Chemical Events in the Atmosphere and their Impact on Environment
Pontifical Academy of Sciences, *Scripta Varia* 56, Vatican City 1985
www.pas.va/content/dam/accademia/pdf/sv56/sv56-brosset.pdf

THE GLOBAL SULFUR BUDGET

CYRILL BROSSET
Swedish Environmental Research Institute
P.O. Box 5207, S-402 24 Gothenburg, Sweden

Introduction

My presentation here on the global sulfur budget has been very much facilitated as I earlier this year received from Professor M.V. Ivanov a monograph (not yet published in English) with the following title: "The global biogeochemical sulfur cycle and influence on it of human activity" (*).

The monograph seems to include probably all our present knowledge concerning the behaviour of sulfur in the environment. All data given are well documented by a very comprehensive list of references. For that reason this monograph will be used as a general reference for all those data and ideas which are discussed in it. Concerning data taken from elsewhere they will be documented in the usual way.

The objective of the present survey

In a paper from 1978 (Atm. Env. Vol. 12), H. Rhode points out that making estimates of the global sulfur budget can be formulated as seeking answers to the following two questions earlier presented in a paper by Kellog *et al.* (Science *175*, pp. 587-596, 1972):

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

(*) General editing: G. K. Skryabin. Editors in chief: M.V. Ivanov (USSR) and J.R. Freney (Australia). This monograph is the result of an international project organized by SCOPE and the Academy of Sciences of USSR. The project has been sponsored by UNEP.

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

It is meant that the material compiled below from the monograph mentioned above and from other papers may give at least a tentative answer to these questions.

The box model

It is generally recognized that the use of box models is a very convenient way to present environmental budgets. This method is also used in the monograph, whereby the time scale has been chosen to one year.

Concerning the space scale it is recognized that *global* budgets may provide limited information because of high local variations in emission density. For that reason several space scales are used.

For the total global model the space scale applied is illustrated in Figure 1.

As shown, the respective states of aggregation are represented by the following reservoirs.

Gas phase:	Continental atmosphere Oceanic atmosphere
Liquid phase:	Ocean water Intracontinental water sheds
Solid phase:	Oceanic sediments Pedosphere Lithosphere

The budgets of the separate boxes are discussed first. Concerning the continental atmosphere it is, to begin with, subdivided into three smaller boxes, i.e., the atmosphere over industrial and urban regions, dusty continental atmosphere, meaning arid regions hit by wind blown dust, and clean continental atmosphere.

The sulfur budgets of all these hoxes and also of the total combination of them will be presented below.

Relevant sulfur compounds and some of their properties

There are certainly many sulfur compounds participating in the fluxes among the different boxes. The most important ones and the correspondent valence states of sulfur have been listed in Table 1.

Of these compounds only H_2SO_4 and the ion SO_4^{2-} are stable in air and airated water.

The compounds of sulfur having the valence state 2− are only stable in systems with much lower oxidation potential.

They are formed biogenetically (coastal zones, decomposition of org. material) or in some cases, pyrolytically (volcanoes).

The gas SO_2 has an intermediate position. It is formed in the first step of the oxidation of S^{2-}-compounds. Further it is produced by thermal decomposition of some sulfates and, as well known, by the combustion of S-containing fuels.

Oxidation of S^{2-}-compounds

As is evident from the above said, all S^{-2}-compounds in Table 1 will be oxidized in air. The principal process is a homogeneous oxidation reaction, usually comprising several steps before the end product H_2SO_4 is arrived at. The main role in this reaction is played by the hydroxy radical. In the troposphere this one is formed according to the following reaction:

$$O_3 + h\nu \rightarrow O(^1D) + O_2$$

$$O(^1D) + H_2O \rightarrow 2\,OH$$

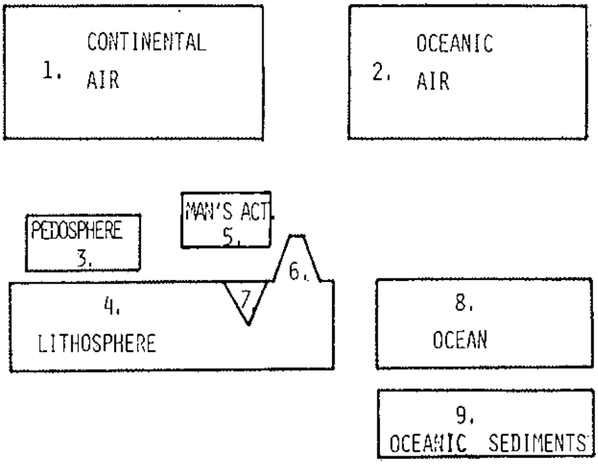

FIG. 1. The global sulfur budget. (Figures in brackets indicate anthropogenic contributions).

TABLE 1

Compound	Valence state of S
H_2S	2−
$(CH_3)_2S$ and other org. sulfides	2−
CS_2	2−
COS	2−
SO_2	4+
H_2SO_4 and its salts	6+

As already mentioned the first product of the reactions of S^{-2}-compounds with this radical is SO_2. The rate of the respective reactions is rather dependent on the type of the compound, which is seen in Table 2. For that reason in the monograph these compounds are divided into two groups which we may call reactive ($(CH_3)_2S$ and H_2S) and non-reactive (CS_2 and COS). In budget calculations the last ones are simply treated as precursors to SO_2.

It may, however, be observed that according to P.J. Crutzen (Geophys. Res. Lett. 1976, Vol. 3, pp. 73-76) the slow oxidation of COS makes possible that this compound is responsible for the sulfate layer in the stratosphere.

Oxidation of SO_2

The most studied reaction in this context is probably the oxidation of SO_2.

TABLE 2

Compound	Rate constant cm^3 molecules^{-1} sec^{-1}
$(CH_3)_2S$	9×10^{-12}
H_2S	5×10^{-12}
CS_2	0.4×10^{-12}
COS	0.04×10^{-12}

Three types of reactions seem to be possible:

1. Homogeneous gas phase reaction
2. Reaction in water solution
3. Reaction on surfaces

It has been shown that several kinds of homogeneous gas phase reactions (reactions with photochemically generated radicals) are occurring. The most important (rapid) ones are the following (Eggleton and Cox. Atm. Env. 1978, Vol. 12, pp. 227-230):

1. The OH-reaction
   $OH + SO_2 \rightarrow HSO_3$
   It has been established that the radical HSO_3 is readily converted to H_2SO_4

2. The HO_2-reaction
   $OH + CO \rightarrow CO_2 + H$
   $H + O_2\ (+ M) \rightarrow HO_2\ (+ M)$
   $HO_2 + SO_2 \rightarrow SO_3 + OH$
   $SO_3 + H_2O \rightarrow H_2SO_4$

3. The CH_3O_2-reaction
   $CH_3O_2 + SO_2 \rightarrow SO_3 + CH_3O$
   $SO_3 + H_2O \rightarrow H_2SO_4$

4. The RO_2-reaction
   (RO_2 stands for peroxy radicals excluding HO_2 and CH_3O_2)
   $RO_2 + SO_2 \rightarrow SO_3 + RO$
   $SO_3 + H_2O \rightarrow H_2SO_4$

The importance of these four reactions are closely connected to the respective reaction rates. These and also the rate constants are given in Table 3 (Eggleton and Cox, 1.c.).
All other photochemically generated reactive species seem to give negligible contributions as compared with those in Table 3.

Earlier it was thought that catalytic oxidation (with Mn as principal catalyst) was mainly responsible for the liquid phase oxidation of SO_2.

However, it has been observed that the decrease in some regions of

TABLE 3

Species	Rate constant for reaction with SO_2 (cm^3 molecules^{-1} sec^{-1})	SO_2 oxidation rate (% h^{-1})
OH	$0.5 - 1.0 \times 10^{-12}$	$1.2 - 2.5$
HO_2	9×10^{-16}	0.84
CH_3O_2	$\leqslant 10 \times 10^{-15}$	$\leqslant 0.8$
RO_2	$\leqslant 10 \times 10^{-15}$	$\leqslant 1.84$

the concentration of smoke particles (carrier of a.o. Mn) was not followed by a decrease of sulfate in precipitation.

In fact, an increase was measured. Therefore, an uncatalyzed reaction seemed to be more probable and was suggested by Penkett (Nat. 240, 105, 1972). In this connection the oxidizing agents O_2, O_3 and H_2O_2 were tested (H_2O_2 is produced in the atmosphere mainly by the reaction $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$). The result of this test is given in Table 4 (Cox and Penkett from Acid Deposition, Ed. Beilke and Elshout. D. Reidel Publ. Comp. 1983).

TABLE 4

CALCULATED RATES OF SO_2 OXIDATION IN WATER SOLUTION BY O_2, O_3 AND H_2O_2 AT 10°C.

INITIAL REACTANT CONCENTRATIONS:
SO_2 = 5 ppbv, O_3 = 50 ppbv, H_2O_2 = 1 ppbv

pH	O_2 µM min^{-1}	O_3 µM min^{-1}	H_2O_2 µM min^{-1}
4.0	0.0001	0.1	
4.3			13.4
5.0	0.003	2.5	
5.4			28.5
6.0	0.6	67.6	
6.6			73.4

The oxidation of SO_2 in rain drops by means of O_3 and H_2O_2 is consequently the dominant non-catalytic reaction. It is interesting to note that the H_2O_2-oxidation is rather insensitive to decrease of pH. These reactions due to their rates are probably quite capable of producing enough sulfate in rain water to account for observed levels.

There has been much work spent on investigations of SO_2 oxidation by means of surface reactions. Results hitherto obtained indicate, however, that conversion of SO_2 to SO_4^{2-} on atmospheric particles at room temperature does not take place in considerable extent (Liberti *et al.*, Atm. Env. 12, 255, 1978).

The distribution of sulfur compounds between air and water

It is well known that compounds of sulfur in different oxidation states have rather different properties, e.g. volatilities and solubilities in water.

A combination of the two last properties is, however, expressed by the respective distribution constants (or Henry law constants). Hence a change in the oxidation state implies a change in the distribution of the compound in question between air and water. This in its turn usually results in a transfer of this compound from one box in the model to another.

The magnitude of this effect is illustrated in Table 5. Here the Henry law constant, $(K_d)_T$, at 20°C for H_2S, SO_2 and H_2SO_4 is given and also an example concerning the respective equilibrium concentrations in mole l^{-1} for water and mole m^{-3} for air.

TABLE 5

Compound	K_d (Total) 20°C dimensionless	Equilibrium conditions mole l^{-1} in water	mole m^{-3} in air
H_2S	6.8	1	6800
SO_2	0.12	1	120
H_2SO_4	~0	1	~0

It shall be pointed out that these "total" constants (Henry law constants) refer to the total content of the respective species in water including hydration and dissociation products.

The right part of Table 5 is a good illustration of what happens if H_2SO_4 in water solution is reduced to H_2S. As is seen almost everything of S-H_2SO_4 will leave the water phase and enter the air as S-H_2S. If the last one now will be oxidized back to H_2SO_4 it will, of course, return as S-H_2SO_4 to the water phase. Such a process is a true cyclic one.

Now, suppose a sulfidic ore has been dug out by man somewhere from the lithosphere and oxidized giving SO_2, which is released into the atmospbere. Here it will be subsequently oxidized to H_2SO_4 and washed out by precipitation into some water shed. By one or another process it may now be reduced to H_2S. It could happen that this one instead of leaving the water phase will react with some heavy metal ions present forming almost insoluble sulfides. The sulfur atoms originating from somewhere in the lithosphere will now be confined in the sediments of the water shed.

As such a process may not readily be considered as a cyclic one, this type will in the following discussion be called a transfer.

For the reason that sulfur displacements in the environment may be both of the cyclic and of the transfer type it is preferred here for the overall processes to use the term budget instead of cycle.

The atmospheric sulfur budget

In the monograph mentioned a very comprehensive examination is presented concerning hitherto published relevant data about concentrations, reaction rates, estimation of emissions and depositions and of fluxes and resident times as well.

The whole material has been evaluated into a number of partial budgets and finally in a total global one.

Special attention has been given to the very important budget of the atmosphere. As already shown in Fig. 1, the total box of the atmosphere has been primarily divided into two: the continental atmosphere and the oceanic one.

Further, the continental atmosphere has been subdivided into 1) The polluted atmosphere over industrial and urban regions, 2) The atmosphere over remote dusty (arid) regions, and 3) The atmosphere over remote clean regions.

For all these regions graphs are given in the monograph. These graphs have here been disguised into tables which seem to facilitate calculation of the total budgets.

All masses in the tables below are given in Tg. The time scale is, as mentioned earlier, one year. The main figures concerning masses in the boxes and fluxes between them are the estimates of the authors of the monograph. In brackets after the main figures are presented the minimum and maximum values found in the literature.

As is seen, Table 6 gives the budget of the industrial and urban atmosphere. The total mass of sulfur within the box has been estimated to 0.145 Tg and its residence time to 0.5 day. It has been suggested that here the contribution from natural sources is negligible.

Steady-state is assumed as in all boxes concerning the gas phase. This assumption has given here a net export of 88 Tg y^{-1}. Half of it is thought to be transferred to the clean continental atmosphere, the other half to the oceanic atmosphere. The total balance for the industrial and urban atmosphere has, in this way, been estimated to 113 Tg y^{-1}.

Table 7 represents the opinion of the authors that the importance of wind blown dust has earlier been underestimated. Their own conclusions indicate that in the budget of the atmosphere, the wind blown dust should be considered as an entry of ~ 20 Tg y^{-1}.

In Table 8 data for the continental clean atmosphere are collected. The total mass is 0.42 Tg and the residence time is estimated to 1.5 days. The total balance amounts to ~ 103.5 Tg y^{-1}.

Summarizing the Tables 6, 7 and 8 one gets for the total continental atmosphere the figures in Table 9.

As is seen the mass of sulfur obtained is 0.59 Tg, the residence time 1.2 days and finally, the grand total balance including transfers from and into oceanic atmosphere 184.5 Tg y^{-1}.

The conditions for the oceanic atmosphere are given in Table 10. Here, the mass of sulfur has been estimated to 0.765 Tg and the residence time to 1.0 day. For the grand total balance (including transfers from and into continental atmosphere) the figure 278 Tg y^{-1} has been obtained.

The data in Tables 9 and 10 finally are summarized in Table 11, which now should give the budget of the total global atmosphere. It should be pointed out that all figures hitherto discussed are valid for the year 1980.

Hence, for this total budget we have got:

Total mass of sulfur	1.36 Tg
Average residence time	1.4 days
Total balance	342 Tg y^{-1}

The total global sulfur budget and the transfer processes of sulfur

Using the data in the Tables 6-11 and also data concerning the liquid and solid phases and with the application of the model in Fig. 1, the authors of the monograph have finally arrived at an estimation of the total global sulfur budget. It is presented in Figure 2.

As the atmospheric boxes have earlier been described in detail and moreover as steady-state has been assumed to prevail in the gas phase it remains now to discuss the fluxes concerning the lithosphere-pedosphere and the ocean (also the intracontinental water sheds).

Table 6

THE SULFUR BUDGET OF THE CONTINENTAL ATMOSPHERE. INDUSTRIAL AND URBAN REGIONS
TOTAL MASS OF S: 0.145 Tg
RESIDENCE TIME: 0.5 Day

INPUT		OUTPUT	
Process	Flux: S Tg y^{-1}	Process	Flux: S Tg y^{-1}
Antropog. emission			
$S\text{-}SO_2$	98 (83-113)	Wet dep.	11 (9-13)
$S\text{-}SO_4^{2-}$	12 (10-14)	Dry dep. ($S\text{-}SO_4^{2-}$)	2 (1-7)
$S\text{-}S_R^{2-}$ x/	3 (1-5)	Dry dep. ($S\text{-}SO_2$)	12 (5-19)
Natural emission	negligible	Transfer into clean cont. atmosphere	44 (34-54)
		Transfer into oceanic atmosphere	44 (34-54)
Total	113 (94-132) Tg y^{-1}	Total	113 (83-147) Tg y^{-1}

x/Index R Stands for Reactive, Such as $(CH_3)_2S$

TABLE 7

THE SULFUR BUDGET OF THE CONTINENTAL ATMOSPHERE.
REMOTE ARID REGIONS
TOTAL MASS OF S: 0.035 Tg
RESIDENCE TIME: 0.6 Day

INPUT		OUTPUT	
Process	Flux: Tg y^{-1}	Process	Flux: Tg y^{-1}
Dust susp.	20 (10-30)	Wet dep.	3 (1.5-4.5)
		Dry dep. ($S\text{-}SO_4^{2-}$)	9 (2-23)
		Transfer into clean cont. atmosphere	8 (3-13)
Total	20 (10-30) Tg y^{-1}	Total	20 (6.5-40.5) Tg y^{-1}

TABLE 8

THE SULFUR BUDGET OF THE CONTINENTAL ATMOSPHERE.
REMOTE CLEAN REGIONS
TOTAL MASS OF S: 0.42 Tg
RESIDENCE TIME: 1.5 Days

INPUT		OUTPUT	
Process	Flux Tg y^{-1}	Process	Flux Tg y^{-1}
Oxid. of COS and CS_2 $S\text{-}SO_2$	1.5 (1-2)	Transfer into oceanic atmosphere	56.5 (31-82)
Transfer from ind. and urban atmosphere	44 (34-54)	Wet dep.	37 (27-47)
Transfer from remote dusty atmosphere	8 (3-13)	Dry dep. ($S\text{-}SO_4^{2-}$)	5 (2-17)
Volcanic emission	14 (7-21)	Dry dep. ($S\text{-}SO_2$)	5 (2-8)
Nat. emission ($S\text{-}S_R^{-2}$)	16 (4-30)		
Transfer from oceanic atm.	20 (10-30)		
Total	103.5 (59-160) Tg y^{-1}	Total	103.5 (62-154) Tg y^{-1}

TABLE 9

THE SULFUR BUDGET OF THE CONTINENTAL GLOBAL ATMOSPHERE (1980)
TOTAL MASS OF SULFUR: 0.59 Tg
RESIDENCE TIME: 1.2 Days

INPUT		OUTPUT	
Process	Flux Tg y^{-1}	Process	Flux Tg y^{-1}
Antropog. emission		Wet dep.	51 (37.5-64.5)
$S\text{-}SO_4^{2-}$	12 (10-14)	Dry dep.	16 (5-47)
$S\text{-}SO_2$	98 (83-113)	($S\text{-}SO_4^{2-}$)	
$S\text{-}S_R^{2-}$	3 (1-5)	Dry dep.	
Volcanic emission	14 (7-21)	($S\text{-}SO_2$)	17 (7-27)
Dust susp.			
$S\text{-}SO_4^{2-}$	20 (10-30)		
Nat. emission			
$S\text{-}S_R^{2-}$	16 (4-30)		
Oxid. of COS and CS_2 $S\text{-}SO_2$	1.5 (1-2)		
Total	164.5 (116-215) Tg y^{-1}	Total	84 (49.5-138.5) Tgy^{-1}
Transfer from oceanic atm.	20 (10-30)	Transfer into oceanic atm.	100.5 (50.5-150.5)
Grand total	184.5 (126-245) Tg y^{-1}	Grand total	184.5 (100-239) Tg y^{-1}

TABLE 10

THE SULFUR BUDGET OF THE OCEANIC GLOBAL ATMOSPHERE (1980)
TOTAL MASS OF SULFUR: 0.765 Tg
RESIDENCE TIME: 1.0 Day

INPUT		OUTPUT	
Process	Flux Tg y^{-1}	Process	Flux Tg y^{-1}
Nat. emission		Wet dep.	230 (160-300)
$S\text{-}S_R^{2-}$	20 (0-40)	Dry dep. ($S\text{-}SO_4^{2-}$)	17 (3-48)
Volcanic emission	14 (7-21)		
Sea spray	140 (77-203)	Dry dep. ($S\text{-}SO_2$)	11 (5-17)
Oxid. of COS and CS_2 $S\text{-}SO_2$	3.5 (2.5-4.5)		
Total	177.5 (86.5-268.5) Tg y^{-1}	Total	258 (168-365) Tg y^{-1}
Transfer from continental atmosphere	100.5 (50.5-250.5)	Transfer into continental atm.	20 (10-30)
Grand total	278 (137-419) Tg y^{-1}	Grand total	278 (178-395) Tg y^{-1}

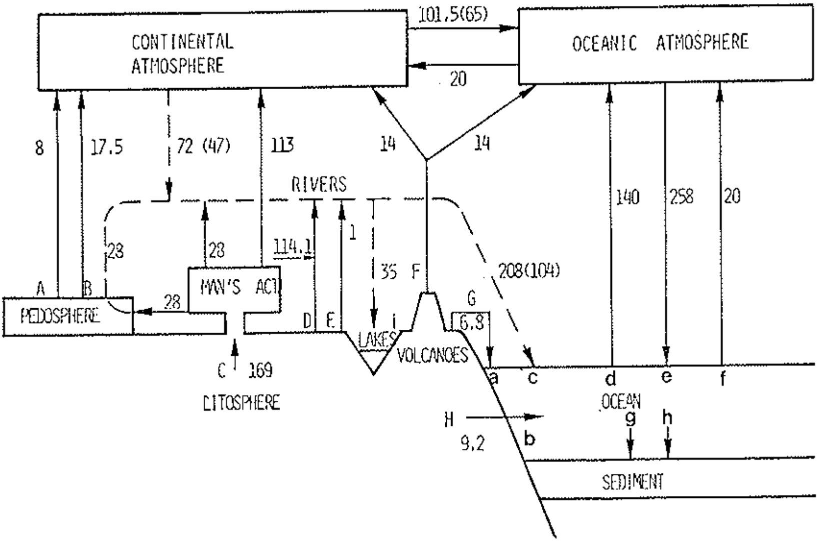

Fig. 2. The space scale of the global box model.

1. Continental atmosphere
2. Oceanic atmosphere
3. Pedosphere
4. Lithosphere
5. Man's activity
6. Volcanoes
7. Intracontinental water sheds
8. Ocean
9. Oceanic sediments

Table 11

THE TOTAL SULFUR BUDGET OF THE GLOBAL ATMOSPHERE (1980)
TOTAL MASS OF SULFUR: 1.36 Tg
RESIDENCE TIME: 1.4 Days

INPUT		OUTPUT	
Continental part	164.5 (116-215)	Continental part	84 (49.5-138.5)
Oceanic part	177.5 (86.5-268.5)	Oceanic part	158 (168-365)
Total	342 (202.5-483.5) Tg y^{-1}	Total	342 (217.5-503.5) Tg y^{-1}

TABLE 12

GLOBAL TRANSFER PROCESS OF SULFUR

OUTPUT FROM LITOSPHERE AND PEDOSPHERE			INPUT INTO THE OCEAN			
Symbol in fig. 2	Process	Flux (Tg y^{-1})	Symbol in fig. 2	Process		Flux (Tg y^{-1})
A.	Net. part. matter	8	a.	Dry dep. (biog. gases)		6.8
B.	Biogenic gasem.	17.5	b.	Underground stream		9.2
C.	Litosphere	169	c.	Transfer with river water		208.1
D.	Weathering	114.1				
E.	Acid mine water	1	d.	Sea spray	140	
F.	Volcanoes	28	e.	Wet and dry dep.	258	
G.	Biogenic gasem.	6.8				
H.	Underground stream	9.2	f.	Biog. emission	20	
			e-d-f	Net. input from atm.		98
	Total	353.6 Tg y^{-1}		Total		322.1 Tg y^{-1}
				OUTPUT FROM OCEAN INTO SEDIMENT		
			g.	Dep. of S-S^{2-}		98.4
			h.	Dep. of S-SO_4^{2-}		27.8
				Total		126.2 Tg y^{-1}
				Net. dep. in the ocean water 322.1-126.2		195.9 Tg y^{-1}
				INPUT INTO INTRACONTINENTAL WATER SHEDS		
			i.			35
				Total		35 Tg y^{-1}

For the sake of clarity, in Fig. 2 the fluxes from the lithosphere-pedosphere have been denoted with capital letters and the fluxes from and into the ocean and the intracontinental water sheds with small letters.

These fluxes and the respective processes, which all correspond to the data in the monograph, are collected in Table 12 and summarized in Table 13. (There seems to be a small error somewhere giving a difference of ~ 1% in the balance).

The conclusions from the figures in Table 13 can be formulated as follows:

TABLE 13

GLOBAL TRANSFER BALANCE OF SULFUR

Emission from litosphere and pedosphere	353.6 Tg y^{-1}	Deposition in ocean water	195.9
		In oceanic sediment	126.2
		In intracontinental watersheds	35
		Total deposition	357.1 Tg y^{-1}

In 1980 a mass of about 355 Tg of sulfur has been removed from somewhere in the lithosphere-pedosphere. Of this mass 195 Tg has been deposited in the ocean water, 35 Tg in intracontinental water sheds and 125 Tg in oceanic sediments.

Some comparisons

Of all the partial budgets given, the one in Table 6 (The sulfur budget of the industrial and urban atmosphere) gives probably the most direct information on the magnitude of man's contribution to the sulfur budget. However, the scale of Table 6 is still too large to give an impression of what is going on in our own European environment. Therefore, an evaluation hy H. Rhode (paper given at IVL Symposium, Gothenburg March 9, 1983) valid for northern Europe will be cited (Table 14).

When comparing Rhode's figures with the ones in Table 6 it may seem that Europe still is responsible for a rather small fraction (~12%) of the total anthropogenic sulfur pollution. However, this fraction seems to have a rather dramatic effect on our nearby environment.

It should be mentioned that in the monograph also the atmospheric budgets for preindustrial time have heen estimated. These are given in Tables 15 and 16. From these tables the total preindustrial atmospheric budget can be calculated (Table 17).

As is seen the balance arrived at is 228 Tg y^{-1} which figure has to be compared with 342 Tg y^{-1} valid for 1980 (Table 11).

TABLE 14

THE ATMOSPHERIC SULFUR BUDGET FOR N. EUROPE (H. Rhode, 1983)

INPUT		OUTPUT	
Process	Flux Tg y^{-1}	Process	Flux Tg y^{-1}
Anthropogenic emission	13	Wet dep. of anthropogenic S	4
Natural emission	0-3	Wet dep. of natural S	0.5
		Dry dep. of anthropogenic S	3-6
		Dry dep. of natural S	0.2-0.3
		Net export	3-6
Total	13-16 Tg y^{-1}	Total	10.7-16.8 Tg y^{-1}

TABLE 15

GLOBAL ATMOSPHERE - PREINDUSTRIAL ERA - CONTINENTAL PART

INPUT		OUTPUT	
Process	Flux Tg y^{-1}	Process	Flux Tg y^{-1}
Vulcanic activity ($S\text{-}SO_2$)	14	Wet dep. ($S\text{-}SO_4^{2-}$, $S\text{-}SO_2$)	26
Wind erosion ($S\text{-}SO_4^{2-}$)	20	Dry dep. ($S\text{-}SO_4^{2-}$)	13
Emission ($S\text{-}S_R^{2-}$)	16	Dry dep. ($S\text{-}SO_2$)	5
Oxid. or red. of COS and CS_2 ($S\text{-}SO_2$ or $S\text{-}H_2S$)	1		
Total	51 Tg y^{-1}	Total	44 Tg y^{-1}
Transfer from oceanic atmosphere	20 Tg y^{-1}	Transfer into oceanic atmosphere	27 Tg y^{-1}
Grand total	71 Tg y^{-1}	Grand total	71 Tg y^{-1}

TABLE 16

THE SULFUR BUDGET OF THE GLOBAL ATMOSPHERE.
PREINDUSTRIAL ERA - OCEANIC PART

INPUT		OUTPUT	
Process	Flux Tg y^{-1}	Process	Flux Tg y^{-1}
Emission ($S\text{-}S_R^{2-}$)	20	Wet dep. ($S\text{-}SO_4^{2-}$, $S\text{-}SO_2$)	161
Volcanic activity ($S\text{-}SO_2$)	14	Dry dep. ($S\text{-}SO_4^{2-}$)	12
Sea spray ($S\text{-}SO_4^{2-}$)	140	Dry dep. ($S\text{-}SO_2$)	11
Oxid. or red. of COS and CS_2 ($S\text{-}SO_2$, $S\text{-}H_2S$)	3		
Total	177 Tg y^{-1}	Total	184 Tg y^{-1}
Transfer from continental atm.	27 Tg y^{-1}	Transfer into continental atmosphere	20 Tg y^{-1}
Grand total	204 Tg y^{-1}	Grand total	204 Tg y^{-1}

TABLE 17

THE TOTAL SULFUR BUDGET OF THE GLOBAL ATMOSPHERE.
PREINDUSTRIAL ERA

INPUT		OUTPUT	
Continental part	51 Tg y^{-1}	Continental part	44 Tg y^{-1}
Oceanic part	177 Tg y^{-1}	Oceanic part	184 Tg y^{-1}
Total	228 Tg y^{-1}	Total	228 Tg y^{-1}

However, the figure 342 Tg y^{-1} is composed of three main terms:

Anthropogenic emission (Table 6)	113 Tg y^{-1}
Sea spray (Table 10)	140 »
Other emissions	89 »
Total (Table 11)	342 Tg y^{-1}

If from this sum of 342 Tg y^{-1} the anthropogenic part (113 Tg y^{-1}) is substracted, one arrives at 229 Tg y^{-1} in good agreement with the result of the little more complicated calculation in Tables 15, 16 and 17.

Surveys similar to this one usually contain a final paragraph describing the conditions which will be met with in, say, the year 2025.

Such forecasts are usually based on statistics indicating the probable increase of the global consumption of sulfur containing combustibles. However, in these very complicated times I think extrapolations of that kind may be rather misleading. For that reason no such forecast will be given here.

DISCUSSION

REVELLE

Did I read your diagram right to understand that there is a net influx of the ocean waters of about 100 million tons a year? That there is a net influx into the ocean waters?

BROSSET

Yes, that is exactly what it is.

REVELLE

If this continued over geologic time, the ocean would consist of nothing but sulphate. You must have some sink in the ocean. There is a possible sink that is the hydrothermal circulation in the bottom of the ocean. The entire volume of ocean water apparently passes through the top one or two kilometers of the crust every ten million years, and the sulphate is probably taken out at that time.

The other question I had is: what about volcanic emissions that go up into the upper atmosphere? They must have a half life a lot longer than one day.

BROSSET

Probably yes. They are only mentioned as a total volcanic emission of 28 teragrams in the air, and they are simply divided into two parts, 14 and 14 for the oceanic and continental atmosphere. That is everything with that. But I am quite aware that part of it does not go up to the stratosphere.

KNABE

You gave different figures on the pre-industrial time and the present time, if I got the number correctly. It was 224 teragrams a year in the pre-industrial time and 342 at present. I would like to see the last of your tables, and then I could make my question more precisely.

BROSSET (showing the table and explaining)

These are the anthropogenic emissions in the atmosphere. These are the sea spray, and these are all other emissions. Now if you put them together, you will get the 342 of today.

KNABE

So far I can follow you, but at the very end of it that means total minus and volcanic conditions... Would this be the pre-industrial budget: 228?

BROSSET

If you just subtract from the total the anthropogenic of today — or from the total of today the anthropogenic of today — you will get there a figure that is identical with the calculation of the pre-industrial.

KNABE

But how much is the sea spray the result of the input by rivers? Any meaning?

BROSSET

Yes, you are quite correct. That is now the total anthropogenic input from the rivers: 208; the anthropogenic part of it is 104; and the sea spray total is 140.

ANDERSON

I would like to speak to the gas phase oxidation rates which you mentioned, and particularly the reaction OH with COS. We have examined that reaction in the laboratory by looking both at reacted products and find it to be 100 times slower than your quotation $0{,}04.10^{-12}$.

CRUTZEN

I would like to make a few corrections here. First of all, the El Chichón volcano did not put out 100 million tons of sulphate — it put out maybe 3. The other thing is that the ocean already contains so much sulphate that I do not think on the short-time scale man's input has modified anything. So the sea spray I think it is pre-industrial. About the sulphur reaction, for many of them it seems that when OH reacts with sulphur compounds there is a very strong oxygen effect. It is not noticed for COS, so I think for COS we can forget about reactions of OH in the atmosphere, but regarding CS_2 and dimethylsulphide very strong oxygen effects have been discovered, mainly work in Germany in the laboratory of Becker.

CHAMEIDES

On this question of COS, the evidence is that $CS_2 + OH$ reaction produces COS, and the problem with that is that COS does not react with OH. We have a real problem removing COS from the atmosphere. I do not think the question of the COS and OH has been properly addressed and I would not be surprised that in low temperature like in the upper troposphere it turns out that that reaction does in fact occur. But at the moment it is a real problem for the sulphur budget where the COS goes.

CRUTZEN

I think that where it goes is rather clear — it will go into the plants. Plants like the stuff, and that has not been considered in the budget so far.

PHILLIPS

I was interested in the results you commented on briefly about the oxidation of sulphur dioxide in the aqueous phase, and you said that there were different oxidizing powers, if you like, and precipitations corresponding to different meteorological conditions, and I think you said that air masses from central Europe have the strongest oxidizing power. Could you comment on what is different about those air masses? What is it in the precipitation which causes this? I mean, how is air from central Europe different from that which has traveled across the North Sea, for instance?

BROSSET

I am not able to do that, and the only thing I can say is that there were a number of special measurements and we observed that we had two or three times higher oxidation powers in the precipitation for southern winds as compared with other wind directions.

LIBERTI

It is quite ambitious for a scientist to describe a natural phenomenon in terms of a specific reaction. The situation in the atmospheric environment is however more complicated as a variety of reactions are occurring simultaneously and a certain species may take part in different reactions affecting the relative equilibria. Most data are coming from laboratory work and experimental conditions are definitely different from the ones observed in the troposphere. As an example the mechanism of oxidation of sulphur dioxide, in gas phase is usually reported occur to a large extent through free radicals. If the presence of humidity and of particulated matter is considered, specifically in the lower part of the troposphere, definitely also heterogeneous reactions play a very important role. I feel that experiments carried on in the atmosphere yield more consistent results to elucidate the chemistry of the atmospheric environment.

BROSSET

Thank you very much, Dr. Liberti. May I ask you now. I avoided to mention the work of Novakov in Berkeley, California; he studied in a number of papers the oxidation of sulphur dioxide on black particles claiming that there *is* a kind of oxidation power of the amorphous carbon itself. Now I never understood myself if carbon is the active re-agent of the catalyst and oxidation is going on on the surface field. Have you any opinion on that?

LIBERTI

I will try to answer your questions. Experiments definitely show that SO_2 absorbed on carbon particles is rapidly oxidized to sulphate and this mechanism is one of the more important for the oxidation of SO_2 in a heterogeneous process. Not all particulated material behaves, however, in the same way and the specific nature of the surface and humidity play an important role on this mechanism.

WANDIGA

Could you also kindly try to elaborate a little more on your biogenic sources of emissions, because I think they may be on the low side, particularly if you restrict yourself to the sources which are occurring in the temperate zones. When you include the biogenic emissions of sulphur which are occurring in the tropical zone, the budget may be very different from what you are saying. In this sense I am referring to forest fires, but also to some of the work we have done on termites as being the source of dimethylsulphide.

BROSSET

You are quite correct, but I cannot elaborate more than I have done at this moment.

MARINI-BETTÒLO

I think it is very interesting this global presentation of the sulphur balance, I would say, more than the cycle. There are also some points that must be cleared, as Dr. Wandiga said, but even another point should be mentioned. We are considering pure reactions in the pure atmosphere. Sometimes it happens that there are also other products that might interfere like particulates. And I think we must bear in mid this when we pass from models to true reality.