

Praca przeglądowa

Leszek Rogalski

**TRANSFORMATIONS OF SULFUR
COMPOUNDS IN THE AEROSPHERE**

**Chair of Air Protection and Environmental Toxicology
University of Warmia and Mazury**

**SOURCES OF SULFUR COMPOUNDS
IN THE AEROSPHERE**

According to KOMARNISKY and others, sulfur compounds belong to the most common aerospheric pollutants. In the troposphere, the lowest layer of the earth's atmosphere, sulfur originates predominantly from natural processes and anthropogenic sources. It usually occurs in the form of dioxide and trioxide, aerosols, sulfuric acid, sulfates (mainly ammonium sulfate), hydrogen sulfide and many other volatile compounds. On the global scale, the mass of sulfur compounds emitted to the atmosphere as a result of anthropogenic activities is similar to the mass of these compounds emitted from natural sources. However, in the urbanized and industrialized areas in Europe and North America natural processes account for 10% of sulfur emission only (FALKOWSKA, KORZENIEWSKI 1998).

NATURAL SOURCES OF SULFUR COMPOUNDS IN THE AEROSPHERE

Sulfur compounds, in the form of hydrogen sulfide and sulfur dioxide, are emitted to the aerosphere during explosive volcano eruptions (SCHÖNWISE 1997). Another major source of these compounds are processes of organic matter decomposition and reduction of inorganic sulfur compounds, e.g. biological reduction of sulfates (HENRY, HIDY 1980) taking place in both marine (oceanic) and terrestrial environments. In the marine environment such processes can be observed first of all in relatively shallow shelves and sandbanks, and in the terrestrial environment – in peatlands, swamps, inland lakes and other sites where anaerobic conditions dominate. During these processes considerable amounts of hydrogen sulfide and some other gaseous sulfur compounds are emitted to the aerosphere, where they oxidize to sulfur dioxide.

A minor, but an important source of sulfur compounds in the aerosphere are sulfate aerosols of marine origin. They may be emitted to the aerosphere from sea and ocean surface. The processes of marine aerosol generation include direct and indirect mechanisms. The direct ones are sea-foam entrainment and spray dispersion on the surface of refracting waves, whereas the indirect processes are all phenomena leading to the formation of gas bubbles in the surface layer of the sea. Marine aerosols are composed of chlorides – 88.7%, and sulfates – 10.8% (FALKOWSKA, KORZENIEWSKI 1998). However, they contain not only sea-salt sulfates, but also sulfates of terrestrial origin (FITZGERALD 1991, O'DAWID et al. 1997).

High atmospheric SO₂ concentrations are also caused by the oxidation of dimethyl sulfide – DMS (chemical formula: (CH₃)₂S), emitted from the sea where it is produced by phytoplankton (NGUYEN et al. 1988, SIMO 2001). This compound is a component of seaweeds containing dimethyl sulfone propionate, a basic constituent of organic matter. Its role has not been investigated in detail yet, but it probably controls osmotic pressure in cells (NGUYEN et al. 1988). Three ways of DMS formation in sea-water are already known:

- from damaged cells formed during seaweed consumption by zooplankton,
- during cell metabolism,
- in the process of phytoplankton population aging (DMS concentrations are different for particular species) (NGUYEN et al. 1988).

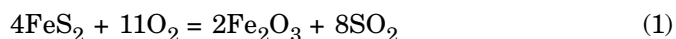
The final effect of SO₂ and DMS changes in the aerosphere is their oxidation to sulfates (CHARLSON et al. 1987, O'NEILL 1998). The atmospheric concentration of dimethyl sulfide is lower than its water concentration, because this compound is reactive and easily undergoes oxidation to sulfur dioxide. It is present in the atmosphere for about one day only (TUNER, LIS 1983).

Terrestrial environments can also be natural sources of sulfate sulfur in the air. Due to wind erosion in dry steppes some amounts of sprayed flowers of sulfur get into the air from the soil surface. Quantification of sulfur compound emission from natural sources is undoubtedly a very difficult task.

ANTHROPOGENIC SOURCES OF SULFUR COMPOUNDS IN THE AEROSPHERE

Considerable quantities of sulfur, in the form of various compounds, are emitted to the atmosphere from anthropogenic sources. The dominant group among those are sulfur oxides emitted as a result of combustion of solid, liquid and gaseous fuels. Major sources of their emission are also the steel industry, oil mining and processing, the chemical industry (processing of sulfur and its compounds), transportation and road traffic, non-ferrous metallurgy and the building industry (KUCOWSKI et al. 1997). The contribution of motor transport in total sulfur compound emission does not exceed 3% (MERKISZ 1994).

All natural fuels, i.e. hard coal, brown coal, petroleum and products of its distillation, and natural gas, contain some amounts of sulfur in the form of organic and inorganic compounds. However, the sulfur content of these fuels is different, depending on their type. For instance, in Poland the average sulfur content of hard coal varies from 0.7 to 3.0%, of brown coal – from 0.6 to 1.2%, of petroleum – from 0.5 to 3.0%. Natural gas contains small amounts of this element, although the sulfur content of some gas deposits may be high. According to rough estimates, approx. half of sulfur contained in hard coal has the form of pyrite (FeS_2), the rest are organic sulfur compounds. During pyrite oxidation SO_2 is formed according to the following reaction:



Considerable quantities of sulfur dioxide are emitted to the atmosphere during ecological catastrophes and military operations. For instance, large quantities of this compound – 4 Mg SO_2 (SCHÖNWISE 1997) were emitted to the air during the Persian Gulf War, when enormous amounts of petroleum were combusted. At present huge quantities of SO_2 are emitted to the air from burning oil-wells.

TRANSFORMATIONS OF SULFUR COMPOUNDS IN THE AEROSPHERE

Sulfur compounds emitted to the atmosphere undergo numerous physical and chemical changes, according to various mechanisms. MAJ (1980) states that authors differ in their opinions on the mechanism of SO₂, and especially H₂S, oxidation in the air, because these changes are significantly affected by many known and unknown factors, such as e.g. daily and seasonal cycles. The courses of reactions are also influenced by the kind and concentration of sulfur compounds, temperature, air humidity, intensity and type of radiation, turbulent diffusion, the presence of other pollutants, e.g. metallic oxides, hydrocarbons and nitrogen oxides, and – according to RYABOSHAPKO et al. (1996) – the duration of their persistence in the aerosphere.

Sulfur dioxide changes in the aerosphere take place mainly under the influence of atmospheric oxygen. Two processes, photochemical and catalytic, play a fundamental role in these changes. The photochemical process takes place in the gaseous phase, and the catalytic one – in the liquid phase. Both these processes lead to the formation of aerosol of sulfuric acid and sulfates.

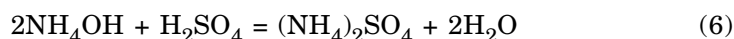
The course of photochemical SO₂ oxidation is as follows:



- * – excited molecules,
- hν – quantum of ultraviolet solar radiation,
- O₃ – chemically active and toxic gas (4).

Ultraviolet radiation plays an important role in this change. SO₂ molecules absorb near ultraviolet quanta ($\lambda > 300$ nm) and enter into the excited state, easily reacting with atmospheric oxygen. The reaction has several stages, and its products are sulfur trioxide (SO₃) and ozone (O₃). Sulfur trioxide absorbs water vapor, forming molecules of sulfur acid, where sulfur has the form of sulfate ions. This reaction can be accelerated by the presence of nitrogen dioxide, ozone or peroxides in the air. If this were the only reaction taking place in the aerosphere, the half-life of sulfur dioxide would be about 30 days. However, the values recorded during investigations are different. According to WEBER (1970), the half-life of SO₂ in the aerosphere is 4 to 5 days, whereas according to PINES (1977) – 30 minutes to 38 hours. There is a close correlation between solar

radiation intensity and sulfur dioxide oxidation (BRICARD 1977). Catalytic oxidation is believed to play a more significant role in the formation of sulfur acid aerosol in the aerosphere. This reaction takes place in the liquid phase, and its course is probably the following: SO_2 dissolved in water drops oxidizes in the presence of catalysts, e.g. salts of Fe, Al., Mn, Cu and other. Spengler MAJ (1980) found that SO_2 oxidation is strongly affected not only by catalysts, but also by pH. For instance, sulfates are not formed in the presence of $1 \mu\text{g Fe}\cdot\text{ml}^{-1}$ at $\text{pH} = 2$. At $\text{pH} = 2.5$ $60 \mu\text{g}$ sulfate ions are formed, and at $\text{pH} = 5$ $150 \mu\text{g}$. Furthermore, according to the Henry's law, water solubility of SO_2 increases with an increase in its atmospheric concentration and a decrease in temperature (KASINA 1981). In the catalytic process light has no effect on oxidation rate, which is affected by the presence of ammonia in the air. In the absence of ammonia oxidation rate is two orders of magnitude lower. Ammonia, passing from the air to the solution, forms ammonium hydroxide which dissociates into NH_4^+ and OH^- ions. The liberated OH^- ions bind H^+ ion excess, which increases the solution pH and accelerates SO_2 oxidation. These processes result in the formation of ammonium sulfate, according to the reaction:



Three kinds of sulfuric acid salts with ammonium ions have been identified in the aerosphere, i.e.: NH_4HSO_4 , $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ and $(\text{NH}_4)_2\text{SO}_4$ (BROSSET 1978). The presence of calcium sulfate, magnesium sulfate and heavy metal sulfates in the aerosphere has been also confirmed (KASINA 1981).

The results of previous studies show that with increasing height above the sea level SO_2 concentration is reduced much faster than SO_4^{-2} concentration, which is less variable (GEORGH 1970). The half-life of SO_4^{-2} is much longer than the half-life of SO_2 ; according to PINES (1971), it can be 43 days long. It was also found that the presence of NO_2 in the aerosphere intensifies SO_2 photooxidation, whereas the presence of NO significantly inhibits the formation of aerosols (MADELAINÉ and oth. 1972, KASPER-GIEBEL, PAXBAUM 1999). The mechanism of the process taking place in the presence of nitrogen dioxide is the following: irradiated nitrogen dioxide absorbs radiation whose wavelength is shorter than 366 nm, and disintegrates into nitrogen dioxide and oxygen atom:

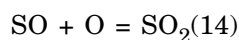
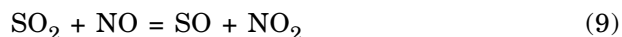


If there is SO_2 in the air, it can oxidize to sulfur trioxide:



MAJ (1980) proved experimentally that in the absence of NO_2 photochemical oxidation of SO_2 (at $\lambda > 300 \text{ nm}$) does not produce aerosol particles in the numbers that could be recorded, whereas in the presence of NO_2 this process leads to the formation of measurable quantities of aerosols. This suggests that reactions with NO_2 are of primary importance in

the formation of condensation nuclei in photochemical changes of SO_2 in the aerosphere. The courses of such changes in the presence of NO_x are most probably as follows:



M – molecule acting as a third body receiving excess energy.

The reaction between SO_2 and NO_2 does not play a major role in this system, as its rate constant is very low. The yield of reactions between atomic oxygen and SO_2 increases with an increase in the $\text{SO}_2 : \text{NO}_x$ ratio. At high values of this ratio, the reaction between atomic oxygen and sulfur dioxide is the dominant. The results obtained by MAJ (1980) show that if the $\text{SO}_2 : \text{NO}_x$ ratio is close to one, the rate of reactions between atomic oxygen and sulfur dioxide is 10 to 20-fold lower than the rate of reactions between nitrogen oxides and atomic oxygen.

The reaction between sulfur dioxide and ozone is also characterized by low efficiency; in the process of SO_2 transformations (SO_2 removal from the atmosphere) a significant role is played by the products of reactions between ozone and nitrogen dioxide (WILSON, LEVY 1970). Reactions in the system SO_2 -hydrocarbons often lead to the formation of aerosols characterized by a disagreeable odor and adverse effects (RADWAŃSKA 1973). Sulfur dioxide, entering into reactions with methane, ethane, propane, *n*-butane and *n*-pentane, forms colorless or pale-yellow non-volatile oily liquid with an unpleasant odor. It was found that SO_2 transformations in the presence of unsaturated hydrocarbons (which are common constituents of polluted atmosphere) do not decide about aerosol formation. If ozone is produced during photochemical oxidation of SO_2 in the presence of unsaturated hydrocarbons, its effects will be visible in the formation of aldehydes and ketones.

The reason for fast changes of sulfur dioxide in the air can be the reactions taking place between SO_2 and different radicals (alkyl, alkoxy and other) in the gaseous phase. CALVERT et al. (1971) proved empirically that methyl radicals easily bind to SO_2 , forming CH_3SO_2 , which in turn attach to double bonds of azomethane. It is possible that such reactions can initiate the formation of aerosols in polluted atmosphere. The main product of the whole complex of photochemical reactions is H_2SO_4 (WILSON, LEVY 1970).

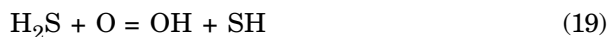
Hydrogen sulfide, containing the most reduced form of sulfur, is rarely present in the air. Some authors are of the opinion that hydrogen sulfide easily undergoes transformation to SO_2 in the process of oxidation in the presence water and oxygen (TUGGLE 1972).



However, in the case of insufficient oxygen supply hydrogen sulfur oxidation is incomplete, and elementary sulfur is produced instead of sulfur dioxide:



Sulfur dioxide can enter into further reactions with water and ammonia, to form $(\text{NH}_4)_2\text{SO}_4$. In the gaseous phase H_2S is not able to react directly with molecular oxygen (O_2) or ozone, but undergoes oxidation with atomic oxygen:



This reaction is followed by a chain of further changes, resulting in the formation of SO_2 , SO_3 , H_2SO_4 , H_2 and H_2O , characteristic of photochemical smog.

Catalytic oxidation of hydrogen sulfide in the aqueous phase may take place in the presence of fog droplets or in clouds. Hydrogen sulfide is partly water-soluble, and in the presence of molecular oxygen (O_2) and trace quantities of transition metals (i.e. scandium group, titanium group, vanadium group, chromium group, manganese group, etc.) it may undergo oxidation to sulfates. Hydrogen sulfide oxidation with atomic oxygen is also possible. Under normal conditions this process may be very slow, but it seems that in higher tropospheric layers hydrogen sulfide easily undergoes oxidation due to relatively high concentrations of atomic oxygen (FRIEND 1973). In solutions (cloud drops) H_2S may be oxidized by ozone (IRIBARNE, CHO 1988):



This reaction results in the occurrence of acid rains that have a harmful effect on the natural environment.

DWORAK (1994) reported that the major constituents of the atmosphere of Venus and Mars are drops of concentrated sulfuric acids, with additions of other acids, mainly hydrochloric (HCl) and fluorosulfuric (HSO_3F).

CONCLUSIONS

1. There are many sulfur compounds of various origin in the atmosphere, undergoing physical and chemical changes according to certain mechanisms which have not been described in detail yet, despite numerous successful attempts. Therefore, there is a need for further investigation of these transformations.

2. Sulfur compounds present in the aerosphere form atmospheric pollutants whose dry or wet deposition results in acidic precipitation and deposition, having a harmful effect on the biosphere.

3. Transformations of sulfur compounds in the aerosphere are also modified by other factors, including climatic ones, discussed in another paper.

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Leszek Rogalski, Leszek Lenart

OCCURRENCE OF SULFUR COMPOUNDS IN THE AEROSPHERE

Key words: sulfur compounds, sources of emission, transformations in the aerosphere, atmospheric pollution, aerosols.

Abstract

The paper presents the main natural and anthropogenic sources of sulfur compounds, the proportion of these compounds in natural fuels and their emission to the aerosphere. Particular attention was paid to conditions of photochemical and catalytic oxidation in the air, as well as the behavior of sulfur compounds in the aerosphere. The transformations of sulfur compounds and their reactions with other compounds or elements contribute to air pollution, including the formation of tropospheric ozone and acid rains.

WYSTĘPOWANIE ZWIĄZKÓW SIARKI W ATMOSFERZE

Słowa kluczowe: związki siarki, źródła emisji, przemiany chemiczne, zanieczyszczenie powietrza, aerozole.

Abstrakt

Praca zawiera opis głównych, naturalnych i antropogenicznych źródeł związków siarki, zawartości takich związków w paliwach naturalnych i emisji atmosferycznych pochodzących ze spalania tych paliw. Szczególną uwagę skierowano na warunki fotochemicznego i katalizowanego utleniania siarki w powietrzu oraz zachowanie się związków siarki w atmosferze. Przemiany chemiczne związków siarki oraz ich reakcje z innymi związkami lub pierwiastkami powodują zwiększone zanieczyszczenie powietrza, łącznie z takimi zjawiskami jak tworzenie się ozonu w troposferze oraz powstawanie kwaśnych deszczy.