric sulfur cycle in equatorial regions. The two main biomes in these regions are the forests and the savannas. It is difficult to estimate the surface of the equatorial forests in the world, as they are evolving constantly and decreasing rapidly as a result of deforestation for cultivation. Lanly and Clement (1979) give a value of 17.6 × 10⁶ km² for all intertropical forests, with primary forests representing less than 3 × 10⁶ km². The total biomass of the equatorial forests comprises about 50% of the continental biomass of the planet. The equatorial forested zones have a high rainfall, usually estimated at 1,400 mm/year (Richards, 1964), and some regions receive more than 3,000 mm/year.

Savannas cover about 20 × 10⁶ km² and receive an annual rainfall of between 120 and 900 mm. The biomass of the savannas decreases with rainfall amount, but no linear relation between these two parameters exists.
2.3 PRODUCTION OF ATMOSPHERIC SULFUR

2.3.1 General Survey of the Transformation of Sulfur

The natural cycle of sulfur in the soils includes a complex chain of oxidation and reduction reactions controlled by microorganisms. In the soils, most sulfur (75% to 99.5%) appears in organic compounds. The proportions of organic sulfur depend largely on the nature of the soil; the inorganic fraction remains low. Plants absorb most of the sulfur in the form of sulfate ions. Organic sulfur compounds then become mineralized due to the action of microorganisms such as bacteria, heterotrophic organisms or fungi. Studies have shown that methyl mercaptan (MeSH), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), and carbonyl sulfide (COS) are produced under aerobic conditions, and carbon disulfide (CS₂), MeSH, DMS, and COS formation prevails under anaerobic conditions (Katoda and Ishida, 1972; Banwart and Bremner, 1975).

Sulfates can be fixed in soil by organisms that use them for cellular synthesis, or absorbed by plants and eventually animals. They can also be reduced to sulfides. Sulfate reduction is the most important cause of the emissions of biogenic sulfur compounds into the atmosphere. One type of sulfate reduction is the assimilatory pathway, in which organisms reduce sulfate in order to meet their nutritional requirement for sulfur. The formation of volatile sulfur by this process is believed to be limited. A second type of sulfate reduction is the dissimilatory pathway. Sulfates serve as a terminal electron acceptor in anaerobic respiration for bacteria of the genera Desulfovibrio and Desulfotomaculum. As a consequence, large amounts of sulfide accumulate in some soils, the main product being H₂S.

Numerous authors have studied the sulfur cycle in soils: Asami and Takai (1963), Postgate (1969), Trudinger (1969), Katoda and Ishida (1972), Schlegel (1974), Banwart and Bremner (1975, 1976) are some of them. Other works present some global analyses (Dommergues and Mangenot, 1970; Alexander, 1977; Adams et al., 1980).

2.3.2 Influence of the Environment on Biogenic Sulfur Sources

Many factors have a direct influence on the emission of gaseous sulfur compounds from the soils: the S-content and composition of the organic matter; the distribution of bacteria; the type and hydrology of the soils, which determine their pH and Eh; the temperature; and the atmospheric proximity of the production zone of S-gases.

The composition of organic matter influences the nature and quantity of sulfur gases emitted. Emission rates were linked positively to soil organic matter by Farwell et al. (1979). However, there seems to be a threshold of
about 2% organic matter below which sulfur volatilization does not occur. Two conditions are necessary for sulfate reduction: the source of sulfates must be unlimited and the content of electron donors (organic acids or hydrogen) must be sufficient. Decomposing litter could be an important site for volatilization (Haines, 1983).

The hydrous state of the soils determines the oxygen content and the emission of sulfur compounds (Table 2.2). Water-saturated soils promote sulfate reduction through dissimilation. A laboratory study on different types of soils carried out by Farwell et al. (1979) showed that emissions of H₂S and CS₂ greatly increase with water content in swamp soils.

The most important sulfur species emitted to the atmosphere is H₂S. Aneja et al. (1980) found that about 50% to 70% of the total measured sulfur flux in the eastern United States consists of H₂S. Saline marshes are strong emitters compared with other types of soils.

Table 2.2  Sulfur fluxes of different soils in North Carolina, USA (Adams et al., 1979)

<table>
<thead>
<tr>
<th>Soil order</th>
<th>Average S flux (g/m²/year)</th>
<th>n</th>
<th>H₂S</th>
<th>OCS</th>
<th>CH₃SH</th>
<th>DMS</th>
<th>CS₂</th>
<th>DMDS</th>
<th>ΣS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alfisol</td>
<td></td>
<td>9</td>
<td>0.010</td>
<td>0.002</td>
<td>-</td>
<td>0.001</td>
<td>0.002</td>
<td>0.002</td>
<td>0.017</td>
</tr>
<tr>
<td>Inceptisol</td>
<td></td>
<td>19</td>
<td>0.0028</td>
<td>0.0022</td>
<td>-</td>
<td>0.0002</td>
<td>0.0012</td>
<td>0.0014</td>
<td>0.008</td>
</tr>
<tr>
<td>Histosol</td>
<td></td>
<td>11</td>
<td>0.0178</td>
<td>-</td>
<td>-</td>
<td>0.0007</td>
<td>0.0001</td>
<td>0.001</td>
<td>0.019</td>
</tr>
<tr>
<td>Saline swamp</td>
<td></td>
<td>1</td>
<td>0.0194</td>
<td>0.0016</td>
<td>-</td>
<td>0.0069</td>
<td>-</td>
<td>-</td>
<td>0.028</td>
</tr>
<tr>
<td>Saline marsh</td>
<td></td>
<td>7</td>
<td>139.50</td>
<td>6.36</td>
<td>6.56</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>152.40</td>
</tr>
<tr>
<td>Alluvial clay</td>
<td></td>
<td>11</td>
<td>0.0004</td>
<td>0.004</td>
<td>-</td>
<td>0.0001</td>
<td>-</td>
<td>-</td>
<td>0.0002</td>
</tr>
</tbody>
</table>

Important variations of H₂S emissions with different soils have been observed by Delmas et al. (1980a) and Jaeschke et al. (1978). The intensity of the emission was much more important under anaerobic conditions, thus confirming the dominance of dissimilatory sulfate reduction as a biogenic source of sulfur.

Soil temperature influences the rate of microbial transformation of sulfur in soils. Enzyme activity is multiplied by a factor 2 to 3 for every 10°C up to 50°C. Above this threshold, enzymes in solution are rapidly inactivated (Katoda and Ishida, 1972). This dependence has been observed by several authors (Hill et al., 1978; Jaeschke et al., 1978). A linear relationship with the mean ambient temperature appears, with a correlation coefficient of
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Figure 2.2 Regression of mean ambient temperature by East-West Sure Grid tiers versus sulfur fluxes (from Adams et al., 1980). Copyright 1980, Electric Power Research Institute (EPRI) report EA-1516, Biogenic Sulfur Emissions in the SURE Region. Reprinted with permission.

0.85, from 158 S-flux measurements performed in the eastern United States (Adams et al., 1980) (Figure 2.2).

Gaseous sulfur compounds are emitted into the atmosphere if the production zone is near the surface. In an oxygen zone, sulfides can be oxidized into sulfates by bacteria such as *Beggiatoa* and *Thiorix*. In this environment, gaseous sulfides cannot reach the atmosphere, which is why hydromorphic soils such as flooded forest soils, swamps, and paddy fields are important sources. This is not the case for lakes and lagoons except near the shores or under eutrophication conditions. The sulfides produced in the sediment layer are oxidized before reaching the surface, as exhibited in a lake of the Amazon basin by Brinkmann and Santos (1974) (Figure 2.3). These results were confirmed recently by Staubes et al. (1986).

It has been believed for years that H$_2$S formed in anaerobic sites in cultivated soils could not escape oxidation by Fe$^{3+}$ ions, but this assertion was disproved recently (Delmas et al., 1980a). From a general point of view, any type of soil can be a source of reduced sulfur compounds either during mineralization of organic matter under aerobic or anaerobic conditions, or during sulfate reduction. This last source is probably the most important, especially under anaerobic conditions.
2.4 BIOGENIC SOURCES

Despite its probable importance, this source is not well known. Detailed studies, such as those carried out by Adams et al. (1980) and Aneja et al. (1979a, b) in midlatitude zones in the USA, have not been undertaken in the tropics. A study of H$_2$S emissions from the humid tropical forests of the Ivory Coast was conducted by Delmas et al. (1980a) and Delmas and Servant (1983). The flux was measured using two methods. The first was by accumulating H$_2$S at night under a forest canopy. The second method involved H$_2$S vertical profile measurements using aircraft at different distances from the coast, in the direction of the horizontal advection of air masses in the monsoon layer (< 2,000 meters alt.). The first method yielded a 12.5 $\mu$g S/m$^2$/hour flux for dry soil and 300 $\mu$g S/m$^2$/hour for partly flooded soil. The second method yielded a similar value: 40 $\mu$g S/m$^2$/hour above swamps and flooded forests (Delmas et al., 1980a).

Soil emissions from forested zones were also calculated using an atmospheric circulation model in which the planetary boundary layer (the monsoon layer in that case) was considered to be a box at equilibrium. The concentration of sulfur in particulate matter (SO$_4^{2-}$), SO$_2$ and H$_2$S were measured over a one-year period at the entry and exit of the box. The results obtained for the exchanges of sulfur compounds allowed the calculation of soil emissions (Figure 2.4).

Sulfur emissions showed pronounced seasonal changes. Values were low during the dry season, 55 $\mu$g S/m$^2$/hour; and high during the wet season, 270 $\mu$g S/m$^2$/hour. The annual mean value was 170 $\mu$g S/m$^2$/hour or 1.5 g
S/m²/year. These values have the same order of magnitude as those deducted from measurements and are in accordance with the relationship between S-flux and latitude, increasing toward the equator. Adams et al. (1980) predict an annual average H₂S flux ranging from 0.5 to 1.0 g S/m²/year near the equator; the total sulfur flux might be as high as 2.3 g S/m²/year at the equator.

The above approach to estimating fluxes accounts for emissions from different types of soils and shows seasonal variations in intensity of the source. However, this determination is not precise due to uncertainties regarding chemical and meteorological parameters, and all S-compounds were not taken into account. The flux of organic sulfides is probably low: during the dry season, (CH₃)₂ SH + C₂H₅ SH emissions reach only 1 to 70 × 10⁻⁴ g S/m²/year in the La Selva rainforest in Costa Rica (Haines et al., 1984), about 20 × 10⁻⁴ the average value calculated for the Ivory Coast.

In a forest at equilibrium, external inputs and outputs of sulfur must
be equal. Outputs are the sum of emissions into the atmosphere from litter, soils, and river run-off. In the tropical rainforests of Costa Rica and Venezuela, net exchanges of sulfur are 1.17 and 0.4 g S/m²/year respectively (Haines, 1983). If river run-off is taken as negligible, these values represent maximum emissions of gaseous sulfur to the atmosphere. They are comparable to the mean H₂S fluxes measured in the Ivory Coast, and correspond to a global emission for the tropical forests of 21 and 7 Tg S/year compared to 27 Tg S/year from the data obtained in the Ivory Coast study. Clearly, any extrapolation from available data presents large uncertainties. Further research is needed in order to evaluate this source accurately. Such studies present difficulties because source intensities vary with the nature of the soils and with soil water status. For example, data obtained for water-saturated soils are an order of magnitude greater than those for dry soils.

A detailed study of all sulfur compounds emitted is needed. Studying fluxes of COS and CS₂ in relation to the global S-cycle would be interesting even though these gases are less important on a regional scale due to their longer residence time in the atmosphere.

2.4.1 Biomass Burning

Biomass burning is an important source of aerosols and gases in tropical areas. Primarily anthropogenic, these burnings occur for three reasons: deforestation for cultivation; clearing associated with shifting agriculture; and annual bushfires, which are traditional in the dry savannas. This phenomenon is particularly important in Africa where 40% to 60% of the savannas located between 5° and 10° N are burned each year (Deschler, 1974). Seiler and Crutzen (1980) (see Table 2.3) estimate the spreading of these fires and the biomass consumed. In their approach the total amount of the biomass burned annually (M) in a biome is:

\[
M = A \times B \times \alpha \times \beta \text{ (gram of dry matter per year)} = \text{g dm/year}
\]

where:

- \( A \) = total land area burned annually (m²/year)
- \( B \) = the average of organic matter per unit area in the individual biome (g dm/m²)
- \( \alpha \) = fraction of the average above-ground biomass relative to the total biomass \( B \)
- \( \beta \) = the burning efficiency of above-ground biomass.

In order to infer the quantities emitted into the atmosphere from biomass burning, the sulfur content of the biomass and the amount of sulfur
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Volatilized during the fires must be determined. Such an estimation is difficult because the S-contents of various plant species in forests and savannas vary, ranging from 0.2 to 2 mg/g (0.02-0.2%). However, the fraction of volatilized sulfur depends on the type of plant and on temperature of the combustion. Two examples are given for a savanna in the Ivory Coast (Table 2.4). The fraction of volatilized sulfur is 67% for a *Loudetia* savanna and 35% for an *Andropogon* savanna. Clearly, it is difficult to evaluate accurately the intensity of this source; more data are needed. An estimation of the magnitude of the source can be made by considering the mean biomass burned annually, 3.6 Tg dm/year (Seiler and Crutzen, 1980), with a max-

<table>
<thead>
<tr>
<th>Activity</th>
<th>Burned area (million hectare)</th>
<th>Biomass exposed to fire</th>
<th>Annually burned biomass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burning due to shifting agriculture</td>
<td>21–62 (42)</td>
<td>24–72 (48)</td>
<td>9–25 (17)</td>
</tr>
<tr>
<td>Deforestation due to population increase and colonization</td>
<td>8.5–15.1 (12.0)</td>
<td>16–25 (20.5)</td>
<td>5.5–8.8 (7.2)</td>
</tr>
<tr>
<td>Burning of savanna and bushlands</td>
<td>(600)</td>
<td>12.2–23.8 (18)</td>
<td>4.8–19 (11.9)</td>
</tr>
</tbody>
</table>

Table 2.4  Sulfur emissions during bushfires in two types of savanna in the Ivory Coast (Delmas, 1982)

<table>
<thead>
<tr>
<th></th>
<th><em>Loudetia</em> savanna</th>
<th><em>Andropogon</em> savanna</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total above-ground biomass before the fire (T(dm)/ha)</td>
<td>7</td>
<td>9</td>
</tr>
<tr>
<td>S content in the dry matter (mg/g)</td>
<td>0.29</td>
<td>0.33</td>
</tr>
<tr>
<td>S amount in above-ground biomass before the fire (kg/ha)</td>
<td>2.03</td>
<td>3.0</td>
</tr>
<tr>
<td>Average percentages of sulfur volatilized</td>
<td>67</td>
<td>35</td>
</tr>
<tr>
<td>S fluxes (kg/ha)</td>
<td>1.40</td>
<td>1.05</td>
</tr>
</tbody>
</table>
mum S-content of 0.2% (Bowen, 1969; Shriner and Henderson, 1978) and an S-volatilization efficiency of 50%. This yields a maximum emission of 3.6 Tg S/year. In the intertropical zone as a whole, this source is weaker than the biological source, but it may be significant in some regions. Our estimate is lower than that of Andreae (1985), which is about 7 Tg S/year, corresponding to an annual biomass burning of 6,800 Tg dry matter. Our calculation concerns only the tropics and does not include the use of wood as fuel, which represents about 1,000 Tg dry matter/year.

Compounds formed during combustion have not been analyzed. Measurements in the Ivory Coast showed that SO$_2$ was dominant in the smoke plume and that H$_2$S was also formed (Delmas, 1982). Very hot air displaced by the wind before the flames causes the vegetation to parch and become partially pyrolized before burning. This is likely the cause of the emission of reduced gases such as H$_2$S. Emissions of COS have also been observed by Crutzen et al. (1979). The ratio of COS/CO$_2$ concentrations = 6 x 10$^{-6}$ obtained from aircraft measurements corresponds to a global source equal to 4 x 10$^{10}$ g (COS-S)/year, or one-tenth of the total emission of COS into the atmosphere (Crutzen et al., 1985).

### 2.4.2 Marine Sources

Oceans are the major natural source of sulfur in the troposphere, with SO$_4^{2-}$ a ubiquitous trace species in the oceanic atmosphere. A large fraction of this SO$_4^{2-}$ is derived from sea-spray and is not discussed further here. An extensive survey on sulfate concentrations from nonmarine origins over 25 regions of the world ocean concluded that the average S-concentration is about 0.7 µg/m$^3$. This concentration differs across regions, e.g. by a factor of 30 to 50 for polluted regions of the Mediterranean Sea and the pristine areas of the southern oceans (Savoie, 1984). In tropical areas, the highest concentrations were recorded to the west of the continents: 1.6 µg/m$^3$ in the Gulf of Guinea, 5 µg/m$^3$ west of South America, 1.1 µg/m$^3$ in the North Atlantic Ocean, 2 µg/m$^3$ in the Gulf of Mexico, and 1.5 µg/m$^3$ in the Bay of Bengal. In the intertropical oceans, values of 0.3 to 0.6 µg/m$^3$ were observed. Higher concentrations are often linked to terrigenous dusts transported from the deserts of Arabia, India, Pakistan, and Sahara. Near the west coast of South America a high sulfate concentration results from industrial activity in Chile. Near the northwest coast of South America the high sulfate concentration can be attributed to either pollution or a natural source.

The SO$_2$ concentration in air is not necessarily linearly correlated with oceanic productivity (Nguyen et al., 1978; Bonsang, 1980; Andreae et al., 1983; Cline and Bates, 1983). However, such a relation between the final products of S-compounds and the emission of DMS has been demonstrated.
2.4.3 Soil-derived Sources

Sulfur derived from soils is associated with wind erosion. At high wind speeds, dusts are suspended in the atmosphere, and the finest aerosol particles are carried by air masses over thousands of kilometers during dry haze episodes (Prospero and Bonatti, 1969; Bertrand et al., 1974; Rahn, 1981; Duce et al., 1980; Bravo et al., 1981; Darzi and Winchester, 1982; Uematsu et al., 1983; Parrington et al., 1983; Ryaboshapko, 1983). In Africa, this source represents 15% of the atmospheric SO$_4^{2-}$ in the equatorial zone (Delmas et al., 1978; Delmas and Servant, 1983). This value was estimated from chemical criteria and explained by the presence of gypsum in the zones where the dry haze originates.

2.4.4 Other Sources

Volcanic emissions and man-made pollution are other potential sources of sulfur compounds in intertropical zones. Active volcanoes in tropical zones are numerous, but most of the sulfur emitted during eruptions, about 2 Tg S/year globally (Müller, 1984a), probably enters the stratosphere directly. Estimations from Naughton et al. (1975) and Cadle (1980) are higher, at 23.5 and 20–30 Tg S/year. If we consider the amount of sulfur in the oceans, sedimentary rocks, and evaporites, these values are too high on a long-term basis. Volcanic emissions into the troposphere during noneruptive periods appear to dominate and a global release rate of 12 Tg S/year is probably a higher limit for the volcanic flux. This source may be important on the regional scale during volcanic episodes.

The present anthropogenic sulfur emissions over the world are estimated as 104 Tg S/year (Cullis and Hirschler, 1980) and 75 Tg S/year (Müller, 1984b). The difference between estimates is due to the higher emission factors for coal and lignite used in Cullis and Hirschler’s work. Global SO$_2$ emissions are expected to increase between 1975 and 2000, mainly due to increased coal combustion. In 1979, man-made sulfur emissions are estimated to have been 1.1, 2.1, and 0.35 Tg S/year for Africa, Central and South America, and Oceania, respectively. The total emissions of these regions represent 8% of the world emissions (Varhelyi, 1985).

2.4.5 Conclusions

The major component of the atmospheric sulfur cycle in the temperate latitudes is anthropogenic. In inter-tropical regions, however, the main terrestrial source is natural biomass decomposition. Recent studies indicate that
most soils and litter decomposition can be major sources of sulfur compounds for the atmosphere, with the greatest emissions occurring under anaerobic conditions. In humid equatorial regions where rains are abundant and anaerobic sites are common, the high temperature and organic content of the soils present favorable conditions for greater S-emissions. Flooded soils, probably the greatest source, depend on the annual rainfall distribution. The emission of sulfur compounds in savanna soils has not been measured, although one might assume that its value is lower than in humid areas because anaerobic conditions are less common. One important source could be biomass burning, but this is a difficult source to evaluate as it is sporadic and occurs during the dry season.

In some tropical countries, particularly those with high population densities in tropical Asia, anthropogenic emissions might exceed natural ones. In China, very high SO$_2$ concentrations are recorded south of the Yangtze River as a result of coal consumption (Zhao and Sun, 1986).

### 2.5 SULFUR COMPOUNDS IN THE TROPICAL ATMOSPHERE

#### 2.5.1 Concentrations of Sulfur Compounds

The data on concentrations of sulfur compounds are limited. Most measurements concern total S or SO$_4^{2-}$ concentrations in particulate matter (Table 2.5). No measurements of carbon sulfide concentrations are available for the tropical zone.

#### 2.5.2 Concentration of Sulfur Compounds in the Equatorial Atmosphere

Several authors have measured the size spectrum of particulate SO$_4^{2-}$. The results obtained in the Amazon basin by Orsini et al. (1982) are shown in Table 2.6. The SO$_4^{2-}$ particles were collected with a cascade impactor six-stage Battelle Model; the analysis of sulfur was carried out by Pixe (particle induced X-ray emission).

The spectrum obtained differs from that of oceanic and continental atmospheric particles. The maximum mass of SO$_4^{2-}$ corresponds to the submicron particles. Similar results were obtained in the Ivory Coast (Delmas, 1980) and in the Congo (Delmas et al., 1986). The cascade impactor used in the latter study was a six-stage high-volume sampler (Weather Measure model), and the analysis was carried out by atomic absorption. About 70% of the SO$_4^{2-}$ mass corresponded to the submicronic fraction. On the other hand, chemical criteria for marine- and soil-derived origins have shown that 70% of the mass of SO$_4^{2-}$ in particulate matter corresponds to airborne sulfates in the Ivory Coast (Delmas et al., 1978).
Table 2.5  Atmospheric concentrations of sulfur compounds in the intertropical zone (average values in parentheses)

<table>
<thead>
<tr>
<th>References</th>
<th>Location</th>
<th>Concentration (ng/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>S particulate</td>
</tr>
<tr>
<td>Lawson and Winchester, 1979</td>
<td>Bolivia, mountain</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>Manaus, Brazil</td>
<td>260</td>
</tr>
<tr>
<td></td>
<td>Salvador, Brazil</td>
<td></td>
</tr>
<tr>
<td>Orsini et al., 1982</td>
<td>Amazon Basin</td>
<td>215–342</td>
</tr>
<tr>
<td>Lodge et al., 1974</td>
<td>Panama, equatorial forest</td>
<td>850–3,150</td>
</tr>
<tr>
<td>Penkett et al., 1979</td>
<td>Sudan</td>
<td></td>
</tr>
<tr>
<td>Delmas et al., 1978 and</td>
<td>Ivory Coast, equatorial forest</td>
<td>500–2,000 (650)</td>
</tr>
</tbody>
</table>
This particle-size distribution, mainly in the submicronic range, implies that \( \text{SO}_4^{2-} \) is formed primarily from homogenous gas-phase reactions. If the formation had been the absorption and subsequent reaction of vapor-phase \( \text{H}_2\text{SO}_4 \) on seasalt or soil-derived particles, the \( \text{SO}_4^{2-} \) mass distribution would have been similar to the surface distribution of these particles. In that case, \( \text{SO}_4^{2-} \) would have shown a mean mass diameter of 4 \( \mu \)m.

No \textit{in situ} study on the mechanism of S-oxidation in equatorial regions has been reported, but results were obtained using a budget method (Delmas and Servant, 1983). Above a forested zone in the Ivory Coast, the calculated monthly mean values of the oxidation rate show a variation from 5.3\% to 12.9\%/hour with an annual arithmetic mean of 8.4\%/hour. This value is an order of magnitude higher than those observed at midlatitude rural zones. It was obtained through an indirect budget method, so precision is likely to be low. However, it seems to account for the concentrations of sulfates observed on the continent. A direct measurement of this oxidation rate in Australia (Ayers, 1986) yielded a lower value of 0.25\%/hour, but the photochemical characteristics of the atmosphere in Australia and equatorial Africa may have been different.

Rapid gas-phase oxidation suggests that the equatorial atmosphere presents favorable features, in particular a relatively high concentration of OH-radicals. Between 15 \( \times \) N and 15 \( \times \) S, the photochemical model of Logan \textit{et al.} (1981) gives an OH-concentration of about \( 2 \times 10^6 \) atoms/cm\(^3\) at ground level. Crutzen and Gidel (1983) obtained similar results.


2.6 SINKS OF SULFUR COMPOUNDS IN INERTROPICAL REGIONS

2.6.1 Sinks

Sulfur compounds leave the atmosphere by dry and wet deposition. The elimination of sulfur in an ecosystem also occurs via horizontal advection and flux of matter outside the limits of the ecosystem. Deposition processes depend on the chemical and physical characteristics of the compounds, such as size spectrum for aerosols and solubility for gases. The residence time of a compound in the atmosphere depends on all these parameters.

2.6.1.1 Dry Deposition

Gases or particles are deposited by mechanisms that depend on near-surface concentrations and on the deposition velocities of the elements. During the day, the near-surface concentration is close to the mixing layer value due to atmospheric turbulence. At night, under stable atmospheric conditions, the near-surface concentration decreases. Deposition velocity is independent of concentration but depends on aerodynamic conditions, the size distribution of the particles, and the solubility (or chemical reactivity) of the gases. For the \( \text{SO}_2 \) example, the Henry's coefficient is 1.3 M/atm, but the effective H-coefficient varies from pH 2 to pH 6 (Schwartz, 1984). Deposition of soluble gases on vegetation depends on whether the stomata are open or closed.

Because of pollution, \( \text{SO}_2 \) is the most extensively studied gas in the industrialized countries (Belot et al., 1974; Garland, 1974; Petit et al., 1976; Garland and Branson, 1977; Fowler, 1978; Shreffler, 1978), where deposition speeds have been measured between 0.3 and 3.2 cm/sec, averaging around 1 cm/sec. No similar study has been carried out in the intertropical regions.

The deposition velocity of \( \text{SO}_4^{2-} \) particles is low (<0.1 cm/sec) and does not depend on gravity due to the particles' submicronic diameter. In the continental zones, Cawse (1974) and Müller and Schumann (1970) indicated a minimum in the 0.1-1 \( \mu \text{m} \) range, and measured a deposition velocity of 0.01 cm/sec. Based on past estimates of dry deposition, Galloway (1985) gives values for dry deposition rates of 0.02 and 0.02 g S/m\(^2\)/year for \( \text{SO}_2 \) and excess \( \text{SO}_4^{2-} \) in remote marine areas, and 0.07 and 0.03 g S/m\(^2\)/year in remote continental areas.

2.6.1.2 Wet Deposition

Wet deposition is proportional to the total annual rainfall and concentration of sulfur compounds in the rainwater. The compounds are mainly sulfates and sulfites, which could result from the dissolution and oxidation of \( \text{SO}_2 \)
in the liquid phase or from rainout and washout of particulate \( \text{SO}_4^{2-} \).

In most experiments, the collectors are not closed between rain events, thus the dry and wet deposits are analyzed together. The data obtained by authors at different sites are displayed in Table 2.7. Concentrations vary by a factor 5, the lowest corresponding to the highest rainfall intensity. Delmas, Mathieu, Galloway \textit{et al.} and Lacaux \textit{et al.}, obtained data under good conditions for collection and analysis. In particular, Galloway \textit{et al.} (1982) used collectors that opened and closed before and after the rain, to preclude dry deposition. The analysis was done by an ionic separation followed by conductivity measurement (Dionex apparatus) giving good precision and reproducibility in the sub-ppm concentration range. Lacaux \textit{et al.} (1986) used an automatic sampler and a Dionex apparatus for \( \text{SO}_4^{2-} \) analysis. They found an \( \text{SO}_4^{2-} \) washout ratio (the ratio of concentration of an element or ion in one liter of rainwater to its concentration in one cubic meter of air) of \( 10^3 \). This is compared to \( 3 \times 10^2 \), the geometric mean of the ratios at Samoa, Miami, and Bermuda, which have been used to calculate the \( \text{SO}_4^{2-} \) deposition flux over the world oceans (Andreae and Raemdonck, 1983).

2.6.1.3 Seasonal Variations in Dry and Wet Deposition

The study undertaken in the Ivory Coast by Delmas (1980) on particulate \( \text{SO}_4^{2-} \) and on the main gaseous S-species \( \text{H}_2\text{S} \) and \( \text{SO}_2 \) affords the opportunity to compare the relative importance of dry and wet depositions in a tropical atmosphere. Studied over a one-year period, the seasonal variations are apparent (Figure 2.5).

Dry depositions are calculated from average monthly concentrations of \( \text{SO}_2 \), \( \text{H}_2\text{S} \), and \( \text{SO}_4^{2-} \) measured in a forested zone, with deposition velocities of 1 cm/sec for \( \text{H}_2\text{S} \) and \( \text{SO}_2 \), and 0.1 cm/sec for \( \text{SO}_4^{2-} \). Wet deposition estimates are based on the weighted means of data obtained at 11 stations in this zone. The wet sulfur deposition, representing about two-thirds of the total, is the highest. This coincides with the assessment of sulfur deposition in remote continental areas given by Galloway (1985). Wet deposition modulates seasonal variations, and total deposition is highest during the wet season due to an increased source of biogenic sulfur in the atmosphere, and due to washout.

2.6.1.4 Acid Rainwater and Influence of Sulfur Compounds

In pristine areas without anthropogenic sources of sulfur, the pH of rainwater is thought to be controlled by the carbonate system buffer \( \text{CO}_2/\text{H}_2\text{CO}_3 \) and has a value of 5.6. The natural parts of the atmospheric cycles of sulfur, nitrogen, and carbon introduce strong acids (\( \text{H}_2\text{SO}_4 \), \( \text{HNO}_3 \)) and weak acids (\( \text{HCOOH} \), \( \text{CH}_3\text{COOH} \)) sufficient to lower the pH of natural rainwater by
Table 2.7  Concentrations of $SO_4^{2-}$ in rainwater in the equatorial zone (average values in parentheses)

<table>
<thead>
<tr>
<th>References</th>
<th>Location</th>
<th>Remarks</th>
<th>Concentration (mg($SO_4^{2-}$-S)/liter)</th>
<th>Rainfall (mm/year)</th>
<th>Deposits (g(S)/m²/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Visser, 1961</td>
<td>Kampala</td>
<td></td>
<td>(0.6)</td>
<td></td>
<td>(0.8)</td>
</tr>
<tr>
<td><em>Reported by Granat et al., 1976</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hesse, 1957</td>
<td>Kiyuhu</td>
<td></td>
<td></td>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>Rodhe <em>et al.</em>, 1981</td>
<td>Kenya, Tanzania</td>
<td>Av. 9 locations, 3 years, Monthly samples</td>
<td>0.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Uganda</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eriksson, 1966</td>
<td>Zaire</td>
<td></td>
<td></td>
<td></td>
<td>0.28</td>
</tr>
<tr>
<td>Bromfield, 1974</td>
<td>Nigeria N.</td>
<td>Av. 11 locations, 2 years</td>
<td>0.13</td>
<td>877</td>
<td>0.11</td>
</tr>
<tr>
<td>Mathieu, 1972</td>
<td>Ivory Coast</td>
<td>Av. 1 location, 2 years</td>
<td>(0.26)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Delmas, 1980</td>
<td>Ivory Coast</td>
<td>Av. 11 locations, 1 year</td>
<td>(0.43)</td>
<td>1,604</td>
<td>(0.69)</td>
</tr>
<tr>
<td>Lacaux <em>et al.</em>, (unpublished)</td>
<td>Lamto,</td>
<td>Av. 1 location, 1 year</td>
<td></td>
<td>687</td>
<td>(0.35)</td>
</tr>
<tr>
<td></td>
<td>Ivory Coast</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><em>Reported by Haines, 1983</em></td>
<td>La Selva,</td>
<td>Av. 1 location, 1 year</td>
<td>(0.35)</td>
<td>3,400</td>
<td>1.25</td>
</tr>
<tr>
<td>Johnson <em>et al.</em>, 1979</td>
<td>Costa Rica</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jordan and Murphy, 1982</td>
<td>San Carlos,</td>
<td>Av. 1 location, 1 year</td>
<td>(0.42)</td>
<td>3,500</td>
<td>1.52</td>
</tr>
<tr>
<td></td>
<td>Venezuela</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Galloway <em>et al.</em>, 1982</td>
<td>San Carlos,</td>
<td>Av. 1 location, 6 months</td>
<td>(0.17)</td>
<td>3,9100</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Venezuela</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
about one unit from that value. The impact of sulfur compounds alone might cause pH values to range from 4.5 to 5.6 (Charlson and Rodhe, 1982). At the most central locations of the Antarctic plateau, before industrial pollution and far from the marine influence, ancient ice cores up to 30,000 years old were found to be acidic at pH 5.2 to 5.5 (Legrand, 1980; Delmas et al., 1980b, 1982). Sources of base-line acidity are probably the biogenic activity of the Antarctic Ocean and atmospheric HNO₃. The volcanic contribution to the total H₂SO₄ fallout on the Antarctic plateau is estimated to be 30% for the last 100 years (Delmas et al., 1982).

Over the oceans, where pollution is low (the estimated total deposition of SO₄²⁻ of nonmarine origin equals the estimated rate of DMS emission), the pH values are 5.4 over the temperate southern Atlantic zones, 5.0 over the northern Atlantic tradewind zones and 5.3 over the north Pacific (Savoie, 1984). Over the continents, pH values may decrease partly due to the S-emission. However, low values are observed over the equatorial belt despite high ammonia (NH₃) emissions and in contrast with the predictions by Daw-
son (1977) based on the acidity of tropical soils. These NH$_3$ emissions have been inferred from the NH$_4^+$ concentration in air and rainwater in the Ivory Coast (Servant et al., 1984). As NH$_3$ is a base, it neutralizes the acidity of H$_2$SO$_4$.

Examples of acidification of natural rainwater are given by the data obtained in the Global Precipitation Chemistry Project (GPCP) (Galloway et al., 1982). Precipitation from five remote areas of the world is analyzed. Two areas are located in the intertropical zone; Katherine, Australia, and St Carlos de Rio Negro in the Venezuelan tropical rainforest (Table 2.8). The average pH values at the different stations were near 4.8. At times the pH was quite acidic, below 4.5, which is the value Charlson and Rodhe (1982) quote as the lowest expected natural value. One interesting new result of this study is the evidence of a fairly constant background of strong mineral acidity with most of the pH-variability associated with organic acids. This finding was suggested by a preliminary analysis of weak organic acids, but requires confirmation at other sites to ensure its generality. This study shows that air and rainwater acidities are linked to the cycle of major elements in the atmosphere of which the sulfur cycle is one. Such a result seems to be confirmed by our recent measurements in the Congo where we have determined the chemical composition of aerosols in a tropical rainforest site (Dimonika, 400 km west of Brazzaville). Organic carbon represents about 70% to 80% of the total mass of particles (Table 2.9). The size spectrum of particulate organic carbon (POC) corresponds to submicron particles (diameter $\leq 1 \mu m$), suggesting a gas-particle conversion from gaseous organic compounds and probably the presence of an acidic component.

In the Ivory Coast, at a site on the border of the savanna forest 200 km from the coast, rainwater was collected for the BAPMON Project. The sampler was opened during rain only, and the water was frozen immediately and sent.

<table>
<thead>
<tr>
<th></th>
<th>St. Georges, Bermuda</th>
<th>Poker Flat, Alaska</th>
<th>Amsterdam Island</th>
<th>Katherine, Australia</th>
<th>St. Carlos, Venezuela</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4.8</td>
<td>4.9</td>
<td>4.7</td>
<td>4.7</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>(4.1-6.0)</td>
<td>(4.7-5.4)</td>
<td>(4.0-5.5)</td>
<td>(4.0-5.4)</td>
<td>(4.0-5.4)</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>$\leq 111$</td>
<td>$\leq 65$</td>
<td>$\leq 73$</td>
<td>$\leq 33$</td>
<td>$\leq 18$</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>$\leq 35$</td>
<td>$\leq 17$</td>
<td>$\leq 14$</td>
<td>$\leq 26$</td>
<td>$\leq 17$</td>
</tr>
<tr>
<td>HX*</td>
<td>$&gt;0$</td>
<td>$&gt;18$</td>
<td>$&gt;13$</td>
<td>$&gt;41$</td>
<td>$&gt;65$</td>
</tr>
</tbody>
</table>

HX* could be HCl, organic acids or H$_3$PO$_4$; the authors believe it was an organic acid.
Table 2.9 Chemical composition of the atmospheric aerosol in a tropical forest site, Dimonika in the Congo (Delmas et al., 1986)

<table>
<thead>
<tr>
<th>Dimonika, Congo</th>
<th>Concentration (ng/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>POC</td>
</tr>
<tr>
<td>End of rainy season</td>
<td>6,850</td>
</tr>
<tr>
<td>End of dry season</td>
<td>7,000</td>
</tr>
</tbody>
</table>

to French laboratories. The pH, conductivity, and concentrations of SO₄²⁻, NO₃⁻, PO₄³⁻, Cl⁻, NH₄⁺ (by ion chromatography) and of Ca²⁺, Mg²⁺, K⁺, Na⁺, Fe³⁺ (by atomic absorption) were measured.

From May 1983 to May 1984, 97 events were recorded with pH values between 4.3 and 6.2 (Figure 2.6). About 19% of the rain events have a pH < 5.0, 46% a pH between ≥ 5.0 and < 5.6, and 35% a pH ≥ 5.6. The more acidic events represent 10% of the total rainfall. In the ionic balance, sulfates and nitrates account for about 70% of the free acidity of rainwater. The remaining 30% might come from organic acids, such as formic acid, the result of isoprene oxidation by OH radicals leading to the formation of formaldehyde. The pH shows slight seasonal variations: values are higher during the dry season when soil-derived particles bring alkaline material from sahelian zones (Lacaux et al., 1986).

Figure 2.6 Histogram of the pH of precipitation collected at the Bapmon site of Lamto, Ivory Coast (from Lacaux et al., 1986)
2.6.1.5 Transport—Influence of Equatorial Regions on the Global Atmospheric Sulfur Cycle

The horizontal transport of trace compounds by air masses depends on their atmospheric residence time. In the continental zones with high precipitation and humidity, the oxidation of S-gases, with the exceptions of CS\textsubscript{2} and COS, is rapid and their residence time is probably less than one day. In these zones, the major source of sulfur is biomass decomposition and most airborne sulfates stay in the planetary boundary layer. This layer presents very efficient rainout with rainfall between 1,500 mm/year and 2,000 mm/year.

In the Ivory Coast, the residence time of aerosols in the atmosphere is estimated at several hours in the rainy season and about two days in the dry season. Under such conditions, transport of the sulfur compounds will be limited mainly to a few hundred kilometers, again with the exceptions of CS\textsubscript{2} and COS. Most of the sulfur emitted is recycled locally or in nearby ecosystems, such as the savanna. On the other hand, bushfires occur during the dry season, and particles formed in the plumes by gas-particle conversion are mostly in the submicronic range. Their residence time in the atmosphere likely approaches two or three weeks, the value usually given for the free troposphere. These particles can be carried away by air masses and dispersed over regions far away from the generating zones. They may, for example, supply the oceanic atmosphere with SO\textsubscript{2}\textsuperscript{−} from nonmarine sources.

In the equatorial regions, a vertical transport of sulfur compounds into the stratosphere is conceivable. These regions are located at latitudes where the tropospheric air enters the stratosphere through the ascending branches of the Hadley cells. Most of the sulfates of the stratospheric layer appear to originate in the COS photolysis over a 20 km altitude during periods with low volcanic activity (Crutzen and Schmaitzl, 1983; Servant, 1986).

2.7 CONCLUSIONS

Attempting to estimate the sulfur budget over the intertropical regions is difficult due to limited and often unreliable atmospheric chemistry data for these regions. According to current knowledge, the sulfur cycle in the tropics still appears to be basically natural. This assertion does not mean that anthropogenic pollution in tropical regions is always negligible, but rather that the background of sulfur in the tropical atmosphere is natural. In the industrialized countries of the Northern Hemisphere, the background of sulfur is anthropogenic. However, man-made emissions may already exceed natural emissions in tropical countries with high population densities and these are expected to increase in the future.

The natural part of the sulfur cycle in the tropics presents some typical features: reaction speeds in the atmosphere and pedosphere are very
The Atmospheric Sulfur Cycle

fast; the main source of sulfur compounds is the biodegradation of organic matter in humid zones; and the turnover of the cycle is dependent on natural and climatic conditions on a regional scale. Rapid degradation of litter due to luxuriant micro-fauna, fungal, and bacterial activity favored by constant high temperatures and soil humidity, and the presence of numerous hydromorphic zones favorable to S-emissions in relation with high rainfall affect source intensity. Features of the tropical sulfur cycle also influence the atmospheric oxidation of sulfur compounds and the recycling of these compounds through wet deposition associated with high rainfall. With a nearly constant year-round air temperature, the atmospheric fraction of the sulfur cycle is modulated by the annual rainfall distribution for both emissions and depositions.

One difficulty in studying the sulfur cycle over tropical regions is the regional variation in climatic conditions. For example, during monsoons the ocean could have a great impact in some regions. In addition, the sulfur cycle should not be studied alone: atmospheric oxidation rates for sulfur are influenced by the nitrogen, carbon cycles through their impact on the concentrations of the hydroxyl radical. The acidification of air and rainwater is caused by sulfur compounds. In the tropics, the pedosphere seems to be a natural source of ammonia, which partly counterbalances the acidifying influence of sulfur compounds. This effect needs further study. Nevertheless, with low anthropogenic emissions, the pH of rainwater can be reduced to below 4.5. One reason could be the presence of organic acids, as is probable in the forested zone, with the atmospheric oxidation of the gaseous organic compounds emitted by the biosphere.

Despite the great intensity of sulfur sources in intertropical regions, they exert only a small influence on the global sulfur cycle. Most of the compounds emitted are recycled locally and contribute to the stability of the primary ecosystems. One exception is carbonyl sulfide (photolized in the stratosphere), which could be emitted in the forested zones where conditions are favorable. This compound might be the source of the sulfate layer in the stratosphere during volcanic ‘quiescent’ periods.

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tions and characteristics from South American Continent. Science, 205, 1267-1269.


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