



Journal of the Air Pollution Control Association

ISSN: 0002-2470 (Print) (Online) Journal homepage: http://www.tandfonline.com/loi/uawm16

# Summary of an APCA International Specialty Conference

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To cite this article: Viney P. Aneja, Donald F. Adams & Charles D. Pratt (1984) Summary of an APCA International Specialty Conference, Journal of the Air Pollution Control Association, 34:8, 799-803, DOI: 10.1080/00022470.1984.10465813

To link to this article: https://doi.org/10.1080/00022470.1984.10465813

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Published online: 08 Mar 2012.



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# ENVIRONMENTAL IMPACT OF NATURAL EMISSIONS Summary of an APCA International Specialty Conference

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Because man now influences the chemistry of the biosphere in so many important ways, it is essential that we understand the complex interrelationships among the chemicals from natural as well as anthropogenic sources and the factors that influence their life cycles. One important grouping of chemical species which influence the atmosphere are the naturally occurring compounds of sulfur, hydrocarbons, halocarbons and nitrogen. While significant efforts have been directed toward the control of similar anthropogenic air pollutants, very limited support has been provided for developing an understanding of the role of natural emissions in air pollution control.

Based on the realization that there may be specific cases where control of anthropogenic sources may have only minimal impact on air quality problems and since resources for basic research on the impacts of natural emissions are limited, the Air Pollution Control Association through the Technical Committee on Interactions with the Total Environment sponsored an International Specialty Conference on the "Environmental Impact of Natural Emissions." The following brief report is only intended to convey the flavor of the conference. The transactions of the conference will be available from APCA headquarters and are highly recommended.

The purpose of this conference was stated in the conference call: "The global sulfur, hydrocarbons, halocarbons and nitrogens  $(NO_x)$  budgets are receiving considerable attention, especially as they relate to anthropogenic and natural sources, and to removal rates. Because of their ubiguitous nature, natural emissions contribute significantly to background levels occurring in the troposphere up to the tropopause. These issues, as well as the significance of the reactions, local, global or upper atmosphere, will be addressed at this meeting. Attention will be directed to natural reduced sulfur compounds, to their oxidation to sulfur dioxide and fine sulfate particulate matter, and thereby to their contribution to reduced visibility, acid precipitation and the stratospheric sulfate aerosol layer."

The technical program to accomplish the purpose for the meeting consisted of seven sessions: Natural Sulfur, Natural Nitrogen, Natural Hydrocarbon, Natural Halocarbon, Atmospheric Reactions, Atmospheric Modeling, and a panel on Assessment of the Impact of Natural Emissions. The conference was held at the U.S. Environmental Protection Agency's Environmental Research Center, Research Triangle Park, North Carolina on March 7, 8 and 9, 1984. It was cosponsored by the South Atlantic Section and the Research Triangle Chapter of APCA.

#### Sulfur

The emission of sulfur into the atmosphere through natural processes has been recognized for at least 40 years. Interest in the magnitude of these emissions, however, has been heightened by recent evidence that biogenic sulfur sources may make significant contributions to the atmospheric loading of particulate sulfate which can be transported over large distances.

Viney Aneja, General Electric Company, reported direct measurements of sulfur emission rates from North Carolina coastal marine sediments. An emission flux reactor (chamber) technique was used to determine the emission rates of sulfur compounds into the atmosphere. The sulfur gases were identified and their concentrations in the emission flux reactor measured with a gas chromatograph equipped with a flame photometric detector specific for sulfur. In general, the emission rates of these gases varied over a wide range of sulfur fluxes (0.05–100 g S m<sup>-2</sup>yr<sup>-1</sup>) under varying conditions of spoils, stage of the tidal cycle, and diurnal variation. It was observed that the emission rates vary inversely with the stage of the tidal cycle. The tidal cycle causes changes in the hy-

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drostatic pressure which affects the gaseous release at the locale. The diurnal studies showed an enhancement in the emission rates at night. The emission rate of gaseous sulfur release appears unrelated to photosynthesis since emission rates were unaffected for increasing light intensity (<90,000 luxes) for constant temperature.

Dian Hitchcock, Hitchcock Associates, compared biogenic H<sub>2</sub>S levels in the atmosphere at an inland region where wetlands were abundant (in Monroe County, near Rochester, New York), and at two sites for a two-week interval in a coastal salt marsh (Wallops Island, Virginia) where previous studies had revealed high concentrations of biogenic sulfur. Hydrogen sulfide levels were extremely variable in both locations, but the range of observed levels were remarkably similar, being slightly but not significantly higher at the inland location than at the coastal marsh. The high concentrations at the inland site were attributed to conditions in local surface waters that promote the metabolism of the bacteria which produce H<sub>2</sub>S as a consequence of high nutrient loadings (eutrophy) due to fertilizer runoff. The data suggest that sulfide releases from the inland marsh system were comparable to those of the coastal salt marsh. If so, the summertime rate of release of hydrogen sulfide from a region of about 8000 km<sup>2</sup> in the southern Lake Ontario plain may lie between about 3 and 16  $\times 10^9$  gm.

Hal Westberg, Washington State University, reported that crops such as alfalfa, corn, beans, tomatoes and peas, as well as oak and pine trees, emit reduced sulfur gases. COS and  $(CH_3)_2S$  were found in quantities ranging from 4 ng S g<sup>-1</sup>h<sup>-1</sup> for pine to 20-40 ng S  $g^{-1}h^{-1}$  for the other vegetation. For typical biomass densities, these emission rates convert to fluxes similar in magnitude to those measured for various inland soils. Dynamic enclosure field measurements of sulfur fluxes from a soil near the western cost of Washington State were in the same range as fluxes obtained over the same soil type in Ohio. A preliminary extrapolation of the available eastern soils data to those of the continental U.S. indicates that biogenic emissions (non-vegetative) amount to approximately 2% of the national anthropogenic emission total. However, an analysis of known errors in the data base indicates that this estimate was a lower limit to the contribution of natural sources.

R. A. Rasmussen, Oregon Graduate Center, reported estimates of global emissions of carbonyl sulfide (COS) and carbon disulfide (CS<sub>2</sub>) from anthropogenic and natural sources suggesting that about 2 million tons (or 2 Tg) of each of these gases are emitted every year. These findings support the contention that only about 25% of the COS and CS<sub>2</sub> comes from anthropogenic sources.

Don Adams, University of Idaho, reviewed the apparent inconsistencies found in sample to sample comparisons. Included in the data set were replicate samples by the same investigator and similar studies by other investigators at different sites. The presentation brought into focus questions of extrapolation from small sampling sites to large geographical area fluxes, and our understanding of atmospheric sulfur chemistry.

## Nitrogen

The nitrogen cycle in nature is extremely complex. The major reservoir for nitrogen is the atmosphere, where it is present as molecular nitrogen and as trace constituents in other compounds that are all directly or indirectly of natural or anthropogenic origin.

In addition to  $N_2$  the atmosphere contains nitrogen as ammonia, nitrous oxide, nitric oxide and nitrogen dioxide. It also contains ammonia and nitrate in solution, as aerosols and as cloud droplets.

With respect to emissions of nitrogenous gases, the state of the art is in many ways at a higher level of development than that relating to other gases. This is due primarily to the long recognized importance of nitrogen cycling to agriculture. Concern over losses of soil nitrogen and the optimum utilization of fertilizers has been the impetus for many such studies. Unfortunately, until very recently, most such studies have dealt with rates of nitrate and ammonium loss without paying much attention to either the quantities of nitrogen removed by different processes or the form in which these compounds are removed. The problem is compounded by the fact that nitrogen losses from non-agricultural soils have been almost totally ignored.

For many nitrogen gases, a complete inventory of all major emission sources is lacking, let alone the availability of quantitative flux estimates. Also, where data do exist there is often considerable controversy over flux magnitudes from various sources.

Direct emission measurements are often difficult or impossible to obtain. Hence, emission estimates have been derived through the application of various models and experiments designed to simulate natural conditions. Nitrogen gas emissions from lightning and from forest and brush fires are prime examples of natural emission sources. Varying assumptions employed in the use of such models can result in substantial differences in emission estimates. Models have also been employed to estimate fluxes where data are poor or unavailable, but where parameters governing emissions, determined through laboratory studies, are reasonably well understood.

Patrick Brezonik, University of Minnesota, reviewed some important concepts and limitations of mass balance models and illustrated by several examples the relative importance of natural versus anthropogenic fluxes for nitrogen, especially in the atmospheric components of the budgets. Mass balances are simple conceptual models of a real system, and they serve to organize and summarize existing knowledge in a succinct and quantitative manner.

George A. Dawson, University of Arizona, reviewed the sources, links, vertical distribution, and surface concentration of ammonia as the only identified gaseous base in the unpolluted troposphere. Background concentrations in the southwestern U.S. which are believed to be primarily of natural origin typically have been found in the range of 1 ppb or a little less. Concentrations greater than 10 ppb have been found to be associated with agricultural activities. As a highly soluble gas, ammonia should have a small mean scale height, probably close to 2 km, though there were very few experimental data. There were essentially no data on the flux of gaseous ammonia to and from soils and vegetation. Simple considerations lead to estimates of the natural flux of ammonia to the atmosphere of between 20 and 40 Tg yr<sup>-1</sup>.

Dennis R. Keeney, University of Wisconsin, reported measurements of nitrous oxide emissions from several natural (unfertilized) and agricultural ecosystems using a closedchamber technique. Emissions from prairie, flooded marsh and deciduous (oak) sites were low ( $< 1 \text{ kg N}_2\text{O-N} \text{ ha}^{-1}\text{yr}^{-1}$ ), whereas that from sites in a coniferous (white pine) forest and a wet meadow were intermediate (1–2 kg N<sub>2</sub>O-N ha<sup>-1</sup>yr<sup>-1</sup>). High N<sub>2</sub>O flux, comparable to agricultural systems, were found in a drained marsh. Highest N<sub>2</sub>O output from agricultural systems occurred at N-fertilized, manured, or alfalfa residue treated sites. All emitted less than 10 kg N<sub>2</sub>O-N ha<sup>-1</sup>yr<sup>-1</sup>.

Large within-site (spatial) variability in N<sub>2</sub>O emissions were encountered (coefficients of variation averaged 100%). The N<sub>2</sub>O flux also varied widely with time, with maximum values after rainfalls, N-fertilization and spring thaw. The spring thaw period was monitored closely. Soil profile N<sub>2</sub>O concentrations increased from ambient in January to very high values at thaw, then decreased again. The mechanisms for this variation are unknown. During the spring-autumn period, N<sub>2</sub>O production was at the soil surface due to nitrification while after heavy rains N<sub>2</sub>O was produced in the subsoil by denitrification of leached nitrates. John Duxbury, Cornell University, summarized the current research on the relative release of  $N_2O$  and  $N_2$  in soils for several variables: aeration, inorganic N species, pH, and available carbon. Although large amounts of  $N_2O$  were frequently found in laboratory studies,  $N_2$  was the dominant denitrification product (>80%) under field conditions.

In a two-year study N<sub>2</sub>O emissions from mineral soil sites ranged from 1 to 3.3 kg N ha<sup>-1</sup>yr<sup>-1</sup> but were close to 100 kg N ha<sup>-1</sup>yr<sup>-1</sup> at cropped organic soil sites. The data illustrated the effects of soil type, crop, and fertilizer management practices on N<sub>2</sub>O emissions from soils. A preliminary analysis of N<sub>2</sub>O emissions from various land uses suggested that agriculture may increase terrestrial N<sub>2</sub>O emissions by 50% of a baseline value.

Dan L. Albritton, National Oceanographic and Atmospheric Administration, reported on measurements of the odd-nitrogen species and particulate nitrate in remote oceanic and polar areas and provided an estimate of the annual averaged global nitrate deposition flux for those regions. It was shown that this nitrate was largely of natural origin. Furthermore, it was demonstrated that the likely natural source was upper-tropospheric lightning, which occurs mainly over the tropics. The odd-nitrogen species produced were long-lived and hence globally distributed. The maximum nitrate deposition flux,  $9 \times 10^8$  molecules cm<sup>-2</sup>s<sup>-1</sup>, occurs near the equator. This upper-tropospheric component of the lightning source deposits 0.12 Tg N yr<sup>-1</sup> over North America. This type of estimate does not depend on stroke frequency and nitrogen production per stroke, which have been used in past estimates. When this value was combined with an estimate of the component produced locally by lower-tropospheric lightning, the net nitrate contribution from lightning to North America was found to be  $0.51 \text{ Tg N yr}^{-1}$ , or about 8% of the anthropogenic emissions from the same region.

# Hydrocarbon

Initial evidence of the amount of natural organic volatiles emitted to the atmosphere was presented by Went in the early 1960s.<sup>1</sup> Interest in these naturally emitted organics increased dramatically in the late 1960s when scientists at the Stanford Research Institute estimated that global natural organic emissions (excluding methane) far exceeded anthropogenic emission. Since that time, research has accelerated to refine emission estimates, to measure ambient air hydrocarbon concentrations and to study the atmospheric chemistry of these compounds.

R. A. Rasmussen, Oregon Graduate Center, has shown that many plants emit measurable quantities of volatile organic compounds into the ambient air. He also has developed methodologies (dynamic flow chambers) to determine the emission rates from various plant species.

C. K. McMahon, USDA, reported that burning of organic soils and forest fires produce large quantities of organic compounds in the particulate form. Highly organic soils can sustain slow combustion for up to several weeks. In laboratory burning studies they found resulting particulate matter was soot free and contained a high percentage of polyaromatic hydrocarbons including benzo(a)pyrene.

Robert L. Seila, U.S. EPA, reported on atmospheric volatile hydrocarbon composition in remote areas of northwestern North Carolina. The nonmethane total hydrocarbon concentrations at the remote sites ranged from 32 to 132 ppbC. The range of identified paraffins, olefins, and aromatics concentrations was 7–65 ppbC, 1–8 ppbC, and 2–20 ppbC, respectively. Isoprene and  $\alpha$ -pinene made up a small portion of NMTHC, ranging from less than 0.05 to 13 ppbC and less than 0.05–9 ppbC, respectively. Unknown peaks eluting mostly in the post-C-9 region of the chromatogram were a significant portion of the NMTHC, ranging from 13 to 108 ppbC. These hydrocarbon species and their sources were not known, although some of the species were probably of biogenic origin. Isoprene and  $\alpha$ -pinene displayed a distinct seasonal variation related to ambient temperature, whereas acetylene and the sum of paraffins, olefins, and aromatics showed no seasonal variation.

Donald B. Hunsaker, Jr., Oak Ridge National Laboratory, reported on the use of the Livermore Regional Air Quality (LIRAQ) model to study hydrocarbons in generating ozone in the San Francisco Bay Area. A nine-county vegetation distribution map prepared from data from the space satellite called Landsat and using vegetative hydrocarbon emission factors developed from results of a Delphi Survey of experts in the field. It was estimated that vegetative sources in the nine-county Bay Area emit about 400 tons per day of hydrocarbons. An estimate of the ozone production in the Bay Area was developed by using the LIRAQ model, a deterministic grid-based photochemical computer model developed for the Bay Area. All inventory components were aggregated to 5 km grid square spatial detail, 1-h temporal detail, and four organic reactivity classes. Model verification improved when the vegetative emissions were included. While the vegetative emissions inventory was relatively large and reactive, the effect on highest hour ozone was modest. However, a greater effect is expected in rural areas located away from the central urban core where biogenic emissions are larger. Inclusion of biogenic sources has a general tendency to dilute the benefits of controls on anthropogenic sources, so that greater emission reductions would be required to project attainment of air quality standards. These results are consistent with independent statistical evaluations of annual ozone trends.

Richard Hutte, University of Colorado, reported on studies of the natural wet removal process for natural atmosphere organic compounds. He concluded that washout was a major mechanism for the removal of organic compounds from the atmosphere. Their conclusions on washout were based on samples collected from a remote mountainous site. The organic compounds isolated from these precipitation samples appear to come predominantly from natural sources.

## Halocarbon

Over the years it has become evident that the atmosphere contains a large number of halocarbon compounds which are predominantly of natural origin. Halogenated compounds have received a great deal of attention in recent years because of their toxicity, their ability to interact with stratospheric ozone, and their potential for atmospheric warming. It is well known that bacteria, algae and sponges produce a variety of halogenated chemicals. These compounds vary from simple halomethanes to highly complex toxins. The simplest and highly volatile species are the most abundant and importnat from an atmospheric viewpoint. Although highest organohalides (>C<sub>1</sub>) are likely to be present, the current knowledge strongly suggests that halogenated methanes are the dominant carriers of organically bound halogens.

Hanwant Singh, SRI International, presented a comprehensive review of the sources, fate, and interrelationships of halogenated methanes. Halogenated methanes are the most important atmospheric carriers of naturally occurring halogens. Methyl chloride and chloroform are two chlorinated species which come from the ocean (it is estimated that 70-80% of CH<sub>3</sub>Cl is of oceanic origin.) A chloroform source of 0.4–0.6 Tg yr<sup>-1</sup> is needed to balance its budget. The oceans appear to be significantly supersaturated with CHCl<sub>3</sub> but the data were too sparse for a full inventory of its sources. Although less abundant, several brominated methanes were found in the troposphere. Methyl bromide, CH2Br2 and CHBr<sub>3</sub> have been measured. The oceans were also supersaturated with methyl bromide, and provide a large natural source. No seawater CH<sub>2</sub>BR<sub>2</sub> data has been discovered. High concentrations of CHBr<sub>3</sub> were found in the eastern Artic Ocean and in the artic air. It is also possible that a number of chloro/bromo methanes were present in remote atmospheres

but have not yet been measured. Methyl iodide appears to be a major carrier of oceanic iodine. Overall, oceans appear to provide a large gaseous organic halogen source contributing 3-5 Tg(Cl) h<sup>-1</sup>, 0.3-0.5 Tg(Br) yr<sup>-1</sup> and 0.3-0.5 Tg(I) yr<sup>-1</sup>. Most naturally occurring chloro/bromo methanes that have been measured have a lifetime of 0.5-2 years. Methyl iodide was an exception and has a lifetime of only 5-10 days. A unique property of these naturally sourced halo-methanes is that they can all cause mutations in bacteria and are toxic at higher concentrations. The mechanism by which halogenated methanes are produced in the marine environment is not well understood.

A. J. Owens, E. I. DuPont de Nemours Company, discussed the role of natural and man-made chlorocarbons and chlorofluorocarbons in the stratosphere and their impact on the ozone layer. Methyl chloride is the most abundant atmospheric halocarbon with a source strength of  $3 \times 10^{12}$  g yr<sup>-1</sup> and a half-life of 1.8 yr. Methyl chloride constitutes approximately 20% of the free tropospheric chlorine and approximately 25% of the upper stratospheric chlorine budget. The other sources of stratospheric chlorine are of industrial origin.

M. A. K. Khalil, Oregon Graduate Center, discussed the emissions of methylhalides (CH<sub>3</sub>I, CH<sub>3</sub>Br, and CH<sub>3</sub>Cl) and chloroform (CHCl<sub>3</sub>) from the oceans and the removal of CCl<sub>3</sub>F (F-11) from the atmosphere. The methylhalides (CCH<sub>3</sub>Br, CH<sub>3</sub>I, and CH<sub>3</sub>Cl) appeared to be the dominant naturally occurring bromide, iodine and chlorine containing trace gases in the atmosphere. Chloroform (CHCl<sub>3</sub>) had been thought to be primarily anthropogenic, however, recent evidence indicates that the oceans may be a large natural source on a global scale. Trichlorofluoromethane (F-11) is an anthropogenic fluorocarbon used in foams, refrigeration and spray cans. It is believed that F-11 can deplete the ozone layer in the stratosphere and thus perturb the global environment.

J. W. Winchester, Florida State University, reported on a study to compare the elemental composition of marine aerosol. By comparing aerosol composition in different locations they were able to estimate the extent of halogen release from the interaction of sea salt aerosol and reactive air pollutants. They observed considerable release of HCl or other gaseous compounds by air pollutant interaction with the natural marine aerosol from the North Atlantic. They suggest that this process may have significant impacts on coastal regions of the eastern U.S. and over the ocean at least 1000 km downwind of anthropogenic sources.

#### **Atmospheric Reactions**

The atmospheric reactions session featured presentations on a variety of atmospheric pollutants in the gaseous, particulate and gas-particulate phase. The speakers reported on recent advances in the measurement, reaction rates, diffusion coefficients, mass concentration and techniques for reaction chamber studies for several of the compounds of interest because of their association with acid deposition and toxicity.

E. S. Saltzman, University of Miami, discussed the atmospheric chemistry of methane sulfonic acid (MSA), an oxidation product of the gas phase reaction of OH radical with dimethyl sulfide. MSA was found in marine aerosols. Model calculations were presented for its photochemical lifetime by free radical destruction pathways. In aerosols >0.1  $\mu$ m, the MSA lifetime is longer than the time for physical removal of the aerosol itself, indicating the stability of MSA in such aerosols. This suggested that MSA might be used as a tracer for organosulfur emissions in the marine environment.

J. L. Durham, U.S. EPA, Research Triangle Park, described the sampling and indirect identification of dimethyl and methyl hydrogen sulfate through use of their diffusion coefficients which control the penetration profile of trace reactive gases in a nylon sample tube. This system follows the modified Gormley-Kennedy diffusion equation.

Linda Cornell, Mississippi State University, reported on the kinetics of the reaction between phenanthrene and ozone in aqueous solution. This research suggests that phenanthrene may be more reactive in aqueous media than some other polycyclic compounds in the formation of secondary pollutants.

D. A. Saucy, University of North Carolina, discussed the atmospheric reactivity of a typical polynuclear aromatic hydrocarbon, 9-nitroanthracene, under simulated atmospheric conditions. Such compounds are associated with particulate matter emissions from combustion. Because of their submicron size, they can penetrate the alveolar regions of the lungs. The research protocol used gave particle concentrations and size distributions similar to those produced by actual fuel combustion, thereby permitting chamber studies of reactions likely to occur in the troposphere.

#### **Atmosphere Modeling**

This session can be divided into presentations that were concerned with: the phenomenon of "acid rain," the photochemistry of natural hydrocarbons and the global carbon monoxide budget.

Julian Chang, National Center for Atmospheric Research, presented a Eulerian acid deposition model. The primary objective of this effort was the development of a system of models suitable for assessing source-receptor relationships and for examining key issues such as the role of natural emissions in the formation of acid rain. The model was actually a system of models that integrate an existing mesoscale meteorological model with a new transport and chemical transformation model. It addressed issues related to the gas phase processes most relevant to acid production, techniques for illuminating source-receptor relationships in a Eulerian model, and the implications of "predictability" in the simulation of source-receptor relationships.

Nels S. Laulainen, Battelle Pacific Northwest Laboratories, discussed wet removal processes, one of the primary phenomena of the acid deposition process. He described the current status of the PLUVIUS series of reactive storm models. Although the PLUVIUS models have been developed for the interpretation of field data, it was shown that they could be used on a predictive mode to examine source-receptor relationships.

Jack D. Shannon, Argonne National Laboratory, addressed the problem of including biogenic sources in a Lagrangian acid deposition model. Model simulations of the relative importance of these two source classes were presented.

Roland B. Stull, University of Wisconsin, presented some results from a preliminary field investigation of the interaction between small cumulus and the mixed layer. The role of fair weather cumulus clouds in the chemical transformation and the vertical transport of various pollutant species has received increasing attention in recent years. Some researchers have hypothesized that fair weather cumulus clouds can transport significant quantities of pollutants out of the atmospheric mixed layer, transform them via aqueous phase reactions and inject the transformed products into the air above the mixed layer.

Frederick W. Lurman, ERT, examined the role of biogenic hydrocarbon emissions on urban ozone formation using a photochemical trajectory model. Emission inventories indicated that the biogenic and anthropogenic HC emission rates were comparable when the biogenic HC is averaged over the entire Tampa-St. Petersburg area. However, the model indicated that less than 10% of the predicted maximum ozone concentration was due to natural emissions. This small contribution was attributed to fast ozone-biogenic HC reactions that scavenge almost as much as is produced by the biogenic HC in the urban environment.

Alan C. Lloyd, ERT, focused on an important aspect of the chemical mechanism to predict ozone formation in mixtures of natural hydrocarbon emissions. The mechnism was then tested against 17 outdoor smog chamber data sets from the University of North Carolina chamber. The mechanism was able to predict with reasonable accuracy maximum ozone concentrations and the time-concentration profiles of other species, such as NO<sub>2</sub>, PAN, and aldehydes. The authors believed that due to the greater availability of kinetic and mechanistic data for isoprene, the mechanism is probably more accurate for that compound than for  $\alpha$ -pinene.

Joyce E. Penner, Lawrence Livermore National Laboratory, described the development of a chemical scheme for representing the photochemistry of isoprene in a complex urban scale photochemical model. She proposed a simplified chemical scheme which adequately simulates the chemistry of isoprene. This finding eliminates the need to use a more computationally involved mechanism in the model.

M. A. K. Khalil, Oregon Graduate Center, discussed the global carbon monoxide budget. The lifetime of CO in the atmosphere is fairly long; thus it can be dispersed to locations far from its sources. They described a study in which a one dimensional, zonal dispersion model, together with a statistical analysis of a large observational data base, was used to examine the global budget of CO and to indicate the role of natural and anthropogenic sources of carbon monoxide.

#### Conclusions

Natural source strengths of sulfur, nitrogen, halocarbon and hydrocarbon compounds were discussed during the conference. Wide variability in the range of emissions for most of these compounds has been reported within a single sampling site, soil order, or plant species. Even greater variability is recorded among different sites, soil orders and plant species. In part, these variations are associated with ambient or substrate temperatures, climate, recency of rainfall, microbiological activity, and site chemistry (both inorganic and organic). Other sources of variability are associated with the varying and generally unvalidated calibration, sampling, and analysis techniques used by the researchers in this field of microchemistry.

Such analytical chemistry problems have been reasonably well addressed for hydrocarbons and halocarbons, but not for the sulfur and nitrogen compounds. Also, as the limit of detection for any given analytical method is approached, the imprecision of the data increases. Accuracy also becomes questionable if there are no validated calibration standards to cover the lower range of the concentration spectrum for many of the field samples.

Especially for sulfur-containing compounds, it is generally conceded that all of these variables combine to provide *reported* natural emission flux data which are lower than the *actual* fluxes.

The major problems associated with calculating global emissions are related to: 1) the lack of sufficient data, 2) the quality of data especially at or near the detectable limits of current measurement methods, and 3) the lack of an adequate understanding of the physical and chemical processes involved in production, distribution and removal of natural emissions.

A. P. Altshuller, U.S. EPA, Research Triangle Park, noted that "with the possible exception of hydrocarbons, the presently reported biogenic emission rates appear too low per unit area to be of concern compared with anthropogenic emissions." In addition, some of the proposed models relating hydrocarbon emissions to regional scale ozone levels did not indicate a significant natural hydrocarbon contribution. However, more accurate and extensive measurements are needed to verify such a conclusion.

Natural sulfur- and nitrogen-containing compounds contribute to the acidity of deposition. The extent of that contribution will vary with the strength of the natural source and in relation to the strength of the associated anthropogenic sources. For receptor areas in the northeastern U.S. and southeastern Canada, biogenic emissions of these compounds would have to be grossly underestimated to contribute substantially to the total deposition. However, this may not be true for unpopulated, tropical regions.

The overall tone of the conference was more that of a series of research presentations than one of defining the significance of natural emission contributions to the environment. The transactions will provide much current information on natural emissions not available elsewhere.

## Acknowledgments

The authors wish to thank all those who assisted in the development and presentation of this conference. The APCA headquarters staff provided excellent support under conditions of great economic uncertainty. The host Section and Chapter provided terrific support from beginning to end.

A very special note of recognition and thanks is hereby extended to the session chairmen and cochairmen. Without their support and efforts this meeting could not have been held. The authors salute: William E. Wilson, Patrick Brezonik, Jay J. Messer, R. A. Rasmussen, Hanwant Singh, Jack Durham, William Pennell, Paulette Middleton and Nels Laulainen.

At the end of most conferences, the attendees are left with many unasked and unanswered questions and without a clear concept of the meaning of what they have heard. Four nationally recognized scientists were recruited to bring the conference presentations into sharp focus. Their comments throughout the conference and their summations at the conclusion of the conference were exceptional. The authors wish to recognize these scientists for their contribution: Dr. Paul Altshuller, U.S. Environmental Protection Agency, Dr. Jennifer Logan, Harvard University, Dr. Nelson Kelly, General Motors Research, and Professor Don Adams, University of Idaho.

#### Reference

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