

ON AEROSOL-GAS RELATIONSHIPS IN THE GROUND LAYER OF THE ATMOSPHERE

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Meteorological parameters of the ground layer of the atmosphere, concentrations of O₃, CO, and CO₂ gases, particle number density, and spectral coefficients of aerosol extinction have been simultaneously measured near Tomsk in summer. Based on the correlation analysis of variations in the measured parameters, it was concluded that there exists a minor sink of O₃ and CO gases on small atmospheric aerosol particles ($r < 0.4 \mu\text{m}$).

Investigations of gaseous and suspended pollutants in the atmosphere over industrial centers indicate a significant impact of anthropogenic factors on the state of the atmosphere.¹⁻³ The main sources of gaseous trace impurities are the products of coal and petroleum combustion (SO₂, CO₂, NO, and hydrocarbons) and exhausts of engines (CO). As a result of photochemical reactions running upon exposure to the ultraviolet radiation in the presence of oxygen and water vapors, some of hydrocarbons, i.e., carbon monoxide (CO) and nitric oxide (NO), are decomposed to the secondary products: nitric dioxide (NO₂), formaldehyde (H₂CO), and ozone (O₃) (see Ref. 3). Some of hydrocarbons form a photochemical aerosol upon exposure to the sun light in the presence of nitric oxides (NO and NO₂), sulfur dioxide (SO₂), and ozone. The enhanced concentrations of carbon monoxide and all the secondary gaseous and suspended impurities in the urban air have harmful effect on public health. Therefore it is of particular importance to study the sinks of these impurities which result in purification of the atmosphere.

At present, there exist several mechanisms to remove the polluting trace impurities from the atmosphere. These are, first of all, chemical reactions converting one substances into the others. The efficiency of gas removal in this case depends on chemical reactivity of the molecules and on their solubility in water. The readily soluble gases, such as SO₂ or NH₃, are rapidly removed from the atmosphere during the rain as well as in the case of their direct contact with water surfaces of seas and oceans. Sedimentation on the Earth's surface is an efficient sink for poorly soluble gases, e.g., CO or O₃. The well-known mechanisms of gas pollutant sinks are also the absorption by biochemical objects, photosynthesis, the above-mentioned photochemical reactions resulting in aerosol formation, and, finally, gas absorption on aerosols.¹

Following Ref. 1, the aerosol entrapment of gases under certain conditions can be an efficient mechanism of removing the poorly soluble gases from the atmosphere. If the absorption rate on the surface of suspended particles is high, then the rate of gas removal will be determined by its thermal motion toward the particle surface, the velocity of which (V_t) depends on particle number density in the atmosphere and on their size (r). The theoretical estimates presented in Ref. 1 for spheres showed that in a strongly turbid atmosphere the r dependence of V_t has a linear character and in a weakly turbid atmosphere the velocity of gas transport V_t is proportional to r^2 . It means that for a strongly turbid atmosphere the

efficiency of gas entrapment by particles of different size is primarily determined by the shape of the particle size distribution function. Thus, e.g., for the Junge distributions, the sink basically takes place on small particles since their number density is much larger.

For a weakly turbid atmosphere a square-law dependence on particle size can lead to the appearance of preferred sink of gases on large particles. The latter is illustrated by Fig. 1 borrowed from Ref. 1, in which the relative contribution of particles of different size to gas absorption on urban and marine aerosols is shown. The ratio of gas amount condensed on the surface of particles with the radius r_i to its amount on the surface of particles with $r \approx 1.0 \mu\text{m}$ is plotted on the ordinate. It can be seen that for marine haze (weak turbidity) gas impurities are mainly condensed on particles with radius 0.2–2 μm . For urban haze, in which the number density of small particles is much larger, the gas entrapment occurs predominantly on particles with $r < 0.5 \mu\text{m}$. It should be noted that in this case the maximum in the curve is attained at $r \approx 0.05 \mu\text{m}$ and the maximum efficiency of gas washout is by three orders of magnitude higher than that for particles with $r = 1.0 \mu\text{m}$.

The experimental check of these theoretical estimates is a very difficult task even under highly controllable laboratory conditions. In the real atmosphere it is impossible to determine aerosol-gas relationships due to the variety of the well-known and unknown factors which act simultaneously. Therefore the only approach for studying aerosol-gas relationships in the atmosphere is the statistical method based on the analysis of correction between the changes in the aerosol number density and variations of the concentration of gas components. In this case the measurements of the absolute brightness angular distribution or of the aerosol extinction coefficients can replace the measurements of the aerosol number density. The applicability of this statistical method to such a problem can be supported by Ref. 7 in which the negative correlation was found between variations of the ozone concentration and the absolute brightness angular distribution at a wavelength of 0.51 μm during sand storm. Since this result was obtained at optical depths $\tau > 3$ in the "off" mode of the ozone source, it was interpreted as aerosol entrapment of ozone.

The studies of aerosol-gas relationships in the ground layer of the atmosphere near the industrial center were started in 1991 as part of the integrated program of the Institute of Atmospheric Optics on studying the tropospheric ozone.

The measurable parameters were: temperature and humidity of air, concentration of O₃, CO, and CO₂ gases, particle number density in different ranges of the particle size, and coefficients of aerosol extinction of visible and infrared radiations. The measurements of the particle number density and spectral aerosol extinction coefficients in the visible and IR ranges were introduced into the integrated program for studying the efficiency of aerosol sink of gases on the particles of different size.

To measure the aforementioned parameters, the following standard and special-purpose instruments were used:

- an acoustic meteorological station⁸ intended for measuring the meteorological parameters of the atmosphere. The error in the measurement of the temperature was ±0.05°C and that of the relative humidity was ±10%;

- GIAM-15 opto-acoustic gas analyzers for measuring CO and CO₂ concentrations in the atmosphere.

The error in the measurement of CO was ±5% and that of CO₂ was ±10%;

- a KG-02P chemiluminescent gas analyzer for measuring the ozone concentration. The error was ±3%. The threshold of recording was about 1 μg/m³;

- an AZ-5 photoelectric aerosol counter for measuring the number density of suspended particles. The error was ±20%, the concentration measuring range was 0-300 cm⁻³;

- a multiwave meter of spectral transmission of the atmosphere for measuring the coefficients of radiation extinction in the wavelength range 0.44-1.06 μm. The measurement error along the 1-km path was about 0.03 km⁻¹ (see Ref. 9).

The aerosol component of extinction was separated out from the total extinction coefficients using the statistical method described in detail in Ref. 10.

Represented below are the measurements performed in June and July, 1991.

The meteorological parameters, gas concentration, and aerosol number density were measured in a local volume, while the extinction coefficients were measured along the extended 1000-m path (the path with reflection and a 500-m baseline).

It should be noted that some individual parameters were not always measured synchronously. Therefore, when the resultant data arrays were formed for statistical processing of different parameters, we obtained somewhat shortened data arrays. Thus, only 69 synchronous measurements were chosen when we formed the data array for studying the relationship among the concentration of O₃, CO, and CO₂, the aerosol particle number density in different ranges of particle size, and the aerosol extinction coefficients.

Table I lists the average values (\bar{x}) and standard deviations (σ_x) of the above-mentioned parameters measured synchronously in the atmospheric ground layer over the entire period of observations. Here, O₃, CO, and CO₂ are gas concentrations measured in a local volume; N₁, N₂, and N₃ are number densities of aerosol particles with diameters $d > 0.4$, $d > 1.0$, and $d > 2.0$ μm, respectively; $\alpha(\lambda)$ are the aerosol extinction coefficients at different wavelengths λ ; F and a are the relative and absolute air humidities; and, t is the air temperature.

TABLE I. Average values and standard deviations of the measurable parameters for summer cycle of investigations ($n = 69$).

Measurable parameter	\bar{x}	σ_x	Measurable parameter	\bar{x}	σ_x
Gas concentration:					
O ₃ , μg/m ³	41.5	16.9	$\alpha(0.63)$, km ⁻¹	0.243	0.093
CO, ppm	10.7	2.59	$\alpha(0.69)$, km ⁻¹	0.236	0.090
CO ₂ , ppm	394	15	$\alpha(0.87)$, km ⁻¹	0.219	0.083
N ₁ , l ⁻¹	6086	6148	$\alpha(0.94)$, km ⁻¹	0.221	0.083
N ₂ , l ⁻¹	647	1066	$\alpha(1.06)$, km ⁻¹	0.242	0.084
N ₃ , l ⁻¹	283	448	F , %	65.9	14.6
$\alpha(0.44)$, km ⁻¹	0.302	0.115	a , g/m ³	8.65	1.4
$\alpha(0.48)$, km ⁻¹	0.282	0.107	t , °C	15.5	2.9
$\alpha(0.55)$, km ⁻¹	0.267	0.102			

Particular attention should be drawn to the flat character of spectral behavior of the average aerosol extinction coefficients which is indicative of the significant contribution of coarse fraction of aerosol to the $\alpha(\lambda)$ dependence and deficit of the finely disperse fraction of particles. This is possibly due to the washing-out effect of rains which often precipitated during the measurements.

TABLE II. Coefficient of absolute correlation $\rho_{N_i F}$, $\rho_{\alpha_\lambda F}$, $\rho_{N_i \text{ gas}}$, $\rho_{\alpha_\lambda \text{ gas}}$, and $\rho_{F \text{ gas}}$ for summer data array ($n = 69$).

Measurable parameter	$\rho_{N_i F}$	$\rho_{N \text{ gas}}$		
		O ₃	CO	CO ₂
N ₁	0.22	-0.57	-0.01	0.50
N ₂	0.08	-0.38	0.02	0.36
N ₃	0.07	-0.42	-0.03	0.38
	$\rho_{\alpha_\lambda F}$	$\rho_{\alpha_\lambda \text{ gas}}$		
$\alpha(0.44)$	0.43	-0.40	-0.16	0.42
$\alpha(0.48)$	0.41	-0.37	-0.13	0.44
$\alpha(0.55)$	0.42	-0.34	-0.09	0.40
$\alpha(0.63)$	0.39	-0.32	-0.12	0.37
$\alpha(0.69)$	0.31	-0.21	-0.14	0.30
$\alpha(0.87)$	0.18	-0.05	-0.17	0.13
$\alpha(0.9)$	0.16	-0.09	-0.02	0.12
$\alpha(1.06)$	-0.11	0.02	-0.15	-0.05
	ρ_{FF}	$\rho_{F \text{ gas}}$		
F	1.00	-0.56	0.20	0.75

Presented in Table II are the correlation coefficients $\rho_{N_i F}$, $\rho_{N_i \text{ gas}}$, $\rho_{\alpha_\lambda F}$, $\rho_{\alpha_\lambda \text{ gas}}$, and $\rho_{F \text{ gas}}$ calculated for the resultant data arrays. It should be noted that even though the dimension of the obtained data array was small, the calculated correlation coefficients, taking into account their significance, can be used in qualitative study of aerosol-gas relationships. Recall that for the data array with $n = 69$, the level of correlation significance is 0.25 and that of substantially significant correlation is 0.32.

It can be seen from the analysis of Table II that in the data array under study there is a significantly negative correlation between the particle number density and the ozone concentration. In this case, the maximum correlation coefficient is attained in the range of N_1 in which the finely disperse aerosol prevails. Formally, a significantly negative correlation between N and O_3 indicates that there is ozone sink on aerosol particles suspended in air. This fact, as well as the predominant ozone sink on the finely disperse fraction of aerosol ($\rho_{N_1O_3} = -0.57$), testify to the qualitative agreement among these data and the theoretical estimates of gas absorption on aerosol¹ and the experimental data.⁷

The zeroth correlation between the CO concentration and the number density of particles of different size shows the absence of CO sink on atmospheric aerosol.

As for CO_2 , we can observe here positive and substantially significant correlation between its concentration and the number density of particles of different size. This testifies to the fact that in the atmosphere there was a common source of aerosol and CO_2 during the measurements which gave rise to synchronous variations of these two components.

Let us finally consider the value and the spectral behavior of the correlation coefficients $\rho_{\alpha\lambda gas}$ given in Table II. Let us start with ozone. It can be seen that the coefficients of correlation between the variations of the ozone concentration and the aerosol extinction coefficients are negative over practically the entire wavelength range, have a pronounced spectral behavior, and decrease with wavelength. The maximum of $\rho_{\alpha\lambda O_3}$ is attained at a wavelength of $0.44 \mu m$ (-0.44). Then it decreases to a wavelength of $0.63 \mu m$ and after that sharply reduces to zero. Note that in the range $\lambda = 0.44-0.55 \mu m$ the correlation coefficients $\rho_{\alpha\lambda O_3}$ are substantially significant.

Thus the measurements of the aerosol extinction coefficients also testify to the possible existence of ozone sink on atmospheric aerosol especially on the finely disperse one ($r < 0.4 \mu m$).

The correlation coefficients $\rho_{\alpha\lambda CO}$ just as $\rho_{\alpha\lambda O_3}$ are negative over the entire wavelength range; however, the level of correlation is below the significant one. The correlation coefficients for α_λ and CO_2 are positive over the entire wavelength range, while in the range $\lambda = 0.44-0.69 \mu m$ they are significant and substantially significant.

On the whole, the results of investigations of the aerosol-gas relationships are qualitatively similar for both microphysical and optical data. However, before we draw the final conclusions concerning the aerosol-gas relationships, we must be convinced of the fact that these relationships are real and are not caused by the indirect effect of the other more important factors. In particular, such an additional factor could be the relative air humidity.

By way of example, let us consider the relationship between the variations of the coefficient α (0.44) and the ozone concentration. It is well known that the variations in α (0.44) are generally caused by changes in the particle number density and size. The latter occurs under the effect of relative air humidity F . And since the efficiency of ozone sink on aerosol is proportional to the surface area of all particles suspended in air, this indicates that the ozone concentration should decrease with air humidity when the particle size (surface) increases. However, in the real atmosphere in summer there is one more negative correlation between the ozone concentration and air humidity (-0.56) associated with the reverse diurnal behavior of these two

parameters. As a result, the measured correlation coefficient $\rho_{\alpha\lambda O_3}$ can be substantially distorted and even incorrectly interpreted.

To avoid this uncertainty in the conclusions, it is expedient to calculate the so-called conditional (partial) correlation coefficients $\rho_{xy/z}$, i.e., when the correlation between the parameters x and y is considered for a fixed parameter z which is also included in the given process.

Assuming that the particle number density also depends on relative air humidity,¹¹ we calculate the coefficients $\rho_{N_i gas/F}$ using the formula¹²

$$\rho_{N_i gas/F} = \frac{r_{N_i gas} - r_{N_i F} \cdot r_{F gas}}{[(1 - \rho_{N_i F}^2)(1 - \rho_{F gas}^2)]^{1/2}}, \quad (1)$$

where $\rho_{N_i gas}$, $\rho_{N_i F}$, and $\rho_{F gas}$ are the normalized coefficients of absolute correlation between the above-mentioned parameters.

The results of $\rho_{N_i gas/F}$ calculation using Eq. (1) are listed in Table III where, for convenience of comparison, the absolute correlation coefficients taken from Table II are also presented. The analysis of these data shows that introduction of conditional correlation coefficients in this case does not change the previous conclusions on aerosol-gas relationships drawn from the microphysical measurements. This testifies to the negligible effect of relative air humidity on the particle number density measured with the AZ-5 aerosol counter.

TABLE III. Absolute and conditional correlation coefficients for N_i and gas components.

N_i	O_3		CO		CO_2	
	$\rho_{N_i O_3}$	$\rho_{N_i O_3/F}$	$\rho_{N_i CO}$	$\rho_{N_i CO/F}$	$\rho_{N_i CO_2}$	$\rho_{N_i CO_2/F}$
N_1	-0.57	-0.55	-0.01	-0.06	0.50	0.51
N_2	-0.38	-0.40	0.02	0.01	0.36	0.45
N_3	-0.42	-0.46	-0.03	-0.04	0.38	0.50

Let us now consider to what extent the conditional correlation coefficients introduced in our consideration could affect the preliminary conclusions on the aerosol-gas relationships derived from the measurements of the aerosol extinction coefficients. In this case, we should measure not only the relative air humidity but also the aerosol extinction coefficient near $\lambda = 1.06 \mu m$ to eliminate the effect of coarse fraction on α_λ variations in the examined wavelength range.

The algorithm for calculating the conditional correlation coefficient for such a four-factor system has the form

$$\rho_{\alpha\lambda gas/F\alpha^*} = \frac{\rho_{\alpha\lambda gas/F} - \rho_{\alpha\lambda\alpha^*/F} \cdot \rho_{\alpha^* gas/F}}{[(1 - \rho_{\alpha\lambda\alpha^*/F}^2)(1 - \rho_{\alpha^* gas/F}^2)]^{1/2}}, \quad (2)$$

where $\alpha^* = \alpha_{1.06}$ and $\rho_{\alpha\lambda gas/F}$, $\rho_{\alpha\lambda\alpha^*/F}$, and $\rho_{\alpha^* gas/F}$ are the conditional correlation coefficients calculated using Eq. (1).

Summarized in Table IV are the spectral autocorrelation coefficients $\rho_{\alpha\lambda\alpha^*}$ and the coefficients of conditional correlation between α_λ and concentration of O_3 , CO , and CO_2 for fixed values of relative air humidity and aerosol extinction coefficients at the wavelength $\lambda = 1.06 \mu m$. The coefficients $\rho_{\alpha\lambda\alpha^*}$ are needed for calculation of the coefficients $\rho_{\alpha\lambda\alpha^*/F}$.

The comparison between the conditional correlation coefficients $\rho_{\alpha_\lambda \text{gas}/F\alpha^*}$ and the absolute correlation coefficients $\rho_{\alpha_\lambda \text{gas}}$ (see Table II) reveals their substantial transformation for all gases and almost for all wavelengths. Thus, in particular, the correlation between the coefficients α_λ (in the range $\lambda = 0.44\text{--}0.63$) and ozone noticeably decreases. As a result, this correlation turns out to be significant only near $\lambda = 0.44 \mu\text{m}$. This transformation of the correlation coefficients for the examined quantities occurs due to the sufficiently strong negative correlation between ozone concentration and relative air humidity in this data array ($\rho_{O_3 F} = -0.56$, see Table II), which makes the anticorrelation between α_λ and O_3 somewhat stronger.

Quite a different character of transformation of the correlation coefficients is found for carbon monoxide. The conditional correlation coefficients in the range $\lambda = 0.44\text{--}0.55 \mu\text{m}$ increase markedly as compared with the absolute ones, and for $\lambda = 0.44 \mu\text{m}$ they become even significant.

For carbon dioxide, the conditional correlation coefficients decrease noticeably as compared with the absolute ones and become insignificant over the entire wavelength range. Such changes of correlation between the parameters under study are due to a strong positive correlation between CO_2 and relative air humidity in the initial data array which can be explained by the diurnal variation of these two parameters. This relationship got stronger and possibly determined the positive correlation between α_λ and CO_2 (see Table IV).

Thus the analysis of the data in Table IV allows us to conclude that in summer hazes in the atmospheric ground layer there is an insignificant sink of ozone and carbon monoxide on small aerosol particles ($r < 0.4 \mu\text{m}$).

This conclusion based on the data of the correlation analysis of the optical measurements is in qualitative agreement with the theoretical estimates given in Ref. 1 for urban aerosol (see Fig. 1).

The comparison of the data in Tables III and IV testifies to the significant difference in the conditional correlation coefficients calculated from the microphysical and optical measurements. A higher coefficient of correlation between the change in the particle number density and variation of the ozone concentration can be considered here which is equal to -0.55 in contrast to -0.29 for optical data. This difference can be explained by the fact that in the first case the measurements of the particle number density and ozone concentration were carried out in a common local volume while the aerosol extinction coefficients were measured along the extended paths. Naturally, in the first case the changes in N and variations of O_3 are more correlated than those of O_3 and α_λ .

TABLE IV. Autocorrelation coefficients $\rho_{\alpha_\lambda \alpha^*}$ and conditional correlation coefficients $\rho_{\alpha_\lambda \text{gas}/F\alpha^*}$ ($n = 69$).

$\lambda, \mu\text{m}$	$\rho_{\alpha_\lambda \alpha^*}$	$\rho_{\alpha_\lambda O_3/F\alpha^*}$	$\rho_{\alpha_\lambda CO/F\alpha^*}$	$\rho_{\alpha_\lambda CO_2/F\alpha^*}$
0.44	0.69	- 0.29	- 0.30	0.22
0.48	0.63	- 0.22	- 0.21	0.27
0.55	0.63	- 0.16	- 0.15	0.16
0.63	0.63	- 0.15	- 0.18	0.15
0.69	0.62	- 0.01	- 0.18	0.10
0.87	0.64	+ 0.12	- 0.17	- 0.05
0.94	0.85	+ 0.08	+ 0.15	- 0.08
1.06	1.0	0.0	0.0	0.0

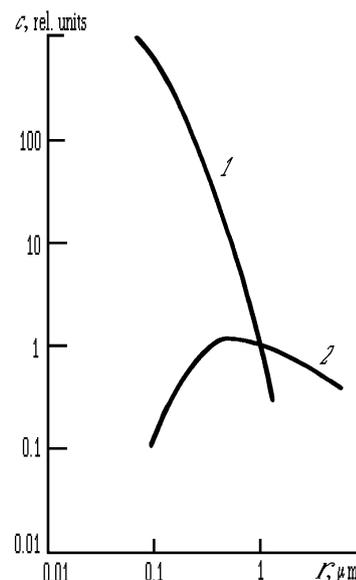


FIG. 1. Relative contribution of aerosol of different size to the gas absorption for urban (1) and marine (2) hazes.

The problem on the absence of correlation between the change in the particle number density and variations of the carbon monoxide concentration and the occurrence of such correlation between $\alpha(0.44)$ and CO , based on the optical data, has not yet been solved. This disagreement can be possibly explained by the fact that the CO sink occurs only on very small particles which cannot be recorded with the AZ-5 counter.

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