POLLUTION OF THE ATMOSPHERE OF NIZHNEVARTOVSK
PART II. COLD SEASON

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The paper presents the results of measurements of gaseous and aerosol composition of atmospheric pollutions over Nizhnevartovsk in the cold season. Their comparison with the results obtained in the warm season shows that the air pollution decreases in the cold season for many components by several times. The reasons of these variations are analyzed.

This paper presents the results of integrated investigations of air quality over Nizhnevartovsk in November–December, i.e., in the cold season, when the conditions of exchange of pollutants between the air and the Earth's surface changed. At this period the additional sources of pollutants, such as heating and technological boiler houses, appeared in the territory of the town.

To carry out the measurements in the same way as in summer,[1] the OPTIK–E AN–30 aircraft–laboratory was used. A mobile station was replaced by a mobile complex with a consequent decrease of the number of measurable characteristics. In particular, we did not measure γ–background and mercury vapor content. Taking into account the results of the experiment carried out in summer[1] which pointed out the safe values of these parameters, we considered the obtained results as the data of complete significance. The rest of the parameters of air were determined by the same procedures and with the same devices as in the experiment carried out in summer. Practically the same parameters were measured by the aircraft–laboratory and ground–based complex.

During the experiment the synoptic situation was characterized by repeated passage of cyclones and weather fronts accompanied by the precipitation that, according to our data,[2] promotes the accumulation of impurities by no means.

SURFACE AIR POLLUTION

The number of sites in which the measurements were carried out reduced from 33 in summer to 13 in the cold season. It was due to two reasons, namely, to severe operational conditions in an unequipped automobile and to short light period determining the vital activity of population. Sites of observation coincided with the most polluted points revealed during the summer experiment.

Without listing all the data of primary measurements note that the concentration of some gases decreases sharply in the cold season down to the values being less than the threshold of sensitivity.

The frequency of recurrence of acetylene, xylene, and benzine decreased sharply. Acetylene was identified only twice (but in both cases its amount exceeds the maximum permissible concentration (MPC)), benzine – three times, once as traces and twice in a very great amount significantly exceeding the maximum permissible concentration. Xylene was recorded three times, once with high concentration and twice as traces.

Ethyl ether was occasionally detected in the same way as in summer only over two sites as traces.

Ammonia, benzene, carbon oxide and dioxide, and sulphur dioxide can be considered as the gases whose concentration remained almost unchanged in passing from warm to cold season. Moreover, NH_3, NO, and NO_2 concentration exceeds the maximum permissible concentration even on the average, benzene exceeds the MPC over one, CO over two, and SO_2 over four of thirteen sites.

This change in gaseous composition of the atmosphere over Nizhnevartovsk in the cold season reflects the decrease of its background concentration in the town. As a result, the local emissions do not spread. As to the background concentration, it decreases because of switching off such a powerful source as evaporation of the petroleum products from the underlying surface which is covered with snow in the cold season.

The second reason for decrease of the concentration of gaseous impurities is more rapid change of gaseous component to aerosol particle[3] as the temperature decreases.

Table I presents the concentration of gases in summer averaged over all the data and 13 sites analogous to the cold season, the average concentration in the cold season, and the results obtained by other authors for comparison.

From comparison of the fall and summer data (Table I) we can see a sharp decrease of the concentration of acetylene, acetone, benzene, xylene, SO_2, H_2S, toluene, total petroleum hydrocarbons, chlorine, ethyl ether, and total hydrocarbons, and on the contrary, the increase of the concentration of NH_3, NO, and CO_2.

TABLE I. Gaseous air composition (mg/m^3).

Air components	Nizhnevartovsk			New–York	Los–Angeles	Leningrad	USSR
	Summer 33 sites	Summer 13 sites	Fall 13 sites	Ref. 4	Ref. 5	Refs. 5 and 6	Ref. 7
Ammonia	0.74	0.44	0.90	0.19	–	–	0.06/0.82
Acetylene	20.10	28.15	1.00	0.58	–	–	–
Acetone	20.32	27.62	<	–	–	–	–
Benzine	8.10	17.14	13.40	–	–	–	–
Benzene	1.16	1.21	0.81	0.71	0.20	0.11	–
Xylene	5.80	6.12	0.43	0.83	0.56	0.12	–
Ozone, μg/m^3	5.00	5,75	3.60	–	–	–	–
NO	0.41	0.47	1.33	–	–	–	0.03/0.35
NO_2	1.49	1.78	0.83	–	–	–	0.04/0.38
CO	2.23	3.63	3.44	–	–	2.00	1.47/12.6
CO_2, %	0.11	0.16	0.71	–	–	–	–
SO_2	0.83	0.82	0.48	–	–	0.04	0.04/0.52
H_2S	6.03	<	<	0.001	–	–	0.002/0.04
Toluene	3.73	5.12	<	0.64	0.53	0.11	–
Σ CH petroleum	39.80	40.07	19.13	–	–	–	–
Chlorine	0.04	0.12	<	–	–	–	0.01/0.14
Ethyl ether	15.40	48.62	1.85	–	–	–	–
Σ CH	214	234	92.30	–	–	–	–

Note: Symbol < means concentration lower than detection threshold and symbol – means that gas was not identified. In the last column numerator stands for concentration averaged over the entire territory of the USSR and denominator – for concentration averaged over its maximum.

It should be noted that the total concentration of nitrogen oxides scarcely changed in 13 comparable sites. There occurs only redistribution of NO and NO_2 contributions, namely, NO concentration increases while NO_2 concentration is nearly halved. This suggests diminishing of the intensity of photochemical processes in this season.

In the comparable sites in addition to ΣNO concentration the carbone oxide concentration scarcely changed that indicated constancy of source of these gases in air over Nizhnevartovsk in the cold and warm seasons.

Thus, the average characteristics also show a considerable decrease of the gaseous pollution of air over Nizhnevartovsk in the cold season.

Data in Table I make it possible to compare the gaseous composition of air over Nizhnevartovsk and air composition in other cities.

So, if only organic gases are considered, we can see that acetylene concentration in New York is only half as high as in Nizhnevartovsk in the cold season. Comparable values of concentration of benzene and xylene were observed in New York and Los Angeles.

The carbone oxide concentration in Nizhnevartovsk is closest in value to that in Leningrad.

The last column of Table I shows the values of gas concentration averaged over the entire territory of the former USSR and concentration averaged over its maximum recorded values borrowed from Ref. 7. It can be seen that concentration of gases recorded in Nizhnevartovsk falls within the range between average concentration and concentration averaged over its maximum values. As to concentration of NO_2, SO_2, and H_2S, in Nizhnevartovsk it is higher than its average maximum values in the USSR.

Hence, against the criterion of comparable gases Nizhnevartovsk can be classified among the group of towns in which the pollution level is higher than average.

An investigation of the suspended substances showed a decrease of concentration of the elements and their number in aerosol particles (see Table II) because of covering of the underlying surface with snow in the cold season.

In this case the values of F^-, Ni, Cu, and B concentration remained practically unchanged, while Cl^- and NH_4^+ content in the composition of particles even increased. Apparently, this resulted from the processes of aerosol formation in the cold season.

One can also see the *pH* increase from 5.26–5.40 to 6.41 in the cold season. According to the data obtained in Ref. 8, this value of *pH* is characteristic of pure water.

Summarizing this section we can conclude that in the surface layer of atmospheric air over Nizhnevartovsk the concentration of many air components very substantially decreases in the cold season. At the same time, the redistribution of mass between gaseous and aerosol components can be identified.

TABLE II. Chemical aerosol composition (μg/m^3) *over Nizhnevartovsk.*

Gases	Summer 33 sites	Summer 13 sites	Fall 13 sites
pH	5.40	5.26	6.41
F^-	2.09	3.13	3.10
Na^+	1.07	1.32	0.63
K^+	2.68	6.30	0.63
Cl^-	11.69	12.34	22.75
Br^-	1.14	0.39	<
NO_3^-	0.44	0.93	<
NH_4^+	0.05	0.11	0.43
SO_4^{2-}	0.81	1.02	0.16
Hg^{2+}	0.004	0.002	<
As^{5+}	0.012	0.008	<
Zn^{2+}	0.20	0.25	0.06
Cd^{2+}	0.002	<*	<
Fe	6.74	6.28	0.74
Mg	20.37	20.60	0.48
Mn	0.30	0.22	0.003
Pb	0.08	0.05	0.03
Cr	0.27	0.34	0.01
Sn	0.09	0.21	<
W	0.09	0.10	<
Ni	0.01	0.02	0.01
Al	10.05	7.89	0.82
Ti	1.28	0.88	0.30
Cu	0.07	0.06	0.05
V	0.01	0.05	0.01
B	0.04	0.02	0.03
Ba	0.11	0.10	<
Ca	26.09	30.40	5.42
Si	17.32	16.06	0.41
Co	0.08	0.22	<

Note: Symbol < means the concentration lower than detection threshold.

VERTICAL DISTRIBUTION OF POLLUTION

Measurement of vertical distribution of the meteorological parameters with the OPTIK–E AN–30 aircraft–laboratory showed that in the cold season all the three types of the air temperature distribution determining the spread of pollutants can be observed over Nizhnevartovsk, namely, surface temperature inversion (the most unfavorable conditions for spreading), elevated temperature inversion (a reservoir for spreading of pollutants enlarges), and temperature lapse (under these conditions accumulation of pollutants is minimum). The altitude of the temperature inversion maximum (even for surface temperature inversion) or of a layer of temperature lapse is rather high and is equal to about 1 km or higher.

Under these conditions the vertical distribution of air pollutants will insignificantly depend on the meteorological conditions that can be proved by the data shown in Fig. 1.

Before proceeding to the analysis of this figure it should be noted that in the cold season we could not detect such components as acetone, toluene, chlorine, and hydrogen sulphide over the town. Ethyl ether, carbon oxide, and acetylene were detected only near the Earth's surface.

It can be seen from Fig. 1 that there are some peculiarities in the vertical distribution of gases. So, for instance, in the fall season benzene and nitric dioxide behavior is close to neutral with the maximum near the Earth's surface. Ammonia, benzine, carbon dioxide, and petroleum hydrocarbons have two maxima in their vertical profiles attained near the Earth's surface and at an altitude of 600 m. Sulphur dioxide also attains two maxima at altitudes of 200 and 600 m. And finally, xylene has only one maximum at an altitude of 200 m.

Such a vertical distribution of the gaseous components indicates that in the cold season there are three sources of emission of gases in the region of Nizhnevartovsk. The first source is located near the Earth's surface and most probably it includes a motor transport. An altitude of the second source is about 200 m and, most probably, it includes the boiler houses. The third source, obviously, includes the powerful gas and oil plumes emitting the great amount of the combustion products at an altitude of 600 m.

In contrast to summer season, in the cold season an ozone hole developed at an altitude of 400 m over Niznevartovsk disappears (see Fig. 1). Vertical ozone distribution becomes more uniform in the boundary layer. Only near the Earth's surface ozone concentration decreases sharply because of destruction by pollutants.

The vertical profiles of gaseous components in the cold and warm seasons are illustrated in Fig. 2 for comparison. It can be seen from Fig. 2 that in the boundary layer as well as in the surface layer the concentration of gaseous pollutants significantly decreases in the cold season. Only sulphur dioxide is an exception.

The vertical distribution of some gases changed as well. So, for instance, in the warm season the NO_2 concentration was maximum near the Earth's surface and had a small secondary maximum at an altitude of 400 m. In the cold season the maximum of NO_2 concentration was still observed near the ground while at higher altitudes the NO_2 concentration considerably decreased. The profile of NO concentration was subject to the wide variations. If in summer this gas had a pronounced maximum at an altitude of 400 m and a secondary maximum near the ground, then in the cold season NO maximum descended down to an altitude of 200 m but its concentration near the Earth's surface became by nearly three times higher. This fact indicates that in the cold season the mechanism of $NO \rightarrow NO_2$ change along the chain

$$NO + O_3 \rightarrow NO_2 + O_2$$

is scarcely effective because of low ozone concentration within the layer 0–200 m and fast consumption of ozone which, judging from the data shown in Fig. 1, is irreducible photochemically in this layer.

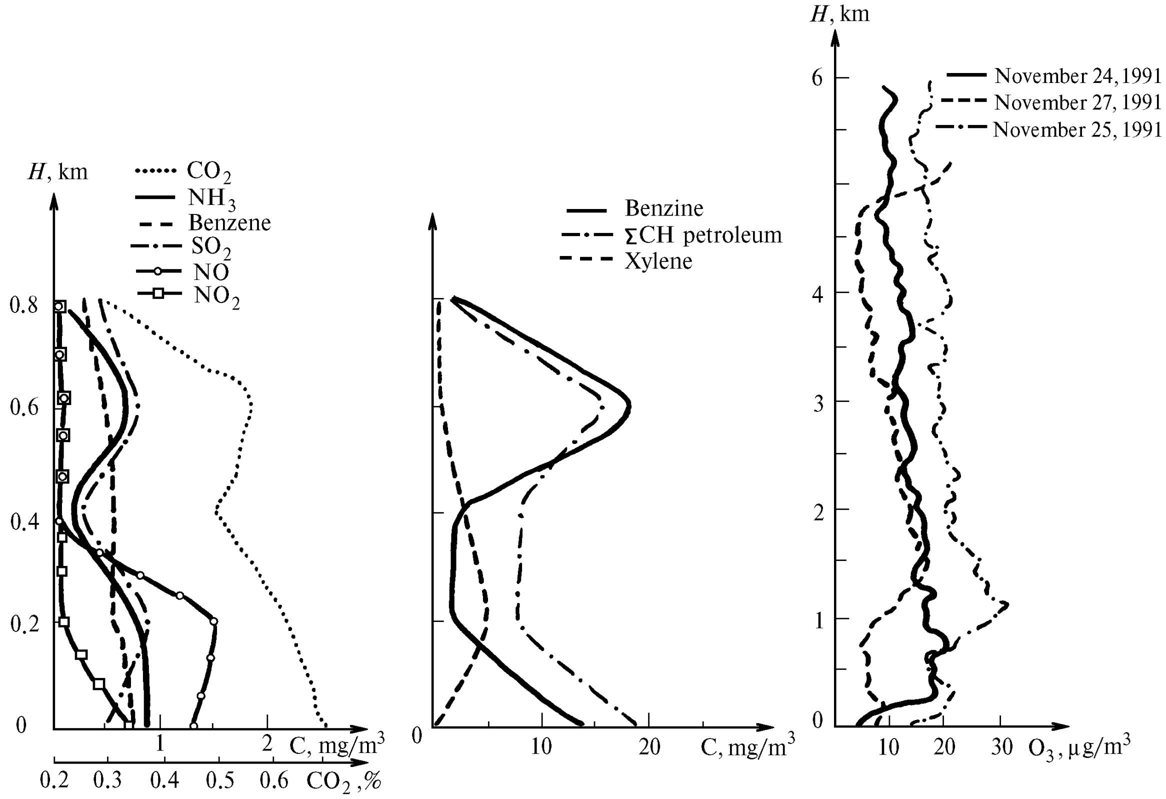

FIG. 1. Vertical distribution of gaseous air components in the cold season.

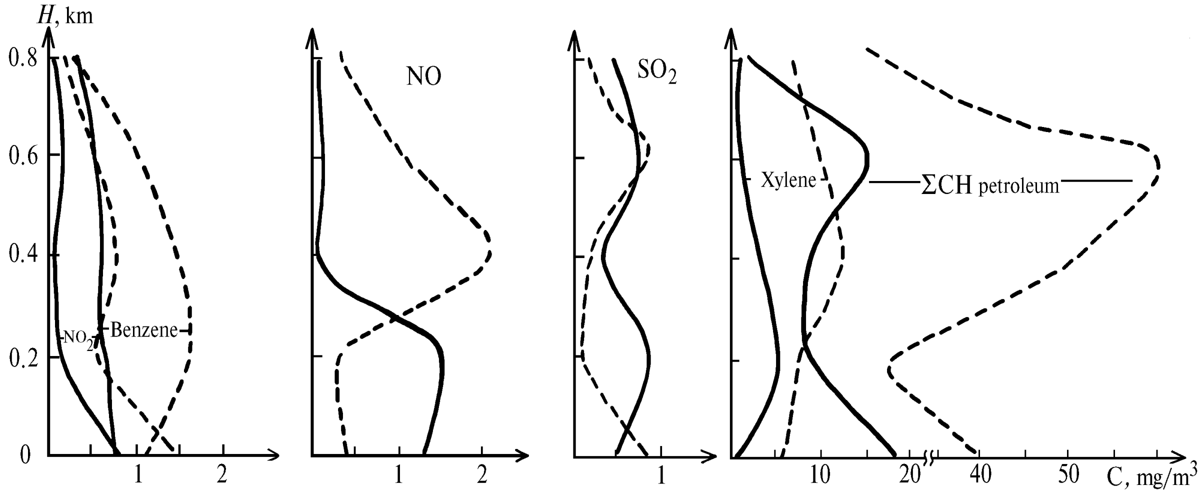

FIG. 2. Vertical distribution of gaseous air components in the cold (solid curve) and warm (dashed curve) seasons.

Organic gases decreased their concentration in the boundary layer in the cold season. Benzene showed almost neutral behavior in this season. Xylene maximum descended from 400 to 200 m. The vertical distribution of the petroleum hydrocarbons retained its profile in the cold season. However, their concentration was halved near the ground and became one fourth at the altitude where the maximum was observed.

Such large amount of decrease of concentration of the polluting gases in the cold season occurred not only near the ground but also throughout the boundary layer and was caused, in our opinion, by the effect of two factors, namely, snow covering of the underlying surface that prevented evaporation of the spilled petroleum products and faster gas–aerosol change at low air temperatures. The latter can be illustrated by Fig. 3 which shows the data on the size distribution of aerosol particles obtained with the help of diffusion battery and photoelectric counter.

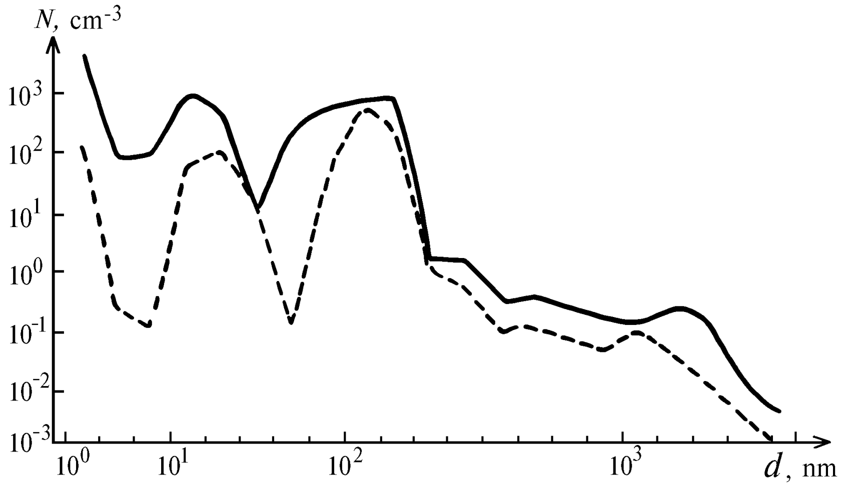

FIG. 3. Size distribution of aerosol particles at an altitude of 200 m *from windward (solid curve)and leeward (dashed curve) sides of Nizhnevartovsk.*

Figure 3 shows that there are two modes, as a rule, in a section of the size spectrum describing the fine fraction of particles. One of them is at the very beginning of the spectrum (d = 5 nm) and indicates that in air there occurs a continuous generation of clusters from aerosol–forming gases. Further the process of coagulation coarsening of the particles starts. Here a difference in the spreading trajectories becomes pronounced with increasing distance from the source. The longer is the distance, the larger is the size of the particles. Therefore, the second mode shifts towards the larger size.

In the region of Nizhnevartovsk such size distributions of particles can be permanently observed that indicates the constancy of the gas–aerosol change. In the regions without the sources of aerosol–forming gases, the concentration of particles of finely dispersed fraction is, as a rule, less[9] by a factor of 10^3.

At the same time, this fraction of particles cannot be trapped with the AFA filters which we employed in determining the chemical composition of aerosol because the particles smaller than 100 nm passed through such filters.[10] Therefore, the change of gases to aerosol particles cannot be detected from the data on their chemical composition measured near the source. It can be identified only at a distance at which the particles will be transformed before they are transformed from finely dispersed fraction to submicron one. This distance, according to previously obtained data,[11] is about several tens of kilometers.

All the above–discussed arguments can be confirmed by the data on the vertical distribution of aerosol chemical composition illustrated in Figs. 4 and 5.

Figure 4 shows that most of aerosol chemical components as well as the gases have their maximum at altitudes of 600 and 200 m or near the ground. Only two substances, namely, SO_4^{2-} and Pb, attain their maximum near the inversion level at an altitude of 800 m.

In contrast to gases, very many components have maximum concentration at an altitude of 400 m. They are Zn^{2+}, Cu, Si, Ca, Ba, Ni, Mo, and V, in other words, those elements which usually comprise the large particles.[12] Probably, their maximum at an altitude of 400 m is connected with sedimentation of heavier particles from the above layer in which pollution is emitted (~ 600 m) and the total aerosol mass (M) reaches its principal sharply defined maximum.

Hence, the data on the chemical composition of aerosol also indicate the same sources of pollution as the gaseous air components do.

The profiles of some chemical aerosol components are illustrated in Fig. 5 for comparison in the cold and warm seasons.

As can be seen from Fig. 5, the concentration of almost all components in the cold season is less than in the warm season. Only Ba and Ti are exceptions.

The hydrogen ion exponent of aerosol changed very significantly. If in summer its value varied from 5 to 5.8 then in fall the pH was not lower than 6.1.

From summer to fall an altitude of concentration maximum changed for a number of elements as well. It descended for Cl^-, Ca, Cr, and Ti, while for Pb and Na^+ it ascended. The profiles of chemical components smoothed. For most of them the secondary maxima disappeared. The absence of the maximum near the Earth's surface can be easily explained by snow covering and effect of screening, but it is still difficult to explain disappearance of the secondary maxima in the profiles for several sources of emissions.

The presence of elevated maxima for almost all of the chemical components of aerosol indicates that their fluxes are directed downwards to the Earth's surface.

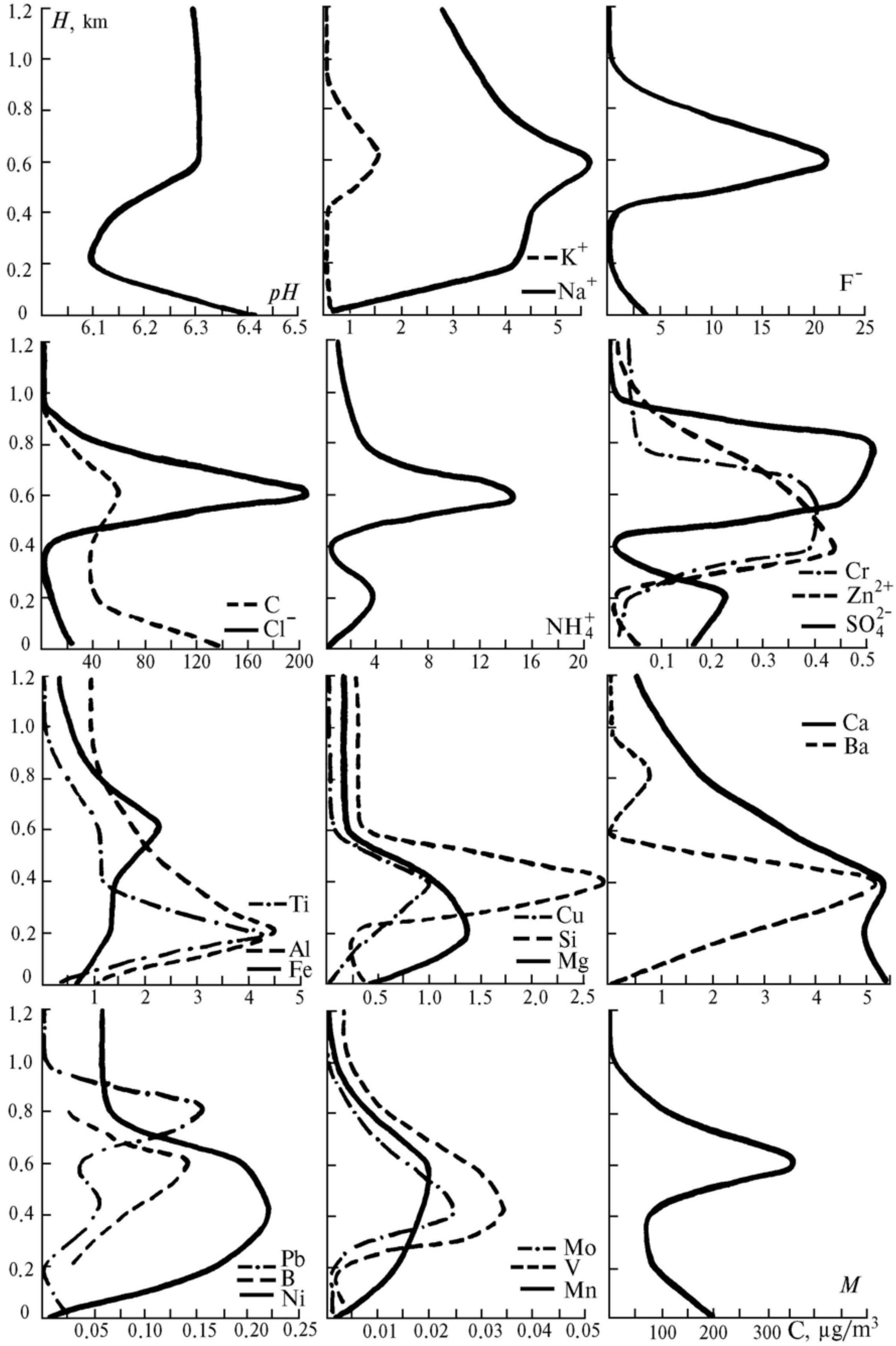

FIG. 4. Chemical composition of suspended substances (mg/m^3) *in the cold season over Nizhnevartovsk.*

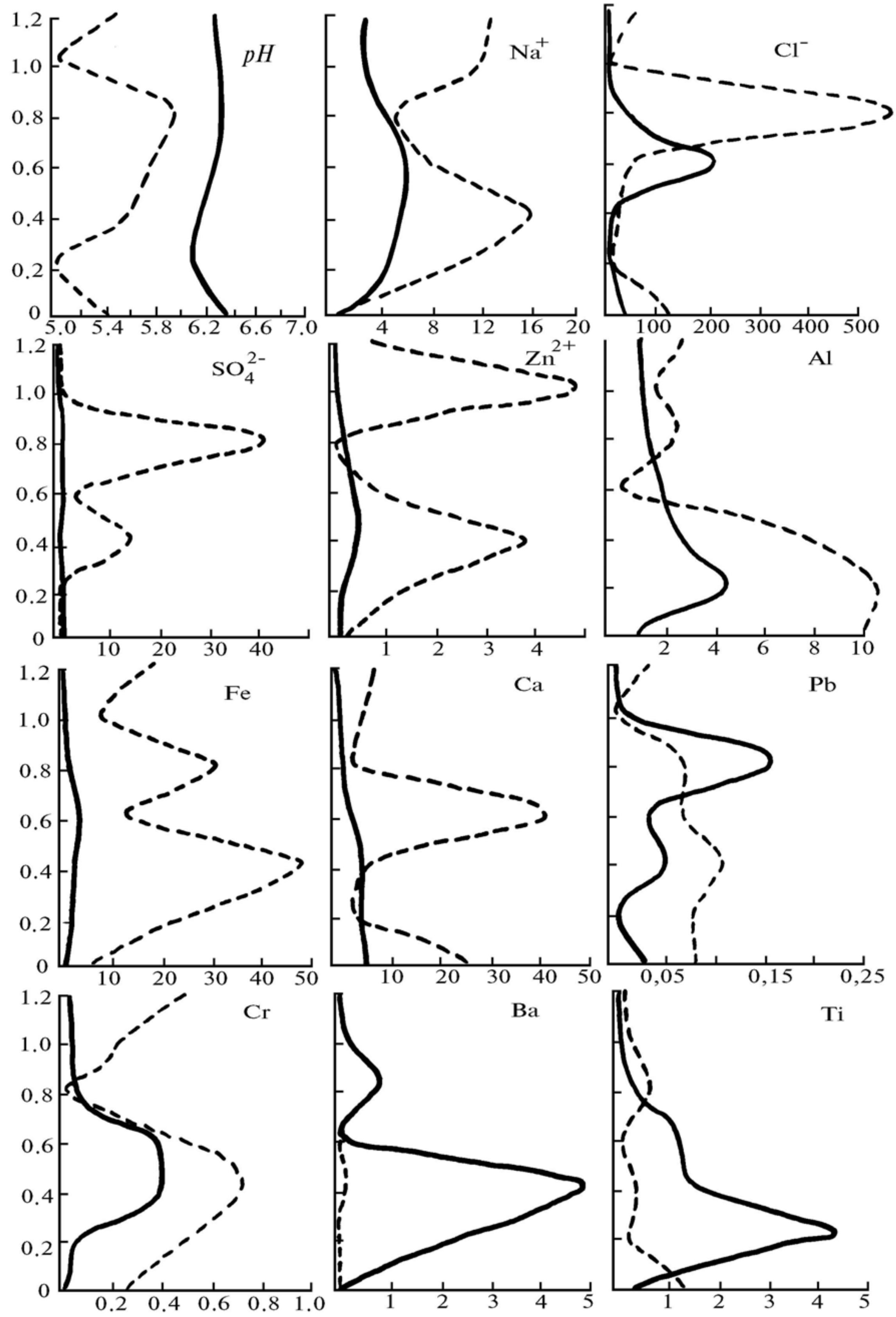

FIG. 5. Chemical composition of suspended substances in the cold (solid curve) and warm (dashed curve) seasons (mg/m^3).

COMPOSITION OF EMISSIONS OF THE MAJOR SOURCES

To carry out an analysis which sources produce different components of pollutants in air over Nizhnevartovsk, the samples from oilfield plumes, boiler houses, and motor transport emissions were tested. Their gaseous and aerosol composition is listed in this section.

As can be seen from Table III, gaseous composition of emission in the region of Nizhnevartovsk is identical to that which is observed in the cold season out of the traces of plumes. It concerns the motor transport as well. It should be noted that the data on its emissions are presented in relative units (gram per kilogram of fuel) which can be easily scaled to concentrations.

TABLE III. Chemical composition of emissions

Gases	Samotlor		Megion	Nizhnevartovsk		Motor transport	
	Oil plume	Gaseous plume	Boiler house	Boiler house No. 1	Boiler house No. 2	Carburetor	Diesel
Ammonia	1.9	0.2	0.8	1.2	0.1	0.02	<
Acetylene	<	<	<	<	3.0	12.44	13.55
Acetone	<	<	<	<	3.2	0.54	1.34
Benzine	31.0	2.2	12.4	2.4	<	3.62	18.11
Benzene	1.8	1.2	0.5	1.2	0.5	1.13	5.49
Xylene	9.6	10.8	5.2	<	5.4	1.84	4.24
NO	1.2	1.3	0.1	2.2	1.6	4.34	8.53
NO_2	0.08	0.2	0.08	1.0	<	0.29	2.58
CO	3.2	3.9	5.6	3.1	2.4	19.82	14.82
SO_2	1.8	1.6	0.8	0.9	0.4	0.77	1.22
Toluene	<	<	<	0.8	0.9	2.05	12.82
Σ CH of petroleum	32.0	14.6	16.2	26.0	12.0	15.76	44.17
Chlorine	<	<	<	0.1	0.5	0.16	0.29
Ethyl ether	<	<	<	<	<	–	–

TABLE IV. Chemical aerosol composition (in units of μg/m^3) in plumes.

Gases	Samotlor		Megion	Nizhnevartovsk
	Oil plume	Gas plume	Boiler house	Boiler house
pH	6.37	6.35	6.25	6.21
Na^+	18.37	5.17	5.29	1.27
K^+	<	<	<	0.04
Cl^-	112.10	<	48.80	13.80
NH_4^+	<	<	<	12.70
SO_4^{2-}	<	<	2.89	3.29
Hg^{2+}	<	0.19	0.03	0.26
Fe	4.38	6.12	3.47	6.48
Mn	0.04	0.003	0.02	0.08
Mg	4.25	<	1.85	1.74
Pb	0.14	0.07	0.02	0.11
Cr	0.10	<	0.02	1.19
Ni	0.41	0.08	0.17	0.26
Al	242.5	3.22	10.80	5.33
Ti	12.0	5.32	4.90	2.96
Cu	0.28	2.13	0.33	1.19
V	0.03	<	0.01	0.04
Mo	<	<	<	0.02
Ca	13.75	3.54	10.30	10.90
Si	0.63	0.03	0.83	0.29
Ba	1.56	<	0.83	3.13
B	0.06	<	0.01	0.09
Co	<	<	0.005	0.002

It would be desirable to obtain the analogous data for the warm season. However, in summer the boiler houses were inoperative and an attempt of the aircraft–laboratory to enter a mouth of plumes of the oilfields led almost to a catastrophe. Sampling at a distance from the mouth from poorly visible plume (without condensation and, consequently, aerosol) would be incorrect.

The chemical composition of emission is indicated in Table IV. It includes the high concentration of Na^+ and Cl^-. Concentration of the elements forming a soil aerosol such as Fe, Mg, Al, Ti, and Ca was higher than near the ground. The NH_4^+, K^+, and SO_4^{2-} ions were identified only in the plumes of boiler houses. This concerns the elements Mo and Co as well.

At the same time, the data in Table IV do not confirm a hypothesis that the vertical distribution of the chemical components of aerosol presented in the foregoing section is formed only by local emissions. Apparently, there occurs a superposition of wind–blown aerosol, emissions, and aerosol rising from the Earth's surface.

CONCLUSION

Experiment carried out in the cold season have shown a qualitative change in air composition over Nizhnevartovsk resulted from switching off such a powerful source of pollution as evaporation of spilled petroleum products. Results obtained in the course of both integrated experiments make it possible to estimate a correlation of factors determining the pollution of air over the town.

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