

MONITORING OF ATMOSPHERIC POLLUTION IN EUROPE: THE EUROTRAC PROGRAM

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An overview is presented of the EUROTRAC program for monitoring of atmospheric pollution in Europe. It includes a discussion of the key aspects of the program: chemical transformation and transport of photo-oxidants (first of all, ozone) in the troposphere; processes leading to atmospheric acidification, particularly those involving aerosols and clouds; assimilation and emission of atmospheric trace gases by the biosphere.

Taking into consideration deterioration of environmental conditions on the European continent, the Commission of the European Communities (CEC) has supported the initiative to develop, as part of the All-European EURECA project, the interdisciplinary EUROTRAC program (of European experiment on the study of transport and transformation of important environmental tropospheric minor gas and aerosol components over Europe), aimed at studying the dynamics of atmospheric pollutants (their transport and chemical transformations).¹⁻³ The general objective of this program is to obtain comprehensive data on the state of the atmosphere over Europe, bearing in mind further use of these data for the scientific foundation of the newly adopted political decisions on the control of the continental environment. Presently the EUROTRAC program is quickly developing into its implementation stage, over 250 research groups from more than 20 European countries participate in it, and their efforts are focused on 15 subprojects.

Among the top-priority developments are the studies of the following problems:

- chemical transformation and transport of photo-oxidants (such as ozone) in the troposphere,
- processes resulting in acidification (particularly those involving aerosols and clouds), and
- assimilation and emission of the minor gas components (MGC's) by the biosphere.

The means to solve these problems include field measurements (ground-based and in the free atmosphere) and laboratory experiments as well as imitation modeling with the participation of experts in many natural sciences (such as meteorology, physics, chemistry, biology, and others) and technology. Below we consider individual subprograms being parts of the general EUROTRAC program and report some results obtained in 1991.

1. FIELD OBSERVATIONAL SUBPROGRAMS

The objectives for the TRACT subprogram are the studies of transport of pollutants over complex (e.g., mountainous) terrain. The objective for the ALPTRAC program, developed as part of the above program, is to monitor the MGC's and their sedimentation on snow cover in the Alps. Studies are underway on the following directions:

Collection of snow samples at 15 stations and subsequent analysis of these samples to reveal the regularities of the spatiotemporal variability of concentrations of the pollutants (principal ions) and of their

sedimentation at altitudes of from 2450 to 3900 m (SNOSP). Observations made in 1991 revealed a 2-3 times increase of the SO_4^{2-} and NO_3^- ions along a 650 km west-to-east path. It is yet to be explained whether this effect resulted from different rates of sedimentation or from rarefaction, which was manifested in the west where the snowfalls were heavier.

Study of interrelation of the properties of the alpine air, clouds, and snow (ALASS), bearing in mind the solution to the following problems on different characteristic time scales:

- relation between the chemical compositions of aerosol and snow,
- relation among chemical composition of precipitation, aerosol, and atmosphere,
- interaction of the MGC's, aerosols, and cloud particles (supercooled droplets and ice crystals), and
- chemical analysis of ice cores for the study of their chemical evolution over decades and centuries (CORE).

The analysis of cores sampled in Col Gniffetti revealed a trend towards decrease of the SO_4^{2-} , H^+ , and NH_4^+ ion concentrations over the last 15 years being about 3-5% every year. However, the data on the isotope of oxygen $\delta^{18}\text{O}$ indicate that such a trend was only partially real. As compared to the preindustrial period, the present concentrations of SO_4^{2-} and NH_4^+ appeared to be 3-5 times higher, while the alkaline reaction of snow changed in acidic one.

The objective of the TOR subprogram is to monitor the tropospheric ozone content and to analyze its variability from the data of observations at 25 stations, performed with the use of direct techniques for measuring the surface ozone concentration, and of lidar sensing. Such studies are important since observational data testify to the ongoing increase of the surface ozone concentrations. Having analyzed the observational data obtained in our century, Varotsos and Cartalis⁴ demonstrated that the surface ozone concentration increased from 20 to 28 ppb in 1901-1920, but then decreased down to 15 ppb in 1940. After that the surface ozone concentration started to increase. According to Bojkov,⁵ the surface ozone concentration (SOC) in rural Europe has approximately doubled over the course of the past century.

The authors of the EUROTRAC Annual Report¹ gave the SOC of 10 ppb in the unpolluted troposphere in 1890, which increased up to 50 ppb by now (naturally, the SOC features a strong spatiotemporal inhomogeneity, primarily

determined by the level of atmospheric pollution and varying climatic conditions). Data obtained at high-mountain observation stations as part of the TOR subprogram indicated that the ozone entering the troposphere from the stratosphere was only a small part of the total tropospheric ozone content. High values of the SOC's in summer are mainly due to photochemical processes. Estimates of the contribution of nitrogen oxides to the ozone formation showed that about 10 molecules of O₃ are produced by each molecule of NO_x in summer, when photochemical processes (chemical chain reactions) are most intensive. Observations revealed a high correlation between the SOC and PAN (peroxyacetyl nitrate) concentrations. Since the background concentration of the PAN is about 2 ppb throughout the year, it opens the way for round-the-year pollution of the troposphere by photo-oxidants.

2. STUDIES OF CLOUDS

The ACE subproject dedicated to certain problems in cloud chemistry such as the study of cloud acidification (that is, chemical reactions in which the nitrogen and sulphur compounds take part) as well as the role of organic substances in cloud chemistry was shelved due to financial problems. These studies envisaged the use of both airborne measurements and laboratory modelling. (It was the need for costly airborne measurements which led to serious financial problems.)

The GCE subproject of highland ground-based measurements of cloud parameters for the study of those physical and chemical factors, which determine the relative contributions of chemical reactions in clouds and washing-out of gases and aerosols from clouds to acidification of clouds and fogs, is carried out better. In particular, this project envisages the study of the following problems:

- factors determining the rate of cloud acidification,
- factors governing concentrations of oxidants and catalysts in droplets,
- the relative contribution of cloud aerosols and chemical reactions running within clouds to their chemical composition as a function of the variable parameters of physics and chemistry of a cloudy medium,
- dependence of the washing-out of condensation nuclei on aerosol microstructure and cloud type, and
- prevailing cloud and fog types in Europe, their annual variation and geophysical variability.

The bulk of initial observational data used to solve the above-mentioned problems was obtained during an integrated field experiment conducted in the valley of the Pau (Italy) in 1991. The analysis of these data led, in particular, to the conclusion that nighttime radiative cooling played but a secondary role in the formation of fogs in the considered area.

The principal factor of the formation of stable dense fogs appeared to be advection of humid air. Fogs in the Pau valley wash out the aerosol particles weakly: only about 1% of particles with diameter larger than 0.01 μm was detected in fog droplets, from 1 to 10% of all the particles of the accumulation fraction (0.1–1.0 μm) were washed out (20–30% of their mass). These values were considerably lower than those obtained earlier for convective clouds (there washing-out efficiency reached 90%). Such a contrast is most probably explained by much lower degree of supersaturation in fogs as compared to clouds (aerosol particles with diameter less than 0.3 μm were not washed out from fogs at all).

Washing out of aerosol particles significantly depends on their chemical composition. The washed-out fraction is characterized by higher content of sulphur, ferrum,

magnesium, and copper, while the high concentration of element carbon is typical of particles remaining in clouds. Possibly, one of the main reasons why fogs in the Pau valley are so special is the presence of organic film on the surface of fog droplets.

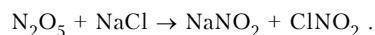
3. LABORATORY STUDIES

The objective of two laboratory subprojects was to obtain reliable data on the characteristics of heterogeneous chemical reactions running in the gas phase, in aqueous solutions, and at the surface of particulate matter, important as they are to understand the regularities of chemistry of the troposphere. Works are underway in three directions as parts of the HALIPP subproject: (1) chemical reactions in aqueous solutions, (2) gas-liquid interactions at phase interfaces, and (3) reactions on particle surfaces including photocatalytic reactions.

As for solutions, their studies concentrate on analyzing the processes of oxidation of sulphur dioxide and sulphites to sulphates, which play the leading role in the formation of acidic precipitation. Work is in progress on the following lines of investigation:

- magnesium-catalysed oxidation of sulphite (what is important is that the reaction is autocatalytic and is affected by synergic interaction between ferrum and magnesium),
- reactions of the sulphate radicals and SO₄²⁻ ions with magnesium,
- co-oxidation of sulphite and ferrum,
- photochemical transformation of oxalate ions into hydroperoxide radicals and hydrogen peroxide in the presence of ferrum,
- oxidation of sulphite by hydrogen peroxide in the presence of metals,
- reactions of sulphite with the SO₅⁻ radicals, and
- photochemical dissociation of hydrogen peroxide in solutions.

The studies of adsorption of the MGC's on water surface were an important part of the above works. In particular, the adhesion coefficients were measured for NH₃ and HONO. This coefficient appeared to reach 0.03 for adsorption of N₂O₅ on water droplets, testifying to the role of adsorption as a factor limiting diffusion. Experiments in a fog chamber demonstrated the possibility of the formation of active chlorine (via ClNO₂ as an intermediate substance) by the reaction of particles of salt in the polluted atmosphere:



Work on the second subproject (LASTOZ) covers five directions: chemistry of hydroxyl OH, reactions of the RO₂ radicals, chemistry of the NO₃ radical, reactions of aromatic and biogenic hydrocarbons, and measurements of the absorption cross sections and quantum yield. Such a choice of priorities is explained by the extremely important role of the OH hydroxyl in the removal of polluting substances from the daytime atmosphere. As for the RO₂ radicals, they are produced by the reaction of OH with volatile organic compounds (VOC's) forming organic radicals, which produce RO₂ in the presence of sufficient amount of oxygen in the atmosphere. The RO₂ radicals take part in the chain reactions of formation of photo-oxidants. The NO₃ radicals, which take part in the fast reaction of photolysis during daytime, play an important role during nighttime,

when they react with hydrocarbons forming nitric acid and hydrocarbon radicals (possibly OH as well).

The odd and even nitrogen oxides, forming NO_x , have comparatively short lifetimes, but may be transported at long distances in the form of PAN or similar compounds, which serve as provisional reservoirs of NO_2 until their thermal dissociation. A new direction is connected with studying reactions of alkenes with ozone. Since such oxidants as ozone are formed from the VOC's via chain reactions in the atmosphere, an important problem is the determination of the ozone formation potential (OFP) (the number of ozone molecules formed by one molecule of hydrocarbon) for each separate volatile organic compound.

Studies promising for the LASTOZ subproject are:

- formation of ozone in the free atmosphere and
- chemical reactions involving VOC and NO_x in the atmospheric boundary layer.

These studies are highly important in the context of the problem of climate changes, since tropospheric ozone and hydroxyl are the substances of critical importance which determine the concentrations of the greenhouse gases. Studies of the sulphate aerosol also acquire particular importance from that point of view.²

4. DEVELOPMENT OF MODELS AND ESTIMATION OF THE AMOUNT OF EMISSIONS

Reliable estimates of the amount of natural and anthropogenic emissions of the most important pollutants into the atmosphere are the objectives of the new GENEMIS subprogram. Meanwhile, an EURAD model has already been developed to describe the long-distance transport of pollutants as part of the other subprogram, EUMAC. This is a 3D Eulerian model specified at the nodes of a grid with an 80-km horizontal step in a 16-layer atmosphere. The model is currently refined to describe better chemical reactions in general and the processes occurring in clouds in particular. A technique is developed to verify the model by the data obtained as part of the TOR subprogram.

The application of the EURAD to reproduce several episodes of heavy pollution yielded satisfactory results. That statement refers, for example, to estimating the distributions of SO_2 , NO_2 , and ozone, as well as that of PAN. One of the crucial factors responsible for the discrepancies between the computational and observational data is an insufficiently reliable account of cloud processes.

The EUMAC studies focus into six principal directions: models of chemical processes, clouds, emissions, embedded submodel (mesoscale processes), model application, and model verification. Chemical aspects of the problem are a top priority.

Europe, as well as other industrial regions of the Northern America and Asia makes a significant contribution to atmospheric pollution on a global scale and receives in its turn such pollutants from other regions. In this connection the challenge of the GLOMAC subproject is to develop and apply a global 3D model of the distributions of ozone, methane, and other hydrocarbons, chemically active compounds of nitrogen, sulphur dioxide, sulphates, etc., allowing for their transport, chemical reactions, and sedimentation, bearing in mind eventually the forecast of dynamics of global atmospheric pollution.

The application of this model should answer three questions:

- What are the sources and sinks of the tropospheric ozone and its predecessors (NO_x , CH_4 , CO, and NMHC)?

- What is the effect of anthropogenic processes (such as industrial emissions, agricultural activities, etc.) in Europe and other regions of the globe upon the chemical composition of the background troposphere and the global climatic system?

- How far may the sulphur compounds and other components oxidizing the atmosphere be transported from the industrial areas?

In this case numerical simulation is based on combining the model of the dynamics of the global atmosphere developed at the European Center for Medium-Range Weather Forecast with various models of chemical processes (in particular, the scheme is applied which allows for reactions involving sulphur and its compounds). Estimates showed that the decrease of the net global radiation flux averaged over the Northern Hemisphere due to sulphate aerosol was about 1 W/m^2 , i.e., was comparable (albeit opposite in sign) to the flux increase caused by intensification of the greenhouse effect due to higher concentrations of carbon dioxide. Such calculations will be continued using a more sophisticated model.

Of particular interest are estimates of the effect of changes in the concentration of carbon monoxide and methane upon the content of hydroxyl. An important problem is to develop the techniques for simulation of the processes of transformation of sulphur compounds and formation of sulphate aerosol.

5. INTERACTION BETWEEN THE ATMOSPHERE AND BIOSPHERE

Studying the exchange of the polluting components and other MGC's between the atmosphere and biosphere, including both dry land areas and water surfaces, is an important part of the EUROTRAC program, since the biosphere is eventually a sink for almost every pollutant or product of its chemical transformation. On the other hand, the biosphere serves a significant source of the MGC's, which may contribute to acidification or formation of photo-oxidants. Therefore, estimates are necessary of both the rates of sedimentation on and amount of emissions from vegetation cover of various types, which may be used to model pollution of the biosphere. These themes form the context of the BIATEX and ASE subprojects.

The BIATEX is one of the most extensive subprojects of the EUROTRAC, including 38 current studies of nitrogen compounds, reduced sulphur, sulphur dioxide, and volatile organic compounds (VOC's) with numerical simulation. Among the important results obtained recently is the study of sedimentation of NO_x on the vegetation cover, which indicated that NO_2 sedimentation is controlled by plant stomata while NO does not practically settle; on the contrary, sometimes it is even emitted by soil. Data on forest pollution due to motor transport near Frankfurt were used to construct a schematic budget of NO_x under these conditions. Soil-emitted nitrogen monoxide is of microbiological origin.

As for ammonia, it may be both settled on and emitted from soil, depending on the level of fertilization, season, and time. The principal compounds settled on the ground in remote areas are HNO_3 and inorganic nitrates, which are contained in raindrops and aerosol particles. Sedimentation of ozone on vegetation is governed by its stomatic conductivity, which varies quite strongly during the vegetation period and features a pronounced diurnal variation. Soil-emitted carbon disulfide (COS) is absorbed by vegetation (same as CO_2). One of the aims of numerical

simulation was particularly to estimate the penetration of a turbulized air into the forest canopy, which strongly intensified sedimentation of pollutants within the forest zone 50 m wide.

The ASE subprogram envisages the study of the exchange of pollutants and MGC's through the air-sea interface bearing in mind that physical, chemical, and biological processes at the atmosphere-sea interface play an important role in the formation of biogeochemical cycles of carbon, sulphur, nitrogen, and metals. Estimating the air-sea mass exchange requires comprehensive data on gas-, liquid-, and solid-phase emissions, dry and liquid sedimentation, and chemical reactions running at that interface. Such emissions significantly affect the chemical composition of the atmosphere. By way of illustration, the biological emissions of sulphur-containing gases (such as dimethylsulfide) noticeably affect acidity of both the atmospheric precipitation and aerosol. The sea also serves as a source of light hydrocarbons and halogen carbon as well as (possibly) of ammonia and methylamine. Since the removal of such chemically important components as nitrates and sulphates from the atmosphere is intensified in the presence of marine salt aerosols, it is important to have the data on the formation of such particles in the European seas and coastal waters. Pollutants contained in that water (e.g., heavy metals, organic matter, and radionuclides) may be re-emitted into the atmosphere and then reach land. These processes need also to be adequately taken into account.

The ASE subprogram covers five main directions of investigations:

- estimate of the contribution from the biological and photochemical processes in the sea surface layer to the air-sea gas exchange,
- measurements of the MGC emissions through the air-sea interface,
- contribution of transformations of the MGC's and aerosols to sedimentation on the water surface,
- air-sea mass exchange of natural and anthropogenic substances in the European region, and
- factors controlling aerosol variability near the water surface.

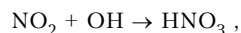
Two ship missions were undertaken in the Mediterranean and Northern Atlantics as parts of the ASE subprogram. A large volume of observations was performed during the mission of scientific-research vessel *Ernst Krenkel* to the Northern Atlantics aimed at the study of the following problems:

- background levels and diurnal variations of photo-oxidants and MGC's related to them in the clear marine atmosphere,
- sources of excess sulphates in the marine atmosphere and the rate of their transport to the European continent,
- atmospheric and continental fluxes of substances affecting both the physical-chemical and biological processes in sea water, into the sea surface layer,
- the role of fronts in the ozone chemistry,
- effects of bioproductivity upon the sea-to-air fluxes of organic matter, and
- parametrization of long-range transport of polluted air masses over ocean using the data on radioactive tracers.

As for the gas components, the principal attention was paid to the problem of the ozone cycle. Aerosol measurements provided the data on condensation nuclei number density and microstructure and chemical composition of aerosol particles.

Shipboard observations under the program of the Northern Sea Experiment (NOSE) revealed a significant decrease in the NO_2 concentration as the distance from

coast increased. Apparently the daytime sink of NO_2 follows the reaction:



while the nighttime reaction with ozone also produces nitric acid in its vapor phase.

The NOSE was aimed to measure microstructure and chemical composition of aerosol with subsequent use of these data for estimation of the sedimentation rate of heavy metals on the sea surface. Observations were performed on a small island in the Kattegat Strait to estimate the sedimentation rate of nitrogen compounds and sulphur dioxide. Analysis of the data of shipboard measurements of the non-methane hydrocarbon concentrations (NMHC's) in the Mediterranean showed that, similar to the Northern Atlantics, the upper sea layer (to depth of several meters) is supersaturated in most hydrocarbons which only feature insignificant spatial variability. Such results indicate the photochemical mechanism of the NMHC formation, leaving the sea quite a minor role as a source of photo-oxidant predecessors, to say the least.

Of particular interest are observational data on the concentration of dimethylsulfide (DMS), indicating that DMS may be a source of sulphur in summer, causing acidification of the atmosphere on a scale similar to that of SO_2 . Observations of DMS emissions into the atmosphere during intense proliferation of phytoplankton and algae in the Northern Atlantics have demonstrated that the flux of DMS was as significant there as in the southern part of the North Sea.

6. INSTRUMENTS

Instruments were designed as parts of three EUROTRAC subprograms: TESLAS, TOPAS, and JETLAG. The aim of TESLAS was to develop lidars for measuring the vertical profiles of ozone concentration. TOPAS uses a technique for differential optical absorption spectroscopy to retrieve the atmospheric content of the MGC's from the data on optical radiation absorption along a 1-2 km path. Appropriate instrumentation has been already routinely used to retrieve the concentrations of such MGC's as NO_2 , SO_2 , HNO_2 , formaldehyde, and ozone in both the urban and rural environments. JETLAG aims to develop techniques for IR absorption spectroscopy employing tunable diode lasers. First prototypes of such instruments have already been developed and will be used for ground-based and airborne measurements. First observations of the Northern-to-Southern Hemisphere differences among the concentrations of CO, NO_2 , HCHO, and H_2O_2 have been already made as part of the TROPOZ project: as expected, the CO concentration in the Southern Hemisphere appeared to be much lower than in the Northern Hemisphere.

In conclusion it should be noted that unfortunately Russian experts do not take part in EUROTRAC studies, except for one episodic expedition, whose preliminary results were discussed in Ref. 5. Undoubtedly, that gap should be covered as soon as possible, so as to ensure studies and monitoring of an enormous part of Europe, European Russia. Further refinement of the objectives of EUROTRAC is necessary as well as a more systematic foundation of its priorities in the light of the recent conceptual studies.⁷⁻¹¹

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