Nitrogen oxides as chemically and optically active trace gaseous constituents of the troposphere

K.Ya. Kondratyev and V.A. Isidorov

*Center of Ecological Safety RAS/Nansen International Center
of Environmental Protection and Remote Sensing, St. Petersburg
St. Petersburg State University*

The paper discusses some recent results of studying the spatiotemporal variability of nitrogen oxides in the troposphere and their role as chemically and optically active trace gaseous constituents of the atmosphere. It is underlined that a much greater attention must be paid to a systematic approach to planning appropriate observations and performing numerical simulation.

Introduction

The chemically active nitrogen oxides NO_x, belong to the trace gaseous constituents (TGCs) of the atmosphere, which play a critically important role in limitation of the rate of atmospheric oxidants formation and, thus, control for the efficiency of the troposphere self-cleaning from different natural and anthropogenic compounds capable of reaching concentrations of toxic levels. The nitrogen oxides, in particular, are of prime importance as factors determining the possibility of formation of the tropospheric ozone through photochemical reactions. Even at concentrations of a few pptv, typical of remote tropical regions of the Pacific Ocean, as well as Arctic and Antarctic regions, the chemically active NO_x determine the rate of ozone production, which is several times higher than the rate of ozone arrival from the stratosphere.

The multi-aspect role of nitrogen oxides in tropospheric chemistry has stirred a great interest in studying factors responsible for formation of NO_x concentration field in the troposphere.[2,12,14] The complexity of the problem is due to the fact that the characteristic rates of reactions with participation of NO_x vary in a wide range from minutes to months. A serious obstacle is a multitude of nitrogen oxide sources, a part of which is located near the earth surface (for example, fossil fuel and biomass combustion, as well as soil nitrification/denitrification processes), others are located in the troposphere itself (including lightning discharges, subsonic aircraft effluxes, NO_x arrival from the stratosphere, and oxidation of reduced nitrogen compounds). All the above causes strong spatiotemporal variability of the NO_x concentration field in the troposphere, that depends on many factors ranging from influence of soil moisture content on microbial activity to conditions of cumulus cloud development.

A considerable progress toward understanding the factors controlling the NO_x concentration field in the troposphere has been made in a series of aircraft observations, especially under conditions of remote (background) troposphere. In this regard, D. Bradshaw et al.[6] reviewed results of such observations over the past fifteen years aimed to collect data on NO_x and many other TGCs reacting with NO_x. These observations were conducted mainly in the course of observational programs in the framework of NASA Global Tropospheric Experiment (GTE), Airborne Arctic Stratospheric Expedition (AASE-I and II), Stratospheric Ozone (STRATOZ-II and III), and INSTAC-1 programs aimed to study stratospheric chemistry. All experiments were made primarily with participation of European specialists and observation facilities.

Main results of the experiments can be summarized as follows:

1) In the greatest part of the background troposphere, the level of NO_x concentration, as determined from NO observations, is sufficiently high to have a considerable impact on photochemical processes there. This primarily refers to formation of the tropospheric ozone concentration field and explains why the mean total ozone content in the troposphere is several times higher than the amount of ozone arriving from the stratosphere.

2) A stable characteristic of the NO concentration field in the background upper troposphere is its three-fold or larger excess over the NO concentration at lower altitudes, which determines the O_3 formation in the upper troposphere and its loss at lower altitudes.

3) Lightning discharges are the most significant source of NO_x in the upper troposphere, and of great importance is convective upward transport from such ground-based sources as fossil fuel and biomass combustion. An important factor maintaining the level of NO_x concentration (especially in the upper troposphere) may be reactions involving other compounds of odd nitrogen. The obtained estimates, however, are characterized by large errors (due to some

uncertainty in contribution of lightning discharges and NH_3 oxidation).

1. Natural and anthropogenic sources of nitrogen oxides

A study of sources of nitrogen oxides arrival in the atmosphere is complicated because they are many and varied. The members of the family of odd nitrogen compounds, denoted by NO_y ($NO_y \equiv NO + NO_2 + NO_3 + N_2O_5$ + nitrogen acid vapors (HNO_3) + aerosol nitrates (NO_{3p}) + peroxyacetyl nitrate (PAN) + other organic nitrates) play an important role in the chemistry of the low troposphere. Not only do they regulate the processes of formation and destruction of the tropospheric ozone, NO, and NO_2, but also influence significantly the content of hydroxyl (OH) and hydrogen peroxide (HO_2) radicals in the troposphere. Through the control over these most important atmospheric oxidants, the nitrogen oxides NO_x ($NO + NO_2$) become efficiently involved in many chemical reactions proceeding in the atmosphere; and thus, the NO_x mixing ratio determines the rate of oxidation removal of many trace gaseous constituents.

Like NO, NO_x are immediately emitted into the atmosphere as a result of combustion processes; but then they rapidly react with different oxidants (O_3, HO_2, peroxide radicals RO_2, etc.), resulting in formation of NO_2. Under exposure to solar radiation, however, NO rapidly (in a few minutes) regenerates because of NO_2 photodissociation. Slower reactions at time scales from several hours to several days may cause NO_2 oxidation to nitrogen acid (HNO_3) or PAN. During night, NO_2 can oxidize to NO_3 (via O_3) or react with NO_3 to form N_2O_5 with a subsequent hydrolysis at the surface of aerosol particles, leading to formation of HNO_3.

The pathway of chemically less active reservoir compounds NO_y (PAN and HNO_3) is somewhat different. As for PAN, it is stable only at low temperatures, and almost insoluble in water; therefore, at lower temperatures it can be transported for long distances in the upper troposphere. Upon arrival at distant regions, PAN is subject to thermal decomposition to NO_x in the descending air. While HNO_3 can react with different gases and particles to form aerosol-bearing nitrates, it is readily soluble in water and adsorbs on the surface of particles. Since HNO_3 has a high deposition rate, it is efficiently removed from the atmosphere through moist and dry deposition during short-range transport.

The HNO_3 removal process is the main NO_y sinking mechanism in the atmosphere. The evolution of HNO_3 is also determined by "fertilization" process of N-deficient ecosystems through HNO_3 sedimentation. The NH_3 is an important biogen for vegetation growth, as well as it is an important acidity factor for the atmospheric aerosol, cloud water, and precipitation.

Most important sources of NH_3 include decomposition of animal's excrements, fertilizer evaporation, biomass burning, and vegetation fading.

Because of the fact that reliable estimates of the processes mentioned above were not available, in 1991−1995 in Harvard Forest (Central Massachusetts, USA) Lefer et al.[16] performed hourly observations of HNO_3 and NH_3 mixing ratios, as well as some other TGCs and aerosol. This work pursued the following goals: (1) to obtain representative set of data; (2) to determine relationships in the diurnal and annual HNO_3 and NH_3 behaviors; (3) to study dependence of the TGCs mixing ratios under consideration on meteorological conditions (temperature, as well as speed and direction of wind); and (4) to compare the roles of the HNO_3 and other chemically active nitrogen compounds in chemical processes in the ground atmospheric layer.

Since both polluted (urban) and clean (rural) air masses enter the region of Harvard Forest, it is characterized by strong variability of the mean daytime HNO_3 mixing ratio: it can increase by a factor of four (to 2000 pptv) when southwest winds blow, and be very low (about 500 pptv) in the case of northwesterly winds. Analysis of diurnal HNO_3 behavior reveals that HNO_3 is involved in the near-ground layer from above at a breakup of the nighttime inversion. Typical mixing ratios of the gaseous HNO_3 range from 200 to 300 pptv and are characterized by only weak diurnal behavior.

High level of sulfate content in the atmosphere causes suppression of NH_3 concentration to the level below the predicted "offset point" of vegetation cover even in periods, when sums of NH_3 and NH_4^+ (NH_x) mixing ratios are large. Control for NH_x components spreading due to sulfate aerosol depends on the temperature. At a fixed SO_4^{2-} concentration, the temperature decrease is accompanied by reduction of NH_3/NH_x. On average, at the about-noon time, the HNO_3 is approximately 20% of NO_y. The sum of concentrations of NO_y components (NO, NO_2, HNO_3, and aerosol NO_3^-) is 60−80% of NO_y, indicating that, in the predominantly forest region, PAN and other organic nitrates make up a considerable portion of NO_y.

An important role in the photochemistry of the troposphere is played by nitrogen oxide (NO), especially because the growth of NO emission (in the presence of solar radiation and hydrocarbon species) causes an increase of tropospheric ozone and other oxidants of photochemical origin. The available estimates suggest that nitrogen oxide emissions from soil contribute as much as 75% to the budget of nitrogen oxides NO_x. In this connection, Roelle et al.[22] have conducted measurements of biogenic emissions of nitrogen oxides from agricultural soils at a wheat-growing (Zea mays) area from May 15 to June 9, 1995. The region of study was located in the District of Washington (near Plimut, North Carolina, USA). To measure the NO emission from soil, they used a system of dynamic flow chamber.

The observational period was characterized by (1) the use of nitrogen fertilizers in the middle of this period and (2) an atypical change in precipitation. Before application of fertilizers, the mean NO flux was (31.5 ± 10.1) ngN/(m^2 · s), while after fertilization it became more than doubled [(77 ± 63.7) ngN/(m^2·s)]. The variations of NO flux followed the diurnal behavior of the soil temperature at maximum (minimum) of emissions coinciding with maximum (minimum) of the temperature. After fertilization, the exponential growth of the NO flux, following the increase of the soil temperature, was observed. Owing to application of the irrigation system, the change in the soil moisture content was minimal; hence, any relation between the moisture content and NO flux was not determined. The analysis of simultaneous measurements of NO_y, NO_2, and NO emissions has revealed that 86% of the NO_y emission from soil was in the form of NO and 8.7% in the form of NO_2. The NO flux was simultaneously measured by the closed chamber technique, and no statistically significant deviations from the above results were found.

When nitrogen oxide, a precursor of tropospheric ozone, is present in the low tropospheric layer in sufficient amounts, it stimulates occurrence here of episodes of strong pollution. To the present time, sources of the NO emission under urban conditions are rather well studied, whereas there is very little similar information for rural (background) conditions. Generally speaking, growth of the near-ground ozone concentration is caused by photochemical reactions between nitrogen oxides and different hydrocarbon compounds of natural and anthropogenic origin[14]:

$$R_1CH_2R_2 + 3NO + O_2 \rightarrow 3NO_2 + R_1COR_2 + {} + R_1'CHO + H_2O$$
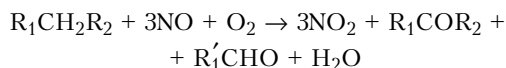
resulting in the reaction

$$NO_2 + O_2 \xrightarrow{h\nu} NO + O_3.$$
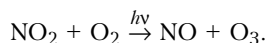
Here R_1 and R_2 are alkyl groups; R_1' determines the alkyl group, which contains one hydrogen atom less than the R_1 group.

Using a unique chamber, allowing a change of the soil moisture, temperature, and pH, Ormeci et al.[18] performed laboratory analysis of mechanical, chemical, and biologic factors controlling the NO emission from agricultural soils to low tropospheric layers. The analysis has shown that all factors under study (temperature, moisture, and pH) influence the NO formation in soil via different biological and chemical processes. The same factors control NO transport from soil to low tropospheric layers by advection and diffusion of NO through pores in the soil. As the temperature increases, the NO flux also increases (at a sacrifice of increasing microbial activity and chemical formation of NO) until reaching maximum values at pH < 5 and pH > 8.

In acid soils, the processes of chemodenitrification cause intense formation of NO. At higher temperatures (> 50°C), the biological formation of NO stops and the biologically-derived NO emission disappears. The NO flux decreases both at very high (> 45%) and very low (< 1%) moisture content. Comparison with field data shows that laboratory simulations somewhat overestimate the magnitude of NO fluxes. In the future, it would be useful to study how the NO emission depends on such factors as size distribution and porosity of soil particles, composition of organic agents in soil, microbial habitat, and presence in the soil of liquids other than water.

Emissions of NO to the atmosphere from soil in rural regions may contribute significantly to the budget of NO_x. The emission rate may increase due to the nitrogen fertilization of soil. Taylor et al.[24] discuss the results of quasi-continuous monitoring of NO emissions from agricultural fields, obtained by the gradient method. A chemiluminescent analyzer was used by them in hourly measurements of the difference between NO concentrations in air and at heights of 0.6 and 1 m. The turbulent mixing coefficient was determined from measurements of the wind velocity profile (using a cap anemometer), corrected for the atmospheric stability. The errors of nitrogen oxide flux calculations were estimated to be less than 0.5 ngN/(m^2 · s).

Analysis of 1833 hourly measurements of NO fluxes from bare soil surface at Elore, Canada, made from January to June, 1995, has shown that the NO fluxes were insignificant in the period before nitrogen fertilization of soil and after that they increased to > 10 ngN/(m^2 · s).

Nitrogen oxides NO and NO_2 are important components of tropospheric chemistry, which determine both the acidity of precipitation and the concentration in the atmosphere of such important oxidants as OH and O_3. The NO reacts with O_3 forming NO_2 which, in turn, can undergo photolysis with further producing of NO. Most important sources of tropospheric NO_x are fossil fuel and biomass combustion, lightning discharges, microbial processes in soil, and arrival from the stratosphere.

In the global emissions of NO_x, reaching about 50 TgN/yr, almost 20 TgN/yr falls on fossil fuel combustion and about 10 TgN/yr on biomass burning. A significant contribution comes from NO emission by soil, which is characterized by strong dependence on the specificity of ecosystems [the emission rates vary in the range 0.1–231 ngN/(m^2·yr) at a mean value of 12.6 ngN/(m^2 · s)]. Until present, very fragmentary data are available for forest midlatitude regions, where the level of emissions is, as a rule, very low [< 0.2 kgN/(ha · yr)], except for the forests with high nitrogen deposition, where the emission rate increases to 1.1 − 5 kgN/(ha · yr).

Pilegaard et al.[20] studied NO emissions from Norway spruce forest floor in Denmark, where a moderate deposition rate N is observed, by the NO flux measurements in dynamic chambers in April and September of 1995. Simultaneously, they measured CO_2 and NO_2 fluxes, soil moisture inside and outside the

chambers, soil temperature at the surface and at a depth of 10 m, and air temperature.

Processing of the measurements has shown that NO emissions in April were low (< 0.3 ngN/m$^2 \cdot$ s), but increased considerably in September [average 21 ngN/(cm$^2 \cdot$s) at the variability range 0–82 ngN/(m$^2 \cdot$ s)]. In April, the soil surface temperature was below 6°C, but relative soil moisture was high (26%). In September, the surface temperature increased to 16°C, but the soil moisture was much lower (14%). A close correlation between CO_2 and NO emissions was observed. The NO_2 fluxes were found to be small and uncorrelating with NO.

The NO emission varied little within this area, but changed considerably from one area to another. Nearly half of NO flux variations in September can be explained by a combined effect of the soil moisture and the distance to tree trunks and moss. However, no marked dependence of NO emissions on soil temperature was found, both at the surface and in depth.

To understand the reasons for the emission variations, it is necessary to take into account the concentration ratio C/N in the soil. Estimates of total NO emissions per year gave the value of 3.15 kgN/(ha · yr), consistent with estimates obtained earlier for forests of Central Europe, experienced nitrogen depositions.

Among major sources of nitrogen oxides NO_x are fossil fuel and biomass combustion, gaseous emissions from soil, arrival from the stratosphere, aircraft effluxes, and lightning discharges. The contribution of lightning discharges to NO_x budget remains most uncertain. The available data indicate that the global contribution is 2–200 TgN/yr, or 2–10 TgN/yr by more realistic estimates. Three-dimensional (3D) simulation of NO_x field with account for lightning discharges requires data on the geophysical distribution (monthly) of lightning flashes, the amount of the produced NO_x per flash, and vertical NO_x distribution.

In this regard, Pickering et al.[19] suggested a technique for parameterization of the vertical NO_x distribution, which can be used in the 3D modeling (according to some calculational data resulting from setting the global annual level of lightning NO_x formation equal to 5 TgN/yr, the lightning discharges are the largest contributors to the upper tropospheric NO_x budget at all latitudes and in all seasons).

They justified typical "lightning" vertical NO_x profiles for continents at midlatitudes and in tropics, as well as for tropical marine troposphere; for this, they used a parameterization of the lightning flash frequency, type, location, and NO_x production rate as applied to scales of transport of tracers in thunderstorm cloud systems. Such a parameterization allowed them to calculate the above characteristics using the variables precomputed based on the two-dimensional Goddard Cumulus Ensemble (GCE) model.

Based on the data on the precomputed wind field, they have obtained information on the lightning NO_x redistribution during a storm.[19] Their calculations of the flash rates and NO_x mixing ratios agree well with observational data. For each storm, the vertical NO_x profiles can be calculated accounting for lightning discharges in clouds. The results for different geographic regions show a presence of NO_x maximum in the upper troposphere, located, as a rule, within 2–4 km from the tropopause. Downward air flows turn to be the strongest in the continental midlatitudes, the evidence of which is intense formation of the "lightning" NO_x (up to 23% of total amount) in the low kilometer layer.

Tropical storm systems, particularly, those over marine areas, are characterized by high frequency of cloud-to-cloud flashes and weaker downward flows. Therefore, only minor amounts of NO_x remain after a storm in the boundary atmospheric layer under such conditions. Even though a substantial portion of NO_x is produced by cloud-to-cloud flashes in the lowest 6-km layer, the most amount of NO_x (55–75%) at the end of the storm is located in the upper troposphere (above 8 km), what agrees with observations. Due to the fact that the lifetime of the lightning NO_x in the upper troposphere is several days, strong storms can be followed by intense photochemical ozone production there. The proposed accounting for typical vertical profiles of NO_x is shown to be very important for reliable estimates of NO_x and O_3 formation in the upper troposphere. Some possible errors of the parameterization under discussion have been analyzed.

A field experiment (LINOX) was performed in the south of Germany in July 1996. Main tasks of the experiment were to study the structure of thunderstorm clouds using radar and satellite observation data, to test the operation of the ground-based network of registration of the lightning discharges, and to conduct the aircraft observation of chemical composition of the atmosphere with the help of the instrumentation installed at a jet aircraft, which could penetrate into the anvil region of thunderstorm clouds.

Analysis of observations made by Höller et al.[11] has shown that a higher concentration of nitrogen oxides (comparative to the surrounding atmosphere) takes place in anvils of thunderstorm clouds, as well as in smaller thunderstorm cumulus clouds, while the CO_2 concentration decreases inside the clouds. The NO_x mixing ratio in anvils is, as a rule, 1–4 ppbv. In narrow discharge channels formed during discharge flashes, as well as near boundaries of thunderstorm clouds, the NO contribution to the total NO_x concentration prevails, probably, because of larger NO_2 photolysis rate in these regions.

To distinguish the lightning-produced NO_x from that coming from the atmospheric boundary layer, the measurement data on the concentration of CO_2 as a tracer of air masses were used. Based on the data on a thick cloud anvil observed on July 23, 1996, Höller et al.[11] have shown that the amount of nitrogen oxides resulting from lightning discharges is comparable with

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the amount of NO_x coming from the atmospheric boundary layer; however, at later stages of the cloud evolution, the lightning NO_x becomes more abundant.

The main features of the spatial NO_x distribution within anvil plume region are well reproduced numerically with the help of a simple 2D model of advection and diffusion of lightning-produced nitrogen oxides. Some of the observed maxima (peaks) of NO_x concentration can be explained by conditions of flash observations in immediate proximity to the aircraft track. Authors of the work,[11] however, note that their results cannot be considered representative for other thunderstorms, and especially for other geographic regions. Hence, further observations are required, with special emphasis on contribution of cloud-to-cloud lightning discharges to the budget of NO_x.

Jones et al.[10] have discussed the results of their study of NO_y concentration in the high latitude troposphere, pointing out to the importance of oxidized nitrogen species for the chemistry of the unpolluted atmosphere and interpretation of data on the nitrate content in ice cores. As was noted above, by definition,

$$NO_y = NO + NO_2 + p\text{-}NO_3 + HNO_2 + HONO + PAN +$$
$$+ \text{ organic nitrates} + 2{\times}N_2O_5 + XONO_2...,$$

where X is the halogen atom. The main purpose of the study of NO_y chemistry is to determine the role of $NO_x(NO + NO_2)$ in the oxidizing capacity of the troposphere, which influences formation of tropospheric ozone and the reaction involving the OH hydroxyl radical.

Since nitrogen oxides have many sources and short lifetime, the NO_x distribution is highly inhomogeneous in space, and cannot be determined adequately on a global scale without numerous observations. Therefore, in summer 1997, an experiment was undertaken at the German Antarctic station (Neumayer, 70°39′S, 8°15′W) to measure simultaneously the concentrations of NO_y, NO, HNO_3, p-NO_3, and methyl and ethyl nitrates (CH_3ONO_2 and $C_2H_5ONO_2$), as well as the NO_2 photolysis rate.[10]

Although inorganic nitrates were thought earlier to be prevailing NO_y compounds in the Antarctic, the data under discussion obtained at a coastal station do not support this hypothesis. The concentration of methyl nitrate was found to be higher than the concentration of inorganic nitrate (with average mixing ratios of 38 pptv for CH_3ONO_2 and 5 pptv for HNO_3). It was also believed earlier that some alkyl nitrates are of maritime origin. If this was the case, a conclusion would follow that ocean was a source of NO_y for the Antarctic troposphere. Thus, it turned to be necessary to estimate the contribution of tropospheric organic nitrates to concentration of nitrates in ice cores.

An important information on nitrogen oxides is contained in the data on their isotopic composition. Five isotopes of nitrous oxide N_2O are of particular interest[21]: most abundant $^{14}N^{14}N^{16}O$ and rare $^{14}N^{15}N^{16}O$, $^{15}N^{14}N^{16}O$, $^{14}N^{14}N^{17}O$, and $^{14}N^{14}N^{18}O$. The present day mass spectrometric systems fail to

distinguish two isotopic forms containing ^{15}N. It was proposed that there is some mass independent relationship between two rare oxygen compounds; however, recent analysis of tropospheric air samples has revealed in them a minor (and mass independent) enrichment with isotope ^{17}O. Usually, the isotopic composition of trace gaseous constituents is given in ppm by $\delta = [(R_{samp}/R_{std}) - 1] \cdot 1000$, where $R_{samp}(R_{std})$ is the concentration ratio of the heavier isotope to the lighter one for the sample (samp) under study and the standard (std).

As a rule, the isotopic analysis of N_2O was earlier made by studying its decomposition products, and therefore either atmospheric N_2 (for ^{15}N) or atmospheric O_2/standard ocean water sample (for O_2 isotopes) served isotope standards for N_2O. Present day instrumentation, however, is capable of separating N_2O from CO_2 and measuring directly the isotopic composition of N_2O (with the help of an appropriate standard). The nitrous oxide is a TGC species formed in the soil microbial habitat via reactions involving both recombined (NH_3) and oxidized (NO_3) nitrogen compounds. Some portion of the produced N_2O enters the troposphere, where it remains chemically inert until reaching the stratosphere. There it is photolyzed under exposure to the solar UV radiation (yielding 90% of N_2O losses) or oxidized by excited oxygen atoms (10% losses), and sometimes it partially returns to the troposphere (via stratosphere-troposphere exchange processes). The portion of N_2O, decomposed through the reaction with $O(^1D)$, is a major source of NO, playing a significant role in the catalytic cycle of the stratospheric ozone.

Current level of N_2O concentration is 313 pptv, which increases by about 0.25% per year. Nitrous oxide lifetime in the atmosphere is approximately 120 years. The relatively high level of nitrous oxide concentration, its temporal growth, and optical activity of N_2O in the IR spectral range have motivated the inclusion of N_2O in Kyoto protocol of six most significant greenhouse gases. Nonetheless, the global nitrous oxide budget is still poorly understood. The available data suggest that the level of different naturally produced components of the N_2O budget is 1–5 TgN/yr for the world ocean and 3.3–9.7 TgN/yr for the soils at tropics and midlatitudes. Estimates of total contribution of anthropogenic N_2O sources vary in the range 3.7–7.7 TgN/yr. These estimates can be significantly improved using the above-mentioned data of isotopic measurements, allowing separation and estimation of contributions of different sources of nitrous oxide. Account for photolytic fractionation of isotopes is of importance in the analysis of isotopic data; and this process calls for further investigation.

2. Transformations (sinks) of nitrogen oxides

As it was noted above, nitrogen oxides in the troposphere and stratosphere can be transformed in

different ways.[1,2,14] One of the most important aspects of the problem is connected with formation of the near-ground ozone concentration (NOC) field. Of most concern is summertime NOC enhancement in populated industrial regions despite anti-pollution measures. The ozone production rate in the troposphere depends on concentration of such ozone precursors as nitrogen oxides NO_x $(= NO + NO_2)$ and volatile organic compounds (VOCs). The complexity of the problem of ozone formation is determined by the necessity to account for such factors of atmospheric dynamics as advection, turbulent diffusion, and dry deposition. A significant role is also played by the temperature, air humidity, and insolation (the latter determines the photolysis rate). Further complexity comes from the fact that anthropogenic and biogenic emissions of the ozone precursors strongly vary in space and time. Taken together, these factors give rise to serious (and still insuperable) difficulties in numerical simulation (and, hence, understanding) of the NOC field variability.

In this regard, NO_y was suggested as an indicator of sensitivity of NOC to emissions of ozone precursors. Vogel et al.[25] performed numerical simulation of connection between O_3 and NO_y under conditions of polluted atmospheric boundary layer using different methods. A box model was used to estimate the sensitivity of transition (between low and high NO_y concentrations) level of concentration to variations of emissions and environmental conditions. The calculations have shown that the transition concentration depends on the intensity of hydrocarbon and NO_x emissions, as well as on such factors as insolation, air temperature, and water vapor content. The greater the hydrocarbon emission rate, water vapor content, insolation, and temperature, the higher the transition level of the NO_y concentration.

One-dimensional simulation model with account for the vertical mixing and dry deposition has demonstrated that some increase in the dry deposition rate may lead to decrease of the transition level of the NO_y concentration. The use of the 3D non-hydrostatic model made it possible to estimate the sensitivity of emission-induced effects on NOC to transfer processes in the atmosphere. In this case, a smoothing was used to reduce the variance of calculated values of the O_3–NO_y relationship. The calculations have shown that in the south-west regions of Germany, the position of the transition level can be used to determine areas, where some decrease of the NO_x concentration leads to maximum fall of NOC.

According to the "box" calculations, the position of the transition level significantly depends on emission rates and environmental conditions. Normalization of simulated and observed data has shown, in particular, that, under conditions of high NO_x concentration, the results of NOC calculations substantially differ, depending on whether advection is taken or not into consideration. It is also shown that the 3D model results are characterized by weaker NOC sensitivity to

variations of NO_x emissions than those obtained under consideration of only chemical processes. Vogel et al.[25] have shown that only more than 50% reduction of NO_x emissions (in order to reduce NOC) may be efficient. Reduction of NO_x emissions is more efficient than reduction of VOC emissions.

In addition to the problem of near-ground ozone concentration, of great concern is anthropogenic increase of ozone in the troposphere. It can manifest itself as a greenhouse gas, or as an agent hazardous for human health and vegetation, necessitating the study of factors responsible for tropospheric ozone (TO) variations. These factors include photochemical ozone production and destruction, ozone transport in the troposphere, stratosphere-troposphere exchange, and ozone deposition at the surface. The anthropogenic TO growth is caused primarily by atmospheric emissions of gaseous precursors of TO, in particular, hydrocarbons with quite long lifetime.

In this regard, Fenneteaux et al.,[9] in context of TOR program of the tropospheric ozone study, have measured O_3, NMHC, PAN, and NO_x concentrations at Porspoder station (north-western France) during 1992–1995, and discussed the results of observations for the period from April 1992 to December 1994. To characterize the origin of air masses coming from the North Atlantic to the region of the Porspoder station, back trajectories of air masses at the 950 hPa level for 5 days were calculated. According to their origin, three types of air masses, coming from the regions of northern and southern latitudes of the North Atlantic and from North American continent, were considered.

The results obtained by Fenneteaux et al.[9] indicate that the high-latitude troposphere over ocean is strongly influenced by emissions from continents, leading to changes in the midlatitude troposphere due to arrival of polar air masses. Their calculations have revealed significant accumulation of anthropogenic species in the Arctic, likely responsible for high springtime level of oxidants. Also, they studied the influence of emissions in North America on the air composition near sea coasts of Europe, which turned to be most substantial in spring. Long-range transport of long-lived species was observed throughout the year; in winter the episodes of transport of such chemically active species as ethane were recorded. An important role is played by meteorological conditions and local photochemical processes as factors responsible for the spread of pollutants over North Atlantic.

Understanding of the processes controlling atmospheric oxidation capacity and, in particular, the role of such short-lived free radicals as hydroxyl (OH), atomic chlorine (Cl), and nitrate (NO_3), is critically important for assessment of the lifetime and role of both greenhouse and ozone-depleting gases including methane and methyl chloroform. Many important trace gaseous constituents (similar to hydrocarbons and halogenated hydrocarbons, carbon oxide, dimethyl sulfide, etc.) are removed from the atmosphere

predominately through the reaction with hydroxyl. Under conditions of polluted air masses, oxidation processes involving Cl and NO_3 may be significant.

Wingenter et al.[27] examined the results of chemical analysis of 1419 air samples taken over oceans of the southern hemisphere during the first field Aerosol Characterization Experiment (ACE-1), aimed at the study of processes of the atmospheric aerosol formation. Of the above samples, 700 pertain to the marine atmosphere boundary layer (MABL), 300 to the free troposphere (FT), and the rest to the so-called Buffer layer located between MABL and FT.

Analysis of the samples has shown that there was a decrease of tetrachloroethene, ethane, ethyne, and propane concentrations for 24 days during Intensive Observations Period (IOP) of the experiment started on November 18, 1995. This decrease is in agreement with available data on annual behavior of hydroxyl concentration and seasonal decrease of biomass burning. Changes in the concentration of these TGCs can be described by a simple empirical model assuming the number concentrations $[OH] = (6.1 \pm 0.3) \cdot 10^5$ cm^{-3} and $[Cl] = (720 \pm 100)$ cm^{-3}. The characteristic time for exchange between MABL and FT was found to be (14 ± 2) days, and $49 + 40/-13$ days for exchange between MABL located over observation site and MABL lying to the north.
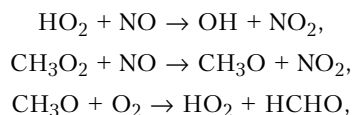
Being a primary oxidizer in the troposphere, the hydroxyl OH is largely responsible for removal of many anthropogenic pollutants and biogenic constituents from the atmosphere. Hydroxyl is formed mainly through photolysis of ozone at wavelengths less than 330 nm in the reactions:
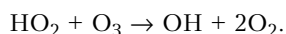
$$O_3 + h\nu \rightarrow O(^1D) + O_2$$

$$O(^1D) + H_2O \rightarrow 2OH.$$
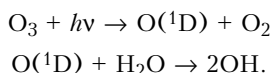
Under conditions of the clean atmosphere, main reactions responsible for OH losses are:

$$OH + CO(+O_2) \rightarrow HO_2 + CO_2,$$

$$OH + CH_4(+O_2) \rightarrow CH_3O_2 + H_2O.$$
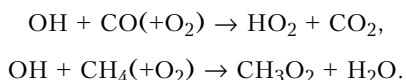
In the presence of NO_x, the following reactions take place:

$$HO_2 + NO \rightarrow OH + NO_2,$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2,$$

$$CH_3O + O_2 \rightarrow HO_2 + HCHO,$$

and some possibility exists for the reaction

$$HO_2 + O_3 \rightarrow OH + 2O_2.$$

In the polluted atmosphere, the hydroxyl may enter into similar reactions involving different non-methane hydrocarbons (NMHC). Since OH and HO_2 have very short lifetimes (1 and 150 s, respectively), their fast mutual transformation can take place. An important intermediate chain between OH and HO_2 may be formaldehyde (HCHO):

$$HCHO + OH(+O_2) \rightarrow H_2O + CO + HO_2,$$

$$HCHO + h\nu(+O_2) \rightarrow CO + 2HO_2.$$
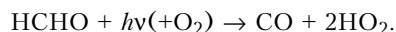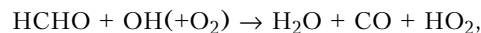
A box model, well describing the above and other processes, was proposed by Carlslow et al.[7,8] to simulate chemical processes in marine atmospheric boundary layer in the region of Mace Head, a remote site at the west coast of Ireland. Subject to limitations imposed by data of NMHC observations, the model was intended to simulate observed concentrations of hydroxyl radicals (OH) and hydrogen peroxide (HO_2), as well as a sum of concentrations of radicals $\Sigma([HO_2] + [RO_2])$, where RO_2 defines a sum of concentrations of all organic peroxy radicals, and R denotes alkyl, akyl, or aryl group.

Carlslow et al.[7] have described in detail the model construction and compared numerical results with observations obtained at Mace Head observatory in July−August 1996 (during field experiment EASE-96). Comparisons made with limited data on OH have revealed that the model overestimated OH and HO_2 concentrations by about 40%, but that discrepancy was within the calculation error ($\pm 31\%$ at 2σ level for OH and $\pm 75\%$, 2σ for HO_2). For HO_2, there appeared the cases of both agreement and disagreement with observational data.

An important product of photochemical oxidation of hydrocarbons, formed in the atmosphere in the presence of NO_x, is peroxyacetyl nitrate $CH_3C(O)OONO_2$ (PAN), first detected in the atmospheric boundary layer (ABL) above Los Angeles in early 1950. PAN serves as a reservoir for NO_x, thus playing a significant role in tropospheric chemistry. Since PAN is very stable at low temperatures, it can efficiently maintain the long-range transport of NO_x in organic form from the middle to high troposphere and remote regions. On the other hand, under conditions of warm ABL, PAN is rapidly decomposed, forming NO_x.

The strong spatiotemporal variability of PAN has stimulated ground based measurements of its concentration both in the clean (background) and polluted atmosphere, especially because PAN and its homologues may serve excellent indicators of photochemical activity and, in particular, photochemical processes of formation of tropospheric ozone. Observations in "background" regions have shown, e.g., that the PAN accumulation is associated with photochemical processes giving rise to springtime maximum of the tropospheric ozone content.

Conducting of simultaneous measurements of PAN, peroxypropionyl nitrate $CH_3CH_2C(O)OONO_2$ (PPN), and peroxymethacryl nitrate $CH_2 = C(CH_3)C(O)OONO_2$ (MPAN) concentrations made it possible to estimate contributions of anthropogenic and biogenic hydrocarbons in the atmosphere, i.e., to photochemical production of near-ground ozone in the Eastern United States.[23] Development and employment of the global chemical transport model (GCTM) have facilitated calculation of the global NO_x and PAN distributions and evaluation

of their contribution to chemical reactions proceeding in the troposphere.

Because of the need for more reliable and full information on PAN with concentration of the order of a few pptv, Tanimoto et al.[23] proposed a method based on combined use of gas chromatographic and mass spectrometric techniques (involving negative ions formed by chemical ionization). This method (abbreviated as GC/NICI MS) permitted measurements of PAN mixing ratio at the detection threshold of (15 ± 4) pptv (for signal-to-noise ratio of 3). The relative and absolute measurement errors were $\pm$ 20% and $\pm$ 15%, respectively. Measurements of PPN and MPAN concentrations were also quite successful.

One of significant sinks of nitrogen oxides is their chemically active assimilation by hydrocarbon soot particles. Main sources of the anthropogenic soot observed in the atmosphere (especially above cities and along flight corridors) are fossil fuel and biomass combustion. The soot particles in the atmosphere exert a substantial influence on many chemical reactions, decelerating them or preventing from proceeding in gas phase. One such reaction, very important for atmospheric chemistry, is the reaction between nitrogen dioxide NO_2 and soot. For instance, one possible mechanism of ozone destruction in the lower stratosphere at midlatitudes is connected with transformation of NO_2 to NO at the surface of soot particles. An evidence of another possible reaction on the surface of soot particles is the presence of anticorrelation between NO_2 and HONO concentrations in the troposphere.

The interaction of NO_2 with soot particles was the subject of many laboratory studies, the results of which have led to conclusion that HONO might be formed during this interaction. Longfellow et al.[17] performed a new laboratory simulation of interaction of NO_2 with different soot particles produced in the laboratory. The obtained results indicate that HONO may arise due to interaction of NO_2 with soot particles formed by methane, propane, hexane, or kerosene burning. The soot produced by combustion of hydrocarbons acts as a catalyst for reaction between NO_2 and H_2O, leading to formation of HONO. However, the rates of NO_2 assimilation by soot particles, obtained in the laboratory, cannot be applied to real atmospheric conditions without additional validity tests.

A significant sink for nitrogen oxides is the process of their deposition on the underlying surface. It is generally recognized that the high deposition rate of atmospheric nitrogen compounds in many regions of Europe and North America is responsible for saturation of forest ecosystems with nitrogen. The saturation means a situation, in which the nitrogen income exceeds the ability of vegetation and soil microbes to accumulate N. Phenomena, accompanying this situation, are the intensification of leaching of soil nitrates (NO_3), soil acidification, and deforestation, all considered as severe ecological hazards.

Under support of European Union, Nitrogen Experiment (NITREX) was initiated to study the nitrogen saturation of eight European forest ecosystems and the reversibility of the process, as well as to estimate the influence of N deposition rate on nitrogen cycle and the efficiency of efforts to mitigate undesired impacts.

Koopmans and Van Dam15 have shown that most forest ecosystems in Holland are nitrogen-saturated due to increase in nitrogen deposition in the past four decades. To analyze consequences of artificially decreased nitrogen arrival, a field experiment was performed at two forest sites with high [37 kgN/(ha·yr)] and artificially lowered [6 kgN/(ha·yr)] levels of nitrogen deposition. To interpret the observational data, they developed an imitation model of biochemical dynamics of forest ecosystems (NICCCE).

In Ref. 15, the calibration and applicability of the model, using biochemical data for nitrogen-saturated Douglas Fir Forest in the central part of the country (52°13′N; 5°39′E) and isotopic data on ^{15}N as a tracer, are under discussion. The main purpose of the field experiment and numerical simulation was to analyze both consequences of the above-mentioned artificial lowering of nitrogen inflow to the forest ecosystem and the high level of nitrogen deposition during the four-year period.

The calibrated model well reproduced the fast response of the chemical composition of the soil water to the lowering of the nitrogen deposition rate and the signal of the tracer ^{15}N in soil water at 90 cm depth. Application of the model version, calibrated for conditions of low N deposition rate, to calculation of trends under conditions of high deposition level was only partly successful. Analysis of the model sensitivity has shown that the influence of variations of the nitrogen arrival is very sensitive to parameters of the microbial habitat in soil. Lowering of nitrogen supply under conditions of nitrogen saturated forest soil has resulted in more than proportional decrease of nitrogen losses due to nitrogen leaching out of the soil. During four years of artificial variation of N inflow, the N-dependent mineralization of soil did not change, but soil nitrification decreased by about one third of the nitrification typical of the site with a high deposition rate of N.

Conclusion

Growing anthropogenic and biogenic impact on the concentration of many chemically and optically active minor constituents in the atmosphere results in changes of the atmospheric chemical composition. The consequences of such changes can manifest themselves in a wide range of scales, from local to global.[1–6,12–14] Of special concern, in this regard, are nitrogen oxides whose spatiotemporal variability remains still poorly understood. This holds true both to observational data and numerical simulation. Much progress was made towards development and application of methods of remote sensing of TGC (including nitrogen oxides) in

the framework of the Earth Observing System (EOS) Program.[26] However, despite a variety of remote sensing instrumentation installed on the EOS satellite, the problem of systematic approach to TGC study based on the problem-oriented approach to planning of observations with the use of different observation facilities (ground-based, airborne, balloon-borne, and satellite) and acquisition of adequate information is still unsolved. The same is true for numerical simulations. Marked advances have been made recently in the study of global carbon cycle[2,5]; while only first steps are made in understanding of the hydrogen cycle. Systematic studies of this cycle (as well as of associated TGCs and attendant processes) must be the subject of future investigations.

References

1. A.A. Grigoryev and K.Ya. Kondratyev, *Ecological Catastrophes* (St. Petersburg Scientific Center RAS, St. Petersburg, 2001), 688 pp.

2. K.Ya. Kondratyev, *Geodynamics and Ecopolytics.* Vol. 1. *Global Problems* (St. Petersburg Scientific Center RAS, St. Petersburg, 1999), 1036 pp.

3. K.Ya. Kondratyev, Izv. Ros. Geofiz. Observ. **132**, Issue 5, 1–17 (2000).

4. K.Ya. Kondratyev, V. Sun, S. Balyunas, K.S. Demirchan, Sh.V. Idso, and E.S. Postmentyer, Izv. Ros. Geofiz. Observ. **133**, Issue 2, 1–19 (2001).

5. K.Ya. Kondratyev and K.S. Demirchan, Vestn. Ros. Akad. Nauk, No. 11 (2001) (in press).

6. J. Bradshaw, D. Davis, G. Grodzinsky, S. Smyth, R. Newell, S. Sandholm, and S. Lin, Rev. Geophys. **38**, No. 1, 61–116 (2000).

7. N. Carlslow, D.J. Creasey, D.E. Heard, A.C. Lewis, J.B. McQuaid, and M.S. Pilling, J. Geophys. Res. D **104**, No. 23, 30241–30255 (1999).

8. N. Carlslow, P.J. Jacobs, and M.J. Pilling, J. Geophys. Res. D **104**, No. 23, 30257–30275 (1999).

9. I. Fenneteaux, P. Colin, A. Etienne, H. Boudries, A.L. Dutor, P.E. Perros, and G. Toupance, J. Atmos. Chem. **32**, No. 2, 233–280 (1999).

10. A.E. Jones, R. Weller, A. Minikin, E.W. Wolff, W.T. Sturges, H.P. McIntyre, S.R. Leonard, O. Schrems, and S. Bauguitte, J. Geophys. Res. D **104**, No. 17, 21355–21366 (1999).

11. F. Höller, U. Finke, H. Huntrieser, M. Hagen, and C. Feigli, J. Geophys. Res. D **104**, No. 11, 13911–13922 (1999).

12. K.Ya. Kondratyev, *Multidimensional Global Change* (Wiley / PRAXIS, Chichester, U.K., 1998), 761 pp.

13. K.Ya. Kondratyev, *Climatic Effects of Aerosols and Clouds* (Springer / PRAXIS, Chichester, U.K., 1999), 264 pp.

14. K.Ya. Kondratyev, and C.A. Varotsos, *Atmospheric Ozone Variability: Implications for Climate Change, Human Health, and Ecosystems* (Springer / PRAXIS, Chichester, U.K., 2000), 617 pp.

15. C.J. Koopmans and O. Van Dam, Water, Air, and Soil Pollut. **104**, Nos. 1–2, 181–203 (1998).

16. B.L. Lefer, R.W. Talbet, and J.W. Munger, J. Geophys. Res. D **104**, No. 1, 1645–1661 (1999).

17. C.A. Longfellow, A.R. Ravishankara, and O.R. Hanson, J. Geophys. Res. D **104**, No. 11, 13833–13840 (1999).

18. B. Ormeci, S.L. Sanin, and J.J. Peirce, J. Geophys. Res. D **104**, No. 1, 1621–1629 (1999).

19. K.E. Pickering, Y. Wang, W.-K. Tao, K. Price, and J.-F. Müller, J. Geophys. Res. D **103**, No. 23, 31203–31216 (1998).

20. K. Pilegaard, P. Hummelshoj, and N.O. Jensen, J. Geophys. Res. D **104**, No. 3, 3433–3445 (1999).

21. T. Rahn, and M. Wahlen, IGAC-tiv. Newsletter, No. 16, 7–10 (1999).

22. P. Roelle, V.P. Aneija, J. O'Connor, W. Robarge, D.-S. Kim, and J.S. Levine, J. Geophys. Res. D **104**, No. 1, 1609–1619 (1999).

23. H. Tanimoto, J. Hirokawa, Y. Kajii, and H. Akimoto, J. Geophys. Res. D **104**, No. 17, 21343–21354 (1999).

24. N.M. Taylor, C. Wagner-Riddle, G.W. Thurtell, and E.G. Beauchamp, J. Geophys. Res. D **104**, No. 10, 12213–12220 (1999).

25. B. Vogel, N. Riemer, H. Vogel, and F. Fiedler, J. Geophys. Res. D **104**, No. 3, 3605–3620 (1999).

26. R. Williams, The Earth Observer **13**, No. 1, 3–9 (2001).

27. O.W. Wingenter, D.R. Blake, N.J. Blake, B.C. Sive, F.S. Rowland, E. Atlas, and F. Flocke, J. Geophys. Res. D **104**, No. 17, 21819–21828 (1999).