

SPECIFIC FEATURES OF PHOTOCHEMICAL PROCESSES IN AIR OVER INDUSTRIAL CENTERS

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Some results of experimental investigation of photochemical processes in air over industrial centers of the Far East of the USSR are presented. It is shown that almost permanent presence of two temperature inversions (near-ground and elevated ones) in the atmosphere over this region results in formation of two layers of pollutant over the cities. The first layer accumulates atmospheric emissions from low-altitude sources and the second — from high-altitude sources. These layers do not mix. The photochemical change of the primary emissions into the secondary products takes place in the upper layer within the 200–400 m altitudes where enhanced content of photochemically active gases takes place. There are no photochemical processes in the near-ground layer because the elevated layer of pollutants screens the UV radiation. However, the secondary products have been detected near the ground. They come here from the upper level due to sedimentation at night. It was noted that over the cities the secondary products of the near-ground layer are rapidly destructed, while outside the cities they live for a longer time. This is caused by the destruction of the secondary products by the atmospheric aerosol especially by its photochemical fraction. It is also shown that after the change of air masses the photochemical equilibrium is reached in a day.

The air over industrial centers of the USSR is of bad quality not only due to gaseous and aerosol pollutants produced primarily by industrial objects and motor transport but also due to their change to secondary products, as a rule, more toxic than the primary ones.

Formaldehyde (H_2CO), nitrogen dioxide (NO_2), and ozone (O_3) are classified among the principal secondary products formed in the atmosphere over industrial centers. They are produced by photochemical reactions running in air. The primary products of these reactions are hydrocarbons (RH), carbon oxide (CO), and nitrogen oxides (NO and NO_2).

Following Ref. 1, the atmospheric cycle of hydrocarbons and carbon oxide is a complicated sequence of radical-chain reactions in which radical OH plays a key role. The start of the chain reaction takes place through the reactions



The active role of individual types of hydrocarbons² can be ascertained by expressing the rate constants of reactions individual substances with OH in terms of the rate constant (k) of reaction of OH with carbon oxide. The rate constant of the latter reaction is assumed to be unity. Then we obtain for methane $k = 0.05$, for paraffins (with respect to butane) $k = 15$, for olefins (with respect to ethylene) $k = 20$, and for aryls (with respect to toluene) $k = 80$.²

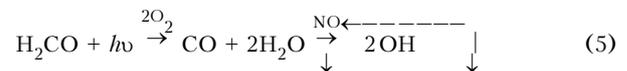
The start of the chain initiates only a multistage process of hydrocarbon change. The point is that the hydroxyl

concentration in air ($10^{-5} \mu\text{g}/\text{m}^3$) is negligible compared to the concentration of the rest of the components of reactions (1) and (2). Therefore, for the chain to be continued an active center OH must be constantly recycled into air, what can be achieved only in the presence of nitrogen oxide quickly reacting with peroxides



where f_i is the stoichiometric coefficient characterizing the formaldehyde yield in the process of oxidation of hydrocarbon of this kind. It was reported in Refs. 3–5 that f_i varies from 0.01 for pentane to 0.80 for ethylene.

Both products of reactions of the NO_2 and H_2CO chain in the daytime undergo photolysis

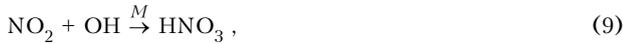


As a result, the chain branches and some fraction of NO recycles.

The chain is caused by ambient air photolysis with formation of energy-excited oxygen atoms¹

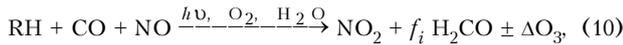


The authors of Ref. 1 claim that the following reaction is the key reaction for the chain break:



due to the fact that nitric acid is quickly removed from the atmosphere.

Thus the group of primary emissions $\text{RH} + \text{CO} + \text{NO}$ which enter the air over an industrial center is changed through the photochemical reactions, into the group of secondary products $\text{NO}_2 + \text{H}_2\text{CO} + \text{O}_3$ according to the molecular equation:



where the signs (\pm) denote the possible variation of the background ozone concentration in the atmosphere resulted from decrease or increase of primary emissions.

Since it is a complicated problem to measure all reactants of the photochemical cycle, in most cases the pathway of photochemical processes in the atmosphere

can be assessed from the excess of the ozone, concentration above the background values typical of this region. This can be explained by the fact that ozone can be easily measured and there is much evidence about its spatio-temporal variability.

However, the experimental studies of air pollution over several industrial centers of the USSR made by instruments placed onboard the AN-30 aircraft-laboratory of the Institute of Atmospheric Optics "Optik-E" showed that such an approach is not always correct. In some cases, in the presence of antagonistic (with respect to ozone) emissions and when sufficiently strong photochemical processes take place, one can observe the reduction of the ozone concentration up to the level below its background value being sometimes less than $1 \mu\text{g}/\text{m}^3$. Such conditions we observed over Khabarovsk and Komsomol'sk-on-Amur. The present paper is concerned with possible reasons for increase and decrease of the ozone concentration due to the photochemical processes.

Let us first examine the general characteristics of dynamics of pollutants over these cities (see Fig. 1).

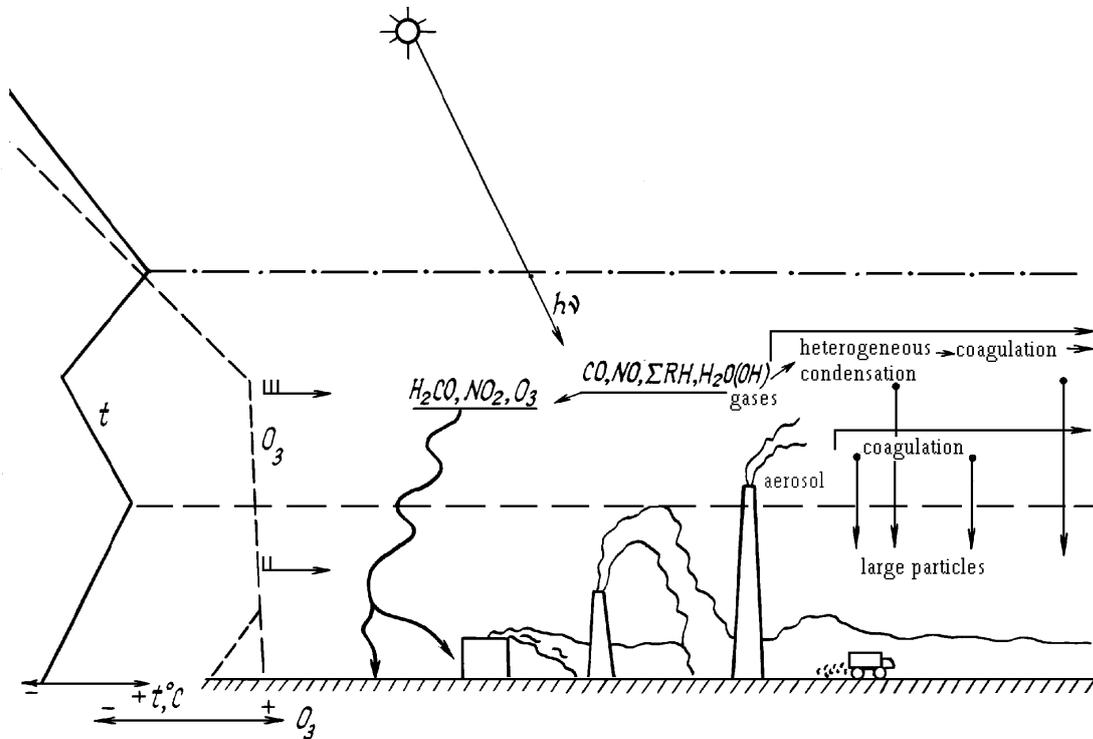


FIG 1. The scheme showing the dynamics of air pollution over an industrial city.

At least two inversions, i.e., near-ground and elevated ones (solid line on the left of the figure), exist over the cities in the Far East of the USSR, being barrier layers that play an active role in the dynamics of pollutants. This results in the formation of two levels of accumulation and transformation of pollutants in the air over these industrial centers.

Emissions from the plant stacks shorter than the altitude of the near-ground inversion boundary (horizontal

dashed line) cannot penetrate into higher layers and at once enter a near-ground layer. As the measurements show, there are no photochemical processes in the near-ground layer because the elevated layer of pollutants screens the UV radiation, although this layer contains almost all components of the above-mentioned cycle. This can be corroborated by Table I which lists the data on air composition over Komsomol'sk-on-Amur in December, 1990 at an altitude of 400 m and near the ground (1.5 m above the ground surface).

TABLE I. Chemical composition of air (mg/m³) over Komsomol'sk –on–Amur.

Position of sampling	Benzol	NH ₃	NO	NO ₂	ΣNO	CO	SO ₂	H ₂ S	ΣRH	Cl ₂	O ₃	Aerosol
Plume of Amursk	0.90	0.20	0.40	0.10	0.50	1.0	1.20	2.00	0.3	0.10	<0.001	0.297
Upon entering Komsomol'sk	0.50	0.20	0.25	0.25	0.50	0.4	0.92	0.90	<0.3	0.05	0.010–0.005	0.140
Heat and electric power plant (HEPP–1) (plume)	0.45	0.25	2.00	0.60	2.60	2.4	0.65	0.01	2.0	0.60	<0.001	0.471
HEPP–2 (plume)	0.40	1.20	2.40	0.40	2.80	0.8	0.50	0.01	0.3	0.50	<0.001	1.368
HEPP–3 (plume)	0.42	0.05	3.20	<0.08	3.20	12.0	0.80	0.01	10.0	0.03	<0.001	2.564
Upon exiting from the city	0.40	0.38	1.20	1.80	3.00	0.9	0.86	0.12	0.8	0.08	<0.001–0.230	0.189
Komsomol'sk (crossings)	2.40	<0.05	1.90	<0.08	1.90	0.9	0.50	0.01	12.0	<0.03	<0.001–0.019	0.051

As can be seen from Table I, concentrations of primary components NO, CO, and ΣRH near the ground reach high quantities. At the same time, concentration of secondary products NO₂ and O₃ (formaldehyde was not measured) is low and does not exceed those typically observed in nature. Thus, the content of NO₂ in air appears to be lower than the threshold of detection (0.08 mg/m³), and that of ozone varies from 19 μg/m³ to zero. Below we consider the ozone destruction in the near–ground layer.

As is well known, the higher stacks emit pollutants above the near–ground inversion. However, the elevated inversion does not allow them to spread in the upward direction and scatter that results in formation of the second layer of pollutants. This being the case, the large aerosol particles sedimentate, a part of them coagulate and also sedimentate. A finer fraction is carried out of the town region. The first row of this table lists the data on suspended substance concentration in the plume of Amursk located 22 km to the South of Komsomol'sk–on–Amur. With southern wind, which was observed during experiment, the plume from Amursk plant stacks spreaded under the inversion and reached the southern periphery of Komsomol'sk–on–Amur. The change of gaseous and suspended substances along this path can be seen from the results of comparison between the first and second rows of Table II. The data on emissions from three heat and electric power plants of Komsomol'sk–on–Amur and characteristics of pollutants detected at the exit from the town are given here too. They allow one to estimate the sedimentation rate of suspended substances from the atmosphere. This process is intense what is supported by the results previously obtained from the data of lidar sensing of plumes⁷ and by Fig. 2 which depicts the transformation of aerosol particle size distribution spectrum in emissions of Amursk when they spread along the 20 km path. It can be seen that as the plume spreads, the submicron fraction of particles decreases and the concentration of moderate and coarse fractions increases.

TABLE II. Average daily concentration (μg/m³) of some components of the near–ground aerosol.

Position of sampling	Cl [–]	Br [–]	NO ₃ [–]	SO ₄ ^{2–}	Sum of the suspended particles
Khabarovsk	13.2	1.2	0.7	0.9	80.2
Komsomol'sk –on–Amur	5.5	8.9	0.3	1.2	43.3

The gaseous phase of emissions can conventionally be divided into three parts. One of them is condensed at once and changes to aerosol which is then transformed according to the above–mentioned scheme. The other part consisting of nonreacting gases is carried out of the city. And, finally, the third part of gases, i.e., CO, NO, and ΣRH takes part in formation of secondary products, according to Eq. (10) in the presence of water vapor upon the action of ultraviolet solar radiation. This can well be seen from the data in Table I obtained at the exit from the town where the highest NO₂ and O₃ concentrations were observed.

The further measurements made onboard the aircraft–laboratory show that the part of the secondary products is carried out by wind and another part of them sedimentates on the ground. This process is traced by the ozone profile which is schematically shown with a vertical dashed line in Fig. 1 and by daily variations of the ozone concentration in the near–ground layer of Khabarovsk and Komsomol'sk–on–Amur (Fig. 3). It should be noted that in Fig. 3 the nighttime maximum near the ground is even more intense than the daytime one. This is indicative of the fact that in the absence of ozone generation (no ultraviolet radiation) the ozone being a conservative constituent is transported to the ground from the layer where the ozone content is high, i.e., from the level of its formation.

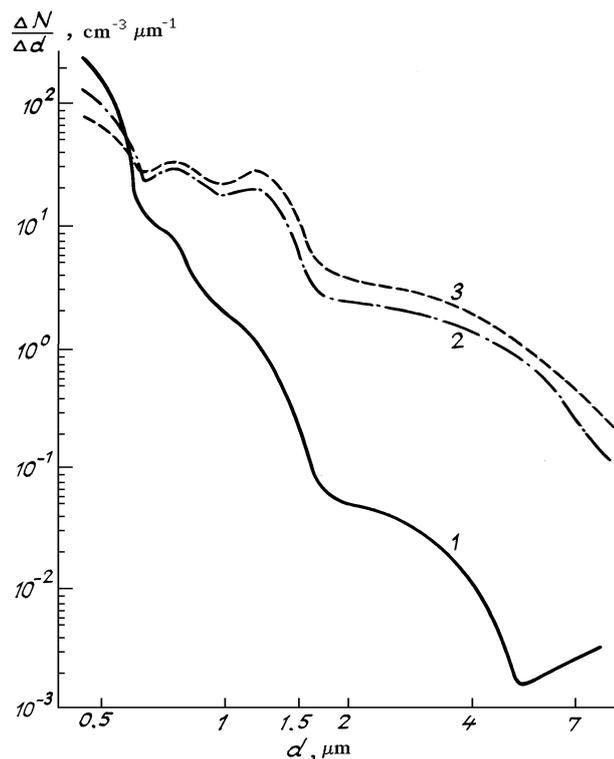


FIG 2. Transformation of aerosol particle size distribution in the plume of Amursk at distances of : 1) 2 km; 2) 20 km; 3) 22 km from the stack mouths.

Let us now consider one more situation observed during the experiments. This is an intense ozone destruction in the near-ground layer of air over the city and almost complete conservation of its concentration out of the city. This fact is conventionally shown in Fig. 1 as the ozone profile splitting. Such a conclusion is based on the results of comparison of ozone vertical profiles obtained during our landing at the airports of the above-mentioned cities and during descents down to an altitude of 50 m over the cities. The lower part of the profile over the city was supplemented by the results of ground-based measurements. This is also seen from comparison of the data in Fig. 4 and Table I. Outside the cities the ozone concentration can exceed $200 \mu\text{g}/\text{m}^3$ and over the cities it does not exceed $20 \mu\text{g}/\text{m}^3$. The rapid ozone reduction under urban conditions was also reported in Ref. 8. The measurements there were performed using another type of instrument and under different climatic conditions. In our opinion, the reduction of the ozone concentration up to nearly zero in the presence of the upper high-power source cannot be accounted for only by its destruction at the ground surface.⁹ Especially because our experiments were performed in winter when the ground surface was covered with snow and ozone destruction would be by a factor of 100 slower than in summer.

Such a conclusion motivates a search for different mechanisms of ozone destruction in the near-ground layer to explain the aforementioned evidences. One of the real mechanisms of the ozone sink is the aerosol, when finely-

dispersed aerosol is formed with the help of ozone what is manifested in the appearance of bluish haze. In addition, Lyubovtseva¹⁰ has reported the reduction (flow-rate) of ozone concentration in the process of synthesizing such natural haze.

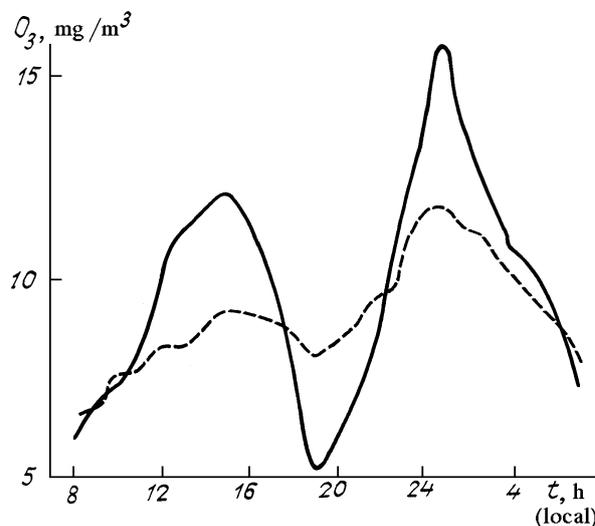
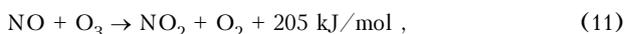


FIG 3. The daytime behavior of the ozone concentration in the near-ground layer of air: the dashed line indicates the data obtained over Khabarovsk and the solid line shows the same over Komsomol'sk-on-Amur.

As can be seen from Fig. 5, however, this process is ambiguous. Thus, if we consider a daytime behavior of ozone concentration and total mass of aerosol they are found to be synchronous. This testifies to the same nature of their formation due to the sedimentation of substances emitted into the elevated layer of pollutants. It should be noted also that if the suspended substances resulted from direct emissions, then ozone would be their derivative. It has been established quite accurate that complete ozone destruction takes place in the plant stack emissions. This was at first shown in Ref. 11 and entirely confirmed in our experiments (Fig. 4). According to Ref. 12 in the haze gases emitted from plant stacks an oxidation of nitrogen oxide with ozone takes place



which runs 10^5 times faster than the oxidation with oxygen. But since the ozone content in air is much lower than that of nitrogen oxide, it reduces rapidly according to reaction (1) and its concentration falls up to zero. This is well seen in Table I and Fig. 4. Moreover, the field of concentrations in Fig. 4 allows one to establish in what area ozone is destructed in the process of the emission spreading.

Nevertheless, this mechanism cannot account for the reduction of the ozone concentration in the near-ground layer over the city. While discussing the aerosol sink hypothesis, it is necessary to analyze the possible ways of aerosol particles formation as a result of heterogeneous reactions or ozone interaction with particle matter.

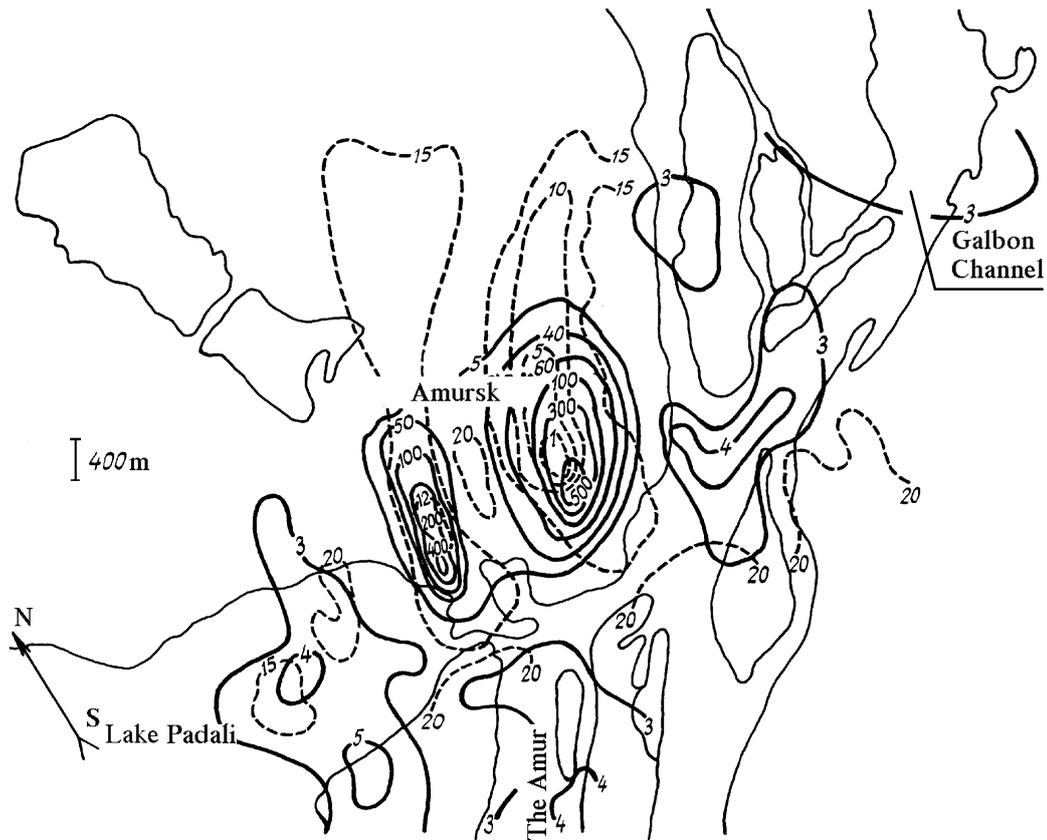
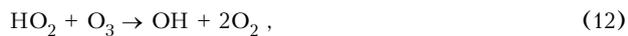


FIG. 4. Horizontal distribution of aerosol (solid lines) and ozone (dashed lines) number densities at an altitude of 400 m over Amursk.

Following Ref. 9, there may exist several cycles of ozone destruction: oxygeneous (following Chapman), nitrogeneous, hydroxyl, and chlorine. The sulfuric¹³ and boric¹⁴ cycles were identified later. The oxygen cycle is peculiar to the stratosphere and of low efficiency in the lower troposphere.

The ozone destruction according to hydroxyl cycle takes place in the following way:



Since the products of reactions (12) and (13) participate in recycles based on Eqs. (1)–(8), their contribution to ozone sinks in the lower troposphere cannot be significant.

The nitrogeneous cycle in the atmosphere starts from reaction (11) and continues through reaction (9). The reaction products are removed from air through formation of droplets of nitrous acid or its salts in the form of aerosol particles.

Natural chlorine by destructing ozone



forms hydrochloric acid HCl or its salts by interacting with aerosol available in air



In most of the oxidation reactions one oxygen atom enters the products composition and two of them form the O_2 molecule. One of exceptions from this rule is the example with SO_2 (see Ref. 9)



When SO_2 is formed a very rapidly running stage of oxidation process takes place, i.e., formation of sulfurous acid



which is removed from the atmosphere in the form of droplets or salt particles (in the processing of interaction with aerosol).

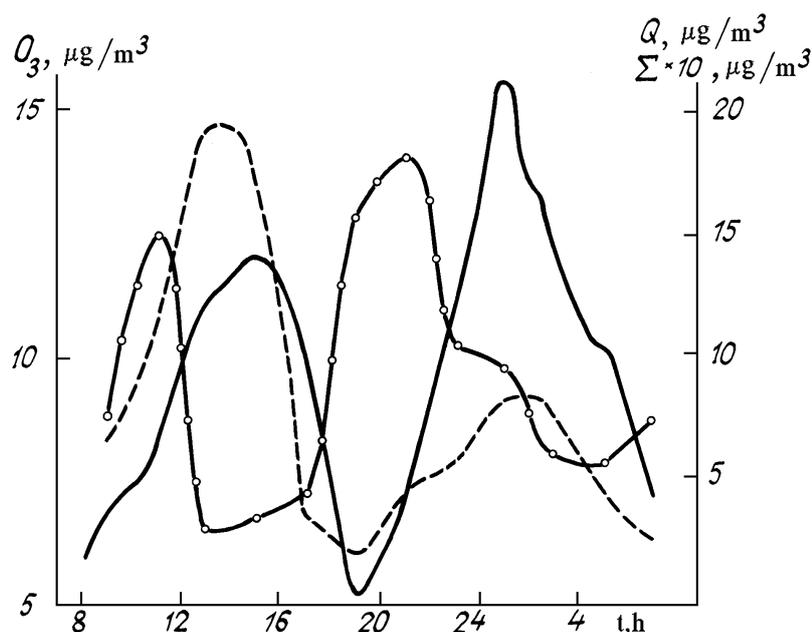
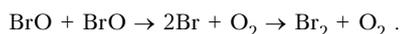
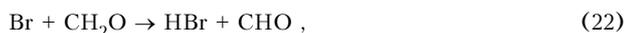
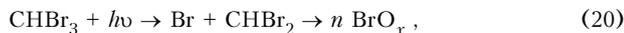


FIG 5. The daytime behavior of ozone concentration (solid line) and mass concentration of suspended particles (dashed lines) and photochemical aerosol component (dot-dash line) over Komsomol'sk-on-Amur.

An important role of the bromide cycle of ozone sink in the lower troposphere was discovered by Canadian scientists.¹⁴ In their opinion, probable mechanism of this cycle is



An important feature of bromide mechanism is that not only ozone but also formaldehyde are destructed in this cycle. Moreover, as was noted in Ref. 14, the amount of NO_x in air decreases simultaneously with ozone. Thus, the bromide cycle stimulates the destruction of all the secondary products formed following Eq. (10) and being more aggressive than the primary ones.

During the diurnal measurements, in addition to ozone concentration the chemical composition of atmospheric aerosol incorporating 43 components was determined. In particular, we were interested in ion products of reactions (9), (11), and (14)–(22). The data on their average daily concentration are given in Table II. Since the ions listed in Table II could be simultaneously a product of ozone destruction and of some other processes, we considered a diurnal variation of their sum in order to determine their resultant contribution to ozone destruction. The results are depicted with a dashed line in Fig. 5.

As can be seen in Fig. 5, the behavior of a photochemical active fraction of aerosol ($\text{Cl}^- + \text{Br}^- + \text{NO}_3^- + \text{SO}_4^{2-}$) is opposite to diurnal variations of ozone and total mass of suspended substances. In our opinion, this fact testifies to a sufficiently important role played by aerosol mechanism of ozone sink in the near-ground layer.

TABLE III. Contribution (%) of different cycles to ozone destruction in the near-ground layer.

City	"Chlorine"	"Bromine"	"Nitrogen"	"Sulfuric"
Khabarovsk	82.5	7.5	4.4	5.6
Komsomol'sk-on-Amur	34.6	56.0	1.9	7.5

Talroze et al.¹⁵ evaluated the contribution of different cycles to destruction of "excess" oxygen. It follows from their estimates that the oxygen cycle constitutes 17%, hydroxyl cycle 9%, nitrogen cycle 70%, and chlorine cycle 4%. The sulfuric and boric cycles were ignored.

If in our case the ozone destruction above the ground is assumed to be much less than aerosol sink and that there are no other mechanisms of sink than those listed in Table II, then the boric and chlorine cycles turn out to be basic for the near-ground layer over the industrial center (Table III). It follows from Table III that they contribute about 90% over each city through their contributions can vary.

One more aspect of photochemical processes in the polluted city should be considered in conclusion. Here we deal with recovering of photochemical equilibrium during a change of air mass which, as is well known, in some cases leads to complete cleaning of air over a city from the impurities. Such situations were observed several times in our experiments.

By way of example let us consider Fig. 6 in which three vertical ozone profiles are shown. The profile obtained on December 12, 1990 can be assumed to be a starting profile. Such a vertical ozone distribution was sufficiently stable and was kept to the noon of December 18. In the afternoon the cold Arctic front accompanied by precipitations passed through the city. Lidar sensing carried out in the back of the front revealed ozone

distribution shown with the dashed line. The ozone concentration was found to be reduced by a factor of nearly 5 (the scale is logarithmic). In a day, on December 19, the vertical ozone contribution was recovered, e.i., in the presence of sources permanently generating ozone-producing gases over the city, the photochemical equilibrium was reached in a day. This recovering takes place several times faster than that of aerosol composition experimentally determined by us earlier. The aerosol profile was recovered in 4 – 5 days.¹⁶

We arrived at a conclusion that an industrial center is not only the "island" of heat in the atmosphere but also an "island" of pollutants whose chemical composition results in the photochemical formation of secondary products with their subsequent accumulation or destruction by some atmospheric constituents.

REFERENCES

1. N.A. Gurevich, E.P. Dombrovskaya, A.M. Kuklin, et al., in: *Thermocatalytic Cleaning and Reduction of Toxic Emissions into the Atmosphere* (Naukova Dumka, Kiev, 1989), p. 138.
2. R. Atkinson, *Chem. Rev.*, No. 1, 69 (1986).
3. W.P.L. Carter and R. Atkinson, *J. Atm. Chem.* **3**, No. 3, 377 (1985).
4. J.P. Killins and G.Z. Whitten, *Atmos. Environ.* **16**, No. 8, 1973 (1982).
5. H. Bandow and N. Washida, *Bull. Chem. Soc.* **58**, No. 9, 2549 (1985).
6. A.Kh. Khrgian, *Meteorol. Gidrol.*, No. 5, 114 (1986).
7. B.D. Belan, V.V. Burkov, I.E. Penner, et al., *Atm. Opt.* (1992) (to be published).
8. L.S. Ivlev and E.F. Mikhailov, in: *Study of Atmospheric Pollutants over Alma-Ata. Part 1. Experiment ANZAG-8* (Galym, Alma-Ata, 1990), p. 119.
9. S.P. Perov and A.Kh. Khrgian, *Current Problems of Atmospheric Ozone* (Gidrometeoizdat, Leningrad 1980), 288 pp.
10. Yu.S. Lyubovtseva, *Izv. Akad. Nauk SSSR, Ser. FAO* **14**, No. 2, 229 (1978).
11. D.D. Davis, G. Smith, and G. Klauber, *Science* **186**, 733 (1974).
12. I.Ya. Sigal, N.A. Gurevich, and E.P. Dombrovskaya, *Teploenergetika*, No. 11, 6 (1980).
13. D.D. Davis and G. Klauber, *Intern. J. Chem. Kinet. Symp.* **1**, 543 (1975).
14. D.M. Uelpdeil and L.A. Barri, *Problems of Monitoring and Environment Protection*, (Gidrometeoizdat, Leningrad, 1989), 320 pp.
15. V.L. Tal'rose, A.I. Poroikova, I.K. Larin, et. al., *Izv. Akad. Nauk SSSR, Ser. FAO* **14**, No. 4, 355 (1978)
16. B.D. Belan, G.O. Zadde, Yu.A. Pkhalagov, and T.M. Rasskazchikova, *Izv. Akad. Nauk SSSR, Ser. FAO* **23**, No. 6, 622 (1987).