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INFLUENCE OF ANTHROPOGENIC ATMOSPHERIC POLLUTION ON THE SMALL GASEOUS COMPONENTS OF AIR IN HIGH – LATITUDE INDUSTRIAL AREA

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Abstract. Chemical transformation of the basic small gaseous components of air by anthropogenic atmospheric pollution is numerically studied. Pollution is supposed to take place during working days (8 – 17 hours). Conversion of different species is studied in the frame of a simplified box model with 9 independent species which are O_3, NO, NO_2, HNO_3 and others. Photodissociation is given as a function of local time with maximum at the noon. It was found that: a) surface ozone concentration (SOC) can be either increased or decreased depending on organic peroxy radical concentration (OPC), limiting value of OPC is approximately 0.001 ppb; SOC grows with the increase of OPC; b) the abrupt diminution of perhydroxyl radical concentration is consequence of nitrogen oxide injection; c) strong intensification of nitric acid generation is observed in process of pollution by nitrogen oxide; industrial zones are sources of nitric acid in the troposphere.

Introduction

Atmospheric pollution renders a strong influence on the small gaseous components (SGC) of air. Distribution of ozone and other SGC are determined by the interaction with the pollution species partly. Solar ultraviolet radiation (UVR) has an effect on this interaction as it is seen in case of ozone. Photodissociation of nitrogen dioxide NO_2 takes part in transformation of nitrogen–rich components of atmospheric pollution to other species. Surface ozone is one of the products of the NO_2 photodissociation. The content of surface ozone depends on concentrations of nitrogen oxides NO_x, perhydroxyl HO_2 , organic peroxy radicals RO_2 and intensity of solar UVR in a nonlinear fashion *(Kondratyev and Varotsos,1998, Vogel et. al.,1999).* Carbon monoxide CO and nitrogen oxide NO are some of the main components of atmospheric pollution including the car exhaust. In this report the mutual transformation of SGC and atmospheric pollution species CO and NO is studied.

Model

The chemical transformation of different atmospheric species are investigated in the framework of a simplified box model with 9 independent species which are O_3, NO, NO_2, NO_3, N_2O_5, HNO_3, CH_3O_2, PAN and HO_2. These species interact with each other in 27 reactions and 3 reactions are NO_2 and NO_3 photodissociation. It is supposed that formation of atomic oxygen proceeds to ozone mainly because the characteristic time of reaction for ozone origin

$$O_2 + O + M \rightarrow O_3 + M$$

$\tau(O) \sim 10^{-5}$ s. is much less then the characteristic times for other interactions of atomic oxygen in the atmosphere. The H_2, H_2O, OH, CH_2O, CO, CH_4, CH_3COO_2 and organic peroxy radicals RO_2 took into account as the given quantities.

Solution of the chemical kinetics equations with dry deposition was found in this model:

$$\frac{dn_i}{dt} = S_i - L_i - \frac{v(i)\,n_i}{h} + S_p(i)$$

where n_i – concentration of *i* component; S_i, L_i – sources and losses of component *i* in the chemical reactions; $v(i)$,h – velocity of dry deposition and the height of mixing layer; $S_p(i)$ – sources of NO and CO from atmospheric pollution by the car exhaust. $S_p(CO)$ is found in the equation for HO_2 because the interaction ($CO+OH+O_2$) is an important way of forming HO_2. Sources of NO and CO act during the working day: $S_p(i) = S(i) = \text{const}$ for $8^{\,h} \leq t \leq 17^{\,h}$; $S_p(i) = 0$ for other local time *t*. Used chemical reactions with its coefficients are taken from *(Yvon et. al.,1996)* and are shown in the Table. The value of *h* is taken as 1000 m. In our model the photodissociation rates are presented as a function of local time with maximum at the noon accordingly to the experimental data *(Lantz et. al.,1996).* Meaning of photodissociation rate at the noon is expressed as a part of experimental value for the mid–latitude. The maximum values of these rates are equal $J(NO_2 \rightarrow NO+O) = 6\cdot10^{-3}\ s^{-1}$, $J(NO_3 \rightarrow NO_2+O) = 0{,}19\ s^{-1}$, $J(NO_3 \rightarrow NO+O_2) = 0{,}016\ s^{-1}$. Diurnal variation of hydroxyl concentration is presented as a function of local time with maximum at the noon *(Elanskii and Smirnova,1997)* like the photodissociation rate. RO_2 concentration was taken as a constant value which was not equal to zero in the time from sunrise to sunset only. The rate of reaction $NO+RO_2$ was used the same as for R18.

Table

Used chemical reactions

R1 $NO_2+h\nu \rightarrow NO+O$	R2 $NO_3+h\nu \rightarrow NO_2+O$	R3 $NO_3+h\nu \rightarrow NO+O_2$
R4 $O_3+NO \rightarrow NO_2+O_2$	R5 $O_3+NO_2 \rightarrow NO_3+O_2$	R6 $O_3+OH \rightarrow HO_2+O_2$
R7 $O_3+HO_2 \rightarrow OH+2O_2$	R8 $NO_3+NO \rightarrow 2NO_2$	R9 $NO_3+NO_2 \rightarrow NO_2+NO+O_2$
R10 $NO_3+NO_2+M \rightarrow N_2O_5+M$	R11 $N_2O_5+M \rightarrow NO_3+NO_2+M$	R12 $NO_3+OH \rightarrow NO_2+HO_2$
R13 $NO_3+HO_2 \rightarrow OH+NO_2+O_2$	R14 $NO_3+CH_2O+O_2 \rightarrow HNO_3+HO_2+CO$	R15 $N_2O_5+H_2O \rightarrow 2HNO_3$
R16 $NO+HO_2 \rightarrow NO_2+OH$	R17 $NO+CH_3COO_2 \rightarrow CH_3+CO_2+NO_2$	R18 $NO+CH_3O_2 \rightarrow CH_3O+NO_2$
R19 $NO_2+CH_3COO_2 \rightarrow PAN$	R20 $PAN+M \rightarrow CH_3COO_2+NO_2$	R21 $OH+NO_2+M \rightarrow HNO_3+M$
R22 $OH+HNO_3 \rightarrow NO_3+H_2O$	R23 $OH+NO+M \rightarrow HNO_2+M$	R24 $OH+HO_2 \rightarrow H_2O+O_2$
R25 $OH+CH_4 \rightarrow CH_3+H_2O$	R26 $OH+CH_2O+O_2 \rightarrow HO_2+CO+H_2O$	R27 $OH+CO+O_2 \rightarrow HO_2+CO_2$
R28 $OH+H_2+O_2 \rightarrow HO_2+H_2O$	R29 $HO_2+HO_2 \rightarrow H_2O_2+O_2$	R30 $RO_2+NO+O_2 \rightarrow NO_2+HO_2$+prod.

Results

The species of atmospheric pollution assist to strong changes of SGC of the air. Atmospheric pollution has significant influence on ozone, perhydroxil and nitric acid above all. Ozone concentration may change significantly during the working day when injection NO takes place. Products of pollution species' action on ozone are, basically, nitrogen oxides. It is determined by RO_2 , first of all, whether positive or negative change of ozone concentration will occur. Let us characterize the pollution influence on ozone by ratio of ozone concentrations at the beginning and the end of working day Y = $[O_3](17\ ^h)/[O_3](8\ ^h)$. The Y value is shown in Fig.1 as a function of pollution source S(NO) for different quantities of $[RO_2]$. The values are taken for next meaning: $[H_2]$ = 500 ppb, $[CH_4]$ = 1600 ppb, [CO] = 200 ppb, $[CH_2O]$ = 1 ppb, $[CH_3COO_2] = 3 \cdot 10^{-4}$ ppb, S(CO) = $5 \cdot 10^{-3}$ ppb/s, maximum value [OH] = $1.35 \cdot 10^{6}$ cm^{-3}, temperature 20° C, rate of photodissociation is 0.8 from the one at mid–latitude. The used values of S(CO) and S(NO) correspond approximately to the pollution intensity in the industrial areas of northern regions of Russia. It is seen that ozone concentration can be increased as well decreased depending on the value $[RO_2]$. Growth of ozone concentration takes place when $[RO_2]$ increases. Function Y(S(NO)) is shown for the day duration of 18 hours (continuous line) and 14 hours (dashed line) (conditions of polar summer). The $[RO_2]$ value separating the regions of increasing and decreasing ozone content is within the limits of 0.002 ppb $\geq RO_2 \geq$ 0.001 ppb for our conditions. The basic change of $[O_3]$ takes place at the atmospheric pollution rate S(NO) < $2 \cdot 10^{-3}$ ppb/s. Concentration of ozone changes quickly at S(NO) < $2 \cdot 10^{-3}$ ppb/s and the changes are small for greater values of S(NO). The pollution of the atmosphere by nitrogen oxide exerts influence upon ozone concentration which may be changed in some times in accordance with Fig. 1.

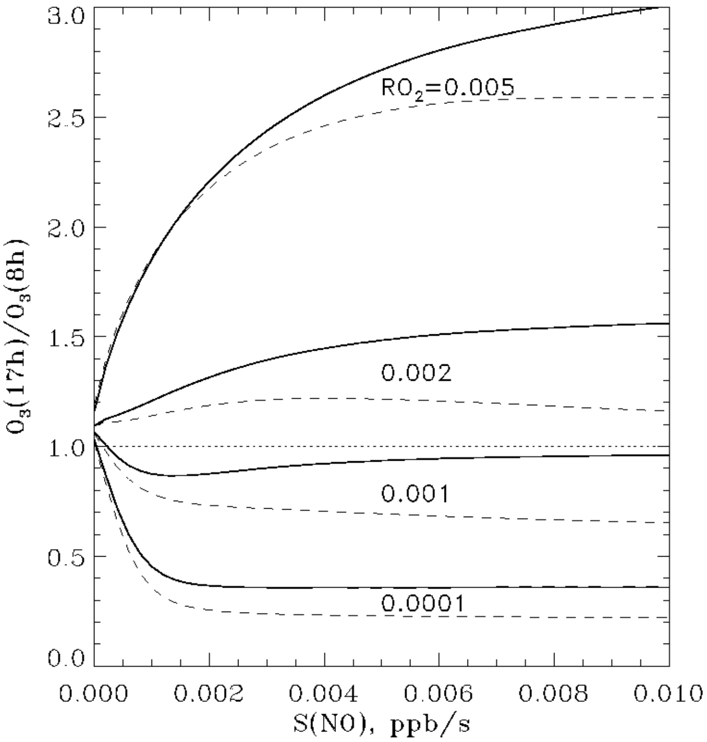

Fig.1 Dependence of the ratio of ozone concentration at the beginning and day on NO pollution rate S(NO) under different concentrations of RO_2 in ppb.

Diminution of $[HO_2]$ and $[CH_3O_2]$ in fast reactions with NO is another important result of this simulation. The behavior of $[HO_2]$ during day and night is shown in Fig. 2. The results of this Figure are given for the day duration of 18 hours; the beginning (at 8 ^{h}) and the end (at 17 ^{h}) of the working day are marked by dashed-dot lines. Perhydroxyl growth begins with formation of OH at 3 ^{h}, then a sharp recession of $[HO_2]$ is observed at 8 ^{h}. The recession value depends on NO rate pollution and its rate increases with augmentation of NO pollution. It is illustrated by three curves in Fig. 2: dotted line for "no pollution", dashed line for the weak pollution rate S(NO) = 10^{-4} ppb/s and the continuous line for the strong pollution rate S(NO) = 10^{-3} ppb/s. The greater values of $[HO_2]$ for polluted cases during 3 ^{h} – 8 ^{h} LT are caused by forming HO_2 through R27. The value of CO pollution rate is the same as for Fig. 1. The $[HO_2]$ recession is caused by reaction R16 with pollutant NO. The characteristic time of this reaction in our conditions ([NO] ≈ 1 ppb ” $[HO_2]$,

$T \approx 300$ °K) is $\tau(HO_2) = 1/k\,[NO] \approx 5$ s., where k is the rate of R16. This result shows that pollution may reduce HO_2 concentration sharply. Diminution of HO_2 means that the oxidants content may be reduced in human organism. It is known that HO_2 molecule electrolitically dissociates in aqueous media of human organism making up superoxide–ion O_2^-. This ion is the reactive oxygen product leading to origination of hydroxyl. The latter is a strong oxidizer inflicting the oxidizing damages to human organism.

Atmospheric pollution by nitrogen oxide causes the intensification of nitric acid generation. Nitrogen dioxide participates in ozone generation and is transformed to PAN and nitric acid partly. It is reflected in Fig. 3 where nitric acid concentration is shown as a function of the local time during the polar summer for different pollution rates. The curve 1 corresponds to the weak pollution intensity (S(NO) = 10^{-5} ppb/s) and the curves 2,3 correspond to the strong pollution (S(NO) = 10^{-3} ppb/s) but different concentration RO_2: $[RO_2] = 5\cdot10^{-5}$ ppb for 2, $[RO_2] = 5\cdot10^{-4}$ ppb for 3. The concentration of HNO_3 increases under atmospheric pollution during the working day. Nitric acid is formed through reaction R21 when OH exists and its formation occurs through reaction R15 after 21^{h} mainly. Nitric acid is a reservoir for nitrogen under these conditions. The volume of this reservoir increases with the growth of NO pollution rate. Industrial areas are sources of HNO_3 because of the interaction of atmospheric pollution with SGC of air.

It is necessary to note the more important role of NO pollution in the interaction with SGC of air in comparison with the one of CO pollution, although the CO pollution rate is several times more than the NO pollution rate.

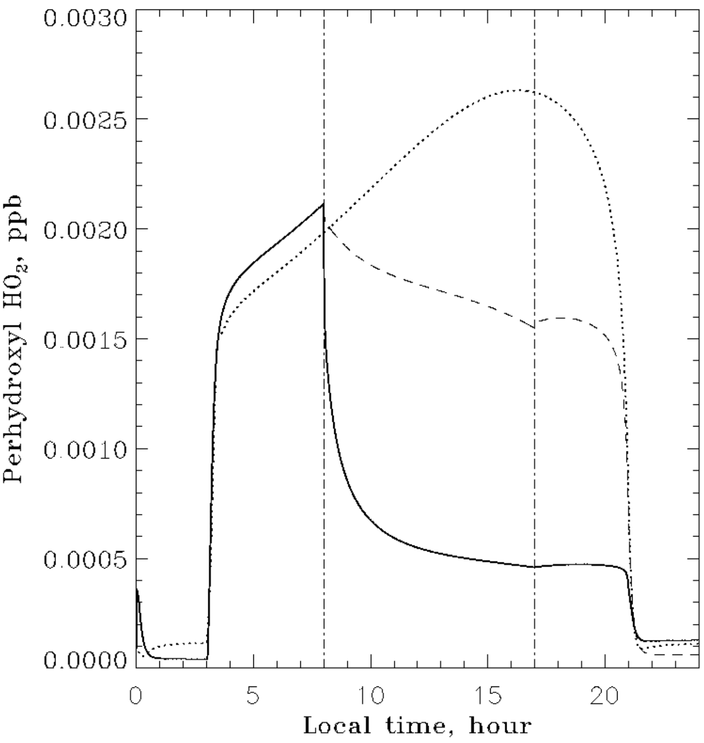

Fig.2. Changing of HO_2 concentration with time at different NO pollution rates

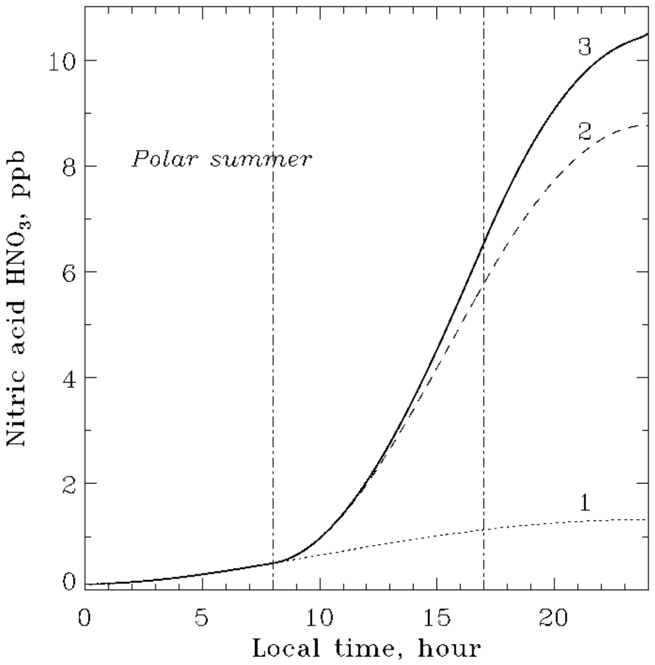

Fig.3. Changing of HNO_3 concentration with time at different NO pollution rates.

Conclusions

The main results of this work are: a) ozone concentration can be increased as well as decreased under pollution conditions, the substance controlling this process is organic peroxy radicals RO_2: the increase of $[RO_2]$ leads to the increase of $[O_3]$; b) atmospheric pollution leads to a sharp diminution of $[HO_2]$ caused by destroying by pollutant NO; c) the pollution increases the nitric acid generation; i.e. industrial areas are the sources of nitric acid in the troposphere.

References

Elanskii N.F. and Smirnova O.I. Ozone and Nitrogen Oxide Concentrations in the Atmospheric Surface Layer over Moscow. RAS News. Atmos. Ocean. Phys. 33, N 5, 597-611, 1997 (in Russian).

Kondratyev K.Ya. and Varotsos C.A. Total and troposphere ozone changes: implications for climate change, human health and ecosystems. Ecol. Chem. 8, N1, 44-59, 1998.

Lantz K.O., Shetter R.E., Cantrell C.A., Floke S.J., Calvert J.G., and Madronich S. Theoretical, actinometric, and radiometric determinations of the photolysis rate coefficient of NO_2 during the Mauna Loa Observatory
Photochemistry Experiment 2. J. Geoph. Res. 101, D9, 14,613-14,629, 1996.

Vogel N., Riemer N., Vogel H., and Fiedler F. Findings of NO_y as an indicator for ozone sensitivity based on different numerical simulation. J. Geoph. Res. 104, D3, 3605-3620, 1999.

Yvon S.A., Salzman E.S., Cooper D.J., Bates T.S., and Thompson A.M. Atmospheric sulfur cycling in the tropical Pacific marine boundary layer (12°S, 135°W): A comparison of field data and model results. 1. Dimethilsulfide.
J. Geoph. Res. 101, D3, 6899-6909, 1996.