Elemental composition of atmospheric aerosols in mass units as a function of soil type exposed to wind erosion

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The paper describes a technique for calculating the concentration of elements in the aerosol substance, in mass units (μg/g or percentage), after analysis of elemental composition of atmospheric aerosols collected on filters having known the weight fraction of aerosol collected on a filter (the mass of the aerosol sampled). This makes it possible to compare the element concentration of atmospheric aerosols with the concentration in soil in comparable units that, in its turn, enables one to analyze and estimate individual aerosol samples and to reveal the short-duration local sources of the anthropogenic origin.

Introduction

Chemical composition of atmospheric aerosols (AA) varies within wide limits. An informative characteristic of AA is its elemental composition that is normally obtained by use of elemental chemical analysis of AA samples collected on filters. Such an analysis gives the value of concentration of the ith chemical element on an operating area of a filter in units of μg/cm^2. Further interpretation of these results is performed as follows.

1. At a given volume of air, pumped through the filter, the concentration C_i of the ith element is expressed in the units of mass per unit volume, i.e., it has the dimensionality [ML^{-3}]. Traditionally, C_i is expressed in ng/m^3. The value of C_i [ng/m^3], which is used to determine the chemical composition of aerosols, is a function of two independent variables, *viz.*, the number of particles per unit volume (mass of all aerosol particles) and of the chemical composition of the particulate matter. At any particular moment in time, one of the above-mentioned properties of AA, either chemical composition or the sample mass that govern the element concentration in the atmosphere, can dominate.

2. One of the widely used methods for interpreting the results of elemental analysis of AA is the use of the so-called enrichment factor (EF). The enrichment factor is the relation between the ith element concentration in an object under study and the concentration of the same element in an object, with which a comparison is being done, i.e., EF = C_i/K_i. It is obvious that in so doing the concentrations must be in the same units. To compare the AA chemical composition either with the soil or with the lithosphere, A. Kist[1] proposed to use EF in the following form:

$$\text{EF} = (C_x/C_{\text{ref}})/(K_x/K_{\text{ref}}), \qquad (1)$$

that is the ratio between the concentrations of an studied and reference elements in a sample under study

(C_x and C_{ref}, respectively) divided by the ratio between the concentrations of the same elements (K_x and K_{ref}) in the system of comparison.

Within this approach it does not matter which units are used for concentration. In our case, the AA system is to be studied and the system of comparison is either lithosphere or soil. As the reference ones, elements Fe, Al, Sc, and Si are most often used as being primarily of soil or lithogenetic origin.

The use of EF does not decrease the number of independent variables because EF, in its turn, depends on two quantities, which are not related to each other, namely, the concentration of an element C_x and the ratio between the reference element concentrations in the system under study and the system of comparison ($C_{\text{ref}}/K_{\text{ref}}$).

One of the main conditions for correct use of EF technique is constant concentration of the reference element.[1] Thus, for example, for aerosols of volcanic origin, silicon is chosen as a reference element. Measurements of the element composition of magma, volcanic lava and ashes of different kind, which are the main source of volcanic aerosols, indicate that the most constant is the content of silicon (50–70%). But even at such careful choice of the reference element (silicon) the error of calculation of EF for most of elements is 20–30% (Ref. 2).

The influence of instability of the reference element in the system under study on the EF value can be decreased significantly when averaging the results over a certain period. Thus, Ref. 3 describes predominantly soil-erosion origin of summer AA of 1997 in the south of Novosibirsk Region when considering the mean relative concentrations of chemical elements in AA over a month-long observation period and when comparing the results with the relative content of elements in the lithosphere.

Thus, the approaches to the interpretation of the results of the elemental analysis of AA available do not enable us to directly relate the chemical composition of AA to the chemical composition of soil.

The paper considers a possibility of extending the interpretation of the results of elemental analysis of samples of atmospheric aerosols thus being an attempt of making a comprehensive study of the relation between the elemental compositions of AA and soil.

Chemical composition of aerosols in mass units

To exclude the effect of AA mass density on the measured element concentration or of the ratio between the reference element concentration in the system under analysis to that in the reference system it is proposed that after the elemental analysis of AA sediment on filters one calculates the element concentration in the units of μg/g (or in the percentage of elements' content) using the mass of a sample collected on a filter

$$C_i = C_i^0 \cdot S / M, \qquad (2)$$

where C_i is the ith element concentration (μg/g); C_i^0 is the concentration of the same element on the operating part of the filter (μg/cm^2); S is the area of the filter operating part (cm^2); M is the sample mass.

This makes it possible to compare immediately the element concentrations in AA with its concentration in soil in relative units that, in turn, allows one to perform AA analysis using single samples of aerosols and to identify short-duration local sources of anthropogenic origin, i.e., to obtain some additional data on AA. Besides, it is possible to relate the biochemical regularities in the plants resulting in the metal migration from the soil to air through cell tissues of plants[4] to the parameters of atmospheric aerosol.
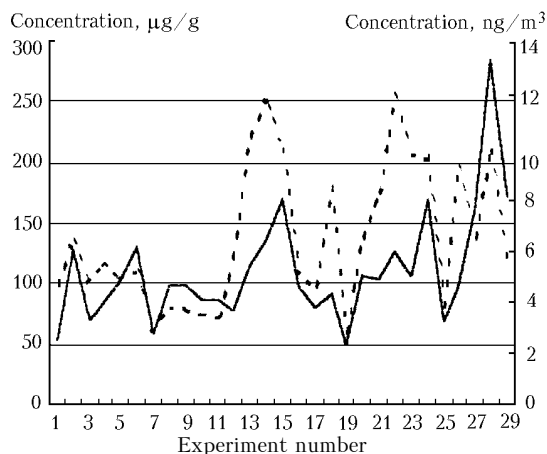

Fig. 1. Dependence of Br concentration in the traditional (ng/m^3, dashed line), and mass units (μg/g, solid line) on the date of sampling. Summer 1997, Karasuk.

A comparison of the behavior of bromine concentration in samples of AA collected during a month period (each sample was collected during 24 hours) in traditional (ng/m^3) and mass (μg/g) units gives an estimate of supplementary potentialities of the approach proposed (see Fig. 1). We notice that at points 7–9 when comparing those with the points

21–23 at constant chemical composition of AA (μg/g) the bromine concentration in the atmosphere varies by 3 to 4 times. In this case, no indications of the action of supplementary sources existed. At the same time, the increase of bromine concentration at the point 28 counts in favor of the existence of a supplementary source of this element (at its mean concentration in soil of 50 μg/g in AA we have 280 μg/g).

Such an approach has not been used so far, to our knowledge, due to the difficulties when measuring the sample mass. For example, in the AA monitoring, performed at the Laboratory of Disperse Systems (IChKC SB RAS) to obtain 3–20 mg of sample about 300 m^3 of air were to be pumped through the filter.

The results presented below have been obtained by use of the proposed approach to the interpretation of the results of the elemental analysis of AA collected during the summer period in the settlement Klyuchi near Novosibirsk and Karasuk in the south of Novosibirsk Region[5] and in the settlement Zav'yalovo (120 km from Novosibirsk in the pine forest). The elemental analysis was performed by use of an X-ray fluorescent method using synchrotron radiation (XRFMSR) at the station of X-ray fluorescent elemental analysis of the center of synchrotron radiation (accumulator of VEPP-3 type) at the Institute of Nuclear Physics SB RAS.

Relation between aerosol chemical composition and soil chemical composition

The variety of soil types, in its element composition, that are the source of AA is mainly determined by the bedrocks. Although the element composition of soil is diverse, there are some so-called reference elements, whose concentration characterizes the type of soil according to commonly accepted classification.[6,7] Among those elements there are titanium (Ti), zirconium (Zr), strontium (Sr), and iron (Fe). The minerals containing zirconium, strontium, and titanium in soils are stable to erosion (solution in water, hydration, hydrolysis, oxidation, reconstruction, etc.) and are present in soils almost in an invariable form. In the literature a review can be found (see, for example, Ref. 8) of the geochemical aspects of the behavior of iron in soils and a possibility is discussed of using the iron distribution for diagnostics of the soil type, i.e., the possibility of using iron as a reference element.

During the field mission to the Middle Ob' in summer of 1999 the following model experiment was performed. During 13 hours the samples of atmospheric aerosol were collected using the filter of AFA-KhA type located close to the dry clay soil at the lee side during fine weather and at wind velocity of 4–5 m/s. The results of elemental analysis of the AA samples (performed using the XRFMSR) are given in Table 1.

It is evident from these results that the obtained concentrations of the reference elements (given in Table 1) agree with the literature data on the clay soil.[1,9]

The increased Mn content as compared with the literature data[1,9] can be explained by the fact that this experiment was performed in the north part of Western Siberia where high Mn content in the soil and water is known. Clay is a good adsorbent of metals and their compounds. This experiment has made it possible to determine correlation between the AA element composition and the soil element composition, at single sample of AA using the above-mentioned filter.

Table 1. Element concentration, %

Element	Clay	AA
S	0.3–0.24	0.35
Cl	0.016–0.018	0.15
K	2.3–2.7	0.95
Ca	2.2–2.5	3.2
Ti	**0.45–0.46**	**0.51**
V	0.013	0.027
Cr	0.01–0.009	0
Mn	0.002–0.13	0.67
Fe	**4.3–4.72**	**4.75**
Co	0.002	0.01
Ni	0.007–0.01	0.006
Cu	0.0045–0.0057	0.013
Zn	0.008–0.01	0.028
Rb	0.014–0.02	0.006
Sr	**0.046**	**0.049**
Y	0.0026–0.003	0.0026
Zr	**0.016–0.02**	**0.018**

The association of chemical composition of atmospheric aerosols and the existence of vegetation (using bromine as an example)

Figure 2 shows the Br concentration in the samples of AA collected in the settlements Klyuchi and Zav'yalovo in summer of 1998. From this figure we notice that if in Klyuchi the Br content in AA is close to the Br content in the soil (10 to 50 µg/g), then in Zav'yalovo the Br concentration is much higher than that in the soil. Aerosol samples in Zav'yalovo were collected in a vast area of pine forest. This area is characterized by the absence of pollution sources of the atmosphere. In this case, the increase of Br content, as compared with its content in soils, is likely to be

connected with the property of vegetation to accumulate Br in green parts of the plants. The elemental analysis of pine-needles, accumulated at different times, shows the presence of Br and the Br content is 2 to 40 µg/g. Bromine and its compounds are volatile and they are easily removed from the plant tissues in the form of vapor-gas fraction, especially during warm season, which is then adsorbed by aerosol particles of the soil origin, particularly, by clay particles.[6]
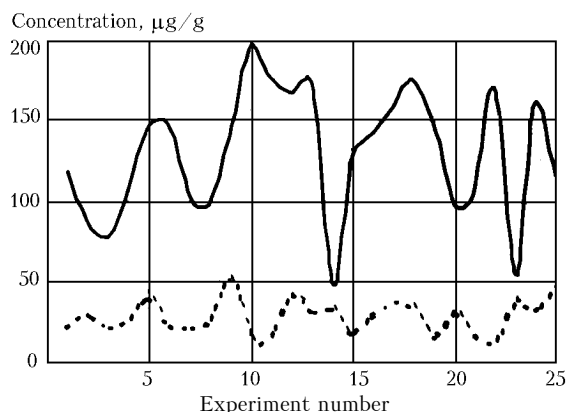

Fig. 2. Br concentration in the mass units in AA samples collected in summer of 1998 simultaneously in Klyuchi (dashed line) and Zav'yalovo (solid line).

Detection of short-duration sources of anthropogenic origin

1. When analyzing samples of AA collected during the expedition in the Middle Ob' in summer 1999, the difference has been revealed among the samples of AA, which were accumulated at freight ports and in the areas without population. In former case, AA composition is affected by the emissions of fuel combustion products from motorboats. If we assume that AA of soil-erosion origin must have the iron concentration of 2–3% (based on the soil characteristics of the Ob' flood-lands), in the freight ports the soil-erosion component is sometimes 20–25% that is seen from analysis of the iron concentration and a great amount of sulfur (S) detected. Some of the obtained results are given in Table 2. The estimate of the amount of soil-erosion component is given in the last column.

Table 2

Data	Place of AA collection	C_{Fe}, %	C_S, %	Soil-erosion, %
07.12	River Tom' in the vicinity of Tomsk	0.57	5.4	25
07.14	Camp located 3 km to the north of Kolpashevo	1.61	0.6	70
07.15	Night camp, there are no populated areas	2.88	0.07	100
07.17	Camp at the freight port (Kargasok)	0.49	3.8	Less than 25
07.19	Between Kargasok and Aleksandrovskoe, a pusher is behind	2.20	0.8	80
07.21	To the north of Aleksandrovskoe, on the way, wind from the side of a pusher	0.68	2.6	30

2. Figure 3 shows the results of elemental analysis of the zinc concentration in samples of AA accumulated in Klyuchi and Karasuk. It is known that in the soils in different regions the zinc content varies from 20 to 400 μg/g.

We note that in Klyuchi the zinc concentration in the sediment collected on the filter is stable and equals 300 to 400 μg/g. In Karasuk sharp oscillations in the concentration are observed. Evidently, this occurs due to the neighborhood of the lead-zinc metallurgical plant in the city of Ust'-Kamenogorsk. Thus, one day the zinc concentration reached 2400 μg/g. Such a large deviation of its concentration from that in soil can be explained only by the contribution of anthropogenic source. In Klyuchi at the same time the increase of zinc concentration is observed but in smaller quantities (up to 1400 μg/g). Analysis of meteorological conditions at a given period, made by A.I. Smirnova, shows that the source of zinc is likely located in the north of Kazakhstan.
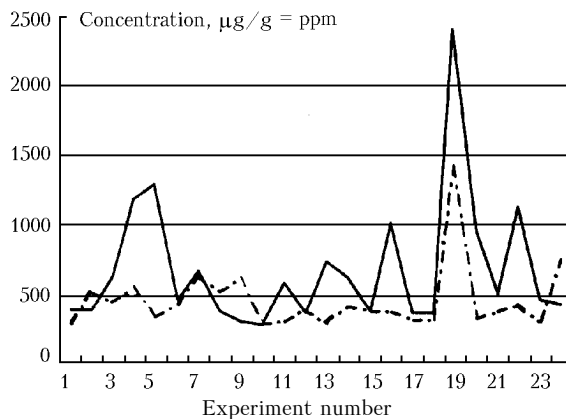

Fig. 3. Zinc concentration in the mass units, in AA samples collected in summer 1997 simultaneously in Klyuchi (dot-and-dash line) and Karasuk (solid line).

Influence of weather conditions on the aerosol chemical composition

1. The process of wind erosion is very complicated and depends primarily on the type and morphology of the soil and on the weather conditions as well. Figure 4 shows the results of elemental analysis of AA samples collected in Zav'yalovo in July–August, 1998. During first 20 days the weather was dry and hot with moderate winds. Regardless the fact that in the soils of the south area of Western Siberia the iron content is 2.5–3%, in the aerosol samples under dry weather conditions the iron concentration increases up to 8%. At the point number 10 the concentration decrease was caused by the wind from Ob' Reservoir while on all other days the wind blew from the dry land. Then, during 10 days of steady drizzling rain the iron concentration in AA decreased down to 1–2%. Here the data on zinc content are given. The zinc concentration increased highly during the rainy period. From the impact experiments[10] it is known that iron is contained

in larger particles in contrast to zinc. Thus, the decrease, due to rain, of the number of large particles and difficulties of wind erosion of damp soil result in a large contribution to chemical composition of AA of small particles.
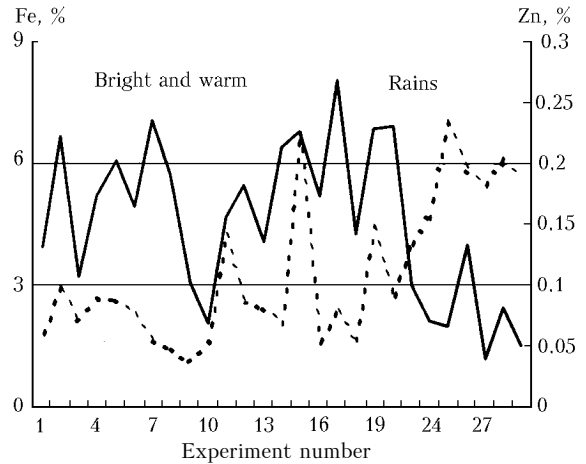

Fig. 4. The influence of weather conditions on the iron (solid line) and zinc (dashed line) concentration, in the mass units, in AA samples, collected in summer of 1998 in Zav'yalovo.

2. During the expedition along the middle part of River Ob' in 1999 a sample of AA was collected under conditions of a very high, dry, and squally wind (up to 25 m/s). The iron concentration in the sample reached 15%, at the same time the iron concentration in samples collected at the same region but at the wind velocity of 3–5 m/s did not exceed 2–3%.

From the above-mentioned examples we conclude that the proposed approach is promising because it enables us to extend the capabilities of interpretation of the results of the elemental analysis of AA.

Conclusions

The proposed approach makes it possible:

1. To consider simultaneously the phenomena in soil (chemical composition, effects of wind erosion, etc.) and AA parameters in the atmospheric boundary layer in relative units.

2. To assess the relation between AA and the soil at single measurements that, in turn, allows the analysis of individual samples of AA, including from the viewpoint of the determination of the short-duration local sources of the anthropogenic origin to be performed.

3. To calculate the enrichment factor without the use of reference elements.

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