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ABSTRACT

The paper considers variations in the chemical composition of the tropospheric aerosol over the background region of the south of Western Siberia in 1997 - 2019. Sounding of the troposphere from 500 to 7000 m above the Karakan pine forest (Novosibirsk region) with an almost monthly frequency is carried out from 1997 to the present using the Optic-E aircraft-laboratory based on the Antonov-30 until 2011 and the Tupolev-134 Optik in this decade. Aerosol sampling is performed at each height and in layers: 500-1000, 1500-2000, 3000-4000, 5500-7000 m onto Petryanov filters (AFA-ChP/ChA-20). Subsequent quantitative analysis for the content of ions and elements in aerosol matter was carried out at the Laboratory for Environmental Monitoring at Tomsk State University. Based on 1200 sample samples (until 2019), the annual cycle of the defined components was built. Their temporal and spatial variability is analyzed. The total variability of the concentration of the inorganic component does not exceed 2 orders of magnitude. Temporary variability of the concentration of trace elements can be more spatial, reaching 4 orders of magnitude. Some data are also presented on organic aerosol, an experimental study of which by the aircraft-laboratory began in the current decade.

Keywords: atmospheric aerosol, airborne sounding, aerosol sampling, elemental and ionic composition, n-alkanes.

1. INTRODUCTION

Aerosol is one of the most important and variable components of the atmosphere that affect the climate of the planet as a whole and its individual regions. One of the main parameters of an aerosol is its chemical composition, which, along with the dispersion and structure of the aerosol substance, determines its physicochemical, optical, and other, including sanitary and hygienic, properties. An explanation of all the complex processes occurring in the atmosphere is impossible without detailed information on the size spectrum of aerosol particles, their calculated and mass concentration, structure, chemical and phase composition, and also the spatio-temporal variability of these characteristics. The refractive index and, accordingly, the laws of scattering and absorption of solar radiation in the atmosphere depend on the chemical composition of the particles, thereby determining its heat balance, which in turn plays a paramount role in the formation of climate.[1] The composition of the aerosol often includes heavy metals and others, including organic microcomponents

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that have carcinogenic and mutagenic properties. The dissolution of sulfate-containing particles in cloudy droplets leads to the formation of acid rain, which ultimately adversely affects the entire landscape-biological system of the regions where they fall. All this determines the high significance of studies of the chemical composition of atmospheric aerosol, which are carried out around the world with increasing intensity.[2]

An aircraft-laboratory can provide the most complete information about the physicochemical properties of an aerosol in the atmosphere above the surface. Such flight experimental studies began to be actively carried out by the Institute of Atmospheric Optics in the 1980s, first on an Ilushin-14; by the end of the 1980s the aircraft laboratory was adapted to the Antonov-30 carrier and certified as Optik-E, hereinafter Optik-Em.[3] However, in the first Russian five-year period (after the collapse of the USSR) since 1992, there were only a few episodes of the flight pilot campaigns. A return to the almost monthly nature (10-12 sounding flights per year) of experimental flight research occurred in mid-1997 after receiving a long-term grant from the International Science Foundation for monitoring greenhouse gases and studying atmospheric processes in the background troposphere of mid-latitude boreal zone of intracontinental Eurasia. Since 2011, the flight program has been ongoing at the jointly created with S.A.Chaplygin Siberian Research Institute of Aviation the aircraft-laboratory Tupolev-134 "Optik".[4]

2. MATERIALS AND METHODS

Research flights are carried out in the background region of the south of Western Siberia over the Karakansky pine forest on the right bank of the southern part of the Novosibirsk reservoir in the tropospheric layer of 500-7000 m. During flights isokinetic sampling of atmospheric aerosol onto Petryanov filters, during which air sampling for analysis the chemical composition of the aerosol and the measurement of its count concentration on the aircraft-laboratory is carried out by direct blowing into the corresponding system by an air flow (when the passing volume after the filters are fixed by gas meters like SGB G 4-1) and then the vacuum created by logging out using a venturi. Aerosol sampling for AFA-ChP/ChA-20 filters is performed at heights and in layers: 500-1000, 1500-2000, 3000-4000, 5500-7000 m.

Subsequent quantitative determination of the main inorganic components of the aerosol matrix - terrigenous elements, more than a dozen trace elements and ions: Si, Al, Fe, Mg, Ca, Ti, Cu, Mn, Pb, Cr, Ag, Ni, V, Ba, Mo, B, Co, Be, K^+, Na^+, Cl^-, SO_4^{2-}, NO_3^-, NH_4^+, Br^-, F^- are produced annually in the chemical analytical laboratory of Tomsk State University. [5]

Also, after the transfer of the laboratory to a new Tupolev-134 aircraft, it became possible to add an additional inlet for sampling organic aerosol onto Grimm 1.113A Teflon filter membranes. In the first 2-3 years, one sample was taken on the Tu-134 for a flight from 500 to 7000 m in the entire studied layer of the troposphere. The refinement of the scheme for such sampling continues and its implementation: the oil-free pump has been replaced by an even more powerful one, which increased the volume of aspiration and, accordingly, lowered the detection threshold for aerosol-forming compounds for hydrocarbon vapors. In each flight, 2 samples are currently taken: in the boundary layer of the atmosphere (500-2000 m) and in the free troposphere (3-7 km). Due to the high volatility of organic aerosol, each filter sample after sampling is placed in an airtight container with acetone, and this extract is analyzed on chromatograph-mass spectrometers in the laboratories of the Institute of Chemical Kinetics and Combustion of the SB RAS and the Institute of Petroleum Chemistry of the SB RAS. [6]

3. RESULTS AND DISCUSSION

In general, for the entire period of a systematic experimental study over the south of Western Siberia from 1997 to 2019, 1225 samples were taken, of which 1205 samples at the beginning of 2019 were analyzed for the main inorganic nomenclature of ions and elements.

Figure 1 shows the course of average annual concentrations of the total mass of the ionic and elemental components of the aerosol from 1997 to 2018 in different tropospheric layers above the main study area.

It should be noted that the average concentration in the entire tropospheric layer of the study area showed, although not pronounced, but maximum values over the past 10 years. However, if earlier the concentration peak of the inorganic component of the entire layer was formed largely due to local sources - due to an increase in concentration in the layers

of the boundary layer of the region, then over the past 2 years there has been a tendency to smooth out peaks in the inorganic component between layers of the troposphere and even the inversion of the maxima of these concentrations, which, on the one hand, indicates the already noted increasing vertical dynamics of the atmosphere, but, on the other hand, may indicate an increase in the role of global sources transmitted through long-distance air transport. To clarify the role of individual inorganic components, we turn to the consideration of the interannual course of a number of the most characteristic of them. Since traditionally the most frequently used to estimate the origin of an element in an aerosol composition by means of geochemical ratios is one of the three elements - aluminum, iron, silicon, and in some cases titanium - it makes sense to turn to at least to consideration the course of one of them. It is believed that the greatest correlation of the inorganic amount with one of them may be an reasonable criterion for choosing the characteristic for our case.

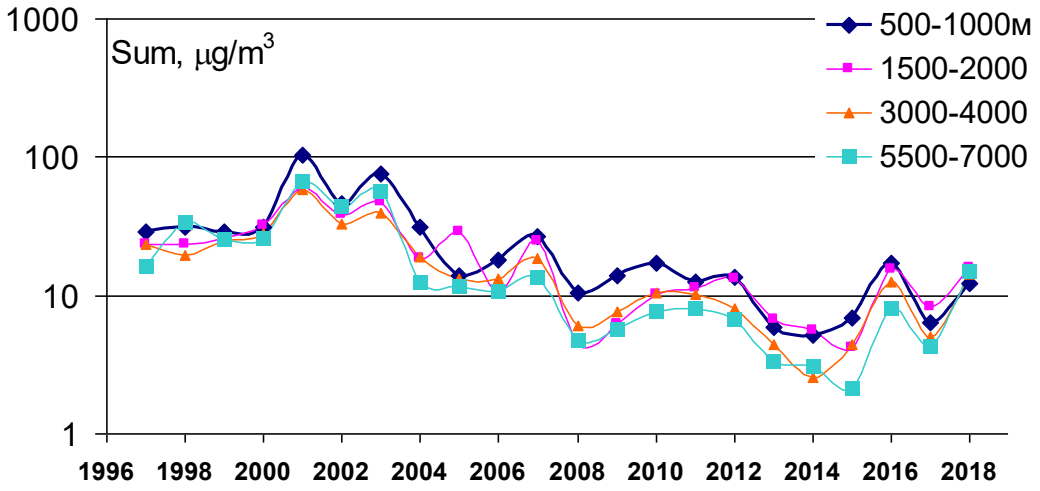

Figure 1. The course of average annual concentrations of the total mass of inorganic ions and elements in the layers of the troposphere from 500 to 7000 m above Western Siberia from 1997 to 2018.

Table 1. Correlation coefficients of the mass sum of ions and elements with the concentrations of individual elements in the samples for three region-specific air masses (sample for measurements for 2010-2018)

	CMM	CAM	CSTM
N=	119	75	68
Height	-0,1892	-0,3726	-0,3698
Al	**0,6039**	**0,3123**	**0,4531**
Ba	0,5373	0,4661	0,4989
Be	0,3787	0,2722	0,2383
Ca	0,5523	0,4906	0,6747
Cd	0,1442	0,0653	0,2808
Co	0,1415	0,1826	0,0902
Cr	0,4447	0,2901	0,225
Cu	0,5753	0,2501	0,3621
Fe	**0,6329**	**0,514**	**0,6269**
Mg	0,5721	0,6327	0,8008
Mn	0,7157	0,4105	0,2608
Mo	0,1454	0,0862	0,4118

	CMM	CAM	CSTM
N=	119	75	68
Ni	0,4267	0,2447	0,423
Pb	0,4324	0,33	0,3559
Si	**0,5476**	**0,4087**	**0,6043**
Sn	0,4301	0,2017	0,2678
Ti	**0,5199**	**0,2513**	**0,3534**
V	0,4402	0,3804	0,524
Zn	0,6032	0,2442	0,4817
Zr	-0,0349	0,0765	0,0071
Na^+	0,138	0,4086	0,4186
K^+	0,0742	0,4987	0,4825
SO_4^{2-}	0,2077	0,5878	0,3815
NO_3^-	0,1475	0,4284	0,7413
Cl^-	0,2942	0,5921	0,4487

(CMM - Continental Moderate Mass, CAM - Continental Arctic, CSTM - Continental subtropical and tropical)

From table 1 it follows that the highest correlation coefficients with the total inorganic mass has the element iron. Therefore, it makes sense to turn to a consideration of the annual course of its concentration in order to estimate, to a first approximation, the interannual trend of the concentration of the inorganic fraction of the tropospheric aerosol in the south of Western Siberia.

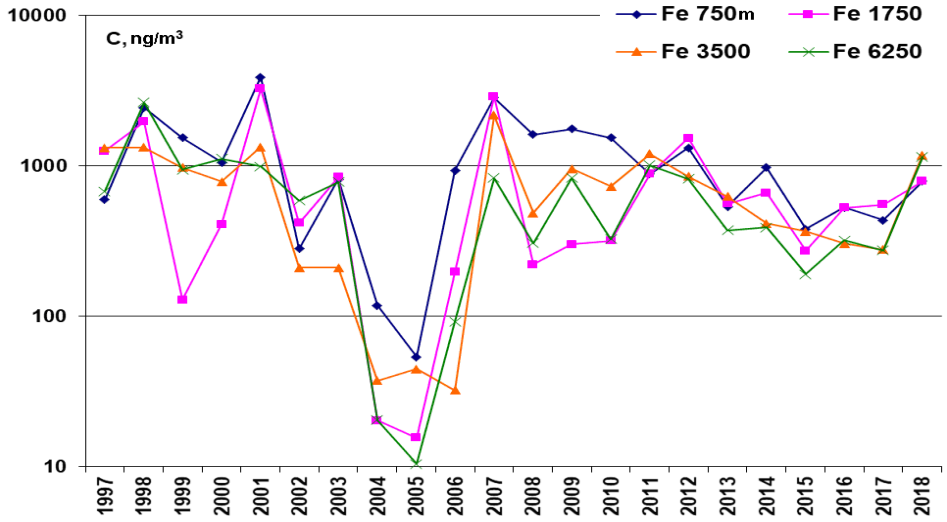

Figure 2. The course of the average annual concentration of the iron element in the troposphere layers is 500-1000 m (designation 750m), 1500-2000 m (1750), 3000-4000 m (3500) and 5500-7000 m (6250) over the background sounding region of the Karakan pine forest.

Figure 2 demonstrates that the interannual variability can exceed 2 orders of magnitude, but the average annual concentrations for different tropospheric layers extremely rarely go beyond the same order, and in the current decade, as a rule, do not exceed 2-3 times. The final coincidence in the current series of the year of measurements (2018) is characterized by the almost coincidence of pairs of average annual concentrations of adjacent PSA layers and the free troposphere - for the first two 0.78 μg/m^3 and for the second - about 1.15 μg/m^3. However, such a trend for average annual iron concentrations occurred almost every second year in the current decade, but with a lesser frequency in the previous years of the flight experiment. Apparently, such a concentration course reflects the corresponding small periodicity of atmospheric processes through a system of not always obvious indirect connections of different scales.

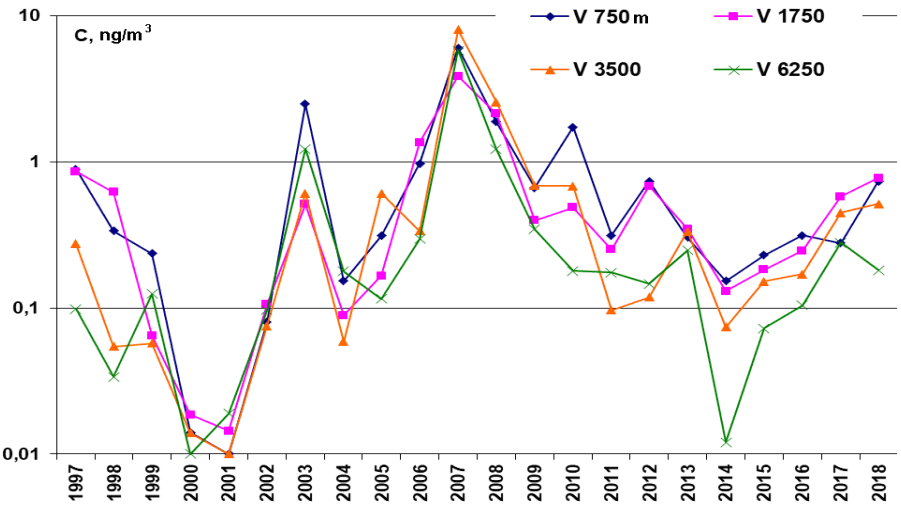

Figure 3. The course of the average annual concentration of vanadium in the layers of the troposphere of the region.

Similar to iron, the distribution of the layers at the end of the measurement period has aluminum, copper and a number of trace elements. The presence of sources in the region reveals an inverse distribution for nickel, vanadium, barium, and potassium cation. The volatile rapper of the oil and gas provinces of vanadium is almost always characterized by its accumulation in the layers of the boundary layer of the atmosphere of the region (Fig. 3).

Over the past three years, there has been a tendency toward a decrease in the ionic components of the aerosol (with the exception of potassium cation) in all layers of the troposphere, especially sharply for oxygen-containing ions (Fig. 4)

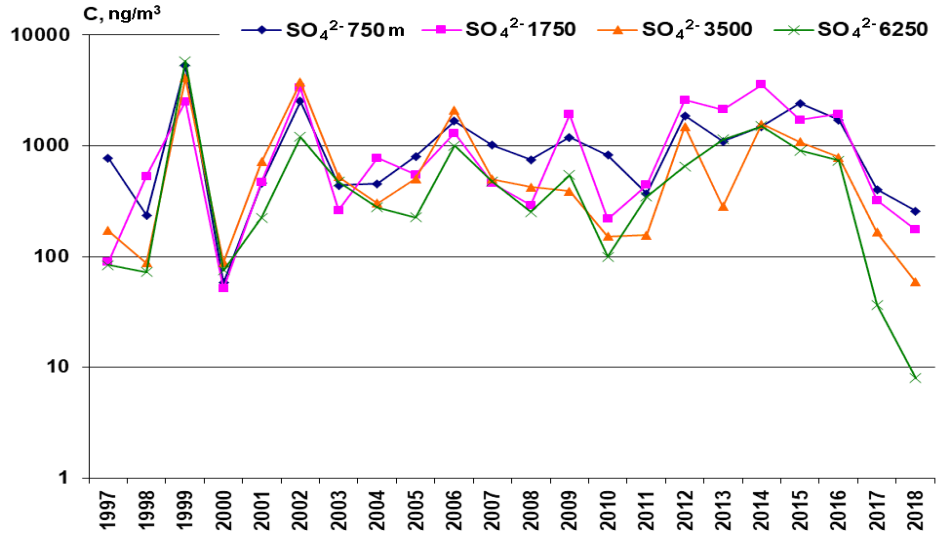

Figure 4. The course of the average annual concentration of sulfate anion in the layers of the troposphere of the region.

It is increasingly evident that the rate of formation of nitrate and sulfate aerosols in the troposphere is related to the activity of the sun, which is reflected in the significant synchronism in the average annual concentration of these anions with the corresponding Wolf numbers (Fig. 5).

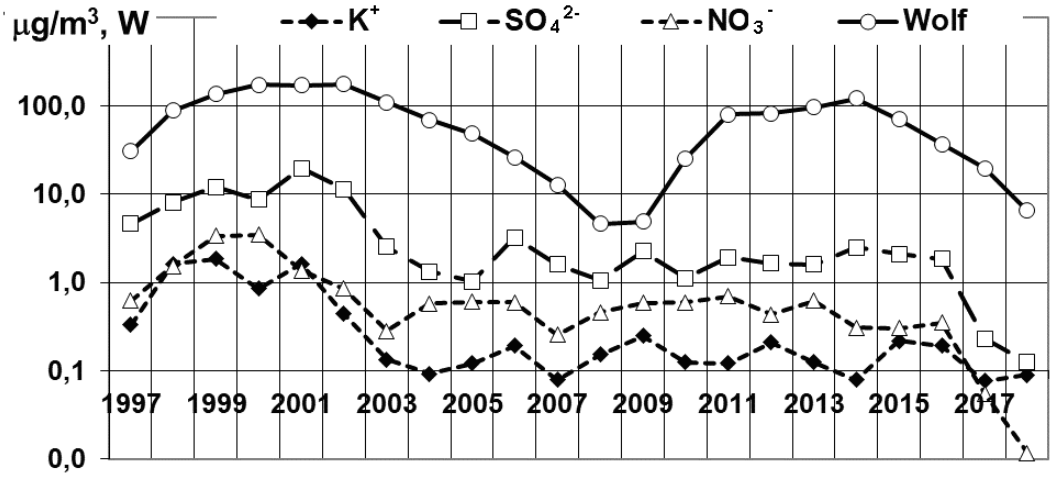

Figure 5. The course of average annual concentrations of a number of ions and Wolf numbers.

The course of potassium is apparently determined by the superposition of both global sources and its emission during the burning of forests in the region, which are also subject to some degree of influence of solar activity. This can be confirmed by the presence of significant relationships with the Wolf numbers of its concentrations in the lower and upper tropospheric layers.

Table 2. Correlation coefficients of average annual concentrations of a number of ions and elements in different sensing layers with Wolf numbers for the period 1997 - 2018 (for n = 22 and P = 0.05 $R_{sign.}$ = 0.36)

	500-1000 m	1500-2000 m	3000-4000 m	5500-7000 m
K^+	**0,3980**	0,3220	0,2449	**0,4568**
NO_3^-	0,0351	**0,3720**	**0,4653**	**0,5220**
SO_4^{2-}	0,2428	0,3575	**0,4514**	0,3359
Si	**0,4372**	**0,5275**	**0,5138**	**0,5198**
Al	**0,4885**	**0,6066**	**0,5836**	**0,4302**
Sum	**0,5530**	**0,6114**	**0,5998**	**0,6349**

For nitrates, this relationship increases with height; for sulfate, there are obviously more factors for its formation. The mechanisms of the influence of solar-terrestrial connections on terrigenous elements are not entirely clear. Moreover, for silicon and aluminum, such a relationship with the noted significance level is observed for all atmospheric layers in which sampling was performed.

Figure 6 shows the course of average annual concentrations of the total mass concentration of inorganic components of the aerosol and normal alkanes in the entire troposphere layer for all years of systematic observations on a laboratory airplane (inorganic samples in 2019 were analyzed only for the first flight by present moment).

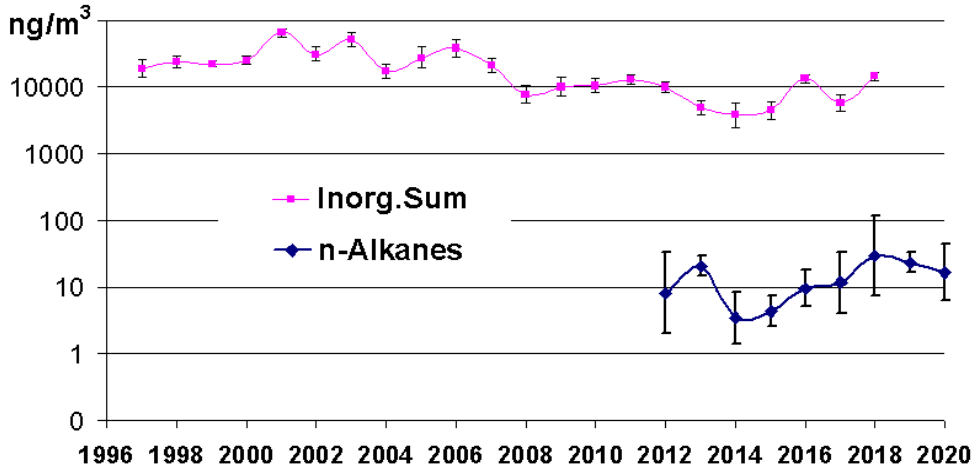

Figure 6. The course of average annual concentrations of the amount of inorganic components for 1997-2018 and the determined hydrocarbon amount of n-alkanes C_8H_{18}-$C_{32}H_{66}$ for 2012 - 2020(1^{st} quarter) in the entire layer of the troposphere, with reliable intervals (P = 0.95) (inorganic samples in 2019 were analyzed only for the first flight).

It is still difficult to decide on the patterns of the interannual variation of the separated hydrocarbon microcomponent of the tropospheric aerosol, but it is already obvious that the intra-annual variability of the sum of n-alkanes is much higher than a variability of the total inorganics in tropospheric aerosol. Most likely, the hydrocarbon component being a

predictor of the secondary aerosol, in comparison with the inorganic, has more significant variability in the troposphere, associated both with a large number of its sources, both natural and man-made, and with significant dependence on atmospheric conditions of its runoff mechanisms.

4. CONCLUSION

The formation of the long-term course of the inorganic component of the tropospheric aerosol is determined by various factors: in the first half of the observation period, the role of local sources is significant, as evidenced by an increase in the concentration in the boundary layer of the region, but in recent years there has been a tendency to smooth the concentration of inorganic component between the layers of the troposphere, which, on the one hand , indicates an increasing vertical dynamics of the atmosphere, but, on the other hand may indicate an increased role for global sources transmitted through long-distance transport. The rate of formation of nitrate and sulfate aerosols in the troposphere is related to the activity of the sun, which is reflected in the significant synchronization of the average annual concentration of these anions with the corresponding Wolf numbers. For nitrates, this relationship increases with height; for sulfate, there are more factors for its formation. The mechanisms of the influence of solar-terrestrial connections on terrigenous elements are not entirely clear.

It is even more difficult to judge the patterns of interannual variation in the amount of n-alkanes. It can be stated for now that the intra-annual variability of the extracted hydrocarbon microcomponent of the tropospheric aerosol is much higher than for the total concentration of inorganic tropospheric aerosol.

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