Investigation on the incorporation of sulfur-dioxide into fog- and rain-droplets

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ABSTRACT

The results of an experimental investigation on washout and rainout of SO_2 by raindrops and fog-droplets of given size-distribution are presented. The laboratory-studies were supplemented by model calculations on the sulfate-concentration in rainwater caused by washout and rainout of SO_2 and sulfate-aerosols. It is shown under which circumstances the rainout resp. the washout mechanism becomes predominant for the chemical composition of rainwater on the ground.

Introduction

This communication summarizes the results of the first part of an extended study on rainout and washout of atmospheric trace-gases and aerosols by fog and precipitation (Beilke & Georgii, 1966). While general agreement on the importance of these processes for the self-cleansing of the atmosphere from trace-constituents is achieved, very little quantitative information is available on the portion of gaseous traces being incorporated into cloud-droplets and precipitation-elements by the abovementioned processes. Earlier investigations carried out by Georgii (1965) under atmospheric conditions give no conclusive data on the scavenging of gaseous traces for the following reasons:

1. During rainfalls the concentration of atmospheric trace-substances is continuously changed by turbulent mixing and advection.
2. Intensity of precipitation as well as droplet-spectra fluctuate considerably during the course of individual rainfalls.
3. Various gases having different absorption characteristics are simultaneously incorporated into cloud and precipitation elements and may react jointly within the droplets.
4. In addition to gas-traces aerosols are also constantly consumed by condensation, by attachment to the droplets and by washout.

For these reasons and investigation on the absorption of trace-gases must be conducted in the laboratory under defined conditions.

Experimental method

Our investigation aimed at determining the attachment coefficient for SO_2 on droplets of rain and fog. A further purpose was to determine the amount of SO_2 washed out by precipitation in relation to (*a*) the intensity of rainfall, (*b*) the size-spectrum of rain-droplets, (*c*) the acidity of rainwater. Sulfur dioxide was selected as a first test substance for its importance as atmospheric trace-gas in continental areas.

The experiments were carried out in a washout-chamber of 1 m^3 volume. This room was filled with a mixture of SO_2 in purified air. The initial SO_2-concentration amounted to 800 $\mu g/m^3$. The change of the concentration was continuously checked by two recording instruments installed at the air-inlet and at the exit of the chamber. Intensity of the artificial rain as well as size-spectrum of droplets were to be varied. For details of the experimental set-up see Beilke & Georgii (1966). Intensity of rain and average size of droplets were selected in such a way as to be in approximate accordance with the relation found by Best (1950) for natural rainfalls. The mean droplet radii for the three different types of precipitation were: $\bar{r}_1 = 0.85$ mm, $\bar{r}_2 = 0.40$ mm, $\bar{r}_3 = 0.15$ mm.

Washout of sulfur-dioxide

The washout tests showed that the SO_2-concentration decreased in the chamber according to the equation:

$c = c_0 e^{-at}$ (t = time, c_0 = initial concentration),

whereby the washout-velocity, a, is a function of precipitation intensity, I, and mean droplet radius as well as of the chemical composition of droplets. The results of our investigation reveal that the decrease of the SO_2-concentration in the chamber takes place the faster the higher the intensity of the rain is, while at constant rain-intensity the washout-velocity depends on the mean droplet-size. However, at intensities above 20 mm/hr the half-life-time of SO_2 becomes practically independent of the droplet-size. The following Table 1 shows the relation between mean droplet-size, half-life-time of SO_2 in the washout-chamber and washout-velocity, a, at a constant rain-intensity of 2 mm/hr. The artificial rain was produced with distilled water.

The decrease of the SO_2-concentration is more rapid in the cloud-filled chamber than in washout-experiments with larger raindrops. This result can also be taken from Table 1. It is practically an extrapolation of the washout-velocity, a, to small droplet-sizes.

Generally, however, the rainout velocity is higher than the corresponding velocities of artificial rain because the total surface of the tiny cloud-droplets at equal liquid water content in the chamber is considerably larger than that of the rain-drops.

As shown in Fig. 1 the effect of different chemical compositions of the rainwater on the washout-velocity, a, was studied at a constant rain intensity of 15 mm/hr and mean droplet-radius of 0.85 mm. The chemical composition was changed by variation of the pH-value between 2.6 and 10.9. Table 2 shows that the washout-velocity increases with increasing pH-value of the rainwater. The reaction-velocity in natural rainwater is obviously higher than in distilled water of the same acidity. This may be due to the effect of catalysts which promote the formation of sulfate ions. This result is in agreement with investigations of the catalytic oxidation of SO_2 by Junge & Ryan (1958).

Table 1. *Half-life-time and washout-velocity of SO_2 in relation to droplet-radius in artificial rain of distilled water*

I (mm/hr)	$\bar{r}$ (mm)		Half-life-time of SO_2 (min)	a (sec^{-1})
2	0.85	rain	25	0.5×10^{-3}
2	0.40	rain	12.4	1.0×10^{-3}
2	0.15	rain	7.5	1.6×10^{-3}
2	0.01	fog	2.5	6.5×10^{-3}

Table 2. *Washout-velocity in relation to pH-value of artificial rain*

Chemical compositions of artificial rain	pH-value	a (sec^{-1})
Distilled water + NaOH	10.9	2.68×10^{-3}
Distilled water	6.4	1.83×10^{-3}
Distilled water + H_3PO_4	2.6	1.70×10^{-3}
Natural rain	5.5	2.50×10^{-3}
Distilled water × H_2O_2	—	3.50×10^{-3}

The washout tests with distilled water to which H_2O_2 had been added resulted in a considerable increase of the washout-velocity. This can be explained by the immediate oxidation of SO_2 to $SO_4^{=}$ by H_2O_2 after the SO_2-molecule had been captured by the droplet.

The variation of the chemical composition of cloud-water was produced in the same way as described for washout in the previous chapter. The effect of the pH-value on the half-life-time of SO_2 leads to the same results as in the case of washout of rain.

Rainout of sulfur-dioxide

An artificial cloud was produced by a droplet-generator, the cloud-droplets having an average radius of 10 μ. The density of the cloud amounted to approximately 100 droplets/ccm.

The concentration of trace substances in cloud-droplets is described after Junge (1963) in first approximation by the equation:

$$K = \frac{\varepsilon c}{L},$$

K = Concentration of trace-substance in cloud water in mg/l,
c = concentration of atmospheric trace-substances in the proximity of droplets in $\mu g/m^3$,
L = liquid water content of cloud in g/m^3,
ε = rainout coefficient $0 < \varepsilon < 1$.

While ε for aerosol-particles is known at least by order of magnitude, no data are available for gaseous traces. During the course of our rainout experiments an attempt was made to determine the rainout coefficient for SO_2 by

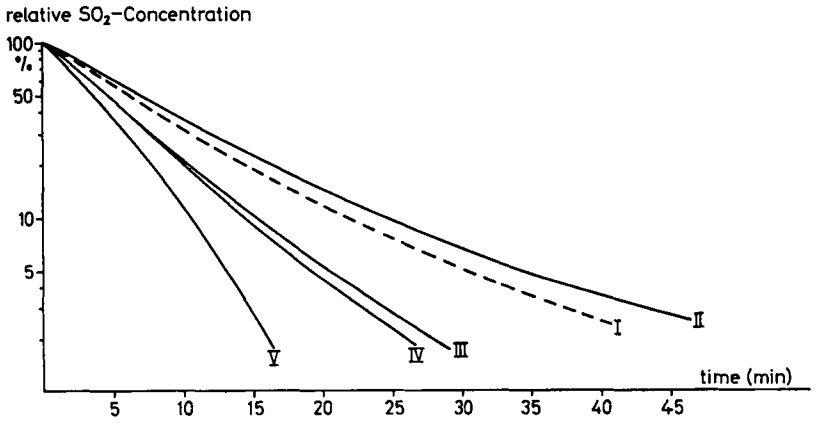

Fig. 1. Decrease of SO_2-concentration by washout during laboratory-experiments. Artificial rain was composed of: distilled water pH = 6.4 (curve I); 0.02 *n* phosphoric acid pH = 2.6 (curve II); natural rainwater pH = 5.5 (curve III); 0.001 *n* sodiumhydroxide solution pH = 10.9 (curve IV); distilled water + H_2O_2 (curve V). Mean droplet size: 0.85 mm; rain intensity: 15 mm/h.

simultaneous measurement of K, c and L. ε can only be determined under equilibrium-conditions between trace-gas concentration and cloud-droplet population in the experimental chamber. This equilibrium, however, is reached in a time-interval below a second. The value obtained was 0.03.

Owing to difficulties in the exact measurement of K and L, the value of ε may be uncertain by a factor of 3 to 5. Therefore it is assumed that ε for SO_2 lies within the range of 0.01 to 0.1. This value certainly is considerably smaller than ε for large and giant aerosol-particles, for which Junge indicates values between 0.1 to 0.8. The rainout of Aitken-nuclei, on the other hand, is of little importance for the mass-budget of chemical traces in precipitation owing to the small total volume concentrated on Aitken-nuclei; although ε for Aitken-nuclei may be close to 1 in a region with very low aerosol-concentration.

Calculations on the incorporation of SO_2 by rainout and washout

Records of atmospheric SO_2-concentration gained during the course of continuous rainfalls and showers for two years in Frankfurt/Main frequently showed a drop of the concentration while it was raining. In most cases an immediate increase of the SO_2-concentration caused by lateral influx of air-masses with unaffected high SO_2-values and continuation of emissions from anthropogeneous sources in the vicinity was observed after the end of the rainfall (Georgii 1962, 1965). Although no quantitative data could be evaluated on the amount of SO_2 removed from the atmosphere by precipitation, we are convinced that the $SO_4^=$-content analyzed in rainwater originates to a good deal from rainout and washout of SO_2.

The following model-calculation was performed to receive more information on this problem. The vertical SO_2-concentration was based on distributions found by Georgii &

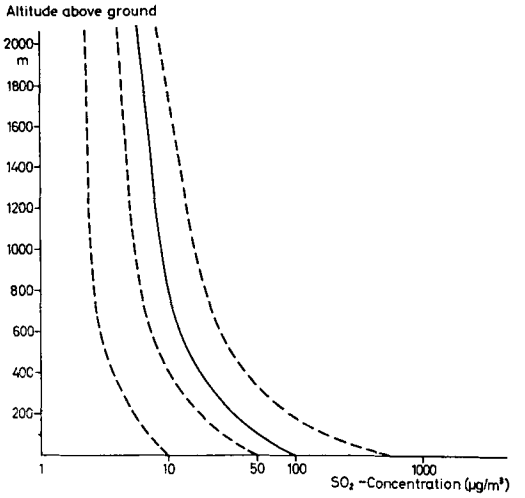

Fig. 2. Vertical decrease of atmospheric SO_2 with altitude. Solid curve: Measurements by Georgii and Jost; dashed curves: model distributions.

Table 3. *Computed $SO_4^=$-concentration in rain in relation to rain-intensity and SO_2-ground-concentration*

Rain-intensity (mm/h)	SO^2-ground-concentration ($\mu g/m^3$)	$SO_4^=$-concentration in rain (mg/l)
1	10	2.7
1	50	7.2
1	100	15.2
1	500	36.5
5	10	1.2
5	50	3.2
5	100	6.8
5	500	16.2
100	10	0.3
100	50	0.8
100	100	1.6
100	500	3.9

Jost (1964) during aircraft-ascents in altitudes up to 6 km. An SO_2-value of 100 $\mu g/m^3$ was chosen as representative ground-concentration for the SO_2-level in a moderately polluted continental atmosphere. Profiles of the vertical SO_2-concentration used in this study are compiled in Fig. 2. As a further assumption the droplet-size was kept constant during the fall of the droplet below the cloud-base. The cloud-free layer was assumed to have a thickness of 2 km. The mean drop-radius was calculated according to Best (1950). All calculations were made under the presumption that the SO_2 incorporated in the drops immediatly oxidizes to $SO_4^=$. The calculations were carried out in dependance of rain-intensity for the following different cases:

(a) *Washout of SO_2*

The amount of SO_2 washed out by falling raindrops was determined by a step to step integration over altitude-intervals of 200 m. The attachment coefficient proved to be primarily proportional to r^2. Different rain-intensities were selected as parameter.

Fig. 3 curve 2 shows the relation between $SO_4^=$-concentration in rain K produced by washout of SO_2 and rain-intensity I which can be expressed by the following power function:

$$K = K_0 \left(\frac{I}{I_0}\right)^{-0.5},$$

where $K_0 = 15.2$ mg $SO_4^=/l$ for $I_0 = 1$ mm/h.

In addition to this, the amount of SO_2 which is washed out by rain at constant intensity but at different vertical SO_2-distributions was calculated. The following SO_2-ground-concentrations were assumed:

$C_0 = 10$ $\mu g/m^3$, 50 $\mu g/m^3$, 100 $\mu g/m^3$, 500 $\mu g/m^3$.

The vertical decrease of SO_2 at these ground-concentrations is given in Fig. 2. The solid line indicates the vertical distribution which is a result of aircraft ascents, found by Georgii & Jost. Table 3 presents the results of this calculation for different rain intensities and different SO_2-ground-concentrations. Table 3 indicates that average SO_2-concentration near the surface primarily determines the $SO_4^=$-concentration in rain by washout. Owing to the characteristics of the vertical distributions of atmospheric SO_2 the lower 1000 m of the atmosphere are responsible for the amount of SO_2 incorporated in falling raindrops by washout.

(b) *Rainout of SO_2*

We assume an average drop-radius of 10 μ, a SO_2-concentration in cloud-level of 10 $\mu g/m^3$, a rainout-coefficient ε of 0.03 and a liquid water content of 0.8 g/m^3 for the calculation of the amount of SO_2 incoroporated in cloud-droplets within the cloud by rainout.

Under these environmental conditions 0.38 mg SO_2/l cloud water equal to 0.57 mg $SO_4^=/l$ is incorporated in the cloud-droplets. This example shows that the amount of SO_2 absorbed by rainout within the cloud is small in relation to the effect of washout on the final $SO_4^=$-concentration in rainwater.

The reason for the small effect of rainout can be seen in the low SO_2-concentration in cloud-level and the small rainout-coefficient. In the case that the SO_2-concentration decreases below 100 $\mu g/m^3$ near the ground, the SO_2 absorption by rainout gains importance, if, however, the SO_2-concentration becomes independent of altitude, incorporation of SO_2 by rainout will be predominant. This result reveals that washout of SO_2 is of particular significance for the $SO_4^=$-concentration in rainwater at ground-level in areas with polluted atmospheres.

Rainout and washout of sulfate-aerosols

Under atmospheric conditions the $SO_4^=$-concentration in rain originates not only from the

gas-phase but also from the incorporation of aerosols containing sulfate.

The calculation for the case including the solid component of atmospheric trace-constituents was based on the following assumptions:

1. The aerosol-concentration near the ground consists of:

   Aitken-nuclei: 10^5 particles/cm^3,
   large nuclei: 10^2 particles/cm^3,
   giant nuclei: 1 particle/cm^3.

   The size ranges of aerosol-particles were selected as follows:

   Aitken-nuclei: 0.01 μ–0.1 μ,
   large nuclei: 0.1 μ–1 μ,
   giant nuclei: 1 μ–10 μ.

2. The decrease of the particle number with altitude is in agreement with vertical aerosol-distributions compiled by Junge (1961).

3. Ten per cent of the entire aerosol substance are sulfate.

4. The collection efficiency E_c, which is a function of the drop-radius and the particle-radius will have the following values as indicated by Facy (1962):

   $E_c = 0.001$ for Aitken-nuclei,
   $E_c = 0.05$ for large nuclei,
   $E_c = 0.3$ for giant nuclei.

5. The vertical distribution of aerosols does not change.

Integration was carried out over appropriately selected radius intervals and over altitude in steps of 200 m. The results are compiled in Table 4 indicating the contribution of the different size-groups of atmospheric aerosols for the total $SO_4^=$-concentration in rain. The results show that the contribution of Aitken-nuclei and large nuclei for the $SO_4^=$-concentration in rain by washout is small compared to that of giant nuclei. They furthermore show that washout of SO_2 is of much greater importance for the sulfate-concentration in precipitation than the washout of sulfate-containing aerosols.

Table 4. *Contribution to the $SO_4^=$-concentration in rain by sulfate-aerosols*

Intensity of rain (mm/h)	$SO_4^=$-concentration by washout (mg/l)		
	Aitken-nuclei	Large nuclei	Giant nuclei
0.1	0.7×10^{-3}	0.15×10^{-1}	2.2
0.5	0.5×10^{-3}	0.11×10^{-1}	1.5
1.0	0.4×10^{-3}	0.09×10^{-1}	1.3
5.0	0.3×10^{-3}	0.06×10^{-1}	0.9
25.0	0.2×10^{-3}	0.05×10^{-1}	0.7

Estimating the effect of aerosol-particles on the sulfate-concentration in rain we need not consider the Aitken-nuclei owing to the negligible mass they contribute.

With respect to the microphysical parameters of stratus-clouds the following values were used for the computation. The values were taken from a report by R. Griffith (1959):

Average drop-size: 10 μ
Number of drops: 200/cm^3
Liquid water content: 0.8 g/m^3

Further it was assumed that only the largest nuclei serve as condensation nuclei. Based on the concentration and size-distribution of the aerosols in an altitude of 2 km a mean value of the particle radii was established. This value depends on the number of nuclei which are consumed by condensation. For the microphysical structure of stratus this value amounts to 0.3 μ.

Based on these assumptions we can estimate that the $SO_4^=$-concentration in layer-clouds will amount to approximately 5.5 mg/l cloud-water. Owing to a higher liquid water content and to a reduced number of cloud-elements in Cumulus cong. and Cb, the $SO_4^=$-concentration is reduced by a factor of about 5 in these convective cloud types.

This means that the $SO_4^=$-concentration within clouds originating from the solid phase is 10 times higher than that part of the $SO_4^=$-concentration which originates from rainout from the gas-phase. Owing to high SO_2-concentrations near the ground this ratio is reversed for the washout mechanism as described in the previous chapter.

Conclusions

We found the following relation for the total $SO_4^=$-concentration in rain (under inclusion of

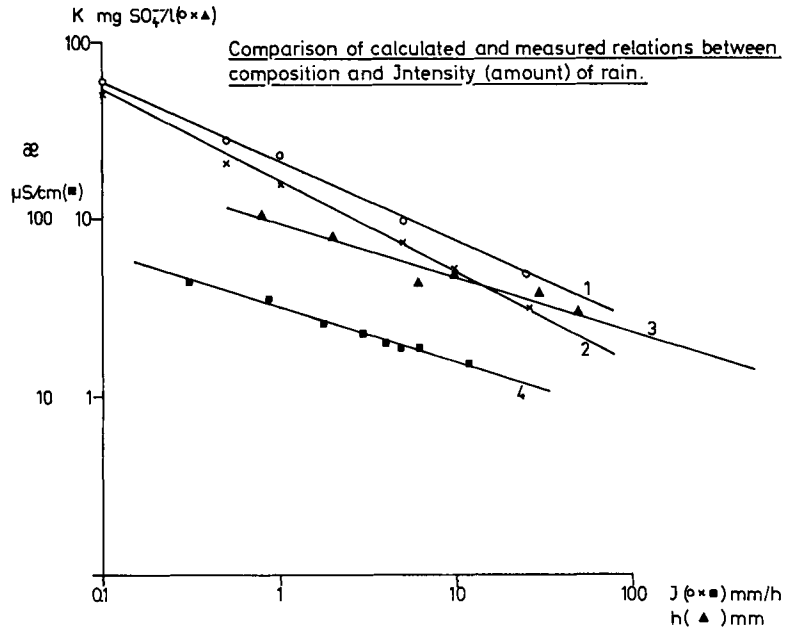

Fig. 3. Comparison between calculated and measured relation between composition and intensity resp. amount of rain. I, Intensity (mm/h); h, amount (mm); K, concentration of trace-substances in rain (mg/l); $\varkappa$, electrolytical conductivity of rain (μS/cm).

Curve 1: $K = K_0\left(\frac{I}{I_0}\right)^{-0.4}$

Curve 2: $K = K_0\left(\frac{I}{I_0}\right)^{-0.5}$

} calculated

Curve 3: $K = K_0\left(\frac{h}{h_0}\right)^{-0.28}$ (Kl. Feldberg/Taunus)

Curve 4: $\varkappa = \varkappa_0\left(\frac{I}{I_0}\right)^{-0.3}$ (Frankfurt/Main)

} measured

rainout and washout of sulfate-particles) to the intensity of rain:

$$K = K_0\left(\frac{I}{I_0}\right)^{-0.4},$$

where $K_0 = 21$ mg SO_4/l for $I_0 = 1$ mm/h.

The slight change of the exponent of this expression compared to the power function governing washout of only SO_2 is not very significant. This is also demonstrated by curve 1 in Fig. 3. Generally rainout and washout of sulfur-components can be described by a power-law. The value of the exponent depends on the relation of gaseous matter to particulate matter incorporated in the droplets as well as on the ratio rainout to washout. The relation between the concentration K and the rain-intensity I confirms earlier measurements under atmospheric conditions carried out by Georgii (1965).

The evaluation of continuous records of the electrolytical conductivity of rainwater made during a number of showers showed that the concentration of ions in rainwater decreased with increasing rain-intensity in all cases. The electrolytical conductivity is proportional to the number of ions in the solution and by this a good indicator for ion-concentration. On the average this relation can be expressed by the equation:

$$\varkappa = \varkappa_0\left(\frac{I}{I_0}\right)^{-0.3},$$

where $\varkappa_0 = 32$ μS/cm for $I_0 = 1$ mm/h.

However it must be stressed that this relation represents the entire composition of rain-water including all soluble inorganic trace-constituents in rain-water and not only sulfur-compounds as in our laboratory-experiments and in

our calculations. Under this consideration the agreement is remarkable. This relation is shown in Fig. 3, curve 4.

Analyses of the sulfate-ion concentration in rainwater were made during individual rainfalls in Frankfurt/Main and on the Taunus Observatory Kleiner Feldberg. After splitting up the 156 individual analyses obtained in Frankfurt and the 62 analyses from the mountain observatory into six different categories according to the quantity of rain we determined the average sulfate-concentration for each of these groups. We found that the relation between quantity of rain of individual cases and $SO_4^=$-concentration can be described by a power function with an exponent of -0.28 for the rainfalls collected on the mountains (see curve 3 in Fig. 1):

$$K = K_0 \left(\frac{h}{h_0}\right)^{-0.28},$$

where $K_0 = 8.6$ mg $So_4^=/l$ for $h_0 = 1$ mm.

The values ascertained from the Frankfurt analyses do not obey exactly a power-law, but show a sharper decrease of the $SO_4^=$-concentration at rain-quantities below 2 mm than at higher quantities. This may be explained by a transposition of two power-functions with different exponents in accordance with the relationship between trace-substance concentration and rainquantity for heavily polluted atmospheres as outlined by Georgii (1965).

We can summarize the results of our computations on rainout and washout of SO_2 and of sulfate-containing aerosol-particles by Table 5 giving the individual contributions of the gaseous and particulate sulfur-compounds for the total $SO_4^=$-concentration in rainwater measured at ground-level:

Table 5. *Contribution by gaseous and particulate sulfur-components to the $SO_4^=$-concentration in rainwater*

	Sulfur dioxide	Sulfate-aerosols
Rainout	5 %	20 %
Washout	70 %	5 %

It must be mentioned once again that the contribution of the gas-phase strongly depends on the vertical distribution of SO_2. It only amounts to the above given percentage if the SO_2-concentration in the lowest 1000 m of the atmosphere exceeds the SO_2-concentration in higher layers of the atmosphere significantly. The distribution of sulfate-containing aerosols in the atmosphere also determines the above given percentages. Since very little information on the vertical distribution of sulfate-aerosols in the troposphere is available present investigations by the authors aim at obtaining data on the concentration of sulfate-aerosols in the lower 5 km of the atmosphere. Our present results also show that in a "pure atmosphere" rainout of aerosols becomes of predominant importance for the chemical composition of rainwater.

Our investigations on rainout and washout are now continued with different trace-gases. With respect to SO_2 they conclusively demonstrate that the gas-phase must not be ignored when the chemical composition of rainwater is considered.

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ИССЛЕДОВАНИЕ ВКЛЮЧЕНИЯ ДВУОКИСИ СЕРЫ В КАПЕЛЬКИ ТУМАНА И ДОЖДЯ

Представлены результаты экспериментального исследования вымывания и выпадения с дождем SO_2 в капельках тумана и дождя. Лабораторные исследования были дополнены модельными расчетами концентрации сульфатов в дождевой воде, вызванной вымыванием и выпадением SO_2 и сульфатных аэрозолей. Показано, при каких обстоятельствах выпадение, соответственно, вымывание, становятся определяющими для химического состава дождевой воды на поверхности земли.