Analysis of the sources of aerosol particles in the atmosphere over Siberia based on measurements of the organic carbon

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The content of organic carbon in atmospheric aerosol was determined in the aerosol samples collected at two sites in Southwestern Siberia and at three sites in Northwestern Siberia. According to many-year observations, the mean mass concentration of the submicron fraction of atmospheric aerosol at the sampling sites in Southwestern Siberia is about 16 μg/m^3. The averaged data on the organic carbon concentration in the samples from Klyuchi and Karasuk for the period since January 2000 until October 2002 give the value of 2.7 μg/m^3. The fraction of the ozone reactions in oxidation of hydrocarbons leading to generation of the aerosol mass of organic carbon was estimated to be up to 20%. For the sampling sites in Southwestern Siberia, no tendency is observed in the dependence of the standard deviation on the concentration. At the sampling sites located in the Northwestern Siberia, the lower is the measured carbon concentration the higher is nonuniformity (fluctuations) in the data set. For this reason one can conclude that for the northern territories the major contribution to the organic carbon mass is due to the long-range transport, while local sources play a less significant role. For the southern regions, the situation is quite different, and this suggests that just these latitudes form the global/regional background, which affects the northern territories.

Introduction

The variability of the concentrations of atmospheric admixtures obeys a simple rule[5,6] that the longer is the admixture residence in the atmosphere the lower is the spatial and temporal variability of its concentration, and *vice versa*. The time of aerosol particles residence in the atmosphere is quite short and varies, depending on the size fraction, from 10 days to seconds. Since aerosol is a short-lived atmospheric admixture, the aerosol concentration is subject to intense time variations or fluctuations. Factors causing fluctuations of the aerosol concentration can be divided into regular and random ones.

The typical regular factors affecting the concentration of atmospheric aerosol include climatic factors. Thus, for example, as the seasons revolve, local sources of bioaerosol or erosive particles are seasonally suppressed. The diurnal variations of irradiation result in the variations of the rate of photochemical production of aerosols. On the other hand, the regular and predictable changes of the aerosol concentration are superimposed by the random variations, which, strictly speaking, should be called fluctuations, because they are processes obeying statistical laws based on the independence of data at different time.

Among the physical properties of an aerosol particle (AP), its lifetime in the atmosphere is of a particular interest. The lifetime determines how long the particle stays in the atmosphere and, if the source intensity is known, how high the quasistationary concentration of particles can be. The analytical relation between the AP lifetime and the particle size is described by the empirical equation[5]:

$$\frac{1}{T}=\frac{1}{C}\left\{\left(\frac{r}{R}\right)^2+\left(\frac{R}{r}\right)^2\right\}+\frac{1}{T_{\text{wet}}}, \tag{1}$$

where T is the particle lifetime; C is a constant (about 4 years); r is the particle radius; R is the radius of the particles with the longest lifetime (about 0.3 μm); T_{wet} is the longest particle lifetime determined by wet scavenging (for the lower troposphere it is about 10 days).

Though Eq. (1) is based on experimental data, its physical meaning is quite clear. Small particles coagulate quickly, while large ones are subject to gravitational sedimentation, so the lifetime of particles in the size range 0.1–1 μm is the longest.

Fluctuations of the concentration of atmospheric admixtures depend on their lifetime.[5,10] The longer lifetime corresponds to smaller variations of the concentration. The equation describing this dependence was derived by Jaenicke[6,8]:

$$\nu^2=\frac{1-\exp(-2T_{\max}/T)}{2[1-\exp(-T_{\max}/T)]^2}\frac{T_{\max}}{T}-1, \tag{2}$$

where ν is the relative standard deviation of fluctuations of the AP number density; T is the AP lifetime; $T_{\max}$ is a constant measured in the units of time.

The physical meaning of Eq. (2) can be explained as follows. If there are processes leading to random alternation of air masses at the measurement point (for example, turbulence), then the higher is the inhomogeneity of an admixture in a rather large volume, the stronger are the fluctuations of its concentration. Whence it follows that an admixture mixed uniformly in a rather large volume has the lower amplitude of fluctuations at a point. The longer is the lifetime, the better is mixing and the lower is the amplitude of concentration fluctuations. Anyway, Eqs. (1) and (2) can be thought empirical, based on the known experimental data.

According to Jaenicke,[5] 10 h $< T_{\max} <$ 30 days.

Because of the similarity of the natural and climatic conditions, as well as terrain over the Siberian territory, two regions have been chosen for the investigation: Western Siberia and Northern Siberia. The southern part of the West-Siberian Plain is characterized by a relatively plain terrain, low height above the sea level, and relatively low mean level of precipitation (250–700 mm a year).

There are several reasons for choosing the northern Siberian territories as a particular region for investigation. First, this region is closest to the Arctic and the study of aerosol properties in this region allows us to draw some conclusions concerning the nature of arctic aerosol – the so-called arctic haze. Second, since this region is hard to reach, only limited investigations with specific instrumentation can be conducted there.

It is of a particular interest to study the so-called blue haze phenomenon. This type of aerosol is observed over the territories with intense plant canopy (for example, rain forest). According to the current ideas, plants emit a great amount of volatile hydrocarbons (for example, terpenes), which take part in chemical atmospheric processes. These processes are induced by photochemistry, include nitrogen compounds (oxides), and lead to production of the low-volatile products, which condense and form aerosol particles.

Traffic, in principle, is one of the very important sources of admixtures in the urban atmosphere. Aerosol directly emitted by cars consists of particles being the products of incomplete combustion of fuel in the internal-combustion engines. An example of such an aerosol is the black plume behind Diesel-powered vehicles, especially, in winter.

The final industrial aerosol is formed by aerosol particles emitted by industrial objects: for example, soot emitted by boiling houses and electric power plants or cement kiln dust emitted by cement production plants.

In addition to aerosol particles, the traffic and industry emit great amount of gases, which can take part in the atmospheric chemical processes leading to production of aerosol. These processes are usually photoinduced, and therefore the aerosol produced in such processes mostly in large industrial centers is called photosmog. Examples of such reactions are the atmospheric cycles of nitrogen and sulfur. The nitrogen oxides NO_x are a forge of radicals for the following oxidation of many atmospheric components, in particular, sulfur compounds with S^{IV} to S^{VI}. As known, sulfates are low-volatile compounds forming the aerosol particles. Therefore, the sulfate aerosol is usually considered as a tracer of anthropogenic pollution of the atmosphere.

Instrumentation

As the initial data, we used the data on the element composition of particles measured in the following way:

The X-ray fluorescence analysis using synchrotron radiation (XFA-SR)[1] has been actively used since the early 1990s to study the composition of aerosol particles.[2,9] The measurements with the source of synchrotron radiation were conducted at the Center of Synchrotron Radiation of the Institute of Nuclear Physics SB RAS. The data were processed at the Institute of Chemical Kinetics and Combustion SB RAS.[2,7]

The content of organic and inorganic components of the aerosol substance was determined in the samples of atmospheric aerosol collected near Klyuchi village situated 30 km south of Novosibirsk and near Karasuk village located at a distance of 400 km southwest of Novosibirsk, as well as at three points in the northern part of Siberia. Aerosol was sampled onto glass-fiber filters at a flow rate of 1.4–1.8 m^3/h. Each of the sampling session took 24 h in every season (winter, spring, summer, and fall). The sampling periods lasted 20 to 30 days, during which 30–40 m^3 air was blown through each of the filters. In parallel with collecting samples for carbon analysis, sampling onto AFA-KhA filters was carried out for determination of the mass concentration by means of filter weighing before and after the exposure. The flow rate of air blowing through the AFA-KhA filters was 13 m^3/h during 24 h.

A quarter of the glass-fiber filter was analyzed to determine the concentrations of organic and inorganic carbon based on the catalytic conversion of organic compounds and elemental carbon into the methane with the following FID gas chromatography. This method is described in Ref. 3. Schematically, the ways of conversion can be presented as follows:

$$C_{org} \xrightarrow{\text{Ar, NiO, 700°C}} CO_2,$$

$$C_{inorg} \xrightarrow{O_2\text{, 700°C}} CO_2,$$

$$CO_2 \xrightarrow{H_2\text{, Ni, 300°C}} CH_4.$$

Results and conclusions

Although the process of formation of the aerosol mass can be caused by both heterogeneous and homogeneous condensation, the formation of low-volatile compounds is a must for any type of condensation. Analysis of the kinetics of aerosol formation still gave no evidence that the low-volatile aerosol can be formed from high-volatile components directly on the surface of aerosol particles due to the heterogeneous reactions.

To be noted are two components playing, according to the current idea, the key role in the processes of photooxidation in the atmosphere, namely, ozone (O_3) and sulfur oxides. The particular role of ozone is connected with the fact that ozone photodecomposition yields excited oxygen, which can lead to formation of OH radicals in reaction with the atmospheric water vapor. The OH radicals, in their turn, are believed to be the main participants of the atmospheric processes, since they are main oxidizing agents for almost any atmospheric admixtures.

The oxidation of sulfur is a very important process from the standpoint of the aerosol formation. The matter is that the compounds of quadrivalent sulfur do largely exist in a gaseous state in the atmosphere, while the compounds of hexavalent sulfur are much more reactive, and under conditions of competition among numerous atmospheric reactions they, nevertheless, lead mostly to the formation of sulfates. The saturation pressure of the sulfates vapor is extremely low, which results in the formation of sulfate aerosol particles.

An alternative way of using ozone as an oxidizing agent leading to the formation of aerosol particles is its participation in oxidation of unsaturated hydrocarbons. Presumably, this mechanism can take place over territories with high natural emission of unsaturated hydrocarbons. For example, plants emit large amount of terpenes (products of dimerization or trimerization of the isoprene) into the atmosphere. These hydrocarbons are unsaturated (including double bond), and their concentration can achieve quite high values over the territories with dense plant canopy (for example, rainforests and boreal forests).

Ozone, reacting with the double bond of unsaturated hydrocarbons, yields biradicals, the so-called Criegee radicals ($R^2O_2^{\cdot\cdot}$). These radicals, in their turn, can take part both in sulfur oxidation (yielding sulfate aerosol) and in the formation of organic aerosol particles, widely known under the name “blue haze.”

Assuming the formation of low-volatile compounds with their following (homogeneous or heterogeneous) condensation is the main mechanism of the aerosol mass formation, the described chemical gas-to-particle transformations can be divided into two groups that are different in principle (depending on the role of unsaturated hydrocarbons taking part in this process). The first group can be called OH-enriched. In this case, the OH radical is the main reagent leading to oxidation of the gas-phase inorganic compounds with the following formation of low-volatile compounds. An example of such a process is the oxidation of SO_2 to compounds of hexavalent sulfur (sulfates). In this case, hydrocarbons present in the atmosphere are involved in the reaction chains as suppliers of oxidizing radicals, that is, they can affect the rate and the ways of the reactions. However, these substances themselves finally degrade to CO_2 and are not involved in the aerosol mass.

The second group or type of reactions assumes the presence of oxidation reactions in the reaction scheme, for example, reaction of ozone with the double bond of unsaturated hydrocarbons. Once the ozone is attached through the double bond and the intermediate structure decomposes, Criegee radical or biradical[10] is formed. It is still unclear what happens then with these highly reactive compounds in the atmosphere. However, under laboratory conditions in the presence of unsaturated hydrocarbons, such as terpenes, and water, organic aerosol is produced[4] via the attack of the double bonds of hydrocarbons by Criegee radicals.

The use of analytical methods, which would allow us to determine the origin of hydrocarbon in the aerosol mass, can elucidate the relative importance of the reactions with the participation of ozone and unsaturated hydrocarbons in the process of formation of the submicron aerosol from the gas phase.

Based on the above ideas and the fact that the OH radical is the main atmospheric oxidizer, we should expect that hydrocarbons present in the atmosphere can serve only catalysts of the oxidation process, and their carbon finally exists in the form of CO_2. However, the ozone reactions with double bonds, which potentially lead to the presence of organic compounds in the submicron aerosol mass, also should be considered. Applying the described analytical technique, we analyzed the samples of atmospheric aerosol collected in different regions of the continental Siberia during several years.

Three of five sampling points were located in the northern sector of Western Siberia (Samburg, Tarko-Sale, and Krasnoselkup), while two others are in the south sector of the Western Siberia (Klyuchi and Karasuk). At two latter points, the submicron fraction of the atmospheric aerosol was continuously monitored. According to many-year observations at the sampling points in Chany and Klyuchi, the mean mass concentration of the submicron fraction of atmospheric aerosol was about 16 $\mu g/m^3$. These data were obtained both by weighing the filters and from the results of mathematical processing of nephelometric observations. The features of sampling for the following analysis of the organic carbon concentration suggest that analysis mostly deals with the submicron fraction. This conclusion is based on that the intakes were not designed for isokinetic sampling. At the nonisokinetic sampling, the efficiency of sampling the particles with the size greater than 10 μm is very low. However, the mass concentration of the coarse aerosol peaks just in this region (about 10 μm) in the case of representation of the particle size distribution according to Whitby’s theory.[11]

The averaged data on the organic carbon concentration in the samples collected in Klyuchi and Karasuk since January 2000 and until October 2002 gave the value of 2.7 $\mu g/m^3$. In the total mass of hydrocarbons, the carbon mass makes up a significant fraction, since the ratio of the molecular mass of carbon to hydrogen amounts to 12, and the ratio of the number of hydrogen atoms to carbon atoms in large unsaturated hydrocarbons tends to 2, but is always less than 4. Thus, the carbon mass in hydrocarbons makes up 60–80%.

All the above-said allows one to draw the following conclusion: despite the ozone reaction with the double bonds of hydrocarbons is not a dominant process, its fraction in the process of hydrocarbon oxidation is estimated to be up to 20% as high.

The standard deviation or fluctuations remain to be very informative parameters in meteorological and other atmospheric measurements. The idea is quite common that the longer is the lifetime of an admixture in the atmosphere (and, consequently, the higher is its homogeneity due to turbulent mixing), the lower are the fluctuations of its concentration.

Figures 1 and 2 show the dependence of the measured organic carbon concentration on the standard deviation in the array of the measurement data.

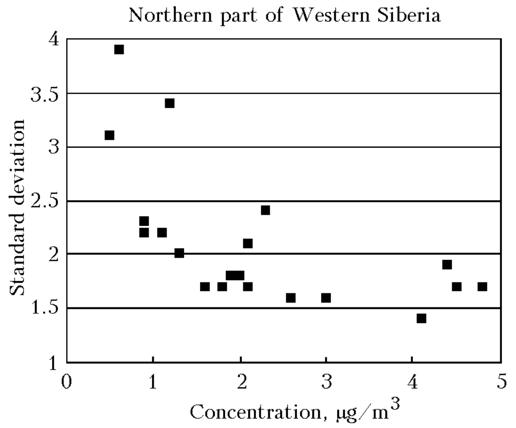

Fig. 1. Measured concentration of the organic carbon in aerosol particles as a function of the standard deviation of the array of measurement data collected at three points in the north.

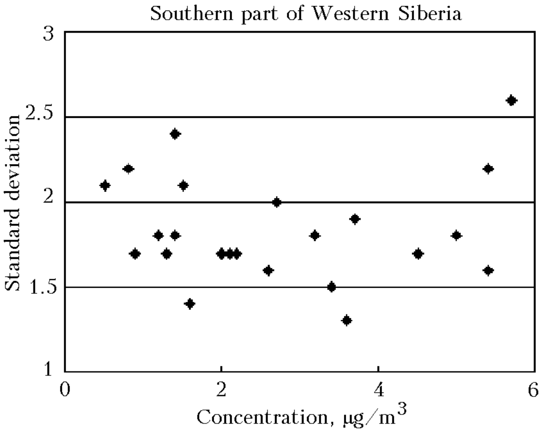

Fig. 2. Measured concentration of organic carbon in aerosol particles as a function of the standard deviation of the array of measurement data collected at two points in the south.

The difference between Figs. 1 and 2 is that Fig. 1 depicts the results measured at the three northern sites, while Fig. 2 gives the data collected at two southern sites. It is clearly seen that for the southern points located in the steppe zone of the Western Siberia there is no pronounced tendency in the concentration dependence on the standard deviation. At the northern points, we can see such a tendency. The dependence is the following: the lower is the measured carbon concentration the higher is the inhomogeneity (fluctuation) of the data. From the standpoint of simple logic, the situation should be quite contrary.

In the case of a well-established concentration field, the observer sees the global, well-mixed aerosol fraction with a relatively long lifetime and the low amplitude of fluctuation in the measured values. The sharp increase in the concentration, leading to the growth of the mean values, against the background of the established concentration can be caused by a local source. So, a relatively new aerosol with the short lifetime is observed. Therefore the fluctuations in the concentration increase.

Consider now the situation with the organic carbon concentration in the northern part of the Western Siberia. The only reasonable explanation can be reduced to the following. If there is a global background of aerosol particles with organic carbon and relatively long lifetime, then the fluctuations of the concentration are low and stable. The concentration is determined by the direction of the global transport at the measurement point. Thus, at the boundary of the Arctic region, the transport from the relatively clean regions of the northern latitudes leads to a decrease in the concentration, while the transport from the relatively polluted south results in a growth of the concentration. In this case, the amplitude of relative variations is constant and corresponds to that for the global atmospheric fraction.

The background value can be distorted by a local source, whose aerosol fraction has the short lifetime and high relative amplitude of variations. If the global fraction corresponding to the admixture transport from the relatively polluted southern regions exceeds the local source in the absolute value, then the variations of the local source turn out to be masked and manifest themselves only when the total concentration decreases down to the level caused by the local sources.

Thus, it can be concluded that in the northern territories the long-range transport processes are responsible for the major contribution to the composition of the organic carbon mass, while local sources play a less significant role. For the southern territories, the situation is different. It suggests that just at these latitudes the global (regional) background is formed, which strongly affects the northern territories.

Figure 3 depicts similar data for lead, which is often associated with the anthropogenic pollution (first of all by traffic and non-ferrous metallurgy). The pattern observed for lead is similar to that for organic carbon at the southern points, but the absolute values have the gradient that decreases from north to south. It is interesting that for both the north and south near the zero values there are some measurements with a wide standard deviation of 5–7 at the mean standard deviation of 2–3.

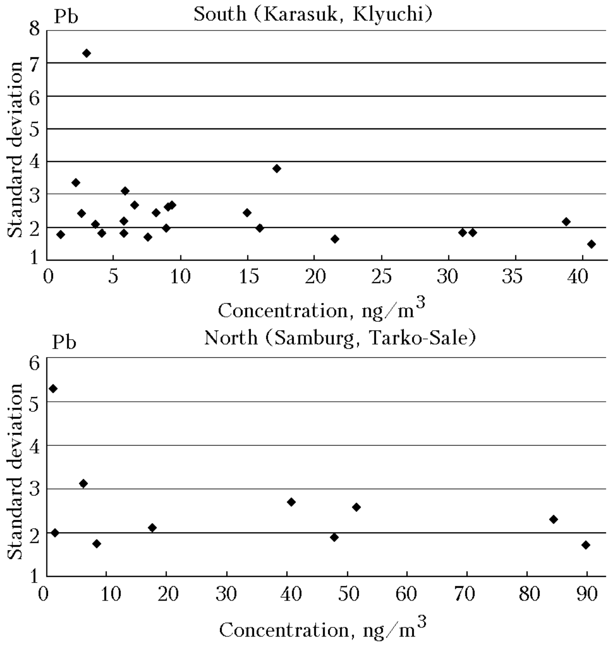

Fig. 3. Measured concentration of Pb in aerosol particles as a function of the standard deviation in the array of the measured data (south and north of Western Siberia).

For the same reasons as were used in explaining the dependence of the concentration on the standard deviation for carbon-containing aerosol particles, we can give the following explanation to this phenomenon. At the low background concentration of lead at the observation point due to the processes of the global and regional transport, the masking effect disappears and the contribution of local sources is seen more clearly. Among the possible local sources, the traffic is the only significant source. Aerosol particles emitted by car exhausts are very fine and have short lifetime. In this case, we should expect high fluctuations of the lead concentration at the low mean values of this concentration.

The presence of the decreasing gradient of the mean lead concentration from the north to the south allows us to draw an unambiguous conclusion that the source of the lead responsible for the principal contribution to the global background over the territory of Siberia is located in its northern part. Since, apart from the traffic, only the non-ferrous metallurgy is a global source of lead, it should be accepted that the sole large non-ferrous metallurgy plant, namely, the Norilsk Nickel Plant, is a source of lead, forming its background values over the vast territory of Siberia.

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