## MULTIELEMENT ANALYSIS OF PLANT POLLEN IN THE SOUTH OF WESTERN SIBERIA

V.V. Golovko, G.A. Koval'skaya, E.I. Kirov, K.P. Kutsenogii, V.L. Istomin, and V.V. Ryzhakov

Institute of Chemical Kinetics and Combustion,
Siberian Branch of the Russian Academy of Sciences, Novosibirsk
M.A. Lavrent'ev Institute of Hydrodynamics,
Siberian Branch of the Russian Academy of Sciences, Novosibirsk
Received February 4, 1998

The pollen of Betula pendula, Pinus silvestris, Picea obovata, Larix sibirica, Populus tremula, Dactylis glomerata, Bromus inermis, Phleum pratense collected in Akademgorodok, Novosibirsk, was studied by the multielement X-ray fluorescence method with synchrotron radiation. The data are presented for 24 elements which concentration is higher than the minimum detectable value ( $10^{-5}$  g/g for elements lighter than Fe and  $10^{-6}$ – $10^{-7}$  g/g for heavier elements).

Atmospheric aerosol is a multi-component system represented by particles of mineral, biological, and anthropogenic origin. Such a variety of composition together with wide variability in content of separate components and their low mass concentration hampers analysis of aerosol chemical composition. At the same time, without this characteristic it is impossible to make conclusions about matter transfer in the atmosphere and, consequently, the state of ecosystems.

In estimating aerosol transfer, it is important to separate its natural and technogenic components. Reliable and comprehensive data about them are necessary in determining the regional geochemical background. The natural component is represented by mineral and biogenic fractions which sharply differ in their composition. The elements Si and Al, most widespread in the crust, do not play any important part in the structure of living substance. At the same time, Co, Cu, Mo, Se, Cd, etc. are not wide-spread but present in live tissues. At present, almost all elements known on the Earth's surface are found in live tissues (total of about 70 elements are found; 47 of them are observed at all times). However, only six elements predominate (H, O, N, C, P, and S). In addition to the six main elements, of greatest importance are four halogens (F, Cl, Br, I) and ten elements: five non-transition elements with constant valence (Na, K, Mg, Ca, and Zn), five transition elements with varying valence (Mn, Fe, Co, Cu, Mo). 1,2

The biogenic fraction of aerosol is rather significant. It accounts for 55-95% of mass concentration of atmospheric aerosol in some regions of the Earth.<sup>3-5</sup> The fraction contains particles of biological origin: viruses, bacteria, spores, pollen, and various remains of living organisms.

Pollen of plants is one of most mass components of bioaerosol. Known are the cases when pollen clouds

were taken for a forest fire from afar. During flowering, pollen is copiously produced. For instance, *Pinus silvestris* produces up to 125 kg/ha, while *Pinus sibirica* produces even up to 150 kg/ha. According to literature data, ash content of their pollen is about 3–4% (Ref. 6). Pollen can play an important part in atmospheric transfer of some biogenic elements due to its mass. Just the pollen was shown to transfer the main part of mineral substances into some oligotrophic lakes in Canada.<sup>7</sup>

In this paper, we present the results of the study of pollen multielement composition for eight anemophilic plants predominating in the vegetable cover.

The pollen was sampled in suburbs of the Novosibirsk city in natural populations of plants using the standard method.  $^{6,8}$  The sampled pollen was thinly sprayed onto filters AFA-KhA with a unit for pulse atomization for powdery materials. Spraying was performed on the testing unit for pulse pneumatic transport of the Department of Pulse Gas Dynamics of the Lavrent'ev Hydrodynamic Institute. All the obtained samples had surface density of pollen deposit less than  $10 \text{ mg/cm}^2$ .

Measurement of element composition of the pollen was performed by use of the X-ray fluorescence method with synchrotron radiation at the station of element analysis in the Institute of Nuclear Physics, SB RAS (accumulator VEPP-3). This method is distinguished by high sensitivity, and its results in fact do not depend on the chemical compound in which the analyzed element is contained in the studied sample. 9,10 In studying samples, we used a beam of X-ray synchrotron radiation with quantum energy of 23 keV. During the processing of the obtained spectra, we considered all the elements with atomic number Z > 19 (beginning from potassium and

heavier) excluding Mo, Ru, Rh, Pd, Ag, Cd, In, Sn. To measure the content of these elements, harder X-ray radiation is required. The reference sample containing 2.2 mg/cm<sup>2</sup> each of Ca, Cr, Fe, Cu, Sr was used for quantitative processing of samples. This was possible due to thinness of layers of the analyzed samples, which allows neglecting of secondary effects including secondary absorption of characteristic quanta.

The Table I presents the results of multielement analysis by the X-ray fluorescence method with

synchrotron radiation applied to the pollen of *Betula pendula, Pinus silvestris, Picea obovata, Larix sibirica, Populus tremula, Dactylis glomerata, Bromus inermis, Phleum pratense* sampled in the Akademgorodok, the Novosibirsk city. The data are presented on 24 elements which concentration is higher than the minimum detectable value  $(10^{-5} \, \text{g/g})$  for elements lighter than Fe and  $10^{-6}$ – $10^{-7} \, \text{g/g}$  for heavier elements). The results on K are of estimation character due to difficulties in calibration for light elements.

TABLE I. Chemical element content in the pollen of eight plants sampled in the Akademgorodok, the Novosibirsk city, g/g.

Elements	Species affiliation of pollen							
	Woody plants					Herbaceous plants		
	Pinus	Larix	Picea	Populus	Betula	Phleum	Bromus	Dactylis
	silvestris	sibirica	obovata	tremula	pendula	pratense	inermis	glomerata
K	0.08551	0.04202	0.1361	0.16302	0.03128	0.08167	0.05365	0.15878
Ca	0.00069	0.00093	0.00077	0.00678	0.00134	0.00217	0.00204	0.00619
Ti	$2.8 \cdot 10^{-5}$	0	0	0	0	$4.2 \cdot 10^{-5}$	$2.8 \cdot 10^{-5}$	$9.1 \cdot 10^{-5}$
Cr	$1.9 \cdot 10^{-5}$	$5.1 \cdot 10^{-5}$	0	0	$3.7 \cdot 10^{-5}$	$1.4 \cdot 10^{-5}$	0	$4.5 \cdot 10^{-5}$
Mn	$4.5 \cdot 10^{-5}$	$8.3 \cdot 10^{-5}$	$4 \cdot 10^{-5}$	0.00021	$4.9 \cdot 10^{-5}$	$3.5 \cdot 10^{-5}$	$2 \cdot 10^{-5}$	$8.3 \cdot 10^{-5}$
Fe	0.00017	$9.5 \cdot 10^{-5}$	0.00015	0	0.0002	0.00019	0.00013	0.00038
Ni	0	$3.3 \cdot 10^{-6}$	0	$2.2 \cdot 10^{-5}$	0	0	0	0
Cu	$1.10^{-5}$	$1.9 \cdot 10^{-6}$	$1.4 \cdot 10^{-5}$	$6.10^{-5}$	$1.6 \cdot 10^{-5}$	$1.8 \cdot 10^{-5}$	$1.6 \cdot 10^{-5}$	$3.9 \cdot 10^{-5}$
Zn	$2.7 \cdot 10^{-5}$	$4.7 \cdot 10^{-5}$	$5.2 \cdot 10^{-5}$	$1.9 \cdot 10^{-6}$	$1.1 \cdot 10^{-6}$	$5.10^{-5}$	$4 \cdot 10^{-5}$	0.00013
As	$1.7 \cdot 10^{-5}$	0	0	$1.1 \cdot 10^{-5}$	$2.2 \cdot 10^{-5}$	$5.1 \cdot 10^{-7}$	$1.3 \cdot 10^{-6}$	$3.10^{-6}$
Br	$1.1 \cdot 10^{-5}$	$8.8 \cdot 10^{-6}$	$2.8 \cdot 10^{-5}$	$1.4 \cdot 10^{-5}$	$2.8 \cdot 10^{-6}$	$4.9 \cdot 10^{-6}$	$4.4 \cdot 10^{-7}$	$3.3 \cdot 10^{-6}$
Rb	$8.7 \cdot 10^{-6}$	$4.8 \cdot 10^{-6}$	$5.2 \cdot 10^{-6}$	$7.6 \cdot 10^{-6}$	$1.5 \cdot 10^{-6}$	$9.6 \cdot 10^{-6}$	$5.2 \cdot 10^{-6}$	$2.5 \cdot 10^{-5}$
Sr	0	$5.5 \cdot 10^{-6}$	$2 \cdot 10^{-7}$	$1.5 \cdot 10^{-6}$	$3.3 \cdot 10^{-7}$	$2.3 \cdot 10^{-6}$	$2.7 \cdot 10^{-6}$	$9.4 \cdot 10^{-6}$
Y	0	$4.3 \cdot 10^{-7}$	0	$5.9 \cdot 10^{-5}$	$2.4 \cdot 10^{-6}$	0	0	0
Zr	$1.3 \cdot 10^{-6}$	$9.8 \cdot 10^{-7}$	$7.9 \cdot 10^{-6}$	0	0	$1.5 \cdot 10^{-6}$	$1.7 \cdot 10^{-6}$	$4.4 \cdot 10^{-6}$
Nb	0	$3.7 \cdot 10^{-7}$	0	0	0.00015	0	0	$3.8 \cdot 10^{-7}$
Sb	$5.10^{-5}$	0	0	0	0	0.00016	0.00011	$4.9 \cdot 10^{-5}$
Sm	$1.5 \cdot 10^{-5}$	$2.9 \cdot 10^{-6}$	0	0	0	0	0	0
Gd	$3.4 \cdot 10^{-7}$	0	$1.3 \cdot 10^{-6}$	0	0	0	0	$2.2 \cdot 10^{-6}$
Yb	$6.5 \cdot 10^{-6}$	0	0	0	$8.6 \cdot 10^{-8}$	0	0	0
Hf	0	0	0	0	$5.7 \cdot 10^{-7}$	$3.9 \cdot 10^{-6}$	0	$2.2 \cdot 10^{-6}$
W	0	0	0	0	$5.5 \cdot 10^{-7}$	0	$2.4 \cdot 10^{-6}$	$2.4 \cdot 10^{-6}$
Bi	0	$2.5 \cdot 10^{-6}$	0	0	0	0	0	0
U	0	0	$5.1 \cdot 10^{-7}$	0	0	0	0	0
Nd	0	0	0	0	0	0	$3.2 \cdot 10^{-6}$	$1.6 \cdot 10^{-5}$
Co	0	0	0	0	0	0	$1.9 \cdot 10^{-6}$	$6.2 \cdot 10^{-6}$
Tm	0	0	0	0	0	0	0	$7.6 \cdot 10^{-6}$
Ra	0	0	0	0	0	0	$8.8 \cdot 10^{-7}$	0

## **RESUME**

- 1. The technique for pollen samples preparing and further multielement analysis by X-ray fluorescence method with synchrotron radiation beams is developed.
- 2. Quantitative data on content of 24 elements in the pollen of anemophillic plants predominating in the vegetable cover near the Novosibirsk city are obtained for the first time.

## REFERENCES

- 1. G.V. Polyakov, ed., *Ecogeochemistry of the Western Siberia. Heavy Metals and Radionuclides* (Publishing House of SB RAS, Novosibirsk, 1996), 248 pp.
- 2. V.N. Vtorova and B. Markert, Izv. RAN, Ser. Biol., No. 4, 447–454 (1995).
- 3. P. Artaxo, H. Storms, F. Bruynseels, R. Van Grieken, and W. Maenhaut, J. Geophys. Res. **93**,

- No. D2, 16005-16015 (1988).
- 4. P. Artaxo, W. Maenhaut, H. Storms, and R. van Grieken, J. Geophys. Res. **95**, No. D10, 16971–16985 (1990)
- 5. H. van Malderen, R. Van Grieken, T.V. Khodzher, N.S. Bufetov, and K.P. Kutsenogii, Atmos. Oceanic Opt. 7, No. 8, 622–628 (1994).
- 6. T.P. Nekrasova, *Pollen and Pollen Regime of Conifers in Siberia* (Nauka, Novosibirsk, 1983), 168 pp.
- 7. P.V. Doskey and B.J. Ugoagwu, Atmospheric Environment **23**, No. 12, 2761–2766 (1989).
- 8. A.N. Ponomarev, in: *Field Geobotany*, (Nauka, Moscow Leningrad, 1960), Vol. 2, pp. 9–19.
- 9. K.P. Kutsenogii, G.A. Koval'skaya, A.I. Smirnova, N.S. Bufetov, and V.B. Baryshev, Atmos. Oceanic Opt. **10**, No. 7, 512–517 (1997).
- 10. G.N. Anoshin and G.N. Kulikov, eds., *Synchrotron Radiation in Geochemistry* (Nauka, Novosibirsk, 1989), 152 pp.