Chemical Events in the Atmosphere and their Impact on Environment
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FINAL CONSIDERATIONS AND CONCLUSIONS

INTRODUCTION

As we approach the dawn of a new century, we feel deeply anxious for the welfare of the planet Earth, and of the generations that must succeed us. Human numbers are growing explosively. Each human being must eat, keep warm and seek shelter. As we do so, in an ever-growing multitude, we place greater stress on the resources that support us. Already the signs of that stress are universal. The last terrestrial frontiers have been removed, the last solitudes penetrated.

Human technology has allowed this growth and must provide for the future. Yet that same technology threatens nature, and may even destroy the very benefits that we seek. Chemistry is at the heart of mankind's remarkable capacity to make needed things, to move mountains and to penetrate far places — even space. Wisely used, chemical technology can immensely enrich our species. Unwisely used, however, it can contaminate nature, most notably the atmosphere and hydrosphere. Technology presents us all with a Faustian bargain.

As scientists we are aware of both gains and hazards. We believe that the immense challenge of the future can be met. We recognize, however, that the global system is an entire whole, and that no one body of knowledge can allow us to use it safely. Nature does not recognize the scientific disciplines into which we have divided scholarship. It is imperative that we seek to use chemical knowledge with as full understanding of the global system as we can command. We recognize, too, that science should not and cannot dictate the manner in which humanity solves its problems. We can offer help, advice and the technical means. Objectives remain the choice of our entire society.

The Pontifical Academy of Sciences brought us together in the full knowledge of the unity and integrity of the global system. It assumed in its planning that we should adopt a holistic stance. Nevertheless, it posed certain specific questions:

— do rising levels of carbon dioxide in the atmosphere pose a threat to future climates?

— what dangers are presented by acid deposition and by the dissemination of heavy metals or other toxics?

— do changes in the stratosphere imply reduced ozone levels, and hence threats to human health and climate? How big are the changes, and the threats they present?

— what is the role of the atmosphere, and especially its chemistry, in the burgeoning problems of the tropical world? What, specifically, can be said of changes in rainforest and arid environments?

— does nuclear war threaten climatic disturbance? What will be the aftermath of such a catastrophe?

The papers written in answer to these questions by the specialists who attended will be published in a separate volume. We present summaries in the following pages, based not only on the original papers, but on thorough and searching discussions. Certain general conclusions emerged that need immediate scrutiny.

Firstly, we noted that many of the problems of atmospheric chemistry are upon us before we notice them, and before we have any chance to study them and modify our technology. The potential for damage arises before any symptoms are noted. And the damage done may be irreversible for decades, or even centuries. This is true, for example, of the carbon dioxide build-up, and of the effect of the chlorofluoromethanes on stratospheric ozone.

Secondly, we were often struck by the inequities that seem to be built into our system. Those who gain from technology may well not be those who suffer the consequences — or, to put it in reverse, the whole world may have to absorb the consequences of actions that have benefited only the industrialized countries. And these consequences occur on a variety of time scales, so that even the future may be mortgaged: acid deposition, for example, works over years and decades, carbon dioxide over centuries. Our descendants will have to clean up the mess we leave behind.

What solutions can we offer? Having arrived at this forbidding situation, can mankind extract itself? Certainly we believed so, or we should not have come to Rome. We defined these needs:

— better factual knowledge, in itself a gigantic challenge involving further technological innovation, more sophisticated laboratories (in more places, including the tropics), the wide use of satellite systems, and above all sustained monitoring of the environmental complex;

— better synthesis of the results of research, in a more holistic and interdisciplinary framework than we have usually adopted;

— better means of communicating the urgency, validity and human implications of what our research reveals. Chemists have not been good communicators, even among themselves. They need to cultivate the art of talking intelligibly to politicians and statesmen, as well as to their fellow scientists.

Those who came to Rome became aware, in fact, that they showed a common concern — that it is our duty to preserve the habitability, beauty and integrity of the planet that has been given to us as a home. In so doing, if this generation of scientists can miraculously overcome its own defects, it will be providing for the future generations of humanity.

It is in that well-intentioned but perhaps over-optimistic spirit that we offer this summary report.

TROPOSPHERIC CHEMISTRY

As a result of advances in our understanding of the tropospheric photochemical system during the past decade, tropospheric chemistry is now viewed as one component of the complex system of biogeochemical cycles through which nature recycles the elements necessary for life on earth. The role of tropospheric chemistry in these cycles is to transform reduced compounds emitted from the surface into the oxidized form in which they are returned to the biosphere, lithosphere, and hydrosphere. These processes influence a wide range of environmental parameters; these include the climate, by controlling the concentration of some "greenhouse gases", such as methane and ozone; the stratospheric ozone layer, by controlling the rate of injection into the stratosphere of chemicals which affect the ozone level; and the biosphere by limiting the levels of toxic gases near the surface.

Although the troposphere is a critical region of the atmosphere, our understanding of this chemical system is far from complete. Of all regions of the atmosphere, the troposphere is spatially and chemically the most heterogeneous and complex. This complexity is derived from the wide variety of species present in the troposphere and from the temporal and spatial variability characteristic of the emissions.

While some effects of pollutants on the local scale are well documented, such as urban photochemical smog, and on the regional scale, such as acid deposition, the effects of man's activities on a global scale are less certain. In particular, the possibility exists that the release of compounds into the atmosphere as a result of anthropogenic activities may be overtaking the ability of the troposphere to oxidize these materials, causing a general perturbation in tropospheric composition. Recent observations of increasing methane concentrations in the atmosphere suggest that these perturbations may be occurring. However, until we understand tropospheric chemistry and its interactions with biospheric processes on a global scale, it will not be possible to assess man's role in this system. As a result, *it is recommended that an international scientific program be launched to study global tropospheric chemistry.* One important element of this program must be an ambitious effort to develop instrumentation to measure atmospheric compounds with high specificity, reliability and accuracy. The major areas where such a program should focus are briefly outlined below.

The key species in tropospheric chemistry is believed to be the free radical species, OH. It is this species that is hypothesized to initiate the oxidation of many of the reduced compounds emitted into the atmosphere and thus has a major role in controlling the trace gas composition of the atmosphere. While photochemical models predict OH to be present in the lower atmosphere, this prediction has yet to be confirmed by direct atmospheric measurements. A major goal of any research program in global tropospheric chemistry should be a test of photochemical theory for OH. This will require not only measurements of OH levels in the atmosphere but also simultaneous measurements of the concentrations of the species which control OH. Concurrently with the test of the OH photochemical theory, more detailed studies of tropospheric chemical transformation and reactions should be prepared.

Another important goal of a tropospheric chemistry research program should be to establish a global air sampling network to characterize the distribution of atmospheric compounds today. In order to determine if the tropospheric composition is changing, a commitment must be made to maintain this network into the 21st century. The interchange of species at the earth's surface due to biologic and lithospheric emissions as well as wet and dry, deposition also needs to be studied, both from the point of view of understanding the flux of material being exchanged and elucidating the physics and chemistry of this interchange. The synthesis of the knowledge gained in this global tropospheric chemistry research program should facilitate the development of a coupled chemical/dynamical model of the troposphere which will facilitate the assessment of future environmental problems of anthropogenic and non-anthropogenic origin so that we may deal with them in an orderly and rational manner.

THE OZONE LAYER

The stratosphere itself exists through the absorption of ultraviolet energy by ozone, and the concentrations of ozone are controlled by complex chemistry dominated by free radical catalytic chains involving species of HO_x, NO_x and ClO_x. The anthropogenic release of long-lived molecules at the earth's surface inevitably results in their eventual transfer to the stratosphere, decomposition by ultraviolet processes and the release of additional free radicals, for participation in these chemical chains. The increasing amounts observed in the troposphere of halogenated compounds such as CCl_2F_2 and CCl_3F and of nitrous oxide and methane provide more ClO_x, NO_x and HO_x in the stratosphere, and can be expected to affect the chemical balance throughout the stratosphere. The effect of additional chlorine is most noticeable in the upper stratosphere, and experimental measurements have confirmed a diminution over the past decade in average ozone concentrations at 40 km altitude. Lesser effects are anticipated at other altitudes and are less certain in magnitude. The atmospheric lifetimes of 50 years and more for some of these compounds will maintain an altered atmospheric composition throughout the 21st century.

There is also present in the stratosphere a particulate aerosol layer which can, at least temporarily, have an impact on the earth's radiation budget and climate. This layer is formed primarily through oxidation of sulphur-bearing precursor gases of tropospheric origin. Anthropogenic activities contribute to the upward flux of these gases.

The major chemical cycles describing catalytic ozone destruction by HO_x, NO_x and ClO_x are now reasonably well characterized. The development of sophisticated computational models has facilitated the unification of field studies with laboratory experiments. At high altitudes where the stratosphere achieves a photostationary state, the chemistry seems well understood, while at lower altitudes, chain termination steps and associated reservoir species have by no means been so accurately characterized.

Field measurements of reservoir species in the lower stratosphere and further laboratory investigations of kinetics governing catalytic chain termination processes must be pursued in order to assess with confidence the effect of further anthropogenic emissions upon the stratosphere.

Our understanding of stratospheric aerosols is still far from being satisfactory. In particular, the gas-to-particle conversion processes involving SO_2 oxidation and condensation nuclei formation are still poorly understood. Future research, therefore, should include in situ measurements of aerosols, trace gases and condensation nuclei involved in aerosol formation. Accompanying laboratory studies of relevant chemical processes are also needed.

The further refinement of direct probes and remote sensing tools based on exquisitely sensitive spectroscopic techniques will play an important role in the continued development of stratospheric chemistry and physics. In this regard, it should be noted that most field studies to date have been conducted in relatively narrow geographical regions. Observation of substantial three-dimensional structure (and fine structure) in the stratosphere calls for more extensive geographical coverage in future experiments.

ATMOSPHERIC CARBON DIOXIDE AND CLIMATE CHANGES

The Present State of Understanding

Highly accurate measurements in many parts of the world show that the concentration of carbon dioxide in the atmosphere increased by nearly 9% between 1958 and 1982, from 315 to 343 parts per million by volume. Credible estimates from the core measurements show that the atmosphere CO_2 content in the middle of the 19th century was about 280 parts per million indicating a 22.5%. Probably two-thirds to three-fourths of this increase came from the burning of fossil fuel — coal, oil and natural gas — and the remainder from clearing of forests to expand agricultural land to meet the needs of rapidly growing human population. It is likely that atmospheric CO_2 will rise to about 600 ppm by the latter half of the 21st century, approximately twice the mid-19th century value.

Because carbon dioxide in the atmosphere absorbs and reradiates infrared radiation, the increase of carbon dioxide will result in a rise in the temperature of the lower atmosphere and the upper layers of the oceans. Model calculations for a CO_2 doubling indicate that after ocean and atmospheric temperatures have approached equilibrium, the average global temperature will be between 1.5 and 4.5°C higher than in the 19th century. The temperature rise at high latitudes will probably be at least twice as large as the global average rise, while temperatures in the tropics will increase by a smaller amount.

The atmosphere content of other infrared-absorbing gases (called greenhouse gases) notably methane, chlorofluorocarbons, tropospheric ozone, and nitrous acids are also increasing. Consequently, temperature in the lower atmosphere during the next century will probably be higher than the above estimates. The world climate will be significantly warmer than at any time during the past 100,000 years. This tendency will persist for many centuries, until the excess atmospheric CO_2 is absorbed into the oceans.

Thermal expansions of the upper ocean waters and disintegration of glaciers will bring about a rise in sea level of at least 70 centimeters during the next century and possibly 5 to 6 meters during the following several centuries. The volume of water in areas of low rain and snow fall will probably decrease by 30 to 40%, with drastic consequences for irrigated agriculture. Rain-fed agriculture in higher latitudes will benefit from a longer growing season and warmer temperatures. Higher carbon dioxide will act as a fertilizer for crop plants, when temperatures are not too warm and sufficient moisture is available. Net photosynthetic production should increase. The effects on natural ecosystems are difficult to predict, in the present state of ecological understanding. Effects in different world regions are likely to be widely different.

What Kinds of Research are needed?

1. Economic and social research on the factors which will determine future emissions of carbon dioxide. This should include the probable rise of future rates of world energy use and the future misuse of energy sources — that is, the ratio of energy from fossil fuel combustion to that from other energy sources. Also needed are better estimates of possible future changes in the areas of forests.

2. Possible changes in atmospheric carbon dioxide related to ocean

circulation and ocean biological production, and to uptake or release of carbon in the land biota and in soil organic matter and soil calcium carbonate.

3. Future changes in atmospheric concentration of other greenhouse gases (methane N_2O, chlorofluorocarbons, tropospheric ozone).

4. How can the fertilizer effect of carbon dioxide be utilized to maximum advantage in human food and fibre production?

5. What changes in river flow can be expected in different areas of the world, resulting from rising temperature and probable changes in precipitation?

6. What will be the likely rate of rise of sea level and the probable range of rates of sea level use? What will be the effects of sea level rise in different areas?

The Need for Assessment of the likely effects of CO_2 increase in different world regions

The CO_2 problem is global, but its net effects will be different in different regions. Though these effects will not be fully manifest for several decades, prudence requires that nations in these regions make their own assessment of the effects and initiate plans to mitigate the deleterious effects and take advantage of the beneficial ones.

ATMOSPHERIC ACIDITY

The atmosphere is an oxidizing medium, and as a consequence, chemical species of anthropogenic origin emitted usually in urban environments, undergo change in oxidation state which may result in increased chemical and biological activity. A specific consequence may be the conversion of material to water-soluble forms, which then can have dramatic impact upon the biosphere with which they come into contact. Such emitted species of importance in industrial nations include sulphur dioxide, oxides of nitrogen, heavy metals, photochemical oxidants and organic materials.

In the specific case of emissions of sulphur dioxide and oxides of nitrogen, the change in oxidizing nature of the atmosphere subsequent to chemical reactions in the atmosphere, and upon deposition, results in changes in the acid base and redox equilibria in the aqueous phases.

These processes are not evenly distributed, since the effects observed in any locality depend upon the emission distribution pattern and transport, the rate of oxidation in the atmosphere, and the rate of deposition, which depends upon climatic factors.

Some local effects are well known, from extensive studies in localities such as Scandinavia, but much less information is available on a global scale, and there are some indications that chemical changes are occurring in remote areas, such as the North Polar region, and effects of this have not been widely studied.

Oxidation in the atmosphere may take place homogeneously in the gas-phase, in the aqueous phase, and heterogeneously, and can lead to particulate formation. The latter is poorly understood.

It must be recognized that transfer of species from the atmosphere by dry deposition is a *continuing* process, whereas that in aqueous phase, through precipitation, is periodic, and strongly dependent upon meteorological conditions.

Dry deposition of different species in the gas-phase is dependent upon their chemical properties and the nature of the surface. When deposited, such species, for example SO_2, may react further in the soil giving substances with increased acid properties. However, the same species may have been produced in the atmospheric process, and are deposited by gravitation.

The wet deposition is of species which have either played the role of condensation nuclei (H_2SO_4 — droplets) or have been washed out during the precipitation event.

A number of observed effects are now with a greater or lesser degree of confidence ascribed to the deposition of acid materials, heavy metals and other species. They include:

(i) Destruction of animal life, particularly fish during the breeding seasons in spring, where run-off of melting snow causes sudden drops in pH. The effects are not solely due to concentration of acid, but clearly involve the solubilization of other elements, notably aluminium, which in higher concentration becomes toxic.

(ii) Damage to plant life, discussed below.

(iii) Damage to buildings, particularly materials such as calcium carbonate stone, and feldspar. However, a detailed scientific understanding of these harmful effects is still lacking.

It is thus recommended that:

1) the oxidation of sulpbur dioxide should be investigated in

greater detail, in the real conditions of the atmosphere where homogeneous as well as heterogeneous reactions occur simultaneously and might affect each other.

2) the causes of the decay of organic materials should be investigated thoroughly in order to evaluate the relative mechanism and the impact of their metabolites on the environment.

EFFECTS OF CHANGES IN CHEMICAL CLIMATE ON WATER, SOILS AND BIOTA

The atmosphere has been used to discharge waste products of human activities, such as fuel burning and industrial processes to a great extent.

The following changes in chemical climate have special importance for biota:

— the increase of photochemically reactive compounds in the atmosphere

— the increase and continuous input of acidity both by wet and dry deposition

— a wide distribution of heavy metals in biota and soils. Besides that, biota and soils are contamined by radioactive fallout and persistent pesticides or other organic compounds or potential hazard to life.

Dealing with the effects we have to differentiate between

— acute and chronic effects by direct impact on plants, animals and human beings, especially by gaseous pollutants such as SO_2, HF, HCl and photochemical oxidants

— long-term effects by accumulation in soils and biota and inclusion into the water and nutrient cycles of ecosystems. The accumulation of acidity in mineral soils and water and the build-up of reservoirs of heavy metals, persistent chlorinated hydrocarbons, and radioactivity to the disposition of living beings are regarded as having great importance.

The following examples stress the importance of immediate counter measures.

— The present decay of many German and other European forests as a result of the impact of air pollution, especially photochemical pollutants and acidic deposition.

— The extinction of many fresh water animals including fish in various Scandinavian and Northeast-American lakes and rivers.

Thus increased research is necessary for a better understanding of the overall change of the biosphere and ecosystems, and detailed studies on the mechanism of pollution effects besides the development of waste-free technology are also required.

Even if we know about the uncertainties of source-effect relations, we strongly recommend immediate action according to the present state of knowledge, even if this is not complete. General aims should be:

— Utmost care in dealing with nature,

— Reducing the amount and number of chemicals put into the environment.

— Developing means of action which will secure life and environment for future generations.

Problems of the Tropical World

Human numbers are growing fastest in the tropical world. With this growth goes an increase in livestock, and in cultivated soil. Pressure is increasing rapidly on life-support resources, and on land. Control depends on an understanding, not only of the social questions involved, but of the demands each living being makes on essential resources.

In humid areas, the rate of world deforestation is estimated at 6 to 10 million hectares per annum, 2 to 4 millions of which are in South America. The biota being destroyed holds the greater part of the nutrients, which are lost to the ecosystem. This deforestation rate represents a tragic loss of plant and animal species. The usual techniques of soil cultivation, especially where precipitation is high — often above 2,200 mm a^{-1} — accelerate the natural loss. Special technology is needed for such humid tropical regions. Existing research on such techniques needs to be increased and intensified.

Despite the known rapidity of chemical cycling and sensitivity to human activities, we still know far too little about the over-all nutrient requirements and their relation to the global biogeochemical cycles. Very little knowledge exists, furthermore, about the sensitivity of tropical ecosystems to soil, air and water pollution. This may be expected to increase in the future due to expanded agriculture and *intensity*. It is important that the gathering of background information needed for studies of such cycling of nutrients, elements and pollutants be accelerated — together with estimates of human impact.

The dry land surfaces of the tropics are also deteriorating rapidly, because of increased human numbers. In tbe past twenty years drought has been severe in many areas. In some parts of Africa large areas have been abandoned. Two feedback processes may be at work:

(i) surfaces denuded of vegetation have increased reflectivity. This may decrease rainfall, by encouraging atmospheric subsidence. Large amounts of fine soil (mineral and organic) have been removed by the wind;

(ii) reduced photosynthesis (due to removal of vegetation) and increased respiration and decomposition (due to soil organisms) may be reducing stored organic material. This in turn (with the loss of fine mineral material) may reduce water storage. Much tropical rainfall comes from re-evaporated rain. Hence such losses may act to reduce rainfall further.

The dry lands of Africa, northeastern Brazil, Australia and possibly other regions have all suffered from these biophysical and biochemical changes. The new countries of Africa, particularly those of the Sahel, of East Africa and of the margins of the Kalahari, have been worst affected.

Future climatic change induced by CO_2 increase may also affect the tropical environment adversely. A temperature rise of 2°K, unless accompanied by a rise in rainfall, will add to the difficulties of farmers and herdsmen. It will also make still more difficult the provision of adequate drinking water, the design of irrigation systems and the maintenance of good health standards.

These problems are so grave that we believe that the scientific community as a whole should give all possible aid and encouragement to those members who live and work in the tropical countries. The need for adequate equipment, funding and even physical access is desperate. So also is the need for trained scientists and for institutions capable of supporting them. Science has a major role to play in the problems of development. Its long tradition of international cooperation can serve to strengthen — even to make possible — the necessary social and political action.

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In this century mankind has reached, for the first time, the point where it can alter its environment in a time scale shorter than the one needed to understand and quantify the implications of such actions. The ozone layer depletion, the global warming due to CO_2 increase, the immission of acid chemicals in the ecosystem are examples of such changes of our environment.

Dramatic changes in atmospheric temperature which would severely strain the survivability of life on earth would also certainly occur in the aftermath of a nuclear explosion due to the accumulation of particulates blocking the sun's light.

In spite of the great progress made in recent years and reported at the present Study Week in the understanding of the physical and chemical phenomena occurring in our atmosphere, major gaps still remain that call for further study and research. As examples, we can cite our limited knowledge of tropospheric chemistry in tropical regions, the lack of information about the CO_2 increase in the atmosphere (and the implication thereof), as well as the various stages of acidic precipitations. This lack of knowledge hinders a precise assessment of what are otherwise generally perceived as possible major alterations of our environment. For example, on the basis of the present knowledge, we cannot today fully appreciate the implications on soil, vegetation and animal life of such phenomena.

It is also felt that besides the need of more theoretical studies, more field research is needed in areas such as the tropics and high latitude regions, as well as volcanic explosions which offer the unique opportunity to study the response of the climatic system to a quantifiable perturbation.

Finally, the need was felt to promote the awareness of Governments and international Institutions as well, about the need to cooperate among themselves with the aim of solving problems that are increasingly perceived as not limited to a single nation but which involve the whole biosphere.