Atmospheric composition observations over Northern Eurasia using the mobile laboratory

TROICA experiments
### TROICA: Transcontinental Observations Into the Chemistry of the Atmosphere

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TROICA experiments

Authors:

Editor: N. F. Elansky
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Preface

This brochure summarizes the long-term studies of the atmosphere over the Russian territory. The data presented here were obtained in the framework of the International Science and Technology Center (ISTC) projects 1235, 2770, 2773, 2757, and 3032. These projects were carried out by a team of scientists and engineers of the A.M. Obukhov Institute of Atmospheric Physics, L.Ya. Karpov Research Institute of Physical Chemistry, Russian Research Institute of Railway Transport, Max Planck Institute for Chemistry, Earth System Research Laboratory NOAA, and other Russian, German, Finnish, and Austrian institutions.

These studies are an important part of the ISTC environmental program addressing growing concerns of irreversible, damaging changes in Earth climate and environment and stimulating scientists to understand processes responsible for those changes and to undertake mitigating measures on regional and national levels. In Russia, as in many other countries, adverse climatic trends and urban-air quality degradation are observed. According to the data of the Russian Hydrometeorological Service, in 2007, the air-pollution level in Russia was specified as high or very high for 67% of the cities with 58.1-million population and as dangerous for 38 cities with 14.9-million population. The anthropogenic climate change, which is particularly visible over the northern regions, may cause significant damage to the Russian economics. During past years, emergency situations associated with permafrost melting and extreme weather conditions are observed with increasing frequency.

The development and support of science and technology projects and promotion of international networks of cooperation in science have been the core activity of ISTC. For 15 years, ISTC supported over 2,600 projects to the amount exceeding US $ 820M; in these projects, over 71,000 scientists and engineers from more than 980 institutes in Russia and other former Soviet Union countries were involved. The ISTC also provides project management and other services stimulating international science cooperation for almost 400 commercial and governmental partners choosing to execute research and development projects within the ISTC partner project framework.

The ISTC supported the international TROICA experiments (TRanscontinental Observations Into the Chemistry of the Atmosphere). These experiments made it possible to increase significantly the information on the atmospheric condition over northern Eurasia. A unique specialized railroad laboratory equipped with modern instrumentation allowed for ground breaking studies of the atmospheric composition on a continental scale. The long-term studies gave important data on the distribution of gaseous and aerosol atmospheric components and its temporal variability, on the air pollution over many cities and industrial regions, and on the harmful effect of different natural and anthropogenic factors on the state of the continental atmosphere.

The TROICA experiments and measurements continue to run on a regular basis, being an important tool of atmosphere monitoring in Russia. I trust that the further promotion of collaboration between scientists of different countries under the aegis of the International Science and Technology Center will be of continued interests of the international science community.

Adriaan van der Meer
Executive Director
International Science and Technology Center
TROICA – the need for research of the atmosphere over the continent

When the eminent scientist Vladimir Vernadsky as early as 1924 did foresee the role of the biosphere in climate and the role of mankind on a global scale, few realized that at the beginning of this century we would already see Climate Change in action. Climate Change constitutes a formidable, if not the most formidable challenge to mankind. Entire ecosystems will change or get obliterated, and not any single country on Earth can claim overall positive effects from Climate Change.

Worldwide, scientists have stepped up their efforts to sufficiently understand weather, climate, the chemistry of the atmosphere, the role of oceans, the biosphere and cryosphere. Despite the measures we fortunately take to reduce greenhouse gas emissions, climate will change. It is imperative that we understand all changes and interactions. In most sciences, observations are of foremost importance, and TROICA performs observations in a very large country indeed.

It is extremely difficult to monitor the atmosphere over a country as vast as Russia, covering different climate and geographical zones. Facing this challenge, and in line with the tradition of excellent quality and innovation in science our Russian colleagues have designed, realized and brought into operation a unique observatory named TROICA (Trans-Continental Observations into the Chemistry of the Atmosphere). TROICA enables Russian scientists to conduct regular and detailed measurements over distances of about 10,000 km.

If any science is international, it is environmental science. In this regard TROICA project also is a fruitful international collaboration. Institutions from other countries partake based on their specific research goals and abilities in TROICA with great success. Integration of scientists, engineers, railway experts has been very successful, and it does great credit to our Russian colleagues.

I hope that support for TROICA will remain strong and that these regular systematic observations thus can contribute to a better understanding of all the changes in the atmosphere and sensitive biosphere across Russia, from Moscow to Vladivostok.

Paul Crutzen
The Nobel Prize Laureate in Chemistry
Introduction

Environmental pollution has become a global ecological problem. The greatest scientific discoveries, advanced technologies and engineering projects of the past centuries have determined a new, higher quality of life for humans on the one hand, but they have also placed life under threat of severe degradation as environment pollution has reached a critical level.

One of the most serious environmental problems is atmospheric pollution. The quality of air we breathe is deteriorating - particularly in large cities, the radiation balance over the Earth is changing and consequently climate is changing. World economic growth has been accompanied by increasing emissions of greenhouse gases, of reactive and toxic compounds, of persistent organic pollutants and their smallest particles, aerosols, into the atmosphere.

Since 1999 the number of cities in Russia with high or very high levels of atmospheric pollution has increased by 1.6 times and 58.1 million people (60% of the urban population) now live in cities with such air pollution. In 37 federal subjects more than 55% of city dwellers live in conditions of highly or very highly polluted air. In seven of those (including the areas of Moscow and St. Petersburg) this applies to over 75% of the population. About 65 million Russians constantly live under high ambient air pollution, which is associated with 40,000 deaths per year, and a three to five-fold increase in the number of bronchial asthma and allergic illnesses since 1990. The most widespread pollutants are perylene and formaldehyde, and also nitric dioxide. The main sources of pollution are the metallurgic and chemical industries, thermal electric power plants and car transport.

During the 2000’s, total anthropogenic emissions into the atmosphere from stationary sources have increased more than by 10%, from traffic – by 30%, and toxic wastes production has risen by 35%.

Simultaneously air composition in rural locations (Siberia and Arctic) is changing quite fast because of long-range transport from Russian industrial centers and neighboring countries (CIS, EU, China, Japan and others). In 2006 the general emission of greenhouse gases (without agriculture and forestry) consisted of 2190 millions of tons of carbon dioxide and the like, which represents 107% of the emission in 2000 and 66% of the emission in 1990. The main producer of greenhouse gas emissions is the energy sector (82% of emissions in 2006).

Ever-growing attention is now also being paid to ecological problems in Russia. At present new Federal target programs “Development of state environment monitoring system in Russia for 2009-2015”, “Clean water”, “Clean air”, and “Clean soil”, which would ensure qualitative changes in Russia’s ecological policy are being elaborated.

The ISTC projects contributed significantly to the minimization/elimination of some of the regional and global ecological concerns and supported efforts leading to sustainable development of ecological systems and to conservation of biodiversity.

Environment (ENV) is one of the largest research areas, where ISTC has been providing its support to the institutes in the form of project funding. As of June 2009 428 projects have been funded. Parties and Partners of ISTC have allocated $133 million for environment related projects. More than 330 Institutes and companies from Russia and CIS countries have been involved in this activity. Implementation of the project results have
resulted in a considerable number of new or improved technologies, analyses and databases related to the natural environment.

This brochure summarizes results of the studies performed by members of the Obukhov Institute of Atmospheric Physics RAS, Russian Research Institute of Rail Transportation, and Karpov Institute of Physical Chemistry. These studies were performed in the framework of the ISTC projects ## 1235, 2773, 2770, 3032, 2757 in cooperation with the colleagues from Germany, USA, Finland, and Austria. Aerosol and gas impurities and radioactive and thermodynamic characteristics of the atmosphere over vast regions of northern Eurasia were studied on the basis of the mobile railroad laboratory in the course of the Transcontinental Observations Into the Chemistry of the Atmosphere (TROICA). The results of these studies supplemented essentially the previous scarce information on the sources, sinks, transport and chemical transformations of atmospheric impurities over the north-Eurasian region, which is extremely important for the state of the global human environment.

The mobile laboratory is unique over the world; it is capable of monitoring along the entire network of electrified railroads of the Former Soviet Union and neighboring states. This laboratory is equipped with modern instruments analogous to those applied at the Global Atmospheric Watch WMO (GAW WMO) and can be considered as the GAW WMO key component, which collects information on the atmospheric state over a significant area of Eurasia, calibrates the measuring networks located in this region, and validates the atmospheric data obtained by the space-based instruments.

We invite all interested partners to join the unique TROICA experiments for the benefit of our natural environment.

Waclaw Gudowski
Professor
Deputy Executive Director
International Science and Technology Center

Valentina Rudneva
Senior Project Manager
Scientific Supervisor of Environmental Program
International Science and Technology Center

N.F. Elansky
Professor
Research Manager of the TROICA Experiments,
Chief of the Department of the A.M. Obukhov
Institute of Atmospheric Physics RAS
Global variations in the atmospheric composition

The atmosphere represents a multi-component chemical system which is in continuous interaction with the global land, ocean, and biosphere. Therefore, the atmospheric composition is not constant. During the last decade, atmospheric composition variations increased significantly as a result of a population upsurge and the intensification of human activity. Industrial enterprises, means of transport, and community services emit harmful chemical substances that have adverse effects on human health and living matter. Some of the harmful atmospheric species are produced in the atmosphere from non-toxic precursors. Such substances as hydrocarbons and oxides of nitrogen, carbon, and sulfur influence the oxidative ability of the atmosphere, thereby influencing the atmosphere’s ability to transform pollutants to neutral substances.

Some of these substances also promote photochemical ozone formation in surface-level air. Increases in ozone concentrations lead to degradation in the biological activity of plants, including crops, and adversely impact human health.

Freons, halons, and other substances that are used in industry and household are characterized by a prolonged lifetime. Because of this, they are able to reach the stratosphere where they can deplete the ozone layer. This process leads to intensification of short-wavelength UV radiation fluxes to the Earth’s surface, resulting in multiform adverse effects on living matter and human health.

In last few decades an additional tendency – namely, the increase in atmospheric concentrations of such greenhouse gases as carbon oxides, methane, CFC, etc. (see Fig. 1.1.1 – 1.1.2) – has revealed itself. As a consequence of this increase, the climatic system has been changing, expressed as a warming at the global scale. This global-scale warming is accompanied by a number of adverse phenomena, such as increasing in the frequency of extreme meteorological and ecological events (heavy showers, floods, hurricanes, landslides, etc.) and desertification of large areas of arid zones.

Worries about these changes in atmospheric composition have resulted in the ratification of several important international agreements containing requirements of limitation of the production and emissions of different substances.

All these agreements contain requirements and recommendations for the organization of a large-scale and multiform monitoring of the chemical composition of the atmosphere.

The state of the atmosphere over Russia

Against the background of the global atmospheric changes, some regional peculiarities reveal themselves. In Russia, as a consequence of the large area of the territory, disparities in the relative industrial development of different regions, the dominance of natural resource-based industry, and varied application of imperfect technologies, have produced non-uniformities in the management of...
natural resources and ecological regions. Over 15% of the Russian territory with a population of more than 60 million has air pollution levels higher than the maximum permissible level (Russian standard). Meanwhile, over 65% of the territory contains almost no economic activity, and the ecosystem state is close to the background conditions. The Russian boreal forests (73% of the world area of such forests) and water-swamp ecosystems are the most capacious reservoir of carbon dioxide and other pollutants absorbed from the atmosphere [Strategy, 2002].

In connection with the economic crisis of the 1990s, the ecological situation in Russia temporarily improved. For a period from 1992 to 2001, the emissions of pollutants decreased by 32%. Namely, the emissions of SO2, NO and NO2, CO and CO2, and solid substances decreased by 35.5, 38, 41, and 46%, respectively [National estimate, 2002]. However, recently, the level of atmospheric pollution began to rise. This tendency is especially pronounced in cities and industrial regions where the enterprises function more and more intensively and the quantity of cars continues to increase rather quickly.

Over European Russia a significant portion of the atmospheric pollutants at the beginning of the 2000s (mercury - up to 95%, benzapyrene - more than 80%, lead and cadmium - more than 50%, sulfur oxides - 12%, and nitrogen oxides - 25%) is caused by atmospheric trans-boundary transport from Western and Central Europe [National estimate, 2002]. In the Far-Eastern region significant atmospheric transport of pollutants including organics from China and during summer from Japan and Korea is also observed. From the Russian Kola and Taimyr Peninsulas, Urals and Southern-Siberian region atmospheric pollutants are transported by air flows to neighboring territories.

For 2007 [Environment, 2008], in 67% of all Russian cities (135 cities) where observations were performed, the level of air pollution was, according to the Russian standard, high or very high. In these cities 58.1 million inhabitants live. A dangerous atmospheric pollution has been formed in 38 cities with population of 14.9 millions.

Air pollution and formation of new toxins within air basins affect adversely the vegetation state. In southern Russia, these adverse effects are especially pronounced [Elansky, 2004]. It is in this region where in the 1990's maximum concentrations of chloro-organic compounds in vegetation (e.g., trichloroacetic acid - up to 70 ng per 1 kg of dry samples [Weissflog et al., 2005]) and the most extensive degradation of natural and planted forest areas (48.8, 8.1, and 6.0 ha/year per 1000 ha of forest area in Kalmykia, Rostov region and Astrakhan region, respectively [Review, 2001]) were found.

Similar effects of air pollution on boreal forests have also been observed [Lisitsyna et al., 2006]. Degradation of these forests can lead to a decrease in their productivity, decreases in the amount of carbon dioxide absorbed, enhancements in water vapor emission and, as a consequence, progressing economic damages and accumulation of the most active greenhouse gases (CO2 and H2O) in the atmosphere. In addition, decrease of water amount in soils worsens and ability of wetland and swamp areas for absorption of organic substances and retardation of the current climatic warming [Weissflog et al., 2009].

The multiplicity of the Russian ecological features is the most important factor allowing for regulation of the balance of greenhouse gases. These features should be necessarily considered when the official positions of the Russian Federation relative to any future international environmental agreements are under formulation. It should be taken into account that the regional trends in the atmospheric composition can differ from the global ones (the negative surface ozone concentration trend at Kislovodsk High-Mountain Station is presented in Fig. 1.1.3).

**Russian Atmospheric Watch System**

On October 16-18, 2007, the All-Russian Conference “Development of the system of atmospheric monitoring” was held in Moscow. Scientists and specialists of 48 organizations affiliated with 16 departments and representatives of the Moscow administration, of the World Meteorological Organization, and of a number of civil society organizations took part in the Conference. On April 3-4, 2008, in the Federal Assembly of the Russian Federation, the International Meeting of Experts “Actual problems of development of ecological investigations in Russia” took place.

The main goals of these two important forums were assessment of the existing system of atmospheric monitoring and elaboration of guidelines for its modernization and development on the basis of analyses of the situation in Russia and world trends in the field under consideration.

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**Fig. 1.1.3. Surface ozone concentration at Kislovodsk High Mountain Station (2070 m.a.s.l.; 43.7°N, 42.7°E)**

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**Atmospheric composition observations**
The resolutions of these forums showed the state of the Russian environment causes anxiety. In recent years the volume of atmospheric emissions has been growing continuously. It can be expected that in the future the quality of air over the Russian territory will become worse.

The main disadvantages of the existing national system of atmospheric monitoring are physical and moral deterioration of measuring instruments, insufficient development of the system of upkeep and control of measurements quality, almost total lack of continuous observations (including automatic ones), insufficient equipment with means of data processing and transmission, its incompatibility with the existing international observation networks and loss of skilled workers for the last years [Elansky, 2004]. The problems accumulated in the national system of atmospheric monitoring at present are caused by the lingering economic crisis and significant defects in legal norms in this field.

The only way out of the existing situations is: to reconstruct radically as soon as possible the Russian system of atmospheric monitoring; to optimize its structure and composition; to apply the up-to-date instruments and procedures including systems of remote sounding providing automated obtaining of 3D data on the atmospheric composition and radiative and meteorological characteristics; and to design special procedures and mathematical models aimed at application of these data for prediction of the weather, climate, and environmental pollution.

Reconstruction of the Russian system of atmospheric monitoring is to be performed with prospects that it ought to be a part of the Integral Global Observation System and, in particular, of the Global Atmospheric Watch system [WMO Global Atmosphere Watch, 2007].
2. TROICA experiments

2.1. Organization

Variations in the Earth’s climate and in atmospheric composition have pronounced regional distinctions. The IPCC (2007) report demonstrates that, for the most recent 100-year period, the most intensive warming occurred in Siberia. Such changes in the climatic system are accompanied by changes in the atmospheric gas and aerosol composition and in terrestrial ecosystems. A rapid development of the global atmospheric monitoring system in the 1990s, unfortunately, didn’t cover Russia.

Moreover, the efficiency of the Russian meteorological network in this period degraded; the stations to monitor background levels of O₃, NOx, SO₂, and aerosol were terminated. In this crucial period (February, 1995) Dr. Prof. P.J. Crutzen proposed to the director of the A.M. Obukhov Institute of Atmospheric Physics (OIAP), academician G.S. Golitsyn, carrying out observations of surface ozone and its precursors from a passenger train moving along the Trans-Siberian Railroad. In November–December 1995 the first experiment of such kind was performed utilizing a specialized car-laboratory. The leader of that first TROICA campaign as all others was Dr. Prof. N.F. Elansky – chief of the Atmospheric Composition Division OIAP. It was shown that reliable information on the regional surface-air composition can be obtained if the car-laboratory is coupled at the head of a train moving along electrified railroads [Crutzen et al., 1998; Elansky et al., 2006].

Thereafter, similar experiments under Max Planck Institute for Chemistry (MPIC) financial support were performed yearly up to 2001. These measurements now comprise the Trans-Continental (or Trans-Siberian) Observations Into the Chemistry of the Atmosphere (TROICA). Owing to the active participation of Dr. C.A.M. Brenninkmeijer and his group, the set of monitored gaseous pollutants was substantially extended and studies of the isotope composition of CO and CH₄ were started. Cooperation with the L.Ya. Karpov Research Institute of Physical Chemistry (KRPC) allowed expansion of the scope of aerosol studies. With time, the researchers from the NOAA Earth System Research Laboratory (ESRL), the University of Helsinki (UH) and the Finnish Meteorological Institute (FMI) joined the project.

Up to 2001, the TROICA experiments were performed yearly (Table 2.1.2). Scientist of the MPIC and of the KRPC have participated in the TROICA experiments since 1996 and 1997, respectively. In 2001, NOAA CMDL (Climate Monitoring and Diagnostics Laboratory, USA), now part of the “Global Monitoring Division” of the NOAA’s Earth System Research Laboratory joined the Project. TROICA expeditions were mainly performed along the Trans-Siberian Railroad on the Moscow-Khabarovsk or Moscow-Vladivostok routes. The most complicated program was performed in 2000; it consisted of monitoring along the railroad from Murmansk to Kislovodsk and monitoring based on stationary scientific stations located on the Kola Peninsula, in central regions of Russia, in the town of Kislovodsk, and in the mountainous North-Caucasian region. The measurements were performed everywhere in “local spring” allowing for study of the transition from winter to summer atmospheric conditions. These measurements allowed us to identify the anthropogenic and natural biogenic sources of CH₄, CO, CO₂, and volatile organic compounds. In the course of this season the laboratory passed thrice along the railroad between Murmansk and Kislovodsk.
In Table 2.1.1 the regularly measuring parameters are presented: surface gases \( \text{O}_3 \), \( \text{NO} \), \( \text{NO}_2 \), \( \text{CO} \), \( \text{CO}_2 \), \( \text{SO}_2 \), \( \text{NH}_3 \), THC, VOC, \( ^{222}\text{Rn} \), and 0,002-10 μm aerosols (including soot), vertical \( \text{O}_3 \) and \( \text{NO}_2 \) profiles, solar radiation, meteorological parameters, 0-600 temperature vertical profiles and some other parameters and atmospheric characteristics. Apart from the regular measuring parameters the additional species, aerosol abilities and atmospheric characteristics were measured by different groups of specialists from Russia and other countries.

Table 2.1.1. TROICA observation system for regular measurements

| Concentration of surface gases | \( \text{O}_3 \), \( \text{NO} \), \( \text{NO}_2 \), \( \text{CO} \), \( \text{CO}_2 \), \( \text{SO}_2 \), \( \text{CH}_4 \), \( \text{NH}_3 \), THC, VOC, \( ^{222}\text{Rn} \) |
| Surface aerosols | Size distribution (2 nm – 10 μm), scattering coefficient, mass concentration, black carbon |
| Remote sensing | \( \text{O}_3 \) and \( \text{NO}_2 \), total content and vertical profile (express Umkehr technique), \( \text{O}_3 \) stratospheric and mesospheric profile (microwave technique), \( \text{NO}_2 \) in boundary layer (MAX-DOAS) |
| Solar radiation | Integral, \( \text{UV-A} \), \( \text{UV-B} \), photodissociation rate \( J(\text{NO}_2) \) |
| Meteorology | Pressure, temperature, humidity, wind (speed and direction), temperature profile (0 – 600 m) |
| Sampling | Green-house gases and VOC; chemical, elements and morphological composition of aerosol, isotope composition of \( \text{CO} \), \( \text{CO}_2 \), and \( \text{CH}_4 \) |
| Others | GPS-data, TV pictures of road-side territory and cloudiness, concentrations of other gases, aerosol properties and different atmospheric characteristics measured not regularly |

Table 2.1.2. TROICA experiments: dates and routes

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<td>1996</td>
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<td>TROICA-3</td>
<td>1997</td>
<td>Nizhny Novgorod-Khabarovsk-Moscow</td>
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<td>TROICA-4</td>
<td>1998</td>
<td>Nizhny Novgorod-Khabarovsk-N Novgorod</td>
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<td>TROICA-5</td>
<td>1999</td>
<td>Nizhny Novgorod-Khabarovsk-Moscow Ob river trip</td>
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2.2. Railway mobile laboratory

Goals and objectives

Components. The TROICA laboratory consists of two specialized railroad cars equipped in accordance with the measurement requirements of the Global Atmospheric Watch (WMO GAW) program. The 1st car represents a laboratory for atmospheric monitoring. The 2nd car represents a chemical laboratory for monitoring the atmospheric chemical pollution and radioactivity as well as for taking and analyzing air, aerosol, water and soil samples.

Goals. Measurements of atmospheric composition determining the emissions of gaseous and aerosol pollutants and determination of the auxiliary atmospheric radiative and thermodynamic parameters.

Tasks. The laboratory addresses a wide circle of scientific, environmental, and applied problems related to the anthropogenic impact on the environment:

- Monitoring of the gas and aerosol composition of the atmosphere and its thermodynamic and radiative characteristics in Russia, the Former Soviet Union republics and other states.
- Identification of the natural and anthropogenic sources of atmospheric pollutants, the characteristics of their atmospheric transport and chemical transformation and understanding of the processes by which they are removed from the atmosphere.
- Monitoring of the fulfillment of international ecological agreements (e.g. the Kyoto and Montreal Protocols, the Conventions on transboundary transport of pollutants and desertification of areas) and for justification of quotas on emissions of greenhouse gases.
- Calibration of the instruments applied by the GAW WMO and other Russian stations and validation of satellite monitoring the atmosphere and environment.
- Revelation and overall study of extreme ecological situations and anthropogenic impacts on the environment.

- Monitoring of the railroad-wayside pollution, and estimation of the railroad effect on the ecological state of the environment.
- Overall study of the air basins of cities and industrial regions and estimation of the adverse
effect of different branches of industry and other human activities (industrial enterprises and power stations, community services, traffic, gas and oil pipelines, etc.).

- Ecological education and advanced training of ecologists.

Contributors to the TROICA design:
- A.M. Obukhov Institute of Atmospheric Physics, Russian Academy of Sciences (OIAP),
- Russian Research Institute of Railway Transport (RRIRT),
- Science and Technology Center (STC) “RADEK”.

Manufactures: Carriage plant, the city of Torzhok.

Contributors to the TROICA instrumentation: OIAP, RRIRT, STC “RADEK”, KRIPC, Institute of Applied Physics RAS and Institute of Chemical Kinetics and Combustion RAS (Russia); MPIC, HORIBA Company, Kipp & Zonen Company, AT-TEX enterprise (Germany); ESRL NOAA (USA); UH, FMI (Finland).

**Equipment.** Each of the cars is supplied with self-sufficient power, air-conditioning, and water-supply systems and can be coupled to passenger, cargo, and specialized trains.

The power systems supply all electrical needs and combine into one system the 110 V storage battery, 28 kWt under-car generator, high-voltage PC transformer, diesel generator, 110 V trainline and three-phase supply. The 220 V A/C line is supplied by a block of reversers transforming the 110-V continuous current from a storage battery, which is used as a buffer. The laboratory is supplied with modern navigational aids (GPS) and telecommunication equipment, which guarantees that data are stamped with the exact geographic coordinates, allows for data exchange between the cars, and permits immediate data transmission to the Moscow data-collection center.

The laboratory is supplied with a jeep from the Ural car factory. This jeep is equipped with devices and instrumentation intended for atmospheric observations and for obtaining air, aerosol and water, soil and vegetation samples.

Each railway car has two 4-seater compartments equipped for both the work and the living needs of the operators. There is a kitchen (refrigerator and electric and microwave ovens), shower cubicle, and bio-lavatory in the compartments.

**Measuring system**

Usually two cars operate together as a single, coordinated system. For some special tasks, such as the estimation of the degree of environment pollution in cities and industrial centers, measurements of emissions of pollutants from different sources, etc., the two cars can be used independently.

As of January 1, 2009, the normal scientific instrumentation consisted of the following capabilities:
- instruments for continuous measurement of the gas concentrations in surface air: gas analyzers, chromatographs, PTR-MS;
- instruments for continuous measurement of concentrations and microphysical characteristics of aerosols: particle counters, nephelometers, aerosol spectrometer, aetholometer, trap for bio-aerosol and radiometer-spectrometer analyzing gamma-radiation;
- instruments for remote sounding of the composition of the troposphere and the middle atmosphere: photometer, spectrophotometers operating in the UV-Vis and IR spectral regions (including MAX-DOAS) and microwave spectro-radiometer;
• instruments for measurements of the solar radiation, optical and meteorological characteristics of the atmosphere: spectrometer, fluxmeters operating in the UV, Vis and IR spectral ranges, photometers for determining the rate of NO₂ photodissociation, a temperature profiler, sonic anemometer and meteorological sensors;

• systems for taking gas and aerosol samples and instruments for express chemical analysis of some samples (gas chromatographs, mass-spectrometer, x-ray fluorimeter);

• integrated (combined with GIS) PC-system for data collection;

• communication TV and audio systems.

For some special experiments precision metering instruments owned by other institutes were deployed at various times during the TROICA experiments: multi-channel chromatograph ACAT-IV, measuring ozone-destroying and greenhouse gases (NOAA-ESRL); proton-transfer-reaction mass spectrometer (MPIC); different mobility particle size, air ion spectrometer, humidity – tandem differential mobility analyzer (UH); particle into liquid sampler with ion chromatograph, aethalometer (FMI); and some others.

A computerized integrated instrumentation set intended for continuous atmospheric monitoring on the basis of the mobile laboratory and stationary observatories was created (Fig. 2.2.1). Ozone concentration was measured with Dasibi 1008RS and 1008AH gas analyzers. These instruments are based on the photometric method. They allow to measure the ozone concentration in the range from 1 to 1000 ppb with a total error of ±1 ppbv.

These instruments undergo scheduled calibrations against the secondary standard, the O3-41M No. 1294 instrument, which undergoes in its turn annual calibrations against the SRP No. 38 standard owned by the Mendeleev Research Metrology Institute (Russia).

NO and NO₂ concentrations were measured at different times with TE42C-TL instrument (Thermo Electron Corp., USA) and with M200AU instrument produced by Teledyne Corp. (USA). These instruments apply the chemiluminescent method. The minimum NO and NO₂ concentrations detectable with these instruments are equal to 0.05 ppb; this allows for measuring the so-called background concentrations not influenced by the pollution sources.

CO concentration was measured with TE48S instrument (Thermo Electron Corp). This instrument uses an advanced method based on the measurements with the so-called correlation of gas filters. It allows for measuring background CO concentrations at a level of less than 100 ppb with the total error of ±10 ppb.

CO₂ concentration was measured with LI-6262 instrument (LiCor, USA). This instrument is based on the well-known method of nondispersion infrared spectrometry (NDIR). The measurement range is 0–3000 ppm; the results are highly reproducible.

Concentrations of CH₄ and nonmethane hydrocarbons (NMHC) were measured with APHA-360 instrument (Horiba Company, Japan). This gas analyzer separates CH₄ and NMHC by using selective catalytic absorbers and measures the gas concentrations with a flame-ionization detector. The total error in the CH₄ and NMHC concentration measurements doesn’t exceed ±5 ppb. To supply the flame-ionization detector with hydrogen, which is necessary for its operation, the instrumentation set has hydrogen generators of different types.

SO₂ concentration was measured with APSA-360 instrument (Horiba Company, Japan). This instrument measures SO₂ chemiluminescence induced by UV-radiation. For scheduled calibrations zero-air generator is used.

NH₃ concentration was measured with M201A instrument (Teledyne Corp., USA). This instrument transforms NH₃ to NO by a catalytic converter and measures the NO concentration by chemiluminescent method.

For calibration of the above-mentioned gas-analyzers, standard gas mixtures from the manufacturers of the instruments are used. The instruments are characterized by high sensitivity and reproducibility. Most types of the instruments under use are taken by the WMO GAW as the standard ones.

The atmospheric surface layer temperature profile up to a height of 600 m was measured with MTP-5 meteorological temperature profiler (ATTEX Company, Russia, Dolgoprudny). The results obtained with this instrument allow for revealing the characteristics of surface inversions.

The instrumentation set also contains the instruments for monitoring the standard meteorological parameters (atmospheric pressure, air temperature
and humidity, wind speed and direction): AT-3M acoustic anemometer (Russia), Skaneks (Russia), Driesen&Kem (Germany), and Vaisala (Finland). This instrumentation set provided measuring an almost continuous series of meteorological parameters averaged over 1 minute. The instrumentation set also includes sensors for integral and ultraviolet (UV-A and UV-B) solar radiation (the sensors are produced by Kipp&Zonen Company, Netherlands).

Compact PTR-MS proton mass spectrometer (Ionicon Company, Austria) was added to the instrumentation set in 2008. It is an instrument allowing for continuous and real-time measuring the concentrations of a number of volatile organic compounds (VOC). The minimum detectable concentration is 0.5 ppb. The list of the VOC measurable by this instrument is based on the available information on the use of similar instruments for atmospheric monitoring. At present, the concentrations of the substances of 42–163 molecular weights can be monitored.

To measure O$_3$ and NO$_2$ total content and vertical distribution, MS260i spectrometer (Oriel Company, USA) was used. Atmospheric O$_3$ and NO$_2$ can be retrieved from spectral measurements of the zenith skylight (the methods are developed in the OIAP).

Concentrations of radon and its daughters were measured by LLRDM instrument (TracerLab, Germany). Atmospheric aerosol was studied with TEOM 1400a instrument (Thermo Electron Corp., USA) and aerosol particle counters (Grimm, Germany).

The instrumentation set is also supplied with an HP 6890 gas chromatograph intended for measurements of some atmospheric organic impurities.

All measurements are fully computerized. The measuring instruments are connected with the PCs through interfaces in such a way that the entire set of measured information is available for one integrating PC. The database contains all parameters measured by the instruments and all features of the operational procedures.

For fast measurements of local ozone in homogeneities from moving laboratory the ozone gas-analyzer with semiconductor sensor has been worked out [Belikov et al., 2008; Obvintsseva et al., 2005; Obvintsseva et al., 2008]. The instrument includes a metal oxide semiconductor sensor, an electronic block and power supply. It is automatically controlled by personal computer. Data transmission cable length can be up to 300 m. The weight of the instrument is 0.5 kg.

The semiconductor sensor is the 1.5×1.5 mm isolating substrate, at the opposite sides of the substrate there is a Pt-heater and measuring electrodes (see Photo). Semiconductor metal oxide layer of ZnO, In$_2$O$_3$, WO$_3$, etc. is deposited over measuring electrodes. Resistance of the sensor depends on concentration of investigated gas impurity. Sensitivity and performance of a sensor depend on the temperature of the sensor. The operating temperature from 20 to 500 °С is chosen accordingly to an optimum sensitivity and performance of the sensor. The sensor is placed in 1 cm$^3$ teflon chamber, through which analyzed air is pumped through. Resistance of the sensor is sensitive to the concentration of different gases in the air besides ozone: NO$_x$, Cl$_2$, HCl, etc. So semiconductor sensors of different types can be used for measurements of the concentration of these gas impurities.

The semiconductor ozone gas analyzers were tested under environmental conditions at the Meteorological Observatory of the Lomonosov Moscow State University and in several TROICA expeditions. In summer 2008 two semiconductor gas analyzers were used in continuous measurement mode with periodical controlling of zero line during international expedition of mobile laboratory “TROICA-12” (from Moscow to Vladivostok). Ozone concentration measurements with developed semiconductor gas analyzer were carried out synchronously with photometer gas analyzer DASIBI 1008-RS. Sensors with ZnO and In$_2$O$_3$ sensitive layers were used.

Good correlation of both tested analyzers and DASIBI 1008-RS data can be found. Results of five days measurements are shown in Fig. 2.2.2. By means of the semiconductor gas analyzer influence of local industrial emission on ozone surface concentration was found.
**Measured parameters**

- concentrations of carbon monoxide (CO), ozone (O$_3$), nitrogen oxides (NO and NO$_2$), carbon dioxide (CO$_2$), methane (CH$_4$), NMHC, sulfur dioxide (SO$_2$), radon (Rn) and its decay products;
- atmospheric pressure, temperature, and humidity, wind velocity and direction;
- integral solar radiation, UV-A and UV-B solar radiation, and photo-dissociation rates J (NO$_2$);
- vertical temperature profiles (0-600 m);
- geographic latitude and longitude, altitude above sea level, and train velocity and direction;
- TV pictures of cloudiness and surrounding territory;

Distinctive features of the measuring system:
- all-around of the measurements obtaining of a file concerted data from different instruments;
- compliance with the data-quality demands of the Global Atmosphere Watch monitoring stations; use of the instrumentation standardized for the CAW network;
- performance of systematic calibrations of the instruments against the standards applied by international programs for atmospheric monitoring;
- integrability of instruments intended for special studies (chromatographs, mass-spectrometers, etc) into the standard instrumentation set;
- prompt transmission of preliminary results and of the processed daily files to the global Internet network.

**Parking of the laboratory in Moscow**

The main part of the TROICA measuring system is parked at the ecological monitoring station (EMS) on the basis of the meteorological observatory of the Moscow State University (MSU).

Between the TROICA campaigns, the instruments from the TROICA observatory are subjected to necessary technical testing, maintenance, and calibration; some of them are also used in a program monitoring the pollution of the Moscow air basin.

Since February 1, 2002, the station has provided continuous atmospheric monitoring of O$_3$, NO, NO$_2$, CO, CO$_2$, CH$_4$, SO$_2$, THC and some volatile organic compounds (VOCs), concentration of aerosol, and meteorological and radiative parameters. Analysis of these data has clarified the annual and daily behavior of atmospheric pollutants. For example in the summer and in the autumn 2002, forest and turf fires were observed over the vicinity of Moscow with the smoke sometimes covering the entire city of Moscow (Fig.2.2.3). These fires worsened the ecological situation significantly with the concentrations of gas pollutants frequently exceeding the maximum permissible level and the visibility decreasing to 200 m. The CO, CH$_4$, and VOC emissions from the forest fires also caused the generation of other harmful air pollutants over Moscow, e.g. ozone (Fig. 2.2.4).

Warming of the regional climate and an intensive increase in the number of modern cars running on high-octane gasoline and modern lubricating oils and additives has led to an increase in the concentrations of reactive pollutants in the atmospheric surface layer over Moscow. This tendency causes an intensification of atmospheric chemical processes and an increase in the frequency with which the summer atmospheric ozone concentrations reach the maximum permissible level. Over the past decade, the city of Moscow has gradually become similar to polluted American and South-European cities in the degree of pollution of the surface air basin.

![Pavilion for monitoring the atmospheric pollutants](image1)

![Fig. 2.2.3. Satellite image, September 3, 2002; red points mark the fire seats](image2)

![Fig. 2.2.4. Variations of daily mean concentrations of O$_3$ and CO in the period from February 2002 to February 2003 in Moscow during two episodes of forest and turf fires; Red line marks the level of maximum permissible concentration according to the Russian standards](image3)
2.3. Database and data quality validation

**Database**

The structure of TROICA-DB Database. The data directory of the TROICA experiments is set up for the collection, storage, and operative extraction of information on the atmospheric gas and aerosol composition and dynamic, radiative, and meteorological parameters. This information is collected from the TROICA experiments and the OIAP stationary stations located in different regions (Table 2.3.1). In addition, this directory contains auxiliary information useful for analyzing and interpretation of the measurements performed in the TROICA experiments and at the network of the OIAP stations.

Table 2.3.2. The OIAP gas measurement system dataset.

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<th>Parameter</th>
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TROICA experiments

such as the diaries of the TROICA operators, air mass trajectories, satellite data on the humidity and temperature fields, etc. This information can be extracted from the data directory with a search system. The database meets the standards of the information storage system of the world network of atmospheric monitoring. The software for the TROICA data processing allows for accessing the data without the analysis of voluminous informative text files, e-mail letters, and www-sites; it includes a simple interface for data extraction and provides an express data analysis. This software is applicable for users with no experience in programming and characterized by a heightened rate of operation and by an extended volume of information being processed.

Each of two cars of the mobile laboratory is connected to the TrendNet TEW410APB radio channel providing data transmission inside and between the cars with a rate of 54 Mbit/s. This instrumentation allows connection of the computers (including notebooks) supplied with Wi-Fi adapters to the observatory local network. The satellite terminal provides connection between the laboratory local network and the global Internet.

The information system TROICA-DB has been based on database relational principles. It is conve-

Table 2.3.1. Atmospheric composition monitoring sites of the A.M. Obukhov Institute of Atmospheric Physics RAS.

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<th>No</th>
<th>Site</th>
<th>Region</th>
<th>Coordinates</th>
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Table 2.3.3. The OIAP and KRIPC aerosol measurement system dataset

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</tr>
</tbody>
</table>

OIAIP:
AE-16 – aethalometer**, (10 – 105 ng/m³)
AZ-6 – photoelectric aerosol size analyzer (0.3 – 1.0 mkm)
GRIMM-1.412 – nephelometer (5 – 1.5*10⁴ mkg/m³)
ADB – Automated Diffusion Battery (1.6 – 200 nm)

KRIPC:
Phenix - nephelometer (1 – 105 mkg/m³)
LAS-P - laser aerosol spectrometer (0.15 – 1.5 mkm)
Roico - photoelectric aerosol size analyzer (0.3 – 15 mkm)
GRIMM - photoelectric aerosol size analyzer (0.5 – 20 mkm)
DAES - aerosol electrostatic analyzer (0.005 – 1.0 mkm)
At the development stage of TROICA-DB designing the all major stages such as system analysis of data structure, infological database analysis, and selection of database type, commercial evaluation, datalogical and physical database designing have been done. The database operated by Firebird (WI-V6.3.1.4481 Firebird 1.5, www.firebirdsql.org) that constructed on Borland InterBase (www.borland.com) database kernel. The database TROICA-DB could be easily transferred to the more powerful database such as a MS SQL or Oracle. The database administration is carried out by IBExpert 2004.09.29 www.ibexpert.com).

**TROICA-DB datasets.** All data which included in database according their derivation could be divided by several groups: the measurement complex datasets, observation operator dataset, video system dataset and datasets of the other organizations and research centers. The measurement complex datasets were divided into sub datasets that were obtained every 10 sec from the major gas measuring system from the aerosol complex dataset and other datasets (Fig. 2.3.1). Additionally data averaged through the 1, 10 minutes and 1 hour, and averaged through the 1, 10 and 50 kilometers have been imported in TROICA–DB as well.

The gas measuring system dataset contains data on gases concentrations, vertical \(\text{O}_3\) and \(\text{NO}_2\) distributions, vertical temperature profiles, meteo-parameters, solar radiation, dissociation rate of \(\text{NO}_2\), \(^{222}\text{Rn}\) concentrations and its decay products (Table 2.3.2). In the Table 2.3.3 the aerosol measuring system dataset is presented. The simi-
lar datasets were created for other measured parameters (Fig. 2.3.1). The special dataset contains data obtained by the foreign participants of TROICA campaigns.

**Data validation**

For adequate interpretation of the results obtained from the TROICA mobile observatory, it is important to estimate the degree of influence of the leading train and of oncoming trains in the area under measurements.

**The effect of the leading train.** Variations in the train speed including ones during deceleration before stops can influence the measurements, so we studied these affects.

Fig. 2.3.2 demonstrates the variations in $O_3$, NO, and NO$_2$ concentrations, meteorological parameters, and temperature gradients in the near-surface atmospheric layer for a height of 0-50 m before and after the stopping point of the train. Variations are given for each railroad section in the form of averaged deviations from the mean values, with the daily variations of the parameters taken into account. In the plots, doubled standard deviations are presented. On the whole, the variations of all parameters are very small. Only the NO$_2$ concentrations notably increase within the boundaries of the populated localities. The ozone concentrations somewhat increase during train decelerations and decrease during stops. If train decelerations and stops proceed outside populated localities, the deviations in the ozone concentrations are smaller still. If the train speed varies with no full stop of the train, the variations are within the measurement errors. No variations in the CO, CO$_2$, and CH$_4$ concentrations and in the radiative characteristics are detected.

In the course of the TROICA expedition performed in 2001, the East-Siberian railroad section was under reconstruction. This caused a number of unscheduled stops of the train along the Irkutsk-Khabarovsk route. As a rule, the trained stopped far from inhabited localities and industrial enterprises. For 18 such events, we estimated the variations in the concentrations of the principal pollutants in the periods of train deceleration and acceleration. Fig. 2.3.3 presents the one-minute mean concentrations of pollutants for the 6-min time intervals before and after each of the stops. It can be seen that the variations in each of the pollutant concentrations are within the double variance, which is marked in the figure by vertical bars. The structures and values of the mean concentration profiles for all these pollutants are similar to those given in Fig. 2.3.2. Apparently, a portion of the air ejected from the ventilation system of the electric locomotive engine (the ventilation system exhaust is located under the locomotive bottom) is sucked in by the air inlet of the laboratory analytical system just before the stop and right after the start of motion, when the train speed is low. This effect reveals itself as "waves" in the $O_3$, NO, profiles registered by the laboratory instrumentation. However, these variations in the $O_3$, NO profiles, similarly to the CO and CO$_2$ variations, are small and hardly influence the results of our analysis and interpretation of the measurement data.

**The effect of oncoming trains.** To estimate the effect of oncoming trains, we consider the instrumentation indications for the periods from 10 min before to 10 min after meetings with oncoming trains. Fig. 2.3.4 presents the variations in the atmospheric contents of minor gases and in the meteorological parameters when sampling near oncoming trains. Data are separately analyzed when a thermal inversion occurred or was absent; the daily variations of the parameters are taken into account. The dashed area corresponds to the time interval when the oncoming train passes by the observatory.

In absence of inversions, the oncoming trains usually lead to insignificant, within 1 ppbv, decreases in the ozone content and to some decrease in the NO$_2$ concentrations. The NO concentrations are almost unaffected, meaning that oncoming electric-traction trains initiate no NO emissions. Under atmospheric inversions, no significant variations in the atmospheric contents of trace gases, temperature stratification, or air humidity are revealed. The concentrations of the minor gases CO, CO$_2$, and CH$_4$, which are not as active as O$_3$, and NO$_2$ vary rare. In the Eastern Siberia the oncoming trains are met seldom in 25-35 min and their effect on observations is negligible. Meanwhile, in the seasons when no snow cover is present, oncoming trains affect significantly the concentration of aerosol, predominantly those with sizes exceeding 0.1 μm. These heightened aerosol concentrations are observed for a distance of about 2-3 km after the meetings with oncoming trains. The oncoming trains that contain tanks with oil products have a sufficient impact on volatile organic compound surface concentrations. Later the emissions of VOC from such trains will be estimated and demonstrated for different conditions. The railroad sections affected by oncoming trains are excluded from the data file intended for subsequent analyses.

This consideration led us to the conclusion that the measurements performed on board of the laboratory moving along electrified railroads (air sampling were taken above the roof just after locomotive) is capable of reflecting the principal peculiarities of the background state of the atmosphere. However, in windless conditions with nighttime temperature inversions, the air pollution along the route sections characterized by intense traffic is rather significant and railroads can be considered as enterprises polluting the atmosphere.

Therefore all data are devided into a few groups obtained in polluted (urban and industrial), rural and background route sections. The special and temporal peculiarities of trace gases variations are analyzed as rule for each group individually.
3. Gases and aerosol over the continent

3.1. Ozone and nitrogen oxides

**Surface ozone**

Surface ozone plays an important role in atmospheric processes. As the strongest oxidant, it helps determine atmospheric chemical composition. As a greenhouse gas, it influences the climate. In addition, ozone is a toxin.

In the course of the 20th century, ozone concentration in the atmospheric surface layer over the Northern Hemisphere increased by a factor of two and the ozone distribution became less geographically uniform. Over some industrial regions, ozone concentrations are high enough to be dangerous to human health. Thus monitoring of ozone concentrations in the atmospheric surface layer has become a leading ecological problem. In Russia, ozone is being monitored only at a small number of observation sites, and this monitoring provides insufficient information on the spatial distribution of this gas [Elansky, 2009]. The TROICA mobile laboratory provides the most effective solution to this problem [Crutzen et al., 1996; Elansky et al., 2001b].

In the course of the TROICA experiments, information on the continental features of ozone distribution, on transport of its precursors and on the photochemical processes leading to its formation and destruction was first obtained (Fig. 3.1.1).

Spatial and temporal variations. Most of the observations (ten of the TROICA expeditions) were performed along the Trans-Siberian Railroad. These observations covered an extended belt of the North-Eurasian area lying between 48° and 58°N and 37° and 135°E (except of the Khabarovsk-Vladivostok meridional route section). The train traversed many cities and industrial regions; however, a significant portion of the route lay in unpolluted areas. The entire data file was divided into two groups of data, which responded to polluted areas (inhabited localities and industrial regions) and to unpolluted rural areas. The regions with the NO and CO concentrations lower than 0.4 ppbv and 0.2 ppmv, respectively, were taken as unpolluted rural areas; the rest regions were considered as the pol-

![Fig. 3.1.1. Ozone concentration along the Moscow-Vladivostok railroad eastern transect, (TROICA-9)](image)

**Table 3.1.1. Surface ozone concentrations variations**

(all data and the data for rural areas only) along the Trans Siberian route (Moscow-Vladivostok) 1995-2008.

<table>
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<th>Season</th>
<th>Conditions</th>
<th>Number of Observation</th>
<th>Mean</th>
<th>St.D.</th>
<th>Median</th>
<th>Mode</th>
<th>Min</th>
<th>Max</th>
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luted ones. These values of NO and CO are characteristic for high-mountain and remote stations.

The complete data series and the data obtained in rural areas, as well as the mean and extreme surface O₃ concentrations observed in all Trans-Siberian expeditions (TROCA-1–TROICA-12) are presented in Table 3.1.1.

Minimum concentrations were observed under conditions of nighttime temperature inversions. Maximum concentrations were observed in the daytime under conditions of ozone generation. The spatial distribution of ozone is characterized by the occurrence of a zonal gradient. The ozone concentration has a mean positive eastward trend of 0.47±0.02 ppbv per 10 degree of longitude (Fig. 3.1.2). Such a gradient is caused by significant biogenic CH₄ and VOC emissions in Siberia, forest fires, transport of ozone precursors from China, intensive air exchange between stratosphere and troposphere over east continental regions, and some other factors [Crutzen et al., 1998; Elansky et al., 2001b].

The expedition-mean ozone concentrations (Fig.3.1.3) show the occurrence of seasonal variations characteristic for rural areas of this latitudinal zone (48° – 58°N). These values were compared with the seasonal variations measured at remote stations (Mace Head (53.33°N, 9.90°W), Zotino (60.75°N, 89.38°E), and Hohenpeissenberg (48°N, 11°W). It is seen that the ozone seasonal variations obtained in the course of TROICA expeditions are similar to those obtained at the Mace Head and Zotino remote stations. The spring maximum is caused by the stratosphere–troposphere exchange, which is active in this season. The absence of the summer maximum, which is characteristic for Central Europe, indicates that in Siberia photochemical ozone production is weak and that ozone depletions under powerful continental temperature inversions proceed more actively than in the coastal zone (the Mace Head station). These processes are displayed at daily variation plots.

In cold versus warm seasons, the mean daily variations in the rural ozone concentrations are different (Fig. 3.1.4). In summer, it is characteristic to see nighttime ozone destruction near the earth’s surface under conditions of temperature inversions and to see active daytime ozone generation. The ozone measurements performed from the mobile laboratory allowed estimation of the rate of ozone dry deposition over extended continental regions: 0.08 and 0.65 cm/s on the surfaces covered and not covered with snow, respectively [Elansky et al., 2001b].

Variations in ozone concentrations can be used as a means of studying atmospheric dynamic processes, such as wave processes within inversion layers (Fig. 3.1.5).

**Stratospheric ozone intrusions.** Ozone is transported from the stratosphere in the regions of downgoing air flows, which are localized in the so-called active (with a pronounced frontogenesis) zones of frontal areas and jet streams. The downgoing flows occupying the layers of the troposphere and lower stratosphere result in a characteristic lowering of the tropopause (folds, funnels, and streamers), which is often related to the high-altitude cutoff lows. Ozone-rich stratospheric air masses may reach the land surface, and regions of increased ozone concentrations, which often have the form of belts stretched along atmospheric fronts, are formed [Khrgian et al., 1973; Elansky, 1975].

In TROICA expeditions intrusions of stratospheric air for examples were observed on February 19, 1998, in the vicinity of Ekaterinburg, April 7, 1997 in Transbaikalia, and July 27, 1996, within a thunderstorm front zone between Novosibirsk and Mariinsk (Fig. 3.1.6).
Fig. 3.1.7. The vertical section of the equivalent temperature fields (dashed lines, in K) and the Ertel potential vorticity (solid lines, in PVU): a) February 19, 1998; b) April 7, 1997; c) July 27, 1996. The position of the registered high ozone concentrations are marked by triangles.

To characterize dynamic processes in the troposphere, the data from a routine objective analysis were used. On the basis of these data, the fields of equivalent temperature and potential vorticity were constructed. Moreover, a number of calculation methods by different authors were used to calculate the fields of maximum wind and jet streams, the dynamic tropopause layer boundaries, and the upper boundary of convective clouds [Shakina et al., 2001].

In Fig 3.1.7 the vertical sections of the equivalent temperature fields and the Ertel potential vorticity (through the places where these episodes were registered) are shown.

An increase in ozone concentration (Episode of February 19, 1998) in the form of abrupt changes from 7 to 20 ppb within the regions (from 5 to 10 km in length) along the train route was noted under low air temperatures (–25ºC) over a snow-covered surface. This case is related to the intrusion of the arctic air masses well to the south in the rear of a deep cyclone (Fig. 3.1.7a).

On April 6-7, 1997 an air “tongue” is seen in the vertical section with a substratospheric PV above the meridian of 60ºE, which slopes steeply down in the rear part of the baroclinic zone of the cold front (Fig. 3.1.7b).

The large-scale structure of atmospheric motions is similar to that for the first case. However the intrusion of air masses with the increased PV is not so powerful and does not reach the land surface, high ozone concentrations over the above-mentioned railroad sector were recorded almost continuously (Fig. 3.1.7).

On July 27, the measurements were taken in the active convection zone (heavy showers and thunderstorms). Stratospheric air masses could arrive to surface in the process of an intensive convective...
mixing under the lowered tropopause located approximately 3 km lower than the convection level. Deep convection itself can generate stable downgoing air flows within sufficiently powerful layers. With the aid of thermodynamic constructions of convection theory, one can estimate the thickness and position of the layers, which feed power to these downgoing flows. We obtain a layer thickness equal to 4 km with the lower boundary at a height of about 5 km. Thus, the downgoing flows in the clouds, on average, were formed in the stratospheric air or in the air of the tropopause layer.

The measurements taken during a series of experiments over a vast territory revealed different effects of stratospheric intrusions on the surface ozone concentration. All of them correspond to already known mechanisms, but (what is important) show the presence of significant nonuniformities in the structure of dynamic processes [Shakina et al., 2001].

Characteristic features of the surface ozone distribution over the Eurasian continent in the latitudinal zone 48 – 58ºN:

- Ozone distribution is influenced mainly by synoptic processes.
- Atmospheric photochemical processes are significantly less intensive over Siberia (rural area) than over Europe.
- The effect of the surface inversions on the surface ozone changes is more significant over Siberia than over Europe.
- The ozone concentration over the continent increases in the eastward direction with a gradient of 0.47 ± 0.02 ppbv/10ºE.
- Stratosphere-troposphere exchange is most intensive over eastern regions of the continent.

**Nitrogen oxides**

Nitrogen oxides (NO and NO₂) are the key components of the atmospheric chemical processes. These gases influence the atmospheric concentrations of free radicals and the intensity of sinks of organic compounds. High concentrations of these gases (several tens of ppbv) are dangerous for human health.

Fuel-consuming transport, heat stations, and industrial enterprises are the main sources of nitrogen oxides. Yearly emission of nitrogen oxides from the Russian territory is about 4∙10⁶ t. [Environment State, 2008]. The effect of these gases does not extend over large distances from their source, because these gases decompose rather quickly in the atmosphere.

To forecast variations in the environment and to estimate consequences, monitoring of atmospheric NOx is necessary. Such monitoring over Russian territory is of special importance because of the scarcity of information on NOx emissions. The TROICA experiments have shown that the mobile laboratory is a highly efficient monitoring mechanism [Markova et al., 2004].

Mean NO and NO₂ atmospheric concentrations and their variations are presented in Table 3.1.2. Over large cities, the concentrations of these pollutants were especially high and achieved several tens of ppbv (Fig. 3.1.8).

The city plumes were as long as several tens of kilometers and, under some conditions, achieved...
several hundreds of kilometers. The anthropogenic effect, on the whole, leads to significant excesses in the NO and NO$_2$ concentrations averaged over the 48-58°N latitudinal belt (all data) in comparison with the NO and NO$_2$ concentrations measured at background scientific stations. The excess in the NO$_2$ concentrations is pronounced to a lesser degree than that in the NO concentration (Fig. 3.1.9). The NO and NO$_2$ concentrations measured over rural areas in all TROICA expeditions were close to those measured at the Hohenpeissenberg station. But for some TROICA expeditions the measured values were close to those obtained at the background Zotino station. The NO$_2$ concentrations are almost seasonally independent. The NO$_2$ concentrations during the day don’t change significantly. The NO concentrations are enhanced in the daytime over small and large cities as a result of house heating (Fig. 3.1.10). Dry grass burning in spring and in autumn also has some impact.

**Vertical O$_3$ and NO$_2$ profiles**

Anthropogenic emissions into the atmosphere change the chemical composition not only of the atmospheric surface layer but also of the free atmosphere. These emissions influence the development of ozone holes over the Antarctic and some regions of the Arctic and depletion of the global atmospheric ozone. The instrumentation of the mobile laboratory is capable of atmospheric remote sounding and of studying the contents of chemically and climatically active gases over the entire atmospheric thickness.

Problems of remote monitoring of the atmosphere could be solved with the mobile laboratory:
- Measurements of the vertical profiles of ozone, nitrogen dioxide, aerosol physical and chemical properties up to a height of 40-50 km over regions not covered by the stationary global atmospheric monitoring network. Validation of satellite retrievals of ozone, NO$_2$, greenhouse gases, and aerosol concentrations measured over extended continental regions by OMI, SAGE, SCIAME-CHI, GOMOS, and other satellite-based instruments.
- Calibration of instruments used for remote sounding at the GAW, NDAAC, and other networks.
The TROICA experiments demonstrated the possibility of using ground-based instruments and well-known measuring procedures for observing the vertical distributions of O$_3$ and NO$_2$ in the atmosphere. The mobile laboratory represents the best means for validation of satellite data, in particular, of data of satellite monitoring of the greenhouse gases.

Figs 3.1.11 - 3.1.13 show retrievals of the vertical O$_3$ and NO$_2$ profiles in the TROICA-4 and TROICA-9 expeditions [Postylyakov et al., 2006]. In both expeditions distributions of the species in the stratosphere over the Moscow-Vladivostok route were approximately uniform. The TROICA total O$_3$ content agrees well with the TOMS data.

A radiative transfer model, which is used for the analysis of remote sensing data, requires ability to calculate derivatives of the radiance field in addition to the radiance intensity itself. In other terms, such derivatives are also known as the weighting function of inverse problem, or the layer/box air mass factors, or the enhanced factors. A linearized radiative transfer model MCC++ is used for interpretation of the atmospheric composition calculated from measurements of scattered solar radiation in the TROICA expeditions [Postylyakov, 2004, Patat et al. 2006].

The MCC++ model employs spherically symmetrical atmosphere. This allows its application for the twilight and near-horizon geometries of observations, which may provide information on the vertical distribution of the atmospheric composition. The model takes into account all orders of
3.2. Carbon compounds CO, CO₂, CH₄

Spatial distribution

Greenhouse gases influence significantly the Earth’s climate, atmospheric radiative processes, and surface air chemical composition. Measurements of the carbon dioxide and methane concentrations in the atmosphere from the mobile laboratory help reveal the natural and anthropogenic sources of these most important greenhouse gases, allowing us to estimate their effect on the atmospheric composition and climate, optimize control strategies for surface air quality, observe extreme ecological situations, and forecast the development of such situations. An example of spatial distributions of CO₂ is presented in Fig. 3.2.1 and 3.2.3.

The most significant effect on Earth’s climate is through variations in CO₂ concentrations. Carbon dioxide is emitted mainly as a result of biogenic processes and through emissions in the transport and industrial sectors.

All high CO₂ concentrations registered at night time, when vegetation and soil respiration fluxes are intensive and CO₂ accumulation under temperature inversions takes place. At the same time there are short peaks of CO₂ in industrial regions as temperature inversions promote the accumulation of anthropogenic CH₄ as well.

Carbon monoxide CO is an important component in atmospheric chemical processes; its oxidation leads to the formation of ozone, a key atmospheric reagent and greenhouse gas.

The most important sources of CO are as follows: methane oxidation, biomass burning, and emissions from the transport sector, heat stations, and industrial enterprises. High concentrations of CO are dangerous for living matter and human health. The TROICA experiments have shown that the Russian regions most polluted by CO are located in central Europe (influenced by transport and industrial enterprises) and in south-eastern Siberia (influenced by electric power generation, atmospheric pollutants transported from China, Japan, and Southern Korea, and forest fires). The CO distribution (TROICA-9) over the Moscow-Vladivostok railroad is shown in Fig. 3.2.2.

Atmospheric methane, CH₄, influences the Earth’s climate, and in very high concentrations
that occur as a result of certain man-made catastrophes it can lead to explosions. The most important natural and anthropogenic sources of methane are its biogenic emissions from swamps and humid soils (see Table 3.2.1) and its leaks from the industry and transportation and from treatment plants and trash dumps, respectively. The highest atmospheric methane concentrations are observed in the central European region in the vicinities of oil-gas-processing enterprises and in West Siberia in the vicinities of natural sources and gas-production enterprises.

Our statistical analysis of greenhouse gas concentrations measured over the course of several expeditions in the period 1997-2004 have revealed some peculiarities of their spatial and temporal variability over Russia [Oberlander et al., 2002; Belikov et al., 2006].

In this section, we consider the results obtained for rural areas, when there were no local anthropogenic sources influencing concentrations.

The characteristic frequency distributions of the concentrations of greenhouse gases measured in cold (winter) and warm (summer) seasons for rural areas are shown in Fig. 3.2.4. In cold periods CO concentration is equal to 0.21±0.03 ppmv. In warm periods, the mean CO concentration is significantly lower, 0.12±0.03 ppmv.

The winter CO$_2$ distribution is almost uniform; all values are concentrated within a narrow range, 380-400 ppmv. In summer period, the CO$_2$ concentrations vary significantly, especially under the influence of intense surface inversions. The mean summertime CO$_2$ concentration is 376±34 ppmv.

The frequency distribution of the CH$_4$ concentration is similar to that of the CO$_2$ concentration; however, the CH$_4$ concentration depends on the surface inversions to a lesser degree than does the CO$_2$ concentration.

Fig. 3.2.5 and 3.2.6 contain the results of analyses of spatial distributions of greenhouse-gases concentrations over the continent.

CO concentration distribution over the continent in cold periods is almost uniform. Meanwhile, in warm periods, a longitudinal gradient in the CO concentration, 0.6 ppbv/degree, is clearly pronounced in Siberia.

CO$_2$ concentration distribution in cold periods is also almost uniform. The non-uniformities observed in warm periods are caused by variations in the landscape, vegetation, and anthropogenic CO$_2$ emissions.

---

**Table 3.2.1. Estimations of CH$_4$ and CO$_2$ from natural sources (June-July, 2001, TROICA-7).**

<table>
<thead>
<tr>
<th>Gas</th>
<th>Region</th>
<th>Emissions, $10^6$/mol/m$^2$ h</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>Max West Siberia</td>
<td>70 ± 35</td>
</tr>
<tr>
<td></td>
<td>Min East Siberia</td>
<td>3.2 ± 1.6</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>Max East Siberia</td>
<td>13.6 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>Min West Siberia</td>
<td>3.35 ± 1.7</td>
</tr>
</tbody>
</table>
Gases and aerosol over continent

CH$_4$ concentration distribution non-uniformities observed in cold periods are caused by anthropogenic sources. The enhance concentration near 70-90°E results the plume of the largest in Russia Kuznetsky coal basin that gives high CH$_4$ emissions in any season. In warm periods, a well-pronounced increase in the CH$_4$ concentrations was observed over West Siberia. This effect is associated with intense CH$_4$ emissions from humid soils of this region.

**Emissions**

The obtained $^{222}$Rn flux values (see section 3.4) can be used to estimate emissions of atmospheric gas components from the sources located on the surface. In particular, such gases are greenhouse gases, CO$_2$ and CH$_4$, as well as CO influencing significantly ozone formation. If anthropogenic influence is absent, these gases are the vital activity products of soil microorganisms and vegetation. In the conditions of temperature inversion they are accumulated in the surface air like radon.

The data obtained in unpolluted conditions only show a high correlation between $^{222}$Rn and CO$_2$, CH$_4$, CO. If the air mass is not polluted (NO ≤0.3 ppbV and CO ≤ 0.2 ppmV), the correlation coefficients between these gases concentrations and $^{222}$Rn concentrations vary from 0.75 to 0.95. Using the $^{222}$Rn flux from the soil and the coefficients of linear regressions between the concentrations of $^{222}$Rn and the carbonaceous gases, the values of night biogenic emissions are calculated. The estimations for summer and winter conditions are presented in Fig. 3.2.7 - 3.2.9.

Fig. 3.2.7. Spatial distribution of CO$_2$ nocturnal biogenic fluxes for summer (TROICA-5 and 7 expeditions) and winter (TROICA-8 expedition)

Fig. 3.2.8. Spatial distributions of CH$_4$ nocturnal fluxes for TROICA-5, 7, 8 – summer and TROICA-8-Winter

Fig. 3.2.9. Spatial distributions of CO$_2$ and CH$_4$ nocturnal fluxes for spring meridional transect Murmansk-Kislovodsk (TROICA-6, red – CO$_2$, blue – CH$_4$)

3.2.10. The δ$^{13}$C and δ$^D$ versus inverse CH$_4$ mixing ratio for samples taken during TROICA-2 expedition
Isotopic composition

Analysis of carbon, oxygen, and hydrogen isotopologues of the atmospheric methane and carbon monoxide using data from the mobile observatory allows to identify the sources of these compounds and to estimate their contribution to the global carbon balance which is closely related with climate change. The $^{13}$C, $^{14}$C, $^{18}$O, and D isotopes analysis of methane and carbon monoxide in the air samples collected in the course of the TROICA expeditions was done in MPIC.

The sources of atmospheric methane can be divided into three groups: biogenic, (emissions from wetlands and rice paddies, animals, landfills), thermogenic (geological processes), and biomass burning (Fig. 3.2.10).

CH$_4$ isotopes measurements in the air samples were performed in the campaigns TROICA-2, 5, 7, 8 along Trans-siberian railroad. The TROICA-5 campaign included also an exploratory expedition along the river Ob using a boat as a measurements platform [Bergamaschi et al., 1998; Oberlander et al., 2002; Rockmann et al., 1997; Tarasova et al., 2006].

An enhanced level of the CH$_4$ was observed during the TROICA-5 expedition over the Western Siberia using the mobile car-observatory and along Ob River using an equipped motor-launch. Analysis of methane isotopic composition ($^{13}$C and D) showed that a predominant source of atmospheric methane observed in the boundary layer has a biogenic origin and is likely emitted to the atmosphere from wetlands and swamps [Fig. 3.2.11]. Natural-gas leakages during the production, processing, and transportation of natural gas also contribute to the atmospheric methane levels. Shipboard measurements showed substantial increases of methane concentration of up to 50% above the background level at a distance of 0.5 km from gas-production points. Methane accumulation took place under temperature inversion, while its isotopic composition has not been analyzed.

In the majority of expeditions an elevated concentration of CH$_4$ was observed in the Perm region where train crosses several gas pipe lines connecting Polar Ural and Western Siberia gas fields with Central Russia. For example in the TROICA-5 the excess of CH$_4$ reached about 200 ppbV above background concentration and identified source isotopic signature $\delta^{13}$C$_{source} = -52.42$‰ showed the presence of the natural gas in the collected air sample.

Due to non-uniform methane sources distribution over Russia it is more efficient to analyze the CH$_4$ distribution and composition in the certain geographical regions, namely European part of Russia (z1), Western (z2) and Central (z3) Siberia, Eastern Siberia and Far East (z4). As an example of such approach Fig. 3.2.12 presents a plot of $\delta^{13}$C versus the inverse of the CH$_4$ mixing ratio for the summer TROICA-7 expedition. It is evident that biogenic methane sources play the principal role not only in Western Siberia but in other parts of Russia. At the same time strong contributions of natural gas can be observed for a few samples. In most of the cases such samples were taken in the vicinity of the objects of gas industry or of the large cities (like Novosibirsk). Several examples of the last mentioned effected were observed in the spring campaign TROICA-8, when the strong local peaks were associated with the gas leakages from the low pressure gas distribution networks.
Gases and aerosol over continent

There are four main CO sources: fossil fuel combustion and biomass burning (both surface sources), and photochemical oxidation of CH$_4$ and of volatile organic compounds (both in situ sources but strongly different distributions depending on OH and on emissions by vegetation). Basically $^{13}$CO reacts slower, and C$^{18}$O faster with OH than $^{12}$C$^{16}$O. On the source side, CO from CH$_4$ oxidation (photochemical or combustion) has a distinctly low $^{13}$C content (CH$_4$ is depleted in $^{13}$C due to its mainly bacterial origin). The $^{18}$O content depends on the oxidation process. High temperature oxidation gives CO with distinctly high C$^{18}$O values, whereas photochemical oxidation gives values that are closer to background values. The photochemical oxidation of CH$_4$, VOC etc, and the burning of biomass contribute to $^{14}$C, whereas CO from fossil fuels is $^{14}$C free.

Analysis of the $^{14}$C and $^{18}$O in CO (see for example Fig. 3.2.13) in combination with trajectory analysis allowed identification of CO source in the summer campaign TROICA-2 as biomass burning, in particular, forest fires and combustion of agriculture waste in China [Bergamshi et al., 1998].

Identified sources of CO along the Ob appear in the TROICA-5 campaign to be connected to methane oxidation based on an inferred $\delta^{13}\text{C}_{\text{source}}=-36.8\pm0.6\%$, while the value for $\delta^{18}\text{O}_{\text{source}}=9.0\pm1.6\%$ identifies it as burning [Tarasova et al., 2005; Tarasova et al., 2007]. Thus flaring in the oil and gas production can be supposed to be a source. The extreme $^{13}$C de-
pletion and concomitant $^{18}$O enrichment for two of the boat samples unambiguously indicates contamination by CO from combustion of natural gas (inferred values $\delta^{13}$C source = -40.3‰ and $\delta^{18}$O source = 17.5‰). The impact of industrial burning was discernable in the vicinity of Perm-Kungur.

**Carbon dioxide $^{14}$CO$_2$**

Fossil fuel derived carbon dioxide (CO$_2$) is entirely devoid of radiocarbon ($^{14}$C) as a result of radioactive decay (mean lifetime = 8,267 yr) whereas other sources of CO$_2$ to the atmosphere contain $^{14}$C at near ambient atmospheric concentrations. Thus, precise measurements of the radiocarbon content of atmospheric CO$_2$ ($\Delta^{14}$CO$_2$) provide an excellent tracer for recently added fossil fuel CO$_2$.

The unique spatial distribution of $^{14}$CO$_2$ over Russia was obtained from Moscow (55° 66’ N, 37° 58’ E) to Khabarovsk (48° 5’ N, 135° 10’ E) as part of TROICA-8 expedition March 19 – April 1, 2004 [Turnbull et al., 2009].

Outside air was drawn from the leading top edge of the laboratory wagon, about four meters above the rails. Samples were collected in 3L electro-polished stainless steel flasks by flushing for 10 minutes. The method of $^{14}$CO$_2$ measurement from these flasks is described by Turnbull et al. (2009). The air from these flasks was analyzed for multiple species, including several halocarbons. These trace gases species as well as others measured continuously using the four channel Airborne Chromatograph for Atmospheric Trace Species (ACATS-IV), were used for selection of samples for $^{14}$CO$_2$ analysis.

It was shown that the greatest influence on the spatial distribution of $\Delta^{14}$CO$_2$ came from fossil fuel, $^{14}$C-free CO$_2$. In addition, $^{14}$CO$_2$ produced by nuclear reactors caused local enhancement in $\Delta^{14}$CO$_2$ in some samples.

Use of back-trajectories allowed us to identify these locally influenced samples, and obtain a background continental boundary layer dataset for this region. $\Delta^{14}$CO$_2$ increases by 5 ± 1.0‰ across the transect from 40° E to 120° E (Fig. 3.2.14.) and this difference is significant at the 99% confidence level. The magnitude of the $\Delta^{14}$CO$_2$ gradient is consistent with the dispersion of fossil fuel CO$_2$ emissions produced in Europe and atmospheric transport across northern Asia dispersing and diluting the fossil fuel plume. The observed isotopic change implies a gradient of 1.8 ppm of fossil fuel derived CO$_2$ (assuming a -2.8‰ change in $\Delta^{14}$CO$_2$ per ppm of fossil fuel CO$_2$ added). $\Delta^{14}$CO$_2$ measurements from Niwot Ridge, Colorado, USA (NWR, 40.05° N, 105.58° W, 3475 m a.s.l.) are believed to represent relatively clean free troposphere air for 3 sampling dates during the time of the TROICA-8 campaign give a mean $\Delta^{14}$CO$_2$ value of 66.8±1.3‰ (grey bar in Fig. 3.2.14). The Eastern Siberian part of the TROICA transect shows values (62.8±0.5‰) most similar to the NWR value, consistent with an easterly dilution of the fossil fuel content in boundary layer air away from the primary source, but suggesting that some influence from the European fossil fuel CO$_2$ source remains in the Eastern Siberian air mass.

The clean air $\Delta^{14}$CO$_2$ observations are compared with simulated spatial gradients from the TM5 atmospheric transport model. The calculations confirmed that the change in $\Delta^{14}$CO$_2$ across the TROICA transect is due almost entirely to emissions of fossil fuel CO$_2$, but that the magnitude of this $\Delta^{14}$CO$_2$ gradient is relatively insensitive to modest uncertainties in the fossil fuel flux. In contrast, the $\Delta^{14}$CO$_2$ gradient is more sensitive to the modeled representation of vertical mixing, suggesting that $\Delta^{14}$CO$_2$ may be a useful tracer for training mixing in atmospheric transport models.

![Figure 3.2.14. $\Delta^{14}$CO$_2$ as a function of longitude. Closed diamonds are the clean air $\Delta^{14}$CO$_2$ dataset. Open symbols indicate samples that may be influenced by either nuclear reactor effluent (triangles) or local city pollution (circles). The shaded bar indicates the Nivot Ridge $\Delta^{14}$CO$_2$ value measured over the same time period and its 1-sigma error envelope. Modeled estimates for each sampling time and location have been done on the basis standard (solid line) and fast (dashed line) mixing (see Turnbull et al., 2009).](image-url)
3.3. Volatile organic compounds

Many volatile organic compounds (VOCs) are toxic, mutagenic, or carcinogenic; when their concentrations are significant, they adversely influence living matter, including humans. Destruction of VOCs in the atmosphere leads to the formation of active radicals, which in turn influence chemical reactions in the atmosphere and the composition of minor atmospheric gases.

No one observation site leads the routine monitoring of VOCs in Russia. Information on VOC natural and anthropogenic sources is extremely scarce. Atmospheric VOC transport from Europe and East Asia to the Russian atmosphere has not been studied. The VOC observations of the TROICA mobile laboratory give some information necessary for estimation of the balance of VOCs and their effect on the atmospheric composition and Earth’s climate [Elansky et al., 2000; Elansky et al., 2001a].

Table 3.3.1. Percentages of different organic substances in VOCs sampled on sorbents over rural areas along the Moscow-Vladivostok railroad

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Alkanes</th>
<th>Alkenes</th>
<th>Aromatics</th>
<th>Carbonils</th>
<th>Alcohols and others</th>
</tr>
</thead>
<tbody>
<tr>
<td>TROICA-2</td>
<td>91.6 ± 6.3</td>
<td>5.5 ± 1.5</td>
<td>0.4 ± 0.3</td>
<td>1.6 ± 0.9</td>
<td>0.9 ± 0.7</td>
</tr>
<tr>
<td>TROICA-3</td>
<td>87.3 ± 6.9</td>
<td>2.9 ± 0.9</td>
<td>1.8 ± 0.8</td>
<td>0.3 ± 0.2</td>
<td>7.7 ± 4.2</td>
</tr>
<tr>
<td>TROICA-4</td>
<td>89.2 ± 7.1</td>
<td>1.3 ± 0.7</td>
<td>0.7 ± 0.3</td>
<td>8.8 ± 4.1</td>
<td>—</td>
</tr>
<tr>
<td>TROICA-5</td>
<td>75.5 ± 15.1</td>
<td>5.5 ± 2.9</td>
<td>6.7 ± 3.8</td>
<td>6.7 ± 3.3</td>
<td>5.6 ± 3.4</td>
</tr>
</tbody>
</table>

Fig. 3.3.2. Spatial distribution of some key VOC along the meridional Kislovodsk-Murmansk railroad on May 27-29, 2000 (PTR-MS, TROICA-6)
The mobile laboratory allows air sampling both while in motion and when stopped. Atmospheric pollutants can be analyzed in samples adsorbed in sorbents or in air samples pumped into stainless-steel canisters. These analyses can be performed in mobile or stationary chemical laboratories. Examples of results of such analyses of sorbent samples are given in Table 3.3.1 and Fig. 3.3.1 [TROICA, 2006].

The highest VOC concentrations during the TROICA campaigns were observed in summer 1999. During performance of the TROICA-5 experiment, high levels and unusual distributions of pollutants were caused by the abnormally torrid weather that led to intense evaporation of organic substances and a high atmospheric oxidative capacity.

In the TROICA-6 experiment the concentrations of those VOCs which are key ones to atmospheric reactions were measured using a proton mass-spectrometer (Fig. 3.3.2).

Along the Murmansk-Kislovodsk railroad, the highest VOC concentrations were seen in the vicinities of the cities of Novocherkassk, Ryazan', Moscow and St. Petersburg. Over the unpolluted rural areas a spring meridional VOC gradient associated with a northward decrease in biogenic emissions was revealed (Table 3.3.2).

Table 3.3.2. Meridional gradient of VOC concentrations for TROICA-6 Kislovodsk-Murmansk route (May 27-29, 2000)

<table>
<thead>
<tr>
<th>Substance</th>
<th>Gradient, ppbv/1000 km</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>2.37 ± 0.11</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>0.08 ± 0.01</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>0.23 ± 0.03</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.89 ± 0.04</td>
</tr>
<tr>
<td>Isoprene, vegetable alcohols</td>
<td>0.06 ± 0.01</td>
</tr>
<tr>
<td>C-pentane</td>
<td>0.03 ± 0.01</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.07 ± 0.01</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.05 ± 0.01</td>
</tr>
<tr>
<td>C8-benzenes</td>
<td>0.03 ± 0.01</td>
</tr>
<tr>
<td>C9-benzenes</td>
<td>0.07 ± 0.01</td>
</tr>
</tbody>
</table>

Detailed Trans-Siberian VOC measurements were carried out using PTR-MS during summer experiment TROICA-12. In Fig. 3.3.3 spatial distribution of isoprene from Moscow to Vladivostok is presented. During the Eastern way the weather at the territory of Trans Siberian railroad was warmer and sunnier on the whole then during back way. The biogenic emission in boreal and broad-leaved forests at the East of the continent on Eastern transect were more active compared with western transect. The concentrations of anthropogenic species benzene and toluene depend mostly on industrial and transport emissions (Fig. 3.3.4).

### 3.4. Radon-222 concentrations and fluxes

Radon ($^{222}$Rn) is widely used as an informative radioactive tracer to describe different atmospheric dynamic processes: determination of air masses formation area and their motion trajectories, estimation of the vertical diffusion coefficient and the mixing layer thickness, determination of the lower atmosphere vertical stratification. The variation of radon concentration can be used to estimate emissions and accumulation of different gas and aerosol admixtures in the surface air as well as their deposition on the surface [Dörr et al., 1983; Biraud et al., 1996; Schmidt et al., 2000]. The main source of $^{222}$Rn emission into the atmosphere is the soil. $^{222}$Rn flux value depends on natural radionuclides content in rocks, soils, underground waters and soil diffusion properties.

$^{222}$Rn concentration was measured by the Low Level Radon Daughters Monitor (LLRDM) produced by Tracer Lab, Germany. An air intake was located at the front part of the railroad car at a height of 4 m above the rails. $^{222}$Rn concentration values were determined every 10 min as the average ones for this period of time. The measurement error is about 30%.

Fig. 3.3.4. Spatial distribution of benzene (a) and toluene (b) concentrations along the eastern transect (TROICA-12, 2008)
Gases and aerosol over continent

According to the TROICA-11 measurements (30.07.07-05.08.07). Sharp increase of $^{222}\text{Rn}$ concentration from the moment of surface night temperature inversions formation and till their destruction is typical for all similar transcontinental profiles. As for the spatial heterogeneities, analysis of the data obtained during the expeditions along the Trans-Siberian Railroad shows the following regions with increased $^{222}\text{Rn}$ concentration: the Urals and Baikal regions, the East Siberia mountain regions and the Amur plain. They are just the regions where high uranium and radium content in rocks is observed.

The mean $^{222}\text{Rn}$ concentration along the Trans-Siberian Railroad varies from 6.2 Bq/m$^3$ (TROICA-5) to 12.6 Bq/m$^3$ (TROICA-9) depending on the season (Table 3.4.1). The differences between the expeditions are caused by soil moisture (atmospheric precipitations) and inversion duration. Fig. 3.4.2 shows $^{222}\text{Rn}$ concentration increase by the end of the summer and the autumn when the inversion duration increases. Large precipitation amount, on the contrary, results in decrease of $^{222}\text{Rn}$ flux into the atmosphere which can be seen while comparing the data of TROICA-7 and TROICA-5.

Table 3.4.1. Mean $^{222}\text{Rn}$ concentrations variation along the Trans-Siberian Railroad

<table>
<thead>
<tr>
<th>Expedition</th>
<th>Period</th>
<th>Mean $^{222}\text{Rn}$ concentration, Bq/m$^3$</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>TROICA-8</td>
<td>19.03.04 - 01.04.04</td>
<td>6.8</td>
<td>6.7</td>
</tr>
<tr>
<td>TROICA-5</td>
<td>26.06.99 - 13.07.99</td>
<td>6.2</td>
<td>6.1</td>
</tr>
<tr>
<td>TROICA-7</td>
<td>27.06.01 - 10.07.01</td>
<td>7.2</td>
<td>8.8</td>
</tr>
<tr>
<td>TROICA-11</td>
<td>22.07.07 - 05.08.07</td>
<td>8.2</td>
<td>8.6</td>
</tr>
<tr>
<td>TROICA-12</td>
<td>21.07.08 - 04.08.08</td>
<td>7.2</td>
<td>7.1</td>
</tr>
<tr>
<td>TROICA-9</td>
<td>04.10.05 - 18.10.05</td>
<td>12.6</td>
<td>10.9</td>
</tr>
</tbody>
</table>

Using the observational data of $^{222}\text{Rn}$ concentrations and inversion depth, radon flux values were estimated. The absence of information about $^{222}\text{Rn}$ vertical distribution is the main source of $^{222}\text{Rn}$ flux estimation uncertainty. The mean accumulation layer depth from Moscow to Vladivostok was about 100 m. The calculated $^{222}\text{Rn}$ fluxes with radon being uniformly distributed in the layer are given in Fig. 3.4.3. The maximum fluxes are noted in Transbaykal, the mountain region of the East Siberia, and the minimum values, as a rule, are observed in the...
3.5. Ozone-depleting substances

The atmospheric loading of ozone-depleting substances (ODS) is currently in decline because of large reductions in the global production during the 1990s. More than 20 years before Russia was one of the most important ODS producers. Therefore there was need for measurement-based estimates of the ODS emissions after reported cessation of their production in 2000 (see Fig. 3.5.1).

During TROICA-7 campaign the concentrations of six main ODS were measured in surface air [Hurst et al., 2004]: CFC-11 that is primary a foam blowing agent, CFC-12 is a refrigerant, halon-1211 is a fire extinguishing agent, and CFC-113, CH₃CCl₃, and CCl₄ are solvents. Carbon tetrachloride is also the precursor chemical (feedstock) for the manufacture of CFC-11 and CFC-12.

The ODS were measured by the four-channel Airborne Chromatograph ACATS-IV between Moscow and Khabarovsk. Fig. 3.5.2 gives the example of CFC-12 and halon-1211 concentrations data obtained at back way from Khabarovsk to Moscow.

Emissions of ODS were calculated from their mixing ratio increases coincident with increases in ²²²Rn activities during 24-hour diurnal periods of the 6.5 day western transect. These transect data were utilized because of low-height temperature inversions existing during all nights in back way (Fig. 3.5.3). For validation of ODS emissions the respiration fluxes of CO₂ were calculated as well using the same method.

The determined average emission ratios and fluxes are representative of the collective upwind sources that influenced measurements. Boundaries of the 6 collective source regions were defined by the position histories of near-surface air masses advec ted to the train, as portrayed by isentropic 9-hour back trajectories. The areas of the 6 collective source regions ranged from 45,000 to 166,000 km² (Fig. 3.5.4). In the 1990’s nearly about 7% of the Russian population lived within this 611,000 km² rail corridor.
Emission rates in this corridor were calculated as the sums of emission rates in each of the 6 collective source regions for which a statistically significant emission ratio was determined. The estimates for all six ODS were scaled to the whole of Russia based on the 15:1 ratio of Russian to rail corridor population. The emission in rail corridor, Russia compared with Global ones are presented in Table 3.5.1.

Our measurement-based estimates indicate that Russian emissions in 2001, even if grossly underestimated because of underreported production, were insufficient in magnitude to play a major role in recent global emission shortfalls [Hurst et al., 2004]. The results also corroborate the reported termination of CFC production in Russia at the end of 2000. The large CFC-12 emissions observed in Russia suggest that a recent estimate of the global CFC-12 reserve is too small.

### 3.6. Aerosols

#### Main characteristics

Atmospheric aerosol particles have significant influences on our environment and the quality of our life. In global and regional scales, aerosol particles have a potential to affect climate and hydrological cycle. More locally, and especially in polluted urban environments, aerosol particles deteriorate visibility and have adverse effects on human health. Better understanding of these aerosol effects requires detailed information on how aerosol particles originating from different sources are distributed in the atmosphere and how the chemical and physical properties of particles vary from location to location. Until now, very little is known about the concentrations and chemical composition of aerosol particles over the Russian territory. Such information would be of great interest for several reasons. First, there are large urban areas and industrial complexes in Russia with poorly known but potentially large emissions of anthropogenic aerosol particles. Aerosol measurements downwind of such sources would be of great benefit for global aerosol modelers, as well as for people planning air quality regulations in Russia. Second, most of the Earth’s boreal forests are located in Russia. They produce large quantities of natural aerosol particles into the atmosphere. Third, aerosol particles formed by agricultural and forest fires in Russia can, under suitable meteorological conditions, deteriorate seriously the air quality all the way through Eurasia and over high Arctic areas. Aerosol measurements in the vicinity of these fire spots would be of great help in developing operational systems by which such air pollution episodes could be predicted in the future.

#### Concentration and size distribution

Since 1996, the concentrations and microphysical and chemical properties of aerosols have been measured in the TROICA experiments. The mobile laboratory is supplied with the following instrumentation developed for these aims at the KRIPC and OIAP:

- nephelometers allowing for determination of the mass concentration of 0.05–15 μm aerosol particles;
- laser analyzer of the size distribution of 0.15–1.0 μm aerosol particles;
- aethalometer allowing for determination of the soot concentration (BC);
- photoelectric analyzer of the size distribution of 0.5–15 μm aerosol particles;
- samplers collecting aerosols for subsequent analyses of their chemical composition and mass concentration.

The instrumentation is computerized and allows measurements on a real time basis. In 2004, the instrumentation system was supplemented with the particle size distribution analyzer (PSDA) designed in the Institute of Chemical Kinetics and Combustion of the Siberian
Division of RAS. This instrument registers fine particles (≥ 0.002 μm).

A great archive of data on aerosol concentration, size distribution and chemical composition was collected. Up-to-now the complete analysis of these data has not been done. Some results were published in articles [Andronova et al., 2002; Andronova et al., 2003]. Here we present some of them as examples.

In the plumes of industrial zones and cities, the mean aerosol mass concentrations were 100-120 μg/m³; with concentrations several times lower on days off than on working days (Fig. 3.6.1). For comparison, the rural aerosol mass concentrations vary from 10 to 20 μg/m³.

Forest fires are another powerful source of atmospheric aerosol. In the plumes of forest fires observed by the TROICA expeditions, maximum identified aerosol mass concentrations exceeded 800 μg/m³.

A comprehensive analysis of the surface-aerosol microphysical characteristics and space-time variability allows determination of the local sources of atmospheric pollutants.

Isolated populated localities and industrial enterprises, oncoming trains, and industrial zones of cities reveal themselves clearly in Figs. 3.6.2 and 3.6.3.

Aerosol chemical composition. Transportation of different goods by railroads results in pollution of the atmosphere, railroad bed, ballast section, and wayside soils. In addition, pollutants transported from remote sources precipitate on the railroad territory.

Our experience shows that mobile observatories represent a suitable means for controlling the ecological state of the regions extended along the railroads. Air, soil, and dust aerosol lifted by moving trains from the railroad bed were sampled for chemical analyses (Fig. 3.6.4).

These samples were analyzed with the following techniques: neutron activation, X-ray analysis, IR-spectrometry, and electron microscopy.

The aerosol enrichment factors for silicon, iron, calcium, potassium, and titanium are significantly lower than 10; this means that these aerosol elements are of soil origin.

The aerosol enrichment factors for nickel, magnesium, manganese, barium, strontium, phospho-
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The aerosol enrichment factors for cesium, sulfur, chlorine, bromine, iodine, copper, and vanadium are higher than 10; perhaps, these aerosol elements have different sources, including mancaused ones.

The highest (17) and smallest (8) numbers of highly enriched elements in the aerosol composition are revealed over the Baikal region and Transbaikalia and over West Siberia, respectively.

Natural radioactivity. Radiolabels are very useful for monitoring atmospheric gaseous pollutants. Such natural radioactive noble gases as radon (Rn) and thoron (Tn) are primarily used for this purpose. Like greenhouse gases, they are emitted from the Earth’s surface and diffuse in the atmosphere under the action of meteorological factors. Rn and Tn are not reactive, and, therefore, their atmospheric trajectories characterize unambiguously the air mass transport from the Rn and Tn sources.

The TROICA instrumentation includes a gamma-radiation radiometer-spectrometer, supplied with a scintillation NaI(Tl) detector resolving on the basis of the cesium line 662 keV with an accuracy of 10%. This instrument allows studies of aerosol particles having no closely-located spectral lines; it is effective in studies of aerosol nuclide composition. The section 3 is devoted to $^{222}$Rn data analysis.

Soot aerosol

Soot aerosol is an important component of the pollution in cities and industrial zones, and it influences the current climate significantly, because of its high light-absorbing efficiency. Soot aerosol particles can be used as a tracer of anthropogenic pollutants in cases where the influence of biomass burning (e.g., forest fires) can be discounted. They absorb some substances, which are harmful for human health (for example, benzpyrene), reveal toxic and cancinogetic properties, and catalyze some atmospheric chemical reactions.

The soot aerosol concentration was measured using the mobile laboratory along the Trans-Siberian and Murmansk-Kislovodsk railroads and around Moscow [Kopeikin V.M., 2007; KopeikinV.M, 2008]. A procedure including atmospheric aerosol sampling with quartz fiber filters and subsequent measurements of the light absorption by the aerosol samples was applied. The different instruments were used simultaneously (see Table 3.6.1).

Along the Murmansk-Kislovodsk railroad the mean level of atmospheric pollution by soot is about 1-2 μg/m$^3$ (Fig. 3.6.5). However, along those railroad sections where diesel locomotives are used, the atmospheric pollution by soot is higher by an order of a magnitude. Along the Trans-Siberian Railroad, large-scale (extended over 500-1000 km) non-uniformities in the soot aerosol distribution in the atmospheric surface layer are seen in winter. This phenomenon is associated with the synoptic and meteorological processes determining the soot transport and accumulation in the atmosphere (Table 3.6.1 and Fig. 3.6.6). As the air-mass transfer decelerates, the soot aerosol concentration increases. In spring of 1997 grass fires produced large-scale polluted zones extending over about 1000 km. In the winter-spring period, the atmospheric soot concentrations over South Siberia and Far East were twice as high as that over European Russia. In the summer period, the atmosphere was not significantly polluted by soot anywhere along the entire railroad.
More detailed information on aerosol physical and chemical properties have been obtained by research groups led by M. Kulmala and V.-M. Kerminen [Kuokka et al., 2007; Vartiainen et al., 2007]. During the TROICA-9 expedition the equipment for continuous monitoring of aerosol parameters with high time resolution was mounted in the moving laboratory.

TROICA-9 was the most “dirty” expedition. Almost all the way from Moscow to Vladivostok and back the trajectories showed the South-West and West air transport from Volga-Ural, Kazakhstan, South Siberia, and China industrial regions. Only during one day in Mid Siberia the transport was from North. And in this case the come air was polluted partly with forest fire products. Besides the warm and sunny weather the largest part of territory was favorable for accumulation pollutants in surface layer.

During the expedition black carbon concentration was measured with 5 minute time resolution using a dual-wavelength aethalometer. The ionic composition of aerosol particles was measured with Particle Into Liquid Sampler (PILS) coupled with two ion chromatographs (IC). Only the fine particle fraction (aerodynamic particle diameter \( D_p < 2.5 \mu m \)) was monitored with PILS-IC. Concentrations of \( \text{Cl}^- \), \( \text{NO}_3^- \), \( \text{SO}_4^{2-} \), \( \text{Na}^+ \), \( \text{NH}_4^+ \), \( \text{K}^+ \), \( \text{Ca}^{2+} \), \( \text{Mg}^{2+} \), oxalate and MSA were analyzed with 15 minutes time resolution. The aerosol particle number size distributions for particles in a diameter range 3-950 nm were measured using a DMPS instrument. Virtual impactor (VI) was used to collect 24-h samples for
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Gravimetric and chemical analysis. The VI divided the sample into fine (aerodynamic particle diameter Dp < 2.5 µm) and coarse fractions (2.5 µm < Dp < 8 µm). Ion chromatography analyses were made from the collected sample. The same ions as measured with the PILS-IC system were determined from the VI samples. The three monosaccharide anhydrides (levoglucosan, galactosan, mannosan) were determined by using a liquid chromatograph mass spectrometry (LC-MS). The trace elements (Al, As, Cd, Co, Cr, Cu, Pb, Mn, Ni, Fe, V, Sb and Zn) were analyzed by using inductively coupled plasma mass spectrometer (ICP-MS).

The total particle concentration was typically of the order of few thousand particles /cm³ varying between 300 and 40 000 particles /cm³. The concentrations were lowest in the rural area between Chita and Khabarovsk and highest near larger villages and towns. Particle concentration levels measured on the way to Vladivostok and back were similar at both ends of the route but differed in the middle, between 4000 and 7000 km, were the concentration was notably lower on the way back to Moscow.

Concentrations of all ions and black carbon were quite low between the 3500 and 6500 km distance from Moscow, whereas high concentrations were observed between Moscow and Novosibirsk and in Asia before and after Khabarovsk on both the way to Vladivostok and back to Moscow. During the way back to Moscow, the concentrations of all ions and black carbon were extremely high near Khabarovsk.

It was evident from trajectory analysis that high concentrations were mostly long-range-transported aerosol particles from North-East China. The increased potassium and oxalate concentrations in this area were indicative of biomass burning.

The mean mass concentrations in PM2.5 and chemical components are shown in Fig. 3.6.7. For example, non-sea-salt sulfate concentrations were between 0.1 and 10 µg/m³ and ammonium-between 0.01 and 10 µg/m³ (Fig. 3.6.8).

Fine particles consisted mainly of soot (BC, 15.8–48.7%, average 27.6%), SO₄²⁻ (2.7–33.5%, 13.0%), NH₄⁺ (1.2–10.5%, 4.1%), and NO₃⁻ (0.5–2.4%, 1.4%). Trace metals together accounted for of 0.4–9.8% of the fine particulate mass. The fraction of monosaccharide anhydrides was in the range 0.4–1.6%, except for one sample (5926-7064 km from Moscow) on the way to Vladivostok when it was as high as 4%. The measured chemical components accounted for 27.7–78.5% of the PM2.5 mass. The unidentified fraction is expected to include organic particulate matter, water-insoluble material and water.

The contribution of BC to PM2.5 was much higher during the whole expedition than what has been observed in Europe, where the BC fraction has estimated to be in the range 5–10%. During the expedition the SO₄²⁻ contribution was lower on the way to Vladivostok, but on the way to Moscow it was close to contributions measured in Europe. The contributions of NO₃⁻ and NH₄⁺ to PM2.5 in Europe have been found to be in the ranges 1.1–18% and 7.0–9.3%.
respectively, which are higher than the values measured during TROICA-9 [Kuokka et al., 2007].

Air ion spectrometer (AIS) classifies air ions according to their electrical mobilities. It allows to measure negative and positive ions from 0.4 to 40 nm: cluster (0.4-1.8 nm), intermediate (1.8-7.5 nm), and large (7.5-40 nm) groups. The half an hour average concentrations of ions are shown in Fig. 3.6.9. The concentrations of negative ions are higher and change in wider limits then positive ones (Vartiainen et al, 2007).

The charge on aerosol particles depends on decay process of radon. As the flux of radon from soil in Siberia is on average high, the production of ion pairs is active. There is an evident correlation between cluster ion and $^{222}\text{Rn}$ concentrations. Snow cover and rainfall decreased the radon activity and ion production.

Two events of formation of fine particles were registered during TROICA-9. On October 10 after 3.30 UTC (about 10:00 local time) the growth of negative ions took place. In Fig. 3.6.10 three lines are shown that display the growth rate. The largest rate 11.4±0.7 nm/h corresponded to ions in diameter range from 4.1 to 9.8 nm. For smaller and larger ions the rate was less: 2.4±0.1 nm/h and 4.4±2.4 nm/h. The similar pictures were observed on October 8 after 5:00 UTC (local time around noon). For negative ions with diameters from 10.2 to 25.6 nm the growth rate was 4.2±0.3 nm/h.

On the way to Vladivostok, between 5925-7064 km from Moscow the concentrations of levoglucosan, oxalate and potassium were extremely high. All these compounds are biomass combustion tracers. The concentrations of BC, sulphate and total particle volume were elevated at the same time with biomass combustion tracers, but to very different extents. They did not coincide with the high oxalate concentrations. These differences in the composition of biomass combustion particles demonstrate differences in burning conditions. Both BC and potassium are emitted to a large extent from flaming fires compared with smoldering fires, whereas oxalate is emitted mostly from smoldering fires (Vartiainen et al, 2007).

Obtained data can be very useful for modeling transport and chemical transformation of the products of biomass burning and distinguishing the man-made ones from the wildfires.
Secondary aerosol in mountain regions

The processes of secondary aerosol formation are scantily investigated. Several mechanisms of particle formation, for instance binary and ternary nucleation, kinetic nucleation, activation of clusters, and ion-induced nucleation are known. Several studies have proven the existence of nucleation events all over the world (Kulmala et al. 2004). But the contribution of each nucleation mechanism and the role of other atmospheric processes in aerosol formation are yet not studied.

The TROICA experiments revealed a new effect associated with the formation of ultra-fine particles within zones of mesoscale orographic perturbations. When the train crossed the East-Siberian mountain ridges, high surface concentrations of 1.6–10-nm aerosol particles (up to 10³ cm⁻³) were observed. These phenomena revealed themselves most clearly in March 2004 (the TROCA-8). Fig. 3.6.11 relates to the events observed when the train traversed the mountain ridges located in vicinities of Irkutsk and Ulan-Ude (on March 28, 2004). An increase of temperature, a decrease of air humidity, and an abrupt increase of concentration of 1.6–10-nm ultra-fine particles were observed in the leeward zone. Over the ridge and in the mountain leeward zone, stationary orographic clouds were observed. The concentrations of SO₂ and volatile organic compounds (VOCs) were enhanced over the entire region, and they were extremely high within the plumes of Irkutsk, Ulan-Ude, and Baikalsk with the Baikal pulp and paper mill.

Numerical simulation of the mountain-ridge airflow (Fig. 3.6.12) demonstrates the occurrence of upward flows in the atmospheric boundary layer (the windward zone) and in the free troposphere (the leeward zone), which lead to formation of orographic stationary cloud system. The region, over which an increase in the concentration of ultra-fine particles was observed, coincides with the region of the downward flow of free-tropospheric air. Under such conditions, the process of formation of the particles can be described as follows. The upward flows occurring in the windward zone of this ridge, similarly to those occurring in the zones of other mountain ridges located in this region carry out SO₂, NH₃, and VOCs to the free atmosphere. Note that NH₃ concentrations were not measured in this TROICA expedition, but they were almost always enhanced in this zone in other TROICA expeditions. The abrupt decrease of temperature and the occurrence of the airflows through orographic clouds activate homogeneous nucleation of aerosol-precursor vapors. The nm-size clusters and detectable particles are produced. In the downward-flow region, where the cloud droplets evaporate, the condensation sink decreases rapidly. The sulfuric acid concentration increases in this zone, promoting the condensation growth of clusters and formation of new particles.

The numerical simulation of photochemical processes and gas–particle interactions occurring under such conditions confirms this mechanism.

Biological aerosol

Biological aerosol includes such objects as viruses, fungal and bacterial spores, pollen, lichen and algae elements, and others, transported passively in the atmosphere. Among them, there are pathogens extremely dangerous for humans, animals, and vegetation, microorganisms, causing bio-damages, and allergens, and toxin producers.

In the mobile laboratory the equipment allowing identification and quantitative analysis of the atmospheric pathogens was successfully tested. The mobile observatory functions in coordination with the MSU observatory, which monitored airborne fungal spores since 1996 [Elansky and Lekomtseva, 1998; Elansky and Ryzhkin, 1999].

Over several regions located along the Moscow–Vladivostok railroad, very high concentrations of pollen and fungal spores were observed (Fig. 3.6.13). The spore types over the European and Tumen’ regions of intense agricultural land-utilization and over the sparsely populated Baikal regions were specified. Monitoring of the pollen and fungal spores over Moscow [Ryzhkin et al., 2002] shows that, in warm seasons, the Cladosporium spores are predominant and the basidiospores are the second most prevalent group (Fig. 3.6.14).
In June-September the total concentration of fungal spores is higher than the pollen concentration (Fig. 3.6.15).

The daily variations of airborne spores concentrations were different for different fungal taxonomic groups. Maximal concentrations of basidiospores and spores of deuteromycetes are observed in the morning, from 4:00 to 10:00, and in the afternoon, from 15:00 to 18:00, respectively (Fig. 3.6.16, 3.6.17).

These peculiarities are associated with the differences in the spores volatilities and mechanisms of the spore emissions in different taxons.

The mobile laboratory can be used to carry out the following tasks:

• Monitoring of the biological aerosol composition and viability associated with the atmospheric state variations.

• Identification of the highly dangerous and quarantine pathogenic living organisms in the atmosphere.

• Revealing the seasonal and daily variations, spatial distribution, and precipitation mechanisms for biological aerosol.

• Identification of the biological aerosol sources and of the ecological state of the sources emitting biological aerosol.
4. Air pollution in cities

Air quality is the main ecological factor influencing human health, the environment, and economics. Cities are areas where both population and the most powerful sources of atmospheric pollutants are concentrated. The photochemical transformation of the different components of urban pollutant plumes produces a different set of toxic substances. For controlling air quality and forecasting extreme ecological situations, it is necessary to monitor the gas and aerosol pollutants and the atmospheric thermodynamic, radiative, and meteorological parameters and to process these data on the basis of techniques of numerical simulation.

The mobile laboratory traverses cities and atmospheric pollution plumes from different sources and monitors them continuously. Repeated expeditions performed along the same railroads under conditions of different wind directions allow systematic determination of local stable sources. Fig. 4.1.1 gives an example of the atmospheric pollutant distribution measured under different wind directions along the railroad traversing the city of Tyumen. This example was obtained in the course of the eastward and westward routes of the TROICA-7 expedition. The structure of the spatial NO distribution allows the conclusion that the same sources were responsible for the NO emissions during the movement of the expedition in both directions and that the observed peculiarities are caused by the plume shifts resulted from the wind-direction variation.

The spatial distribution of pollutants over areas of cities depends not only on the location of the sources of pollutants but also on the relief, vegetation state, and other factors.

Fig. 4.1.2 presents the concentration distributions for some atmospheric pollutants along the railroad traversing the city of Krasnoyarsk. Over the city center and industrial zone, high concentrations of atmospheric pollutants are observed. Over the cold and breezy bed of the Yenisei, the concentrations of pollutants are at a minimum.

Having a laboratory along the railroad network provides a possibility for comparing the air pollution over different populated localities and cities and the ecological states in different regions.

During the TROICA expeditions, the train going along the Trans-Siberian Railroad traversed repeatedly about 110 cities populated by 20 to 1500 thousand people (except Moscow). In addition, several tens of cities were traversed by the train in the course of the Kislovodsk–Murmansk expedition (TROICA-6). One expedition (TROICA-10) was aimed at the study of the atmosphere over the Moscow megapolis. These long-term studies give a possibility for revealing the features of atmospheric composition and their trends inherent in different cities.

The ozone concentrations averaged over the cities traversed in the course of the Trans-Siberian expeditions are presented in Fig. 4.1.3. As a rule, they were slightly lower than the ozone concentrations...
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observed in rural areas due to ozone destruction by nitrogen oxides in urban air. The exception to this rule was the data file obtained in the TROICA-5 expedition. In this expedition, the ozone concentration level in cities was slightly higher than that in rural areas. This feature can be explained by the predominant warm (the temperature was 23-35°C) sunny weather that accompanied the Moscow-Vladivostok-Moscow expedition. High urban VOC concentrations caused by evaporation of automobile fuel were observed everywhere.

Comparison of the ozone-concentration seasonal behaviors for Russian cities and the Hohenpeissenberg and Zotino stations shows that, in the February-November period, the concentration level over Russian cities is less variable. In Russia (in comparison with central Europe), the ozone-concentration spring maximum is lower and the summer ozone generation is weaker. The ozone destruction intensity in polluted air is significantly higher in Moscow than in the other Russian cities located along the Trans-Siberian Railroad (Fig. 4.1.3), where the ozone behavior corresponds, on the average, to that in slightly polluted areas. Table 4.1.1 gives the data on the ozone and other gases concentrations measured in different expeditions over the cities, city vicinities, and remote areas. The mean values and the values averaged over the period from 11:00 to 18:00 local time are presented. Apparently, the mean urban-air pollution is not very severe. The atmospheric concentrations of ozone precursors are also not high. As a rule, weather conditions over the latitudinal belt 48-58° N don’t promote active photochemical processes. Therefore, in the cities, the excess in the ozone concentration level over the background one is little if any even in the daytime (11:00-18:00 local time).

To find out the correlation between the urban-air composition and the scale of the city area and population, we classified all the cities into the large, medium, and small ones (see Table 4.1.2). Fig. 4.1.4 compares the O₃, NOₓ, and CO mean concentrations over the central and suburban areas of cities with those over remote (background) areas. In all seasons, the concentrations of ozone precursors increase as the distance from the city center decreases. Over medium and small cities, the daytime ozone concentrations exceed the background level.

Table 4.1.2. Cities distribution according to population

<table>
<thead>
<tr>
<th>City group</th>
<th>Population</th>
<th>Number of cities</th>
</tr>
</thead>
<tbody>
<tr>
<td>Large</td>
<td>&gt; 500 000</td>
<td>11</td>
</tr>
<tr>
<td>Middle</td>
<td>50 000 ÷ 500 000</td>
<td>34</td>
</tr>
<tr>
<td>Small</td>
<td>&lt; 50 000</td>
<td>62</td>
</tr>
</tbody>
</table>

Within large cities ozone destruction by nitrogen oxides prevails over ozone generation. But into the plumes of polluted air going out the large cities of the

Table 4.1.1. Mean trace gases concentrations for different seasons (spring – TROICA-8; summer – TROICA – 5,7,11,12; autumn TROICA-9) over the territory of cities, their suburbs compared with background conditions (Bgr)

<table>
<thead>
<tr>
<th>Gases</th>
<th>Spring</th>
<th>Summer</th>
<th>Autumn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bgr</td>
<td>Suburb</td>
<td>City</td>
</tr>
<tr>
<td>O₃</td>
<td>47.1</td>
<td>41.4</td>
<td>36.3</td>
</tr>
<tr>
<td>NOₓ</td>
<td>1.1</td>
<td>6.2</td>
<td>15.9</td>
</tr>
<tr>
<td>CO</td>
<td>180</td>
<td>240</td>
<td>330</td>
</tr>
<tr>
<td>SO₂</td>
<td>1.5</td>
<td>3.1</td>
<td>5.3</td>
</tr>
<tr>
<td>CH₄</td>
<td>1840</td>
<td>1880</td>
<td>1900</td>
</tr>
<tr>
<td>NMHC</td>
<td>110</td>
<td>130</td>
<td>200</td>
</tr>
</tbody>
</table>

Fig. 4.1.3. Trans-Siberian TROICA expedition mean O₃ concentrations in all cities crossed in TROICA expedition in comparison with O₃ seasonal variations at three sites: Moscow (2002 – 2008), Zotino (2006 – 2008) and Hohenpeissenberg (1995 – 2007)

Fig. 4.1.4. Daytime mean (11:00-18:00 h. local time) O₃, NOₓ, CO concentrations averaged on the background (brg) and different parts of cities territories for spring, summer and autumn and for three groups of cities (TROICA-3 – TROICA-11)
excess of ozone compared with the remote areas for this corridor could take place in a warm period of the year.

The daily mean variations in the concentrations of some other atmospheric pollutants over all cities but Moscow are given in Fig. 4.1.5 and 4.1.6. It is apparent that the daily variations in the gas concentrations are mainly determined by the traffic, in less stage are dependent on the functioning of industrial enterprises, and are influenced by the origination and destruction of the temperature inversions, which are rather intensive in Siberia. If morning and evening rush hours often coincide with the inversion period, fast accumulation of pollutants in surface air occurs. Such a situation is characteristic for cold seasons. As the summer nights and time of temperature inversions existence are short, active emissions of pollutants take place in the hours when the air mixing processes are already intensified and, therefore, no accumulation of pollutants proceeds. In Fig. 4.1.5 this effect is well pronounced by the example of NOx diurnal variations.

In the period of TROICA-8 and 9 expeditions in many cities the heating systems were functioning. Comparison between the observations performed in the Russian cities through which the Trans-Siberian railroad goes and in the Moscow megapolis with its population of more than 10 million people reveals significant differences in the O3 concentration mean daily behaviors calculated for the same months (Fig. 4.1.7). (The O3 concentrations in the Moscow megapolis are calculated on the basis of the measurements performed at the site of Moscow. These differences are mainly caused by the intensive nighttime ozone destruction in the Moscow megapolis due to the intensive round-the-clock traffic and horizontal advection bringing polluted air from the suburban industrial regions. However, the July–August noon surface O3 concentrations observed in all these cities are almost the same and are higher than that observed in rural areas.

This difference increases from year to year as the city traffic grows and the industrial activity intensifies after the economic crisis of 1991-1995. This conclusion is illustrated by Fig. 4.1.8 where the NOx-concentration trend calculated on the basis of the measurements performed in the course of all 1996-2007
expeditions is displayed. In the Figure the trend of number of motor vehicles in Russian cities is shown as well. It is seen that both trends coincide well. The same is true for CO concentration (Fig. 4.1.9).

Fig. 4.1.10 shows that, in summer 1996, the concentrations of different VOCs over a number of Russian cities were significantly higher than those over rural areas.

The mobile observatory allows monitoring of the pollution plumes propagating from cities and industrial zones. Sometimes, the plumes propagate over several hundreds of kilometers. As an example, the 650-km plume extending from Novosibirsk to Omsk is shown in Fig. 4.1.11 (TROICA-5).

As a result of photochemical reactions proceeding within plumes, pollutants transform to different toxic products, including ozone, the concentration of which can be significant. In this figure, an ozone generation zone, where the ozone concentration exceeds its local background value by more than 20 ppbv, is shown (the ozone-concentration daily variation is taken into account).

4.2. Moscow experiment

In the period of October 3-7, 2006 the unique experiment (TROICA-10) on monitoring the surface air composition in the Moscow megapolis was performed. The mobile two-car laboratory coupled to an locomotive made three circles along the Moscow circular railroad. The road length is 526 km; the distance between the road and the center of Moscow ranges from 50 km for the northwestern section of the road to 95 km for its northeastern section. In addition, at the beginning and at the end of the experiment, the observations were performed along the radial northward railroad from the center of Moscow to the circular railroad.

The monitoring was performed in the period when the North-Atlantic cyclone replaced the powerful anticyclone that prevailed in September over the European Russia. During the entire observation period, stable western air transport was predomi-
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4.2. Moscow experiment

Minimum concentrations of pollutants and maximum concentrations of ozone were measured in the airflow incoming to Moscow. Short-term peaks in the concentrations of different substances brought from small towns, industrial enterprises, and highways stand out against this general background (Fig. 4.2.4). It is interesting that the concentrations of aromatic hydrocarbons in airflows coming out of the megapolis is higher than that in surface air in the center of Moscow. This phenomenon is caused by predominant locations of industrial enterprises and traffic in the eastern sector of the Moscow region and accumulation of VOC down a wind. For example, the location of metallurgical plants in this sector revealed itself in enhanced concentrations of SO₂, which was not actually identified in measurements performed along other sections of the route.

4.3. Caucasus experiment

In the framework of the TROICA-6 experiment, mobile railroad-car and autocar laboratories were used together in the Kavkazskie Mineral'nye Vody (Kavminvody) region for monitoring of the spatial concentration variability of atmospheric minor gases and aerosol under almost stable weather conditions in the period of April 13-25, 2000 [Belikov et al., 2001]. This combination of two mobile laboratories allowed rather quick complex estimation of the state of the atmospheric basin chemistry for the extended region (Fig. 4.3.1).

In different towns and populated localities of the Kavminvody region, these laboratories performed daytime and nighttime observation sessions of 20-60-min duration. The
Regional atmospheric pollution observations were performed at points located in park zones remote from pollution sources and near motor roads (or in immediate proximity of motor roads) with different traffic intensities.

Over 50% of all cities, the atmospheric state differed from the background one almost not at all, and, over only 10% of them, high levels of pollution were observed. All highest pollution levels were observed when the autocar laboratory was located at driveways characterized by intense traffic and lying at a mountainside (Table 4.3.1).

Over all populated localities, the pollution daily behavior was similar. Fig. 4.3.2 presents the ozone, NOx, carbon oxides, fine aerosol, soot, and benzpyrene daily behaviors averaged over all observation points. For each of the pollutants, the daily behavior is similar to the averaged daily behavior measured repeatedly at any one observation site. This result means that the photochemical reactions of the pollutants are similar over the entire region under consideration.

The regional degree of pollution is determined by the motor vehicle traffic intensity and by the functioning of industrial enterprises. The atmospheric pollution is maximum in the period between 15:00 and 17:00. In the evening, the down slope wind from the foothills reduces rapidly the degree of atmospheric pollution to its background level. The high quality of the regional air can be explained by the weakness of harmful flows from the ground-based sources, high oxidative activity of the atmosphere, and intense atmospheric photochemical and dynamic processes promoting purification of the air basin. The similarity of the photochemical processes proceeding over the entire region provides rather reliable prognostic estimations.

<table>
<thead>
<tr>
<th>Pollution level</th>
<th>Background, very pure conditions</th>
<th>Background, pure conditions</th>
<th>Moderate</th>
<th>Permissible</th>
<th>High</th>
<th>Very high</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of observations,%</td>
<td>13</td>
<td>39</td>
<td>25</td>
<td>13</td>
<td>5</td>
<td>5</td>
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<tr>
<td>Aerosol, ( \mu g/m^3 )</td>
<td>18</td>
<td>31</td>
<td>40</td>
<td>55</td>
<td>56</td>
<td>68</td>
</tr>
<tr>
<td>Soot, ( \mu g/m^3 )</td>
<td>0.7</td>
<td>2</td>
<td>4.3</td>
<td>6</td>
<td>11.1</td>
<td>16.1</td>
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<tr>
<td>Nitrogen oxide, ppbv</td>
<td>0.1</td>
<td>0.3</td>
<td>3.1</td>
<td>14</td>
<td>30</td>
<td>77</td>
</tr>
<tr>
<td>Nitrogen dioxide, ppbv</td>
<td>0.4</td>
<td>1.5</td>
<td>2.5</td>
<td>3.3</td>
<td>1.9</td>
<td>1.2</td>
</tr>
<tr>
<td>Carbon monoxide, ppm/m^3</td>
<td>0.3</td>
<td>0.8</td>
<td>1.7</td>
<td>2.4</td>
<td>6</td>
<td>10.7</td>
</tr>
<tr>
<td>Ozone, ppbv</td>
<td>29</td>
<td>32</td>
<td>35</td>
<td>24</td>
<td>29</td>
<td>26</td>
</tr>
<tr>
<td>Benzpyrene, ng/m^3</td>
<td>0.25</td>
<td>0.46</td>
<td>0.75</td>
<td>0.76</td>
<td>0.58</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Fig. 4.3.1. Kavkazskie Mineral’nye Vody Region.

Fig. 4.3.2. Mean daily behavior of different pollutants.
Observations performed on the basis of the mobile laboratory not only revealed the harmful emissions into the environment but also allows for forecast of extreme situations associated with the formation of toxic substances in the atmosphere.

One of these substances is trichloroacetic acid (TCA). TCA is a pesticide that can be produced in the atmosphere from almost non-hazardous substances. From the atmosphere TCA penetrates into vegetation bodies. Enhanced concentrations of TCA were found in tree leaves and needles collected in different regions of the world [Weissflog et al., 2001; Weissflog et al., 2003].

On the basis of the data obtained during the TROICA-6 expedition, model calculations for TCA formation in the atmosphere over Kalmykia, the Kola Peninsula, and Central Russia are performed (Fig. 4.5.1) [Weissflog et al., 1999].

The studies performed in Kalmykia show that atmospheric pollutants transported by airflows from remote regions can unexpectedly cause a very strong adverse effect under specific local conditions. Atmospheric flows transport great amounts of organic pollutants from Ukraine and from the Volgograd and Astrakhan' regions to Kalmykia, where the pollutants precipitate to the underlying surface. In air and water saturated with salt aerosol of domestic and Central Asian origin, active oxidizing processes lead to the formation of reactive haloid-containing substances. Under the conditions of a dry and hot climate, photochemical interactions between these substances and neutral organic pollutants lead to the formation of toxic substances, for example, of Cl-substituted acetic acids [Elansky, 2004; Weissflog et al., 2006].

Fig. 4.4.2 shows the main natural reaction routes leading to TCA formation.

The TCA effect on vegetation includes the intensification of water evaporation and deceleration of CO₂ assimilation. TCA is distributed over large ter-
ritories. Therefore, the depression of forests and other continental vegetation and an associated increase in the atmospheric H2O and CO2 concentrations can lead to significant regional and global climatic changes.

At high concentrations of TCA, its harmful effect can lead to the degradation and disappearance of forests. Similar processes proceed in some regions of Central Europe [Weissflog et al., 2009].

Recent studies showed [Weissflog et al., 2004; Weissflog et al., 2005] that TCA precursors, such as methyl-chloroform, tetrachloroethylene, trichloroethylene, and tetrachloromethane, can also be produced under the salt crust in the water depth of salt lakes and be desorbed together with salt aerosol into the atmosphere; production of the TCA precursors is promoted by halobacteria (Table 4.4.1).

### 4.5. Examples of extreme situations

Zones of high ozone concentrations arise often in the regions influenced by local and remote sources of air pollution. Meanwhile, ozone has direct harmful effect upon human health and promotes formation of other toxic substances in the atmosphere. The mobile laboratory allows monitoring of the atmospheric concentrations of ozone and its precursors and obtaining all information necessary for forecasting dangerous situations associated with changes in the air chemical composition.

Local regions of abnormally high ozone concentrations can originate in the vicinities of forest fire zones, in the plumes of cities, industrial objects, and burning dumps, and near power transportation lines (Fig. 4.5.1).

Intense processes of ozone generation were observed in the daytime in the cities and the industrial zones under conditions of hot weather and intense solar illumination. Such conditions are characteristic of the monsoon periods in the Far East region (Fig. 4.5.2).

High atmospheric concentrations of CO and VOCs are also necessary for ozone generation. CO and VOCs can be emitted from sources located within the region under consideration or transported from remote territories. The mobile obser-
Regional atmospheric pollution

On July 1 and 2, 1999, polluted air was transported to the cities of the Kabarovsk krai from Japan and Korea. The air-mass trajectories in the lower atmosphere are shown in Fig. 4.5.3.

Within moving air masses, oxidation of primary VOCs, decreasing in the NOx concentration, and fast increasing in the concentrations of secondary hydrocarbons proceed (Fig. 4.5.4). Diffusion of urban pollutants into this air mass leads to intense generation of ozone. The start of such a process is illustrated in the above figure [Elansky et al., 2005].

According to the data of the TROICA-5 expedition, the ozone concentration over the city of Birobidzhan increased quickly in the evening of July 2, 1999 and reached a critical value of 230 ppbv, which exceeded the MPC by a factor of 3 (Fig. 4.5.5).

Fig. 4.5.4. Photochemical transformation of anthropogenic components in atmospheric plumes from cities

Fig. 4.5.5. Ozone concentration peak over the city of Birobidzhan (July 2, 1999)
5. Local impacts on the atmospheric composition

5.1. Railway transport impact

The total adverse effect of railroad systems on the environment consists of sub-effects of stationary industrial objects (freight terminals, repair plants and depots) and freight and passenger trains.

The atmospheric pollution caused by loaded trains is associated with abrasion of solid surfaces of car and locomotive components, with pouring, leaking, and dusting out of transported loads, with the functioning of locomotive diesels, and with smoke emissions from coal car-heating boilers.

From trains transporting ores, coal, and other loose goods, large amounts of solids of different chemical composition can be blown away by airflows. Upward airflows blow solid particles up from the railroad bed. The majority of these particles are coarse, and, therefore, they are deposited back to the surface rather quickly.

In Fig. 5.1.1, the effect of oncoming freight trains on the size distribution of atmospheric particles is shown. An abrupt increase of the portion of coarse particles after the passage of oncoming trains is caused by the lifting of solid particles from railroad beds and from freight cars. In contrast, oncoming trains have almost no influence on the atmospheric concentration of fine particles.

An abrupt increase in the aerosol concentration is observed immediately after the passage of trains. The height of the concentration peak depends on the length and speed of the oncoming train and on its type: long freight trains increase aerosol concentrations to a greater extent than do passenger trains (Fig. 5.1.2).

The atmosphere along electrified railroads is enriched with heavy metals as a result of the wearing-off the wire-pantograph rubbing surface. The concentration of different metals in aerosols depends on the supply current system (Fig. 5.1.3).

For example, when changing 3 kV of direct current for 25 kV of alternating current, Cu and Zn concentrations decrease by 20 – 80 % and Ni and Cd concentrations increase by 2 – 5 times. Sharp increase of Se concentration (by 10 – 20 times) is observed.

The study of the chemical composition of railroad embankments showed that the degree of their enrichment by such heavy metals as Cu, Zn, V, Pb, Ni, Ti, and Cd relative to their mean content in the Earth's crust ranges
between 102 and 104. These elements enter into the composition of different alloys used in the railroad engineering industry and in the production of overhead contact lines and represent the components of different ores transported in open railroad cars (Fig. 5.1.4).

The atmosphere along railroads is polluted by stationary and mobile sources of pollutants. The contribution of mobile sources can be estimated through measurements of pollutants in railroad tunnels. For example, along the Buriya-Birobidzhan section of the Trans-Siberian Railroad, the TROICA-8 expedition (March 2004) revealed enhanced concentrations of almost all pollutants characteristic of railroad areas; therein, the aerosol and NOx concentrations often exceeded the maximum permissible concentrations (MPC) (Fig. 5.1.5).

Enhanced atmospheric concentrations of unsaturated hydrocarbons (UHCs) were measured when trains containing oil-gasoline tanks passed by and also in vicinities of stations and siding lines where similar tanks were concentrated (Fig. 5.1.6).

Such emissions caused by trains consisting of tanks only and of different cars, including tanks, were estimated. The degree of UHC enhancement depends on the tank quantity in the train, the type of the transported good, hermeticity of the tank hatches, wind speed and direction, air temperature, and landscape. It is important that hatches of empty railroad oil-gasoline tanks are open to avoid explosive vapor concentrations within tanks containing hydrocarbon residuals.

A number of ecological problems associated with harmful emissions from diesel locomotives are well known. The studies performed on the basis of the mobile observatory allowed comparative estimation of the degree of pollution by diesel locomotives and electric locomotives and fixation of the variations in the concentrations of harmful substances along passenger trains (Fig. 5.1.7).

The functioning of diesel-locomotive shunters and stationary objects causes enhanced concentrations of atmospheric pollutants within station areas as compared with the concentrations of atmospheric pollutants within areas of cities and their vicinities. These differences are most significant in small towns (especially if these towns are the traffic centers); in cities, harmful emissions from industrial enterprises and motor transport prevail (Fig. 5.1.8).

The level of atmospheric pollution characteristic for cold seasons exceeds significantly that characteristic for warm seasons due to the contribution of urban heating systems and coal heating systems functioning in passenger cars at railroad stations.
Fig. 5.1.8. Effect of the population size on the degree of pollution of air over the areas of railroad stations, cities, and suburbs in warm and cold seasons
5.2. Leakage of natural gas

Methane leakages from pipelines and gas tanks represent a real danger, because they can stimulate accidents and eco-catastrophes, which are rather possible if pipelines and equipment are worn out. The information on gas leakages in the territories of Russia and the FSU was ambiguous (see Table 5.2.1).

<table>
<thead>
<tr>
<th>Source of methane leakage</th>
<th>FSU</th>
<th>Russia</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dedikov et al.</td>
<td>Reshetnikov et al.</td>
</tr>
<tr>
<td>Production</td>
<td>0.6</td>
<td>11.0-13.5</td>
</tr>
<tr>
<td>Transportation</td>
<td>4.4</td>
<td>16.0-19.7</td>
</tr>
<tr>
<td>Supply</td>
<td>-</td>
<td>4.0-11.8</td>
</tr>
<tr>
<td>Total (accidents are not considered)</td>
<td>5.0</td>
<td>-</td>
</tr>
<tr>
<td>Total (accidents are considered)</td>
<td>-</td>
<td>31-45</td>
</tr>
</tbody>
</table>

The railroad car-observatory is capable of continuous on-line monitoring and exact identification of methane leakages in the regions where the systems of transportation, processing, storage, and supply are located in the vicinity of the railroad bed.

Trans-Siberian railroad crosses about 10 large magistral pipelines. At these points, significant peaks in the concentrations of methane and other volatile organic components of natural gas were usually registered.

Fig. 5.2.1 presents an example an abrupt increase in the CH₄ and NMHC concentrations over the point of intersection of the railroad and two main pipelines. This point is located in the area remote from swamps and anthropogenic sources; this fact is confirmed by low background values of the NOₓ and CO concentrations. Such a local increase in the atmospheric content of natural gas is difficult to explain by anything but leakages from the gas-transport system.

Among the Russian regions, Western Siberia and northern areas of European Russia are notable for enhanced concentrations of methane and nonmethane hydrocarbons. It was assumed that this enhancement is largely associated with natural gas leakages from the oil-and-gas production system. However, the CH₄ isotopic-composition studies performed aboard the mobile railroad and ship laboratories in the course of expeditions along the Trans-Siberian Railroad and along the Ob River showed that, in these areas, the greatest portion of above-background methane is of biogenic origin.

The portion of anthropogenic methane increases from 2% over the southern and eastern
boundaries of Western Siberia to its center and amounts to 30-50% in the vicinity of gas-extraction points [Tarasova et al., 2006]. Although the obtained estimates of methane leakages from the gas-extraction system lowered the value used earlier by some experts from 40 to 10 Mt/year (Fig. 5.2.2), they confirmed the hazard of leakages of methane and other natural-gas components to the ecosystem of Western and Central Siberia [TROICA, 2006].

Fig. 5.2.3 illustrates an example of crossing one such plume from a big gas-producing field in Western Siberia. This plume during the train moving shifted westward and its structure consists of many peaks of CH₄ concentrations and results the combined effects of biogenic and anthropogenic methane emissions. The detail satellite image of gas and oil fields has been shown on the additional picture. The derricks and gas field local pipelines have been clearly seen.

Considerable leakages of natural gas were regularly observed in cities and sometimes from compressing stations. In Fig. 5.2.4 an example of the injection of methane in the atmosphere at a compressing station and a gas pipe-line during the maintenance check-up work is presented. The estimation of CH₄ emission gives the value which is about $2.1 \times 10^{10}$ μkg/h. It should be noted that the method back-forward GIS analysis for reconstruction emission source and evaluation emission rate, which include relation database, geoinformation system, satellite photos, regional air transportation models (TROICA- DB / ArcInfo / GoogleMap / NOAA-hysplit or RAMS/HYPACT) is representative for investigation leakage from the gas-oil fields, compressing stations and transportation systems [Safronov and Elansky, 2008].
Local impacts on the atmospheric composition

Fig. 5.2.3. Methane transport from a West Siberian gas field to Trans-Siberian railroad (TROICA-5). Yellow line – the back trajectories to the train points during its moving.

Fig. 5.2.4. The natural gas plume from the place of gas transportation system repairing. (TROICA-7)
5.3. Power transmission lines

The use of the TROICA laboratory showed that it is capable of determining small variations in the concentrations of anthropogenic pollutants in the atmospheric surface layer in spite of its significant natural temporal variability.

The TROICA experiments allowed pioneering measurements of the atmospheric ozone concentration variability in the points where railroad beds intersect power transmission lines (PTLs) [Elansky et al., 2001]. No specific variations in the ozone concentration were revealed under 110-kV PTLs. Passages of the car-observatory under 220- and 500-kV PTLs were associated with ozone concentration peaks rising above the background level by (2.1±0.5) and (2.9±0.6) ppbv, respectively (Fig. 5.3.1). By and large, these peaks are not very high and went beyond the natural ozone concentration variability only slightly. However, first, under conditions of nighttime temperature inversions, such peaks stably exceed the mean deviations in the ozone concentration and, second, these peaks are repeatedly observed when the car-observatory passes under PTLs. If the density of PTLs is rather high, they can influence the ozone concentration over prolonged regions, for example, in West and Central Europe.

The hypothesis on ozone formation as a result of atmospheric charges and on changes in the oxidative activity of the atmosphere along PTLs was tested by using experiments and a numerical photochemical model. Such experiments were performed in the Moscow region on the basis of a specialized autocar that was moving in vicinities of a 500-kV PTL. Concentrations of O3 and of O and NO2 radicals were measured under different seasonal and weather conditions when the autocar traversed zones of PTL location. The mean O3 concentration increase caused by the PTL is equal 2.5±0.5 ppbv, similarly to the effect measured by the railroad observatory.

These results and calculated data on formation of other radicals under the action of corona discharges were applied for estimation of the PTL effect on oxidation of organic pollutants and on the surface-air oxidative ability.

Models for the daytime and nighttime background and polluted conditions were developed. The simulations showed that rather large volumes of ozone can be produced near PTLs as a result of interaction between atomic and molecular oxygen. The hydroxyl radicals produced in the corona discharges promote oxidation of hydrocarbons and other organic substances. It was stated that the content of peroxy-radicals near PTLs is always higher than their background content.

Thus, PTLs represent specific treatment plants, which can be useful within urban areas for purification of polluted air. Ozone generated by PTLs is quickly consumed in the atmospheric redox reactions.

If air in the PTL vicinities is rather pure, an enhanced ozone concentration is stabilized at some constant level. Under the Russian climate, the ozone concentration enhancement in the vicinities of PTLs is not great and it is unlikely that the adverse ozone effect on living organisms is significant. However, PTLs can be harmful for the ecosystems of different regions of South Europe, USA, Japan, and China, where the PTL network is rather dense.
5.4. Plumes from industrial sources

As a tool for monitoring the gaseous and aerosol atmospheric constituents, the mobile laboratory has a number of important advantages over the network of stationary observation stations. For example, the mobile laboratory allows for identification of the concentrations of atmospheric pollutants in sections of industrial plumes with such high resolutions as several tenths of meters along the railroad. A combined analysis of these data and the data of remote measurements of the temperature and wind vertical stratifications in the atmospheric boundary layer gives a possibility for estimation of the gas and aerosol emissions from the local and extended sources. If the laboratory moves along a plume, the processes of photochemical transformation of pollutants and formation of secondary aerosols in polluted air and also the peculiarities and scale of the anthropogenic effect on the environment can be studied.

The TROICA expeditions registered plumes resulted from different anthropogenic and natural sources. Multiple traversing of the areas of cities under conditions of different wind directions allowed for revealing the locations and intensities of transport, industrial, and municipal sources of pollutants.

Fig. 5.4.1 presents an example of correlation between the observed variations in the concentration of pollutants and the calculated plumes from a large-scale source of these pollutants. The Industrial Source Complex Short Term dispersion model was used for the calculations. An analysis of the backward NOAA hysplit 4.8 trajectories at 100, 500, and 1000 m allows for
supposition that the plume source is the copper metallurgic plant that is located near the Pervouralsk city. The plume was calculated with the Pasqual atmospheric stability parameters obtained from the temperature vertical profiles measured in the TROICA expeditions. There is a good coincidence between the regions of the calculated plume and enhanced $\text{SO}_2$ concentration. The use of the observational data and dispersive model allowed estimation of the emis-
Local impacts on the atmospheric composition

The SO\(_2\) emissions for the observation period are equal to 6500 ton/Y.

The measured concentrations of atmospheric constituents in the mesoscale plumes can be effectively used for validation of the disperse and transport-photochemical models. Models RAMS 6.0, MM5 v3, WRF 3.1 (Fig. 5.4.2.) have been tested to construct a meteorological field with a resolution of 10 – 20 km.

Fig. 5.4.3 demonstrates an example of application of these models for explanation of the enhanced SO\(_2\) concentration in the Eastern Siberia near the China boundary. The backward trajectories show that the enhanced SO\(_2\) concentrations observed along the 7700 – 8300 km railroad section are caused by the plume from Harbin industrial objects. The large Harbin power plant is one of these objects.

The plumes from the Harbin power plant have been calculated by the NOAA hysplit dispersion model with the dry and wet deposition taken into account. These plumes are shown in Fig. 5.4.4 for the RAMS, MM5, and WRF meteorological fields. The intercomparison of the plumes calculated for different meteorological fields provides insight into the accuracy requirement. The WRF plume does not cross the railroad, the MM5 plume flows over the railroad, and the RAMS plume stretches along the railroad. The shapes and directions of the plumes vary in time.

In the Fig. 5.4.5 several two-hour-averaged plume sections located along the Trans-Siberian Railroad are presented. These plume sections are calculated for the MM5 meteorological field by the NOAA hysplit dispersion model without consideration of deposition. The Top-Hat Puff approach for the horizontal direction and the Particle approach for the vertical direction in the 0–150 m mixing layer were applied.

Fig. 5.4.5. SO\(_2\) surface concentration relative values measured by the mobile laboratory and averaged over two-hour intervals and calculated for these intervals (black lines) (Harbin plumes, TROICA-9, westward direction)
Researchers and technicians from different countries participated in the TROICA experiments. Due to close cooperation and unification of technical capabilities the obtained results added to our knowledge about atmospheric conditions above North Eurasia. The mobile laboratory is surely to be the basis of the whole work. It was specially developed and constructed for carrying out observations on the network of electrified railroads in the countries of the former Soviet Union.

By January 2009, the TROICA laboratory was equipped with the up-to-date measuring system. Field testing of the laboratory performed in the framework of the TROICA international experiments shows that this laboratory has unique characteristics and offers the following advantages over other Russian means of monitoring the atmospheric gas and aerosol constituents:

1. Wide variety of the parameters can be measured, namely, almost all key gaseous and aerosol pollutants, the radiative and thermodynamic parameters characterizing atmospheric photochemical activity, and the parameters of controlling transport and dry deposition of atmospheric components;

2. Wide range of detectable concentrations from small natural variations of the concentrations of potential pollutants in the non-polluted atmosphere to variations of the concentrations of pollutants under conditions of extreme ecological situations when their critical levels are significantly exceeded;

3. Multifunctionality, namely, the concentrations of atmospheric components, the chemical composition of water, soils, and vegetation bodies, the biological composition of aerosols, natural radioactivity, and some other characteristics are detectable and thus not only the atmospheric composition and parameters can be monitored but also the effects of pollutants on the state of ecosystems and on the environment can be studied;

4. Conformance with the international standards, namely, the instruments applied at the TROICA laboratory are recommended by the WMO GAW, are supplied with international certificates, and undergo regular calibrations and standard validations of their applicability;

5. Universality of the measuring methods used in the moving platform, namely, individual elements of the instrumentation can be transported into other mobile platform or any buildings and installed there as mobile or stationary observation stations, and, in addition, simplified variants of the measuring system and software can be replicated and used for equipping future Russian network stations;

6. On-line functioning, namely, the software allows on-line analysis of the measurements, numerical simulation of photochemical and dynamic processes, prediction of extreme ecological situations, and on-line danger warning on the basis of satellite communications.

Work on further modernization of the TROICA mobile laboratory and its measuring instrumentation is in progress. Several series of observations along the Moscow-Vladivostok, Murmansk-Kislodvsk, Moscow ring, and some other railroads are planned. We anticipate that the TROICA laboratory will be included in the WMO GAW network. Monitoring of the concentrations and emissions of greenhouse gases, which is aimed at management of the Kyoto Protocol, is one of the primary tasks of the modernized TROICA laboratory.

The support of TROICA experiments by the International Science and Technology Center played a very important role. The center united many organizations and made the collaboration very effective. We hope that TROICA experiments will continue and the number of participants will increase.
A large number of institutions participated in the TROICA project. The Max Planck Institute for Chemistry has been the most active and reliable partner of Russian participants of the project for the long-term work. A great assistance in equipping the modern mobile laboratory was rendered by the Earth System Research Laboratory NOAA (ESRL). The close cooperation between the ESRL and the A.M. Obukhov Institute of Atmospheric Physics and recognition of the importance of this project resulted in rewarding of Dr. Prof. N.F. Elansky by the NOAA Environmental Hero Award in 2004.

The organization and performance of the TROICA experiments required a significant financing. It was very important that International Science and Technology Center, Russian Foundation for Basic Research and also INCO-COPERNICUS and INTAS International Programs gave necessary financial support to the project. Creation of the modern mobile laboratory wouldn’t be possible without efficient support from the managers and experts of Russian Ministry of Communications, J.S.C. “Russian Railways” and Russian Research Institute of Railway Transport, namely, V.A. Gapanovich, A.L. Lisitsyn, I.S. Besedin, A.E. Semechkin, V.V. Sevostyanov, V.M. Bogdanov, V.S. Mozgrin and I.V. Bogorodskaya. A great assistance in the organization and performance of the experiments was rendered by the following members of the International Science and Technology Center: W.Gudowski, V.Ya. Rudneva, and E.V. Ryabeva. The benevolence and interest of the collaborators: H. Akimoto, M. Heimann, V-M. Kerminen, M. Kulmala, J. Lelieveld favored the successful performance of the project.

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# Specialized Abbreviations and Acronyms

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ACATS</td>
<td>Airborne Chromatograph for Atmospheric Trace Species</td>
</tr>
<tr>
<td>ADB</td>
<td>Automated Diffusion Battery</td>
</tr>
<tr>
<td>AE</td>
<td>aethalometer</td>
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<tr>
<td>AIS</td>
<td>air ion spectrometer</td>
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<tr>
<td>BC</td>
<td>black carbon</td>
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<tr>
<td>CFC</td>
<td>chlorofluorocarbon</td>
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<tr>
<td>DMPS</td>
<td>Differential Mobility Particle Sizer</td>
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<tr>
<td>EMS</td>
<td>Ecological Monitoring Station</td>
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<tr>
<td>ESRL</td>
<td>Earth System Research Laboratory (NOAA)</td>
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<tr>
<td>FMI</td>
<td>Finnish Meteorological Institute</td>
</tr>
<tr>
<td>FSU</td>
<td>Former Soviet Union</td>
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<tr>
<td>GAW</td>
<td>Global Atmospheric Watch</td>
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<tr>
<td>GOMOS</td>
<td>Global Ozone Monitoring by Occultation of Stars</td>
</tr>
<tr>
<td>GPS</td>
<td>Global Positioning System</td>
</tr>
<tr>
<td>HYPACT</td>
<td>HYbrid PArticle and Concentration Transport Model</td>
</tr>
<tr>
<td>HYSPLIT</td>
<td>HYbrid Single-Particle Lagrangian Integrated Trajectory</td>
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<tr>
<td>IC</td>
<td>ion chromatograph</td>
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<tr>
<td>ICP-MS</td>
<td>Inductively Coupled Plasma Mass Spectrometer</td>
</tr>
<tr>
<td>INTAS</td>
<td>International Association for the promotion of co-operation with scientists from the New Independent States of the former Soviet Union (NIS)</td>
</tr>
<tr>
<td>IPCC</td>
<td>Intergovernmental Panel on Climate Change</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>KRIPC</td>
<td>L.Ya. Karpov Research Institute of Physical Chemistry</td>
</tr>
<tr>
<td>LAS-P</td>
<td>Laser Aerosol Spectrometer</td>
</tr>
<tr>
<td>LC-MS</td>
<td>Liquid Chromatograph Mass Spectrometry</td>
</tr>
<tr>
<td>LLRDM</td>
<td>Low Level Radon Daughters Monitor</td>
</tr>
<tr>
<td>MM5</td>
<td>PSU/NCAR mesoscale model</td>
</tr>
<tr>
<td>MPC</td>
<td>maximum permissible concentrations</td>
</tr>
<tr>
<td>MPIC</td>
<td>Max Planck Institute for Chemistry</td>
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<tr>
<td>MSA</td>
<td>methanesulfonic acid</td>
</tr>
<tr>
<td>MSU</td>
<td>Moscow State University</td>
</tr>
<tr>
<td>MPC</td>
<td>maximum permissible concentrations</td>
</tr>
<tr>
<td>NDAAC</td>
<td>Network for the Detection of Atmospheric Composition Change</td>
</tr>
<tr>
<td>NMHC</td>
<td>nonmethane hydrocarbons</td>
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<tr>
<td>NOAA</td>
<td>National Oceanic and Atmospheric Administration</td>
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<tr>
<td>NWR</td>
<td>Niwot Ridge Station (Colorado, USA)</td>
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<tr>
<td>ODS</td>
<td>ozone-depleting substances</td>
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<tr>
<td>OIAP</td>
<td>A.M. Obukhov Institute of Atmospheric Physics (Moscow, Russia)</td>
</tr>
<tr>
<td>OZA</td>
<td>observation zenith angle</td>
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<tr>
<td>PILS</td>
<td>Particle- into liquid Sampler</td>
</tr>
<tr>
<td>PILS-IC</td>
<td>Particle- into-liquid Sampler equipped with ion chromatographs</td>
</tr>
<tr>
<td>PSDA</td>
<td>Particle Size Distribution Analyzer</td>
</tr>
<tr>
<td>PTLs</td>
<td>power transmission lines</td>
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<tr>
<td>PTR-MS</td>
<td>Proton Transfer Reaction Mass Spectrometer</td>
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<tr>
<td>RAMS</td>
<td>Regional Atmospheric Modeling System</td>
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<tr>
<td>RAS</td>
<td>Russian Academy of Sciences</td>
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<tr>
<td>RRIRT</td>
<td>Russian Research Institute of Railway Transport</td>
</tr>
<tr>
<td>ISTC</td>
<td>International Science and Technology Center</td>
</tr>
<tr>
<td>TCA</td>
<td>trichloroacetic acid</td>
</tr>
<tr>
<td>TOMS</td>
<td>Total Ozone Mapping Spectrometer</td>
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<tr>
<td>TROICA</td>
<td>Transcontinental Observations Into the Chemistry of the Atmosphere</td>
</tr>
<tr>
<td>UH</td>
<td>University of Helsinki</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
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<tr>
<td>VI</td>
<td>virtual impactor</td>
</tr>
<tr>
<td>VIS</td>
<td>visible</td>
</tr>
<tr>
<td>VOC</td>
<td>volatile organic compounds</td>
</tr>
<tr>
<td>WMO</td>
<td>World Meteorological Organisation</td>
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<tr>
<td>WRF</td>
<td>Weather Research and Forecasting Model</td>
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</table>
ISTC is an intergovernmental organization holding diplomatic status, created to prevent nuclear weapons proliferation and to link the demands of international markets with the exceptional pool of scientific talent available in Russian and other Commonwealth of Independent States (CIS) institutes. ISTC was established in 1992 by the European Union, Japan, the Russian Federation, and the United States of America on the basis of a multinational agreement. Norway and the Republic of Korea are signatories to the agreement, and Canada joined as a full Governing Board member in 2004.

Based in Moscow, Russia, but with Branch offices in 6 other countries, ISTC’s core activity is associated with the development of international science projects. Since 1994, ISTC has managed financial support exceeding US$ 820 M to 2,660 projects, encompassing over 71,000 scientists and technicians at more than 980 institutes in Russia and CIS. ISTC also provides a project management, and tax and customs-duty exempt mechanism for its 390 commercial and governmental agency Partners choosing to fund research with ISTC beneficiary institutes.

ISTC has established strategic partnerships with Russian and CIS innovation foundations and organizations, has engaged in technology transfer using its internationally agreed procedures, and has assisted a broad range of other international institutions, government organizations, business schools, legal companies, foundations, and investors to deliver their R&D and commercialization objectives.

ISTC operates a Partner Program to assist private companies, government agencies and non-governmental organizations to partner with highly skilled Russian and CIS scientists and R&D project teams. The Program offers:

- Cost free technology-demand matchmaking
- Moderate R&D costs
- Experienced project management
- Tax-free payments to project teams and scientists via ISTC
- Customs and duty-free imports of equipment via ISTC
- Intellectual Property Rights (IPR) integral to Projects

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