

Conf-9107104--18

ANL/CP--71762

DE92 003403

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AND FEEDBACKS.

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October 1991

Invited paper accepted for publication in the
proceedings of the 5th International Conference
on Precipitation Scavenging and Atmospheric-
Surface Exchange Processes, Richland, WA, July
15-19, 1991.

The submitted manuscript has been authored by a
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POTENTIAL CHANGES IN ATMOSPHERIC CHEMISTRY IN THE DECADES AHEAD: CLIMATE AND BIOSPHERE INTERACTIONS AND FEEDBACKS.

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ABSTRACT

Atmospheric chemistry is a challenging area of research where much knowledge is needed if we are to continue to survive as a species. This paper outlines research needs in the decades ahead in this key area of scientific endeavor. Highlighted are areas of research that are likely to lead to climatic and biospheric impacts and have been given little attention in the past. In particular, the possible organic transformation chemistries that may lead to chemical and physical changes in tropospheric cloud chemistries are highlighted and emphasized as an area where research is needed in the future.

1. INTRODUCTION

This paper will attempt to outline some of the areas of atmospheric chemistry that we believe

will be key areas for future research efforts in the next few decades. As we gaze into our crystal ball and attempt to identify the environmental research needs in atmospheric chemistry, we will focus primarily on the troposphere, while briefly mentioning stratospheric concerns with the recognition that these are coupled systems. Since this is by necessity a limited review and atmospheric chemistry is now recognized as an extremely complex science, we will obviously not be able to touch upon all the research needs in the coming decades. We will attempt to focus on two aspects of the future atmospheric environmental impact issues: climate and biosphere interactions and feedbacks, with particular attention being given to non-criteria pollutants. As other papers in this symposium are dealing with the currently identified criteria pollutant issues (i.e. acid rain, tropospheric ozone, etc.) we will only briefly touch upon these issues as they relate to the major unknowns as identified in this paper. The detailed chemistry of the atmosphere as presently understood has been summarized (Finlayson-Pitts and Pitts, 1986) and will not be reviewed in detail here. Readers are referred to this reference for the basic atmospheric chemistry upon which this paper will base its discussion of future needs for research in the upcoming decades. We will also focus upon those perceived issues that are likely to have the greatest impact upon our atmosphere and where the largest unknowns exist.

2. FUTURE RESEARCH TOPICS - BEYOND CRITERIA ISSUES

Criteria issues as discussed in this paper are those environmental problems that have already been identified and have been under study and mitigation for sometime. These issues include acid rain, tropospheric ozone (urban and rural), visibility reduction, greenhouse gas warming (carbon dioxide), and stratospheric ozone depletion (chlorofluorocarbons, CFC's). In this section we will attempt to look beyond these identified criteria issues to future environmental research problems.

2.1 Beyond Acid Rain

For the last decade or so, we have become aware that the oxidation products from gaseous air pollution can be removed by wet and dry deposition. The best known aspect of this removal process has been popularized as acid rain. Our knowledge of acid deposition has been summarized in the National Acid Precipitation Assessment Program (NAPAP) documents (e.g. Sisterson, et.al. 1990). However, as pointed out in previous work (Gaffney, et.al., 1987), there are numerous atmospheric species that are quite water soluble and are being co-deposited with sulfuric and nitric acid that are not criteria pollutants. These include but are not limited to: hydrogen peroxide, organic peroxides, organic peracids, oxalate, formaldehyde (methylene glyoxal), formic acid, acetic acid, phenol, nitro-phenols, and other oxidized organics. Hydrogen peroxide levels as high as 200 micromolar have been reported, after the available sulfur dioxide has been titrated to sulfuric acid (Kelly, Daum, and Schwartz, 1985; Lee, Shen, and Klotz, 1986). The other species are abundant and quite toxic (Gaffney and Senum, 1984; Lee, Shen, and Klotz, 1986; Hewitt and Kok, 1991), however, few studies have been performed to determine their impacts on our ecosystems. However, it has been reported that hydrogen peroxide in acidic solution can cause damage to spruce (Masuch, et.al. 1986).

It is also likely that similar to the acid catalyzed oxidation of dissolved sulfur dioxide by hydrogen peroxide in solution, that other acid catalyzed aqueous reactions may be important in the production of organic acids, particularly oxalate. It is quite likely that the aqueous oxidation of keto-acids produced from the photooxidation of primary organic emissions in the troposphere lead to the formation of this toxic species (i.e. oxalate). Similarly the oxidation of aromatic hydrocarbons will lead to the formation of nitro-phenols which are quite water soluble (Finlayson-Pitts and Pitts, 1986). Levels of dissolved hydrogen peroxide and formaldehyde can be appreciable in precipitation and cloudwater, ranging in the high micromolar range in the east-

ern United States (Kelly, et.al., 1985; Lee, et.al. 1986).

2.2 Beyond Tropospheric Ozone

Having been identified as an important component of photochemical smog, ozone has become the criteria oxidant in the troposphere (Penkett, 1991). Considerable concern has been given to the synergistic production of elevated tropospheric ozone levels caused by the photochemical oxidation of organics by NO_x catalyzed reactions. These reactions involve a number of key radical species including hydroxyl radical, hydroperoxyl radicals, organoperoxy radicals, organoperoxyacetyl radicals, and nitrate radical (Finlayson-Pitts and Pitts, 1986). In order to control the production of ozone in the troposphere, one can limit the amount of reactive hydrocarbons or nitrogen dioxides emitted, or both. Current control strategies are aimed primarily at limiting the emissions of hydrocarbons to lower urban ozone levels.

One serious limitation of this approach is that in many urban centers the biogenic background of the reactive natural hydrocarbons, particularly isoprene, may limit the effectiveness of this control strategy (Chameides, et.al. 1988; Gaffney, et.al. 1987; Gaffney and Senum, 1984; Gaffney and Marley, 1991). This is due to the fact that isoprene emissions from plants (principally deciduous trees) can be appreciable (with steady state levels at the ppb level) and that OH reacts rapidly with isoprene leading to the formation of peroxy radicals and peroxy radical precursors (i.e. formaldehyde) which will convert NO to NO₂ rapidly leading to the formation of ozone. There are known to be a number of oxidants other than ozone that can be important in the chemistry of the troposphere. These include hydrogen peroxide, methyl hydroperoxide, peracetic acid, peroxyacetyl nitrate (PAN) and their higher analogs (Gaffney and Senum, 1984; Gaffney et.al., 1987; Gaffney, Marley, and Prestbo, 1989; Hewitt and Kok, 1991). The chemistry of the peroxyacetyl nitrates (PANs) has been recently reviewed (Gaffney, Marley, and Prestbo, 1989). PAN is a

potent phytotoxin and lachrymator. It can lead to the long range transport of NO_x in the troposphere and since it is in thermal equilibrium with the peroxyacetyl radical, it can play an important role in initiation of nighttime chemistry free radical chain reactions. PAN and associated organic nitrates are also greenhouse gases, like ozone, and should be considered as such.

As pointed out in the previous section the aqueous reactions of the peroxides and the peracids are important in the conversion of sulfur dioxide to sulfuric acid in the troposphere. Other aqueous reactions of these oxidants need to be considered in aerosols, fogs, and clouds, particularly the oxidation of dissolved organic species such as formaldehyde (methylene glyoxal). The pH dependence of these oxidation reactions needs to be explored as well. The organic peracids and peroxides are likely to be potent phytotoxins and like ozone must be considered as a health and ecosystem hazard. The effects of increased ultraviolet radiation upon the photochemistry of the troposphere must also be examined as our stratosphere's light-filtering ability changes in the future due to the injection of chlorofluorocarbons in to our air (McElroy and Salawitch, 1990; Rowland, 1991).

2.3 Beyond Carbon Dioxide

A great deal of research has been focussed upon the increased levels of carbon dioxide in the atmosphere due to the burning of fossil fuels. Carbon dioxide is a greenhouse gas and the concern is that higher levels of this important gas will lead to global warming and climate change. A number of other trace gases have been identified as being important in this regard, including nitrous oxide, methane, carbon monoxide, and the chlorofluorocarbons (CFCs). These stable species have received considerable attention, while the more reactive greenhouse gases, ozone, peroxyacetyl nitrate, and the various organic primary and secondary pollutants have not been considered.

One key issue that has been identified is the formation of clouds, which can act to scatter

light and lead to cooling effects. The oxidation of sulfur gasses (e.g. sulfur dioxide, dimethylsulfide) can lead to the formation of sulfuric acid which can be an effective cloud condensation nuclei (Charlson et.al. 1987; Schwartz, 1988, 1989). As well, recent work by these authors has shown that dissolved inorganic and organic species in water have strong infrared absorption bands in the window region. Thus, gases, aerosols, dissolved species in clouds and fogs, must all be considered if we are to begin to accurately predict the radiative balance in our ecosystems. This includes both absorptive properties and light scattering characteristics of the cloud and aerosol droplets.

3. Biospheric and Climatic Feedbacks

A last but important area of future research will be the impacts of air pollution on our biosphere and its feedbacks. For example, increased temperature will likely lead to increased isoprene emissions from deciduous trees, which in turn will lead to increased levels of formaldehyde, ozone, hydrogen peroxide, and to conversion of sulfur dioxide to sulfate. How will this effect other species and their emissions?

A number of areas of research will be needed if we are to assure ourselves of effective air pollution control strategies. These include:

- o Knowledge of the effects of temperature, rainfall, pollution, etc. on the emissions of isoprene, terpenes, methane, and other compounds from the biosphere. The feedbacks from these emissions must be understood as they relate to changing energy related emissions of nitrogen oxides due to combustion.
- o Detailed information on the trace gas emissions from various species, as they increase or decrease depending on biospheric stresses.

- o The sensitivities of various biota to air pollutant and climatic stresses.
- o Hydrological cycle impacts due to changing biota patterns (i.e. species distributions). A number of similar issues has been outlined in a previous paper (Gaffney and Marley, 1991).

o The effect of increased ultraviolet radiation due to ozone depletions in the stratosphere upon biota.

The increased usage of satellite data (e.g. leaf index information) should be pursued in future evaluations of biospheric/atmospheric linkages (Fishman, 1991).

CONCLUSION

It is clear from this brief overview, that there is no scarcity of research needs in atmospheric chemistry in the decades ahead. In particular, we need to keep in mind that the atmosphere/biosphere/geosphere is an very dynamic system that requires some understanding before it can be successfully manipulated. We can no longer pigeon-hole and over-simplify environmental issues as we have done in the past (e.g. "acid rain", "urban ozone", etc.). Research needs to be carried out on non-criteria and criteria pollutants to obtain a better fundamental understanding of the system as a whole. This will require interactions between a number of different disciplinary areas. To accomplish this research, a significant increase in the quantity and quality of scientists trained in these areas will be needed, particularly in the area of atmospheric transformation chemistry.

ACKNOWLEDGEMENTS

The authors wish to thank the Department of Energy's Office of Health and Environmental Research, Office of Energy Research, for supporting this work as part of the Atmospheric Chemistry Program (ACP) under contract W-31-109-ENG-38.

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QUESTIONS AND COMMENTS:

Dr. V.M. Voloshcuck: If I understood you correctly, you talked in your paper on the increasing role of hydrogen peroxide in acidic pollution of the atmosphere. Have you any data from which one could judge on the climatic trend of the content of hydrogen peroxide in the atmosphere for the last decades?

Dr. J.S. Gaffney: We have a limited data set that indicates that hydrogen peroxide levels are important in the conversion of sulfur dioxide to sulfate and that the sulfate is a key species in producing cloud condensation nuclei and haze. The role of clouds and haze in climate modification is a current area of intense interest and discussion among the leading scientists in these areas. However, we do not have the type of long term data set to which you refer to determine changes in hydrogen peroxide levels and its direct effects on climate.

Dr. J.B. Shukla: One of the reasons affecting the ecosystem in water is the dumping of organic materials in rivers and seas leading to the depletion of oxygen. Could you please comment.

Dr. J.S. Gaffney: You have brought up an important point with regard to water pollution issues. We have attempted in this short report to address air pollution impacts of organics, but certainly they have important impacts on water pollution as well.

Dr. J. Slanina: The possible impact of peroxides on vegetation could be considerable, but the major contribution may result from dry deposition of these compounds on water layers produced by dew or precipitation?

Dr. J.S. Gaffney: Indeed, it is well established that hydrogen peroxide is highly water soluble. Thus it will play an important role in both wet (i.e. precipitation) and dry deposition onto wet surfaces such as dew deposited onto vegetation.

Dr. J. Slanina: You describe that background volatile organic carbon (VOC) concentrations could be limiting effective abatement strategies. What are the consequences of this situation both for future levels of oxidants and abatement measures/

Dr. J.S. Gaffney: It is becoming increasingly clear that the natural reactive hydrocarbons in our atmosphere can interact with nitrogen oxides produced from energy related activities to produce ozone, PAN, and other tropospheric oxidants. In the northern hemisphere, the sources of these pollutants are seasonal, with the maximum output of natural hydrocarbons being produced in the spring and summer. In the southern states, the natural hydrocarbon output from biota can be appreciable throughout the year. It appears to us that hydrocarbon control strategies will not be as effective as nitrogen oxide control.

Dr. J. Slanina: You mention the possible role of organic peroxides in sulfur oxidation of clouds. Is the reactivity of these compounds not much lower compared to hydrogen peroxide or ozone?

Dr. J.S. Gaffney: The actual reactivity of these compounds with dissolved sulfur (IV) is roughly equivalent to hydrogen peroxide. They are somewhat less effective than hydrogen peroxide as they are somewhat less soluble and therefore their effective concentrations are less. However, under circumstances where the hydrogen peroxide is reacted away (i.e. high SO_2), these organic oxidants may be important.

Dr. J. Slanina: Can you indicate the importance of in cloud infrared absorption in relation to other processes, eg. light scattering?

Dr. J.S. Gaffney: We believe that the absorption of infrared radiation by clouds may be very important when attempting to understand radiative balance. Certainly light scattering is also an important aspect of this issue, and must be seriously considered when addressing the effects of clouds and aerosols on climate.

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