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DIURNAL AND WEEKLY VARIATIONS OF PEROXY RADICAL CONCENTRATION DUE TO VARYING INDUSTRIAL LOAD IN MOSCOW

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Concentrations of some minor gas components were measured in Moscow in the winter-spring period of 1996. The dynamics of peroxy radical concentrations was evaluated on the basis of a one-dimensional photochemical model, taking into account the variable insolation, which depends on the cloud cover and the level of urban atmosphere pollution. Diurnal and weekly periods were found in the concentration behavior. They are associated with the city's industrial rhythm. The total concentration of peroxy radicals can serve as an air purity indicator.

The task of monitoring the chemical composition of the air basin is a long-standing challenge, especially in large cities, where the man-made impact on the environment is very great.

The nitrogen oxides (NO and NO_2) and ozone are the principal reagents in photochemical processes both in polluted industrial regions and in unpolluted remote and oceanic areas which can be regarded as the pollution background. In the absence of other pollutions, these impurities constitute a system which is close to the state of a photochemical equilibrium in accordance with the reactions [1]

$$(R1) \quad NO + O_3 \rightarrow NO_2 + O_2,$$
$$(R2) \quad NO_2 + h\nu \rightarrow NO + O, \quad \lambda < 420 \text{ nm},$$
$$(R3) \quad O + O_2 + M \rightarrow O_3 + M.$$

Carbon oxide and hydrocarbonates violate the system's equilibrium. Extra oxygen may appear due to the following reactions:

$$(R4) \quad CO + OH \xrightarrow{O_2} CO_2 + HO_2,$$
$$(R5) \quad HO_2 + NO \rightarrow OH + NO_2$$

and

$$(R6) \quad RH + OH \xrightarrow{O_2} H_2O + RO_2,$$
$$(R7) \quad RO_2 + NO \rightarrow RO + NO_2.$$

The reaction ($R7$) shows that the extra removal of nitrogen oxide is due to compounds with the general formula RO_2 (peroxy radicals) [2], where R denotes any organic radical. In this paper the concentration of peroxy radicals is understood as the total concentration of $[RO_2] + [HO_2]$.

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Parish [3] was the first to propose a method for calculating the concentration of peroxy radicals as a quantity that characterizes the deviation of O_3- and NO_x-containing systems from the state of a photochemical equilibrium. The adequacy of this method has been validated by numerous measurements conducted in different regions.

Assuming the system of equations $(R1)$–$(R7)$ to be closed, we have a photochemical model for evaluating the variability of the concentrations of its gaseous components. For a closed system, $d[\mathrm{NO}]/dt = 0$, the rates of reactions $(R5)$ and $(R7)$ are nearly equal, and the total concentration of peroxy radicals is given by

$$[\mathrm{RO_2}] + [\mathrm{HO_2}] = \frac{J_{\mathrm{NO_2}}}{k_5}\frac{[\mathrm{NO_2}]}{[\mathrm{NO}]} - \frac{k_1}{k_5}[\mathrm{O_3}],$$

where k_i denote the rates of the respective reactions, and $J_{\mathrm{NO_2}}$ is the rate of nitrogen dioxide photodissociation.

This model was used in our study for calculating the concentration of peroxy radicals on the basis of long-term measurements that were conducted in Moscow for the first time. Of special interest was the possibility of using this model in the conditions of varying industrial load on the Moscow air basin, i.e., the opportunity of evaluating the dynamic behavior of the RO_2 concentration under industrial pollution of the city.

Measurements of the concentrations of gaseous components (O_3, NO, NO_2), weather parameters, and a radiation flux were carried out at the Atmospheric Physics Institute, Russian Academy of Sciences, which is located in Moscow's center, in the period of February 17 to March 3, 1996. Over the entire observation period, the concentrations of the gaseous components varied between 3 and 30 ppb for O_3 and between 10 and 15 ppb for NO_2 (1 ppb is a concentration that corresponds to one molecule of the substance per 10^9 air molecules). The concentrations varied significantly over a 24-hour period due to diurnal variations in the removal of pollutants by automobiles, ranging from 3 to 25 ppb. The observation period coincided with a fire at the Moscow Tire Plant, which gave rise to an abrupt growth of the NO concentration up to 80–90 ppb. The concentrations of all minor gases were measured with an accuracy of 1 ppb.

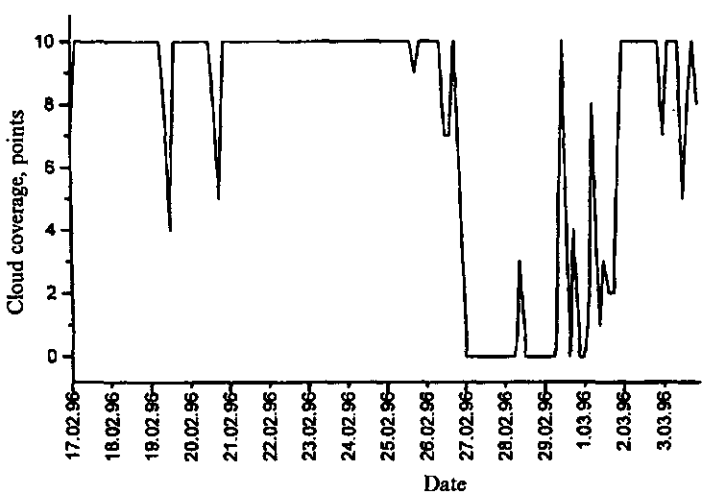

Fig. 1

Cloud coverage variation over the measurement period.

Weather conditions were mainly characterized by the cloud coverage, because it is the clouds that limit the amount of radiation which determines photochemical processes. When evaluating the NO_2 photodissociation rate, the cloud coverage (Fig. 1) was taken into account using both the integral radiation flux and the flux of UV radiation ($\lambda = 0.3$–$0.4\ \mu$m), whose spectrum is the closest to the the NO_2 absorption region. The feasibility of this approach to evaluating the photodissociation rate (using the UV flux) was demonstrated by Madronich [4].

Different approaches were employed for calculating the concentration of peroxy radicals. Because the nitrogen dioxide photodissociation rate was not measured during our experiment, it was calculated by the formula

$$J_{NO_2} = 0.01305 \exp(-0.360 \sec\theta),$$

where θ is the solar zenith angle.

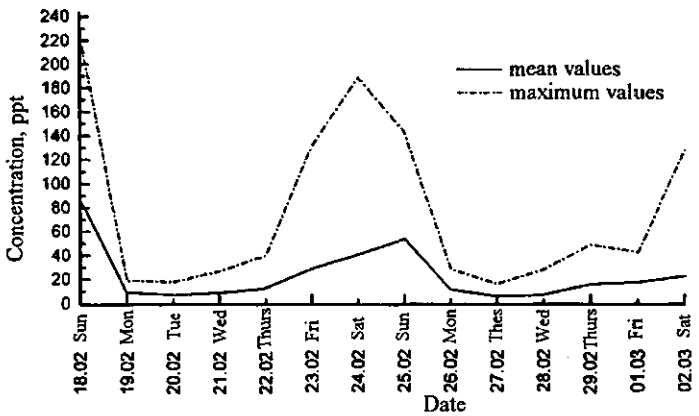

Fig. 2

Model behavior of peroxy radical concentration.

The values of peroxy radical concentration calculated using the photodissociation rate were highly overestimated, especially on weekends, owing, in particular, to the fact that the cloud conditions were not taken into account when evaluating J_{NO_2}. The range of mean $[RO_2]+[HO_2]$ concentrations calculated using data from [5] extends from 5.8 ppt (1 ppt $= 10^{-3}$ ppb) on weekdays to 87 ppt on weekends and holidays (Fig. 2), which agrees with the data of [6, 7].

We corrected our values using another method of calculating the photodissociation rate. Since the diurnal behavior of the photodissociation rate is controlled by the diurnal behavior of the radiation fluxes, their values (those of the integral radiation flux and the flux of UV radiation) were taken as a basis for recalculating the nitrogen dioxide photodissociation rate to incorporate the cloud cover influence on the atmosphere's photochemical state. A clear cloudless day was selected as a reference, and all other values were normalized based on that day.

The concentrations of peroxy radicals calculated with cloud coverage taken into account are shown in Fig. 3. The errors in these data were mainly due to errors in the values of the NO_2 photodissociation rate (max. 25%). Moreover, inaccuracies in the reaction constants were taken into consideration. For these reasons, the total error for the average daytime values of the peroxy radical concentration was about 30%, becoming greater for very low concentrations.

Analysis of our data revealed two basic periods, daily and weekly, in the variation of the peroxy radical concentration in Moscow.

In the weekly period, low peroxy radical concentrations fall on busy workdays and high concentrations fall on weekends and holidays. An opposite picture was observed for the ozone production rate (Fig. 4). This was due to a higher NO removal on workdays. Therefore it can be concluded that the concentration of peroxy radicals is an indicator of the atmosphere's degree of purity.

The diurnal variation of the RO_2 concentration follows the variation of the radiation fluxes which determine the nitrogen dioxide photodissociation rate.

An interesting correlation was revealed between the humidity and the peroxy radical concentration. The coefficient of correlation between these parameters varied from day to day but always negative, varying from –0.36 to –0.91 (an example is shown in Fig. 5). This correlation is difficult to explain in the framework of our model. We suppose it to be due to the additional generation of OH groups through water vapor

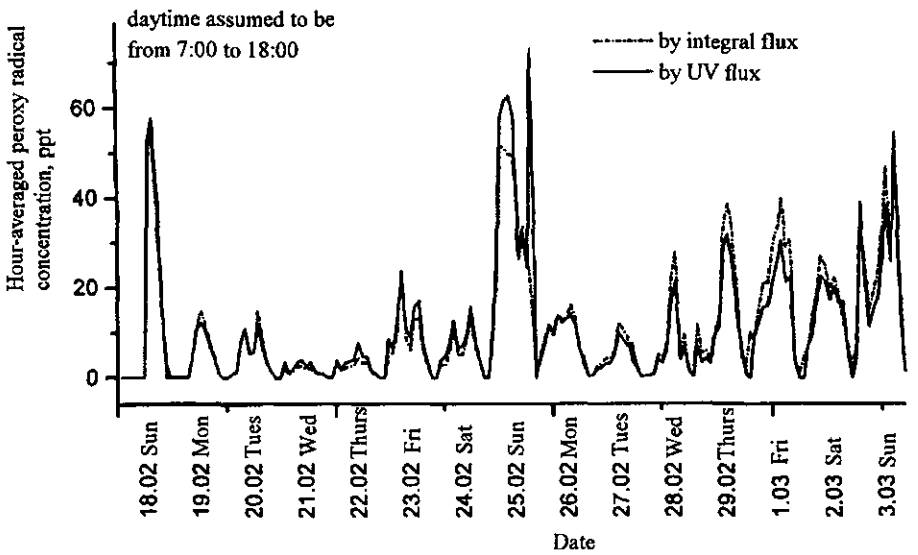

Fig. 3

Peroxy radical concentration corrected for cloud coverage.

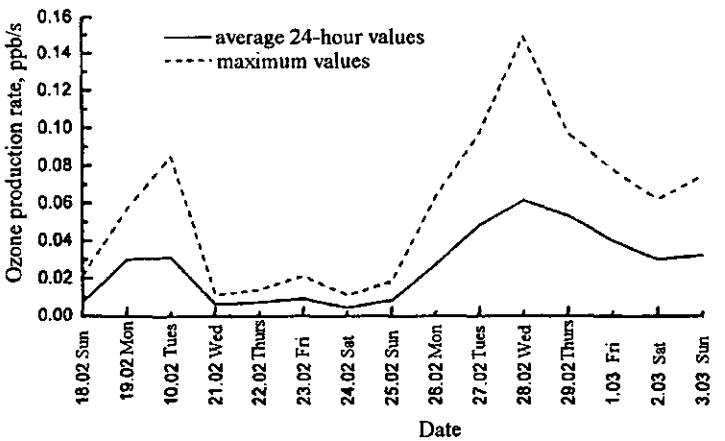

Fig. 4

Ozone production rate during the measurement period.

photolysis. A further refinement of the model will make it possible to evaluate the influence of H_2O on the chemical composition of the atmosphere in quantitative and qualitative terms.

A negative correlation between the concentration of peroxy radicals and the humidity is clearly seen in Fig. 5. This fact justifies the addition into a refined model of the reactions between the hydroxyl and the nitrogen oxides and the reaction of the odd oxygen. The series of measurements should be extended to different illumination conditions for specific estimates of the photodissociation rate of nitrogen dioxide which participates in the reactions of the gaseous components.

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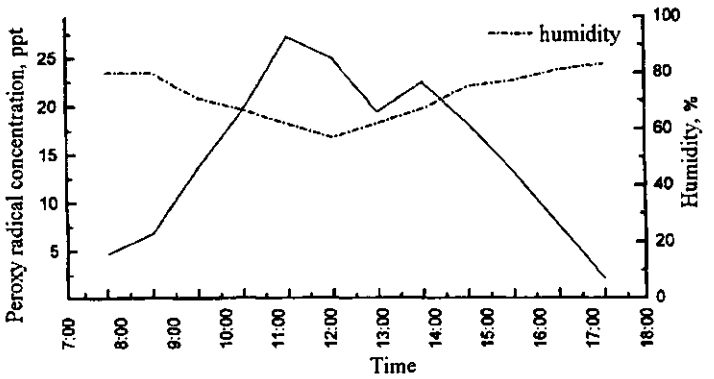

Fig. 5

Peroxy radical concentration and humidity variations on March 2, 1996.

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