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MAJOR CONCERNS AND RESEARCH NEEDS FOR OUR UNDERSTANDING OF THE CHEMISTRY OF THE ATMOSPHERE

(Technical Report)

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Major concerns and research needs for our understanding of the chemistry of the atmosphere (Technical Report)

Synopsis. Inputs of a questionnaire survey classified under global, regional/urban, and indoor/workplace are presented. Major concerns and research needs for our understanding of the chemistry of the atmosphere are identified together with suggestions for IUPAC's role expected in each of the three fields.

Introduction

The scope of the interest of the chemists studying the atmosphere has been broadened significantly in recent years since they realized that chemists should and could play a central role in the research for global-scale atmospheric change in addition to regional- and urban-scale, and indoor and workplace air pollution. IUPAC Commission on Atmospheric Chemistry judged that it is timely and worthwhile to identify " Major Concerns and Research Needs for Our Understanding of the Chemistry of the Atmosphere " at this point in time, and adopted it as a project. This document was prepared as an output for the project.

The survey was made by sending a questionnaire to the Commission Members and their inputs were organized and classified so as to clarify the points of major concerns and research needs for our understanding of the chemistry of the atmosphere in each scale of global, regional / urban, and indoor / workplace. In hope that this Commission could find a way to play a role in facilitating researches in the chemistry of the atmosphere in an international perspective, this document also contains suggestions for expected IUPAC's role in each field of the concerned research.

I. Global

1. Global Climate Change

<u>Major Concerns</u> It is widely thought that changes in the chemical composition of the earth's atmosphere are capable of inducing changes in the earth's climate through influences on the longwave transmittance of the atmosphere by increased concentration of infrared absorbing gases, and through influences by aerosol particles on the shortwave reflectivity of the planet and on cloud microphysical properties. The processes controlling the loading and distribution of trace gases and aerosol particles in the atmosphere must be understood to permit confident formulation of policies to mitigate such chemically induced climate changes. Additionally, there are indications that such composition changes may be influencing the oxidizing capacity of the earth's atmosphere. Although generally increasing trends of CO_2, CH_4, N_2O and CFCs are well documented, precise measurements of CO_2 and CH_4 concentrations indicate that the rate of increase is not uniform year-to-year. This implies some interaction between climate and source and/or sink rates.

Research Needs Atmospheric concentrations of trace gases should be measured accurately, including spatial distributions and temporal trends, to provide data that will constrain models of source and sink processes that will lead to an understanding of feedback mechanisms relating climate and atmospheric composition. A network of aerosol monitoring stations covering much of the troposphere should be established.

Natural and anthropogenic sources and emissions should be quantified more precisely, and worldwide inventories of the trace gas emissions in each country should be made. Laboratory studies of the rates, branching ratios and photodissociation channels of atmospheric reactions of trace gases are important. Better information on the infrared spectra of the trace gases in the atmosphere, including the temperature dependence of the absorption cross sections, should be very valuable. Improved understanding is required of the sources, sinks, and chemical, microphysical and optical properties of atmospheric aerosols, especially anthropogenic aerosols.

More sophisticated climate models need to be developed which allow more accurate estimation of the magnitude of global warming expected for various emission scenarios of infrared absorbing gases. Climate-chemistry interactions should be studied by two- and three-dimensional models in order to understand the influence of climate change on the oxidizing capacity of the earth's atmosphere.

IUPAC's Role Compilation of current information on the absorption cross sections of trace gases in the atmosphere should be IUPAC's role. IUPAC should facilitate development of measurement protocols to be adhered to by participants in a global aerosol monitoring network. Education of the public and the dissemination of the information by preparing documents should be an important IUPAC activity.

2. Stratospheric Ozone Depletion

Major concerns Depletion of stratospheric ozone both in the polar and non-polar regions except for tropics is well documented. It is well established that the polar ozone depletion is mainly caused by the ozone-destroying chain reaction of chlorine which is ascribed to anthropogenically emitted CFCs. It is generally thought that heterogeneous chemistry plays an important role not only in polar stratospheric clouds (PSCs) in the polar region but in or on other aerosol particulates characteristic of stratosphere in the non-polar region. In addition to CFCs, many other trace gases with long enough lifetimes to reach stratosphere cause ozone change either directly by involvement in the chemical chain reaction or indirectly through causing the change in stratospheric temperature. The development of alternative compounds to CFCs and the evaluation of the alternatives and other potential ozone destroying compounds with respect to the influence on the ozone layer is of much concern.

Research Needs Although a global network for ozone trend observation is well implemented in the mid- and high-latitudes in the northern hemisphere, monitoring sites are still scare in the sub-tropical and tropical regions and in the southern hemisphere, and need to be intensified. The observation of all key radicals predicted to be important in controlling stratospheric ozone is of particular significance to evaluate theoretical prediction, and new instruments for this purpose await further development.

Photochemical reactions under stratospheric conditions and OH radical reactions of halocarbons and their substituents need to be studied. The products of the reaction of OH with HCFCs their atmospheric reactions and their ultimate fate need to be determined. Heterogeneous reactions on aerosol particulates characteristic of the stratosphere need to be studied and quantified. Stratospheric reactions of bromine and fluorine containing species need further research.

Prediction of ozone change from the combined effects of changes in CFCs, N_2O, CH_4 and CO_2 is an important research subject and needs to be explored. To this end, better understanding of the role of PSCs and stratospheric aerosols in heterogeneous chemistry of ozone depletion is needed. The coupling of ozone depletion and global climate change should be studied using global circulation models.

Better worldwide emission inventories of anthropogenic halocarbons are needed for each country as well as measurement of emission fluxes of natural organohalogens containing chlorine and bromine. The development of alternative CFC compounds for use in refrigeration, propellants, etc., which have low potential for ozone destruction, is of immediate necessity as is the study of the atmospheric chemistry of these compounds and their reaction products. In addition a better understanding of the atmospheric cycles of natural organohalogens is needed.

IUPAC's Role IUPAC should encourage the establishment of a global monitoring network for ozone and trace gases. Working through our Atmospheric Commission Members and National Representatives, IUPAC should obtain current information on production rate of halocarbons in each country and review our understanding of the emissions of halocarbons. Organizing an international workshop and reviewing the methods of estimation of the ozone-reducing potential of halocarbons would be IUPAC's role.

II. Regional / Urban

1. Tropospheric Ozone Increase

Major Concerns The increase of tropospheric ozone in northern hemisphere has been fairly well documented based on long-term observation data at remote monitoring stations. Reflecting the relatively short lifetime of ozone and the importance of regional scale photochemistry in the build-up of ozone, the rate of increase of tropospheric ozone is not uniform either spatially or temporally. Since the background ozone level in the remote area of the northern hemisphere has often reached as high as 30-50 ppb, it tends to push up oxidant levels of urban and suburban photochemical air pollution, which is a major concern from the point of both health and ecological effects. Further increase of tropospheric ozone may be caused by the enhanced UV radiation due to stratospheric ozone destruction. Tropospheric ozone levels and distributions may also be affected by global climate change. Oxidizing capacity of the earth's atmosphere would have been and will be changed by the tropospheric ozone change.

Research Needs The world-wide, long-term monitoring and compilation of data on surface level ozone is necessary to established the global trend and to anticipate the effects on ecosystems. There is an absolute need for the long-term change of the vertical profile data including both in the boundary layer and free troposphere in order to understand the mechanism of ozone increase. More complete coverage of measurement stations particularly in the tropics and the southern hemisphere is needed for obtaining a global picture of the tropospheric ozone increase.

Accurate emission inventories of precursors to ozone generation including both natural and anthropogenic emissions of hydrocarbons, NO_x and CO are needed. Projection of future anthropogenic emissions of these compounds is important for constructing scenarios for the use of the model prediction of future trends of tropospheric ozone. There are significant research needs in the reproduction and prediction of tropospheric ozone build-up by the application of three dimensional models on regional and global scales. Tropospheric ozone increase caused by enhanced UV radiation due to stratospheric ozone depletion and global climate change should also be evaluated.

IUPAC's Role IUPAC should support WMO in ensuring that the ozone network is maintained and enhanced and is conducted with adequate quality assurance and quality control. IUPAC should also conduct or cosponsor workshops on the measurement and atmospheric chemistry of tropospheric ozone.

2. Tropospheric Short-lived Trace Gases and Oxidizing Capacity

Major Concerns Short-lived trace gases such as CO, hydrocarbons, and NO_x are of concern from the view of their impacts on ozone formation both in the urban and regional scale, and on the oxidizing capacity of the atmosphere which is mostly determined by the OH radical concentration. The oxidizing capacity of the troposphere determines atmospheric lifetimes of most of trace gases including important infrared-absorbing and ozone-destroying gases such as CH_4, HCFC, CH_3B_r, etc. Quantitative discussion on sources and sinks, and biogeochemical cycling of most of naturally originated gases requires the knowledge of the oxidizing consumption rates as well as oxidation products.

Research Needs Measurement networks which utilize modern unambiguous instrumentation for the detection of key trace gases and which provide information on the atmospheric concentration over long periods of time need to be developed. Data formatting, storage and access has to be standardized to allow the scientific community to utilize such information. Continuing development and deployment of instruments for measuring free radicals, especially OH and HO_2, are needed as well as the development of measuring techniques for partially oxidized products of hydrocarbons. Further, because of the great importance of the NO_x chemistry in the formation of tropospheric ozone, the NO_x transformation products such as gaseous nitric acid, peroxyacetyl nitrate and other organic nitrate should be monitored in both urban and clean atmospheres. An accurate inventory of emissions of CO, hydrocarbons and NO_x from fossil fuel use and natural sources is needed. Particularly, tropical biomass burning as a source of these gases requires the study of their emission factors and the impact on atmospheric chemistry.

In order to define the fates and lifetimes of the tropospheric trace gases, atmospheric reaction mechanisms of hydrocarbons and their oxidation products should be investigated further in the laboratory. In particular, the oxidation chemistry of terpenes and aromatic hydrocarbons needs further study. There are also research needs for measurements of the absorption cross sections and the photochemical pathways of dissociation of the various trace gases including many hydrocarbon oxidation products. Evaluation and testing of present simplified chemical and transport regional models are necessary. Further, inclusion of chemistry models involving short-lived trace gases into three dimensional models is required for evaluating the global oxidizing capacity of the earth's atmosphere.

IUPAC's Role Evaluation of current instrumentation employed in measurement networks and recommendation for the best instrumentation would be a role of IUPAC. Compilation of evaluated rate constants required for the regional and urban photochemical models should be a task of IUPAC.

3. Aerosol Chemistry

Major Concerns In many areas of the developed and developing world, the concentration of tropospheric aerosols has increased to levels significantly affecting the environment in various aspects. Reducing the amount of solar radiation reaching the ground has the potential for important effects on climate by reducing ground temperature, and increasing cloud albedo and stability, which result in global cooling. Increased aerosols in the boundary layer reduce visibility, and have important effects on human health leading to respiratory diseases by inhalation and to rickets due to inadequate sunlight for the production of vitamin D. Reduced solar radiation and changes in atmospheric stability has important effects on atmospheric photochemistry and modeling.

Research Needs As for aerosol sampling, the conversion of gaseous SO_2 and HNO_3 to sulfate and nitrate, respectively, during sampling, and the evaporation of semi-volatile components such as organic compounds and NH_4NO_3 during and after sampling needs further investigation. New instrumental techniques are needed to monitor the vertical distribution of aerosols worldwide. Collection and analysis of atmospheric aerosol data are needed on a global basis to clarify concentration, size distribution, optical properties and elemental and molecular composition.

Comparing with information on inorganic aerosols, our knowledge of the composition of the organic fraction associated with atmospheric particles is insufficient. Quantification of organic components of aerosols should be explored.

IUPAC's Role Evaluation of current understanding of the role of aerosols in the chemistry of the atmosphere and evaluation of possible sources of the observed aerosol components should be an IUPAC's role.

4. Acid deposition

Major Concerns Acid deposition is a well documented environmental issue both in Europe and North America. Although acid deposition in Asia has not been widely known, it is also of serious concern in China and other countries in East Asia. It is well established that sulfur dioxide and nitrogen oxides are precursors to acids which mainly consist of sulfuric acid and nitric acid. Importance of organic acids is usually marginal in the acid rain in temperate and boreal regions but is known to increase in tropics. It is generally thought that both wet and dry deposition are important as processes of acid deposition. The processes controlling oxidation of nitrogen oxides is believed to be mainly homogeneous gas phase reaction, whereas liquid phase reaction is thought to be important as well in the case of sulfur dioxide.

Research Needs Although international networks for observation of acid deposition has been well developed in Europe and North America, such a network system has not been developed yet in Asia and other part of the world, and needs to be intensified. Particularly, standardization of monitoring techniques for acidic species with quality control and assurance is required for making international comparison of data possible. New instrumental techniques are needed to monitor dry deposition rates since it is general estimated by aerosol loading multiplied by dry deposition velocity which is not necessarily well established.

As compared to the fairly well established gas phase oxidation mechanism to form acids, processes involving liquid phase need further research. In order to quantify the reaction processes related to acid species, measurement of the Henry's Law constants for the various trace gases and determination of the gas-liquid transfer coefficients are necessary. Liquid phase radical reactions, and reaction mechanisms for the aqueous phase chemistry in clouds, and the associated rate constants need to be studied. The role of aerosols in chemical reactions including acids and oxidants has to be evaluated by studying the chemical mechanism of in-cloud and below-cloud scavenging. Laboratory experiments on cloud chemistry with wind tunnels and cloud chambers are also important to clarify atmospheric processes taking place inside clouds. The rate of dry deposition of the various atmospheric species needs to be determined more accurately.

Contribution of natural sources of sulfur, nitrogen and hydrocarbon compounds to acid deposition should be evaluated based on accurate measurements and emission inventories of precursors to sulfuric acid, nitric acid and organic acids. Development of a simplified model for describing acidification in cloud, fog and rain drops is needed as well as cloud models linking gas and liquid phase chemistry. In order to evaluate health and environmental impacts of acid rain, acid aerosols and acid gases, the establishment of exposure-effect relations for human health and ecological effects, and the development of integrated long range transport, deposition, and effect models are necessary.

IUPAC's Role IUPAC could play a role in standardization of acid deposition monitoring techniques and data archiving in the newly developed acid deposition monitoring networks in Asia and other developing part of the world. Evaluation of the knowledge on atmosphere-surface chemistry in relation to dry deposition should be reviewed by IUPAC.

III. Indoor / Workplace

Major Concerns Regulations and standards on workplace air quality are well-established at a national level as far as gases are concerned and there are significant moves toward harmonization of these standards. Regulations and standards on indoor air quality are also well developed, and exist in many countries. The quantification of chemical species relevant to workplace air quality is very important and there is a major concern in the development of analytical methods.

For the quantification of chemical species relevant to workplace air quality, the development of analytical method based on gas-chromatograph-mass spectrometry (GC-MS) and other techniques should be explored. There is also a need for monitoring dust, microorganism and allergenic compounds. In this respect, not only the concentration has to be determined but also the identification of the compounds is of critical importance.

Research Needs While the regulations and standards on indoor air quality exist in many countries, standarized methodology of the measurement of air quality is lacking and there are major needs for progress on standardized sampling strategy, measurement methodology, and quality control. In particular, most available measurement methods are expensive and technically complex, and there is a need for simpler, more cost-effective methods especially for developing countries. Diffusive sampling is a particularly attractive alternative to conventional active sampling in providing a more cost-effective solution. There remains significant research needs in the area of the theory of diffusional sampling through finite beds, and the calculation of sampling rates for non-ideal solvents.

IUPAC's Role Moves towards a standardization of measurement strategy and performance characteristics of methods are being actively promoted in Technical Committee of European Committee for Standardization (CEN/TC). Alongside these specific developments, IUPAC should promote further developments of diffusive sampling and air quality regulations at an international level.

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