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Dedicated to the doctor of chemical sciences, Professor Vladimir Andreevich Mikhailov, a man of honor and word, outstanding scientist

Composition of Atmospheric Aerosols as the Global Invariant

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Abstract

Examples of the elemental composition of atmospheric aerosols in various points of the Earth were considered and the connection with the average level of the suburban background (ALSB) was established. The data on concentrations of ALSB for 49 elements and calculation data of the regression analysis were given. It was shown that, as a whole, the global atmospheric aerosol was characterized by the constancy of the elemental composition and differs only by the dilution degree (or concentrating) depending on the region under study.

Key words: atmospheric aerosol, ALSB

INTRODUCTION

Atmospheric aerosol is an important geochemical component of the atmosphere that affects climatic factors and the biosphere. It is considered that its quantitative and qualitative elemental composition changes depending on natural conditions of the area and the presence of anthropogenic sources of pollution. Accordingly, the further is it from the pollution source, the more pure the air is. At that, the elemental composition itself is considered as a function of the coefficient of elements enrichment relatively to their average contents in the earth crust.

As shown in the works [1, 2], concentrations of individual elements of the atmospheric aerosol may differ greatly, depending on the region of the planet. *However, the total elemental composition of the atmospheric aerosol characterized by the set of ratios of elements concentrations to each other is a global constant, unchanged in space and time.* At least, such a picture was observed in the second half of the 20th century. At that, *the elemental composition itself can be considered as the function of multidimensional vector of the average level of the suburban background* (C_{ALSB}). The work [1] presents concentrations of ALSB for 49 elements that are averaged values from the minimally registered in the air of suburban areas of a number of cities in Europe, America, Asia, Africa, as well as some cities of Siberia are given (ng/m^3): S 6000, Si 1300, Cl 760, Fe 520, Ca 460, Al 420, Mg 400, K 350, Na 300, Pb 140, Ti 84, F 80, Zn 63, Cu 40, Mn 30, Ba 13, Ni 10, Cr 5, Br 4.8, Sr 4.7, Rb 3.3, V 2.5, As 2.4, Cd 2, Mo 2, I 1.4, Se 1.3, Ce 1, Ru 0.7, W 0.7, La 0.6, Hg 0.55, Co 0.55, Ag 0.54, Sb 0.53, Ga 0.5, Sc 0.3, Cs 0.23, Th 0.2, U 0.2, Sm 0.082, Ta 0.05, Hf 0.045, Yb 0.037, Eu 0.033, In 0.025, Re 0.02, Au 0.01, Lu 0.003. The selec-

tion of the data of concentrations as the universal characteristic in the form of the vector of ALSB is based upon the comparison of two independent estimates: 1) the analysis of extensive literature data on the elemental composition of atmospheric aerosols in various suburban areas of our planet (C^{lit}_{ALSB}) and 2) results of the neutron activation analysis conducted in suburban areas and in the territories of Siberian cities under favourable meteorological conditions, viz, Novosibirsk, Novokuznetsk and Kemerovo (C^{sib}_{ALSB}). The regression analysis gives the equation of the regression line:

$$\log C^{sib}_{ALSB} = 0.06 + 0.97 \log C^{lit}_{ALSB}$$

with the correlation coefficient, equal to 0.98. This allows to consider two independent assessments as two approximately equally accurate assessments of ALSB as the global vector and to assume that the average composition of the aerosol at the level of the ALSB in the world is virtually the same [1, 2].

The above rule is fulfilled on the territory of these cities under the condition of favourable meteorological conditions and fairly long (seasonal, annual) sampling, which provides the necessary statistical processing of measurement results. And, of course, we are not talking about the aerosols in the direct vicinity of emission sources.

In connection with the aforesaid, it is expedient to carry out the analysis of the modern data on the elemental composition of atmospheric aerosols to confirm the regularities established.

EXPERIMENTAL

The data on the elemental composition of atmospheric aerosols in a number of countries at the turn of 20th and 21st centuries were investigated by us. When comparing measured concentrations of elements with the data of the ALSB, sustainable correlation relationships wererevealed. They are discovered at the analysis of equations of regression lines when building logarithmic dependenciesof the type:

$$\log C_{i,N} = a(N) + b \log C_{ALSB,i} \quad (1)$$

where $\log C_{i,N}$ and $C_{ALSB,i}$ are the concentration of i-th element in N region and corresponding component of the vector C_{ALSB}. These relations may be assessed using the validity coefficient of approximation (R^2) (the squared correlation coefficient) and mean square deviation (MSD) σ from the regression line (Table 1). The regression coefficient (b) is the tangent of the slope of the regression line (the straight line); it tends to unity and shows the presence of a relationship between the ALSB and elemental composition of the aerosol in the region considered. The coefficient (a) is a segment that is cut off by a straight line on the y axis; tends to zero and characterizes the degree of the aerosol contamination air in the region, in comparison with the ALSB [3].

When the coefficient $b$insignificantly different from one, the equation is true:

$$C_{i,N} = 10^{a(N)} C_{ALSB,i} \quad (2)$$

Thus, different regions differ only by the degree of dilution (or, on the contrary, concentration) of the global aerosol. For example, for the South Pole $a_{S/P} \approx -3$ and for Tashkent in the late 1970, $a(N) \approx 2$. This means that at the virtually identical aerosol composition (the proportionality $C_{i,N}$ and $C_{ALSB,i}$), the air in the South Pole is approximately 1000 times more pure, in comparison with ALSB, while the air of Tashkent is 100 times dirtier [1, 4].

RESULTS AND DISCUSSION

As can be seen from the data of Table 1, the atmospheric aerosol in various points of the globe has a clearly pronounced connection with the ALSB. In Indonesia, according to the data of 1996, the coefficient b almost does not go below the value of 0.9. This is characteristic and for cities (even for so big, as Jakarta) and coastal regions, despite the increased content of chlorine due to the supply from the sea. The samples were selected in the spring on the height of 1.5 m from the ground surface during 1.5–2 h with the rate of air bleeding of 20 L/min [5]. These territories are distinguished by unusually high concentrations of chromium in the air, besides, in the coast, they are higher than in the cities. According to the opinion of researchers, this is conditioned by the soil origin chromium. An analogous situation is observed in the northwest of China.

In Russia, according to data of the mass spectrometric and X-ray fluorescence analysis

TABLE 1

Form of equations of regression lines and their assessment for various regions of the Earth at the turn of 20th and 21st centuries

Equation regression line type, $y = bx + a$	R^2	Place sampling, height above the sea level	Number of determined lements	MSD (σ)
		Indonesia (1996., Cr)**		
$y = 0.902x + 0.078$	0.665	Carita (coast)	14	0.53
$y = 0.898x + 0.060$	0.824	Jakarta (city)	14	0.35
$y = 1.019x + 0.035$	0.840	Bandung (city), 709 m	14	0.37
$y = 1.100x - 0.510$	0.893	Yogyakarta (city), 116 m	14	0.31
$y = 0.898x - 0.088$	0.647	Lake Bali (coast)	14	0.55
		Arctic (1985–1995)		
$y = 0.892x - 0.587$	0.848	Severnaya Zemlya archipelago	29, Au**(6)	0.53
$y = 0.888x - 0.141$	0.919	Wrangel Island	29	0.38
$y = 1.112x - 0.664$	0.902	Station "North Pole-28"	16	0.38
$y = 1.147x - 0.963$	0.799	Barents Sea	16, Na**(6)	0.74
		Russia, railroad Moscow–Vladivostok (2004–2005)		
$y = 1.025x + 0.551$	0.897	East European plain, autumn	40	0.54
$y = 0.946x + 0.175$	0.866	The same, spring	42	0.58
$y = 1.107x + 0.458$	0.932	Middle Ural, autumn	42	0.46
$y = 1.013x + 0.042$	0.871	The same, spring	40	0.59
$y = 0.967x + 0.545$	0.902	West Siberian plain, autumn	43	0.48
$y = 1.040x + 0.102$	0.923	The same, spring	42	0.47
$y = 0.984x + 0.560$	0.908	Mountains of South Siberia, Transbaikalia, autumn	42	0.49
$y = 0.983x - 0.022$	0.923	The same, spring	39	0.46
$y = 1.133x + 0.219$	0.918	Amur Zeya plain	37	0.49
$y = 0.981x - 0.103$	0.922	The same, spring	37	0.44
		Russia, the coastal territory of the Lake Baikal (1990–1993)		
$y = 0.905x + 0.097$	0.942	Listvyanka village, winter	28	0.30
$y = 0.978x + 0.356$	0.954	The same, spring	29	0.34
$y = 0.985x - 0.052$	0.953	The same, summer	28	0.27
$y = 0.957x - 0.058$	0.947	The same, autumn	28	0.34
$y = 0.947x - 0.104$	0.969	Station Observatory winter, 750 m	24	0.25
$y = 0.942x - 0.012$	0.966	The same, summer, 750 m	23	0.23
		Northwest China (1994)		
$y = 0.795x + 0.340$	0.789	Glacier of the Tien Shan (mountains), 3370 m	13	0.43
$y = 0.799x + 0.270$	0.773	Lake Bosten, 1048 м	15	0.46
$y = 0.905x + 0.820$	0.763	Yulai, Takla Makan (desert)	15, Sc**(250)	0.44
$y = 0.956x + 1.088$	0.765	Ruok'yang, Takla Makan, 885 m	14, Sc**(65)	0.32
$y = 0.818x + 1.235$	0.725	Kimo, Takla Makan, 1240 m	13	0.45
$y = 0.893x + 0.828$	0.807	Minfeng, Takla Makan, 1410 m	14	0.44
$y = 0.880x + 0.445$	0.765	Eraydeyk, Kunlun (mountains) 2150 m	13	0.46
$y = 0.809x + 1.057$	0.747	Yutyan, Takla Makan, 1390 m	15	0.47
$y = 0.874x + 0.720$	0.777	Tuleyk, Takla Makan, 1720 m	14	0.48
$y = 0.884x + 1.477$	0.686	Hotan, Takla Makan, 1420 m	13, Sc**(800)	0.58
$y = 0.993x + 0.840$	0.824	Yurungkash, Takla Makan, 2150 m	14, Sc**(130)	0.55
$y = 0.792x + 2.057$	0.65	Yarkant, Takla Makan, 1315 m	13, Sc**(2300)	0.58
$y = 0.842x + 0.589$	0.695	Tashkurgan, Pamir (mountains), 3010 m	14	0.56
		Cuba (2007)		
$y = 0.875x + 0.075$	0.739	Havana (city)	13, V**(15), Br*(4)	0.49
		Bangladesh (2002–2003)		
$y = 0.805x + 0.729$	0.704	Dhaka (city)	15, Br*(8), Zn*(10)	0.41
		Mexico (1994)		
$y = 0.934x + 0.634$	0.662	Mexico (city, northeast)	13,V**(20),Cr*(14), Ca*,Si*(15)	0.56
$y = 0.916x + 0.700$	0.691	Mexico (city, southwest)	13, V**(150),Cr*(17)Ca*,Si*(10)	0.51

* Elements, concentrations of which exceeded significantly the ALSB (the multiplicity is indicated in brackets).

** Elements, concentrations of which exceeded significantly the ALSB and were excluded from the analysis.

of 2004–2005, for more than 40 elements, in the whole territory along the railroad Moscow–Vladivostok from West to East the close connection of the atmospheric aerosol with the ALSB is traced. It can be seen (see Table 1) that the coefficient b is not very different from one. Judging from the values of the coefficient a, in autumn, the aerosol is quite stable and on average 3.5 times more contaminated, in comparison with the suburban background, except for the eastern part of the country (see Table 1). In spring, concentrations of elements are changeable, however, as a whole; they are close by value to the level of the suburban background or even below it, as along the railroad in Transbaikalia and the Far East. The samples were selected on the height of 4 m from the railroad with the air consumption of 12 m^3/h during 1 h and longer. No less than seven samples were selected in each region; further, averaging was carried out [7].

In the coastal area of the Lake Baikal, the elemental composition of atmospheric aerosols, according to the data of the neutron activation analysis for a broad spectrum of elements also has qualitative similarities with the data of the ALSB (Fig. 1). The coefficient of regression is close to one, while the coefficient of dilution is close to zero. At that, in the spring, when the amount of precipitations is minimal and the land is poorly covered with vegetation, the atmospheric aerosol is most polluted. According to researches' opinion, this is conditioned by the inflow of the erosional soil dust in the air. At the same time, in winter, in this territory the atmospheric aerosol is enriched with the elements Sb, As, Co and some rare earth metals due to the fuel combustion during the heating season. Studies were carried out on the basis of the Limnological Institute and Baikal Astrophysical Observatory of the Institute of Solar-Terrestrial Physics, SB RAS, in 1990–1993. The samples were selected by standard methods, and averaging was performed by 3–24 samples [8].

Highly valuable data for the analysis were collected in the northwest of China [9]. Judging by the results, correlation connections between the ALSB and harsh conditions of the desert and mountains are saved, despite the fact that in the southern part of the Takla Makan desert the samples were selected in several days after sandstorms. The concentrations of calcium and silicon in the aerosol reached 118 and 171 μg/m^3, correspondingly, what exceeds the indicators of ALSB in hundreds of times. Abnormally high concentrations of scandium were excluded from the analysis in the places of its discovery (see Table 1). It is noteworthy that the samples in this region were collected in different altitudinal belts (height above the sea level is 900–3500 m, see Table 1).

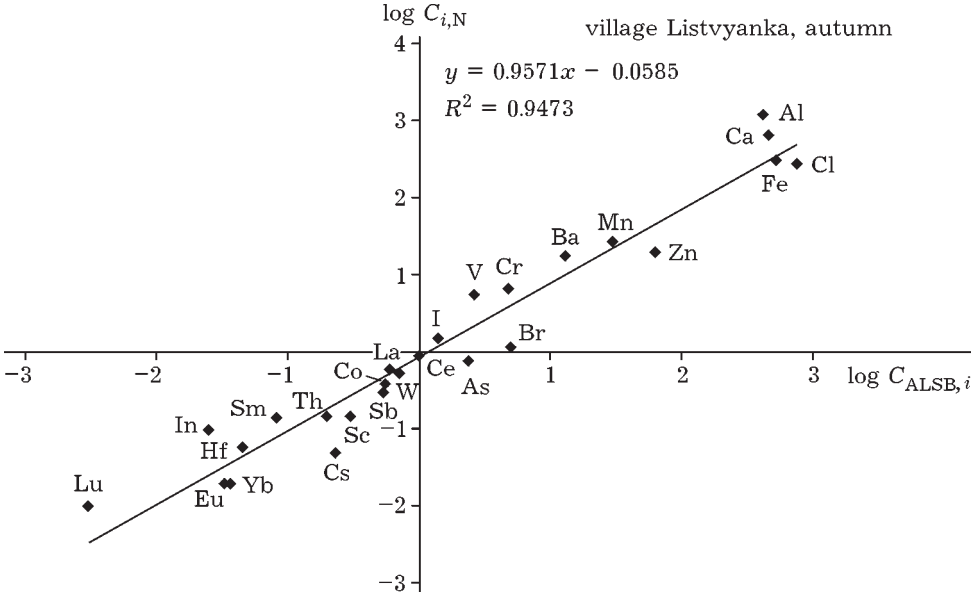

Fig. 1. Distribution of elements along the regression line for samples selected in the village Listvyanka.

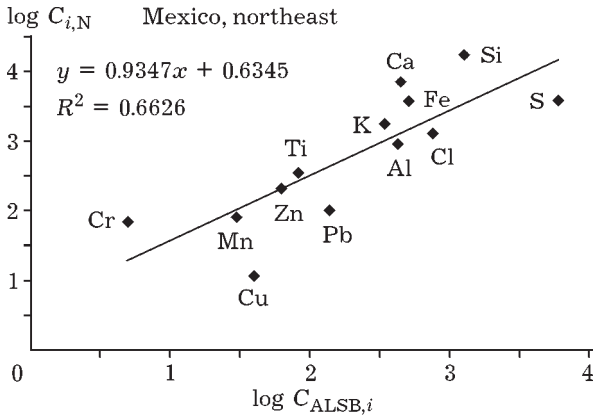

Fig. 2. Distribution of elements along the regression line for samples selected in Mexico.

Thus, one can assume that with the height, the qualitative stability of the elemental composition of atmospheric aerosols was maintained. The samples here were selected in the summer on the height of 1.5 m from the ground surface during 1.5–2 h with the rate of air bleeding of 20 L/min [9].

In big capitals of various countries, the dependence between the ALSB and elemental composition of aerosols can be traced just as clearly. The atmospheric aerosol in Havana is characterized by an increased content of vanadium what is due to the fuel combustion by industrial enterprises and the auto transport. Samples in Cuba were selected during 24 h with the air consumption of 20 L/min each second day during five months from November to April [10]. A similar picture is observed in Dhaka (Bangladesh) and Mexico (Mexico). In Dhaka, samples were selected during 6–20 h with the air consumption of 15–17 L/min two times a week during one year [11]. In Mexico, samples were selected during 6 h once a week during four months simultaneously in different parts of the city [12] (Fig. 2). High concentrations of silicon, calcium and iron in aerosol are related to the general dustiness of the atmosphere of large cities. Samples of atmospheric aerosols in the capitals, in the northwest of China and Indonesia were analysed by the XRF method with an excited beam of accelerated protons (PIXE analysis).

The analysis of the data of Table 1 shows that the coefficient of validity approximation on average is equal to 0.8, which indicates a good approximation of measurement results towards the linear dependence. The value of the mean-square deviation of the measurement results from the regression line is on average close to 0.5, which agrees with the assessments of natural variability of individual components of matched vectors of concentrations indicated earlier [1].

It should be noted that the amount of certain elements affects strongly the results of the analysis. Besides, when analysing the composition of atmospheric aerosols, significantly elevated concentrations of individual elements, in comparison with the ALSB, are often observed. Points corresponding to these elements deviate noticeable from the regression line distorting the overall picture of the distribution of the rest of the spectrum of elements. This is explained by local features of the region of consideration. However, it should also be taken into account the pursuit to symmetrical aligning elements along the regression line requires a certain time and dilution volume of air masses and that such a phenomenon occurs mainly at a small number of certain elements, when there are no sufficient data for finding compensating points.

Thus, in the work [1], when building a logarithmic dependence for the South Pole, bromine, iodine, sodium and mercury were excluded from the analysis, since the sea makes a significant contribution to their content. A high content of mercury in Antarctica is probably related to its freezing out from the impinging low-latitude air flows. For this reason, the global warming faces increasing the concentration of mercury in the global aerosol.

For evaluating the enrichment of the atmospheric aerosol on a separate component, one can use the formula proposed by V. A. Mikhailov:

$$dM_i = V dC_i + (VC_i/t_i)dt \quad (3)$$

where M_i is the total delivery of the i-th element in the volume (V) for the time (dt).

CONCLUSION

Thus, the stability of the atmospheric aerosol all over the world can serve the indicator of the sustainable development and is probably related to the fact that the technogenic pollution of the atmosphere, capable of affecting

significantly the total dust content of the air, is capable of affecting its total elemental content to a much lesser extent. Mechanisms of such stability are a subject to research and can be linked to self-organization processes. Thus, the atmospheric aerosol forms the unified sustainable global system that can be defined as *aerosol sphere*.

REFERENCES

1 Pushkin S. G., Mikhailov V. A., Komparatorny Neytronno-Aktivatsionny Analiz. Izucheniye Atmosfernykh Aerozoley, Nauka, Novosibirsk, 1989.

2 Mikhailov V. A., Pushkin S. G., Arsinevich E. A., XVI Mendeleevskiy S'yezd po Obshchey i Prikladnoy Khimii: Referaty Dokladov i Soobshcheniy No. 3 (Proceedings), St. Ptersburg, 1998, pp. 181–182.

3 Derffel K., Statistika v Analiticheskoy Khimii [Statistics in Analytical Chemistry], Mir, Moscow, 1994.

4 Mikhailov V. A., Kardanov S. Z., in V. P. Meshalkin (Ed.), Mezhdunar. Nauch.-Tekhn. Konf. "Ustoichivoye Razvitiye. Ratsionalnoye Prirodopolzovaniye. Tekhnologii Zdorov'ya" (Proceedings), Tula, 2011.

5 Makra L., Borbely-Kiss I., Koltay E. and Sutikno, *Acta Climatol. Universitatis Szegediensis*, 32–33 (1999) 65.

6 Vinigradova A. A., Antropogenny Atmosferny Aerozol' nad Moryami Severnogo Ledovitogo Okeana (Doctoral Dissertation in Geography), Moscow, 2005.

7 Andronova A. M., Iordanskiy M. A., Minashkin V. M., Nevskiy I. A., Obvintsev Yu. I., Trefilova A. V., in: Obzornye Doklady na Zasedanii v RAN, Moscow, 2007, pp. 102–127.

8 Khodzher T. V., Obolkin V. A., Potemkin V. L., Tomza U., Ran K., *Chem. Sust. Dev.*, 5 (1997) 547.

9 Makra L., Borbely-Kiss I., Koltay E., Chen Y., *Acta Climatol. Universitatis Szegediensis,* 32–33 (1999) 77.

10 Zayas G. P., Hernõndez I. P., Aruca M. R., Gala R. G., Esquivel E. M., Varona M. M., Arocha A. F., Ugalde F. A., Maldonado J. F., *Nucleus*, 46 (2009) 27.

11 Begum B. A., Biswas S. K., Hopke P. K., Cohen D. D., *Aerosol and Air Quality Res.*, 6, 4 (2006) 334.

12 Paredes-Gutierrez R., Lopez-Suarez A., Miranda J., Andrade E., Gonzalez A. J., *Rev. Int. Contam. Ambient*, 13, 2 (2009) 81.