CHAPTER 4

The Global Biogeochemical Sulphur Cycle*

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ABSTRACT

The major sulphur fluxes of both natural and anthropogenic origin have been assessed by generalization of the results of our studies and data available in the literature. Annually about 120 Tg S are extracted by man from the lithosphere in fossil fuels and sulphur-containing raw materials for the chemical industry. Of this amount 70 Tg S are emitted to the atmosphere with the products of fuel combustion. About half of the remaining 50 Tg S directly enters rivers with sewage and residual waters, and another part is applied with fertilizers to agricultural land. Parallel with anthropogenic sulphur, volcanic gases contribute markedly to the atmospheric sulphur cycle over continents where, according to our data, the sulphur flux amounts to 29 Tg yr\(^{-1}\). The major transfer of sulphur from continents to the ocean is brought about by river runoff with an annual sulphur load of 224 Tg in which the sulphur of anthropogenic pollution accounts for 109 Tg. Tremendous amounts of sulphur are involved in processes of internal turnover between the oceanic atmosphere and its waters. The total flux of various sulphur forms (organic, sulphate, and pyrite) from oceanic water to sediments and further to the lithosphere amounts to 130 Tg yr\(^{-1}\); thus, our estimates point to the fact that the anthropogenic sulphur fluxes to the atmosphere and hydrosphere have reached a level comparable with that of natural fluxes. The analysis of prospects for future uses of various fossil fuels and fertilizers suggests that by the end of this century the anthropogenic sulphur fluxes will increase notably in all regions of the world.

The present report is a preliminary account of the work of Soviet scientists on preparing the SCOPE report as part of project 1.3, 'The global biogeochemical sulphur cycle'. The resolution on conducting this work was adopted at the Paris meeting of the SCOPE Executive Committee in May 1977 and supported by the Open Session of the SCOPE Executive Committee in London (October 1977).

*The work on this project was carried out with the assistance of Prof. V. A. Grinenko and Drs. A. A. Migdisov (Institute of Geochemistry and Analytical Chemistry), A. Yu. Lein (Institute of Biochemistry and Physiology of Microorganisms), A. G. Ryaboshapko (Institute of Applied Geophysics), I. I. Volkov and A. G. Rozanov (Institute of Oceanology), and A. L. Rabinovich (Hydrochemistry Institute).
At the time our work started, several surveys had already been published assessing the content of sulphur compounds in the atmosphere, hydrosphere, and lithosphere, and considering magnitudes of some sulphur fluxes (Eriksson, 1963; Friend, 1973; Kellogg et al., 1972; Robinson and Robbins, 1970; Granat et al., 1976). Particular attention was paid to the sulphur cycle in the atmosphere; the remaining fluxes were considered only to balance the atmospheric cycle (see Table 4.1). Therefore, many of the fluxes were calculated arithmetically, from values obtained by analysis of the processes occurring in the atmosphere. Because of the relatively numerous and informative data on the atmospheric processes as compared to the less investigated processes occurring in the lithosphere and hydrosphere, such an
approach is not only reasonable but also the only one possible. However, this approach leads to considerable variations in estimates of the other biogeochemical processes of the sulphur cycle, as can be seen clearly from the data of Table 4.1.

If we consider that the estimate of the atmospheric sulphur cycle is based on rather limited data with a number of a priori assumptions, there arises a natural desire, or rather a vital necessity, to find an independent approach to the estimation of the separate fluxes which together constitute the entire global biogeochemical sulphur cycle.

Our first task was to compile the primary information on the content of different sulphur forms in separate reservoirs and geospheres and to estimate the magnitudes of each flux, where possible, by different methods. These several approaches were based on the analytical geochemical data of the sulphur compounds and on the in situ experimental studies which constitute the basis of dynamic biogeochemistry.

In recent years the ever-growing interest in global cycles is explained not only by our rapidly increasing scientific knowledge in this field but also by the eagerness of the scientists to investigate the quantitative and global processes involved in the cycles of major elements. Such interest is stimulated by fears that the scope of industrial and agricultural activity of man may have an unpredictable impact on the environment not only in the industrialized regions of the earth but also on a global scale.

It is noteworthy that the possible consequences of global pollution of the environment by sulphur compounds have not attracted as much attention as, for example, the investigations of atmospheric pollution by anthropogenic CO₂. Both scientific and popular literature widely discuss the possible climatic and ecological impacts of CO₂ accumulation in the atmosphere. But pollution of the atmosphere and hydrosphere by such chemically active compounds as hydrogen sulphide and sulphur oxides presents even now a real problem for vast regions of industrialized countries. Many ecological aspects of this problem have been treated in detail by Nriagu (1978b, 1978c).

For example, the Scandinavian countries and some other industrialized countries of Europe and North America are now facing a problem of pollution of river and lake waters and soil by fallout of sulphuric acid.

It is fairly simple to estimate the total anthropogenic sulphur flux on a regional and global scale. For this purpose it is sufficient to use information on the amount of the different kinds of sulphur-containing raw materials consumed by different branches of industry and agriculture.

Such data, particularly the anthropogenic sulphur flux to the atmosphere, are available in many published studies (see Table 4.1). The variation in the estimates is more conditioned by the use of data from different years than by the methods of approach of the various authors. In other words, these differences reflect an objective increase in consumption rate of sulphurous raw materials and, primarily, of fossil fuel over the last two decades.
The quantitative estimate of different natural processes involved in the global sulphur cycle appears much more complicated. For many of these estimates there is not only a lack of factual material, but also an absence of methodical approach to the estimate. Therefore, we sought, where possible, not only to indicate the natural and anthropogenic contributions to the sulphur fluxes separately, but also paid particular attention to the natural processes.

Finally, one more feature of our work was an attempt to estimate the fluxes of some other elements involved with the biogeochemistry of the sulphur compounds. As seen from Figure 4.1 all of the main reactions of the sulphur cycle involving living organisms are closely related to the carbon cycle.

The amount of carbon involved in the fluxes of the sulphur cycle through biogenic processes varies depending on the type of organisms undertaking the metabolism of the sulphur compounds. In the processes of bacterial chemosynthesis, which are characterized by low amounts of energy utilized for the CO$_2$ assimilation, only relatively small amounts of carbon are transformed into organic matter.

In anaerobic, bacterial photo-assimilation of CO$_2$ where sulphur compounds are used as electron donors, the amounts of oxidized sulphur and assimilated carbon are comparable. In anaerobic sulphate-reduction, 24 g of organic carbon are mineralized for each 32 g of reduced sulphate sulphur. Thus, in ecosystems with an advanced development of photoautotrophic and sulphate-reducing bacteria both groups of microorganisms transform significant amounts of carbon compounds and, consequently, these organisms should be considered not only as participants in the sulphur cycle but as active biogeochemical agents of the carbon cycle.

The extremely important geochemical role of plant photosynthesis in both carbon and sulphur cycles is evident [see Figure 4.1 (VIII) and chapter 6, this volume], although sulphur is not reduced in photosynthesis and sulphur-organic compounds are formed in secondary metabolic processes.

The role of key reactions in the sulphur cycle on the geochemistry of different metals is important and diverse. Hydrogen sulphide released in sulphate reduction plays a principal role in the immobilization of metals as sulphides, most of which are insoluble in water. On the other hand, sulphuric acid and dissolved metals are formed in the weathered zone by biological and chemical oxidation of metal sulphides and elemental sulphur. During intensive weathering by acid sulphate, e.g. in volcanic sulphur-sulphide deposits, sulphuric acid decomposes not only the ores but also the volcanic rocks (Lein and Ivanov, 1970; Ivanov, 1971). As a result the sulphate solutions are enriched in Al$^{3+}$, Fe$^{2+}$, Fe$^{3+}$, Ti$^{2+}$ and even in silicic acid.

The great importance of many reactions of the sulphur cycle for the turnover of oxygen is indisputable. In many aquatic reservoirs much of the dissolved oxygen is used to oxidise hydrogen sulphide and elemental sulphur, and these reactions influence significantly the oxygen cycle and overall geochemistry in reservoirs (Kuznetsov, 1970).

Thus, our attention has been focused on the less investigated problems of the global sulphur cycle: the direct estimate of fluxes, the separate estimate of natural
Figure 4.1 Relationship between general biological processes of the sulphur cycle and some reactions of the carbon cycle.

Chemooautotrophic bacteria

\[2H_2S + O_2 = 2S^0 + 2H_2O\] (I)
\[H_2S + 2O_2 = SO_4^{2-} + 2H^+\] (II)
\[2S^0 + 3O_2 + 2H_2O\]
\[= 2SO_4^{2-} + 2H^+\] (III)

Photoautotrophic bacteria

\[2H_2S + CO_2\]
\[= 2S^0 + (CH_2O) + H_2O\] (IV)
\[H_2S + 2CO_2 + H_2O\]
\[= SO_4^{2-} + (CH_2O) + 2H^+\] (V)
\[S^0 + 2CO_2 + 2H_2O\]
\[= SO_4^{2-} + 2(CH_2O) + 2H^+\] (VI)

Sulphate-reducing bacteria

\[SO_4^{2-} + 2\text{C}_{\text{org}} = S^{2-} + 2\text{CO}_2\] (VII)

Photosynthesis (VIII)

Putrefaction (IX)

and anthropogenic components of individual fluxes and the relation of the sulphur cycle to the cycles of other elements.

4.2 GLOBAL SULPHUR CYCLE, ANTHROPOGENIC FLUXES

A summary diagram of the global sulphur cycle with quantitative estimates of the sulphur fluxes is given in Figure 4.2. The numbers near the arrows designate the
Figure 4.2 Fluxes of the global biogeochemical sulphur cycle. The figures following the flux numbers designate the magnitude of a total sulphur flux, while those in parentheses show anthropogenic contributions.

Symbols: $P_1$—sulphur flux from the lithosphere due to all kinds of mining; $P_2$—sulphur flux to the soil with fertilizers; $P_3$—sulphur flux with industrial sewage waters; $P_4$—flux of anthropogenic sulphur to the atmosphere; $P_5$—sulphur flux from water erosion processes; $P_6$—flux of biogenic sulphur; $P_7$—flux of volcanic sulphur; $P_8$—sulphur of dust emission; $P_9$—sulphur flux to land with atmospheric precipitation; $P_{10}$—sulphur flux with river runoff; $P_{11}$—anthropogenic and natural sulphur flux from continents to ocean; $P_{12}$—flux of biogenic $\text{H}_2\text{S}$ from coastal shallow sediments; $P_{13}$—flux of marine sulphur with the sea-spray; $P_{14}$—flux of marine sulphur to continents; $P_{15}$—sulphur flux from the oceanic atmosphere to ocean; $P_{16}$—emission of reduced sulphur from the oceanic surface; $P_{17}$—sulphur in biomass of marine plants; $P_{18}$—mineralized sulphur of dead marine plants and other organisms; $P_{19}$—flux of organic sulphur to the sea bottom; $P_{20}$—organic sulphur oxidized to sulphate and returned to sea water; $P_{21}$—organic sulphur buried in marine sediments; $P_{22}$—sulphate sulphur buried in marine sediments; $P_{23}$—reduced sulphur buried in marine sediments.

total sulphur flux in Tg S yr$^{-1}$ for all compounds. The contributions from anthropogenic activities are indicated by numbers in parentheses. So the flux $P_1$ is the sum value of sulphur extraction from all kinds of mining on the globe. The main part of this flux (about 70 Tg S yr$^{-1}$) is from the fossil fuel and polymetallic sulphide ores. The combustion of fuel and metal smelting from ores are accompanied by an intensive emission of sulphur oxides to the atmosphere (flux $P_4$).

We consider that all sulphur of the flux $P_4$ enters the continental atmosphere and mixes therein with other sulphur forms from the natural sources (see fluxes $P_6$, $P_7$, $P_8$, $P_{14}$). Most of the sulphur of the continental atmosphere returns as dry and wet deposition on to the continental surface (flux $P_9$), and a smaller part enters the oceanic atmosphere (flux $P_{11}$).
Two other anthropogenic fluxes—P$_2$ and P$_3$—are the final by-product of processing the sulphurous raw materials in different branches of industry. The sulphurous raw materials (some 50 Tg yr$^{-1}$) are supplied by the mining industry in the form of pyrites, elemental sulphur, or sulphur from gas deposits (Nriagu, 1978a).

According to Cote's data (1970) cited in the work of Nriagu (1978a) about half of the sulphur extracted in the world in 1970 was used for production of fertilizers and (see Figure 4.3), consequently, brought with them into the soil (flux P$_2$). Then this sulphur appeared in the water draining from the soil and joined the river runoff (P$_{10}$). The second half of the sulphur obtained from pyrites, sulphate, and gas deposits is consumed by the chemical industry and finally is discharged with domestic or industrial sewage (flux P$_3$) and also enters the rivers.

Two important fluxes of anthropogenic sulphur through the soil (P$_2$) and sewage (P$_3$) entering the runoff are added with another 60 Tg of anthropogenic sulphur falling on to the land surface with precipitation (see the flux P$_9$). So, currently rivers annually bring about 108 Tg of anthropogenic sulphur to the ocean.

Moreover, 10 Tg of anthropogenic sulphur, as a minimum, is transferred by air flows from the continental atmosphere to the atmosphere over the ocean (flux P$_{11}$). This sulphur also finally enters the ocean waters. Thus, the annual anthropogenic pollution of the ocean by sulphur compounds amounts to 120 Tg S yr$^{-1}$ and exceeds the magnitude of natural river runoff of sulphur compounds (see section 3).
Table 4.2 Average Content and Weight Ratio of Sulphates/Chlorides in the River Waters of the Various Basins of the USSR (according to Alyokin and Brajnikova, 1964)

<table>
<thead>
<tr>
<th>Basin</th>
<th>Content (mg litre⁻¹)</th>
<th>SO₄²⁻</th>
<th>Cl⁻</th>
<th>SO₄²⁻/Cl⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Siberian rivers</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>The Chukotsk, East Siberian,</td>
<td>17.5</td>
<td>17.7</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>Kara and Laptev Seas</td>
<td>8.8</td>
<td>7.3</td>
<td>1.20</td>
<td></td>
</tr>
<tr>
<td>Rivers of the European part of</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>the USSR</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>The Baltic, Barents,</td>
<td>7.0</td>
<td>4.0</td>
<td>1.75</td>
<td></td>
</tr>
<tr>
<td>White, Black, Azov and</td>
<td>14.8</td>
<td>5.0</td>
<td>2.96</td>
<td></td>
</tr>
<tr>
<td>Caspian Seas</td>
<td>41.5</td>
<td>16.5</td>
<td>2.51</td>
<td></td>
</tr>
<tr>
<td></td>
<td>62.1</td>
<td>18.9</td>
<td>3.28</td>
<td></td>
</tr>
</tbody>
</table>

4.3 NATURAL SULPHUR IN RUNOFF

The estimate of the natural sulphur flux by rivers (Figure 4.2, P₁₀) is based on the well-known data of Livingstone (1963) and the results given by Alyokin and Brajnikova (1964) on the ionic runoff of the USSR rivers. Since these data characterize both the runoff from the regions polluted by anthropogenic sulphur and from non-polluted areas, to estimate the natural sulphur flux it was necessary to find an objective index for the low level of water pollution. When analyzing the data relating to the USSR’s rivers (Table 4.2) we noticed that in the runoff of Siberian rivers the weight ratio of sulphates/chlorides was close to unity, whereas for the European rivers of the USSR where industry was more developed in the catchment, the relative sulphate content was much higher.

If we use the same approach for analysing Livingstone’s data for the different continents, in the rivers of Africa, Asia, and South America with relatively low water pollution the ratio of sulphates/chlorides is also close to unity, whereas in the rivers of North America and, particularly, in those of Europe the waters are considerably enriched in sulphate (Table 4.3).

Having assumed that the weight content of sulphates is equal to chlorides in the river waters of all continents and using the recent data about volume of river runoff taken from the monograph ‘World Water Budget and Water Resources of the Earth’ (Korzun et al., 1974), we obtained a value for the yearly runoff of natural sulphur of 104 Tg (Table 4.4).

The separate sulphur fluxes of the runoff both natural and anthropogenic are shown in Figure 4.4. We would only draw attention to the grand total: 224 Tg S yr⁻¹, of which 109 Tg is anthropogenic sulphur.
Table 4.3 Average Content and Weight Ratio of Sulphates/Chlorides in River Waters of Various Continents (according to Livingstone, 1963)

<table>
<thead>
<tr>
<th>Continent</th>
<th>SO$_4^{2-}$</th>
<th>Cl$^-$</th>
<th>SO$_4^{2-}$/Cl$^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Europe</td>
<td>24.0</td>
<td>6.9</td>
<td>3.48</td>
</tr>
<tr>
<td>North America</td>
<td>20.0</td>
<td>8.0</td>
<td>2.50</td>
</tr>
<tr>
<td>South America</td>
<td>4.8</td>
<td>4.9</td>
<td>0.98</td>
</tr>
<tr>
<td>Asia</td>
<td>8.4</td>
<td>8.7</td>
<td>0.96</td>
</tr>
<tr>
<td>Africa</td>
<td>13.5</td>
<td>12.1</td>
<td>1.11</td>
</tr>
<tr>
<td>Australia</td>
<td>2.6</td>
<td>10.0</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Table 4.4 Sulphur Flux to the Ocean in the Form of Dissolved Sulphates in River Runoff

<table>
<thead>
<tr>
<th>Continent</th>
<th>Area having runoff to the ocean (millions of km$^2$)$^a$</th>
<th>Annual runoff (thousands of km$^3$)$^a$</th>
<th>Average SO$_4^{2-}$ content (mg litre$^{-1}$)</th>
<th>Annual runoff (Tg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N. America</td>
<td>19.5</td>
<td>7.84</td>
<td>8.0$^b$</td>
<td>62.72</td>
</tr>
<tr>
<td>S. America</td>
<td>16.4</td>
<td>11.70</td>
<td>4.3$^c$</td>
<td>50.31</td>
</tr>
<tr>
<td>Euro-Asia</td>
<td>39.1</td>
<td>16.40</td>
<td>8.4$^d$</td>
<td>137.76</td>
</tr>
<tr>
<td>Africa</td>
<td>20.5</td>
<td>4.11</td>
<td>13.5$^e$</td>
<td>55.48</td>
</tr>
<tr>
<td>Australia and Oceania</td>
<td>4.8</td>
<td>2.37</td>
<td>2.6$^e$</td>
<td>6.16</td>
</tr>
<tr>
<td>Total</td>
<td>100.3</td>
<td>42.42</td>
<td></td>
<td>312.43</td>
</tr>
</tbody>
</table>

$^a$According to Korzun et al., 1974; $^b$Estimated from chlorides (Table 4.3); $^c$According to Gibbs, 1972; $^d$Livingstone’s data for Asia; $^e$Livingstone, 1963.

4.4 ATMOSPHERIC SULPHUR CYCLE

In the upper and right-hand parts of Figure 4.2 are given some principal fluxes of the atmospheric sulphur cycle. We shall consider only the fluxes which differ considerably from those published previously. First of all for flux $P_7$ the emission of volcanic sulphur, our estimate exceeds by a factor of 10 and even more the data published by Kellogg et al. (1972), Friend (1973), and Granat et al. (1976). Such a discrepancy is not spurious. The above-cited authors took into account only the emissions of hydrogen sulphide and sulphur oxides occurring during volcanic eruptions. In contrast, we also considered the quantitative estimates of all year-round
Some Perspectives of the Major Biogeochemical Cycles

Figure 4.4 Scheme showing the major natural and anthropogenic sulphur fluxes contributing to the flux of sulphate sulphur from continents to oceans. Figures by the flux indices denote the amount of sulphur in Tg yr⁻¹. Symbols: R₁–R₇, natural sulphur fluxes: R₁, volcanic sulphur; R₂, biogenic sulphur; R₃, sulphur of dust emission; R₄, sulphur flux from continental atmosphere to oceanic; R₅, marine sulphur flux to continent; R₆, total flux of natural sulphur from atmosphere to continents; R₇, sulphur of water erosion processes; R₈, sulphur transferred to soil drainage waters with fertilizers; R₉, sulphur of sewage waters; R₁₀, sulphur of underground flux; R₁₁, sulphur of sewage waters of mining manufacturing; R₁₂, anthropogenic sulphur flux to atmosphere; R₁₃, atmospheric sulphur precipitating to continents; R₁₄, anthropogenic and natural sulphur transfer from continents to ocean.

I, sulphur output from lithosphere as a result of mining; II, processing of pyrites, native sulphur and sulphur-containing gases in chemical industry; III, fossil fuel combustion and sulphide ore processing.

sulphur emissions from the fumaroles, hot springs, and lakes made by a number of Soviet, American, and Japanese investigators (Berlyand, 1975; Okita and Shimosuzu, 1975; Stoiber and Jepsen, 1973).

To estimate the emission of biologic sulphur to the atmosphere was quite difficult and was complicated by the variation in estimated values from different surveys, that is from 170 Tg S yr⁻¹ (Eriksson, 1960, 1963) to 27 Tg S yr⁻¹ (Granat et al., 1976). Throughout this range the estimates were not obtained from factual data but by difference from the atmospheric sulphur budget.
The factual data from the measurement of biogenic emissions of hydrogen sulphide from the shallow sediments of Limfjord were obtained four years ago by the Danish ecologists Hansen et al. (1978) and Jørgensen (1977, 1978). In parallel with these experiments Jørgensen obtained a vast amount of factual material on the intensity of sulphate reduction in the sediments of Limfjord using radioactive sulphate. By comparing the intensity of sulphate reduction in shallow coastal samples from various parts of the ocean with direct measurements of hydrogen sulphide emission to the atmosphere we managed to estimate this flux (Figure 4.1, P12). The maximum value for this estimate would be 10–12 Tg S yr⁻¹ (Ivanov, 1979). To confirm this value we need, however, to obtain some additional experimental data on the emission of hydrogen sulphide to the atmosphere in various climatic zones.

Two more fluxes of biogenic sulphur (Figure 4.2, Flux P6 from land to atmosphere, 23 Tg; and flux P16 from sea to atmosphere, 7 Tg) were calculated from the actual content of reduced sulphur in the atmosphere. The analysis of results obtained by Brazilian hydrochemists (Brinkmann and Santos, 1974) on the hydrogen sulphide emission from the flood plain of the Amazon River to the atmosphere shows that the sulphur flux from the flood-plain surface of 6000 km² 0.2–0.25 Tg during only four months (Ivanov, 1979). The other estimates of atmospheric sulphur fluxes obtained in our version of the global sulphur cycle approximate more or less to the values cited in the review of Swedish investigators published by SCOPE in 1976 (Granat et al., 1976).

4.5 SULPHUR CYCLE IN THE OCEAN

Previous works on the global sulphur cycle have usually considered only the fluxes connecting oceanic and atmospheric sulphur reservoirs (Figure 4.2, P13, P15, P16). The internal oceanic sulphur cycle, as far as we know, was not assessed quantitatively. However, this cycle includes important processes such as the incorporation of sulphur into biomass of sea plants (Figure 4.2, P17) and the reverse process of mineralization of organic sulphur compounds after aerobic and anaerobic decay of dead plants and other organisms (Figure 4.2, P18).

This part of the global sulphur cycle was evaluated from data on the carbon cycle in the ocean. The calculations were based on results published by Romankevich (1977). From these data the annual primary production of organic matter in the ocean is 36 000 Tg. Let us assume that the sulphur content of phytoplankton biomass is one per cent, then about 360 Tg of sulphate sulphur of sea water is accumulated by living biomass annually (Figure 4.2, P17).

After death the decay of organisms proceeds mainly in oceanic water. Not more than 10 per cent of the organic matter synthesized by phytoplankton is assumed to reach the bottom as particles (Romankevich, 1977). From this analysis, flux P19 is 36 Tg of sulphur per year, and flux P18 reaches 324 Tg per year.

Organic sulphur compounds which arrive at the bottom of the ocean are intensively decayed by microorganisms in the uppermost horizons of the sediments.
Some Perspectives of the Major Biogeochemical Cycles

Table 4.5 Total Sulphate Sulphur Flux from Water to the Oceanic Sediments

<table>
<thead>
<tr>
<th>Forms of sulphate in sediments</th>
<th>Mass of sulphur (Tg yr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In solid phase of clay sediments</td>
<td>11.9</td>
</tr>
<tr>
<td>In silt water</td>
<td>7.1</td>
</tr>
<tr>
<td>In form of barium sulphate (baryte)</td>
<td>4.0</td>
</tr>
<tr>
<td>In biogenic carbonates</td>
<td>1.4</td>
</tr>
</tbody>
</table>

About 90-95 per cent of the organic sulphur is oxidized there to sulphate which returns to the water (flux P₂₀). The rest of the sulphur, about 2 Tg, is buried with silt in the sediments as organic sulphur compounds (flux P₂₁).

Of special interest for estimation of the global sulphur cycle are the data on sulphate and sulphide sulphur fluxes from the water column of the ocean to the sediments (Figure 4.2, fluxes P₂₂ and P₂₃). During the present period of geological history the formation of evaporites occurs less extensively, primarily in some continental basins (Strakhov, 1960). Nevertheless, sulphate sulphur is buried with the sediments in the oceans as skeletons, shells and remains of various organisms and as minerals of terrigenic drifts. In addition some sulphates are buried in dissolved form in the interstitial waters of sediments. The total value of this sulphate flux (P₂₂), calculated by Dr. I. Volkov specially for this report, is 30 Tg per year. The components of this flux are tabulated in Table 4.5.

The world oceanological and geochemical literature contains several important works on the biogeochemical processes of sulphate reduction in seas and oceans, and the distribution of reduced forms of sulphur in modern sediments (Strakhov, 1960, 1972; Berner, 1971; Goldhaber and Kaplan, 1974). However, in none of these papers was the global sulphur cycle evaluated quantitatively. Only a few attempts to calculate the annual formation of hydrogen sulphide have been made, for example in the Black Sea (Datsko, 1959; Skopintsev, 1975).

In both these works the annual production of hydrogen sulphide in the sea was estimated at 2 Tg by Datsko (1959) and 3.2 Tg by Skopintsev (1975). Datsko’s calculations are based on the balance of organic matter in the Black Sea, while Skopintsev used experimental data on the intensity of sulphate reduction published by Sorokin (1962).

These workers considered the processes of hydrogen sulphide formation in the whole basin including the water column and sediments; a possible burial of a part of the hydrogen sulphide and its derivatives in sediments was not taken into account. Therefore from these data it is impossible to evaluate how much sulphur leaves the cycle and is buried in newly formed sediments.

We can use several different techniques for quantitative evaluation of the reduced sulphur flux to bottom sediments.
Table 4.6 Amount of Reduced Sulphur Buried Annually in Sediments of the Baltic Sea (after Lein, 1978)

<table>
<thead>
<tr>
<th>Method of flux calculation</th>
<th>Flux value (Tg yr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Method of absolute masses: area of aleuritopelitic sediments</td>
<td>0.440</td>
</tr>
<tr>
<td>298 X 10⁵ km², rate of dry sediment accumulation 10.87 g cm⁻² per 1000 years, S content/H₂S 1.37% by dry weight of sediment</td>
<td></td>
</tr>
<tr>
<td>2. Method of annual inputs of material to the sea: total 46.10⁶ Tg, S content/H₂S 1.37% by dry weight of sediment</td>
<td>0.580</td>
</tr>
<tr>
<td>3. Balance of sulphur fluxes in the runoff, precipitation from atmosphere, and water exchange through Danish channels</td>
<td>0.702</td>
</tr>
<tr>
<td>Average</td>
<td>0.574</td>
</tr>
</tbody>
</table>

1. Generalization of analytical data on the content of reduced sulphur in modern sediments of various types in different geomorphological areas of some seas and the world ocean (shelf, continental slope, etc.). This value, the rate of sediment formation, and the area of sedimentation allowed us to calculate the rate of annual sulphur flux to the sediments.

2. For more or less separated basins (inland seas, large gulfs of the ocean, etc.) this value may be obtained by multiplying the average sulphur content in reduced sediments by the amount of sedimentary material entering the basin from runoff and other sources.

3. The sulphur budget of some studied seas was calculated on the basis of the sulphate sulphur influx with surface and underground runoff and the amounts of reduced sulphur withdrawn from the sulphur cycle and buried in silts.

4. For a comparative analysis of the rate of sulphate reduction in various geomorphological zones and sediments of the ocean, the results on the sulphate reduction activity with radioactive sulphate were used (Ivanov, 1956, 1968, 1979).

5. To calculate the budget of sulphur compounds, in a number of cases the data on the balances of other components, such as organic carbon and barium were used.

To illustrate, some initial values and final results of the sulphur budget calculated for the Baltic sea are tabulated in Table 4.6. As seen from Table 4.6, the calculations done by these three different methods agree very closely.

It is noteworthy that the total flux of reduced sulphur alone to the sediments makes up 100 Tg per year (Figure 4.2, flux P₂₃). From the sum of fluxes P₂₂ and P₂₃, about 130 Tg of sulphur in oxidized and reduced forms is transferred annually from the ocean to the lithosphere.

Therefore, these data make it possible to close the global biogeochemical sulphur cycle and to show that disregarding anthropogenic activity, the natural sulphur flux
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from the lithosphere, its main reservoir, is compensated by the reverse flux of sulphur compounds to the lithospheric sediments of the ocean.

4.6 QUANTITATIVE EVALUATION OF OTHER CYCLES FROM THE SULPHUR CYCLE

To illustrate possibilities for the quantitative evaluation of fluxes of other elements based on the sulphur fluxes let us consider only one example: the geochemical result of sulphate reduction in bottom sediments of the ocean. It is well known that pyrite is the main form of sulphur buried in sediments (Goldhaber and Kaplan, 1974; Volkov et al., 1972, 1976).

Knowing the value of sulphur flux (Figure 4.2, P23) we may assert that about 85 Tg of iron are preserved annually in sediments as pyrite.

From the same data and based on the sulphate reduction reaction (Figure 4.1, VII) it is possible to calculate the minimum quantity of organic carbon that would be mineralized during microbial sulphate reduction. It should be noted here, however, that the entire amount of H₂S formed during sulphate reduction in sediments would surely not be preserved as water insoluble compounds. Thus, to evaluate the amount of carbon involved in metabolism by sulphate reducing bacteria, it would be more correct to use values for the intensity of sulphate reduction. According to our calculations the annual value for sulphate reduction in the ocean sediments approximates 400 Tg. Therefore about 300 Tg of organic carbon is consumed during this process, i.e. 15-30 per cent of the total carbon deposited annually in the sediments of the ocean (Romankevich, 1977). Surely, such a large value is extremely important in the budget of organic matter or carbon in the ocean, as well as in the global sulphur cycle.

Carbon dioxide formed during mineralization of organic carbon in anaerobic conditions is responsible for the increase in the total alkalinity of interstitial waters in reduced sediments. One half of this carbon dioxide and bicarbonates enters the water, the other half is bound to calcium ions in water in the sediments. This partitioning results in the formation of diagenetic carbonates which have an anomalously light isotopic composition for carbon (Ivanov, 1968; Lein, 1978). As shown in the work of Lein (1978) in the Pacific and Indian oceans, the amount of such diagenetic carbonate in terrigenic sediments may be as high as 60 per cent of the total carbonate minerals found in sediments.

Therefore, a combined and systematic consideration of processes of the sulphur cycle and their connection with other elements gives valuable quantitative information on separate aspects of cycles for a number of elements including carbon, calcium, oxygen, and various metals.

4.7 CHANGES IN THE GLOBAL BIOGEOCHEMICAL SULPHUR CYCLE AS A RESULT OF MAN-MADE CONTRIBUTIONS

We have also studied the literature on possible changes in anthropogenic fluxes of sulphur during decades to come. The curves showing the increased output of raw
Figure 4.5 Production of sulphur from various sources since 1960. The projected worldwide production of sulphur in the coming decade is expected to lie within the hatched area; the historical trend line is shown as the broken curve (after Nriagu, 1978a).

Materials containing sulphur for the chemical industry are given in Figure 4.5. As seen from the figure, the output of elemental, pyrite, and gaseous sulphur and production of sulphuric acid will increase by 30 per cent from 1975 to 1985. Nriagu (1978a) underlines also, that with agricultural development the consumption of sulphur will be greatly increased in developing countries of Africa and South America, where it will be double during 10 years. Thus, sulphur contamination of drainage waters and rivers will increase and will occur in new regions of the globe.

The curves in Figure 4.6 show the increase in atmospheric contamination with various energy sources. During conditions of an energy crisis and ever-rising prices of liquid and gaseous fuels the most realistic prognosis should take into account a substantial increase in coal consumption. As seen from the data presented, even with the present systems of fuel gas purification of SO₂, there is a most gloomy prospect for sulphur contamination of the global environment.

Actually, the correlation between values of natural and anthropogenic sulphur fluxes (Figure 4.2) shows that already by the mid-1970s the total amount of sulphur entering the atmosphere and hydrosphere has doubled since 1900 because of anthropogenic sulphur. Thus the natural biogeochemical systems for neutralization of sulphur oxides in the atmosphere and sulphuric acid in the hydrosphere and soils must already double their rate as compared to 1900.

The irregularity of the distribution of sulphur contamination source and the short average residence time of sulphur compounds, especially in the atmosphere,
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Figure 4.6 Predicted trends of global anthropogenic SO₂ emission into the atmosphere (after A. Ryaboshapko, 1978). 1, Spale and Harrington, 1971 (209): 1(1), fossil fuel version; 1(2), fossil fuel-nuclear version with use of breeder-reactors; 2, Shvedov, 1976 (51), on basis of coal and oil use for energy; 3, this paper; 4, Roderick, 1975 (181); 5, Kellogg et al., 1972 (146), 6, Land, 1971 (150): 6(1), fossil fuel version without treating systems; 6(2), using treating systems; 7, Smill, 1975 (190): 7(1), fossil fuel version with treating systems; 7(2), fossil fuel-nuclear version; 7(3), nuclear version

enhance the menace of regional situations of crisis from sulphuric acid contamination of the atmosphere, hydrosphere, and soil.

The acidification of lake water and soil, the increase in sulphate content, and the appearance of hydrogen sulphide in river, lake, and even sea waters show that in a number of cases the natural systems are unable to manage the ever-increasing sulphur contamination.

A possible way out of the present situation may be the development and introduction of utterly new systems of full gas purification from sulphur oxides. The additional amount of sulphuric acid obtained may in turn decrease the demands for the expansion of pyrite and native sulphur outputs. As an alternative to sulphur contamination we may suggest the wide-spread development of nuclear power.
4.8 REFERENCES


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