Localization of sulfur dioxide and sulfate sources using back trajectory analysis and data of local monitoring

O.M. Zhukova,[1] V.P. Kabashnikov,[2] B.B. Kozeruk,[1] V.N. Kuz'min,[3]
N.S. Metelskaya,[2] and A.P. Chaikovskii[2]

[1]*Republican Center of Radiation Control and Monitoring of Environment, Minsk, Belarus*
[2]*Institute of Physics, Belarus National Academy of Sciences, Minsk, Belarus*
[3]*ECOMIR Republican Scientific and Technical Center, Minsk, Belarus*

Received April 17, 2008

The residence time method is used to determine for each element of the area under study the concentrations of sulfur dioxide and sulfates, which on the average are recorded at the monitoring station under condition of the preliminary passage of the analyzed air masses over this area element. The calculated concentration fields reflect the degree of influence of different regions on the state of air environment; they were used for localization of the regions, responsible for pollution of air basin of the Berezinsk reserve (republic Belarus) by sulfur dioxide and sulfates. The error, arising from a limited amount of the monitoring data on the concentration field, was estimated. Since the regions with a high concentration can be considered as probable admixture sources, the calculated fields of annually mean concentrations of sulfur dioxide and sulfates were compared with EMEP expert data about the spatial distribution of sulfur dioxide emission rates in 2004. The calculated distributions of concentration well agree with the EMEP data. The arising discrepancies, possibly, are associated with the processes of chemical conversion of sulfur dioxide on the way from the source to the receptor station.

Introduction

Sulfur dioxide is one of the most important atmospheric pollutants. Its main sources are fossil fuel combustion, oxidation of organic substances in soils and ocean, volcanic eruptions, and biomass burning.[1] The SO_2 lifetime in the atmosphere ranges from one to a few days and is determined by the dry and moist deposition, as well as its conversion to sulfate particles.[2] The sulfate particles are among the primary aerosol components, which scatter light in the visible spectral range and deteriorate the atmospheric transparency. They increase the Earth's albedo, favoring the reduction of the incoming solar energy flux and the change of the climate.[3] Under continental conditions, practically all sulfate particles are formed from sulfur dioxide.[4] Characteristic conversion times of sulfur dioxide to sulfates depend on the humidity, the presence of ammonium and other admixtures in the atmosphere, and may range from a few hours in the moist polluted atmosphere to a few days in clean dry air.[2] Expected lifetime of sulfates in the atmosphere is 1–2 weeks.

At present, in many countries the emissions of sulfur-containing gases are analyzed and systematized with indication of the emission rates and location of emission sources. However, the large-scale pattern of emissions at areas, including several countries, is made, as a rule, on the basis of expert estimates,[5] because the national data do not always contain all the necessary information. Therefore, the data, obtained by some independent way, may be of interest. Note that the influence of pollution sources on the air quality at some region-receptor is determined not only by their emission rates and distance from the receptor, but also by the processes of their chemical transformation, associated with conditions of the pollution transport. The purpose of our study is identification of the main geographic regions, being the sources of sulfur dioxide and sulfates and estimation of the degree of their influence on the content of these admixtures in air in the region of the station of background monitoring in the Berezinsk biospheric reserve, located 100 km to north-east from Minsk (Belarus).

Presently, the so-called method of residence time is widely used to detect the source-regions of airborne pollutants.[6–8] Input parameters for this method are monitoring data on the admixture content for a long time period (e.g., one or a few years) and a set of back trajectories of air masses arriving at the monitoring site at the times of concentration measurement. It is assumed that the air mass, passing at quite low altitude (mainly, within the atmospheric boundary layer (ABL)) over emission source territory, intercepts the pollutant and carries it on. On the way, the pollutant concentration reduces through diffusion, deposition, and chemical conversion.

A single trajectory carries no information about the place, where the pollutant was trapped on the way of the air mass motion. However, by means of statistical processing of the monitoring data and back trajectories, it is possible to determine certain relation between the concentration level at the monitoring site and areas, over which the air masses had passed before its arrival at the monitoring site; thereby, it is possible to identify regions causing the elevated

0235-6880/08/11 842-06 $02.00

pollutant concentration at the monitoring site. The considered method was used to detect source regions of sulfur dioxide,[7,10,11] nitrogen oxide,[11] ozone,[12] acid precipitation,[13] aerosols,[9] and sources and sinks of CO_2 [Ref. 14] and radioactive ^{7}Be [Ref. 15].

Method of calculation and initial data

When applying the method of residence time, the geographic region, surrounding the monitoring site (receptor), is divided into cells by a grid. Let i, j enumerate the geographic coordinates (longitude and latitude) of the cell (i, j) center. To each cell, an average concentration P_{ij}, is assigned, which is at the receptor provided an air mass has passed above the considered cell:

$$P_{ij} = \sum_{l=1}^{L} c(l)\tau_{ij}(l) \Big/ \sum_{l=1}^{L} \tau_{ij}(l), \qquad (1)$$

where l enumerates the trajectories passed over the (i, j) cell; L is the total number of trajectories; $c(l)$ is the concentration of admixture, which is recorded at the receptor at the moment of arrival of the lth trajectory; $\tau_{ij}(l)$ is the residence time of the lth trajectory above the territory of the (i, j) cell. The parameter P_{ij} has a simple physical meaning of the concentration occurring at the receptor on the average, if the air mass passed above the territory of the (i, j) cell prior to arrival to the receptor. Cells with a high P_{ij} are considered as probable pollution sources.

We used the data on near-ground concentrations of sulfur dioxide and sulfates, measured at the background monitoring station in Berezinsk biospheric reserve (Belarus) from October, 2004 to July, 2007. The diurnal sampling proceeded from 09.00 LT of the day, to which the measurements were assigned, till 09.00 LT of the next day. More than 1000 measurements were used. The concentrations at the receptor were assumed constant throughout the sampling period.

The trajectories were calculated, using data on the wind and temperature field in the Northern Hemisphere, presented by Republican Hydrometeorological Center of the Republic Belarus. These data are arrays of horizontal (along latitude and along meridian) components and the vertical component of the wind speed, as well as arrays of temperature and height of standard isobaric surfaces with a grid step of 2.5° at moments of 00.00 and 12.00 UTC. Fields of the horizontal wind are specified on standard isobaric surfaces of 1000, 925, 850, 700, 500, 400, 300, 250, 200, 150, 100, 75, and 50 hPa. The fields of vertical wind speed and air temperature are specified on isobaric surfaces of 1000, 850, 700, 500, 300, and 200 hPa.

For period from October, 2004 to August, 2005, the data on vertical component of the wind speed were lacking. For that period, the vertical wind speed was calculated from data on the temperature and the horizontal speed under assumption of the flow adiabaticity.[16] Data of Republican Hydrometeorologic Center were also added by calculations of wind speed inside ABL at three intermediate surfaces between 1000 and 925 hPa. To do this, the methods of parameterization of ABL characteristics were used,[17,18] which require as input data the heights of isobaric surfaces of 1000, 850, and 700 hPa, air temperatures at these surfaces, and surface roughness heights.

The trajectory equation of physically infinitesimally small liquid particle has the form[19]:

$$\mathrm{d}X/\mathrm{d}t = V\big[X(t),t\big], \qquad (2)$$

where t is the time; X is the vector of the particle position; and V is the wind velocity.

The algorithm of numerical solution of equation (2) at the time step Δt has the form[19]:

$$X(t_1) \approx X(t_0) + \frac{1}{2}\Delta t\Big(V(X(t_0),t_0) + V(X(t_1),t_1)\Big), \qquad (3)$$

where subscripts 0 and 1 indicate the initial and final instants of the time step. Equation (3) was solved by iterations, because the coordinates of the point, at which the particle arrives after time Δt are *a priori* unknown. Speeds outside the spatiotemporal grid nodes of the initial data were calculated using the time linear interpolation and the space beta-spline second-order interpolation.

Using the program, developed by us, we calculated five-day 3D back trajectories for the monitoring site of the Berezinsk reserve (indicated by star in Fig. 1).

To each concentration, averaged over diurnal interval, we assigned back trajectories, starting from the monitoring site 4 times daily: at 12.00, 18.00, and 24.00 LT of the current day and at 06.00 LT of the next day. In each start, there were three trajectories, beginning at heights of 975, 950, and 850 hPa, approximately corresponding to geometric heights of 200, 430, and 1350 m. Relative contribution of each of these three trajectories to the content of the observed pollutant was assumed proportional to the time of residing each trajectory within ABL over all territories.

An example of the calculated trajectories is presented in Fig. 1, which gives the so-called “dirty” trajectories, along which in warm seasons (May – October) the receptor site received air masses at a height of 950 hPa during days with SO_2 concentration, exceeding its mean value by more than a factor of two. Overall 224 such trajectories were recorded over the considered time period. Totally, 1648 trajectories were recorded in warm seasons and nearly the same amount in cold seasons for each of three above-indicated heights.

Calculated results

The sulfur dioxide and sulfate contents in air of the Berezinsk reserve have a pronounced seasonal behavior. The concentration of these substances is much higher in winter months than in summer ones, therefore, the annually mean capacity of the sources is approximately equal to the capacity of winter munths. Consequently, for brevity, we consider only annually mean sources and sources of warm seasons.

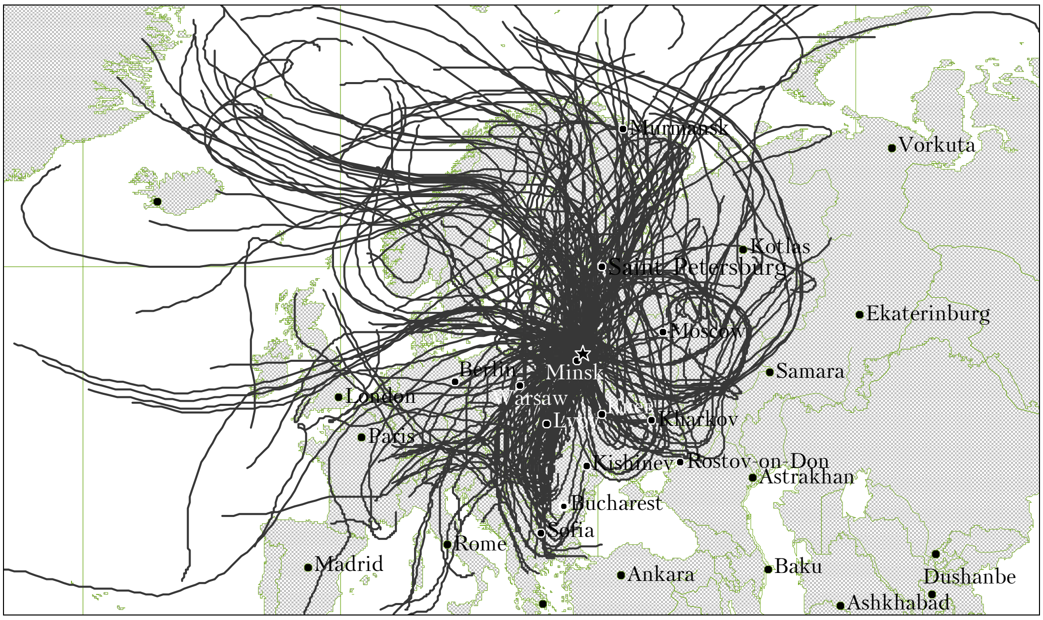


Fig. 1. Trajectories of polluted air masses, arrived at the Berezinsk reserve in warm seasons at a height of 950 hPa.

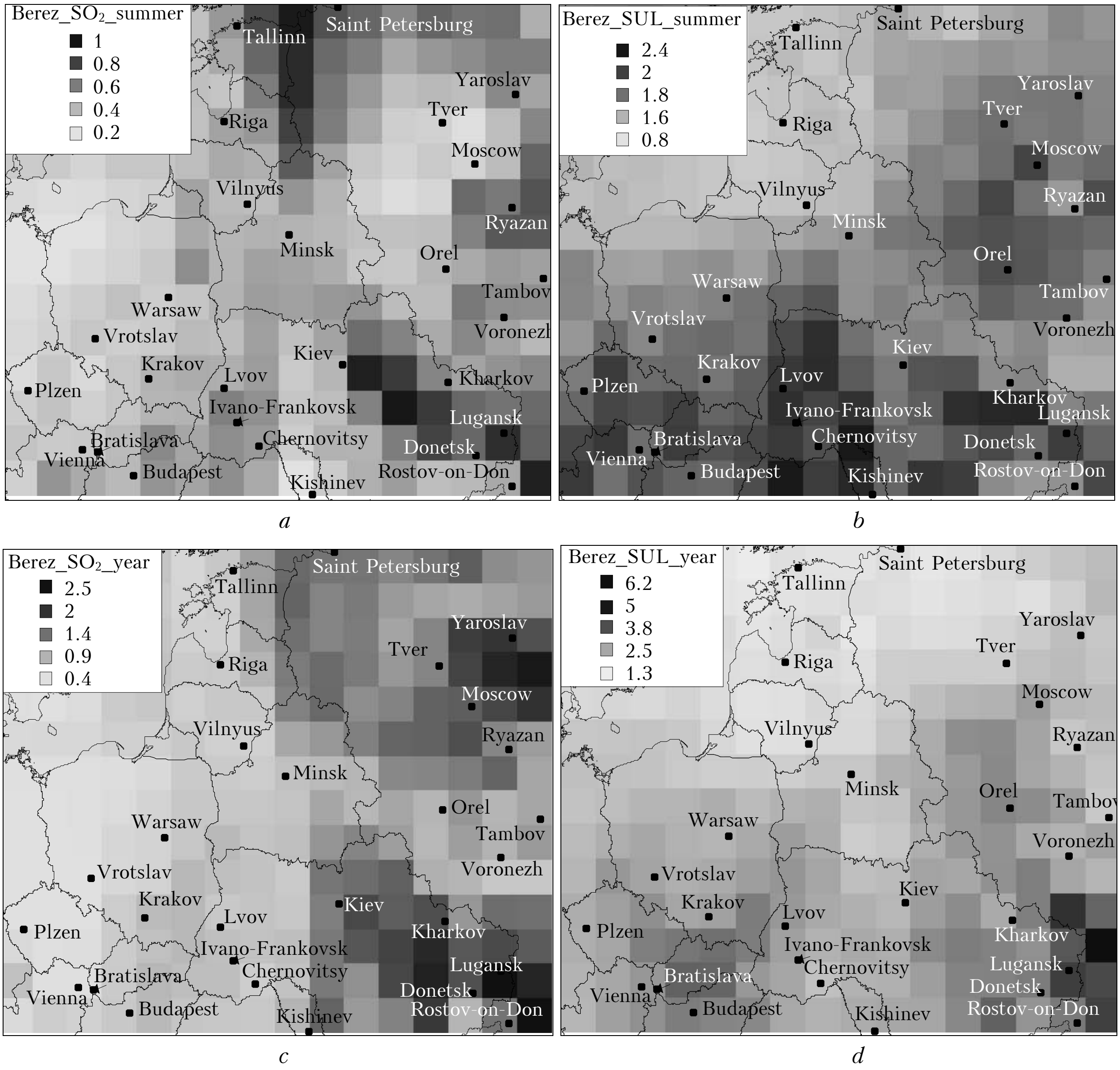
Using the method of time residence, for each grid cell we found such P_{ij}, which is recorded, on the average, at the monitoring site provided that the analyzed air masses have preliminarily passed over the territory assigned to this cell. Figure 2 presents the results of the use of formula (1) for calculation of P_{ij} field from data on sulfur dioxide and sulfate contents in air of the Berezinsk reserve.

The concentration is taken in μg/m^3. The grid cell size is 2° and 1° (by longitude and latitude, respectively), that corresponds approximately to 133 × 110 km at the Minsk latitude. Each cell, presented in the map, was traversed by no less than 30 trajectories. Figures *2a* and *b* present the sources of sulfur dioxide and sulfates, respectively, for warm seasons. It is seen that in summer months the largest concentrations of sulfur dioxide in the Berezinsk reserve are brought by air flows from industrial regions of Ukraine, the region of Saint Petersburg – Tallinn, and the region of Moscow. The increased sulfate concentrations were caused by sources, located in Ukraine, Romania, Slovakia, Czechia, Poland, as well as in the Moscow region. Figures 2*c* and *d* present annually mean sources of sulfur dioxide and sulfates, respectively. Annually, the primary areas, responsible for the increased sulfur dioxide concentration, are those, which are located to the east, north-east, and south-east of the Berezinsk reserve, especially regions of Moscow and the Donetsk basin region. Sulfate sources of the less intensity are nearly uniformly distributed in south and east sectors, centered in the Berezinsk reserve.

Keeping in mind that the regions with sulfur dioxide and sulfate high concentrations can be considered as probable pollution sources, the calculated fields of annually mean concentrations of the matters can be compared with EMEP expert data[5] on the spatial distribution of emission rates of sulfur dioxide in 2004 (Fig. 3).

Comparing Figs. 3 and 2*c* and *d*, we can conclude that the EMEP data on the location of SO_2 emission sources in the region of Moscow, south-east, south, and west of Ukraine, and south of Poland approximately agree with ours. Since sulfates are formed from sulfur dioxide, the sources of sulfur dioxide and sulfates are to coincide. Partly this is true, mainly, for summer conditions. However, the sulfate sources of the Moscow region affect the Beresinsk reserve much weaker than the sulfur dioxide ones. They are more distinct only in summer. Possibly, this is because the dry air in summer months comes from the east regions more frequently and on the way from Moscow to Berzinsk reserve, lasting 1–1.5 days, sulfates have no time to be formed.

The calculated concentration fields and EMEP data on emission rates of sulfur dioxide most notably disagree for the south of Poland. The EMEP data suggest that just there are the most powerful sources of sulfur dioxide. However, their effect is weak in the Berezinsk reserve. As is seen from Fig. 1, west winds rarely bring extrimely polluted air. The air masses from the south of Poland, on average, bring sulfur dioxide in small concentrations. Possibly, this is because the west winds are moist, in which sulfur dioxide is rapidly transformed to sulfuric acid or sulfates. However, figures 2*c* and *d* show that the south of Poland does not refer to most intense sources of sulfates. Possibly, the most amount of SO_2, emitted in this region, is captured by cloud droplets, leading to reduction of both SO_2 and sulfate concentrations in air. The same argument is used by *Rúa* et al.[11] to explain why Spanish monitoring sites do not fill the effect of powerful sulfur dioxide sources, located on British islands.



a *b*

c *d*

Fig. 2. Spatial distribution of conditionally averaged concentrations of sulfur dioxide (to the left) and sulfates (to the right). Data relate to warm seasons (top) and annually mean data (bottom).

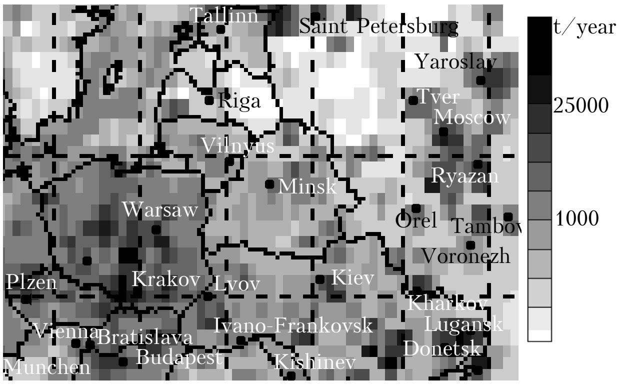


Fig. 3. Spatial distribution of emission rates of sulfur dioxide sources in 2004 according to the EMEP expert data.

P_{ij} uncertainty caused by a limited volume of monitoring data

The results of calculations of P_{ij} fields depend on a particular sample from the concentration monitoring data and the corresponding trajectories. The estimate of uncertainty of P_{ij}, calculated from the final sample of P_{ij} (and, hence, random), could be the variance of P_{ij} arising from the passage to other samples of the same volume. However, we have a unique set of monitoring data and trajectories. In this case, to estimate the variance of P_{ij}, the bootstrapping method[20] can be used.

This method implies the formation of repeating samples with substitution inside the same original sample. Let there be an original sample of volume N. We create a new sample. To do this, in the original sample we randomly select (with the $1/N$ probability) data of a certain single measurement, duplicate them, and place the copy in a new sample in such a way that the initial sample is not destructed. Iterating this operation N times, we obtain a new sample of the volume N, in which certain data from the original sample may be missed, while some other data may be met more than once.

Calculate the P_{ij} field from the new sample. It will differ from the P_{ij} field of the original sample. Iterating this procedure many times, we obtain different P_{ij} values, which will allow us to find average values and variances of P_{ij}.

The calculations terminate, when the maximal change of the standard deviation during next 100 repetitions turn out to be less than 0.5%. The calculation results on the fields of the variation coefficients, expressed in percent, are presented in Fig. 3 for annually mean sources of sulfur dioxide and sulfates.

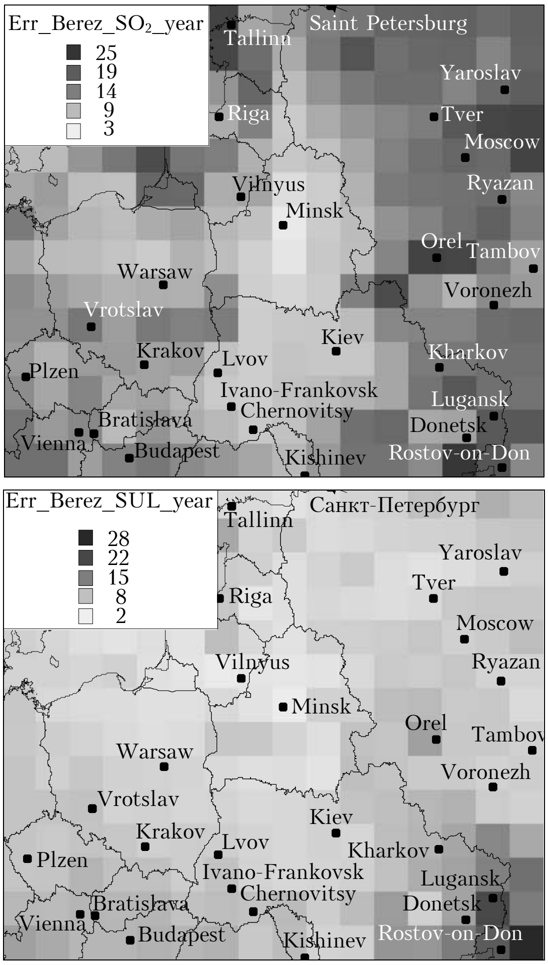


Fig. 4. Spatial distribution of variation coefficients of concentration fields (in percents), presented in Figs. 2*c* and *d*.

The variation coefficients characterize the uncertainty of P_{ij}, caused by the limited volume of the monitoring data. The variation coefficients of P_{ij} decrease with the increase of the data volume and the number of trajectories passing over the selected cell. The fluctuations and uncertainty P_{ij} are maximal in cells far removed from the receptor, because, for a fixed data volume, the shorter the distance between the cell and the receptor, the greater the number of trajectories passing over the cell. The uncertainty, associated with the limited data volume, will affect weaker the results, if the standard deviations are much less than the mean P_{ij} in the cell. As is seen from Fig. 4, in case of annually average sources of sulfate dioxide and sulfates, the uncertainty does not exceed 25–30% (10-15%) for most sulfate dioxide (sulfate) sources, except for the south-east of Ukraine, characterized by an uncertainty of 26%.

Conclusion

Using the residence time method, for each element of the area we found such a concentration, which, on the average, is recorded at the monitoring site, provided that the analyzed air masses preliminarily have passed over this element of the area. Thus, we found the geographic regions responsible for the episodes of increased concentration of sulfur dioxide and sulfates in the Berezinsk reserve. We used the monitoring data obtained from October, 2004 to July, 2007. Tree-dimensional five-day back trajectories of air masses were calculated from fields of the wind velocity and temperature, provided for by the Hydrometeorologic Center of the Republic Belarus.

On the average, for this time interval, the main areas, responsible for increased sulfur dioxide concentration in Berezinsk reserve, are located to the east, north-east, and south-east of the Berezinsk reserve. Especially active are regions of Moscow and south-east of Ukraine. The highest sulfate concentrations were caused by sources of the Donetsk basin. Less intensive sulfate sources are nearly uniformly distributed in south and east sectors, centered at the Berezinsk reserve.

The calculated fields of annually mean concentrations of sulfur dioxide and sulfates mostly agree with distribution of sulfur dioxide emission rate from EMEP expert data. The calculated concentration fields and EMEP data on sulfur dioxide emission rates most considerably disagree in the south of Poland, where the EMEP data indicate the most powerful sulfur dioxide sources. However, the air masses, arriving at the Berezinsk reserve from the south of Poland, are characterized by low concentrations of sulfur dioxide and sulfates. Probably, the west winds are most often cause clouds and the elevated air humidity. As well, a considerable part of SO_2, emitted in the south part of Poland, is captured by cloud droplets, that decreases both SO_2 and sulfate concentrations in air.

The error caused by a limited volume of the monitoring data, was estimated by the bootstrapping method. The error increases with the distance from the monitoring site. This paper presents data for the area, where the error was largely 10–20% and reached 38% only in areas, sufficiently far removed from the monitoring site.

Acknowledgements

This work is partially supported by ISTC (Grant B-1063).

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