INTERNATIONAL COOPERATION AND SOME RESEARCH NEEDS TO IMPROVE OUR UNDERSTANDING OF THE CHEMISTRY OF THE ATMOSPHERE

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THE CHEMISTRY OF THE ATMOSPHERE:

ITS IMPACT ON GLOBAL CHANGE

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As is known, CHEMRAWN is the acronym for Chemical Research Applied to World Needs. The purposes of IUPAC CHEMRAWN Conferences are indentifying and supporting basic and applied research that help to solve global human problems.

Among many global needs which the mankind has recognized by the end of the 20th century, the most important one is the need for sustainable development in a situation when population is growing, natural non-renewable resources becoming more and more limited, environmental degradation more and more visible and dangerous. The cumulative impact of the mankind's activities has reached a point where the life on Planet Earth is at risk in connection with global environmental changes.

This is the reason why the United Nations decided to convene in June 1992 a special UN Conference on Environment and Development (UNCED) in order to analyse the international collaboration concerning global changes and to work out a programme of actions for the 21st century based on the scientific approach (AGENDA-21).

Among other important topics, the UNCED will pay attention to the protection of the atmosphere with the emphasis on the greenhouse effect, ozone layer depletion and transboundary air pollution.

So, the CHEMRAWN-VII Conference "The Chemistry of the Atmosphere: Its Impact on Global Change" may be considered as a part of the preparatory work of the world chemical community for the UN Conference.

In the frame of the preparatory work to the UNCED, the International Union of Pure and Applied Chemistry has also launched a broader mission-oriented Programme on Chemistry and Environment [1]. We are now studying possible liaisons of this programme with other international programmes and trying to recognize the areas which are not sufficiently covered by the existing programmes relating to the chemical aspects of environmental pollution.

Environmental problems including atmospheric pollution have been attracting attention of the United Nations since the 1970s. Their anxiety on the state of the atmosphere is illustrated in particular by the documents in Table 1.

The current UN activity in this area is concentrated on three main aspects of the atmospheric pollution:

= estimating the effects of increasing concentrations of greenhouse gases on the Earth's climate and recognizing the ways how to avoid possible negative consequences;

= supporting monitoring and developing recommendations how to keep "ozone umbrella" against the dangerous ultraviolet radiation:

= developing recommendations and coming up to an agreement how to prevent acid rains.

The UNCED Preparatory Committee has presented at its 3rd session (August 1991) a set of documents with the analysis of:

= interrelations between air pollution, ozone layer depletion and climate changes [3],

= existing systems of monitoring transboundary air pollution and basis for international actions [4],

= recent scientific findings on ozone depletion and basis for international actions [5],

= probable consequences of climate change [3,6],

= possible ways of restructuring systems of energy production and using, and of transport sector (as the key sources of atmospheric problems and climate change) in accordance with the requirements of sustainbale development [3],

Table 1

International Agreement in the Field of Atmosphere Protection [2]

- Convention on Long-Range Transboundary Air Pollution, Geneva, 1979.
  = Protocol to the 1979 Geneva Convention. Long-Term Financing of the Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe (EMEP), Geneva, 1984.

  = Protocol to the 1979 Geneva Convention. Reduction of Sulphur Emissions or their Transboundary Fluxes by at least 30 per cent, Helsinki, 1985.

  = Protocol to the 1979 Geneva Convention. Control of Emission of Nitrogen Oxides or their Transboundary Fluxes, Sofia, 1988*.

- Vienna Convention for the Protection of Ozone Layer, Vienna, 1985
  = Montreal Protocol on Substances that Deplete the Ozone Layer, Montreal, 1987.

  = Amendment to the Montreal Protocol on Substances that Deplete the Ozone Layer, London, 1990.

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*)There exists the 1991 draft protocol on volatile organic compounds

= most important goals that rise from the preceding item for the AGENDA-21 (agenda of science for environment and development in the 21st century) [7].

The above mentioned global aspects of atmospheric pollution are fundamental for many existing international programmes [8], including the International Global Atmospheric Chemistry (IGAC) Programme [8,9]. This programme is a core project of the well known International Geosphere·Biosphere Programme (IGBP) established by ICSU in 1986 and seeks to understand quantitatively the chemical and physical processes that determine the atmospheric composition. The structure of the IGAC Programme is shown in Table 2. It is mainly based on the earlier created programme of the International Association of Meteorology and Atmospheric Physics and partly overlaps with SCOPE project on Trace Gas Exchange between Biosphere and Atmosphere.

In many cases the IGAC Programme will be built on the existing national programmes. This explains a regional character of the main part of the projects.

Very close to the IGAC Programme is the Stratosphere-Troposphere Interactions and Biosphere (STIB) Programme [8]. Its structure is shown in Table 3.

If we now look at the agenda of the CHEMRAWN-VII Conference, we will see that it corresponds to the well recognized global problems of atmospheric pollution which are considered through the prism of chemical science. The chemistry as a scientific branch of knowledge is concentrated in this case on photochemically induced free radical reactions in which quite simple species such as molecules of oxygen, ozone, nitrogen and sulphur oxides, chlorofluorocarbons are involved. Many of corresponding elementary reactions are or can be well studied but their combination in the open dynamic system of the atmosphere leads to many difficulties and uncertainties in the estimation of global results.

Table 2

Structure of the IGAC Programme

I. Natural Variability and Anthropogenic Perturbations of the Marine Atmosphere:

- North Atlantic Regional Study,
- Marine Aerosol and Gas Exchange-Interaction with Atmospheric Chemistry and Climate,
- East-Asian-North Pacific Regional Study.

II. Natural Variability and Anthropogenic Perturbations of Tropical Atmospheric Chemistry:

- Biosphere-Atmosphere Trace Gas Exchange in the Tropics,
- Deposition of Biogeochemically Important Trace Species,
- Impact of Tropical Biomass Burning on Atmospheric Chemistry and Biogeochemical Cycles,
- Chemical Transformations in Tropical Atmosphere and Their Interaction with Biosphere,
- Rice Cultivation and Release of CH_4 and N_2O.

III. The Role of Polar Regions in Changing Atmosphere Composition:

- Polar Atmospheric Chemistry,
- Polar Air-Snow Experiment.

IV. The Role of Boreal Regions in Biosphere-Atmosphere Interaction:

- High-Latitude Ecosystems as Sources and Sinks of Trace Gases and their Sensitivity to Environmental Distribution.

V. Trace Gas Fluxes in Mid-Latitude Ecosystems.

VI. Global Distributions, Transformations, Trends and Modelling:

- Global Tropospheric Ozone Network,
- Global Atmospheric Chemistry Survey,
- Development of Global Emission Inventories.

VII. Cloud Condensation Nuclei as Controllers of Cloud Properties.

VIII. Intercalibration/Intercomparison.

Table 3

Structure of the STIB Programme

I. Stratospheric Changes and the Penetration of UV-Radiation

II. Stratosphere-Troposphere Exchange

III. Anthropogenic Trends and Natural Variability

IV. Stratospheric Aerosols and their Climate Effects

V. The Impact of Stratospheric Changes on Climate

I will not further regard the main problems of global changes and their causes. Instead I would like to draw attention to other important aspects of chemical pollution of the atmosphere which in my opinion introduce some additional complications and are not enough covered by international programmes and projects.

The atmosphere of the Earth is a life-supporting and life-protecting system. But in our days it has also turned into a reservoir for many of by-products of the human activity. This reservoir is simultaneously playing the role of a flow reactor for chemical transformation of pollutants, and the role of a transport system for delivering pollutants and products of their transformation, many of which are harmful, to sensitive parts of the ecosystems.

So, we should take into consideration not only a change of protecting properties of the atmosphere ("green house" effect, destroying "ozone umbrella") but also the distribution of various harmful substances and products of their transformation through the atmospheric channels. In the second direction the most part of international efforts are directed to the acid rains and their origins.

But we should not forget other dangerous groups of pollutants. Among them are metals.

There exists a danger of poisoning the biosphere by global metal pollution [10,11]. This type of pollution involves not only soil and aquatic systems but also the atmosphere. Tables 4 and 5 give a general picture of trace metals emissions from natural and anthropogenic sources to the atmosphere. As is seen from these data, the anthropogenic emissions have become dominantly responsible for the most trace elements in the atmosphere. Anthropogenic emissions of lead, cadmium, vanadium and zinc exceed the fluxes from natural sources by 28-, 5-, 3- and 3-fold, respectively. Industrial contribution of arsenic, copper, mercury, nickel and

Table 4

WORLDWIDE EMISSIONS OF TRACE METALS FROM NATURAL SOURCES TO THE ATMOSPHERE (thousand tonnes per year) [10]

Elements	Wind-borne soil particles	Sea salt spray	Volcanoes	Forest fires	Biogenic sources	Total
Antimony	0,78	0,56	0,71	0,22	0,29	2,6
Arsenic	2,6	1,7	3,8	0,19	3,9	12
Cadmium	0,21	0,06	0,82	0,11	0,24	1,4
Chromium	27	0,07	15	0,09	1,1	43
Cobalt	4,1	0,07	0,96	0,31	0,66	6,1
Copper	8,0	3,6	9,4	3,8	3,3	28
Lead	3,9	1,4	3,3	1,9	1,7	12
Manganese	221	0,86	42	23	30	317
Mercury	0,05	0,02	1,0	0,02	1,4	2,5
Molybdenum	1,3	0,22	0,40	0,57	0,54	3,0
Nickel	11	1,3	14	2,3	0,73	29
Selenium	0,18	0,55	0,95	0,26	8,4	10
Vanadium	16	3,1	5,6	1,8	1,2	28
Zinc	19	0,44	9,6	7,6	8,1	45

Table 5

WORLDWIDE EMISSIONS OF TRACE METALS FROM ANTHROPOGENIC SOURCES TO THE ATMOSPHERE (thousand tonnes per year) [10]

Elements	Mining + smelting and refining	Manufacturing processes + commercial uses[a)]	Energy production	Waste incineration	Total
Antimony	0,10+1,42	...	1,30	0,67	3,5
Arsenic	0,06+12,3	1,95+2,02	2,22	0,31	19
Cadmium	... +5,43	0,60+...	0,79	0,75	7,6
Chromium	...	17,0+...	12,7	0,84	31
Copper	0,42+23,2	2,01+...	8,04	1,58	35
Lead	2,55+46,5	15,7+4,50	12,7[b)]	2,37	332
Manganese	0,62+2,55	14,7+...	12,1	8,26	38
Mercury	... +0,13	...	2,26	1,16	3,6
Nickel	0,80+3,99	4,47+...	42,0	0,35	52
Selenium	0,16+2,18	...	3,85	0,11	6,3
Thalium	...	4,01+...	1,13	...	5,1
Tin	... +1,06	...	3,27	0,81	5,1
Vanadium	... +0,06	0,74+...	84,0	1,15	86
Zinc	0,46+72,0	33,4+3,25	16,8	5,90	132

a: Including agricultural use

b: + 248 thousand tonnes for transportation antimony amounts 100 to 200 percent of the emissions from natural sources.

Of cource, there are some uncertainties in the estimation of global emissions of heavy metals in the atmosphere (cf. Table 6) due to large amounts of natural and anthropogenic sources with the different and in some cases variable level of emission, but general conclusions are reliable.

The International Institute for Applied Systems Analysis has emphasized:"As with acid pollutants, atmospheric emissions of heavy metals are an international problem, often travelling 1000 or 1500 kilometres before deposition" [12].

The problem is really international, but at the same time a coordinated international heavy metals monitoring programme is not yet launched. We can judge it using the data of Table 7 on the number and location of the WMO GAW stations [4].

The global WMO Background Air Pollution Monitoring Network (BAPMoN) run by WMO and UNEP has traced long-range transboundary air pollution since 1968 and has provided most of the atmospheric data to the UNEP Global Environment Monitoring System (GEMS). Together with the Global Ozone Observing System, it is now a part of the WMO Global Atmosphere Watch (GAW), which operates a network of 337 stations in 78 countries altogether [4].

The well developed Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) in its fifth-phase projects (1990-92) includes gas particles measurements of SO_2, $SO_4^{=}$, NO_2, O_3, NO_3^-, NH_3, NH_4^+, NHO_3 and precipitation measurements of pH, $SO_4^{=}$, NO_3^-, Cl^-, NH_4^+, K, Na, Mg, Ca. But the measurements of heavy metals are still in the stage of planning.

Efforts are now underway to develop global inventories under an atmospheric chemistry project within the International Geosphere-Biosphere Programme of the ICSU [4,8].

Table 6

COMPARISON OF TOTAL EMISSIONS OF TRACE METALS IN THE ATMOSPHERE ACCORDING TO TWO RECENT REVIEWS (thousand tonnes per year)

Element	Sources			
	natural[10]	anthropogenic[10]	natural[11][a]	anthropogenic[11][a]
Antimony	2,6	3,5	1(0,5-1,8)	24 (18-38)
Arsenic	12	19	8(3 -13)	40 (25-80)
Cadmium	1,4	7,6	1(0,3-7)	7,7(5,5-11)
Chromium	43	31	60(44-130)	50(21-94)
Copper	28	35	20(18-22)	140(56-260)
Lead	12	332	27(4-45)	425(300-470)
Manganese	317	38	600(516-750)	215(107-320)
Mercury	2,5	3,6	20(2,5-150)	6(1,7-11)
Nickel	29	52	27(8,5-54)	80(43-98)
Selenium	10	6,3	10(6-14)	7(1,1-11,7)
Vanadium	28	86	65(40-79)	170(110-210)
Zinc	45	132	90(36-200)	500(315-840)

a. Values in parentheses indicate a spread of data of various authors

Table 7

GAW STATIONS [4]

(by 31 December 1990)

Parameters measured	Regions							
	Africa	Asia	South America	North and Central America	Pacific (SW)	Europe	Antarctic	All regions
Precipitation chemistry	14	17	7	41	14	74	1	168
Particles	8	5	2	11	20	33	1	80
Sulphur dioxide	1	1	1	-	2	28	-	34
Oxides of Nitrogen	-	1	-	1	4	20	9	28
Carbon dioxide	4	1	1	14	6	12	2	40
Ozone	9	43	5	17	11	49	7	141
Heavy metals	-	-	-	-	-	4	-	4

The worldwide contamination of the environment (air, water and soils) with toxic metals (especially with Pb, Cd, Hg, As) is a matter of concern. In many urban areas and around some point sources the natural emissions are insignificant in comparison with the anthropogenic metal pollution. The influence of heavy metals on human health is usually considered from the point of view of acute rather than chronic effects. In the situation of our days the long-term effects of exposing human populations to small doses of toxic metals in the environment should receive adequate attention. The reliable information for the estimation of postponed effects of small doses of toxic elements can be obtained through the medical survey of population (including the genetic level) in the regions of geochemical anomalies, characterized by the high content of some heavy metals, with the simultaneous investigation of surrounding ecosystems, taking into account some heavy metals tendency to accumulate in components of ecosystems. Therefore it is believed that launching joint projects of this type by the WHO, UNEP (programmes "Biogeochemical Cycles" and "Health and Toxicology") and IUPAC will be very important for understanding a scale of hazard.

The main sources of heavy metals pollution of the biosphere including atmosphere are connected with mining, smelting and refining in non-ferrous metallurgy, with energy production and transport sector (exhaust gases of cars and trucks, burning leaded gasoline).

The most important way to preclude anthropogenic changes of the atmosphere is the reduction of the emission of harmful chemical substances by industry, energetics, transport and municipal utilities. Introducing some international restrictions on the emission is demonstrated by the above mentioned conventions and protocols. Of course this way should be supported by vast technological changes in the area of production. Therefore a conjugated giant problem emerges - how to develop industry in the context of a new vision of future in connection with environmental problems, in the context of sustainable development of our civilization.

This is the reason why the next CHEMRAWN-VIII Conference will be devoted to Chemistry and Sustainable Development (sub-heading - Towards a Clean Environment, Zero Waste and Highest Energy Efficiency).

The toxic effects of heavy metals is one side of the problem of global environmental pollution, including atmospheric, by trace metals. Another side - a catalytic effect of many metals has direct relation to the chemistry of the atmosphere. The role of catalysis in the atmospheric chemistry is an area that is open for fruitful international scientific collaboration. The same is related to the more general area - to the investigation of the role of aerosols and heterogeneous processes in the chemistry of the atmosphere [13] (N 11,p.1729).

Another important direction of international activity seems to be the creation of kinetic data bases for adsorption processes, gas-phase and surface reactions, photochemical transformations. The IUPAC Commission on Chemical Kinetics (former Chairman Prof.E.T.Denisov, now - Dr.J.T.Herron) is trying to join efforts of specialists of many countries in this direction. In April 1991 the special international workshop "Databases in Chemical Kinetics" was held in Novosibirsk and discussed the situation in this area.

Databases on chemical kinetics are very important for developing mathematical models of chemical processes in the atmosphere [13] (N 10, p.1627, N 11, p.1757).

It is my pleasure as the editor-in-chief of the Russian review journal "Uspekhi Chimii" (Advances in Chemistry) to inform you that after we had decided to devote two issues of this journal to the chemistry of the atmosphere, a group of specialists invited by Prof.Yu.N.Molin covered, among others; almost all of the above mentioned "hot" areas by prepared papers [13].

Now I would like to return to the IUPAC Chemistry and the Environment Programme and to put a question - what is being done and what can be done under the aegis of the IUPAC in relation to the chemistry of the atmoshere?

First of all, it is necessary to stress the importance of this CHEMRAWN-VII Conference that should additionally stimulate international collaboration in many discussed areas. The recommendations that will be developed by the Future Action Committee will serve as a guide in this joint work.

A list of ongoing IUPAC projects relating to the problem under discussion is given in Table 8.

The projects of Section I and partly Section II are coordinated by the Commission on Atmospheric Chemistry (the former Chairman Prof.J.G.Calvert, now - Dr.J.Slanina), of Section III - by the Sub-Committee on Gas Kinetic Data Evaluation for Atmospheric Chemistry (Chairman Prof.J.A.Kerr) and of Section IV - by the Commission on Environmental Analytical Chemistry (Chairman Dr.J.Buffle).

I would like to draw attention mainly to Sections I and IV.

The workshop organized in July 1990 by the Commission on Atmospheric Chemistry on the assessment of uncertainties in the projected concentrations of carbon dioxide in the atmosphere demonstrated that the predictions of trends in increasing radiatively active gases and their greenhouse effect are subject to a large margin of uncertainty [14] (cf.[15]). The participants of this workshop identified most important causes for the uncertainty in the projection of future carbon dioxide concentrations and proposed corresponding recommendations for future research.

The methodological consistency of potential global change assessment is very important, taking into account the possible scale of the economical and social response to be required. Therefore the scientific community should pay adequate attention to the analysis of all basic data and models

Table 8

IUPAC Projects Relating to the Chemistry of the Atmosphere

I. Analysis of Situation and Methodological Aspects

= Compendium of Agencies, Institutes and Ongoing Activities in the Field of Atmospheric Chemistry

= Inventory of Regulations for Emissions and Standards on Ambient and Workplace Atmosphere

= Inventory of Current Tropospheric Sampling Programmes, PAC, 62, N 1, 163-176 (1990)

= Evaluation and Harmonization of Current Tropospheric Sampling Networks Worldwide

= Assessment of Uncertainties in the Projected Concentration of the Carbon Dioxide in the Atmosphere, PAC, 63, N 5, 764-796 (1991)

= Inventory of Missing Emission Data Necessary to Evaluate Global Atmospheric Changes

= The Use of Passive Samplers for Monitoring Atmospheric Constituents

= Major Concerns and Research Needs for our Understading of the Chemistry of the Atmosphere

II. Nomenclature and Units

= Glossary of Atmospheric Chemistry Terms, PAC, 62, N 11, 2167-2219 (1990)

= Glossary of Terms Used in Environmental Analytical Chemistry

= Evaluation and Recommendation of Units for Use in Atmospheric Chemistry

III. Kinetic Data

= Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry, J.Phys.Chem.Reference Data, 18, 881-1087 (1989)

= Kinetic Data Evaluation for Application in Modelling Studies of Global Atmospheric Chemistry

IV. Characterization, Transport and Reactions of Atmospheric Particles

= Source Apportionment of Atmospheric Particles

= Sampling of Airborne Particulate Matter for Analysis

= Sampling and Analysis of Carbonaceous Particles in the Atmosphere

= Characterization of Individual Environmental Particles by Beam Techniques

= Characterization of Environmental Particle Surface by Fourier-Transform Infrared and Nuclear Magnetic Resonance Spectroscopies

= Characterization of Particle Surface Charge

= Microanalysis of Individual Aerosol Particles

= Characterization of the Cr(III)/Cr(VI) Ratios in Aerosols

= Interaction of Electromagnetic Radiation with Airborne Particulate Matter

= Acid-Base Equilibria on Particles in the Atmosphere

= Mass Transport by Airborne Particulate Matter

V. Other areas

= Recommendation for the Determination of pH in Acid Rain

= Analysis of Wet Deposition (Acid Rain): Determination of the Major Anionic Constituents by Ion Chromatography, PAC, 63, 907-915 (1991)

= Pesticides in Air

used for forecasting.

The importance of this area for the international collaboration may be additionally demonstrated by the existing disagreement in the relative roles of the effect of anthropogenic chemical substances and natural processes in the "ozone hole" formation.

The projects of Section IV illustrate the IUPAC entering in the heterogenous chemistry of the atmosphere. The ongoing projects are mainly related to the problem of the characterization of particles and their surface. The reactions on the surface, the catalytical role of components, including heavy metals, and the fate of products are waiting for the initiatives of chemical community in joining efforts.

It is also desirable to mention the importance of a study of the aerosols' role in the transport and transformation of radioactive substances (SCOPE project on Biogeochemical Pathways of Artificial Radionuclides) and of using the chemical composition features of particulate matter, emitted by industry, especially particles containing heavy metals,as a tracer for the identification of the source of emission at long distances.

A proposal of the International Union of Testing and Research Laboratories for Materials and Structures (RILEM) to the IUPAC to organize collaboration on the problems of atmospheric actions on various materials, including the materials for the façades of buildings, should be taken into account as well. This is also a part of heterogeneous atmospheric chemistry.

In conclusion I would like to stress once more that the transition to sustainable development requires a significant strengthening interaction between chemical science and industry in all areas, and in connection with this to attract your attention to George Whitesides' papers "What Will Chemistry Do in the Next Twenty Years?" and of Wolfgang Jentzsch "What Does Chemical Industry Expect from Physical and Industrial Chemistry" presented to the Jubilee Symposium devoted to the BASF 125 years.

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