COMPUTER SIMULATION OF ACID RAINS

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Abstract. *One of the key problems of the present global ecodynamics is a study of conditions for acid rains formation and their prediction. For the first time, this problem was widely discussed at the 28th General Assembly of the International Unit on Theoretical and Applied Chemistry held in Madrid in September, 1975. Subsequent conferences and various international programs made it possible to accumulate data and knowledge in this sphere. It follows from them that sulphur compounds emitted to the atmosphere from natural and anthropogenic sources are an important precursor of acid rains strongly damaging the environment. Sulphur resides in the atmosphere mainly in the form of gas-phase SO_2 and H_2S as well as sulphate ion SO_4^{2-} .*
Keywords: *acid rains, prediction, computer simulation.*

Introduction

Sulphur dioxide is a basic precursor of acid rains. Its concentration at the surface level is estimated at 1 μg m^{-3}. The participation of SO_2 in the acid rains formation is realized in two ways: through dry deposition onto a wet surface and formation of H_2SO_4 directly in the atmosphere with subsequent deposition either onto the surface or in water basins. Sulphur dioxide reacts with water and gives sulphuric acid:

$$SO_2 + H_2O + 1/2\ O_2 \rightarrow H_2SO_4 \qquad (1)$$
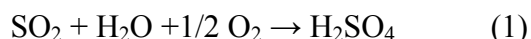
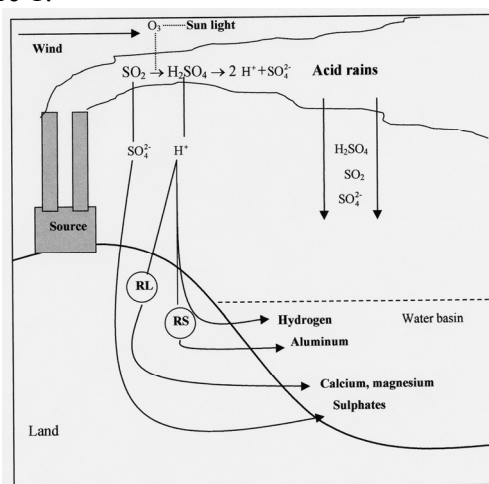Schematically these processes are shown in Figure 1.

Figure 1. The conceptual scheme of the impact of anthropogenic sulphur emissions on the aquatic medium quality.

Notations for the figure 1:
- RL – reactions with limestone minerals;
- RS – reactions with aluminum-containing silicate minerals.

The SO_2 residence in the atmosphere depends strongly on the way of its removal. Due to dry deposition, SO_2 is removed from the atmosphere during 7.6 day, and due to its transformation into SO_4^{2-} - during 13 days. The rate of dry deposition depends on the type of surface and many other environmental parameters. This rate averages 2 cm·s^{-1} over land and 0.9 cm s^{-1} over the ocean. Due to the combination of the processes of SO_2 removal from the atmosphere its residence can shorten to 4.8 day.

A simplified formula of acid rain is:

$$acid\ rain = H_2O + SO_2 + NO_2 \qquad (2)$$

Natural and anthropogenic emissions of SO_2 to the atmosphere are responsible for 60-70% of acid rains over the globe. Deposition from the atmosphere of excessive sulphate is estimated at 360 Tg·yr^{-1} at an average rate of their emission to the atmosphere 110 Tg·yr^{-1}, with 31% of excessive sulphate in case of rain water being of anthropogenic origin. On the whole, the anthropogenic sources emit to the atmosphere >90% S. Such sources are:
- coal burning (coal contains 2-3% S, and its burning gives SO_2);

- oil burning and its refining (the power of sulphur sources is 4-5 times lower than in case of coal burning);
- ore melting to obtain metals, such as copper, nickel, and Zink;
- volcanic eruptions;
- organics decomposition;
- weathering the sulphur-containing rocks (~15 $Tg \cdot yr^{-1}$);
- input of sulphur to the atmosphere with sea spray (~45 $Tg \cdot yr^{-1}$);
- fertilization of soil with sulphates and their subsequent input to the atmosphere with dust (~10 $Tg \cdot yr^{-1}$);
- aviation and car engines.

Natural sources of sulphur compounds in the form of hydrocarbons, dimethylsulfide (DMS), carbonyl sulfide, and methyl mercaptan include soils, marshes, forests, volcanoes, hydrosphere and agricultural soils. It is known that from the World Ocean surface DMS gets to the atmosphere and is rapidly oxidized to give sulphates residing in the atmosphere in not more than five days. From available estimates, volcanoes emit annually to the atmosphere from 4 to 16 million tons of sulphides (recalculated for SO_2). The sulphur-containing compounds form also as a result of geothermal activity and living organisms' activity on land and in water. Rivers bring sulphur to seas and oceans ~100 $Tg \cdot yr^{-1}$. Natural sources of sulphur are rather small. For instance, in the USA and Canada emissions of sulphur products from natural sources constitute, respectively, not more than 4 and 18% of total emissions of sulphur.

The model of sulphur cycle in the environment

The spectrum of anthropogenic sources of sulphur compounds is diverse and varies with an addition of new names. Sulphur is known to be present in many useful minerals, such as coal, oil, iron, copper, and other ores. Their use by man leads to emissions of sulphur to the atmosphere despite the use of purification devices. The main by-product of industrial processes and fossil fuel burning is sulphur dioxide. For instance, in the USA, SO_2 emissions are distributed by the types of sources as follows: electric power stations – 67%, fossil fuel burning – 3%, industrial enterprises – 15%, transport – 7%, and other sources – 8%. On a global scale, these indicators vary strongly both in space and in time. In particular, in Canada, in contrast to the USA, electric power stations emit 20% SO_2, whereas non-ferrous metallurgy gives 43% SO_2. On the whole, in Canada the industrial enterprises are the main source of SO_2 (74%). It should be noted that the sources of sulphur in the USA are responsible for more than 50% of acid rains in the Canada territory, and territories bordering the Quebec province get up to 75% of acid rains due to SO_2 emissions in the USA. By different estimates, the transboundary SO_2 transport from the USA to the Canada territory varies within 3.5-4.2 million tons per year.

In most countries, with the intense use of petroleum, the problem of acid rain is closely connected with economic problems. The current sorts of petroleum contain sulphur from 150 to 600 ppm. The economic losses because of acid rains force the developed countries to work out technologies to obtain petroleum with a low content of sulphur.

The structure of sulphur dioxide emissions is similar in various countries. In Germany the share of heat power stations and boiler-houses constitutes about 90% of total emissions of sulphur dioxide, and the share of industrial enterprises and transport reaches only 7.5% and 2.5%, respectively. Emissions of sulphur compounds to the atmosphere in high latitudes are of clearly seasonal nature.

Getting to the atmosphere from different sources in a given territory, sulphur compounds can be transported by air masses for long distances and deposit in other territories. It is clear that knowledge of spatial distribution of the concentration of sulphur compounds with the meteorological information taken into account will make it possible to predict acid rains. The expert system ESPhAP which takes into account a totality of the models of the atmospheric transport of pollutants, and the model of sulphur cycle in the environment included into ESPhAP

as an independent unit, make such predictions possible. Of course, certain limitations appear here connected both with the limited global database and with the absence of some functional descriptions. This difficulty can be overcome with the use of the global simulation model (GSM) within which the sulphur cycle is parameterized with due regard to the role of many sub-systems of the biosphere and anthropogenic processes. Moreover, an inclusion of the sulphur unit to GSM broadens its functions, since it is dictated by the dependence of biotic processes on the content of sulphur in the biospheric compartments. Available data on supplies and fluxes of sulphur compounds in the atmosphere, soils, vegetation cover, and hydrosphere enable one to formulate mathematical relationships to simulate the global sulphur cycle.

On a global scale, the sulphur cycle is a mosaic structure of local fluxes of its compounds with other elements produced due to water migration and atmospheric processes. The conceptual schemes of global and regional sulphur cycles have been described in detail by many authors [1], [2], [3]. However, the available models have been designed for autonomous functioning and application, which does not permit to include them in the GSM without substantial changes in their parametric spaces. Here is one of the solutions for this problem.

Sulphur as a non-metal is widely spread in nature and is one of the components of global biogeochemical cycles. From the viewpoint of humans, sulphur belongs to elements which can negatively affect the vital media. The harmful impact of sulphur on the environment is manifested mainly through acid rains. The water basins acidity due to acid rains and subsequent transport of sulphur compounds with the runoff from adjacent lands are one of such manifestations.

Processes causing the acidification of water basins are mainly connected with anthropogenic sources of sulphur and, of course, other chemical elements such as nitrogen. In the pre-industrial period, the acidity of inland water basins had not exceeded pH=8, as a rule. With the growing anthropogenic impact on the environment the water basins acidity increased overcoming for many of them the level pH=5.7 in the middle of the last century. At present, in the zones of high industrialization the natural water basins acidity reaches pH <5. The increasing trend of acidity causes serious problems of the fish reserve control. Many lakes and rivers in North America and Europe have been excessively acidified, and therefore the aquatic biota in them has suffered irreversible changes. For instance, in the USA [5] about 4.2 % of lakes and 2.7% of river systems are in a state when their capability to neutralize a high acidity in a natural way is equal to zero. The chronic excess acidification of water basins (pH<5.2) leads to irreversible changes in ecosystems.

As seen in Fig. 1, many factors affect the composition of water, among them of importance being vegetation cover and type of soils in the aquatic system's basin. Therefore to solve the problem of their acidity regulation all factors should be considered in complex, which is only possible with the use of numerical models. Experimental technologies cannot be used for this purpose due to unique character of natural systems. Acid rains are a serious cause of the forests damage, especially coniferous forests. As a rule, forests grow in the regions with sufficiently high amount of rains and, hence, can get large dozes of harmful elements with acid rains which damage leaves and pine-needles as well as change the soil composition. At $pH \in [2; 2.6]$ the vegetation productivity lowers drastically, and at $pH \leq 2$ young sprouts get withered. On the whole, at $pH \in [0.5]$ there appears a danger of acid rains and changes in the parameters of soil-plant formations. The level of danger depends on the climatic zone and the type of the soil-plant formation. At $pH \geq 5.6$, precipitation does not threaten the environment.

The soils of most forests have $pH \in [3.2, 5.5]$. This interval is provided by stability of ion-exchange processes in soil, which preserves the living conditions for the root systems of trees. An excess in soil of cations H^+ affecting the leaching of nutrients as well as the conversion of

unsoluble aluminum compounds to soluble ones leads to a substitution of ion-forming centres and, hence, external conditions for the root system get strongly violated.

On the whole, for the global assessment of the role of acid rains, the respective data base is needed which would characterize the regional level of pH and give the structure of pH-forming processes. Fragments of such a data base are formed in many developed countries, but it is not enough for parameterization of the global pattern of acid rains formation. As shown in [4], such data are collected, for instance, for the territory of India. Using data of observations of the rains composition in India for the period 1984-2002, Safai et al. [4] found out that in rainy seasons the content of SO_4 and NO_3 in rain water is steadily growing over many regions of India, but the pH level remains within the interval of alkalinity. Such data and knowledge of the values of trans-boundary fluxes of sulphur make it possible to calculate the pH levels with due regard to the growth of industrial production and development of transport. Another example of data base accumulation for acid rains control is an analysis of trends in changes of SO_2 and SO_4^{2-} concentrations in the atmosphere over the urban territories of the western and mid-Atlantic regions of the USA for the period 1990-1999. Here of importance is an assessment of the spatial variability of these concentrations (30-42%), which makes it possible to more reliably calculate the parameters of the respective equations in biogeochemical units in the models of the atmospheric aerosol transport.

The model of global sulphur cycle (MGSC) proposed

The model of global sulphur cycle (MGSC) proposed here is a unit of GSM with inputs and outputs compatible with other units of the global model. In contrast to hydrogen, sulphur compounds cannot be attributed to long-lived elements of the biosphere. Therefore in the unit of sulphur the spatial digitization of its natural and anthropogenic reservoirs should be planned to reflect the local distributions of sulphur in the vicinity of its sources and to enable one to estimate the intensities of the inter-regional fluxes of sulphur compounds. The version of the sulphur unit proposed here, in contrast to the known hydrodynamic models of the long-distance transport, takes into account the fluxes of sulfur compounds between the hydrosphere, atmosphere, soil, and biota. The model does not consider the vertical stratification of the atmosphere. The characteristics of sulphur fluxes over land and oceans averaged vertically are calculated. The spatial digitization of the biosphere and the World Ocean corresponds to the criterion inherent to the GSM. The block-scheme of the model of the biogeochemical cycle of sulphur is shown in Fig. 2, a description of the fluxes of sulphur compounds is given in Table 1. This scheme is realized in every cell Ω_{ij} of the Earth's surface and in every compartment Ω_{ijk} of the World Ocean. The interaction between the cells and the compartments is organized through the climate unit of the GSM. Therefore the equations of the sulphur unit lack the terms reflecting the dynamic pattern of the spatial transformation of the sulfur reservoirs. With due regard to notations assumed in Fig. 2 and in Table 1, the equations describing the balance relationships between the reservoirs of sulphur compounds are written in the form of the system of ordinary differential equations [1]
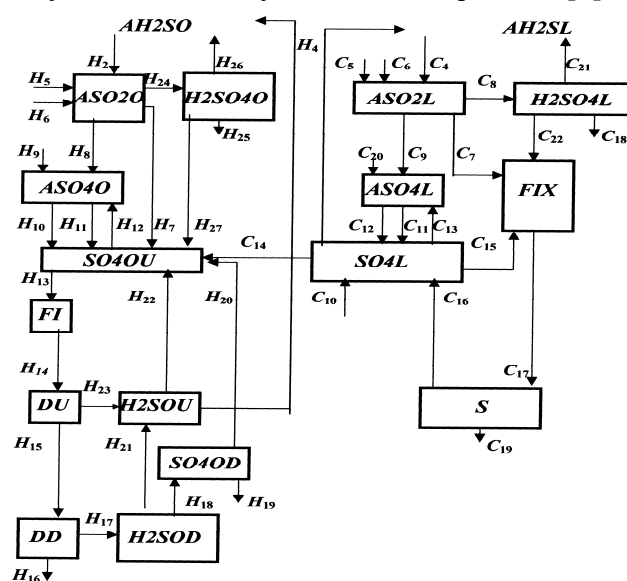

Figure 2. The scheme of sulphur fluxes in the environment considered in the MGSC.

Table 1. Characteristics of the land and hydrospheric fluxes of sulphur shown in Fig. 2. Assessments of fluxes (mg m^{-3}day^{-1}) obtained by averaging over the respective territories

Sulfur flux	Land		Hydrosphere	
	Identifier	Estimate	Identifier	Estimate
Volcanic eruptions				
H_2S	C_1	0.018	H_3	0.0068
SO_2	C_5	0.036	H_5	0.0073
SO_4^{2-}	C_{20}	0.035	H_9	0.0074
Anthropogenic emissions				
H_2S	C_2	0.072	H_1	0.00076
SO_2	C_6	0.92	H_6	0.038
SO_4^{2-}	C_{10}	0.47		
Oxidation of H_2S to SO_2	C_4	1.13	H_2	0.3
Oxidation of SO_2 to SO_4^{2-}	C_9	1.35	H_8	0.16
Dry sedimentation of SO_4^{2-}	C_{12}	0.37	H_{11}	0.11
Fall-out of SO_4^{2-} with rain	C_{11}	1.26	H_{10}	0.38
Biological decomposition and emission of H_2S into the atmosphere	C_3	1.03	H_4	0.31
Assimilation of SO_4^{2-} by biota	C_{15}	0.41	H_{13}	1.09
Biological decomposition and formation of SO_4^{2-}	C_{16}	1.13	H_{17} (H_{23})	0.43(0.12)
Sedimentation and deposits	C_{18}	0.22	H_{15} (H_{25})	0.98 (0.036)
	C_{19}	0.11	H_{16} (H_{19})	0.55 (0.0076)
Wind-driven return to the atmosphere	C_{13}	0.25	H_{12}	0.33
Replenishing sulphur supplies due to dead biomass	C_{17}	0.86	H_{14}	1.1
Assimilation of atmospheric SO_2	C_7	0.46	H_7	0.18
Washing-out of SO_2 from the atmosphere	C_8	0.27	H_{24}	0.061
River run-off of SO_4^{2-} to the ocean	C_{14}	1.17		
Transformation of gas-phase H_2SO_4 to H_2S	C_{21}	0.018	H_{26}	0.0076
Assimilation of the washed-out part of atmospheric SO_2 by biota	C_{22}	0.036	H_{27}	0.015
Oxidation of H_2S to SO_2 in water medium			H_{18} (H_{22})	0.045(0.19)
Advection of SO_2			H_{20}	0.38
Advection of H_2S			H_{21}	0.37

The GSM sulphur unit, like all units of biogeochemical cycles, has the similar level of accuracy of parameterization like other GSM units, and therefore there is no deregulation of the global model, and the stability of results of simulation experiments is ensured. To check this stability, we have undertaken some numerical experiments, taking the parameters of

the sulphur unit from [1] and assuming $\Delta\varphi = 4^{o}$, $\Delta\lambda = 5^{o}$, $\Delta z_1 = 10$ m, $\Delta z_2 = 100$ m. As follows from Fig. 3, an enhancement of initial sulphur supplies affects the system's dynamics during first two years, whereas a decrease of initial data prevents the system's output to a stationary regime during five years.
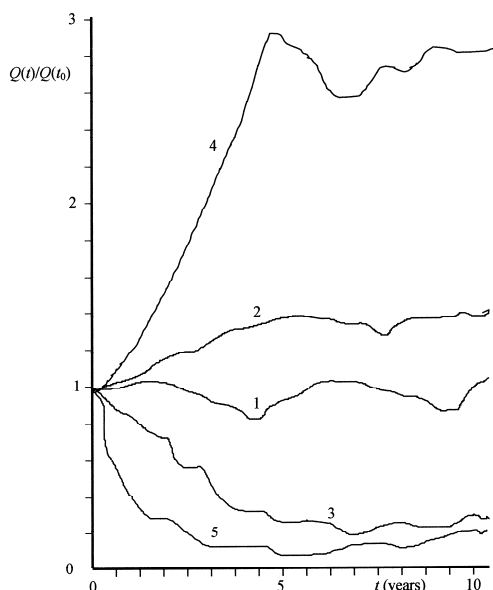

Figure 3. Dependence of dynamics of sulphur concentrations $Q(t)/Q(t_0)$, normalized to initial conditions averaged over Ω on initial conditions: 1-initial conditions correspond to standard data; 2- reduced by 50%; 3-increased by 50%; 4- reduced by70%; 5-increased by 70%.

The curves in Fig. 4 are marked with the time after the beginning of the experiment. pH is calculated with the formula $pH = lg\, H^{+}$.

The curves in Fig. 4 characterize the dependence of acid rains on the level of anthropogenic activity. Calculations have shown that the pH value of precipitation stabilizes, on the average, during 30 days from the moment of changing the regime of anthropogenic emissions of sulphur. The spatial distribution of pH of rains with an even increase of the fluxes of C_2, C_6, C_{10}, H_1 and H_6 by 0.2% $year^{-1}$ does not markedly change during 3 years. The ratio of acid rains rates for latitudinal bands $70^{o} - 90^{o}N$ and $70^{o} - 90^{o}S$ remains, on the average, at a level of 2.5.
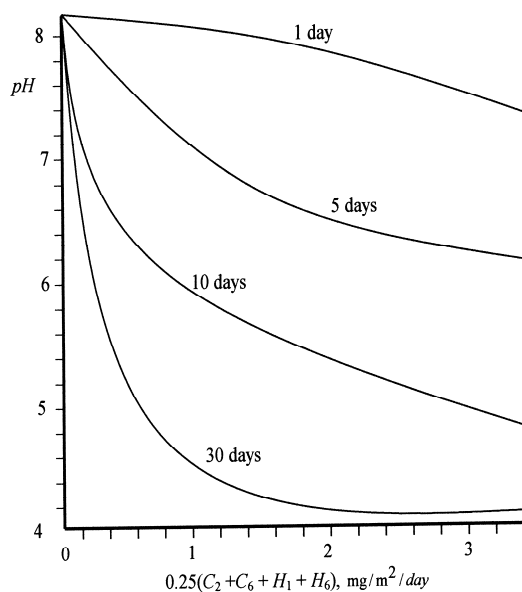

Figure 4. Dependence of average acidity of rain on anthropogenic sulphur fluxes. Change of anthropogenic activity is assumed to be homogeneous in all territories.

Of interest is an estimate of the contribution of various regions to the Arctic pollution. With the stable state of the mean annual concentration of gas-phase H_2SO_4 in the arctic atmosphere assumed to be 100%, the shares of participation in the formation of this level are as follows: the USA – 17%, Canada – 21%, Europe – 37%, and the eastern territory of Russia – 25%. These estimates correlate with the structure of anthropogenic sulphur fluxes prescribed by the scenario of anthropogenic activity and determined by the relationship of all parameters of the global sulphur cycle. As seen from Figure 5, the intensity of the biological decomposition in water is distributed non-uniformly, and this means that hydrocarbon production in the oceans is a function of the vertical structure of their ecosystems. For instance, in the Indian Ocean there are two distinct maxima of H_2S production. A weak second maximum of hydrocarbon appears at depths ~1.5 km in the Atlantic Ocean. In other oceans, one maximum of the vertical distribution of H_2S is observed.
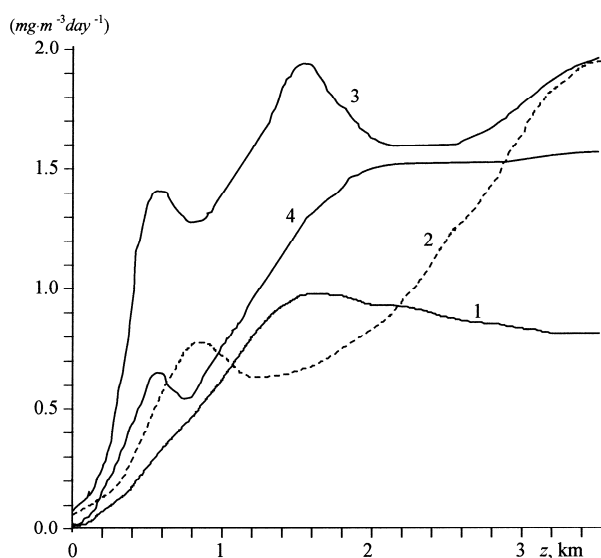
Figure 5. Average production of H$_2$S (mg m^{-3} day^{-1}) in the oceans: 1 0 the Arctic Ocean; 2 – the Pacific Ocean; 3 – the Indian Ocean; 4 – the Atlantic Ocean.

Conclusions

The above numerical modeling has shown that a reliable assessment of the spatial distributions of pH levels depends on many factors, among which the accuracy of parameters in equations of the MGSC unit and the form of its referencing to GSM are important and decisive. To increase the reliability of acid rains forecast, it is necessary to further improve the MGSC unit by filling it with new biogeochemical cycles of other chemicals, such as carbon bisulfide and sulphurous anhydride. Consideration of only sulphur dioxide, sulphates and hydrocarbon in the models of global sulphur cycle limits the accuracy of these models. Unfortunately, most of international and national programs on studies of sulphur cycle are confined to these elements.

References

[1] Kondratyev K.Ya., Ivlev L.S., Krapivin V.F., and Varotsos C.A. (2006) *Atmospheric aerosol properties*. Springer/PRAXIS, Chichester UK, London, 852 pp.

[2] Nitu C., Krapivin V.F., and Pruteanu E. (2004) *Intelligent Systems in Ecology*. Onesti, Bucharest, 410 pp

[3] Nitu C., Krapivin V.F., and Bruno A.(2000) *System modeling in ecology*. Printech, Bucharest, 260 pp.

[4] Safai P.D., Rao P.S.P., Momin G.A., All K., Chate D.M., and Praveen P.S. (2004) *Chemical composition of precipitation during 1984-2002 at Pune*, India. // *Atmospheric Environment,* vol.38, no.12, pp. 1705-1714.

[5] Stoddard J.L., Kahl J.S., Deviney F.A. et al. (2003) *Response of Surface Water Chemistry to the Clean Air Act Amendments of 1990*. U.S. Environmental Protection Agency, EPA/6201R-02/04, New York, 92 pp