# POLLUTION OF THE ATMOSPHERE OF NIZHNEVARTOVSK PART I. WARM SEASON

# B.D. Belan, V.I. Vaver, V.K. Kovalevskii, O.Yu. Luk'yanov, V.E. Meleshkin, M.K. Mikushev, M.V. Panchenko, A.V. Podanev, E.V. Pokrovskii, T.M. Rasskazchikova, A.V. Sibirko, S.A. Terpugova, G.N. Tolmachev, A.I. Shcherbatov, and A.V. Shcherbatova

Institute of Atmospheric Optics, Siberian Branch of the Russian Academy of Sciences, Tomsk Received February 5, 1993

The paper considers the data of experimental determination of more than 50 ingredients of gaseous and aerosol composition of air over the region of Nizhnevartovsk.

The pollution composition and distribution in the near-ground layer over the city and the vertical profiles of the impurities are determined. The diurnal variations of different air components are analyzed. The impurity budget is calculated over the region of the town and the Lake Samotlor oilfield. It is shown that three pollution sources act in the Nizhnevartovsk region in summer. They are the motor transport, plumes of combustion of the accompanying gases, and evaporation of petroleum products spilled on the underlying surface; the intensive photochemical processes in the urban air; and, the hydrocarbon sedimentation which is observed in the nighttime from the upper air layers. The impurity fluxes over the city and the oilfield are estimated.

## INTRODUCTION

The intensive development of oil production industry in the north of Western Siberia resulted in sharp worsening of the ecological situation in this region. The reasons are the complete neglect of salvaging our environment during exploitation of the oilfields and subsequent wrong estimate of the principal sources of pollution. The Institute of Atmospheric Optics, Siberian Branch of the Russian Academy of Sciences, Tomsk (IOA SB RAS) carried out the integrated observation of Nizhnevartovsk and the adjacent oilfields by means of the OPTIK-É AN-30 aircraft– laboratory and mobile station in 1991. Measurements were carried out in warm and cold seasons. The results obtained in August are presented in this paper.

The aims of the expedition were the following:

- determination  $% \left( {\left[ {{{\rm{T}}_{{\rm{T}}}} \right]_{{\rm{T}}}} \right)$  of quantitative and qualitative composition of pollution,

- analysis of spatial and temporal dynamics of pollution inside and outside the town,

- revealing of the main pollutants, and

 $- \mbox{ identification }$  of the reasons and sources of pollution.

The mobile ecological station assembled on the basis of the GAS-66 truck (IAO SB RAS and the Scientific-Production Enterprise "Ekotekhnologiya") was completed with the following means of routine air monitoring<sup>1</sup>:

meteorological complex,

- KG–02 and GIAM–15 gas analyzers (ozone and carbone oxides),

- RGA-11 gas analyzer (Hg vapor),

- indicator of the radioactive background  $(\gamma$ - background),

- KPM-4 small-size field chromatograph,

- AZ-5 photoelectric counter, and

– FAN photoelectric nephelometer.

The OPTIK-É AN-30 aircraft-laboratory included the MAKREL-2 lidar<sup>2</sup> in addition to the aforementioned complexes.

Thus, the measuring complexes of the aircraft– laboratory and mobile station were almost identical. They were capable of measuring 17 gaseous components of air and about 40 elements and ions in the suspended substance composition. The meteorological parameters and the  $\gamma$ – background of the region were simultaneously monitored.

In order to determine the pollution concentration in the near-ground layer over the town and out of it, 33 measuring sites were selected. These sites were distributed almost uniformly over the town area and were at the main crossroads, inside the microdistricts, and in industrial zones.

The aircraft–laboratory operated simultaneously with the ground–based complex by the procedure described in Ref. 3.

The obtained data made it possible to construct the maps of distribution of all measurable air components not only near the ground surface, but also at some altitudes. That made it possible to understand better the mechanism of the proceeding processes.

## POLLUTION OF THE NEAR-GROUND AIR LAYER

Before proceeding to an analysis of the obtained data, it is necessary to give some methodical comments.

Since our objective was to inspect the ecological situation in the town, we paid most attention to the selection of the measurement sites which cause considerable concern of the Municipal Environmental Protection Agencies. Therefore, the presented data of measurements in individual sites and their average values characterize the sites of enhanced anthropogeneous loading, and one should consider them as instantaneous not trying to expand them to the town as a whole. It should be also noted that

 $^{\odot}$ 

1993 Institute of Atmospheric Optics

in August, 1991, and therefore the results were preliminary for the whole summer season, to say nothing of the data averaged over the period of several years.

In the beginning let us dwell on the most general characteristics of air pollution. The averaged gas concentration over 33 ground-based sites and an entire data array are given in Table I (maximum excess of the maximum permissible concentration obtained in individual measurements is also given here).

TABLE I. Average concentration of gases in Nizhnevartovsk in warm season.

Component,	Average	Excess of maximum
$mg/m^3$	value	permissible concentration
0		(MIPC)*
O <sub>3</sub> , μg/m <sup>3</sup>	5.00	—
NH <sub>3</sub>	0.74	21
Acetylene	20.10	_
Acetone	20.32	314
Benzine	8.10	10.4
Benzene	1.16	2.8
Xylene	5.80	105
ΣΝΟ	1.90	—
NO	0.41	—
$NO_2$	1.49	57.6
CO	2.23	8.3
CO <sub>2</sub> , %	0.11	_
$SO_2$	0.83	5.8
H <sub>2</sub> S	6.03	25
Tolyene	3.73	35
$\Sigma$ CH of petroleum	39.80	—
Cl <sub>2</sub>	0.04	5
Ethyl ether	15.40	_
$\Sigma \ CH$	214.00	—

(MIPC)\* means the maximum instantaneous permissible concentration.

It can be seen from Table I that 12 from 19 measurable gases exceed the maximum permissible concentration (MPC) over Nizhnevartovsk in summer. They are  $NH_3$  (~ 20), acetone (~ 300), benzine (~ 10), benzene (~ 3), xylene (~ 100),  $NO_2$  (~ 60), CO (~ 8),  $SO_2$  (~ 6),  $H_2S$  (~ 20), toluene (~ 30), and  $Cl_2$  (~ 5 MPC). Only ozone and mercury vapor do not exceed the MPC. For the other 6 gases, which also have the high concentration, the MPC was not determined. Noteworthy is carbon dioxide, whose concentration in individual sites of Nizhnevartovsk was 15 times higher than the background concentration with an average value of 0.11% (normal concentration is 0.034%).

The fact that the average concentration of some gases over the sites of heavy anthropogeneous loading exceeds the value of the maximum instantaneous permissible concentration (MIPC) has engaged our attention. This is true for ammonia (~ 3), acetone (~ 6), benzine (~ 1.5), xylene (~ 10), NO<sub>2</sub> (~ 18), SO<sub>2</sub> (~ 1.5), and toluene (~ 6 MIPC). This is caused by both the high concentration of the above-enumerated gases over individual sites and the frequent recurrence of these gases over the territory of the town.

Table II gives an indication of the average chemical composition of suspended substances in the warm season.

TABLE II. Average aerosol chemical composition ( $\mu g/m^3$ ) in Nizhnevartovsk in warm season.

			$K^+$			0	-	-	
5.40	2.09	1.07	2.68	11.69	1.14 (	).44 (	0.05 (	0.81 0	.004
			-						
			+ Fe						W
0.012	2 0.20	0.00	2 6.74	20.37	0.30	0.08	0.27	0.09	0.09
Ni	Al	Ti		V		Ba	Ca	-	Со
0.01	10.0	5 1.28	3 0.07	0.007	0.038	0.11	26.09	17.32	0.08

Although Nizhnevartovsk ranks among the towns being most polluted by the suspended substances,<sup>4</sup> the data in Table II do not confirm that. Apparently, frequent rain during the experiment resulted in purification of the atmosphere and affected the data, because the aerosol field had no time to reproduce itself, since this took about 4-5 days.<sup>5</sup>

Table II gives the low value of the hydrogen ion exponent pH, which is equal to 5.4 and is close to the values characteristic of the acid rain,<sup>6</sup> and the high concentration of Mg (~ 20 mg/m<sup>3</sup>) which was not observed over other towns.

In addition to the substances enumerated in Table II, we also determined Mo, Ag, Ga, Jn, and P in the aerosol composition, but their concentration was lower than the detection threshold.

The preliminary information about the emission sources pointed out that the main source in the city was the motor transport. The analysis of the spatial distribution of the impurities over the town confirmed this fact only partially.

If we consider the CO distribution over the town (Fig. 1), we can see that its maximum concentration is observed in the central part and decreases to the periphery. Since the maxima of the CO content correspond to the intersections of the main stream of traffic, the transport can be assumed, with high degree of confidence, the main source of CO.

The distribution of other gases in air indicates the existence of additional sources. Thus, we can identify two possible sources in the field of total hydrocarbons shown in Fig. 2. They are the airport zone that is quite understandable if we take into account the intensity of air transport and the plume of the Lake Samotlor oilfield. The CO concentration over the town increases due to local emissions. Thus, Fig. 2 shows that the oilfields affect the near-ground air layer.



FIG. 1. Distribution of the carbon oxide concentration over Nizhnevartovsk (mg/m<sup>3</sup>).



FIG. 2. Distribution of the total hydrocarbons concentration (mg/m<sup>3</sup>).

#### VERTICAL DISTRIBUTION OF POLLUTION

The existence of two oilfields such as Megion and Samotlor, in which the accompanying gas is still burnt, near Nizhnevartovsk calls for the obligatory analysis of the vertical distribution of the impurities, since they can enter the territory of the town for the appropriate wind directions. The average profiles of the gaseous components of air are shown in Fig. 3. The general conclusion which follows from the data is that the source of gaseous impurities is elevated above the town and is situated at an altitude of about 400 m at which 7 from 11 gases have their maxima. Two gases such as petroleum hydrocarbons and SO<sub>2</sub> have their maximum concentration at an altitude of 600 m.



FIG. 3. Vertical profiles of the gaseous impurities over Nizhnevartovsk.

In addition, it can be seen that a number of gases have their powerful source near the ground. They are acetylene,  $NO_2$ ,  $SO_2$ , and CO.

Let us pay our attention to the special character of the ozone vertical distribution over the town, namely, to the decrease of its concentration almost to zero at an altitude of 400 m at which the maximum concentration of most of gases is observed. The analysis of the maps of the corresponding levels of concentration shows that this is not a single fact but results from the action of permanent factor.

It is known that nitric oxide, as a rule, is formed in the combustion products. It changes to nitric dioxide in the presence of ozone by the reaction

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

Figure 3 shows that the power of the NO source at an altitude of 400 m is so high that ozone has no time to be produced or to enter this level in order to provide the complete change of NO to  $NO_2$ . Thus, the local ozone hole is formed over Nizhnevartovsk at an altitude of 400 m in the warm season. The maximum concentration of many aerosol chemical components is detected at the same altitude in addition to the maxima of the gaseous components. Among them are Si, Fe, Pb,  $NO_3^-$ , K<sup>+</sup>, Na<sup>+</sup>, and Zn<sup>2+</sup>. However, the chemical components of the

suspended substances are stratified much more distinctly than gases. Some of them have the maxima of concentration at an altitude of 200 m (Al,  $As^{5+}$ , and  $Cd^{2+}$ ), 600 m (Mn, Ca, and F<sup>-</sup>), and 1000 m (Zn<sup>2+</sup> and Ni). An altitude of 800 m is especially distinguished. The concentration of such substances as Cl<sup>-</sup>, Br<sup>-</sup>, SO<sup>2</sup><sub>4</sub>, and Hg<sup>2+</sup> at this altitude is much higher than at the other altitudes.

The data of Fig. 4 show that the elevated emissions spreading upwards are the source of many aerosol components in the near-ground layer (Table II). Only Pb and Mg are produced near the ground.

The stratified character of the ion and element distribution results in the complex character of the vertical profile of pH. It reaches its minima at an altitudes of 0.2 and 1 km and maximum at an altitude of 0.8 km.

The above-presented data on the air composition over Nizhnevartovsk provide strong evidence that the atmosphere of the town is heavily polluted by emission from the plumes of adjacent oilfields.

# DUIRNAL VARIATIONS OF AIR POLLUTION

The duirnal variations of air impurity concentration were measured at the most polluted site of the town located on the crossroad of Mira and Neftyanikov Streets. It reflects the action of all the aforementioned factors. The duirnal variations of some components are shown in Fig. 5.



FIG. 4. Vertical distribution of the aerosol chemical components ( $\mu g/m^3$ ).

It can be seen from Fig. 5 that in the profiles of mass aerosol concentration M and concentration of petroleum hydrocarbons, acetylene,  $CO_2$ , and NO there occur two maxima corresponding to the duirnal rhythm of operation of technological motor transport. On the one hand, its operation is accompanied by gas emissions, on the other, the soil dust rises up as evidenced by the behavior of concentration of Ca and Si.

In Sec. 2 we have noted the high concentration of Mg in the composition of the suspended substances. Taking into account that the technological motor transport drives up to the oilfields in the morning and drives back in the evening, we can conclude that Mg is brought to the town from the outside (Fig. 5). Inside the town Ti is the dominant component of suspended substance composition.

Apparently, the maximum in the CO concentration in the morning is connected with the motor transport operation, since the mechanisms start to operate without preliminary warming and emit unburnt gases. The evening maximum is not observed by two reasons. First, the amount of emission of CO is less, and CO changes to secondary impurities in the course of photochemical processes. The duirnal variations of  $CO_2$  confirm this (Fig. 5).

The impact of the second factor – the oilfield plumes –is demonstrated by the duirnal variations of  $SO_2$ , benzine, and xylene. Their concentration is low during all day and becomes 2–3 times higher at night. In our opinion, this is caused by the sedimentation of these gases from the upper air layers when the intensity of turbulent mixing is minimum.

The next factor that may strongly affect the concentration of some gases over Nizhnevartovsk is the evaporation of the petroleum products spilled on the underlying surface. We failed to explain the duirnal variations of benzine, toluene, chlorine, and total hydrocarbons by the other processes.

Finally, the temporal dynamics of NO, NO<sub>2</sub>, O<sub>3</sub>, and CO indicates that the intensive photochemical processes proceed in the atmosphere of the town. This quite closely corresponds to the available concept of the photochemical processes in the polluted atmosphere.<sup>8</sup>

Thus we can identify not one but three sources of air pollution in Nizhnevartovsk in summer. They are the motor transport, combustion products from oilfield plumes, and evaporation of petroleum products. The dynamics of the primary and secondary gaseous impurities indicates the presence of the photochemical processes.



FIG. 5. Duirnal variations of the gaseous  $(mg/m^3)$  and aerosol  $(\mu g/m^3)$  air components.

## CORRELATION OF DIFFERENT COMPONENTS OF AIR POLLUTION

The problem of minimization of the number of measurable parameters is quite important for constructing the systems of routine air monitoring. One of the approaches to its solution is the determination of correlations between different pollutants. When they are present, by the variations of concentration of one of them we can infer the concentration of the other by way of preliminarily determination of the regression relation between different components. The second point is that we can follow the reason of their appearance, i.e., the emission source, from synchronism in variations of different components of air pollution.

The calculated coefficients of correlation between gaseous components of air are presented in Table III. According to Ref. 9, the significant correlation coefficient for the given length of sample is 0.4 with probability 0.995 and 0.49 with probability 0.9995, respectively.

It follows from Table III that such gases as  $O_3$ ,  $NH_3$ , acetone, NO,  $CO_2$ , and  $SO_2$  are uncorrelated with the others. Possibly, this reflects the fact that the source of their appearance in air is the action of different factors that are divorced from each other.

To the contrary, hydrocarbons that are present in all aforementioned sources are quite well correlated, namely, acetylene with benzene, toluene, petroleum hydrocarbons, and otal hydrocarbons; benzene with toluene; xylene with petroleum hydrocarbons and total hydrocarbons; toluene with petroleum and total hydrocarbons; and, petroleum hydrocarbons with total ones.

The motor transport emissions are detected from the correlation of  $\Sigma$ NO, NO, and NO<sub>2</sub>, on the one hand, and of benzine, xylene, CO, and toluene on the other.

Component	t	O <sub>3</sub>	NH3	Acetylene	Acetone	Benzine	Benzene	Xylene	Σ ΝΟ	NO	NO <sub>2</sub>	со	CO <sub>2</sub>	SO <sub>2</sub>	$H_2S$	Toluene	$\Sigma \ CH \ of$ petroleum	Cl <sub>2</sub>	Σ CH
t	<u> </u>			0.40						0.00		0.40	0.00	0.10	0.04	0.54	0.07		
	1	0.0	-0.32	0.49	-0.48	0.41	0.41	0.36	0.49	0.39	0.40			-0.19	0.01	0.51	0.37	-0.23	0.33
O <sub>3</sub>		1	-0.01	-0.04	-0.04	0.09	0.08	-0.28	-0.14	-0.01	-0.18	-0.00	-0.30	0.09	0.01	-0.03	-0.06	-0.30	-
NII																			0.11
NH <sub>3</sub>			1	-0.28	0.02	-0.33	-0.13	-0.36	-0.25	-0.12	-0.24	-0.18	0.13	-0.01	-0.12	-0.35	-0.37	0.22	-
A t 1																			0.35
Acetylene				1	-0.29	0.14	0.40	0.38	0.18	0.14	0.15		-0.02	-0.09	0.06	0.53	0.53	-0.30	0.58
Acetone					1	-0.21	-0.26	-0.10	-0.16	-0.16	-0.11	-0.10	0.07	0.12	-0.02	-0.25	-0.27	0,15	0.11
Benzine						1	0.17	0.28	0.51	0.23	0.51	0.02	0.27	-0.11	-0.06	0.38	0.21	-0.11	0.35
Benzene							1	0.33	0.39	0.09	0.35	0.01	-0.14	0.07	-0.00	0.57	0.36	0.10	0.37
Xylene								1	0.48	0.20	0.49	0.00	-0.02	0.12	-0.13	0.48	0.53	0.15	0.55
Σ ΝΟ									1	0.65	0.88	0.42	0,26	-0.29	0.36	0.44	0.26	0.32	0.35
NO										1	0.21	0.34	0.10	-0.35	0.37	0.21	0.08	0.04	0.13
$NO_2$											1	0.32	0.27	-0.15	0.23	0.43	0.29	0.39	0.37
СО												1	0.04	-0.16	0.94	0.03	0.06	-0.12	0.09
CO <sub>2</sub>														-0.15		-0.07	-0.12	0.03	0.13
SO <sub>2</sub>													-		-0.20	0.06	0.23	0.00	0.10
$H_2 \hat{S}$														-	1	-0.05	-0.11	-0.07	_
2															1	0.00	0.11	0.01	0.07
Toluene																1	0.65	-0.08	0.61
$\Sigma$ CH of petroleum																	1	-0.13	0.77
Cl <sub>2</sub>																		1	_
																			0.13
Σ CH																			1

TABLE III. Correlation of gaseous components of air in Nizhnevartovsk.

The especially close relationship between CO and  $H_2S$  is not clear yet. Possibly, it is also the result of the motor transport action.

We may explain the high positive correlation of temperature with concentration of hydrocarbons and nitric oxides by the intensification of turbulent mixing and increase of the evaporation capacity of the petroleum products with temperature. However, the reason of the negative correlation between temperature and acetone is not clear. The coefficients of correlation between air temperature at the instant of measurement and all the gases are given in the first row of Table III.

At the end of discussion of the data in Table III it should be noted that they confirm the above conclusions about the multiplicity of the sources of air pollution in Nizhnevartovsk.

# POLLUTION BUDGET IN THE REGION OF NIZHNEVARTOVSK

In order to study the budget of the air impurities coming from outside and produced over the town, sounding of the atmosphere was carried out by the procedure described in detail in Ref. 3. The principal relations used for calculation of the budget were also given there. Taking into account that the numerical value of the budget is not enough informative, we calculated the upwelling and downwelling pollution fluxes over Nizhnevartovsk and Lake Samotlor from the numerical value of the budget. The calculated results are given in Table IV.

TABLE IV. Annual fluxes of impurities  $(t/km^2)$  in the region of Nizhnevartovsk.

Substance	Nizhnevartovsk	Lake Samotlor
NH <sub>3</sub>	-0.4	-0.4
Acetylene	+28.3	+112.8
Acetone	-152.1	-64.6
Benzine	-51.5	-12.2
Benzene	+0.3	+1.5
Xylene	+32.7	+8.3
$NO_2$	+2.1	-2.3
CO	+3.6	-1.4
$SO_2$	-0.2	-0.2
$H_2S$	-0.04	+1.0
Toluene	-10.9	+11.6
$\Sigma$ CH of petroleum	-21.0	+9.5
Suspended substances	-0.1	+2.0
Downwelling flux (–)	-236.24	-81.7
Upwelling flux (+)	+67.0	+146.7
Budget	-169.24	+65.6

It can be seen from Table IV that, on the average, the annual downwelling flux is 240 t/km<sup>2</sup>. Ammonia, acetone, benzine, sulphur dioxide,  $\rm H_2S$ , toluene, petroleum hydrocarbons, and suspended substances are among the substances with the downwelling flux. Acetylene, benzene, xylene, nitric dioxide, and carbon oxide have upwelling fluxes and are removed from the town. The net annual upwelling flux is 70 t/km<sup>2</sup>. The net annual downwelling flux is equal to 170 t/km<sup>2</sup>.

The reverse dependence is observed over Lake Samotlor. The estimated upwelling flux of substances is  $65 \text{ t/km}^2$  greater than the annual downwelling flux. The downwelling fluxes have ammonia, acetone, benzine, nitric dioxide, carbon oxide, and sulphur dioxide, while the other substances have upwelling fluxes.

Thus, the net budget of pollutants given in Table IV shows that sedimentation of impurities takes place over Nizhnevartovsk, and their removal - over Lake Samotlor.

The obtained values of fluxes are in a good agreement with the data reported for Munich in Ref. 10. The estimated pollution transfer for Netherlands<sup>11</sup> also agrees by an order of magnitude with the estimates for Nizhnevartovsk.

#### REFERENCES

1. B.D. Belan, M.V. Panchenko, and N.P. Soldatkin, in: *Proceedings of the First School–Seminar on Ecology of the Atmosphere* (1991), pp 17–20.

2. V.E. Zuev, B.D. Belan, D.M. Kabanov, et al., Atmos. and Oceanic Opt. 5, No. 10, 658–663 (1992).

3. B.D. Belan, Atmos. and Oceanic Opt. 6, No. 2, 124–135 (1993).

4. É.Yu. Bezuglaya, G.N. Rastorgueva, and I.V. Smirnova, *The Breathing of an Industrial City* (Gidrometeoizdat, Leningrad, 1991), 256 pp.

5. B.D. Belan, G.O. Zadde, Yu. A. Pkhalagov, et al., Izv. Akad. Nauk SSSR, Fiz. Atmos. Okeana **28**, No. 6, 622 (1987).

6. L. Khorvat, Acid Rains (Stroiizdat, Moscow, 1990), 81 pp.

7. J.L. Sigal, Protection of the Atmosphere on Combustion of Fuel (Nedra, Leningrad, 1988), 312 pp.

8. Photochemical Processes in the Earth's Atmosphere (Nauka, Moscow, 1990), 252 pp.

9. P. Muller, P. Noyman, and R. Storm, *Tables on Mathematical Statistics* [Russian translation] (Finansy i Statistika, Moscow, 1982), 278 pp.

10. D. Paffrath, in: Abstracts of Reports at Alpbach Simp. School, Noordwijk (1990), pp. 43–49.

11. J. Lelieveld, F.W. Jansen, and J.F. Den Tonkelaar, Atmos. Environ. **21**, No. 10, 2133–2143 (1987).