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TOWARD A BETTER UNDERSTANDING OF ATMOSPHERIC CHEMISTRY

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It is with mixed feelings that I address the topic assigned to me.

First, it is clear that the subject of atmospheric chemistry has emerged over the past two decades as one of the "frontier research" areas in the atmospheric sciences.

Second, it is equally clear that thoughtful consideration of the issues involved leads to the conclusion that a uniquely international effort is required, and this is therefore a particularly appropriate topic to be addressed by the Pontifical Academy of Sciences.

Third, I can claim no special competence in the intricate details of the subject, and must be constrained to view its development from the perspective of the Chairman of the Board on Atmospheric Sciences and Climate of the National Academy of Sciences.

With these considerations in mind, permit me to address (1) the essence of the subject, as it appears to me, (2) the context within which the topic is properly considered, and (3) some specific suggestions regarding future scientific strategies that have emerged from two thoughtful analyses by the National Academy of Sciences [1, 2].

As the world approaches the threshold of the twenty-first century, higher levels of understanding of the physical environment are becoming necessary and attainable. Just as science and technology have permitted world human population to grow and life expectancy to increase through modern industry and agriculture, so they permit more rigorous investigations into how the earth's planetary life support system works. Prudent management will become imperative if the general health and stability of human life on this planet is to be assured. Effective management will require a good understanding of the complex physical, chemical and biological processes in that system which enable it to combine solar radiant energy with the cycling of chemical nutrients through the biosphere to sustain plant, animal, and human life.

The important role of chemical and physical processes in the troposphere in the planetary life support system has been brought into sharp focus in recent years not only by our research discoveries, but also by a disturbing, recurring sequence of problem identification and response, e.g., impacts of smog on health, of acid on lakes, forests, and agriculture, of increasing carbon dioxide and other trace gases on climate, and of chemicals moving upward through the troposphere to the stratosphere. It has become clear that the troposphere is an integral component of the planetary life support system — receiving, transporting, transforming and depositing substances that either contribute to the efficiency of the system or deleteriously perturb it. Yet there has been relatively little effort expended in obtaining fundamental understanding of the global troposphere, its dynamical behavior and cycles. Perturbations can be expected to increase in frequency and variety during the next several decades, and their significant economic impact will grow. Because the atmosphere is a moving and restless continuum enveloping the planet, the issues are international; since physical, chemical and biological processes are inextricably intertwined, the effort to understand them must be interdisciplinary.

Accordingly, it is timely that a conceptual framework and scientific strategy for the study of the chemistry of the global troposphere be initiated. Rapid advances in theoretical understanding of chemical reactions in the troposphere, field-measurement capabilities, remote sensing, laboratory techniques, data handling, and numerical modeling capacities strongly support the conviction that a coordinated international effort can lead, before the end of the century, to the kind of understanding that would provide the predictive capability necessary to anticipate the impact on our planetary ecosystem of natural or anthropogenic changes in the chemistry of the lower atmosphere.

Three specific issues and four generic programs constitute the context within which a major international effort is warranted.

The first issue is the possibility raised in the early 1970's that human activities might add certain chlorine, nitrogen, and other catalytic substances to the stratosphere. These substances, in turn, would upset the balance between the production and destruction of ozone in a manner that could increase the intensity of ultraviolet light reaching the biosphere with potentially deleterious results on animals, marine life, plants, and humans (increased incidence of basal cell carcinoma and squamus cell carcinoma). Increasingly sophisticated models of the chemical and physical processes deemed to be important, laboratory experiments to determine the photochemical rate coefficients used in the models, and increasingly reliable techniques of field measurements from balloons and satellites have illuminated the matter but have underscored the complexity of the problem. In brief, the most recent assessment [3] suggests that the theory of humanly inducted changes in the stratosphere remains valid. The exchange of trace gases between the stratosphere and the troposphere is emerging as one of the essential steps in the ozone perturbation process. Coupled, three-dimensional, dynamical-radiative-photochemical simulation models will be required for definitive studies and a sustained global observational system will be required to validate the models.

A second issue in acid deposition (popularly known as "acid rain") resulting from the emissions of oxides of sulfur and nitrogen associated with the combustion of fossil fuels. The potentially harmful effects on ecosystems have been documented, especially in areas with low geochemical capacities for neutralizing acid inputs. The matter is complex, involving the generation and interpretation of scientific evidence, assessment of risks, costs and benefits and domestic and international political considerations. Crucial to the decision-making process is the development of realistic, validated models of the meteorological processes of transport, mixing, physical and chemical reactions, and deposition of gases, suspended particles and water droplets as well as the relationship between emissions and deposition. Again, the listing of research needs embraces field studies, laboratory investigations as well as the modeling effort. A review of the current scientific understanding is available for North America [4] and the scientific issues are again being assessed for Western Europe.

Finally, there is the issue of the possible influence on global climate of the buildup of carbon dioxide in the atmosphere from the combustion of fossil fuels. Since this topic is covered of this study week by Professor R. Revelle, mention will be limited to reference to a sustained attempt by a group with a wide range of expertise to achieve a comprehensive and internally consistent assessment [5]. It is worth noting, however, that resolution of this intrinsically international problem requires a sustained program of geophysical and biospheric monitoring and an array of physical, biogeochemical and econometric models sufficiently credible that global decision-making can proceed before irreversible climate changes take place to the advantage of some regions and the disadvantage of others. So broad is the subject and so global its scope that as the Academy Report noted: "It is conceivable that CO_2 could serve as a stimulus not only for tbe integration of the sciences but for increasingly effective cooperative treatment of world issues".

Among the generic programs there is, first, the Global Atmospheric Research Program — GARP — [6], first suggested by President Kennedy in an address to the United Nations in 1961, and developed under the guidance of a Joint Organizing Committee established by the nongovernmental International Council of Scientific Unions and the Intergovernmental World Meteorological Organization. Implemented in 1979-80 as the First Garp Global Experimental, this international collaborative effort broke new ground in international scientific cooperation. Premised on the contention that an understanding of the dynamics of global weather circulation patterns had outstripped the observational power that clearly lay within each, GARP succeeded brilliantly in advancing our knowledge of the dynamics of large-scale atmospheric circulation and extending by a significant degree the time interval over which meaningful weather predictions can be made. Five geostationary satellites were launched by several nations, networks of drifting buoys were placed in the oceans, and fleets of aircraft and ships were deployed to fill gaps in the global network of meteorological organizations. Notably lacking, however, is a meaningful insight into the physical processes linking ocean and atmosphere and the chemical and biological processes by which the behavior of the global atmosphere is linked to the underlying marine and terrestrial ecosystems. It is now clear that without addressing these facets of a complex hydrodynamic, thermodynamic and biogeochemical system, our understanding and predictive capability will be severly limited.

More recently, emphasis has been focused on the mesoscale phenomena of the atmosphere [7], since these features are embedded within the global circulation patterns and exercise a strong influence on — and are influenced by — anthropogenic activity, as well as by the natural interaction between the atmosphere and its boundary of land, vegetation, and water. Just as global observational capacity and computer modeling opened up new dimensions in the analysis of large circulation patterns in the 1970's, so have advances in mesoscale modeling and the measurement of the internal structure and motion within individual clouds by doppler radar opened an avenue to observe and predict small-scale weather phenomena — squall lines, thunderstorms, flash floods, freezing rain or dense fog — with the accuracy and reliability necessary to protect the public, and make effective use of climate and weather information by government, industry, and agriculture. It will be important to include in the research phase of this study an examination in the mesoscale of the chemical flux to land and water surface and the acqueous-phase reaction mechanism and scavenging processes.

A third generic program is the World Climate Research Program [8] which built upon the Global Atmospheric Research Program and is guided by a Joint Scientific Committee of the International Council of Scientific Unions and the World Meteorological Organization. The objectives are to determine (a) to what extent climate can be predicted, and (b) the extent of man's influence on climate. Understanding climate and climate variability involves a detailed study of a great many physical, chemical and biological processes of the atmosphere, oceans, land and sea ice as well as the terrestrial ecosystems that influence the atmosphere over time scales of several weeks to several decades. The program is structured in three streams:

(a) The first stream seeks to establish the physical basis for the prediction of weather anomalies over periods of several weeks.

(b) Tbe second stream is concerned with interannual variability of tbe global atmospheric climate over periods of one to several years.

(c) The third stream seeks to illuminate the long-term variations and the response of the planetary climate to man-made or natural forcing factors over periods of several decades.

There is an intimate interaction among the cycling of chemical elements such as nitrogen, oxygen, carbon and sulphur through the soil air, water and biomass and the characteristics of the natural or man-made ecosystems which, in turn, influence climate. Increasingly, trace gases are recognized as contributing significantly to the earth's radiative equilibrium temperature and may turn out to be as important in the aggregate as carbon dioxide. As this program proceeds, the need for better information on tropospheric chemistry will become more urgent.

Finally, there is the program of the Scientific Committee on Problems of the Environment (SCOPE) of the International Council of Scientific Unions whicb for the past decade has been focused on the major biogeocbemical cycles and their interaction [9], as well as methods for assessing the effects of chemicals on reproductive functions [10]. Particular attention has been directed to:

(a) the effect upon carbon storage in sediments, soils, and vegetation (primary production) of additional N, P, and S from fossil fuel burning and deforestation;

(b) soil management practices — the potential deterioration of soils through alteration of the N, P, and S via cultivation;

(c) the biosphere as a source of trace gases which influence the chemistry of the atmosphere; the processes within the biosphere that produce these gases;

(d) the eutrophication of coastal marine waters through the entry of N, P, and S by man's activities;

(e) water quality changes from the mountains to the sea as a consequence of N, P, and S entry from man's activities;

(f) the long term effects of population increases and material utilization via N, P, and S dispersion upon the carrying of the earth for humanity.

The study of methodology for assessing the consequences of releasing chemicals into natural and modified ecosystems is the first step in a projected series which seeks, through a collaboration effort, to explore a rapidly enlarging problem. In addition to homocentric considerations, there are important implications emerging of nonhuman reproduction. This is a facet of tropospheric chemistry that is far more than an exercise in toxicology.

In concluding this discussion of the context for a global troposphere chemistry program, mention should be made of the outline of a research program on biogeochemical cycles developed under sponsorship of the National Aeronautics and Space Administration under the rubric of "habitability" and reported by McElroy [11]. Five major goals are persuasively set forth:

(a) to understand the principal components of the hydrological cycle;

(b) to understand the processes which regulate the distribution and abundance of lower atmospheric oxidants, notably O_3, SO_2, and NO_2's;

(c) to define the factors which influence the chemistry of deposition both dry and moist;

(d) to identify processes which affect the abundance of aerosols and of gases such as CO_2, N_2O, CH_2, NH_3 and H_3O;

(e) to assess the impact of anthropogenic infrared absorbers on the radiative budget of the atmosphere and on climate.

It seems clear from this brief reference to issues and programs that the stage is set for a comprehensive investigation of the chemistry of the global troposphere. As outlined by the report of the National Academy of Sciences [2], the goals would be:

(a) to understand the basic chemical cycles in the troposphere through field investigations, theory aided by numerical modeling, and laboratory studies;

(b) to predict tropospheric responses to perturbations, both natural and human-induced, of these cycles; and

(c) to provide the information required for the maintenance and effective future management of the atmospheric component of our global life support system.

The following specific objectives are proposed to achieve these goals:

(a) *To evaluate biological sources of chemical substances in the troposphere.* Primary emphasis should be placed on investigations of temperate and tropical forests and grasslands, intensely cultivated areas, coastal waters and salt marshes, open ocean regions, tundra regions, and biomass burning.

(b) *To determine the global distribution of tropospheric trace gases and aerosol particles and to assess relevant physical properties.* This program calls for field measurements and analyses coordinated with the development and validation of tropospheric chemical-transport models, the development of tropospheric chemical-transport models, the development of a regional and global data base for key species in chemical cycles, and the continuation and improvement of existing monitoring programs for the accurate measurement of long term trends in environmentally important trace gases and aerosol particles.

(c) *To test photochemical theory through field and laboratory investigations of photochemically driven transformation processes.* Particularly important tests will be investigations over tropical oceans and rain forests with additional studies in midlatitudes.

(d) *To investigate wet and dry removal processes for trace gases and aerosol particles.* Research should be directed not only toward evaluating chemical fluxes to land and water surfaces, but also toward a fundamental understanding of aqueous-phase reaction mechanisms and scavenging processes.

(e) *To develop global tropospheric chemistry systems models (TCSMs)* *and the critical sub-models required for the successful application of TCSMs.* A wide range of models must be developed of individual processes important for tropospheric chemistry as well as comprehensive global models that include the most important chemical and meteorological processes. Modeling, laboratory, and field studies are necessarily symbiotic; progress in each area is dependent upon contributions from the others.

The institutional framework exists in the International Council of Scientific Unions. Now would seem to be a propitious time to act.

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DISCUSSION

Marini-Bettòlo

In effect biologists are not represented here as are other scientists, but tomorrow we will have with us Silvio Ranzi, Professor of Zoology at the University of Milan, who for many years has been responsible for the Consiglio Nazionale delle Ricerche's program for lake and river pollution of northern Italy.

Malone

I did not intend that as a criticism but more as a commentary on the good statement.

Marini-Bettòlo

In my plans there was an invitation to a botanist, but it is quite difficult to find somebody who is working in this field.

Hare

I really wanted to say, Mr. Chairman, that the trouble with botanists is that many of them do not know anything about plants. Biologists these days are so much concerned with the cell, with the nucleus and with the genome that the questions that are important in the area — and I am serious about this — are now largely tackled by non-botanists, non-biologists, because they are so much concerned with the molecular control of their discipline that they have forgotten to a large extent the things that we are discussing. The problem that you have, Sir, is the problem that we all have when you try to involve biologists in these discussions.

Marini-Bettòlo

Thank you, Professor Hare. I think that it is quite a problem. We need taxonomists and ecologists. Even the ecologists have their own programs. In effect we miss very much the presence of Dr. Di Castri, secretary of the

Biosphere program at the UNESCO, who could not come because of the coincidence with the UNESCO general conference.

KNABE

Professor Malone, you gave quite a good explanation of a program for future work. The difficulty is that at present decisions had to be made and I would like to make some statement from the point of view of the ecologist on the chemistry of the troposphere. What we observe and what we are concerned about are several items. First, there has been an increase of the masses of SO_2 and NO_2 or NO, NO_x you could say, and hydrocarbons in general, all over the world over the last decades, especially after World War II. Secondly, the emissions of those gases have been concentrated on two sources, one source of high stacks at relatively high elevations between 200 and 300 meters, and so the concentrations downwind for each stack is at levels which they have not reached before. The other source is the automobile traffic fumes may be half a meter, or a truck may be 2 or 3 meters; so that you have dense concentrations near the ground. What has changed not only in recent times and makes us concerned is the amount of masses but also the number of chemicals. We do know a bit about the effects of SO_2 or NO_x and ozone, but we do not know really anytbing about many organic chemicals which are so numerous today. What has also changed is the combination of solid components of the atmosphere, dust and fine particles on the one hand and the gases on the other hand. So by the removal of the ash from the stack we have quite a change in the industrial region. And this might also effect then the air pollution in the regions far off.

The present change in conditions is the increase of pollution in the regions far from industrial areas, and this demands — and that is the only reason I mention it — the measuring of pollution not only in the industrial areas but in a well distributed network over the whole globe. It has also changed the relation of acidic and of photochemical reactive parts, that means the oxidants, the photo-oxidant cycle. SO_2 is also included in this, I know this, but the special line of building up and also other oxidant hydrocarbons which has started in the Los Angeles basin is now present in many parts of Europe, and this should be of concern. However, at the same time we have the great impact of acidity.

I do not want to go into Professor Liberti's paper — he will do this in more detail — but it is a fact we have a very great input of acids, not only sulphuric acid but also nitric acid. We are asking you as chemists: could you help us to explain what is going on on the plant surface? You have to make measurements with very fine instrumentation in the stratosphere, and discover radicals and other components, but we are missing the same experiments, the same measurements at the plant surface. What is going on there? Do you believe the same radicals occur there? Can they help us to explain the present damage? Well, just these general remarks, or thoughts, are necessary because you have just given the program for the future and so as an ecologist I want to add my problems.

MALONE

I cannot take exception to anything you said at all. I concur. I might have mentioned in this matter of the relation between plant life and chemistry of the atmosphere, as you are all aware, that when the atmosphere was first present, three and a half billion years ago, there was no oxygen at all, and it was not until one billion years later that there was about 1% oxygen, and it was not until 670 million years ago that it was about 7%; then it rose to its approximate level today, about 400 million years ago at the time of the flowering of plants in the middle paleozoic. I am not trying to divert attention from the immediate problems by going back 100 million years. I am just saying that this geological record suggests the importance of the very thing you are underscoring.

WANDIGA

Professor Malone, I would like you to possibly comment on the topics listed. I saw you listed "The Study of Tropical Forests" as one of the areas that need to be further studied. As you might recall, forests in most tropical regions are an endangered species. There is much more activity occurring in the savanna regions, which I believe are going to have a greater impact on the regional climate or the global climate in the long run. I would mention the encroaching deserts, the solid particles being emitted into the atmosphere and other such activities due to lack of vegetational covers. Furthermore, there is also the estuarine siltation which is affecting the aquatic life and altering quite a number of systems, even the aquatic system. Would it not also be proper to include studies of such nature in this program?

MALONE

Very much so. You will find a very nice analysis of these problems and the discrepancies in the estimates of tropical forests in the paper by Mr. McElroy. He also goes into some detail about the coastal marine problem, the issues that need to be resolved there, and the outflow of nutrients from the rivers into the ocean.

ROWLAND

Perhaps you should just give a reference to the McElroy article.

MALONE

Its publisher is the Jet Propulsion Laboratory - Publication 85-51, July 15, 1983.

REVELLE

We need biogeochemists, people who are concerned with the whole ecosystem and how it reacts. That is a rather special kind of biology You won't get much out of botanists or physiologists; you do get something out of the ecologists, and more out of people who would treat ecology in a quantitative way.

MALONE

Your colleague, Ed Goldberg, is a classical example.

REVELLE

So are Michael McElroy, and James McCarthy both at Harvard, and some people in Germany.