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ABSTRACT

The research activities making up the programs in the Environmental Chemistry Division of the Department of Applied Science are presented. Some of the more significant accomplishments during 1989 are described and plans for 1990 are discussed briefly. Publications for the period are listed and abstracts are provided. Research objectives and principal investigators are given for each of the active programs. A list of personnel and collaborators during the past year is presented. The support distribution for FY 1989 is approximately 85% from the Department of Energy (65% Office of Health and Environmental Research), and 15% other agencies (principally from the Electric Power Research Institute).

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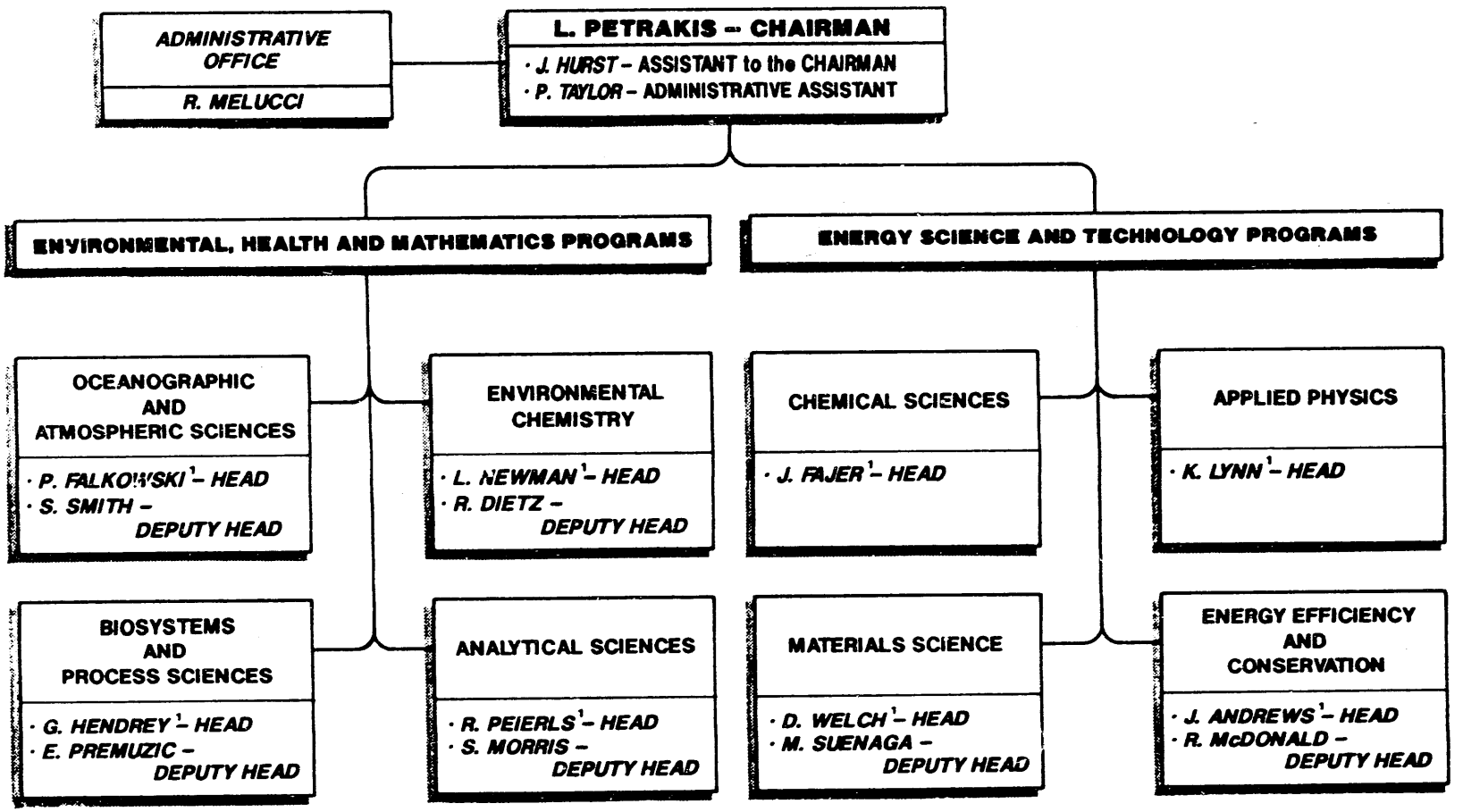

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(1) Members of Dept. Council

INTRODUCTION

The Environmental Chemistry Division is engaged in a wide range of programs encompassing theoretical studies, measurement methodology, laboratory studies and field experiments. Areas of research include (1) the development of methods and practical instruments for the detection and measurement in real-time of a variety of atmospheric constituents at ambient levels for use in field studies and laboratory experiments, (2) the development and applications of gaseous tracers employed at extremely low concentration levels in studies of atmospheric transport and dispersion, building air infiltration and ventilation, geophysics of oil and gas recovery from production wells, and other leak detection applications, (3) theoretical, laboratory, and field studies directed at understanding the formation and behavior of aerosols, (4) studies engaged in the measurement and understanding of the formation of gaseous and particulate pollutants as they mix with ambient air, (5) modeling studies involving the kinetics of chemical reactions taking place among pollutants and with water vapor in the atmosphere, and (6) laboratory and field studies directed at understanding the mechanisms involved in the incorporation of sulfur and nitrogen into cloud water with the consequent formation of acid rain. An Analytical Chemistry Group is operated to provide support services for this and other Divisions (especially Atmospheric Sciences) within the Department and the Laboratory.

SIGNIFICANT ACCOMPLISHMENTS

Research in the Environmental Chemistry Division is directed toward the determination of the concentrations of environmental pollutants arising from anthropogenic sources and the study of their interactions, by the development of measurement methodologies, laboratory investigations, field experiments, and analysis and interpretation of data.

Emphasis within the Division has been placed on: the development of highly sensitive techniques for measuring gaseous pollutants as well as tracer compounds and their transport and dispersion; the development of methods for determining the size distribution and molecular composition of ambient aerosols; theoretical studies and laboratory measurements of aerosol properties; the modeling of chemical reactions of pollutants, laboratory studies of the mechanisms and rates of reactions occurring under ambient conditions which include investigations under clear air, cloudy and rain conditions; field experiments to elucidate the interdependence of transport and transformation; and, analysis of data relevant to global climate change. The disciplines represented on the staff include chemistry, biochemistry, physics, engineering, applied mathematics, as well as meteorology (collaboration with the Atmospheric Sciences Division). Subgroups within the Division include a Tracer Technology Center and an Analytical Chemistry Group which provides support for the above programs and other efforts in the Department and the Laboratory as a whole.

1. Analysis and Interpretation

<u>H_2O_2, SO_2, and related compounds from field measurements</u>. Analysis of data from field studies, particularly data from the DOE-sponsored PRECP (<u>PR</u>ocessing of <u>E</u>missions by <u>C</u>louds and <u>P</u>recipitation) program has been a major focus this year. Particular interest in the study of the concentration fields of H_2O_2, SO_2, and related compounds derives from the recognition that reaction of SO_2 and H_2O_2 in clouds may be a significant source of the sulfuric acid deposited in precipitation. Thus, the spatial and temporal characteristics of sulfate wet deposition may be determined not only by the amount of SO_2, but also by the amount of H_2O_2 available for its oxidation.

Analysis of H_2O_2 and SO_2 concentration fields adjacent to convective clouds revealed several characteristics which may have significant implications with respect to the importance of the H_2O_2/SO_2 reaction in summer convective storms. Vertical profiles of H_2O_2 concentration exhibited a characteristic shape with concentrations near the surface frequently less than aloft. Typically a "bulge" in the concentration was observed near the top of the boundary layer. Concentrations above the boundary layer typically decreased slowly with increasing altitude. In contrast, vertical profiles of SO_2 exhibited the highest concentrations in the lowest portion of the boundary layer near the earth's surface. Concentrations dropped off rapidly with altitude, and were frequently too low to be measured above the boundary layer. Comparison of the H_2O_2/SO_2 vertical profiles showed that the H_2O_2 concentration in the boundary layer was seldom sufficient to oxidize the available SO_2, whereas above the boundary layer, H_2O_2 was frequently in excess. These observations imply that mixing processes may be an important factor in controlling the extent to which the SO_2/H_2O_2 reaction occurs in convective storms. Further study of the H_2O_2 vertical profiles showed that although the shapes of the profiles were similar day to day, concentrations varied significantly between days. A radical budget calculation showed that most of this variability could be ascribed to changes in the water vapor concentration. Changes in H_2O_2 with altitude above the boundary layer were also ascribed to changes in water vapor concentration. The generally lower, and for the most part, highly variable H_2O concentrations found near the surface (in comparison to observations aloft) were attributed to changes in the distribution of radical consumption pathways (i.e., the enhanced importance of NO_x in the boundary layer for radical consumption in comparison to radical combination processes producing H_2O_2) and to the enhanced importance of other H_2O_2 loss processes such as dry deposition.

<u>In-cloud measurements</u>. Analysis of in-cloud data showed evidence for a strong seasonal trend in H_2O_2 concentration. Average concentrations of H_2O_2 during the spring and summer were approximately a factor of 10 higher than concentrations in winter. This observation was found to be consistent with a photochemical source for H_2O_2, and with the seasonal dependency of atmospheric water vapor concentration.

The mutual exclusiveness exhibited by H_2O_2 and SO_2 in non-precipitating clouds was not observed in precipitating clouds; significant quantities of SO_2 were observed to co-exist with H_2O_2. This observation was attributed to the transport of H_2O_2 from aloft by falling rain drops. Thus, the measured H_2O_2 would not have had sufficient time to react with the local gas-phase SO_2.

Drop-size dependent chemistry in clouds. Techniques previously developed for modeling gas-aqueous reactions in clouds have been extended to treat clouds having a realistic drop size distribution, as determined by field measurements. Mass-transport coupling between gas and aqueous phases is more rapid for smaller drops, which, therefore, scrub soluble gases, such as HNO_3, more rapidly than larger drops and are thus initially more acidic. As a consequence, SO_2 oxidation of O_3 (which is inhibited by acid) is initially much more rapid in larger drops. However, as a consequence of the acidity produced by that reaction, the H^+ and $SO_4^=$ concentrations soon become relatively uniform as a function of drop size.

Influence of aerosol sulfate on cloud albedo and climate. Previous work at BNL and elsewhere has suggested that increased concentrations of sulfate-containing aerosol particles can, by increasing cloud albedo, decrease heating of the earth by direct solar radiation. This work has been extended to estimate the magnitude of this forcing on local and regional scales. Preliminary estimates suggest that this forcing can be significant on scales of several thousand kilometers, and be of magnitude 1 to 2 W m^{-2}. Such a forcing is comparable to that of increased concentrations of CO_2, but of opposite sign, and should be considered in analyses of global climate change.

Droplet evaporation kinetics. In the study of photochemical formation of organic aerosols in the atmosphere, it is usually necessary to know the vapor pressures of the condensing species. Unfortunately, however, such data are often difficult to obtain for species of practical interest, because their volatility at ambient temperatures is too low to render measurements by conventional experimental methods. Although the single-particle evaporation technique recently developed at BNL and elsewhere offers a good chance to determine ultra-low vapor pressures, a knowledge of the diffusivities and/or

evaporation coefficients of the evaporating organic molecules is a prerequisite that is again hard to acquire. A mathematical analysis was, therefore, undertaken to incorporate the temperature dependence of diffusivity into the droplet evaporation kinetics. The temperature coefficients of the vapor pressure equation can then be determined without having to know the actual values of the diffusivity. If, in addition, some high-temperature vapor pressure data are available in the literature for the organic compound of interest, a best-fit, self-consistent vapor pressure curve can then be deduced from all data points over the entire temperature range under consideration. This procedure eliminates the uncertainty associated with a long extrapolation, which normally spans many orders of magnitude on the pressure scale. The mathematical analysis was carried out for both the continuum regime (760 torr) and the free-molecule regime (0.05 torr), in which different droplet evaporation kinetics operate.

Relationship between PAN and O_3 concentrations at a surface site. The relationships between the concentrations of PAN and O_3, measured at a surface site, have been investigated. Daytime measurements showed that both species have a photochemical source and the magnitude of daytime increases was dependent upon NO_y concentration. Nightime behavior showed O_3 to be rapidly deposited at the surface, under stable nocturnal inversions, whereas, PAN was not. The presence of high NO concentrations, from stationary sources at night, resulted in reduction of both species concentrations to virtually zero.

Soil gas diffusion models applied to subsurface tracing. Subsurface transport of both intentionally added tracers as well as that of pollutants from previous releases and contaminated aquifers was examined with the use of models for the applicability of near-surface measurements to the characterization of deeper subsurface sources. In one case, in order to reduce the cost of decommissioning an experimental site consisting of about 35 barrels of sand in a lined trench into which was released 25 gallons of perfluorocarbon tracer (PFT)-tagged high voltage insulating fluid, the near-surface (5-inches below the surface) measurements of PFT concentration were used in a model to predict the location of the oil-laden sand; the model indicated that the oil should be confined to only about 2.3 barrels of the sand, which could

reduce clean-up costs by as much as $10,000. The oil content of the sand can also be quantified by the analysis of the PFT content with a limit of detection of 5 ppb of oil in sand. In another case, a preliminary model evaluation of pollutant-laden subsurface spills and aquifers implied that the PFT sampling and analysis technology, with small modifications, could be adapted to detection and pinpointing of chlorinated solvent-laden subsurface sources. Both approaches will be further confirmed by field measurements.

2. Measurement Methodology

Measurement of odd-nitrogen species. There have been many improvements in the measurement techniques for odd-nitrogen (NO_y) species. The use of a CO-doped gold catalyst has made the measurement of NO_y by catalytic conversion-O_3 chemiluminescence more reliable. In the measurement of NO_2 by photolytic conversion-O_3 chemiluminescence, the addition of an IR beam splitter results in less interference from deposited aerosol decomposition products and an AL reflective coating of the photolysis cell betters the conversion efficiency. A two column system in the packed column GC/ECD measurement of PAN eliminates water and permits an analysis time of 5 minutes. In the capillary GC/ECD measurement of PAN and alkyl nitrates, a trifluoro-propyl silicone phase offers much better separation of PAN and 2-propyl nitrate. The packed and capillary column systems have been intercompared with laboratory standards and show excellent agreement at mixing ratios from 10 ppbv to below 0.5 ppbv.

Measurement of atmospheric species. A commercial NO_x instrument was modified to reduce the noise level. These improvements yielded a factor of ten enhancement of the minimum detectable quantity (<0.2 ppbv).

Single particle Raman spectroscopy. Effort in the improvement of sensitivity of the single particle Raman spectroscopy is continued. The basic design of this Raman spectrometer remains unchanged. The charged particle is trapped at the null point of a quadrupole electric field. The radiation pressure due to the excitation laser is counteracted by the additional dc potential. Both the data collection efficiency and Raman frequency measurement are improved by the introduction of a recently acquired optical multichannel analyzer (OMA). The accuracy in the present setup is greatly

increased by keeping the setting of the monochromator fixed between the scanning of the samples and the wavelength standard. The ultimate resolution of the Raman spectrometer is currently in the order of 0.25 cm^{-1}. In actual practice, the slit of the monochromator is set for 1.0 cm^{-1} resolution. However, the accuracy of individual Raman vibration frequency determination is dependent on the actual line width of the chemical species under investigation. The line width observed usually is about 2 to 4 cm^{-1} for most solid inorganic-salt particles and 6 to 10 cm^{-1} for solution droplets.

Initial investigation is made to study the resonance Raman effects on a single particle. One of the major difficulties with such studies is excessive heating by the excitation laser. Consequently, the suspended particle can be disintegrated instantaneously as soon as the laser beam is focussed on it. Even for bulk samples, two common methods are used to dissipate this heating effect: a) specially designed rotating cells to reduce local heating of a solid sample; and, b) capillary tube to contain a liquid sample. In the present study of the chromate compounds, which are yellow crystals having a very small absorption cross-section in the excitation wavelength, Raman spectra of excellent S/N were obtained only by using a gated sampling technique. In such an experiment, the laser beam was also blocked periodically to allow the absorbed laser energy in the particle to dissipate. The observed enhancement factor is about 20 (±15%) with respect to nitrate. However, when the laser excitation is closer to the absorption band, as in the case of permanganate ion, the resonance enhancement factor can be more dramatic. For permanganate ion, the enhancement factor is measured to be about 500 (±15%) with respect to nitrate ion.

Analytical Chemistry Group (ACG). Nearly 1,800 analyses were performed by the Analytical Chemistry Group during 1989. As in previous years, a significant number of requests were initiated by investigators in the Environmental Chemistry and Atmospheric Science Divisions of DAS, although in the absence of a field program, fewer samples were submitted. A substantial number of samples were received from organizations outside BNL. Analyses were completed for the Acurex Corporation, the Pierce Foundation, which is associated with Gale University and the Naval Research Laboratory.

In addition to the above requests, samples were analyzed for the Accelerator Development, Medical, Nuclear Energy, and Physics Departments, and the Reactor Division.

One ACG member continues to be employed on an almost full time basis within the Environmental Chemistry Division, repairing, modifying, and calibrating real-time analytical instruments which are primarily used in various aircraft and the Shasta van during field programs. A second analytical chemist was assigned to the Medical Department on a continual basis to assist in developing a new technique for the production of ^{127}Xe. Unfortunately, this program was interrupted by the extended shut-down of the High Flux Beam Reactor.

Much time was spent testing equipment to be used in the Sao Paulo Atmospheric Characterization Experiment. Since HNO_3 was of major importance, a nitric acid generator was constructed and utilized in testing both the Annular Denuder System, which was obtained from the University Research Glassware Corp., and a modified TECO 8840 Oxides of Nitrogen Analyzer.

Improvements in the collection and analysis of perfluorocarbon tracers (PFTs). Adding an active electronic filter with a cutoff frequency of 0.02 Hz significantly reduced noise and facilitated the automatic detection of tracer quantities less than 40 femtoliters (40×10^{-15} liters); above those levels, filtering is maintained at 0.05 Hz. A longer precut column (increased from 20-inches to 4-feet) is temperature programmed from 100°C to 190°C; excellent separation between potentially-interfering low boiling chlorofluorocarbon compounds and the first eluting PFT allows those to be entirely discarded from the reconcentrating trap. Preliminary tests have shown that the trap temperature control can be handled with the spare Detector A temperature controller which will be incorporated for the first time on the new Varian 3600 gas chromatograph (GC) being built for the Japan Atomic Energy Research Institute (JAERI). The Florisil reconcentrating trap was run in an open configuration; PFTs could be collected and then desorbed for analysis with no loss in spite of being continually open, which would eliminate the need for its valve, but interferents also appeared to be collected.

Three prototype, commercially-produced programmable samplers incorporating pocket-computer control and state-of-the-art mass flow measurement have been evaluated. Previous hardware problems have been corrected, but a number of software changes or improvements are needed prior to production of a final version. Seventeen units have been ordered by JAERI for their long-range atmospheric tracing program.

3. Laboratory Investigations

Aqueous phase PAN reactions. Peroxyacetyl nitrate (PAN) is an important and ubiquitous atmospheric nitrogen species. The knowledge of its aqueous-phase reactions in terms of kinetics and stoichiometries is a prerequisite to the evaluation of its contributions to the removal of nitrogen species from the atmosphere and the supply of fixed nitrogen species to water bodies such as estuaries and oceans. The effects of ionic strength and temperature on the reaction kinetics of PAN hydrolysis were studies and it was found that the rate of hydrolysis increases only slightly with salt concentration consistent with the primary pathway in which only neutral reacting species are involved. The positive temperature dependence of the reaction kinetics slows the reaction down at low temperatures. However, since the Henry's law solubility of PAN exhibits a greater temperature dependence of the opposite sign, the uptake of PAN by liquid water, such as ocean surface water, is expected to be more significant in winter than in summer dispite the slower reaction rates. Product analysis showed that NO_2^- is the predominant reaction product for pH 6 and higher, and NO_3^- for pH less than 4. This indicates that PAN is a NO_2^- precursor for ocean surface water (pH ~8.4), and a NO_3^- precursor for acidic aerosols (pH <1).

Chemistry of reduced sulfur species. Reduced sulfur species, such as $(CH_3)_2S$ and COS, are important precursors of cloud condensation nuclei, especially in remote atmospheres. The chemistry of these compounds which governs atmospheric budgets of these species must be determined in order to assess their contributions to cloud formation. We have initiated the study of the kinetics of aqueous-phase reactions of COS. Initial effort directed to the quantitative measurement of this compound using UV absorption and

hemiluminescence technique coupled to an FPD has allowed us to devise a method to study the COS aqueous reactions in homogeneous solutions using alcohol as a transfer agent.

Radiation chemistry studies of reactions in cloudwater. Studies have continued of the rate of H_2O_2 formation from HO_2 in cloudwater induced by γ-radiolysis of synthetic solutions whose composition is representative of cloudwater, and of actual rainwater samples. These studies have confirmed the suitability of this approach to examining H_2O_2 yields per free radical formed. In the absence of transition metal ions, yields are consistent with HO_2 radicals exclusively forming H_2O_2. However, the presence of iron(III) at micromolar concentrations markedly influences the free-radical chemistry, decreasing H_2O_2 yields and, at low radiation intensities, actually decreasing H_2O_2 to below its initial concentration. These results can be modeled with known reactions and rate coefficients, supporting the use of these models for atmospheric application.

Atmospheric trace gas sampling and detection. A new experimental method is needed for those trace gases whose mass-accommodation coefficients are greater than 1×10^{-2}. Efforts have been directed toward developing the ultra-sensitive detectors necessary for the determination of trace amounts of dissolved H_2O_2 or OH radicals absorbed in aerosol solution droplets.

As a result of the above investigation, a new non-enzymatic method has been developed for the determination of H_2O_2 in condensed phase atmospheric samples. This method is based on the Fe(II)-catalyzed oxidation of benzoic acid by H_2O_2 to form hydroxylated products, which are analyzed by sensitive fluorescence detection. The sensitivity and linearity of the new method are comparable to that of the well known and frequently used enzymatic POHPAA method. Moreover, the newly developed non-enzymatic technique has the advantage of (a) using inexpensive, stable, easily available non-enzymatic reagents which do not require refrigeration, and (b) being insensitive to the moderate transition metal levels often found in atmospheric samples.

In order to apply this new technique for ambient gas-phase H_2O_2 measurements, the sampling system was tested with the well established enzyme

catalyzed POHPAA method. Several different calibration methods were employed to assess the ability of the system to measure ambient gaseous H_2O_2 concentration.

1. Aqueous H_2O_2 standard was introduced temporarily in place of stripping solution to obtain a calibration curve, which was found to be linear, reproducible, and independent of the ambient atmospheric conditions. In addition, it was also found that this calibration method was very insensitive to the sampling line condition.

2. Zero air was sampled with addition of gaseous standard H_2O_2 at three different positions: (a) near the stripping coil, (b) middle of the sampling line, and (c) near the ambient air inlet. They produced characteristic calibration curves similar to those of the aqueous H_2O_2 standard method. A linear calibration curve could be obtained when gaseous standard H_2O_2 was introduced near the ambient air inlet. However, it was found to be not only nonreproducible but also to depend on the sampling line age, i.e., the cleanliness.

3. Ambient air was sampled with and without the addition of gaseous standard H_2O_2. In general, calibration curves were found to be heavily dependent on ambient atmospheric conditions and on the cleanliness of the sampling line. In the worst case, no difference was found between the signals with and without the addition of gaseous standard H_2O_2 into the ambient air sampling line.

The results from this careful investigation can be summarized as follows:

(a) The measurement of gaseous H_2O_2 is very sensitive to ambient atmospheric and sampling line conditions.

(b) A measured gaseous H_2O_2 concentration can easily vary as high as factor of 10 or more depending on the calibration method used.

(c) It is necessary to elucidate the heterogeneous H_2O_2 loss mechanism in order to minimize the measurement error.

Single particle evaporation studies. A systematic investigation of the volatility of some environmentally important organic compounds having very low vapor pressures was initiated. Experiments were carried out in two separate single particle levitation apparatus designed to accommodate a wide range of volatilities. One apparatus was designed for high pressure experiments in which a levitated droplet was evaporating in a flow of nitrogen gas at one atmosphere. The high pressure operation was necessary for those organic compounds whose vapor pressures are in the order of 10^{-4} mm Hg at ambient temperatures. The other apparatus was a high vacuum system suitable for droplets whose vapor pressures are in the order of 10^{-7} mm Hg.

In a typical experiment, a droplet was levitated in a quadrupole cell housed in a thermostated enclosure. The droplet size was continuously monitored during evaporation by light scattering at 90° from an He-Ne laser used as the illuminating source. The droplet size as a function of time was accurately determined from the recorded Mie resonance spectrum. Measurements were made in the temperature range 322-294 K.

The vapor pressures as a function of temperature were expressed by the standard equation,

$$\ln p = A + \frac{B}{T} + C \ln T + DT^{n} .$$

The coefficients A, B, C, D, and the exponent n were determined for each system from measured evaporation kinetics and the available high-temperature vapor pressure data, using a least-squares fitting procedure. The evaporation kinetics of the following organic compounds have been investigated: Glycerol and methane sulfonic acid by the high pressure flowing experiments; dioctyl phthalate and oleic acid by the high vacuum evaporation experiment. Equations were deduced for those compounds covering a vapor pressure range over six to eight orders of magnitude.

Single particle Raman spectroscopy. Effort has been made to study the spectroscopic properties of supersaturated solutions of ammonium bisulfate, potassium bisulfate and sodium bisulfate in the region between 650 and 1300 cm^{-1}. Historically, bisulfate ion exhibits unusual asymmetry in its

Raman vibration bands, which are located around 892 cm^{-1} and 1048 cm^{-1}. Under normal circumstances, it is extremely difficult to study the nature of this asymmetry due to the overlapping bands from the co-existing sulfate ion (980 cm^{-1}). However, the single particle suspension method has provided a new approach to create supersaturated solutions, in which the sulfate ion is almost completely suppressed. As a result, the existance of an ion-pair is observed in the supersaturated bisulfate solution. The cation effect can be also demonstrated using appropriate substitution. Based on these studies, the proposed form for the ion-pair is $M^+HSO_4^-(H_2O)_n$; where M^+ is the cation and n is probably equal to or less than unity. The new vibrational frequencies observed for the ion-pair in the supersaturated bisulfate solutions are: 869 cm^{-1} and 1020 cm^{-1} for ammonium bisulfate; 869 cm^{-1} and 1027 cm^{-1} for potassium bisulfate; 883 cm^{-1} and 1033 cm^{-1} for sodium bisulfate.

Chemical characterization of carbonaceous aerosols from North Bay, Canada. An exploratory investigation is underway to evaluate the feasibility of carbonaceous species measurement and identification from aerosol samples collected by the BNL Environmental Chemistry Division. Test aerosol samples were generated from the Canadian North Bay field program. Filter composites were made for surface aerosol samples, aircraft samples, and for travel blanks. Levels of elemental and organic carbon have been determined for each composite.

Peroxycarboxylic nitric anhydride and hydroxy nitrates predicted by modeling studies. Study of the chemistry of peroxymethacrylic nitric (MPAN) anhydride commenced with the exploration of methods for the liquid phase synthesis of MPAN. Significant decomposition and polymerization was noted in attempts to form peroxymethacrylic acid, and upon reaction with HNO_3. The synthesis of 1,4-hydroxy nitrates was also undertaken. Conventional reactions of parent hydroxy bromides with $AgNO_3$ did not yield the desired product, but instead appeared to produce cyclic products. This may have interesting implications concerning the behavior of 1,4 product species thought to be present in the atmosphere.

Column preparation using plasmas. The initial goal of achieving a non-extractable phase was accomplished. The columns prepared were characterized. Technical problems with plasma generation made future studies impractical at this time, thus, work in this area was concluded.

Integrated capillary cryofocusing injection. The capillary trap was shown to perform well in gas chromatography under a variety of conditions. The trap temperature can be determined from the resistance of the trap without adding the thermal mass of an external sensing unit. The trap allows 1-mL vapor phase injections without degrading efficiency.

Database of building ventilation air flows. The second half of this database was completed, taking home air infiltration measurement results previously run on a Tektronix computer using software that did not include an error analysis routine for assessing data reliability, and imparting the raw data into the PC-based system for re-coputing all relevant information including the error analysis. The database now contains over 4000 home measurement periods in many locations throughout the U.S. for use by investigators of energy use patterns and in indoor air quality studies.

Leak detection for the utility industry. A tutorial on this subject based on PFT technology was presented to about 20 representatives from the utility industry. Two demonstrations were also presented--one on detecting a hydraulic leak from high pressure gas lines during their commission testing, and the other on locating and pinpointing the subsurface loss of dielectric fluid from underground high voltage cables. The hydraulic fluid (water) was successfully tagged at about 2 ppm with a PFT; using a real-time analyzer, a simulated leak of 0.25 mL/hour was successfully demonstrated. About 25 gallons of PFT-tagged oil was released near the bottom of a 1-meter deep lined trench about 1 year earlier. Using a concentrating-type real-time analyzer in a van, determining the approximate location of the subsurface leak was demonstrated with the bumper-mounted, ground surface, air sampling device. Subsequent pinpointing with the real-time continuous analyzer sniffing air from barholes was demonstrated to be feasible to within less than 3 feet of the actual leak location.

A separate study on detecting a leak in an out-of-service commercial utility generator stator bar was performed using 3 ppm PMCP in hydrogen, pressurizing the bar to 200 psig. In normal operation, up to 100 bars carry the current produced in a commercial generator; the bars are internally water-cooled at a pressure of 22 psig, but the generator housing itself is at about 35 psig with H_2 (a heat transfer medium for the windings), so normal leakage results in H_2 getting into the cooling water which is then detected, signaling a leak. Excessive leakage can lead to the formation of a ground fault which, if unchecked, could lead to catastrophic failure. An electric phase triangulation procedure was used by Con Ed to locate the failed bar, but the exact location of the leak on the 19-foot long element could not be found, even with hydraulic testing in another lab. The PFT technique successfully pinpointed the leak location and magnitude, which was then visibly confirmed by submersion in water; a leak rate of 1.4 mL/min of H_2 was equivalent to a water leak of 10^{-4} gallons/hour, which is why hydraulic testing would fail.

4. Field Studies

Vertical profiles and removal processes. Vertical profiles taken in the vicinity of Columbus, OH, in June 1987 have been examined relative to source and removal processes of nitrogen oxides (NO_x), carbon monoxide, and aerosol particles, all of which have source terms in the boundary layer and are subject to upward motion in convective cells. Although all of these species exhibit decreasing concentrations as a function of altitude consistent with their boundary layer source, concentrations of aerosol particles (0.2 to 2 μm) fall off much faster than those of CO and NO_x. Comparison of particle concentrations with absolute humidity suggests that incorporation of soluble aerosol particles into cloudwater followed by precipitation is responsible for the observed sharp decrease in particle concentration with altitude.

NASA biomass burn project. Smoke plume particles were sampled by NASA field personnel during a prescribed burn of boreal forest vegetation that occurred in Ontario, Canada, during July 1989. The chemical composition and the ambient mass concentrations of the carbonaceous aerosol particles will be determined. The particulate carbon data generated and the possible organic

molecular tracers found from this example of biomass combustion will augment the gaseous species data, particularly those for the greenhouse gases, that are measured by NASA personnel during the biomass burn field experiments. The overall goal of the NASA program is to describe the magnitude of biomass combustion emissions on a global scale and to assess what impact these global emissions may have on climate.

Tracers in oil and gas reservoirs. Several PFTs have been injected in separate studies, into both a gas reservoir and an oil reservoir in the North Sea. The purpose of the former was to document the mixing and dilution of tracer in the reservoir served by that well which would provide some measure of the interactive volume or rate of diffusional spread in the section of the reservoir; the decrease in initial tracer concentration from recovered gas was in accord with engineering predictions. To date, of the three PFTs used to tag the gas entering a gas injection well within the oil reservoir, only about 0.1% has been accounted for in the intervening three years of oil production from the 28 production wells; this also corroborates the experience with two radioactive tracers also injected at about the same time and location. Concern has arisen, however, in regard to the gas sampling protocol used at the well site as well as with the efficiency of transferring samples to adsorbent tubes and their subsequent analysis. Problems with interfering hydrocarbon gases are being studied separately in the laboratory. The use of multiple PFTs in oil reservoirs holds the promise of not only tracking fluid movement in such reservoirs, but also the ability to characterize residual oil content during these enhanced oil recovery operations.

Building ventilation measurements. The PFT technology applied to air flow determinations in an occupied building on site confirmed that in most cases the fresh air exchange was sufficient. In one case, elevated CO_2 levels of about 1500 ppm were consistent with the occupancy by 3 to 4 people having average CO_2 production of 0.024 m^3/h. The base case, before weatherization, for an older 2 story house with a finished basement was shown to have wintertime cold air inleakage that was almost 3 times the national average. Preliminary steps at weatherization showed little real reduction in air leakage implying a need for extensive care in such attempts. Measurements were performed at a test house at Lawrence Berkeley Laboratory (LBL),

comparing the programmable sampler PFT technology with the real-time mass spectrometer-based tracer system employed by LBL. Building windows and door openings were varied to collect information under different flow conditions, but results will be available next year. The PFT technology was also employed at a home in Huntsville, AL, at which Oak Ridge National Laboratory is studying radon ingress via peculiar perculation or solution pipes present in the ground caused by dissolution of limestone veins with the clay layers of the soil. PFTs placed in the soil in the immediate proximity of the house were shown to be present in the house, but none could be detected from solution pipes as close as 20 feet to the house.

PLANS FOR 1990

1. Analysis and Interpretation

Cloudwater acidification mechanisms. Interpretation of measurements obtained in previous field projects will continue and will focus on mechanisms and rates of cloudwater acidification. Also, the relations between gases, aerosols, and water vapor will be examined to deduce scavenging efficiences of trace species relative to the removal efficiency of water itself.

Sulfate influences on cloud abedo. A project will be undertaken to search for evidence, principally in satellite data, for the enhancement of cloud albedo by emissions. The evaluation of the magnitude of perturbation as a function of time and location, in the context of other sources of cloud condensation nuclei, principally biogenic sulfur compounds, should permit critical testing of hypothesis linking responses of the earth climate to changes in radiative forcing.

Vertical redistribution of materials. The purpose of this study is to examine vertical profile data collected principally during PRECP-V for transport of materials from the boundary layer to the upper troposphere. Such transport can be effected by several mechanisms. One mechanism is by so called "eddy diffusion", whereby materials are mixed from regions of high concentration to regions of low concentration; the time constant for mixing of pollutants from the surface to air altitude of 10 km by this process is on the order of several months. Another mechanism is transported by clouds and storms. The latter transport process can be much faster than the former with large quantities of boundary layer air being moved to the upper troposphere on a time scale of hours. The study will be focussed on obtaining direct evidence for vertical transport by convective storm systems. If such evidence is found, several additional questions will be addressed. On question is whether all species are transported by such storms to the same extent, or whether significant portioning occurs during the transport process. More directly, are soluble species, such as aerosol and HNO_3, transported to the same extent as insoluble and relatively unreactive species such as CO, NO and NO_2? A second question is what influence these transported species migh have on upper tropospheric chemistry.

Relationships between PAN, O_3 and NO_y. Quantitative aspects of the relationships between PAN, O_3, and NO_y, measured at North American surface sites, will be examined. The efficiency of PAN and O_3 production for a given NO_y concentration will be studied in data from sites having a variety of hydrocarbon and NO_x impacts. The nighttime behavior of PAN and O_3 will be compared to see if PAN deposition velocity can be estimated.

Modeling utility power station flow rates. Preliminary assessment of the application of PFT technology to commercial power plant stations has shown that, in many areas, significant energy and materials degradation savings can be obtained. Several million dollars per year can be lost due to problems related to condenser air inleakage, tube failure with incipient intrusion of cooling seawater into clean boiler water, and improper cooling water flow rates. The corrosion effects of resultant dissolved oxygen plus seawater salts in the high temperature furnace and boiler tubes can cause significant economic consequences. In addition, improvements in waste equipment heat recovery by proper air flow balancing within the station building has the potential for saving hundreds of thousands of dollars per year. Models will be developed to convert tracer tagging and analysis results in each of the applicable areas above into quantitative determination of air and water inleakage as well as fluid flow. The PFT technology will also aid in locating and pinpointing the equipment leaks, thereby reducing both the time for repairs as well as the magnitude of "acceptable" leaks. The first year of effort will use the support from a single utility or possibly a conglomerate of northeast area utilities to examine the feasibility of an on-line system for condenser air inleakage localization at a nearby utility station.

2. Measurement Methodology

Hydrocarbon and oxygenated products. The measurements of hydrocarbon and oxygenated product species will commence. Hydrocarbons of the size range C_2-C_{10} will be measured by cryogenic collection followed by capillary GC separation with FID. Two columns will be used: an Al_2O_3 plot column for the range C_2-C_6 and a methane silicone column for C_6-C_{10}. Conditions will be

sought that will permit simultaneous analysis, with the same GC oven conditions, and a dual FID system. Oxygenated species will be measured by the following methods: a GC-ECD method based on derivatization with pentafluorophenylhydrazine, and a coupled packed/capillary GC-FID system. An integrated calibration scheme will be developed based on a continuous FID instrument. A catalyst train that first oxidizes all organic carbon to CO_2, then reduced it to CH_4, will permit the intercalibration of various standards, including National Institute of Standards and Technology (NIST) standard reference material (SRM), CH_4, propane, and benzene standards. Standards of unstable oxygenated species such as methacrolein and methyl vinyl ketone can then be directly calibrated on a per-carbon basis.

Measurement of aerosol sulfate. Efforts will be directed at improving the response of a flame photometric detector toward aerosol sulfate. Major problems with surface effects presently degrade both the sensitivity and the speed of response. Alternative detection methods will be investigated.

Single particle Raman spectroscopy. A continuing effort will be made to develop the single particle Raman spectroscopic technique for studying heterogeneous reactions. Gated sampling methods and more efficient collection optics will be evaluated for their improvement factors in the pulsed excitation experiments. The heating effects of the excitation laser will also be studied. Parallel effort will be made to utilize monodispersed particle stream to study the resonance Raman effects in micron-sized droplets. Success of these techniques is extremely importanmt to future experiments such as the Raman microprobe, single particle resonance Raman spectroscopy, *in situ* particle composition analysis and heterogeneous reactions.

Analytical Chemistry Group (ACG). The Analytical Chemistry Group will be significantly involved in the PRECP "Frontal Boundary Study" field experiment, to be conducted in the Columbus, OH, area. Further involvement of the group in a proposed summer field program is anticipated.

Analytical services will continue to be supplied to the ECD and various departments of the laboratory when requested, and outside agencies when possible.

One member of the ACG will devote a minimum of 50% of his time to the maintenance, calibrtion, and development of new aircraft and ground based real-time analytical instrumentation. It is expected that a second group member will again be assigned to the Medical Department's Radionuclide and Radiopharmaceutical Research Division when their program for the development of a new technique for the production of ^{127}Xe is reactivated.

PFT technology improvements and applications. Discussion will be had with the manufacturer of PFTs to provide samples of new tracer compounds. A new calibration curve procedure for the laboratory GC system will be investigated. Preliminary results will be obtained on the feasibility of an ohmically heated main chromatograph column in order to reduce baseline drift and noise from the normal, inadvertent concurrent heating of nearby components such as catalyst beds in the injector ovens, the permeation and detector mounted on top of the oven, and valves mounted in the oven; ohmic heating will only heat the column located in the oven, not the oven itself, which will also reduce cool-down time. The precut subsystem catalyst bed will be relocated or simply removed to determine if the downstream florisil reconcentrating trap can be operated in an open mode all the time. This would eliminate the trap valve, which normally is opened and closed twice during a single GC cycle. A new reactive, indicating cleanup trap will be added to the carrier gas system and the quality of the carrier gas and the performance of *in situ* cleanup traps will be evaluated to reduce interfering peaks during GC operations. A complete laboratory GC system, including hardware and software, will be built for JAERI for use in atmospheric tracing studies. Another system will be prepared for the Tracer Research Corporation (TRC) for use in leak monitoring of underground storage tanks (USTs) and related piping. Studies will begin to automate the catalytic preoxidation step into the laboratory GC system. This will allow on-line removal of interfering HCs in tracer studies at oil and gas reservoirs as well as in leak monitoring applications in some of the HC-contaminated environment around USTs.

3. Laboratory Investigations

Aqueous reactions of PAN with dissolved species in surface water. In order to describe quantitatively the rate of deposition of PAN to surface water, the kinetics of the reactions of PAN with dissolved species in these waters must be first characterized. We will study the reactions of PAN with two important constituents of ocean surface water, i.e., humic acid and sulfur containing compounds, e.g., H_2S. The former is believed to be susceptible to redox reactions involving free-radical pathways and may react rapidly with PAN, which is itself in equilibrium with peroxyacetyl radicals and NO_2 radicals. H_2S and/or HS^- may react with PAN because it has been demonstrated that PAN reacts rapidly with glutathion by attacking the sulfhydro group.

Chemistry of reduced sulfur species. The chemistry of reduced sulfur species, such as dimethyl sulfide and carbonyl sulfide, is important in controlling the budgets of these species in the atmosphere, and consequently the concentration of cloud condensation nuclei which in turn influence the climate change by way of cloud albedo. We will study the aqueous-phase reactions of COS by first examining its hydrolysis reaction and its dependences on pH and temperature. Methods have been developed to study the kinetics of this reaction by UV absorption in homogeneous aqueous solutions using alcohol as a transfer agent for COS, which has a somewhat limited solubility in water.

Deposition of O_3 to ocean surface water. Exchange of reactive gases between the atmosphere and ocean water is a key process influencing the distribution of these gases in remote marine atmosphere and as such plays a dominant role in the global chemistry of infrared active gases. The dry deposition flux of reactive gases to surface water can be described theoretically by coupling the atmospheric mass transport rate with the chemical reaction rate at the interface. We will design, construct, and test an instrument to measure the rate of reactive uptake of O_3 by ocean water, and to test the theoretical model by simultaneously measuring reactive uptake, pertinent micrometeorological variables, and net O_3 deposition flux.

A validation of the theoretical model by such an experiment would lend strong support to its application to assessing the dry deposition rate of other important trace radiatively active gases to the oceans.

Cloudwater free-radical chemistry. Studies of the yields and kinetics of H_2O_2 formation in synthetic and authentic precipitation samples, initiated by radiolysis, will be continued.

Peroxymethacrylic nitric anhydride and related compounds. Continued study of MPAN (and related compounds) is envisioned starting with gas- and liquid-phase synthetic techniques. The thermal decomposition rate of MPAN will be determined, and its behavior in the capillary GC-ECD system investigated to see if atmospheric measurement of this compound is possible.

Single particle Raman spectroscopy. Raman spectroscopy of supersaturated solutions will remain as the major interest of laboratory studies. The role of hydrogen bonding in these supersaturated solution droplets will be explored and investigated. A logical approach in this direction would be isotopic substitutions, because participating ions in the "ion-pair bonding" will be generally more susceptible to mass changes. In addition, controlled environment studies will be carried out to elucidate the conditions for the formation of complexes.

Single particle studies. Measurements of the thermodynamic and optical properties of concentrated electrolyte solution droplets, which constitute a large portion of the ambient aerosol, will continue, as will a systematic investigation of the volatility of many environmentally important organic compounds having ultra-low vapor pressures.

Heterogeneous reaction kinetics. Work will be initiated to develop experimental techniques for studying heterogeneous reactions of atmospheric trace gases with organic pollutants either adsorbed on particle surfaces or dissolved in droplets. An aerosol flow reactor will be designed and constructed in FY 1990 for these studies. Advanced spectroscopic techniques will be incorporated in the flow system to perform *in situ* chemical analysis of the aerosol particles.

Atmospheric trace gas sampling and detection. Mass-accommodation coefficient measurements for trace gases on water surfaces will be continued, with efforts devoted to the construction of a combined aerosol flow reactor and laser induced fluorescence detection. The system will be calibrate for OH radicals.

Concurrently, some efforts will be devoted to the elucidation of the heterogeneous H_2O_2 loss mechanism in the sampling line and to the development of the atmospheric OH radical measurement system.

Chemical characterization of carbonaceous aerosols from North Bay, Canada. An exploratory investigation has been underway to evaluate the feasibility of carbonaceous species measurement and identification from aerosol samples collected by the Brookhaven National Laboratory Environmental Chemistry Division. Test aerosol samples were generated from the Canadian North Bay field program. Filter composites were made for surface aerosol samples, aircraft samples, and for travel blanks. Levels of elemental and organic carbon have been determined for each composite. Solvent-soluble organic species will be measured. The resulting data will be used to estimate the minimum air volumes required for identification and speciation of carbonaceous particle-bound aerosol compounds. Evaluation of possible organic sampling artifacts will also be conducted.

PFT Technology: HC interferences. Detailed studies of the effectiveness of a catalytic pretreatment procedure on removing HC interferences in the analyses of adsorbent-collected PFT samples as well as possibly on-line during sample collection (e.g., prior to sampling PFT-tagged oil and gas reservoir gas streams). Effects of temperature, oxygen concentration, flow rate, rate of sample desorption, etc., will be quantified using a thermal conductivity detector (TCD)-GC to look at residual HC levels. Separate laboratory studies will also commence on documenting the effects of various HC vapor concentrations on the passive as well as active sampling of PFTs near HC-contaminated sampling sites (e.g., when monitoring for leaks near USTs). Additionally, the ability of the current design passive CATS sampler to quantitatively collect and recover various subsurface pollutant HCs and

halocarbon solvent contaminants will be assessed for potential application in subsurface pollutant plume mapping of both shallow as well as deep (up to 100 m) contaminated aquifers and soil gas.

Henry's law for PFT in water/seawater. An accurate determination of the effect of temperature on the Henry's law partitioning of PFTs between an air phase and both fresh water and seawater will be determined. It has been shown that, using 2 or more PFTs dissolved into a moving stream of water, the unknown fluid flow rate as well as the unknown extent of partitioning to an air phase in mass transport equilibrium with such fluid stream can be uniquely determined. The application of this approach is in calibrating very high fluid flow rates (100,000 + gallons per minute) used in cooling condensers in electric power generating stations.

4. Field Studies

Identification of organic compounds from emission sources of primary fine particle aerosols. Analyses of extractable organics from primary emission sources of fine aerosol particulate carbon using high-resolution gas chromatography have been performed at Caltech. The California State Air Resources Board has requested a joint proposal from Caltech and Brookhaven National Laboratory for further analyses of the ~40 authentic source samples. High-resolution gas chromatography-mass spectrometry analyses of the source samples are currently underway at UCLA. The primary focus of the proposal to the California Air Resources Board will be to interpret the GC-MS data. This task can be accomplished at BNL with the installation of the INCOS Data System. Once completed, the organic species data will function as data base inventory that can be accessed for comparison of unknown aerosol organic compounds to the array of organics present in these fully characterized source emissions.

Field boundary study (Fall 1990; Columbus, OH). During Fall 1990, the Environmental Chemistry Division is participating in a field program to study the distribution of materials across frontal boundaries in extra-tropical cyclones, and to examine the ability of these systems to transport materials to the mid to upper troposphere. This program will be conducted in central

Ohio and will be done in conjunction with PNL. Major facilities include PNL's G-1 aircraft, and a surface network of computerized precipitation collectors.

Preliminary discussions are also underway on a study of coastal storms, to assess their importance in the transport of pollutants across the North Atlantic.

Southeast Regional Oxidant Network (SERON). Partipation in the proposed Southeast Regional Oxidant Network is planned. This study will involve measurement of inorganic and organic species at a ground site in the southeast during the summer of 1990 for a period of about 6 weeks. NO_y species, O_3, CO, SO_2, H_2O_2, and aerosol constituents will be measured, as well as C_2-C_{10} hydrocarbons, oxygenated organic product species, and particle-phase organic compounds. The objective will be to better define the role of natural hydrocarbons and NO_x in the production of oxidants (O_3, H_2O_2) on a regional scale, in order to determine the kinds of control strategies necessary to meet regional air quality goals.

NASA biomass burn project. Burning events of Brazilian tropical rain forests will be sampled by NASA personnel in the first half of 1990. Smoke plume aerosols will be collected for the analysis of the particulate carbon fraction. Chemical analyses will be conducted by Brookhaven National Laboratory. Of key interest is the solvent-soluble fraction of the smoke aerosols where special attention will be focused on potential molecular tracers of rain forest combustion. Such marker compounds are valuable parameters that can be applied to the transport and removal of aerosol particles from combusted rain forest vegetation. Overall, the carbonaceous aerosol mass emission data will provide better estimates of particulate carbon fluxes to the global troposphere from large-scale burning of tropical rain forests.

New BNL aircraft. A new BNL aircraft will be outfitted for field measurements with consideration made for operation in a pressurized cabin. Several instruments will be redesigned for enhanced performance; all will be integrated into a single data system for electronic storage.

Building ventilation studies. Studies will continue on the effectiveness of weatherization of a small home documented by reduced air infiltration as measured by the passive PFT technology. The results from an intercomparison of the PFT technique with the LBL mass spectrometric-based system (MS) will be completed for measurements taken in an experimental 2-story home. Up to 28 commercial buildings built according to the Energy Edge protocols in the northwest area of the country will be measured for total ventilation using the PFT technology; attempts will be made to apply a simple home weather-dependent ventilation model in order to normalize the measurements to a standard weather condition. Six homes will be studied in detail both with the PFT technology and the LBL-MS system to demonstrate the small (<6%) extent of bias in the passive PFT ventilation measurement approach caused by the diurnal cycling of outside temperature and wind speeds. Miscellaneous building and home ventilation and indoor air quality-related studies will be conducted worldwide.

Atmospheric tracer studies. Brookhaven will participate in a tracer study to assess the impact of the Kennecott Copper Inc. smelter stack emissions on air quality in the Grand Canyon area. Two PFTs will be used to distinguish ground-level from elevated emissions as they impact at 25 ground level sites up to several hundred kilometers away. A total of 68 BATS lids will be used during the approximate 45-day tracer release period. Brookhaven will prepare the samplers and analyze over 1500 collected samples as well as characterize the purity of the released tracer. Brookhaven will also assist with implementation of a quality assurance component of the tracer studies to be conducted in the San Joaquin Valley region of California; intercomparison of standards, analysis of duplicate collected samples, and intercomparison of sample collection procedures and hardware are several of the aspects to be covered.

PROGRAM SUMMARIES

Title: PRECP-PRocessing of Emissions by Clouds and Precipitation

FY 89: $2,070,000

FY 90: $2,095,000

Principal Investigators:
P. Michael and L. Newman

Sponsor: Office of Health and Environmental Research, DOE

This project is a multilaboratory effort aimed at determining relations between emissions of sulfur and nitrogen oxides, amounts of airborne acidic or acidifying pollutants, and amounts of these materials that are deposited to the surface. The specific objective of this program is to obtain a scientific basis so that the dependence of wet deposition of pollutants upon pollutant input can be determined; to do this one must study the PRocessing of Emissions by Clouds and Precipitation (PRECP).

The research consists of three highly interactive components: diagnostic modeling, field measurements, and laboratory experiments. Diagnostic modeling has been used to explore possible causes and extent of nonlinearity of source-receptor relations. The results of laboratory studies have provided parameterizations to be used in models and have identified species that should be measured in field studies. Field measurements have provided information on ambient concentrations of reactants and catalysts to guide laboratory studies, and have identified important transport transformation and deposition processes. Field measurements have also provided data for model development and evaluation.

Principal achievements of the PRECP project to date include demonstration of the importance of in-cloud oxidation of SO_2 by H_2O_2, based on field, laboratory, and modeling research; demonstration of the importance of vertical mixing processes in governing the extent of the SO_2-H_2O_2 reaction; and elucidation of the role of vertical transport and scavenging in the removal of soluble pollutants in convective cells.

This project at Brookhaven is a joint effort of the Environmental Chemistry and Atmospheric Sciences Divisions and is carried out in conjunction with Argonne National Laboratory and Battelle Pacific Northwest Laboratory.

Title: Aerosol Chemistry and Dynamics

FY 89: $245,000

FY 90: $245,000

Principal Investigator:
I. N. Tang

Sponsor: Office of Health and Environmental Research, DOE

Aerosols are known to play an important role in many atmospheric processes affecting local visibility and regional to global climatic conditions. Both the primary and the secondary combustion products constitute a substantial portion of the ambient aerosol. The formation of these airborne particles and their subsequent chemical and physical transformation in the atmosphere not only determine the air quality, but may cause grave ecological concerns as well. The objective of this research program is to elucidate the fundamental processes governing the chemical and dynamic behavior of ambient aerosols. Current research activities include: (1) theoretical and experimental studies of the evaporation kinetics of droplets containing either a pure component or a volatile solute, (2) measurements of thermodynamic and optical properties of concentrated electrolyte solution droplets, which constitute a large portion of the ambient aerosol, and (3) development of experimental techniques for quantifying the interaction of reactive trace gases with aerosol particles. The results of this research program will lead to a better understanding of the basic mechanisms by which pollutants from energy-related activities are transformed and transported in the environment. Furthermore, the thermodynamic and optical data obtained for aerosol particles are essential as input to mathematical models describing important atmospheric processes such as acid precipitation and radiation balance.

Title: Analytical Techniques and Applications of Microparticles

FY 89: $45,000

FY 90: $90,000

Principal Investigators:
I. N. Tang and K. H. Fung

Sponsor: Basic Energy Sciences, Office of Energy Research, DOE

Analytical techniques are being developed for in situ chemical analysis of suspended particles whose individual mass is on the order of nanograms. Knowledge of the particle shape, size, and chemical composition of microscopic particles is vital to the understanding and control of the heterogeneous processes in which these suspended particles are playing a central role. Current effort centers on applying laser Raman spectroscopy to chemical characterization of a flowing particle stream. An investigation of Raman intensity enhancement by resonance absorption will be undertaken in order to measure trace constituents in particles. Other advanced technologies such as fourier transform (FT)-Raman spectroscopy employing a Nd:YAG laser and fluorescence spectroscopy using a tunable light source will also be investigated for chemical characterization of microscopic particles. An immediate application of the present work is to couple the spectroscopic techniques developed here with an evaporative light-scattering detector, currently being developed elsewhere for liquid chromatography of high-molecular-weight organic compounds whose structural information cannot otherwise be obtained with conventional LC detectors.

Title: Atmospheric Organic Chemistry: Investigation of Primary and Secondary Species

FY 89: $240,000

FY 90: $220,000

Principal Investigator: J. M. Roberts

Sponsor: Office of Health and Environmental Research, DOE

The goal of this task is to obtain information on important aspects of atmospheric organic compounds so that the participation of these compounds in important atmospheric processes may be assessed. The approaches used are to make field measurements of primary and secondary organic compounds in order to elucidate reaction pathways and rates, and to conduct laboratory studies on individual processes involved in the formation or removal of organic compounds. Field measurements of the key secondary species, formaldehyde, acetaldehyde, and "peroxyacetyl nitrate" (PAN), are being made in conjunction with measurements of other important species (ozone, oxides of nitrogen). These measurements are focusing on the oxidant formation potential of NO_x-hydrocarbon chemistry and the regional impacts thereof. Methods are being developed and applied to the measurement of primary and secondary organic species with special emphasis on following important compounds, such as isoprene, through atmospheric photooxidation processes. Laboratory studies of the thermal and photolytic decomposition rates of important secondary species will be undertaken. Special emphasis has been placed on organic nitrates, which are relatively stable product species that may be transported over wide areas of the troposphere.

Title: Atmospheric Tracer and Instrumentation Development

FY 89: $145,000

FY 90: $180,000

Principal Investigator:
R. N. Dietz

Sponsor: Office of Health and Environmental Research, DOE

The Atmospheric Tracer and Instrumentation Development task has as its objectives the identification and utilization of new atmospheric tracer compounds for dispersion and long-range atmospheric transport studies, and the support of these studies through development, validation, and application of new unique instrumentation. Efforts are directed at the testing and validation of state-of-the-art samplers and analytical procedures for a family of perfluorocarbon tracers (PFTs), the search for new PFTs with lower ambient background levels, the preparation of the respective gas standards, and participation in interlaboratory testing studies, field validation programs, and applied short- and long-range dispersion and transport studies. An immediate objective for this task is improved resolution of PFTs through the use of different packings with and without temperature programming. A second objective is to improve overall sampling and analysis precision including examination of the calibration curve-fitting procedures, study of the benefits of using peak heights instead of peak areas, and the use of reference tracers for the inherent determination of sample volume. In addition, changes in the analytical train will be studied to reduce interferences from unknown constituents in sampled air. A new generation programmable atmospheric tracer sampler has been developed in a final prototype form and 17 units will be commercially produced for the Japan Atomic Energy Research Institute. Modifications to a real-time, dual-trap analyzer will improve its use in urban environments. The results of this task will be an improved tracer technology for the assessment of risk and impact of long-range atmospheric transport and subsurface transport, dispersion, and fate of energy-related pollutants.

Title: Advancements in Atmospheric Tracers and Related Instrumentation

FY 89: $80,000

Principal Investigator:
G. I. Senum

FY 90: $100,000

Sponsor: Office of Health and Environmental Research, DOE

With the increasing use of perfluorocarbon tracers (PFTs) in long-range atmospheric transport and dispersion experiments, a corresponding continued need for ongoing improvements in the laboratory gas chromatographic analysis system is manifested. Every newly proposed atmospheric tracer experiment increasingly requires the laboratory analysis system to routinely perform at the limits of its PFT sensitivity. The increasing number of PFTs and their increasing diverse atmospheric application subjects the laboratory analysis system to a multitude of background interferents which must be systematically and efficiently removed for continued, reliable operation of the laboratory analysis system. As long-range atmospheric transport and dispersion experiments become more sophisticated with results which are to be used for comparison and validation of atmospheric transport and dispersion models, an increased importance must be given to maintaining the quality of the analytical results of the laboratory analysis system. This program will be directed by the increased PFT application needs in order to extend and apply the PFT multitracer technology to the diverse tracer application scenarios. These, along with other concerns which may arise with increased PFT applications and in other nonatmospheric PFT applications, require an ongoing programmatic effort to maintain the laboratory analysis system at its optimal efficiency for the range of PFT analyses it is required to perform, and to extend the range of available PFT experiments.

Title: Perfluorocarbon Tracer Tagging for the Deep Probe Project

FY 89: $10,000

Principal Investigators:
G. I. Senum and R. N. Dietz

FY 90: $0

Sponsor: Savannah River Plant, E.I. Dupont and Company; Office of Health and Environmental Research, DOE

Perfluorocarbon tracers (PFTs), a class of liquid, nontoxic, perfluorinated organic compounds have been used for the first time to tag the drilling muds of the Subsurface Microbiology Deep Probe Project's Fourth Investigators Hole (FIH). The muds were tagged with PFTs to provide a method for quantifying the residual drilling-mud contamination levels of the pared sample cores which are used for subsequent microbiology analysis. The PFT technology which has been developed at the Tracer Technology Center (TTC) is a multitracer technology, allowing both the drilling mud of the core well and the sample well to be tagged with different PFTs, to assess the residual contamination from both wells and any future wells at a particular site. The muds were solubilized with PFTs to levels in the ppm range and can be subsequently detected in the pared sample core down to the femtogram (10^{-15}) range, providing eight orders of magnitude of dilution range. Consequently, the ratio of PFT concentration in the pared core to the drilling mud can quantify the residual drilling mud contamination down to the 10^{-8} level. The drilling muds were tagged by adding an aliquot of a 1% PFT emulsion in water to each 100-gallon lot of drilling mud as it was made. Samples of the pared core, about 1 mL, were sent to the TTC for subsequent PFT analysis. This study will provide a quantitative measure of the residual drilling-mud contamination level, a necessary quality-assurance technique to guarantee the results of microbiological analyses at other drilling sites within the Deep Probe project in future years. In addition to tagging for fluid intrusion, preliminary experiments will assess the potential of the PFT tagging of microorganisms or microspheres for studying the transport and fate of such organisms. Support for preliminary work in FY 1988 was from the Savannah River Plant. In FY 1989, DOE assumed partial support for this application of the PFT technology to their Subsurface Microbiology program.

Title: Adapting Perfluorocarbon Tracer Technologies for Use in DOE-Site Contamination Studies

FY 89: $0

FY 90: $15,000

Principal Investigators:
G. I. Senum and R. N. Dietz

Sponsor: Office of Energy Research, DOE

The perfluorocarbon tracer (PFT) technology developed by the Tracer Technology Center (TTC) at Brookhaven National Laboratory (BNL) has been successfully applied to various geophysical, hydrological and atmospheric studies. This task will provide a mechanism for implementing the presently available cost-effective PFT technology to various U.S. Department of Energy (DOE)-site directed and funded remedial contamination studies. This will provide for the adaptation and initial optimization of the present PFT technology to the experimental needs of the DOE-site studies. This includes initial site visits for consultation, demonstration of PFT feasibilities, and short-term research to allow the effective selection of the most appropriate PFT technology for each DOE-site study. This task will provide only for the initial interfacing between the PFT technologies and the diverse tracer application needs of the DOE-site contamination remediation studies.

Title: Application of Multitracer Technology to Petroleum Reservoir Studies

FY 89: $175,000

FY 90: $215,000

Principal Investigators:
G. I. Senum and R. N. Dietz

Sponsor: Bartlesville Project Office, DOE

The Tracer Technology Center (TTC) at Brookhaven National Laboratory (BNL) has developed a multitracer perfluorocarbon tracer (PFT) technology, initially for atmospheric transport and dispersion experiments. In previous years, this technology has been successfully extended to hydrological and subsurface-based experiments. This program is aimed at extending this technology to petroleum reservoir studies, specifically by exploiting the potential 1000-fold reduction in tracer costs for PFTs compared to radioactive tracers and by demonstrating the applicability of multiple PFTs, having different volatilities, to the characterization and study of petroleum reservoirs. Specific areas to be addressed include (1) development and evaluation of tracer-injection techniques adapted to conditions of injection, (2) validation of the effectiveness and representativeness of the sampling procedures for various phases extracted, (3) development and implementation of pretreatment procedures and analytical-system modifications needed to eliminate hydrocarbon (HC) interferences, (4) evaluation of physical and chemical interactions that might occur between the PFTs and the subsurface constituents, and (5) demonstration of the potential tagging and tracing capability of the PFT technology through actual oil-field injection tests in cooperation with other petroleum researchers. In addition, this task will directly benefit joint cooperative tracer studies being conducted between BNL and the Institute for Energy Technology (IFE) in Kjeller, Norway, and is relevant to the Memorandum of Agreement (MOA) between the U.S. Department of Energy (DOE) and the Norwegian Ministry of Petroleum and Energy (MOPE) for cooperative research in enhanced oil recovery (EOR).

Title: Gas Reservoir Tracing

FY 89: $10,000

FY 90: $0

Principal Investigator:
R. N. Dietz

Sponsor: Morgantown Energy Technology Center, DOE

Brookhaven National Laboratory (BNL) has developed a highly sensitive tracer technique utilizing perfluoro hydrocarbons and has successfully applied the method to monitoring global wind and weather patterns. The rarity of the specific compounds in the environment and the extreme sensitivity of detectors to these compounds allows very small quantities of tracer to be used in large-scale gas flows. This technique appears to have the potential to yield valuable information about the flow through gas reservoirs and could also be useful in establishing flow patterns for underground coal gasification and modified *in situ* oil shale technologies. BNL personnel will work with Morgantown Energy Technology Center (METC) to define a tracer experiment of interest to the extraction program. BNL will estimate the number of tracer injection and sampling points required, the total volume of tracer required, the sensitivity of the experiment to errors including absorption of the tracer by liquids or solids, and the resolution of the flow patterns achievable with the defined experiment. BNL will also identify a schedule and resource requirement to carry out the experiment.

Title: Tracer Tagging of Gas and Seawater Injections in Gas and Petroleum Reservoir Studies

FY 89: $20,000

FY 90: $5,000

Principal Investigators:
G. I. Senum and R. N. Dietz

Sponsor: Institute for Energy Technology, IFE, Norway

For nearly two decades, radioactive tracers have been used to monitor the effectiveness of gas reinjection for enhanced oil recovery (EOR). In May 1986, Brookhaven began an informal cooperative experiment with IFE to tag one injection well with three PFTs in the Ekofisk North Sea oil field, where two radioactive tracers, Kr^{85} and CH_3T, had just been used to tag the other four of the five injection wells.

Periodically, gas samples were collected from a number of the 28 production wells, a portion transferred onto adsorbent samplers to retain PFTs, and subsequently analyzed at BNL. All three PFTs have been seen in a number of production wells less than 1000 m from the injection well at maximum concentrations of 5 to 7 femtoliters/liter, comparable to levels found for the radioactive tracers based on the relative quantities injected. The PFTs' appearance at the wells was in the order of their volatility, indicating a potential for estimating the quantity of pore residual oil in the reservoir.

The petroleum reservoir studies will continue, including subsequent studies with seawater injection. Another experiment was started in August 1988, in which two PFTs were injected to estimate the permeability and porosity of a gas reservoir being used for storage of reinjected surplus gas recovered during oil production operations.

Title: Feasibility of Detecting PFT-Tagged Oil Leaks from High-Pressure Oil-Filled Underground Transmission Cables

FY 89: $15,000

FY 90: $135,000

Principal Investigators:
R. N. Dietz and G. I. Senum

Sponsor: Electric Power Research Institute, EPRI

Leakage of oil from underground high-pressure oil-filled (HPOF) high voltage transmission cables can be detected most readily by the addition of a perfluorocarbon tracer (PFT) vapor to the oil with subsequent measurement of those PFT vapors above the ground. Field experiments have shown that tagging cable oil with a PFT at about 0.1% by weight has provided detection of a 0.5 gal/h leak after one day of leakage when sniffing the air at up to 100 m from the leak location; the cost of the PFT taggant would be about 5% of the cost of the oil. The approach has been successfully applied in field experiments at BNL and in New York City. Approximately 25 gallons of 0.1% tagged oil were leaked below the surface; using a variety of PFT sampling technology, it was demonstrated that aerial sampling could locate the leak to within $^1/_2$ a block, and that bore hole sampling could then be used to pinpoint the leak to within less than 5 feet.

Independent investigation by the Cablec Corporation of the compatibility of 0.1% PFT in the oil of an operating cable in terms of breakdown voltage and power factor indicates no performance problems to date.

A reinvestigation one year later of the Brookhaven experimental oil leak trench site showed that the tagged oil (25 gallons) in the lined trench was still localized to within two feet and that the PFT signal would persist with a half-life greater than five years. That site will soon be decommissioned for environmental reasons, but additional field studies in urban settings will be performed in the next fiscal year to finalize the protocols for locating, localizing, and pinpointing HPOF cable oil leaks at unknown leak sites.

Title: Utility Research and Development Center
Technology Transfer Projects

FY 89:	$25,000	Principal Investigators: W. M. Loss and R. N. Dietz
FY 90:	$65,000	Sponsor: Various Northeast U.S. Utilities

The Tracer Technology Center (TTC) has, for more than two years, been studying the feasibility of tagging cable oil used in underground high pressure oil filled (HPOF) high voltage electric cable feeders for detecting and pinpointing subsurface oil leaks.

Discussions with numerous utilities in the Northeast have examined other leak detection applications, including gas pipeline leaks, condenser air and water leaks, building waste heat recovery, hydrogen storage and turbine-generator leaks, and underground storage tank leaks.

A tutorial was held for northeast utility representatives to familiarize them with the perfluorocarbon tracer (PFT) technology and to demonstrate its applicability.

A more comprehensive program is planned for this fiscal year to evaluate the applicability to leak detection at a power station for condenser air inleakage, tube leakage, cooling water flow rates, and waste heat recovery.

Title: Building Infiltration and Ventilation

FY 89: $60,000

Principal Investigator:
R. N. Dietz

FY 90: $0

Sponsor: Office of Buildings and Community Systems, DOE

The objective of this research is to apply multiple perfluorocarbon tracers (PFTs) in multizone buildings to determine natural air infiltration, air exchange between zones, and mechanical ventilation; to establish protocols for certifying the performance of air-handling equipment in large buildings; to develop multizone modeling approaches to quantify the magnitude and errors in determining flow rates and pollutant source and decay rates in indoor air quality (IAQ) studies; and to improve the PFT measurement technology and encourage its use in the private sector. These studies would answer objective questions such as 1) how efficiently is fan energy being utilized to provide fresh air in all zones of a building, 2) does the air-handling equipment operate as designed, 3) can a specific building make more use of natural infiltration to save fan energy, and 4) to what extent does conditioned air leak from ductwork, etc. The basic approach is to apply the passive PFT technology as well as programmable and real-time sampling equipment in large buildings using as many as six tracer types to study the interaction of multiple zones with one another and the outside. The flow performance will be evaluated under various meteorological and operating conditions. The results will be compared both with the system design and its performance as determined by other measurement techniques. Such studies should result in the more efficient operation of existing heating, ventilating, and air conditioning (HVAC) systems and possibly suggest equipment design changes.

Title: A Database of PFT Ventilation Measurements

FY 89: $40,000

Principal Investigator:
R. W. Goodrich

FY 90: $0

Sponsor: Versar, Inc.
Subcontract, US EPA

The ventilation characteristics of a building can be described by treating the building as a group of interconnected, well-mixed chambers or zones and by measuring all of the air flows between the zones as well as flows to the outdoors. Brookhaven has pioneered the use of multiple tracers to measure building ventilation. Since 1982, BNL has measured ventilation in more than 4000 homes, comprising about 100 separate research projects throughout the world. This measurement set is unique in that it is the only set of ventilation measurements that acknowledge and measure the multizone characteristics of residences. Other large measurement sets assume that a home can be treated as a single, well-mixed zone.

This work has created a database of all PFT ventilation measurements encompassing single family, residential, detached buildings. Included in the database are a full description of the house structure, the zonal divisions within the homes, the measured ventilation flows and their associated error estimates, the geographic locations of the homes, and the local meteorology during the measurement period. The database is available for use on any IBM- or Apple Macintosh-based personal computer system.

This work was supported by the EPA through a subcontract from Versar, Inc., parent company of GEOMET Technologies. GEOMET is currently involved in a long-term project which is attempting to mathematically model the release and transport in residential buildings of indoor air pollutants. Their need to describe the flow patterns within various types of residential structures at different times of the year and at different geographic locations has resulted in the creation of this database. In addition to its utility in modeling indoor pollutant dispersion, this database may also be useful to those people studying energy conservation, thermal comfort, and heating system design in residential buildings.

Title: Miscellaneous Air Infiltration Programs

FY 89: $20,000

Principal Investigator:
R. Dietz

FY 90: $40,000

Sponsor: Numerous State and Private Institutions and Companies

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Concern for the degradation of indoor air quality due to weatherization of homes and buildings and the energy performance of such facilities has resulted in a need for advanced measurement technology to determine the multizone flow characteristics of buildings.

The Brookhaven Air Infiltration Measurement System (BNL/AIMS) is the only technique currently available to cost-effectively provide a measure of internal and external air flow patterns into, out of, and within buildings. As such, we are supplying this system capability to universities, architectural firms, air handling system designers, etc., to establish the protocols for the implementation of the measurement technique in various scenarios. In addition, we will continue to assist in the transfer of this technology to the private sector. Since the measurement capability now resides in the commercial sector at the National Association of Home Builders National Research Center, Brookhaven will emphasize its research studies in the large building area.

Title: Improved Gas Chromatograph System for PFT Determinations in Japan

FY 89: $50,000

FY 90: $40,000

Principal Investigator: R. N. Dietz

Sponsor: Japan Atomic Energy Research Institute, JAERI

JAERI has been conducting long-range atmospheric tracer experiments and would like to incorporate the Brookhaven-developed perfluorocarbon tracer (PFT) technology in their future studies.

Under this program, Brookhaven will provide to JAERI a complete laboratory gas chromatograph (GC) system including a new unit based on the Varian 3600 GC, a passive sampler desorption rack, manuals and training, PFT standards, and a fully programmed data acquisition system. In addition, we are assisting JAERI with overseeing of the production of 17 new-generation programmable PFT samplers.

A longer precut column has been developed to minimize low molecular weight gaseous interferents from the PFT analyses; the column can be temperature programmed directly under control of the Varian 3600 auxiliary temperature controller using direct ohmic heating. In addition, for the first time, we are able to control and read the Florisil reconcentration trap temperature directly. The system will be completed in Fiscal Year 1990, with final training and installation in Japan.

Title: Cloudwater Acidity Measurements and Formation Mechanisms

FY 89: $100,000

Principal Investigator:
S. E. Schwartz

FY 90: $150,000

Sponsor: Electric Power Research Institute, EPRI

The overall objective of this project is development of enhanced understanding of the role of liquid-water clouds in formation of acid precipitation. Processes examined include: 1) incorporation by clouds of soluble gaseous and aerosol species present in pre-cloud air and 2) in-cloud gas-aqueous reaction, i.e., dissolution of reactive gases followed by aqueous-phase reaction. Substances of concern include gaseous SO_2, NO, NO_2, HNO_3, NH_3, and O_3; aerosol H^+, NH_4^+, $SO_4^=$, and NO_3^-; aqueous H^+, NH_4^+, $SO_4^=$, NO_3^-, and H_2O_2. Determination of species concentrations in the several phases in conjunction with laboratory-determined equilibrium and kinetic data permits examination of chemical equilibria and evaluation of reaction rates, thereby enabling the important in-cloud processes to be identified.

Principal components of this project have been field measurements, principally by instrumented aircraft; interpretation of measurements in terms of processes responsible for cloudwater composition; development and evaluation of instrumentation in support of the aircraft measurements; and directed laboratory studies of processes identified as potentially important to description of gas-aqueous reactions in clouds. At present, this project is focusing on continued interpretation of field measurements.

Title: Grand Canyon Visibility Project

FY 89: $0

Principal Investigator:
M. A. Mazurek

FY 90: $35,000

Sponsor: National Park Service

Objectives of the Grand Canyon Visibility Project are to relate the composition of aerosol particles collected at two elevations (i.e., Hopi Point at 7000 feet above sea level, at the top southern rim; and Indian Gardens, at 3300 feet, within the canyon) to visibility measurements and upper-air wind trajectories during summer ambient conditions. Relating the aerosol composition to simultaneous measurements of visibility and air-mass trajectories will provide a basis for an assessment of the sources and impact of visibility-reducing aerosols found in Grand Canyon National Park.

Local sources of aerosol carbon within the Grand Canyon are of interest in terms of describing the total ambient mass concentrations of carbonaceous aerosols. Two important local sources of aerosol carbon are: (1) wood smoke emissions from wildfires and campfires; and (2) plant waxes and exudates from local vegetation. Aerosol collection from these local sources will help identify and quantify contributions of wood smoke and vegetation emissions to the Grand Canyon airshed.

Title: Analytical Chemistry Group

FY 89: $150,000

Principal Investigator:
L. Newman

FY 90: $50,000

Sponsor: Distributed Account*

This is a service group mainly dedicated to fulfilling the analytical chemistry requirements of the Department of Applied Science and thereby presently devotes most of its efforts to the programmatic needs of the Environmental Chemistry and Atmospheric Sciences Divisions. However, their services, both through analytical chemical measurements and direct programmatic involvement, are available for and indeed used by the rest of the Department and the Laboratory as a whole. Most samples are submitted for analyses to be performed at the central analytical facility, but when the need for more intensive analytical support dictates, chemists from the group are loaned for various periods of time to other Divisions and Departments within the Laboratory. The analytical techniques most frequently utilized are ion chromatography, automated colorimetry, atomic absorption, spectrophotometry, liquid and gas chromatography, and mass spectrometry. Computer-assisted data analysis has been instituted for several of these techniques.

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*This distributed account derives support approximately as follows: 60% from Environmental Chemistry Division programs presented in this report, 20% from Atmospheric Sciences Division, 10% from other Divisions in DAS, and 10% from other Departments in the Laboratory.

PUBLICATION LISTINGS

(Publications are listed alphabetically by author, within subdivisions consisting of: Articles; Meetings, Proceedings and Abstracts; and Reports. BNL Numbers are provided for reference.)

ARTICLES

Daum, P. H. Kelly, T. J., Tanner, R. L., Tang, X., Anlauf, K., Bottenheim, J., Brice, K. A., and Wiebe, A. Winter measurements of trace gas and aerosol composition at a rural site in southern Ontario. Atmos. Environ. 23, 161-173 (1989). [BNL 40342 R2]

Daum, P. H. Observations of H_2O_2 and S(IV) in air, cloudwater and precipitation and their implications for the reactive scavenging of SO_2. Atmos. Res., accepted (1989). [BNL 42337R]

Daum, P. H., Kleinman, L. I., Hills, A. J., Lazrus, A. L., Leslie, A. C. D., Busness, K., and Boatman, J. Measurement and interpretation of concentrations of H_2O_2 and related species in the upper midwest during summer. J. Geophys. Res., submitted (1989). [BNL 43091R]

Dietz, R. N., Spandau, D., D'Ottavio, T., Goodrich, R., and Senum, G. Description and design of perfluorocarbon tracer (PFT) analysis system. In Description, Ground-Level Sampling at Primary Sites, and Meteorology, R. R. Draxler and J. L. Heffter, Eds., pp. 19-36, NOAA Air Resources Laboratory, ERL ARL-167, 1989. [BNL 43731]

Forrest, J. and Newman, L. Determination and speciation of ambient particulate sulfur compounds. In Methods of Air Sampling and Analysis, 3rd Ed., J. P. Lodge, Jr., Ed., Intersociety Committee, Chapter 2, Part IV, pp. 715-730, Lewis Publishers, Inc., Chelsea, MI, 1989. [BNL 37014]

Fung, K. H. and Tang, I. N. Composition analysis of suspended aerosol particles by raman spectroscopy: Sulfates and nitrates. J. Coll. Interface Sci. 130, 219-224 (1989). [BNL 41350]

Fung, K. H. and Tang, I. N. Raman spectral studies of supersaturated bisulfate solution droplets. Chem. Phys. Lttrs 163, 560-564 (1989). [BNL 43165]

Kelly, T. J., Schwartz, S. E., and Daum, P. H. Detectability of acid producing reactions in natural clouds. Atmos. Environ. 23, 569-583 (1989). [BNL 40964R]

Kelly, T. J., McLaren, S. E., and Kadlecek, J. A. Seasonal variations in atmospheric SO_x and NO_y species in the Adirondacks. Atmos. Environ. 23, 1315-1332 (1989). [BNL 41335R]

Kleinman, L. I. and Daum, P. H. Oxidant limitation to the formation of H_2SO_4 near a SO_2 source region. Atmos. Environ., submitted (1989). [BNL 43362]

Newman, L. and Forrest, J. Sulfur isotope measurements relevant to power plant emissions in northeast United States. In Stable Isotopes in the Assessment of Natural and Anthropogenic Sulfur in the Environment, SCOPE/UNEP, R. Krouse, Ed., in press, John Wiley and Sons, Inc., New York, 1988. [BNL 36451R]

Newman, L. Awakening concerns in India with degradation of the environment. Atmos. Environ. 23, 891-897 (1989). [BNL 40054R]

Patrinos, A. A. N., Leach, M. J., Brown, R. M., Tanner, R. L., and Binkowski, F. S. An acid rain study in the Washington, DC, area. J. Appl. Meteorol. 28, 948-968 (1989). [BNL 41711]

Roberts, J. M. and Fajer, R. W. UV absorption cross sections of organic nitrates of potential atmospheric importance and estimation of atmospheric lifetimes. Environ. Sci. Technol. 23, 945-951 (1989). [BNL 41682 R2]

Roberts, J. M., Fajer, R. W., and Springston, S. R. The capillary gas chromatographic separation of alkyl nitrates and peroxycarboxylic nitric anhydrides (PAN-type compounds). Anal. Chem. 61, 771-772 (1989). [BNL 42032]

Roberts, J. M. The atmospheric chemistry of organic nitrates. Atmos. Environ., accepted (1989). [BNL 42332]

Schwartz, S. E. Acid deposition: Unraveling a regional phenomenon. Science 243, 753-763 (1989). [BNL 42350]

Schwartz, S. E. Sulphate aerosols and climate. Nature 340, 515-516 (1989). [BNL 42305R]

Sisterson, D. L., Shannon, J. D., Daum, P. H., Klotz, P. J., Luecken, D. J., and Hall, D. J. The snowfall chemistry collector intercomparison test (SCCIT). Water, Air, Soil Pollut., accepted (1989). [BNL 43543]

Springston, S. R. and Dezaro, D. A. Nonextractable stationary phases for gas chromatography cross-linked by exposure to low-temperature plasmas. J. Chromatogr. 473, 79-92 (1989). [BNL 42057R]

Springston, S. R. A cryogenic-focusing ohmically-heated on-column trap for capillary gas chromatography. J. Chromatogr., submitted (1989). [BNL 43139R]

Tang, I. N. and Munkelwitz, H. R. Evaporation kinetics of ammonium chloride solution droplets in water vapor. J. Colloid Interface Sci. 128, 289-295 (1989). [BNL 41135]

Tang, I. N. and Fung, K. H. Characterization of inorganic salt particles by raman spectroscopy. J. Aerosol Sci. 20, 609-618 (1989). [BNL 41749R]

Tanner, R. L. The measurement of strong acids in atmospheric samples. In Methods of Air Sampling and Analysis, 3rd Ed., J. P. Lodge, Jr., Ed., pp. 703-714, Lewis Publishers, Inc., Chelsea, MI, 1989. [BNL 36791]

Tanner, R. L. Analysis of sulfur-containing gases in the atmosphere (continuous method with flame photometric detector). In Methods of Air Sampling and Analysis, 3rd Ed., J. P. Lodge, Jr., Ed., in press, American Public Health Association, Washington, DC, 1988. [BNL 37204]

Tanner, R. L. Sources of acids, bases and their precursors in the atmosphere. In Advances in Environmental Science, Acid Precipitation Series, Vol. 2. Sources, Emissions, and Mitigation, D. C. Adriano, Coordinating Editor, Springer-Verlag, Heidelburg, 1988, in press. [BNL 40657R]

Tanner, R. L. and Miguel, A. H. Carbonaceous aerosol sources in Rio de Janeiro. Aerosol Sci. Technol. 10, 213-223 (1989). [BNL 40523R]

Tanner, R. L. and Shen, J. Measurement of hydrogen peroxide in ambient air by impinger and diffusion scrubber. Aerosol Sci. Technol., accepted (1988). [BNL 40823 R3]

Tanner, R. L. and Kelly, T. J. Discussion: A method for determination of hydrogen peroxide in air. Atmos. Environ. 23, 283-284 (1989). [BNL 40902]

Tanner, R. L., Kelly, T. J., Dezaro, D. A., and Forrest, J. A comparison of filter, denuder, and real-time chemiluminescence techniques for nitric acid determination in ambient air. Atmos. Environ. 23, 2213-2222 (1989). [BNL 42352R]

Tanner, R. L., Daum, P. H., Slinn, W. G. N., and Dana, M. T. Comparison of cloudwater and rain composition from airborne and surface measurements: Limits of homogeneity of wet deposition. Tellus-B, submitted (1989). [BNL 43146]

Tanner, R. L. and de Andrade, J. B. Determination of formaldehyde by HPLC as the DNPH derivative following high volume air sampling onto bisulfite-coated cellulose filters. Anal. Chem., submitted (1989). [BNL 43820]

MEETINGS, PROCEEDINGS AND ABSTRACTS

Daum, P. H. Reactive scavenging in clouds. Symposium on the Role of Clouds in Atmospheric Chemistry and Global Climate, Anaheim, CA, January 29-February 3, 1989, Preprint Volume, pp. 236-238, American Meteorological Society, 1988. [BNL 41951]

Daum, P. H. Cloud chemistry and acidic precipitation. American Chemical Society Northeast Regional Meeting, Environmental Chemistry Session, Albany, NY, June 20, 1989. [BNL 42344]

Dezaro, D. A., Springston, S. R. and Schidlovsky, G. Electron beam-induced fluorescence as a liquid chromatographic detection technique. Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlanta, GA, March 6-10, 1989. [BNL 41748]

Dietz, R. N., D'Ottavio, T. W., and Goodrich, R. W. Use of perfluorocarbon tracer technology for short-term and real-time building ventilation determinations. Conference on Thermal Performance of Exterior Envelopes of Buildings IV, Orlando, FL, December 4-7, 1989. [BNL 41932]

Dietz, R. N. and Goodrich, R. W. Evaluation of home weatherization, ventilation and heating system "improvements". Indoor Air '90, the 5th International Conference on Indoor Air Quality and Climate, Toronto, Canada, July 29-August 3, 1990. [BNL 43548]

Dietz, R. N. and Senum, G. I. Overview of the perfluorocarbon tracer technology. First International Symposium on Microbiology of the Deep Subsurface, Orlando, FL, January 15-19, 1990. [BNL 43764]

Downs, J. L., Lin, C.-C., Lev-On, M., and Tanner, R. L. Atmospheric hydrogen peroxide measurements during the 1987 southern California air quality study. Air Pollution Control Association 82nd Annual Meeting and Exhibition, Anaheim, CA, June 25-30, 1989. [BNL 42054A]

Hildemann, L. M., Mazurek, M. A., and Cass, G. R. Distinctive features of fine organic aerosols emitted from various combustion sources. AAAR Annual Meeting, Reno, NV, October 10-13, 1989. [BNL 43545]

Hildemann, L. M., Cass, G. R., and Mazurek, M. A. Mathematical modeling of fine organic aerosol characteristics: The effect of Direct source emissions on an urban atmosphere. ASCE Conference on Environmental Engineering, Washington, DC, July 9-11, 1990. [BNL 43544]

Mazurek, M. A., Hildemann, L. M., and Cass, G. R. Measurement and flux of carbonaceous aerosol species from pine and oak wood combustion. Chapman Conference on Global Biomass Burning: Atmospheric, Climate, and Biospheric Implications, Williamsburg, VA, March 19-23, 1990. [BNL 43547]

Mazurek, M. A., Cofer, W. R., III, and Levine, J. S. Chemical speciation of carbonaceous aerosols from prescribed burning of a boreal forest ecosystem. Chapman Conference on Global Biomass Burning: Atmospheric, Climate, and Biospheric Implications, Williamsburg, VA, March 19-23, 1990. [BNL 43546]

Schwartz, S. E. Control of global cloud albedo and climate by marine dimethylsulfide emissions: A test by anthropogenic sulfur dioxide emissions. Symposium on the Role of Clouds in Atmospheric Chemistry and Global Climate, Anaheim, CA, January 29-February 3, 1989, Preprint Volume, pp. 4-8, American Meteorological Society, 1988. [BNL 41952]

Schwartz, S. E. Climate regulation by marine phytoplankton? A test by anthropogenic SO_2 emissions. 28th Liege International Astrophysical Colloquium, "Our Changing Atmosphere", Liege, Belgium, June 26-30, 1989. [BNL 42744]

Schwartz, S. E. Acid deposition. In Proceedings of the Ninth Seminar on Nuclear War: The New Emergencies, August 19-24, 1989, Erice, Sicily (Italy), A. Zichichi, Ed., in press, 1989. [BNL 43550]

Schwartz, S. E. and Weinstein-Lloyd, J. Laboratory studies of free radical reactions in cloudwater. Symposium on Chemical Kinetics and the Environment, American Chemical Society 199th National Meeting, Boston, MA, April 22-27, 1990. [BNL 43551]

Senum, G. I. and Dietz, R. N. Perfluorocarbon tracer technology: Overview and a hydrological application. Annual Meeting of the Association of Ground Water Scientists and Engineers, Houston, TX, October 31-November 1, 1989; Ground Water, submitted (1989). [BNL 42933]

Senum, G. I. and Dietz, R. N. Perfluorocarbon tracer tagging of drilling muds for the assessment of sample contamination. First International Symposium on Microbiology of the Deep Subsurface, Orlando, FL, January 15-18, 1990. [BNL 43145]

Springston, S. R. and Dezaro, D. A. Cross-linking stationary phases for gas chromatography by exposure to low-temperature plasmas. Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlanta, GA, March 6-10, 1989. [BNL 41631]

Tang, I. N. and Fung, K. H. Resonance raman spectroscopy of suspended aerosol particles. American Association for Aerosol Research, 1989 Annual Meeting, Reno, NV, October 10-13, 1989. [BNL 42362]

Tang, I. N. and Munkelwitz, H. R. Simultaneous determination of optical and thermodynamic properties of an evaporating aqueous solution droplet. 3rd International Aerosol Conference, Kyoto, Japan, September 24-27, 1990. [BNL 43549]

REPORTS

Loss, W. M., Dietz, R. N., and Senum, G. I. Detection of leaks in a water-cooled generator stator bar using perfluorocarbon tracers. Informal Report, BNL 43654, December 1989.

Newman, L. Environmental Chemistry Division Annual Report - 1988. Informal Report, BNL 42277, January 1989.

Senum, G. I., Cote, E. A., D'Ottavio, T. W., and Dietz, R. N. Hydrocarbon precombusting catalyst survey and optimization for perfluorocarbon tracer analysis in subsurface tracer applications. Informal Report, BNL 42769, May 1989.

Senum, G. I. and Dietz, R. N. Application of multitracer technology to petroleum reservoir studies. In Enhanced Oil Recovery, U.S. Department of Energy Progress Review, Quarter Ending December 31, 1988, Quarterly Report, BNL 43171, July 1989.

Senum, G. I. and Dietz, R. N. Application of multitracer technology to petroleum reservoir studies. In Enhanced Oil Recovery, U.S. Department of Energy Progress Review, Quarter Ending March 31, 1989, Quarterly Report, BNL 43172, July 1989.

Senum, G. I. and Dietz, R. N. Application of multitracer technology to petroleum reservoir studies. In Enhanced Oil Recovery, U.S. Department of Energy Progress Review, Quarter Ending June 30, 1989, Quarterly Report, BNL 43167, July 1989.

ABSTRACTS OF THE PUBLICATIONS

(Listed by BNL Number)

BNL 36451R

SULFUR ISOTOPE MEASUREMENTS RELEVANT TO POWER PLANT EMISSIONS IN NORTHEAST UNITED STATES

L. NEWMAN and J. FORREST

In Stable Isotopes in the Assessment of Natural and Anthropogenic Sulfur in the Environment, SCOPE/UNEP, R. Krouse, Ed., in press, John Wiley and Sons, Inc., New York, 1988.

A body of data has been obtained whereby we compile the isotopic ratio of sulfur in fuels that are in use in the northeastern part of the U.S. We have explored the variation with time in the isotopic ratio in typical oil and coal fired power plants. The isotopic ratio of sulfur in sulfur dioxide was measured in an extensive set of samples collected both at ground level and at elevations within the mixed layer, over a period of eight years and at a number of sites in the northeast.

There is no sensible difference between ground level and airborne measurements and the grand average of all results yields a ^{34}S del value of 2.4 with more than 90% of the values within the range of 0 to 4 del units. The isotopic ratio of sulfur in sulfate in the atmosphere was found to be significantly more positive than sulfur dioxide with an average ^{34}S del value of 5.0 and a range containing 90% of the values lying between 3 and 8 del units. The isotopic ratio of sulfur of a number of fuels is documented. Sources of sulfur containing substances suitable for use as short range tracers for power plant plumes have been identified.

BNL 36791

THE MEASUREMENT OF STRONG ACIDS IN ATMOSPHERIC SAMPLES

R.L. TANNER

In Methods of Air Sampling and Analysis, 3rd Ed., J. P. Lodge, Jr., Ed., pp. 703-714, Lewis Publishers, Inc., Chelsea, MI, 1989.

Atmospheric strong acids consist principally of nitric and sulfuric acids derived from the oxidation of sulfur dioxide and nitrogen oxides which in turn were emitted from stationary and (for NO_x) mobile combustion sources. Some evidence suggests that hydrochloric acid may also be present in the atmosphere directly from coal-fired utility emissions or from filter interactions between sea salt and acidic sulfate aerosols. These species are neutralized principally by atmospheric gaseous ammonia (the latter emitted from mostly surface biogenic and anthropogenic sources) and soil-derived particulate matter to produce the observed composition of sulfate and nitrate aerosols and the levels of nitric acid found in the atmosphere. Despite the acknowledged general validity of the above summary statements, many questions remain to be fully addressed: What is the relative strong acid content of atmospheric aerosols, especially its spatial and temporal variability? Is aerosol strong acid content associated only with aerosol sulfate and nitrate? Are ammonia and nitric acid in equilibrium with atmospheric aerosols? Are atmospheric gaseous strong acids (HNO_3, HCl, etc.) present in amounts comparable with aerosol species. Do weak acids contribute significantly to the acidity of atmospheric samples? What are the relationships of gaseous and aerosol strong acids to the composition of clouds and precipitation?

Active research efforts are in progress in all of the above question areas. These efforts are dependent on the development and application in the last 10-20 yr of technique for rapid, accurate, microscale determination of total strong acid and of individual acidic species in atmospheric aerosol and gaseous/samples. It is the purpose of this state-of-the-art review first to detail these technique developments, which consist in large measure of filter-based schemes but with some continuous and/or real-time approaches. The analytical complications derived from sampling anomalies and artifact formation problems will be reviewed, and some sampling/analysis protocols recommended which will minimize these complications. Lastly, some results of aerosol and gaseous composition studies in which strong acid measurements were critically important will be briefly summarized and the implication of these studies for future atmospheric pollution studies reviewed.

BNL 37014

DETERMINATION AND SPECIATION OF AMBIENT PARTICULATE SULFUR COMPOUNDS

J. FORREST and L. NEWMAN

In Methods of Air Sampling and Analysis, 3rd Ed., Ch. 2, Part IV, J. P. Lodge, Jr., Ed., pp. 715-730, Lewis Publishers, Inc., Chelsea, MI, 1989.

Our knowledge of atmospheric sulfur chemistry has been vastly enlarged during the past decade, attributable partially to the significant amount of progress which has been made in the measurement of ambient particulate sulfur compounds. Previous errors associated with sample collection have been more clearly defined, and procedures to minimize filter artifact sulfate formation and particle reactions have been devised. Ion chromatography has rapidly arisen as the popular method for analysis of routine soluble sulfate simultaneous with other anions as well. Real-time aerosol sulfate instruments utilizing flame photometric detection have been constructed, with modifications even for sulfate speciation. Sulfate speciation has been further enhanced by application of the principle of light scattering by airborne particles as a function of relative humidity, and through temperature programming and addition of ammonia, the degree of quantification may be enhanced. Although significant inroads have been established in determining the oxidation state of aerosol sulfur, further progress is till needed to clarify some of the existing discrepancies.

BNL 37204

ANALYSIS OF SULFUR-CONTAINING GASES IN THE ATMOSPHERE (CONTINUOUS METHOD WITH FLAME PHOTOMETRIC DETECTOR)

R.L. TANNER

In Methods of Air Sampling and Analysis, 3rd Ed., J. P. Lodge, Jr., Ed., in press, American Public Health Association, Washington, DC, 1988.

The methods for determination of sulfur-containing gases in the atmosphere, both total gaseous sulfur and individual sulfur compounds following gas chromatographic (GC) separation, using the flame photometric detector are described in parallel in this chapter. The principle of operation of the flame photometric detector (FPD) is described followed by a section on sensitivity, limit of detection and range of this detector. Interferences are discussed along with factors controlling precision and accuracy of continuous and GC-FPD systems. The apparatus, reagents and operational procedures are discussed in detail. The chapter then ends with a discussion of calibration procedures, use of standards, and calculational techniques for obtaining the reported sulfur gas concentrations.

BNL 40054R

AWAKENING CONCERNS IN INDIA WITH DEGRADATION OF THE ENVIRONMENT

L. NEWMAN

Atmos. Environ. 23, 891-897 (1989).

An invitation to visit India was accepted in order to present lectures and have discussions at the Indian Institute of Technology (Delhi), Andhra University, Indira Gandhi Centre for Atomic Research, Indian Institute of Science, and Bhabha Atomic Research Centre. Selections from eight lectures on environmental protection, acid rain, and atmospheric chemistry were presented and served as a means to introduce environmental questions being addressed in the United States and to initiate discussions on scientific programs being formulated in India. Impressions of the country and interests of its scientists are described. In general, there is an awakening concern in India with the need to protect the environment, and there is a cadre of scientists that are well informed in world environmental issues through whom a number of major activities are just getting underway. Their resources are modest and they yearn for assistance from and cooperation and involvement with foreign scientists.

BNL 40342 R2

WINTER MEASUREMENTS OF TRACE GAS AND AEROSOL COMPOSITION AT A RURAL SITE IN SOUTHERN ONTARIO

P.H. DAUM, T.J. KELLY, R.L. TANNER, X. TANG, K. ANLAUF, J. BOTTENHEIM, K.A. BRICE, and A. WIEBE

Atmos. Environ. 23, 161-173 (1989).

This paper reports the results of continuous measurements of concentrations of trace gas and aerosol species at Powassan, Ontario, a rural location in southern Ontario, from January 20 - February 24, 1984. The measurements included aerosol H^+, NH_4^+, Na^+, Ca^{++}, NO_3^-, $SO_4^=$, and Cl^-, gaseous SO_2, NO, NO_y (= NO + NO_2 + PAN + HNO_3), HNO_3, PAN, and O_3. Average values of concentrations for key species during the project were: SO_2, 7.3 ppb; NO_y, 7.5 ppb; HNO_3, 0.85 ppb; O_3, 33 ppb; NH_4^+, 1.5 ppb; NO_3^-, 0.4 ppb; and $SO_4^=$, 0.9 ppb. Concentrations of primary pollutants (e.g., SO_2) were typically much higher, and concentrations of secondary species (e.g., $SO_4^=$) typically lower, than observed at this location in summer. However, clear-air t-$NO_3^-/SO_4^=$ ratios averaged 5-10 times higher in the winter than in summer which suggests that HNO_3 is a more important source of atmospheric acidity, relative to $SO_4^=$ aerosol, in winter than in summer. Pollutant concentrations were highly variable; back trajectory calculations indicate that periods of high concentrations of both primary and secondary species were typically associated with air-mass back trajectories from the southern sectors while periods of low concentrations of secondary species were associated with back trajectories from the north. Comparison of these measurements with those at other locations suggests that concentrations at Powassan were characteristic of those prevailing over a much larger, possibly regional, area.

BNL 40523R

CARBONACEOUS AEROSOL SOURCES IN RIO DE JANEIRO

R.L. TANNER and A.H. MIGUEL

Aero. Sci. Technol. 10, 213-223 (1989).

Aerosol carbon concentrations, organic/elemental speciation, and carbon isotopic composition data ($^{13}C/^{12}C$ ratios and ^{14}C content) are reported from the second Rio de Janeiro Aerosol Characterization Study (RIO-JACS II), along with supplemental meteorological and inorganic aerosol data. These data and their diurnal and weekday/weekend variability are used to identify sources of carbonaceous aerosols in the urban Rio air basin. Specifically, contributions from biogenic sources, anthropogenic emissions (principally transportation sources), and sugar cane-derived alcohol-fueled vehicular emissions to aerosol carbon levels in Rio are estimated from measurements of carbon-14, organic and elemental carbon and $^{13}C/^{12}C$ isotopic composition in total aerosol samples collected at two ambient Rio sites and in a heavily travelled tunnel. The major source of elemental (soot) carbon appears to be diesel vehicles, but secondary sources of both biogenic and fossil organic aerosol carbon are indicated.

BNL 40657R

SOURCES OF ACIDS, BASES AND THEIR PRECURSORS IN THE ATMOSPHERE

R.L. TANNER

In Advances in Environmental Science, Acid Precipitation Series, Vol. 2. Sources, Emissions, and Mitigation, D. C. Adriano, Coord. Ed., in press, 1988.

A summary of the sources of acidic and basic substances in the atmosphere is given. The primary combustion sources and secondary homogenous and heterogenous pathways by which acidic sulfate aerosols and gaseous nitric and hydrochloric acids enter or are formed in the atmosphere are delineated, and emission sources and fates of the principal atmospheric base, ammonia, are discussed. Homogenous reactions of SO_2 and NO_2 with OH radicals are important for sulfuric and nitric acid formation, respectively, but aqueous-phase oxidation reactions also convert dissolved S(IV) to sulfuric acid within typical cloud and rain droplet lifetimes. Evidence for rapid reaction of ammonia emissions with the principal atmospheric acids (H_2SO_4 and HNO_3) is reviewed. Discussion then follows concerning how these reactions combine with boundary layer mixing processes to establish vertical gradiants in the mixing ratios of acidic aerosols and gases.

BNL 40823 R3

MEASUREMENT OF HYDROGEN PEROXIDE IN AMBIENT AIR BY IMPINGER AND DIFFUSION SCRUBBER

R.L. TANNER and J. SHEN

Aerosol Sci. Technol., accepted (1989).

Two methods for the determination of gaseous hydrogen peroxide in ambient air were tested during the Carbon Species Methods Comparison Study conducted at Glendora, CA, August 12-20, 1986. Air was sampled by the BNL dual impinger/diffusion scrubber apparatus after ambient ozone removal by addition of NO. Sampling was done during daylight hours (~0800-2000 hr) from a sampling line shared with the National Center for Atmospheric Research (NCAR) and Texas Tech University (TTU) groups. Impinger data were formally compared with results from other methods; they showed afternoon maxima which were generally <1 ppbv for the first 5 days, and >1 ppbv the last 4 days of the study, respectively. Data from the diffusion scrubber agreed well with the impinger data if the former are corrected for an ~40% aqueous phase loss of collected H_2O_2. Error sources for impinger and scrubber data resulting from potential interferences and loss mechanisms are discussed.

BNL 40902

DISCUSSION: A METHOD FOR DETERMINATION OF HYDROGEN PEROXIDE IN AIR

R.L. TANNER and T.J. KELLY

Atmos. Environ. 23, 283-284 (1989).

Hartkamp and Bachhausen [Atmos. Environ. 21, 2207-2213 (1987)] describe a new technique for gaseous H_2O_2 determination. Although this technique is promising, it shows no clear advantage over available techniques when all current literature is surveyed.

BNL 40964R

DETECTABILITY OF ACID PRODUCING REACTIONS IN NATURAL CLOUDS

T.J. KELLY, S.E. SCHWARTZ, and P.H. DAUM

Atmos. Environ. 23, 569-583 (1989).

Oxidation reactions of SO_2 and NO_2 in clouds are considered important atmospheric acid formation processes. This paper evaluates the feasibility of detecting the occurrence of these oxidation reactions in natural clouds by means of field measurements. This evaluation is performed by calculating the changes expected in reagent and product concentrations resulting from these reactions in representative cloud types, and comparing those changes with concentration differences detectable by available analytical methods in the context of typical atmospheric variability. Four in-cloud oxidation reactions are considered: aqueous-phase reactions of SO_2 with O_3 and with H_2O_2, and gas-phase reactions of NO_2 with OH radical and with O_3, the latter leading to acid formation by reaction of N_2O_5 with cloud liquid water. The cloud types considered are fog, stratus, cumulus, and mountain lee wave. This evaluation indicates that oxidation of SO_2 by H_2O_2 should be detectable in a wide variety of cloud conditions, but that oxidation of SO_2 by O_3 is unlikely to be detected by field measurements. Oxidation of NO_2 may be detectable in fog and stratus clouds, which provide long in-cloud residence times. The paper includes discussion of factors which favor or hinder detection of acid producing reactions in clouds, and reviews evidence from published field studies on the occurrence of these reactions.

BNL 41135

EVAPORATION KINETICS OF AMMONIUM CHLORIDE SOLUTION DROPLETS IN WATER VAPOR

I.N. TANG and H.R. MUNKELWITZ

J. Colloid Interface Sci. 128, 289-295 (1989).

The evaporation kinetics of aqueous NH_4Cl droplets have been measured in a single particle suspension apparatus in conjunction with Mie resonance spectroscopy. Evaporation coefficients for NH_3 and HCl, heretofore inaccessible to any measurements, have been deduced from the droplet evaporation rate data using a mathematical model considering equal-molar evaporation of the solute gases. The values are 0.29 ± 0.03 for NH_3 and 0.45 ± 0.04 for HCl, based on the partial pressures of the solute gases estimated from the best available thermodynamic properties.

BNL 41335R

SEASONAL VARIATIONS IN ATMOSPHERIC SO_x AND NO_y SPECIES IN THE ADIRONDACKS

T.J. KELLY, S.E. MC LAREN, and J.A. KADLECEK

Atmos. Environ. 23, 1315-1332 (1989).

This paper reports the results of over two years of measurements of species comprising atmospheric SO_x (= SO_2 + $SO_4^=$) and NO_y (= NO + NO_2 + PAN + HNO_3 + organic nitrates) at Whiteface Mountain, New York. Continuous real-time measurements of SO_2 and total gaseous NO_y provided data for about 50% and 65% of the period, respectively, and 122 filter pack samples were obtained for HNO_3, SO_2, and aerosol $SO_4^=$, NO_3^-, H^+, and NH_4^+. Concentrations of SO_2 and NO_y were greatest in winter, whereas concentrations of the reaction products $SO_4^=$ and HNO_3 were greatest in summer. The seasonal variation in $SO_4^=$ was considerably more pronounced than that of HNO_3, and the high concentrations of $SO_4^=$ aerosol present in summer were also relatively more acidic than $SO_4^=$ aerosol in other seasons. As a result, $SO_4^=$ aerosol was the predominant acidic species present in summer, HNO_3 was predominant in other seasons. Aerosol NO_3^- concentrations were low in all seasons and appeared unrelated to simultaneous NO_y or HNO_3 concentrations. These data are consistent with seasonal variations in photochemical oxidation rates, and with existing data on seasonal variations in precipitation composition. The results of this study suggest that emission reductions targeted at the summer season might be a cost-effective way to reduce deposition of sulfur species, but would not be similarly cost-effective in reducing deposition of nitrogen species.

BNL 41350

COMPOSITION ANALYSIS OF SUSPENDED AEROSOL PARTICLES BY RAMAN SPECTROSCOPY: SULFATES AND NITRATES

K.H. FUNG and I.N. TANG

J. Colloid Interface Sci. 130, 219-224 (1989).

Raman spectra of singly suspended aerosol particles were obtained for several environmentally important species, such as sulfates and nitrates. Experiments were carried out using a quadrupole cell as the particle containment chamber and the 4880 Å line of an argon ion laser as excitation source. Raman spectral shifts were measured for the above-mentioned species with a resolution of 4 cm^{-1}. Quantitative measurements were also established for sulfate and nitrate mixtures in both crystalline and aqueous states under controlled laboratory conditions. The present work demonstrates the feasibility of a non-destructive and unique technique for aerosol composition analysis.

BNL 41631

CROSS-LINKING STATIONARY PHASES FOR GAS CHROMATOGRAPHY BY EXPOSURE TO LOW-TEMPERATURE PLASMAS

S.R. SPRINGSTON and D.A. DEZARO

Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlanta, GA, March 6-10, 1989.

Many recent developments in capillary gas chromatography have focussed on techniques for cross-linking stationary phases. Cross-linking can prevent the breakup of polar films at higher temperatures by increasing the viscosity of the liquid phase. Properly cross-linked stationary phases also resist dissolution by large solvent injections. Thermal decomposition of free-radical initiators, such as azo compounds or organic peroxides, is a popular approach for achieving these goals. However, heating may disrupt marginally stable films before they are successfully cross-linked. In addition, chemical agents, particularly peroxides, cause undesirable polar decomposition products to be incorporated within the phase.

Low-temperature plasmas were explored as a source of free radicals for the treatment of stationary phases. Plasmas can be controlled to minimize surface heating. Low pressures and pure reagent gases should minimize the presence of unwanted byproducts. Various polymers were deposited on microscope coverslips and exposed to an argon plasma (P = 1 torr). The treated films subsequently resisted solvent dissolution and were judged to be fully cross-linked. Similarly, SE-30 coated on glass beads was also rendered insoluble by plasma treatment. Chromatographic tests showed both the polarity and the separation power were virtually unaffected by plasma exposure.

Plasmas have also been generated within coated capillary columns. *In situ* cross-linked phases resisted solvent rinses. The chromatographic behavior of several different stationary phases will be discussed.

BNL 41682 R2

UV ABSORPTION CROSS SECTIONS OF ORGANIC NITRATES OF POTENTIAL ATMOSPHERIC IMPORTANCE AND ESTIMATION OF ATMOSPHERIC LIFETIMES

J.M. ROBERTS and R.W. FAJER

Environ. Sci. Technol. 23, 945-951 (1989).

Organic nitrates, $RONO_2$, produced in the atmosphere through photochemical reactions involving hydrocarbons and oxides of nitrogen, may comprise a significant fraction of reactive odd-nitrogen, NO_y. Ultra violet absorption cross-sections (σ) of methyl, ethyl, 1- and 2-propyl, 1-, 2-, and tert-butyl, 2-, 3-, and cyclo-pentyl nitrates, nitrooxy-acetone, and nitrooxy-ethanol were measured to provide estimates of atmospheric removal rates. The spectra were very similar in the range of atmospheric interest (>290 nm) and decreased from $\sigma \sim 10^{-20}$ cm^2-molecule^{-1} to $<10^{-22}$ cm^2-molecule^{-1} above 330 nm. An increasing trend in σ was observed with length and degree of substitution of the alkyl substituent. Nitrooxy-acetone exhibited a cross-section approximately 10 times higher than that of methyl nitrate, while nitrooxy-ethanol had a cross section approximately a factor of 3 lower than methyl nitrate at 300 nm. The atmospheric lifetimes and possible significance of $RONO_2$ are also discussed.

BNL 41748

ELECTRON BEAM-INDUCED FLUORESCENCE AS A LIQUID CHROMATOGRAPHIC DETECTION TECHNIQUE

D.A. DEZARO, S.R. SPRINGSTON, and G. SCHIDLOVSKY

The Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlanta, GA, March 6-10, 1989.

Electron beam-induced fluorescence, in the liquid phase, has been investigated as a chromatographic detection technique. The electron gun from a Siemens TEM was used to produce a stable high energy electron beam (1-50 microamps at 40-100 kilovolts), which impinged upon a specially designed liquid flow-cell (10 μL). The electron beam penetrated a flow-cell window (4 μM thick) and was dissipated in the liquid mobile phase. The dissipation of electron beam energy produced ionization and excitation of mobile phase molecules, some fraction of which transfer their energy to excite eluting fluorescent molecules. Fluorescent light output was collected through a transparent flow-cell window and monitored by a photomultiplier tube.

This prototype detector has been used to monitor fluorescent polyaromatic compounds as they elute from flow injection and HPLC systems. Characteristics of the detector such as flow-cell construction, voltage, current, electron beam-illuminated volume, sensitivity, linearity, and selectivity will be discussed.

BNL 41749R

CHARACTERIZATION OF INORGANIC SALT PARTICLES BY RAMAN SPECTROSCOPY

I.N. TANG and K.H. FUNG

J. Aerosol Sci. 20, 609-618 (1989).

Raman spectra have been obtained for single aerosol particles levitated in an electrodynamic cell. The particles are composed of common inorganic salts such as sulfates, nitrates, phosphates and chromates in either pure or mixed form. The Raman vibrational frequencies observed for these compounds present in aerosol particles are found to be in good agreement with those of bulk samples. Moreover, the high resolution (± 1 cm^{-1}) developed in this work has made it possible to identify hydrated or mixed salts, which may be present in ambient aerosols under a variety of atmospheric conditions. It is shown that the Raman technique is a unique and non-destructive method for physical and chemical characterization of aerosol particles.

BNL 41932

USE OF PERFLUOROCARBON TRACER TECHNOLOGY FOR SHORT-TERM AND REAL-TIME BUILDING VENTILATION DETERMINATIONS

R.N. DIETZ, T.W. D'OTTAVIO, and R.W. GOODRICH

Conference on Thermal Performance of Exterior Envelopes of Buildings IV, Orlando, FL, December 4-7, 1989.

The application of the perfluorocarbon tracer (PFT) technology to the determination of multizone building ventilation measurements is best known for the facility of the passive PFT permeation source and passive adsorbent sampler (CATS) in estimating multizone air flows over long periods, from days to months. Although economically very attractive, there are negative biases (generally < 15%) in such results when the building air flow rates are varying during the sampling period. In certain instances, for example, when adjusting ventilation systems, there may be a desire to measure the flows in periods too short (< 1 h) for detection using the passive sampler. This paper will address the use of less well known PFT sampling technology that is applicable not only to such short-term measurement periods, but also to real-time building flow determinations.

In February 1988, in an intercomparison of three tracer technologies (Princeton constant concentration single tracer gas system, Lawrence Berkeley Laboratory (LBL) multiple tracer measurement system, and Brookhaven PFT technology), three types of PFT sampling were used: the CATS, the BATS (a programmable multitube sampler, and the DTA (a dual trap analyzer for multiple PFT determinations in about 5 min). Versions of these three PFT sampling modes have been available for more than eight years, the last two having been originally developed for long range atmospheric tracer studies. The building studied was variously tested in either 4-zone or 5-zone configurations, which the PFT technology can accommodate. In these tests, the high concentrations of other tracers (Princeton used about 100 ppb of SF_6, LBL about 10 ppm of halocarbons) interfered with the detection of the 10 ppt PFT levels in only the DTA real-time analyzer; the lab analyzer needed for the CATS and BATS was not affected by the other high tracer concentrations. Interpretation of the BATS 15-min interval data during which three substantial changes in either air infiltration or interzonal air exchange were induced, showed that the technology was able to measure the new rates to better than ±15% in just one interval. Thus the PFT technology responds and stabilizes in less than 15 min to large step changes in ventilation rates when measured in the steady-state mode. This means that there is a real need for a very short cycle time (~1 to 2 min) real-time PFT analyzer.

Complete details of the short-term results obtained in those tests as well as another performed in a condominium unit with a forced air heating system will be presented.

BNL 41951

REACTIVE SCAVENGING IN CLOUDS

P.H. DAUM

Symposium on the Role of Clouds in Atmospheric Chemistry and Global Climate, Anaheim, CA, January 29-February 3, 1989, Preprint Volume, pp. 236-238, American Meteorological Society, 1988.

Clouds represent an ideal medium for atmospheric aqueous-phase chemical reaction in view of their high liquid water content, high dispersion, and the generally high thermodynamic driving force resulting from the dissolution of soluble materials in water. Aqueous-phase transformation is of particular importance in the study of wet deposition since clouds are the immediate precursors to precipitation, but cloud processes may also be important contributors to species found in clear-air since most clouds evaporate, releasing trace gases and aerosols to the atmosphere.

BNL 41952

CONTROL OF GLOBAL CLOUD ALBEDO AND CLIMATE BY MARINE DIMETHYLSULFIDE EMISSIONS: A TEST BY ANTHROPOGENIC SULFUR DIOXIDE EMISSIONS

S.E. SCHWARTZ

Symposium on the Role of Clouds in Atmospheric Chemistry and Global Climate, Anaheim, CA, January 29-February 3, 1989, Preprint Volume, pp. 4-8, American Meteorological Society, 1988.

It has been hypothesized (Charlson et al., 1987) that mean global albedo and temperature are controlled by emissions by marine phytoplankton of dimethylsulfide, which is oxidized in the atmosphere to form aerosol sulfate particles that serve as cloud condensation nuclei, enhancing cloud albedo, and thereby effecting global cooling. This hypothesis is tested by noting that anthropogenic SO_2 emissions exceed marine dimethylsulfide emissions and are comparable to biogenic gaseous sulfur emissions globally, are confined largely to the Northern Hemisphere, and have reached their present level largely within the past 100 years. Concentrations of non sea salt aerosol sulfate at remote locations in the Northern Hemisphere substantially exceed those in the Southern Hemisphere, consistent with an anthropogenic SO_2 source. The absence of a Northern Hemisphere excess in mean cloud albedo and of a global cooling or interhemispheric difference in warming rate over this time period precludes any major influence of anthropogenic SO_2 emissions on global or hemispheric mean albedo and temperature and by extension also any such influence due to marine dimethylsulfide. This talk will treat the following subjects: a) Global and hemispheric sulfur emissions; b) Geographical distribution of aerosol sulfate; c) Sulfate in precipitation and ice cores, NH and SH; d) Interhemispheric differences in cloud albedo expected from Charlson hypothesis and observed; e) Temporal changes and interhemispheric differences in mean temperature expected from Charlson hypothesis and observed; and, f) Alternative explanations for the lack of the expected signals in mean albedo and temperature.

BNL 42032

THE CAPILLARY GAS CHROMATOGRAPHIC SEPARATION OF ALKYL NITRATES AND PEROXYCARBOXYLIC NITRIC ANHYDRIDES, (PAN-TYPE COMPOUNDS)

J.M. ROBERTS, R.W. FAJER, and S.R. SPRINGSTON

Anal. Chem. 61, 771-772 (1989).

The measurement of peroxyacetic nitric anhydride (PAN) and related compounds, which is crucial to the study of atmospheric reactive odd-nitrogen (NO_y) chemistry, is generally accomplished by packed column gas chromatography (GC) coupled with electron capture detection (ECD). Recent observations of alkyl nitrates ($RONO_2$) in rural and remote atmospheres have prompted the extension of this method to these compounds; however, a typical packed column consisting of Carbowax 400 on Chromosorb W HP, packed in a 0.6 m x 1/8" OD Teflon tube, operated under typical conditions 40 cc/min N_2 flow, 30-35°C, cannot separate 2-propyl nitrate from ethyl nitrate, and 2-butyl nitrate from 1-propyl nitrate. Since the lower flow rates and narrower elution peaks associated with capillary columns provide a great improvement in sensitivity relative to packed columns, the capillary column separation of PAN, peroxypropionic nitric anhydride (PPN), and methyl, ethyl, 1- and 2-propyl, 1- and 2-butyl, and were studied here to determine if these compounds could be measured simultaneously. A commercial capillary column, consisting of 30 m x 0.32 mm i.d. fused silica with a 1 μm coating of cross-linked methyl silicone (J and W Scientific, DB-1) was found to completely separate all of the above compounds at 30°C, and to provide separation from potentially interfering chlorinated hydrocarbons; however, a relatively long analysis time was required. The optimization of a capillary GC/ECD system for atmospheric measurements is discussed.

BNL 42054A

ATMOSPHERIC HYDROGEN PEROXIDE MEASUREMENTS DURING THE 1987 SOUTHERN CALIFORNIA AIR QUALITY STUDY

J.L. DOWNS, C.-C. LIN, M. LEV-ON, and R.L. TANNER

Air Pollution Control Association 82nd Annual Meeting and Exhibition, Anaheim, CA, June 25-30, 1989.

Ambient atmospheric concentrtions of hydrogen peroxide were measured as part of the Southern California Air Quality Study (SCAQS). These measurements were conducted the four sites, on eleven summer intensive test days in 1987. The sites were located at Claremont, downtowna Los Angeles, Long Beach and Rubidoux. Eight samples were collected at each site on each test day, with a time resolution ranging from one hour (in the afternoon) to seven hours (around midnight).

The tandem impinger method developed by the Brookhaven National Laboratory was used to collect air samples. Potential negative interferences from sulfur dioxide were eliminated by the presence of 2 mm of formaldehyde in the impinger solution, while positive artifacts due to the presence of ozone in the air sampled were handled by titrating it with excess nitric oxide upon sampling, prior to the first impinger. The samples were derivatized in the field with a p-hydroxyphenylacetic acid (POHPAA) reagent containing peroxidase thus forming the POHPAA dimer, which was subsequently analyzed fluorimetrically in the laboratory within 48 hours of sampling.

Measured atmospheric concentrations of hydrogen peroxide ranged from 0 to 5 ppbv. The diurnal concentration profiles were similar for all four sites, exhibiting mid-afternoon peaks and late-night valleys. However, the absolute values were variable with observed concentrations generally higher at receptor area sites, such as Claremont and Rubidoux. The integrity of the entire measurement system was verified by performing gas-phase calibrations, with a portable calibrator, to test for line losses. Recorded line losses ranged from 20-30% for the Claremont and Rubidoux sites, to 7% at the Long Beach site.

BNL 42057R

NONEXTRACTABLE STATIONARY PHASES FOR GAS CHROMATOGRAPHY CROSS-LINKED BY EXPOSURE TO LOW-TEMPERATURE PLASMAS

S.R. SPRINGSTON and D.A. DEZARO

J. Chromatogr. 473, 79-92 (1989).

Non-polar and medium-polarity stationary phases, such as SE-30, SE-52, and SE-54, can be completely cross-linked by exposure to low-temperature plasmas. Plasma-exposed polymers on glass coverslips resist solvent dissolution and were judged fully cross-linked. SE-30 coated on glass beads was also rendered insoluble by plasma treatment. Columns packed with treated beads show no reduction in chromatographic performance. A simple method for generating plasmas within evacuated capillaries is presented. Tests mad with *in situ* cross-linked capillary columns demonstrate plasma exposure does not affect retention characteristics. The advantages of plasmas are described, and additional applications are proposed.

BNL 42277

ENVIRONMENTAL CHEMISTRY DIVISION ANNUAL REPORT - 1988.

L. NEWMAN

Informal Report, January 1989.

The research activities making up the programs in the Environmental Chemistry Division of the Department of Applied Science are presented. Some of the more significant accomplishments during 1988 are described and plans for 1989 are discussed briefly. Publications for the period are listed and abstracts are provided. Research objectives and principal investigators are given for each of the active programs. A list of personnel and collaborators during the past year is presented. The support distribution for FY 1989 is approximately 85% from the Department of Energy (65% Office of Health and Environmental Research), and 15% other agencies (principally from the Electric Power Research Institute).

BNL 42305R

SULPHATE AEROSOLS AND CLIMATE

S.E. SCHWARTZ

Nature 340, 515-516 (1989).

My paper [Nature 336, 441-445 (1988)] proposed that anthropogenic SO_2 emissions serve as a surrogate for enhanced marine dimethylsulfide (DMS) emissions to test the hypothesis of Charlson et al. [Nature 326, 655-661 (1987)] that marine DMS emissions regulate global cloud albedo and mean temperature by enhancing the number density of aerosol sulfate particles that serve as cloud condensation nuclei (CCN). I concluded that no influence of anthropogenic SO_2 emissions (confined largely to the Northern Hemisphere, NH) could be found in interhemispheric comparisons of the cloud contribution to planetary albedo or in hundred-year temperature records. Ghan et al. and Gavin et al. raise several concerns with the suitability of anthropogenic SO_2 as a surrogate for enhanced marine DMS emissions and with the interpretation of albedo and temperature measurements in my paper.

BNL 42332

THE ATMOSPHERIC CHEMISTRY OF ORGANIC NITRATES

J.M. ROBERTS

Atmos. Environ., accepted (1989).

The chemistry of organic compounds containing the covalently-bound nitrate group is reviewed with the purpose of summarizing the state of knowledge concerning their importance in atmospheric chemistry. Information pertinent to the conduct of research is contained in sections titled Nomenclature; Preparation, Properties and Spectroscopic Data; and Measurement Techniques. Information specific to atmospheric chemistry is contained in sections titled Atmospheric Formation Processes, Atmospheric Removal Processes, and Atmospheric Observations. Areas of potential importance and areas of major uncertainty are identified throughout to provide focus for future research activities.

BNL 42337R

OBSERVATIONS OF H_2O_2 AND S(IV) IN AIR, CLOUDWATER AND PRECIPITATION AND THEIR IMPLICATIONS FOR THE REACTIVE SCAVENGING OF SO_2

P.H. DAUM

Atmos. Res., accepted (1989).

In-cloud oxidation of atmospheric SO_2 by H_2O_2 to produce H_2SO_4 has been demonstrated by several recent field studies. This reaction appears rapid and quantitative with the amount of sulfate determined by the concentration of either SO_2 of H_2O_2 whichever reagent is present in lesser amount. We report here measurements of H_2O_2 and S(IV) in air, precipitating clouds, and in surface precipitation made in the several field studies conducted as part of the DOE PRECP program, and during a field study in southern Ontario in the winter of 1984. Clear air concentrations measured in the midwest during June 1987 were found to be quite variable from day to day, and even within days when different air masses were sampled. The SO_2/H_2O_2 vertical profiles show that while SO_2 is largely confined to the boundary layer, H_2O_2 is present over a much wider range of altitudes. The H_2O_2 in the boundary layer was seldom present at concentrations sufficient to completely oxidize the available SO_2. This implies that mixing processes associated with clouds may be an important factor in controlling the extent to which the reaction of these two species occurs. The mutual exclusiveness of H_2O_2 and SO_2 previously found in non-precipitating clouds was not observed in precipitating clouds; substantial quantities of these two species frequently coexisted. This is attributed to material dissolved in falling hydrometeors which has not had time to react with SO_2. Analysis of the seasonal dependency of cloudwater and precipitation H_2O_2 concentrations shows a strong seasonal trend with concentrations much higher in summer than winter, consistent with a photochemical source for H_2O_2.

BNL 42344

CLOUD CHEMISTRY AND ACIDIC PRECIPITATION

P.H. DAUM

American Chemical Society Northeast Regional Meeting, Environmental Chemistry Session, Albany, NY, June 20, 1989.

This paper presents an analysis of aircraft data from various field studies of the relative importance of various mechanisms contributing to the composition of cloudwater. In clouds studied at various locations in the eastern US during spring, summer, and fall, it has been found that the composition of cloudwater cannot be accounted for soley by nucleation scavenging of aerosol particles and scavenging of soluble gases from pre-cloud air, suggesting occurrence of reactive scavenging processes. One such process, the in-cloud aqueous-phase oxidation of SO_2 by H_2O_2 has been identified and found to be an important contributor to cloudwater acidity and sulfate. In contrast, reactive scavenging does not appear to be an important contributor to the composition of clouds in winter. In a study conducted in southern Ontario during winter 1984, low level stratus clouds were found to exhibit concentrations of major ions nearly identical to concentrations of these species in below-cloud air. This observation suggests that nucleation scavenging of sulfate aerosol and scavenging of gaseous nitric acid were the principal processes determining compositon of clouds sampled during this study. The unimportance of reactive scavenging processes in these clouds is consistent with the reduced solar intensity prevailing in winter which leads to lower concentrations of oxidants available for reactive scavenging processes in winter, relative to other seasons of the year.

BNL 42350

ACID DEPOSITION: UNRAVELING A REGIONAL PHENOMENON

S.E. SCHWARTZ

Science 243, 753-763 (1989).

Because sources of sulfur and nitrogen oxides distributed broadly across eastern North America have greatly overlapping zones of influence, it is difficult to determine detailed relations between emissions and the resulting acid deposition. Although substantial progress has been made in the past decade in understanding the pertinent atmospheric processes and in describing them in numerical models, because of the complexities of these processes and the wide range of the time and space scales involved, credible source-receptor relations for regional-scale acid deposition are not yet at hand. Consequently, near-term strategies for reducing acid deposition should be based on considerations other than detailed atmospheric source-receptor relations, but with confidence that regional deposition will be reduced equivalently to any reduction in regional emissions.

BNL 42352R

A COMPARISON OF FILTER, DENUDER, AND REAL-TIME CHEMILUMINESCENCE TECHNIQUES FOR NITRIC ACID DETERMINATION IN AMBIENT AIR

T.L. TANNER, T.J. KELLY, D.A. DEZARO, and J. FORREST

Atmos. Environ. 23, 2213-2222 (1989).

Measurements of gas-phase nitric acid were made by four separate techniques during a 7-day summertime period at a near-coastal site on Long Island, NY. Results from methods intercomparison data for nitric acid, and their relationship to particulate nitrate and other odd nitrogen and oxidant species show the following: (a) high-volume filter pack nitric acid concentrations are well correlated with diffusion denuder difference (DD) results, except for small absolute losses with the former; (b) daytime real-time 2-channel chemiluminescence HNO_3 levels correlated well with DD results, but were higher during nighttime periods; (c) results by a new $Al_2(SO_4)_3$ denuder/thermal evolution technique were not in agreement with other techniques. Based on HNO_3 and particulate nitrate results reported herein, it appears that negative errors in HNO_3 filter-sampling techniques resulting from nitric acid loss by sorption generally exceed positive errors from ammonium nitrate volatilization at this site.

BNL 42362

RESONANCE RAMAN SPECTROSCOPY OF SUSPENDED AEROSOL PARTICLES

I.N. TANG and K.H. FUNG

American Association for Aerosol Research 1989 Annual Meeting, Reno, NV, October 10-13, 1989.

Recent work has demonstrated that Raman spectroscopy is a very effective technique for chemical characterization of individually levitated aerosol particles. The main advantage of Raman spectroscopy is that it can be applied to a minute sample either in solid or liquid phase. Moreover, Raman spectroscopy can provide simple spectral features for identifying functional groups found in inorganic compounds as well as organic substances. However, the small Raman scattering cross-section is always a great barrier to overcome in chemical analyses. In this work, we take advantage of resonance absorption to enhance the low Raman scattering intensities. The excitation laser beam in the present experiment is modulated by a mechanical chopper, so that the excess heat due to absorption can be dissipated during the laser-off cycles. The sensitivity and spectral resolution are both increased by collecting the Raman scattering signal with a gated photo-diode array detector.

Using this technique, the resonance Raman spectra were measured for particles containing small amounts of chromates and permanganates. About 1-10% mixtures of these color compounds imbedded in nitrate particles were used in the present study. The spectral intensity dependence on the excitation frequency was also studies. Based on the relative Raman cross-sections and mixture composition, apparent enhancement factors in the order of 100-1000 were obtained.

BNL 42744

CLIMATE REGULATION BY MARINE PHYTOPLANKTON? A TEST BY ANTHROPOGENIC SO_2 EMISSIONS

S.E. SCHWARTZ

28th Liege International Astrophysical Colloquium, "Our Changing Atmosphere", Liege, Belgium, June 26-30, 1989.

Because of their high albedo relative to the underlying land or ocean surfaces, clouds exert a major influence on the short-wave (solar) forcing of the earth radiation budget. A possible mechanism for perturbing cloud albedo noted by Twomey (1977) was a change in the number density of cloud droplets, N. An increase in N would increase cloud albedo even if all other cloud properties remained constant. Such a perturbation might result from industrial emissions producing a greater number density of aerosol particles (AP) that serve as cloud condensation nuclei (CCN). The potential sensitivity of global mean albedo and temperature to N prompted a novel suggestion (Charlson et al., 1987) that global climate is regulated by emission of dimethylsulfide (DMS) by marine phytoplankton, which is arguably the principal source of sulfate aerosol in the absence of industrial SO_2 emissions. However these industrial emissions are large compared to DMS emissions, and consequently they may be used to test the Charlson et al. hypothesis. The absence of an observable global or hemispheric climatic influence of industrial SO_2 emissions makes it unlikely that climate is regulated by marine DMS emissions.

BNL 42769

HYDROCARBON PRECOMBUSTING CATALYST SURVEY AND OPTIMIZATION FOR PERFLUOROCARBON TRACER ANALYSIS IN SUBSURFACE TRACER APPLICATIONS

G.I. SENUM, E.A. COTE, T.W. D'OTTAVIO, and R.N. DIETZ

Informal Report, May 1989.

The extension of the perfluorocarbon tracer (PFT) technology, as developed for atmospheric dispersion and transport studies to petroleum reservoir characterization studies, required the development of a more robust catalyst to remove analysis interferents. This was required by the orders of magnitude increase in interferents caused by the adsorption of 5 liter hydrocarbon reservoir gas samples containing PFT onto carbonaceous adsorbent samplers. Two approaches were studies: (1) Replacement of the present internal laboratory PFT analysis system catalyst with a more effective catalyst and, if this was not viable, (2) Development of an external preprocessing catalyst train, to significantly reduce the hydrocarbon levels in the sample, without affecting the perfluorocarbon tracers. The second approach was found viable, consequently, a 9" x 1/8" O.D. column of 10% V_2O_5 on alumina, fed with 5 mL/min of O_2 and 15 mL/min of N_2, was found acceptable with respect to hydrocarbon interferent reduction while not effecting the perfluorocarbon tracers, i.e., this catalyst would significantly combust the 5 liters of hydrocarbon standard (as derived from petroleum reservoir samples) without destroying any PFT down to the 50 femtoliter level.

BNL 42933

PERFLUOROCARBON TRACER TECHNOLOGY: OVERVIEW AND A HYDROLOGICAL APPLICATION

G.I. SENUM and R.N. DIETZ

Annual Meeting of the Association of Ground Water Scientists and Engineers, Houston, TX, October 31-November 1, 1989; Ground Water, submitted (1989).

The perfluorocarbon tracer (PFT) technology has been developed by the Tracer Technology Center (TTC) at Brookhaven National Laboratory, initially for application to atmospheric dispersion and transport studies. More recently this developed technology has been extended to subsurface applications. The PFTs are a family of eight non-toxic, inert, and non-radioactive perfluorinated alkyl substituted cycloalkanes, uniquely detectable at subfemtoliter (10^{-15} ℓ) to femtoliter quantities. The PFTs are analyzed by gas chromatography/electron capture detection with an analysis time of twelve minutes. The TTC has also developed real-time PFT monitors, automated field samplers and laboratory based analysis systems which have analyzed 8,000 to 10,000 field samples per year. Ancillary equipment for the application of PFTs has been fully developed. The PFT technology has been applied to the Deep Probe experiment as tracers of hydrological transport. Four different PFTs were used to tag drilling muds used a differing depths and wells at the PFT solubility level of ~1 ppm. The PFTs were applied as a 1% PFT emulsion in H_2O during the preparation of the drilling muds. Subsequent PFT analysis of various well samples provided quantification of the degree of transport of the PFT tagged drilling muds.

BNL 43091R

MEASUREMENT AND INTERPRETATION OF CONCENTRATIONS OF H_2O_2 AND RELATED SPECIES IN THE UPPER MIDWEST DURING SUMMER

P.H. DAUM, L.I. KLEINMAN, A.J. HILLS, A.L. LAZRUS, A.C.D. LESLIE, K. BUSNESS, and J. BOATMAN

J. Geophys. Res., submitted (1989).

Measurements of H_2O_2 and related species were made by aircraft on 18 flights over 11 days during June 1987, over Ohio. Measurements typically encompassed an altitude range from the surface to 5.5 km msl, and were conducted under a variety of meteorological conditions, but focussed on conditions conducive to the formation of convective storms. Concentrations of H_2O_2 ranged from < 0.2 to 7 ppb and exhibited as much as a factor of 10 variability even on a given day at fixed altitude, as well as between days. Hydrogen peroxide concentration typically was low near the surface, rose to a maximum near the top of the boundary layer, than slowly decreased with altitude. In contrast, SO_2 and NO_y were largely confined to the surface layer. A simple photochemical calculation shows that where NO_x concentrations are low, $[H_2O_2]$ is strongly influenced by the water vapor concentration. The $[H_2O_2]$ tracked changes in dewpoint, and measured and calculated H_2O_2 concentrations were in general agreement. The low $[H_2O_2]$ in the boundary layer is ascribed to consumption of radicals by reactions other than combination reactions, and to loss of H_2O_2 by dry deposition. Comparison of the profile shapes for H_2O_2 and SO_2 suggests that mixing processes will have a large influence on the extent to which these two species will react in convective systems.

BNL 43139R

A CRYOGENIC-FOCUSING OHMICALLY-HEATED ON-COLUMN TRAP FOR CAPILLARY GAS CHROMATOGRAPHY

S.R. SPRINGSTON

J. Chromatogr., submitted (1989).

A new method is presented for thermally desorbing solutes which have been cryogenically trapped on a capillary column. The trap heater is a thin layer of metallic gold applied to columns near their inlet. This layer is ohmically heated to initiate the separation. The temperature within the trap is related to the resistance of the gold layer. The trap is shown to not degrade column performance relative to a split injection. Other advantages are discussed. Examples showing trace analyses of alkanes in air are given.

BNL 43145

PERFLUOROCARBON TRACER TAGGING OF DRILLING MUDS FOR THE ASSESSMENT OF SAMPLE CONTAMINATION

G.I. SENUM and R.N. DIETZ

First International Symposium on Microbiology of the Deep Subsurface, Orlando, FL, January 15-18, 1990.

Perfluorocarbon tracers, PFTs, a multitracer technology of seven chemical tracers were used to tag the drilling muds used in the Fourth Investigators Hole of the Deep Probe experiment. PFTs are fully fluorinated alkyl substituted cycloalkanes, which are inert, non-toxic and chemically non-reactive, detectable in these applications to 1 picoliter/gram of sample by gas chromatographic electron capture detection. PFTs were incorporated into the drilling muds at the 100,000 pl/gm level by addition of a 1% PFT micro-emulsion in H_2O during the periodic preparation of the drilling muds. A total of four different PFTs were used to tag the drilling mud used in the stratigraphic core and sample wells; two PFTs were used in the core well and two further PFTs in the sample well. After sampling, a small aliquot of sample was forwarded to the Tracer Technology Center (TTC) for PFT analysis along with samples of the tagged muds. The samples were centrifuged and headspace sampled for PFT. Results of the PFT analysis were then used to assess the degree of drilling mud contamination of the retrieved samples. The results indicated some contamination of the retrieved samples and some transport of fluids from the core well to the sampling well, which are quantitated by the measured PFT concentrations.

BNL 43146

COMPARISON OF CLOUDWATER AND RAIN COMPOSITION FROM AIRBORNE AND SURFACE MEASUREMENTS: LIMITS OF HOMOGENEITY OF WET DEPOSITION

R.L. TANNER, P.H. DAUM, W.G.N. SLINN, and M.T. DANA

Tellus-B, submitted (1989).

Measurements of cloudwater and rain composition were made during a non-convective rain event in West-Central Ohio. Cloud and rainwater samples were collected aloft from aircraft traversing precipitating clouds, together with event rain samples collected on the surface along the ground track, and analyzed for major ions and for peroxides. Concentrations of H^+, NH_4^+, SO_4^{2-} and NO_3^- were uniform in airborne samples obtained by the same type of collector at constant altitude between Columbus and Dayton, OH. Measured hydrogen peroxide levels were lower in samples collected to the west. Systematic differences were observed between rain samples and mixed cloud-water and rain samples, from which it is deduced that H^+, NH_4^+, SO_4^{2-} and NO_3^- concentrations were higher, but H_2O_2 concentrations were lower in cloud-water than in rain collected within the same precipitating cloud. Surface concentrations of H^+, NH_4^+ and SO_4^{2-} in event samples were not significantly different from those in rain samples collected aloft, but surface nitrate levels were about 15 μM higher. The data suggest that, in this event, the rain chemical composition resulted from droplets falling from "cleaner" regions above 4000 ft through polluted boundary layer clouds to the surface, with noticeable contribution from below-cloud scavenging of nitric acid.

BNL 43165

RAMAN SPECTRAL STUDIES OF SUPERSATURATED BISULFATE SOLUTION DROPLETS

K.H. FUNG and I.N. TANG

Chem. Phys. Lttrs. 163, 560-564 (1989).

Raman spectra of supersaturated solution droplets of ammonium bisulfate, potassium bisulfate and sodium bisulfate were obtained in the region between 800 cm^{-1} and 1300 cm^{-1} with a resolution of 1 cm^{-1}. Under supersaturation condition, these solution droplets show new molecular vibrations that are not found in the spectra of either the bulk crystalline or the solution samples. The results clearly demonstrate the existence of an ion-pair in the supersaturated bisulfate solution, which consists of both the cation and the anion of the dissociated solute as well as the solvent molecules. It also provides new interpretation of the asymmetry commonly found in the 1050 cm^{-1} bisulfate ion vibration band.

BNL 43167

APPLICATION OF MULTITRACER TECHNOLOGY TO PETROLEUM RESERVOIR STUDIES (QUARTERLY REPORT FOR THE PERIOD ENDING JUNE 30, 1989)

G.I. SENUM and R.N. DIETZ

In Enhanced Oil Recovery, U.S. Department of Energy Progress Review, Quarter Ending June 30, 1989, July 1989.

The objectives of this research program are to improve the assessment of the character of petroleum reservoirs using tracer technology for the monitoring and improvement of EOR techniques, specifically, a) To apply the presently available multitracer perfluorocarbon tracer (PFT) technology to the study of petroleum reservoir in characterizing reservoir bulk subsurface flow transport and dispersion, and b) To demonstrate that PFTs with differing physical properties will interact with differing rates of adsorption and dispersion within such reservoirs, from which may be inferred differences in the character and/or extent of petroleum in those reservoirs.

BNL 43171

APPLICATION OF MULTITRACER TECHNOLOGY TO PETROLEUM RESERVOIR STUDIES

G.I. SENUM and R.N. DIETZ

In Enhanced Oil Recovery, U.S. Department of Energy Progress Review, Quarter Ending December 31, 1988, July 1989.

The objectives of this research program are to improve the assessment of the character of petroleum reservoirs using tracer technology for the monitoring and improvement of EOR techniques, specifically, a) To apply the presently available multitracer perfluorocarbon tracer (PFT) technology to the study of petroleum reservoir in characterizing reservoir bulk subsurface flow transport and dispersion, and b) To demonstrate that PFTs with differing physical properties will interact with differing rates of adsorption and dispersion within such reservoirs, from which may be inferred differences in the character and/or extent of petroleum in those reservoirs.

BNL 43172

APPLICATION OF MULTITRACER TECHNOLOGY TO PETROLEUM RESERVOIR STUDIES (QUARTERLY REPORT FOR THE PERIOD ENDING MARCH 31, 1989)

G.I. SENUM and R.N. DIETZ

In Enhanced Oil Recovery, U.S. Department of Energy Progress Review, Quarter Ending March 31, 1989, July 1989.

The objectives of this research program are to improve the assessment of the character of petroleum reservoirs using tracer technology for the monitoring and improvement of EOR techniques, specifically, a) To apply the presently available multitracer perfluorocarbon tracer (PFT) technology to the study of petroleum reservoir in characterizing reservoir bulk subsurface flow transport and dispersion, and b) To demonstrate that PFTs with differing physical properties will interact with differing rates of adsorption and dispersion within such reservoirs, from which may be inferred differences in the character and/or extent of petroleum in those reservoirs.

BNL 43362

OXIDANT LIMITATION TO THE FORMATION OF H_2SO_4 NEAR A SO_2 SOURCE REGION

L.I. KLEINMAN and P.H. DAUM

Atmos. Environ., submitted (1989).

The question of whether the aqueous-phase formation of H_2SO_4 is limited by the availability of oxidant is examined using concurrently measured concentrations of H_2O_2 and SO_2 from the mid-western U.S. in a summer month. Between the surface, and an altitude of 850 mb, $[SO_2] > [H_2O_2]$ on most days. The reverse is true above 850 mb. Oxidant limitations, defined here simply as situations in which $[SO_2] > [H_2O_2]$, thereby depend upon the altitude at which a cloud ingests air. Even allowing for complete mixing between SO_2-rich boundary layer air and H_2O_2-rich free tropospheric air (up to 600 mb), oxidant limited conditions existed on 9 out of 12 experimental days. Measurements were made in an area with high SO_2 emission rates. According to previous SO_2 monitoring data, similar SO_2 concentrations exist over a large area in the eastern U.S.

BNL 43543

THE SNOWFALL CHEMISTRY COLLECTOR INTERCOMPARISON TEST (SCCIT)

D.L. SISTERSON, J.D. SHANNON, P.H. DAUM, P.J. KLOTZ,
D.J. LUECKEN, and D.J. HALL

Water, Air, Soil Pollut., accepted (1989).

The Snowfall Chemistry Collector Intercomparison Test (SCCIT) took place as part of a field experiment of the PRocessing of Emissions by Clouds and Precipitation (PRECP) program during January and February 1986 in western New York. SCCIT compared the chemical composition and equivalent water depth of snow collected with a large, bag-lined can (used by the PRECP community for a concurrent surface snowfall network); the most widely used automatic wet/dry collector; an aerosynamically designed, heated, funnel and bottle system; and a large plastic sheet. The aerodynamically designed system had significantly higher concentrations of analytes than the other systems, particularly H^+ and SO_4^{2-}, apparently because of evaporative losses. Samples from the bag-lined can were more acidic than those from the automatic wet/dry collector. The aerodynamically designed system and the bag-lined can indicated greater snow amounts than the other methods.

BNL 43544

MATHEMATICAL MODELING OF FINE ORGANIC AEROSOL CHARACTERISTICS: THE EFFECT OF DIRECT SOURCE EMISSIONS ON AN URBAN ATMOSPHERE

L.M. HILDEMANN, G.R. CASS, and M.A. MAZUREK

ASCE Conference on Environmental Engineering, Washington, DC, July 9-11, 1990.

Approximately one-third of the fine particulate matter present in the atmospheres of urban areas like Los Angeles consists of organic material, and many organic compounds present in ambient air have been found to be carcinogenic or mutagenic. Little was known at the outset of this research about the contributions of emissions from specific sources to the concentrations of organic aerosol found in the ambient air of urban areas. Using a literature-based estimate of carbonaceous aerosol emissions in the Los Angeles area, the major sources of fine organic aerosol were tentatively identified, and source types were selected for sampling that accounted for close to 80% of the organic aerosol emissions. Dilution sampling techniques were developed and then used to sample sources that included an industrial-scale boiler, a home fireplace, a charbroiler, cigarette smoke, a roofing tar pot, and a fleet of gasoline- and diesel-powered vehicles. Grab sampling techniques were used to characterize tire wear debris, paved road dust, and brake dust.

BNL 43545

DISTINCTIVE FEATURES OF FINE ORGANIC AEROSOLS EMITTED FROM VARIOUS COMBUSTION SOURCES

L.M. HILDEMANN, M.A. MAZUREK, and G.R. CASS

American Association for Aerosol Research (AAAR) Annual Meeting, Reno, NV, October 10-13, 1989.

A portable dilution stack sampling system specifically intended to collect representative organic aerosol samples has been used to collect combustion emissions from a variety of organic aerosol sources, including industrial-scale boilers, a home fireplace, a charbroiler, and gasoline and diesel vehicles. This system simulates the condensation processes occurring when source emissions are cooled and diluted in the atmosphere. In addition to bulk chemical analysis of these source samples, it is possible to investigate the speciation of the organic fraction of the fine aerosol emissions.

BNL 43546

CHEMICAL SPECIATION OF CARBONACEOUS AEROSOLS FROM PRESCRIBED BURNING OF A BOREAL FOREST ECOSYSTEM

M.A. MAZUREK, W.R. COFER III, and J.S. LEVINE

Chapman Conference on Global Biomass Burning: Atmospheric, Climate, and Biospheric Implications, Williamsburg, VA, March 19-23, 1990.

A boreal forest prescribed burn was conducted in northern Ontario, Canada, in August 1989. Nonsize-segregated airborne particles were collected for the identification and mass concentrations of carbonaceous species present in the smoke plumes for smoldering and full-fire conditions using a helicopter sampling platform. Out-of-plume aerosols were collected also during full-fire conditions to compare these carbonaceous ambient mass concentrations to those present in the defined smoke plumes.

BNL 43547

MEASUREMENT AND FLUX OF CARBONACEOUS AEROSOL SPECIES FROM PINE AND OAK WOOD COMBUSTION

M.A. MAZUREK, L.M. HILDEMANN, and G.R. CASS

Chapman Conference on Global Biomass Burning: Atmospheric, Climate, and Biospheric Implications, Williamsburg, VA, March 19-23, 1990.

Methods have been developed for the collection and analysis of wood smoke aerosols to estimate the mass flux and the chemical composition of particulate carbon to the atmosphere. Fine wood smoke particles ($d_p < 2.1$ μm) were sampled from two burn experiments involving separate combustion of pine and oak wood. A specially designed source sampler which simulates the cooling and dilution processes that smoke plume effluents undergo under ambient conditions was used to collect the fine wood smoke aerosols.

BNL 43548

EVALUATION OF HOME WEATHERIZATION, VENTILATION, AND HEATING SYSTEM "IMPROVEMENTS"

R.N. DIETZ and R.W. GOODRICH

Indoor Air '90, The 5th International Conference on Indoor Air Quality and Climate, Toronto, Canada, July 29-August 3, 1990.

Many of the homes on Long Island are from 30 to 40 years old with oil-fired hot-water heating systems. Proper retrofit weatherization of windows, doors, sills, etc. can reduce air infiltration and thus, exfiltration heat losses. Minimal bathroom ventilation can significantly reduce moisture problems while inside dryer venting can reduce exfiltration and recover heat. Heating system updates (retention head burner, proper stack draft control, furnace cleaning) can also reduce air infiltration requirements, improve combustion efficiency, and reduce standby heat losses. The economic consequences of such changes can be substantial with no degradation in indoor air quality while improving occupancy comfort, but may not be significant given current consumer awareness and current levels of technical service.

BNL 43549

SIMULTANEOUS DETERMINATION OF OPTICAL AND THERMODYNAMIC PROPERTIES OF AN EVAPORATING AQUEOUS SOLUTION DROPLET

I.N. TANG and H.R. MUNKELWITZ

3rd International Aerosol Conference, Kyoto, Japan, September 24-27, 1990.

Aerosols are known to play an important role in many atmospheric processes affecting local visibility and regional/global climatic conditions. Thus, it is essential to have extensive data on the optical and thermodynamic properties of ambient aerosols for use in mathematical models being developed to describe the relevant atmospheric processes. Recent advances in the single-particle levitation technique have made it possible to investigate the evaporation of an aqueous solution droplet under controlled humidity conditions. The technique involves the levitation of a charged micron-sized inorganic salt particle in a quadrupole cell, which can be evacuated to $\sim 10^{-7}$ torr and back filled with water vapor to a pre-determined pressure at a fixed temperature. Water evaporation takes place as the cell is evacuated slowly through a precision leak valve. The droplet mass change is measured by the dc voltage that is needed to counterbalance gravity; whereas the droplet size is continuously monitored by the 90°-angle laser light scattering. By fitting the light scattering data with Mie computations using appropriate refractive index and density estimates, it is possible to obtain these optical and thermodynamic properties over a wide concentratin range from high dilution to high supersaturation. Such a wide concentration range can only be achieved with a suspended solution droplet. Results are presented for aqueous sulfate and nitrate solution droplets that are of atmospheric interest.

BNL 43550

ACID DEPOSITION

S.E. SCHWARTZ

Proceedings of the Ninth Seminar on Nuclear War: The New Emergencies, August 19-24, 1989, Erice, Sicily (Italy), A. Zichichi, Ed., in press, 1989.

The acid deposition phenomenon is a well documented example of the influence of industrial activities on atmospheric composition and precipitation composition. This phenomenon consists of emissions of sulfur and nitrogen oxides into the atmosphere, largely from fossil-fueled combustion, followed by transport, chemical transformation, and deposition to the surface. This deposition consists principally of deposition of sulfuric and nitric acids in precipitation (wet deposition) and deposition of gaseous SO_2, NO_2, and HNO_3 in the absence of precipitation (dry deposition). The acid deposition phenomenon is widely held to be responsible for deleterious effects on ecological systems, structural and ornamental materials, and visibility in the atmosphere. Because of the density of emission sources in eastern North America, it is not yet possible to specify precisely the contribution to deposition at particular receptor sites to particular emission sources. Present understanding of atmospheric transport velocities and rates of transformation and deposition processes suggest mean source-receptor distances of 500 to 1500 km. Regional emission densities in the Northeast United States substantially exceed standards that have been suggested to protect sensitive ecosystems. Recognition of the properties of the acid deposition phenomenon is explicitly noted in prospective legislation in the United States.

BNL 43551

LABORATORY STUDIES OF FREE RADICAL REACTIONS IN CLOUDWATER

S.E. SCHWARTZ and J. WEINSTEIN-LLOYD

Symposium on Chemical Kinetics and the Environment, American Chemical Society 199th National Meeting, Boston, MA, April 22-27, 1990.

Reactions in cloudwater can be important pathways for chemical transformation of atmospheric trace gases because of high solubility of reagent gases, rapid aqueous-phase kinetics, and large thermodynamic driving force. A key cloudwater reaction is oxidation of dissolved SO_2 and H_2O_2. It is thus important to understand processes controlling H_2O_2 formation in the atmosphere by gas- and aqueous-phase reactions of HO_2 free radicals. A concern with models of free radical chemistry in cloudwater is that of the applicability of present chemical kinetic schemes to such complex milieus. This concern arises because, at the low free-radical concentrations expected for cloudwater, reactions of radicals with trace ipurities are favored over radical-radical reactions, which dominate at high radical concentrations commonly employed in laboratory investigations. We report initial results of a study in which the rate of change in H_2O_2 concentration is monitored in synthetic and authentic cloudwater in which HO_2 radicals are produced by $^{60}Co\gamma$ radiolysis at rates comparable to those expected upon transfer of HO_2 from interstitial cloud air to cloudwater. These results indicate that micromolar concentrations of Fe(III) decrease H_2O_2 yields and can even lead to H_2O_2 loss rather than formation. Implications on cloud chemistry will be discussed.

BNL 43654

DETECTION OF LEAKS IN A WATER-COOLED GENERATOR STATOR BAR USING PERFLUOROCARBON TRACERS

W.M. LOSS, R.N. DIETZ, and G.I. SENUM

Informal Report, December 1989.

A generator stator bar with a suspected leak was removed from the ConEdison Ravenswood power plant and shipped to an independent laboratory for hydraulic pressure testing. The test failed to demonstrate the location and magnitude of leaks. The stator bar was subsequently investigated at Brookhaven's Tracer Technology Center. Pressurization with 3 ppm PMCP (perfluoromethylcyclopentane) in hydrogen as carrier gas revealed a leak close to the turbine end of the generator. The equivalent water leak rate was calculated to be about 1/2 mL per day at 30 psi water pressure. A series of tests was designed to first verify the existence of potential leaks and then to locate these leaks as accurately as possible. Enclosing the bar in a flexible hose, introducing nitrogen gas into the hose and analyzing the hose exhaust with Brookhaven's Dual Trap Analyzer successfully identified the existence of a laminar flow regime inside the hose prevented the formation of uniform concentration levels and, hence, consistent readings. Successful leak pinpointing was accomplished by wrapping short sections of the bar in plastic bags. This approach with some suggested improvements is also recommended for future experiments with stator bars.

BNL 43731

DESCRIPTION AND DESIGN OF PERFLUOROCARBON TRACER (PFT) ANALYSIS SYSTEM

R.N. DIETZ, D. SPANDAU, T. D'OTTAVIO, R. GOODRICH, and G. SENUM

In Across North America Tracer Experiment (ANATEX), Vol. I: Description, Ground-Level Sampling at Primary Sites, and Meteorology, R. R. Draxler and J. L. Heffter, Eds., pp. 19-36, NOAA Air Resources Laboratory, ERL ARL-167, 1989.

The goal of ANATEX was to provide 3 months of ground and aerial sampling of tracers released routinely for three hours, every 2.5 days, regardless of synoptic weather conditions, but at sampling distances up to 3000 km from the sources. Such a program would have required about 75,000 kg of perfluorocarbon tracers (PFTs) at a cost of over $7,000,000 using the then existing PFTs with background concentrations of about 3 to 4 femtoliters per liter (fL/L is equivalent to parts per 10^{15}). The goal of the tracer technology part of the ANATEX program was to identify at least two new tracer compounds having ambient concentrations an order-of-magnitude lower (less than 0.3 fL/L) in order to reduce tracer cost by about 10-fold. This paper describes the identification and quantification of all PFTs currently measured in the background troposphere, the selection of oc-PDCH (ortho, cis-perfluorodimethylcyclohexane) and PTCH (perfluorotrimethylcyclohexane) with background concentrations of about 0.25 and 0.1 fL/L, respectively, as the primary ANATEX tracers, and the operation of the analytical gas chromatograph system used to determine such low levels in the ambient air.

BNL 43811

A PERFLUOROCARBON TRACER TRANSPORT AND DISPERSION EXPERIMENT IN THE NORTH SEA EKOFISK OIL FIELD

G.I. SENUM, R.N. DIETZ, T.W. D'OTTAVIO,
R.W. GOODRICH, E.A. COTE, and D.J. SPANDAU

Informal Report, December 1989.

A perfluorocarbon tracer (PFT) transport and dispersion experiment has been performed in the Ekofisk section of the North Sea Oil fields. Fifty grams each of three PFTs were injected into a well and 28 surrounding wells were sampled for the presence of PFT. Sampling was accomplished by initially collecting bottles of reservoir hydrocarbon gas and subsequently transferring 5 liter (gas phase) aliquots onto Capillary Adsorbent Tracer (CAT) samplers. The resulting CATS samplers were analyzed for PFT in a specially configured laboratory gas chromatograph with electron capture detection. The limit of detection for PFT as determined by standard addition experiments was circa 1 to 10 femtoliters (10^{-15} L) per liter of sampled reservoir gas.

Sampling was performed up to two years past the injection time; approximately two hundred samples were analyzed. PFT was observed only in four sampling wells at four different times, though the PFT analysis of earlier samples lack sufficient sensitivity to PFT detection due to a hydrocarbon interferent problem which was resolved during this experiment.

The PFT concentrations observed in these four wells appeared to follow an exponential dilution law with a dilution half-life of approximately 70 days in the reservoir.

Recommendations for future experiments of this nature are made based on the problems encountered in this initial study.

BNL 43820

DETERMINATION OF FORMALDEHYDE BY HPLC AS THE DNPH DERIVATIVE FOLLOWING HIGH VOLUME AIR SAMPLING ONTO BISULFITE-COATED CELLULOSE FILTERS

J.B. deANDRADE and R.L. TANNER

Analytical Chemistry, submitted (1989).

A method is described for the determination of formaldehyde using collection as hydroxymethanesulfonate on bisulfite-coated cellulose filters. Following extraction in aqueous acid and removal of unreacted bisulfite, the hydroxymethanesulfonate is decomposed by base and HCHO determined by DNPH-derivatization and HPLC. Since collection efficiency for formaldehyde is high even when sampling ambient air at high-volume flow rates, limits of detection of 0.2 ppbv can be achieved for 30 min sampling times. Interference from acetaldehyde co-collected as 1-hydroxy-ethanesulfonate is <5% using this procedure. The technique shows promise for both short-term airborne sampling, and as a means of collecting mg-sized samples of HCHO on an inorganic matrix for carbon isotopic analysis.

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Biographies of the Scientific and Professional staff members follow.

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Education	Polytechnic Institute of Brooklyn (B.S., Chemistry, 1952); Massachusetts Institute of Technology (Ph.D., Chemistry, 1956); Royal Institute of Technology, Sweden (Visiting Scientist, 1962-63).
Research Interests	Studies of the atmospheric chemistry of sulfur and nitrogen compounds as they relate to the impacts of air pollution; Identification and measurement of the chemical composition of gases and aerosols.
Professional Affiliations	Adjunct Professor, New York University; American Chemical Society and its Environmental Chemistry Division and the New York Section; American Association for the Advancement of Science; NY Academy of Sciences; Air Pollution Control Association; Sigma Xi.
Committees	BNL Scientific Council; Chairman, BNL Lecture Committee; Editorial Advisory Board, Environmental Science and Technology; Program Planning MAP3S; Nuclear Methods Environmental Measurements (ANS); Technical Advisor, Public Service Commission (WI); Chairman, Measurement of Impurities in Liquid Metal Breeder Reactors (ASTM); University of Chicago Review Committee for the Chemical Technology Division (ANL); Chairman, Review Committee Chemical Research and Development Center (U.S. Army); Research Operations Group (PRECP).
Summary of Experience	Design, conduct, and interpret experiments directed at understanding the formation of acid rain; Involved with power plant plume and ambient measurements directed at determining the mechanisms and rate of oxidation of sulfur and nitrogen oxides; Development of analytical techniques for measuring the concentration and composition of atmospheric pollutants; Studies of complex ion equilibria of simple and mixed ligand complexes, hydrolysis reactions, solvent extraction principles, chemistry of actinide and less familiar elements, kinetic mechanisms, electrochemistry, and nuclear reactor fuel processing chemistry.
Selected Publications	Lee, Y.-N., Shen, J., Klotz, P. J., Schwartz, S. E., and Newman, L. Kinetics of the hydrogen peroxide-sulfur(IV) reaction in rainwater collected at a northeastern U.S. site. J. Geophys. Res. 91, 13264-74 (1986).
	Forrest, J. and Newman, L. Determination and speciation of ambient particulate sulfur compounds. In Methods of Air Sampling and Analysis, 3rd Edition, Intersociety Committee, J. P. Lodge, Jr., Editor, pp. 715-30, Lewis Publishers, Inc., Chelsea, MI, 1989.
	Newman, L. Awakening concerns in India with degradation of the environment. Atmos. Environ. 23, 891-7 (1989).

TED W. D'OTTAVIO Staff Engineer

Education	Cornell University (B.S., Chemistry, 1977); University of California at Berkeley (M.S., Chemical Engineering, 1982); State University of New York, Stony Brook (M.S., Electrical Engineering, 1988).
Research Interests	Instrumentation development; Indoor air pollution studies; Aerosol science.
Summary of Experience	Chronological development includes: The measurement of fluorescence deactivation rates; Computer calculations of rotational barriers in strained molecules; Field measurements of gaseous and particulate air pollutants; Development of a real-time monitor for sulfate and sulfuric acid; The measurement and modeling of impaction losses of aerosols passing through packed beds; Development of a semi-real-time instrument for the measurement of perfluorocarbon tracers; Multi-zone model development for indoor air quality studies; Implementation of a computerized data acquisition system to measure perfluorocarbon tracers.
Selected Publications	D'Ottavio, T. W., Senum, G. I., and Dietz, R. N. Error analysis techniques for perfluorocarbon tracer derived multizone ventilation rates. Building and Environ. 23(3), 187-94 (1988).
	D'Ottavio, T. W., Reisman, J. G., and Dietz, R. N. Calculations and experiments concerning bias in the PFT-derived determination of building ventilation. Infiltration and Ventilation Measurement Techniques Workshop, Copenhagen, Denmark, Mar. 1988.
	D'Ottavio, T. W., Goodrich, R. W., Spandau, D. J., and Dietz, R. N. A database of PFT ventilation measurements. BNL 41680, Aug. 1988.

PETER H. DAUM Chemist

Education	Drexel Institute of Technology (B.S., Chemistry, 1965); Princeton University (1965-66); Michigan State University (Ph.D., Chemistry, 1969).
Research Interests	Environmental chemistry; Chemical instrumentation; Electrochemistry.
Professional Affiliations	American Chemical Society.
Summary of Experience	Technician, Methods Development Group; Rohm and Haas Co., Bristol, PA, 1961-65; Professor, Department of Chemistry, Northern Illinois University, Dekalb, IL, 1969-75 (assistant), 1975-80 (associate); Taught and conducted research in the areas of chemical instrumentation and electrochemistry; Visiting Professor, University of North Carolina at Chapel Hill, 1978-79; Conducted research involving the characterization of polymer-modified electrodes; Chemist, Environmental Chemistry Division, 1980-present.
Selected Publications	Daum, P. H. Processes determining cloudwater composition: Inferences from field measurements. In Acid Deposition Processes at High Elevation Sites, M. H. Unsworth and D. Fowler, Editors, pp. 139-53, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1988.
	Daum, P. H. Observations of H_2O_2 and S(IV) in air, cloudwater and precipitation and their implications for the reactive scavenging of SO_2. Atmos. Res., accepted.
	Daum, P. H., Kelly, T. J., Tanner, R. L., Tang, X., Anlauf, K., Bottenheim, J., Brice, K. A., and Wiebe, H. A. Winter measurements of trace gas and aerosol composition at a rural site in southern Ontario. Atmos. Environ. 23, 161-73 (1989).

RUSSELL N. DIETZ Chemical Engineer

Education	Polytechnic Institute of Brooklyn (B.S., Chemical Engineering, cum laude, 1960; Ph.D., Chemical Engineering, 1964); National Science Foundation Fellow, 1960-64.
Research Interests	Correlation of stationary source combustion emissions; Development of ultra-sensitive atmospheric tracer instrumentation; Detection of clandestine explosives; Tracer techniques for natural air infiltration, mechanical ventilation, and indoor air quality studies in homes and buildings; Tracers for subsurface exploration and transport in aquifers and oil and gas reservoir studies; Leak detection for the electric and gas utility industry.
Professional Affiliations	American Chemical Society; Air Pollution Control Association.
Summary of Experience	Early activities included computer correlation of unsaturated hydrocarbon yields from the pyrolysis of light hydrocarbons; the application of gamma irradiation processes for the fixation of nitrogen from air, the synthesis of ozone at cryogenic temperatures, and the dissociation of carbon dioxide; The kinetics of oxides of nitrogen formation in furnaces; Iodine hydrolysis reactions pertaining to nuclear reactor loss-of-coolant accidents; Development of novel permeation devices; Tertiary treatment of waste waters by irradiation and ozonation; Effect of combustion parameters on pollutant emissions of fossil-fueled utility boilers; Most recent activities include: Instrumentation for sub-part-per-quadrillion detection of atmospheric tracers; Detection of clandestine explosives at airport environments; Development of a miniature tracer system for air infiltration measurements in buildings; Applications of tracers in the subsurface environment including enhanced oil recovery in the North Sea, oil leaks from high voltage cables under city streets, and aquifer transport. Currently, head of the Tracer Technology Center at Brookhaven.
Selected Publications	Dietz, R. N. Overview of tracer technology instrumentation for short-term and real-time building ventilation determinations. Air Infiltration and Ventilation Center (AIVC) Workshop on Measurement Techniques, Koge, Denmark, Mar. 1988; In Technical Note AIVC 24, 101-41, June 1988.
	Baron, S. and Dietz, R. N. Transferring 'taxpayer' technology. ASME News 8(2), 8 (1988).
	Dietz, R. N., Spandau, D., D'Ottavio, T., Goodrich, R., and Senum, G. Description and design of perfluorocarbon tracer (PFT) analysis system. In Across North America Tracer Experiment (ANATEX): Description, Ground-Level Sampling at Primary Sites, and Meteorology, R. R. Draxler and J. L. Heffter, Editors, Vol. 1, pp. 19-36, NOAA Air Resources Laboratory, ERL ARL-167, 1989.

RUBY W. FAJER Chemistry Associate II

Education Brandeis University (B.A., Organic Chemistry, 1958; M.A., Organic Chemistry, 1960).

Research Interests Preparation and analysis of nitrooxy organic pollutants.

Summary of Experience Organic syntheses of dyes for color film development at Polaroid Corporation; Preparation of bridged ferrocene compounds including general preparation, I.R. spectroscopy, and gas chromatography; Derivitization of trace nitrate and sulfate anions and polynuclear aromatic hydrocarbons with subsequent analysis by gas chromatography; Preparation of PAN and its analogues; Analysis of PAN and its decomposition products by gas chromatography; Analysis by gas chromatography of perfluorohydrocarbons for tracer technology; Syntheses of nitrooxy alkanes, alcohols, and acetone; Analyses of these compounds by FTIR and UV-VIS spectroscopy; Analyses of PAN and nitrooxy alkanes by capillary gas chromatography.

Selected Publications

Roberts, J. M., Fajer, R. W., and McIntire, D. M. Characterization of a calibration source and gas chromatographic system for the measurement of ambient PAN. Presented at the American Chemical Society 196th National Meeting, Los Angeles, Sept. 1988.

Roberts, J. M. and Fajer R. W. UV absorption cross sections of organic nitrates of potential atmospheric importance and estimation of atmospheric lifetimes. Environ. Sci. Technol. 23, 945-51 (1989).

Roberts, J. M., Fajer, R. W., and Springston, S. R. The capillary gas chromatographic separation of alkyl nitrates and peroxycarboxylic nitric anhydrides. Anal. Chem. 61, 771-2 (1989).

K. HANG FUNG	Associate Chemist
Education	University of Waterloo, Ontario (B.S., Chemistry, 1976); University of Chicago (M.S., Chemistry, 1977; Ph.D., Chemistry, 1980).
Research Interests	Photophysics of aerosols; Light scattering; Electronic and Raman spectroscopy; Kinetics of heat and mass transport; Photothermal spectroscopy; Kinetics of clusters and aerosols formation; Gas phase vibrational circular dichroism spectroscopy; Intramolecular electronic interactions; Doppler-free high resolution spectroscopy; Spectroscopy of free radicals.
Professional Affiliations	American Chemical Society.
Summary of Experience	Developed Raman spectroscopy for chemical analysis on suspended single particles; Determined the thermal accommodation coefficient for helium and mass accommodation coefficient for water by high resolution Mie scattering spectroscopy; Developed Laser Intra-Cavity Photothermal Spectroscopy (LIPS) and applied it to gas chromatography; 1980-82, Research Associate at Technical University of Munich; 1982-84, Research Associate at the National Research Council of Canada; 1985-1987, Assistant Chemist, Environmental Chemistry Division; 1987-present, Associate Chemist.
Selected Publications	Fung, K. H. and Tang, I. N. Composition analysis of suspended aerosol particles by Raman spectroscopy: sulfates and nitrates. J. Colloid Interface Sci. 130, 219-24 (1989).
	Tang, I. N. and Fung K. H. Characterization of inorganic salt particles by Raman spectroscopy. J. Aerosol Sci. 20, 609-17 (1989).
	Fung, K. H. and Tang, I. N. Raman spectral studies of supersaturated bisulfate solution droplets. Chem. Phys. Letters, in press.

ROBERT W. GOODRICH Chemistry Associate I

Education	West Virginia Wesleyan College (B.S., Chemistry, 1952); Oklahoma State University (M.S., Chemistry, 1955; Phys. Chem., 1957-60).
Research Interests	Physical-inorganic chemistry; Instrument development; Data acquisition and computer interfacing.
Summary of Experience	Coordination of analysis, data handling, and computer programs for tracer studies, instrumentation development in atmospheric tracer monitors.
Selected Publications	Dietz, R. N., Goodrich, R. W., D'Ottavio, T. W., Spandau, D. J., and Senum, G. I. Multiple PFT tracer-determined air flow and duct leakage in a forced-air-equipped condominium. Presented at the 9th Annual Conference on Effective Ventilation, Ghent, Belgium, Sept. 1988. Dietz, R. N., Spandau, D. J., Senum, G. I., D'Ottavio, T. W., and Goodrich, R. W. Determination of femtoliter (fL) quantities of perfluorocarbon compounds. Presented at the American Chemical Society 196th National Meeting, Los Angeles, Sept. 1988.

MARY T. KINSLEY Chemistry Associate I

Education	St. John's University (B.S., Chemistry, 1948); University of Kentucky (M.S., Chemistry, 1950).
Research Interests	Analytical chemistry; Environmental studies; Radiochemistry; Waste management.
Professional Affiliations	American Chemical Society.
Summary of Experience	Analyzed many different types of samples using the following chemical and radiochemical methods: Wet chemical, flame and flameless atomic absorption spectrometry, UV and visible spectrophotometry, gel and ion chromatography, automated colorimetry, specific-ion electrodes, counting of alpha, beta, and gamma photons, and X-ray and gamma-ray spectrometry; Developed methods for aerosol and acid rain studies utilizing atomic absorption, radionuclide tracer, and spectrophotometric techniques; Developed methods for the production of isotopes for medical use and for the separation of fission products; This work involved neutron and proton activations, and radiochemical separations; Studied the chemistry of trench waters from commercially-operated radioactive waste disposal sites and the migration of radionuclides and radionuclide complexes along the flow paths of groundwaters at these sites; Analyzed sections of down-core samples from the Bering Sea for organic carbon, nitrogen, and ^{210}Pb; Currently studying ice-phase chemistry of chemical species important to atmospheric chemistry; These studies include the adsorption on ice of hydrogen peroxide, nitrate, and sulfur dioxide and the chemical reactions on ice of hydrogen peroxide or ozone with sulfur dioxide; Also currently studying the kinetics of peroxyacetyl nitrate (PAN) hydrolysis.
Selected Publications	Lee, Y.-N. and Kinsley, M. T. Kinetics of peroxyacetyl nitrate (PAN) hydrolysis and its atmospheric implications (abstract). Presented at the American Chemical Society 196th National Meeting, Los Angeles, Sept. 1988. Lee, Y.-N. and Kinsley, M. T. Oxidation of sulfur dioxide by hydrogen peroxide on ice. Presented at the American Chemical Society 196th National Meeting, Los Angeles, Sept. 1988.

PAUL J. KLOTZ Senior Chemistry Associate

Education St. John's University (B.S., Chemistry, 1958).

Research Interests Analytical chemistry; Chemical analysis of atmospheric samples; Applications of ion chromatography; Kinetics and mechanisms of atmospheric gas-liquid interactions.

Professional Affiliations American Chemical Society.

Summary of Experience Investigated the properties of milk proteins using electrophoresis and ultracentrifugation while employed in the Physical Chemistry Group of the National Dairy Research Corporation. As a member of the Analytical Chemistry Group at Brookhaven has analyzed numerous samples using wet chemical methods, specific ion electrodes, UV, visible and atomic absorption spectrophotometry, radiochemical methods, gas, high performance liquid, and ion chromatography. Due to considerable work with the actinide elements, gained much expertise in glove-box techniques. Operated van instrumented for use in the ground level sampling of atmospheric pollutants during field experiments. Conducted research in the following areas: solvent extraction, chemical equilibria involving mixed metal complexes, production of radionuclides, atmospheric chemistry, chemical mutation of plants, analysis of ocean sediments, and kinetics and mechanisms of atmospheric gas-liquid interactions.

Selected Publications

Lee, Y.-N., Shen, J., Klotz, P. J., Schwartz, S. E., and Newman, L. Kinetics of the hydrogen peroxide-sulfur(IV) reaction in rainwater collected at a northeastern U.S. site. J. Geophys. Res. 91, 13264-74 (1986).

Lee, Y.-N., Shen, J., and Klotz, P. J. Chemical composition of precipitation at Long Island, NY. Water, Air, Soil Pollut. 30, 143-52 (1986).

Sisterson, D. L., Shannon, J. D., Daum, P. H., Klotz, P. J., Luecken, D. J., and Hall, D. J. The snowfall chemistry collector intercomparison test (SCCIT). Water, Air, Soil Pollut., accepted.

DANIEL F. LEAHY Chemistry Associate I

Education	State University of New York at Farmingdale (A.A.S., Chemistry, 1956); Adelphi University (B.S., Chemistry, 1961).
Research Interests	Analytical chemistry; Air pollution and cloud water chemistry studies.
Summary of Experience	Have served as a crewmember for more than 300 flights investigating air pollution and cloud water chemistry. The missions are conducted using specially equipped aircraft and involve the simultaneous operation of a variety of instruments and sample collecting devices. Duties include adaptation, installation, calibration and maintenance of on-board equipment. Major contributor to the development and technique required for preparation of filters used in the filter pack system. Have participated in numerous field studies and have a primary role in the transport and set up of supplies and equipment necessary for extended time periods involving aircraft and mobile ground monitoring operations.
Selected Publications	Schwartz, S. E., Leahy, D. F., and Fink, S. Aircraft release of sulfur hexafluoride as an atmospheric tracer. J. Air Pollut. Contr. Assoc. 35, 555-7 (1985).
	Leahy, D. F. and Spandau, D. J. Mobile laboratory van. BNL 39666, Mar. 1987.
	Schwartz, S. E., Daum, P. H., Kelly, T. J., Leahy, D. F., Lee, Y.-N., and Newman, L. Cloudwater acidity measurements and formation mechanisms: Report of findings. BNL 40459, Nov. 1987.

JAI H. LEE	Chemist
Education	Seoul National University, Korea (B.S., Chemistry, 1966); Catholic University of America (M.S. and Ph.D., Physical Chemistry, 1971 and 1975, respectively).
Research Interests	Chemical kinetics in the gas phase including thermal, photochemical reactions; Atmospheric chemistry including tropospheric and stratospheric chemistry; Combustion chemistry particularly on the pollutant formation and reduction in the combustion processes; Interstellar and planetary chemistry; Atomic and radical reactions with substrates; Gas-particle interaction reactions and heterogeneous chemical kinetics.
Professional Affiliations	American Chemical Society and its Physical Chemistry Division; American Geophysics Union; Guest Scientist at NASA/Goddard Space Flight Center.
Summary of Experience	NAS-NRC Resident Research Associate at NASA/Goddard Space Flight Center, 1975-77; Research Associate (6 mo.) at Catholic University of America; Gas phase chemical kinetic studies of oxygen, hydrogen, deuterium, nitrogen, bromine, chlorine atoms, and OH-radical with simple organic and inorganic molecules which are of interest in the atmospheric, interstellar, and planetary environments using three different detection methods; Electron spin resonance, mass-spectrometer and atomic, OH-radical resonance fluorescence which are coupled with the fast flow discharge systems and the flash photolysis technique; Laser-induced fluorescence detection of NH_2 radical using CW dye laser pumped with argon ion laser in the fast flow discharge system.
Selected Publications	Lee, J. H. and Tang, I. N. Accommodation coefficient of gaseous NO_2 on water surfaces. Atmos. Environ. 22, 1147-51 (1988). Tang, I. N., Munkelwitz, H. R., and Lee, J. H. Vapor-liquid equilibrium measurements for dilute nitric acid solutions. Atmos. Environ. 22, 2579-85 (1988).

YIN-NAN LEE	Chemist
Education	Tunghai University, Taiwan (B.S., Chemistry, 1969); Washington University, St. Louis, MO (M.A., Chemistry, 1972; Ph.D., Physical Organic Chemistry, 1976).
Research Interests	Mechanistic investigation of homogeneous and heterogeneous chemical reactions and catalyses in the field of organic and atmospheric chemistry.
Professional Affiliations	American Chemical Society and its Physical and Environmental Chemistry Divisions; American Geophysical Union.
Summary of Experience	Areas of research experience include: (1) Kinetics and mechanisms of gas-aqueous reactions of nitrogen oxides and oxyacid species; Determination of physical solubilities and chemical reaction kinetics and mechanisms of various atmospheric constituents and pollutants, such as photooxidants; (2) Nucliophilic displacement reactions; Measurement and interpretation of heat capacity of activation; and (3) Acyl transfer reactions; Identification of tetrahedral addition intermediates and characterization of their susceptibility to acid-base catalysis.
Selected Publications	Park, J.-Y. and Lee, Y.-N. Solubility and decomposition kinetics of nitrous acid in aqueous solution. J. Phys. Chem. 92, 6294-302 (1988).
	Lee, Y.-N. and Kinsley, M. T. Kinetics of peroxyacetyl nitrate (PAN) hydrolysis and its atmospheric implications (abstract). Presented at the American Chemical Society 196th National Meeting, Los Angeles, Sept. 1988.
	Lee, Y.-N. Transformation and deposition of atmospheric species--a view from the aqueous side (abstract). Presented at the International Conference on Global and Regional Environmental Atmospheric Chemistry, Beijing, China, May 1989.

WALTER M. LOSS Research Engineer II

Education	University of Vienna, Austria (B.S., Civil Engineering, 1973); Colorado State University (M.S., Environmental Engineering, 1975).
Research Interests	Solar energy and heat transfer; Fluid dynamics.
Summary of Experience	Principal Investigator of "Performance of Materials" program at BNL's Environmental Buildings Division; Technical and Program Coordinator of BNL's "International Housing Village". Performed PFT leak detection in stator bar experiments; Calculated infiltration and air balancing for commercial high-rise buildings. Directly responsible for evaluation of phase change materials in light weight frame buildings; Instrumented and monitored passive solar house; Developed phase change simulation model; Designed solar rockbed and direct contact storage collector, including innovative efficiency improvements; Created computer simulations for collectors and storage devices at Solar Research Institute.
Selected Publications	Loss, W. Cost effective improvements of rockbeds used in solar air heating systems. DOE Report 31-109-38-5692, 1982.
	Dennehy, G., Loss, W., and Jones, R. F. Evaluation of modifications to the Mastin double-envelope house. BNL 51803, Apr. 1984.
	Loss, W., Jones, R. F., Dennehy, G., and Ghaffari, H. T. Case study of the Brookhaven thermal storage house. BNL 51680, Sept. 1984.

MONICA A. MAZUREK Assistant Chemist

Education	Pasadena City College (A.A., Pre-Pharmacy, 1974); University of California, Los Angeles (B.S., Chemistry, 1977); University of California, Los Angeles (Ph.D., Geochemistry, 1985).
Research Interests	Organic aerosol emissions from biomass combustion; Sources and global distributions of carbonaceous aerosols; Trace analysis organic pollutants; Environmental organic geochemistry.
Professional Affiliations	American Chemical Society, Analytical Chemistry and Environmental Divisions; American Geophysical Union, Atmospheric Sciences Division.
Summary of Experience	Current and recent research activities include: Analysis of organic aerosols from authentic source emissions for identification of unique molecular tracers; Measurement and identification of carbonaceous particles from biomass combustion; Investigation of visibility-reducing aerosols in remote airsheds and the relation of measured organic aerosol species to local and long-range emission sources; Development of analytical techniques for identifying and measuring trace organic aerosol compounds.
Selected Publications	Mazurek, M. A., Cass, G. R., and Simoneit, B. R. T. Quantification of the source contributions to organic aerosols in the remote desert atmosphere. Final report to the Electric Power Research Institute, Report No. 1630-11, 1989. Simoneit, B. R. T. and Mazurek, M. A. Organic tracers in ambient aerosols and rain. Aerosol Sci. Technol. 10, 267-91 (1989). Mazurek, M. A., Simoneit, B. R. T., and Cass, G. R. Interpretation of high-resolution gas chromatography and high-resolution gas chromatography/mass spectrometry data acquired from atmospheric organic aerosol samples. Aerosol Sci. Technol. 10, 408-20 (1989).

HARRY R. MUNKELWITZ Chemistry Associate I

Education	C.W. Post College (B.A., Chemistry, 1970).
Research Interests	Particle growth; Gas-to-particle conversion; Chemical kinetics; High temperature chemistry; Nuclear reactor safety.
Professional Affiliations	American Association for the Advancement of Science; American Geophysical Union.
Summary of Experience	Employed initially as a technician on advanced reactor concepts by the Nuclear Engineering Department, was responsible for designing and building many of the remote tools and fixtures used to remove the LMFR experimental loop from the BGR; Subsequently worked as a technical specialist on the fast reactor safety program and was responsible for developing the methods and instrumentation used to make preliminary laboratory measurements of fission product diffusion, migration, and transport in high temperature reactor fuels; Most recently has been concerned with the development and application of remote sensing techniques to the in situ study of aerosol growth and interaction with trace chemicals.
Selected Publications	Fung, K. H., Tang, I. N., and Munkelwitz, H. R. Study of condensational growth of water droplets by Mie resonance spectroscopy. Appl. Opt. 26, 1282-7 (1987). Tang, I. N., Munkelwitz, H. R., and Lee, J. H. Vapor-liquid equilibrium measurements for dilute nitric acid solutions. Atmos. Environ. 22, 2579-85 (1988). Tang, I. N. and Munkelwitz, H. R. Evaporation kinetics of ammonium chloride solution droplets in water vapor. J. Colloid Interface Sci. 128, 289-95 (1989).

JAMES M. ROBERTS Associate Chemist

Education	California Polytechnic State University (B.S., Chemistry and Environmental Engineering, 1978); University of Colorado (Ph.D., Chemistry, 1983).
Research Interests	Study of the distribution, transformation and fates of atmospheric organic compounds; Study of atmospheric organic nitrogen chemistry; Trace analysis of organic compounds in the atmosphere; Regional photochemical oxidant production.
Committees	Expert Analyst, Chemtracts, John Wiley and Sons.
Summary of Experience	Developed and applied gas chromatographic methods for the identification and quantitation of organic compounds in the atmosphere; Studied the chemistry of simple aromatic hydrocarbons and monoterpene hydrocarbon in rural atmospheres; Developed a tungsten oxide diffusion/denuder tube system for the atmospheric measurement of nitric acid and ammonia and made measurements at remote tropospheric sites; Applied the method to the measurement of ammonia in the troposphere. Recent research has involved: The systematic study of important atmospheric secondary organic compounds; The development of capillary and multi-dimensional chromatographic techniques for the measurement of oxygenated organics and organic nitrates in the atmosphere; The laboratory determination of thermal and photolytic decomposition rates of organic nitrates; Studies of the chemical distribution of atmospheric-odd-nitrogen; Field studies of regional photochemical oxidant production.
Selected Publications	Roberts, J. M. and Fajer R. W. UV absorption cross sections of organic nitrates of potential atmospheric importance and estimation of atmospheric lifetimes. Environ. Sci. Technol. 23, 945-51 (1989). Roberts, J. M., Fajer, R. W., and Springston, S. R. The capillary gas chromatographic separation of alkyl nitrates and peroxycarboxylic nitric anhydrides. Anal. Chem. 61, 771-2 (1989). Roberts, J. M. The atmospheric chemistry of organic nitrates. Atmos. Environ., in press.

STEPHEN E. SCHWARTZ Chemist

Education	Harvard College (A.B., Chemistry, 1963); University of California, Berkeley (Ph.D., Chemistry, 1968); University of Cambridge, England (Postdoctoral Fellow, 1968-69).
Research Interests	Atmospheric Chemistry: Transformation of trace atmospheric constituents; Laboratory investigation of model systems; Field measurements and interpretation; Chemical modeling. Physical Chemistry: Reaction kinetics; Chemical thermodynamics; Mass transport; Molecular spectroscopy; Photochemistry.
Professional Affiliations	American Chemical Society and its Physical and Environmental Divisions; American Geophysical Union; American Physical Society; American Meteorological Society; American Association for the Advancement of Science.
Committees	Associate Editor, Atmospheric Environment, 1984-present; Committee on Atmospheric Chemistry, American Meteorological Society, 1985-present; Associate Editor, Journal of Geophysical Research-Atmospheres, 1986-89; Committee on Atmospheric Chemistry, National Academy of Sciences, 1988-present; BNL Council, 1987-present.
Summary of Experience	Current and recent research activities include: Design, conduct, and interpretation of measurements of acids, acid precursors, and other relevant species in and about liquid water clouds; Laboratory studies of gas- and aqueous-phase kinetics; Modeling gas-phase and heterogeneous atmospheric kinetics; Interpretation of atmospheric residence times and scales of transport; Examination of cloud-climate interactions. Principal investigator, "Cloudwater Acidity Measurements and Formation Mechanisms" (Electric Power Research Institute, 1981-1990); Principal investigator, "Investigation of Tropospheric Rainout Process" (Federal Aviation Agency, 1978-1982). Brookhaven National Laboratory: Associate Chemist, 1975-1977; Chemist, 1977-present. State University of New York at Stony Brook: Assistant Professor of Chemistry, 1969-1975.
Selected Publications	Schwartz, S. E. Are global cloud albedo and climate controlled by marine phytoplankton? Nature 336, 441-5 (1988).
	Schwartz, S. E. Acid deposition: Unraveling a regional phenomenon. Science 243, 753-63 (1989); Letters 244, 127-8 (1989).
	Kelly, T. J., Schwartz, S. E. and Daum, P. H. Detectability of acid producing reactions in natural clouds. Atmos. Environ. 23, 569-83 (1989).

GUNNAR I. SENUM Chemist

Education	Brooklyn College of the City University of New York (B.S., Chemistry, 1970); State University of New York at Stony Brook (Ph.D., Chemistry, 1975).
Research Interests	Application and modeling of chromatographic systems for the development of techniques for the detection and quantification of trace components with the consequent application to geophysical trace gases, indoor pollution and various industrial applications.
Professional Affiliations	American Chemical Society; American Physical Society; American Association for the Advancement of Science.
Summary of Experience	Presently responsible for the development and new applications of perfluorocarbon tracers in the Tracer Technology Center, including atmospheric hydrological and geophysical applications. Was responsible for the experimental program, Evaluation of Vapor Taggants and Substrates for the Tagging of Blasting Caps, which developed a technique for the predetonation detection of explosives by trace detection of a specific vapor taggant emitted by explosives.
Selected Publications	D'Ottavio, T. W., Senum, G. I., and Dietz, R. N. Error analysis techniques for perfluorocarbon tracer derived multizone ventilation rates. Building and Environ. 23(3), 187-94 (1988).
	Dietz, R. N., Goodrich, R. W., D'Ottavio, T. W., Spandau, D. J., and Senum, G. I. Multiple PFT tracer-determined air flow and duct leakage in a forced-air-equipped condominium. Presented at the 9th Annual Conference on Effective Ventilation, Ghent, Belgium, Sept. 1988.
	Senum, G. I. and Dietz, R. N. Perfluorocarbon tracer technology: Review and hydrological application. Presented at the Annual Meeting of the Association of Ground Water Scientists and Engineers, Houston, Oct. 1989.

STEPHEN R. SPRINGSTON Associate Chemist

Education	Virginia Polytechnic Institute and State University (B.S., Chemistry, 1978); Indiana University (Ph.D., Chemistry, 1984); University of Utah (Postdoctoral Fellow, 1984-1986).
Research Interests	Development of analytical instrumentation for high-efficiency separations and the measurement of atmospheric constituents; Column technology for liquid, supercritical fluid, and gas chromatography.
Professional Affiliations	American Chemical Society and its Analytical Chemistry Division.
Summary of Experience	Developed and constructed a capillary supercritical fluid chromatograph for analytical separations and the precise measurement of physicochemical properties of solutes in supercritical fluids; Novel approaches were investigated for synthesizing and coating chromatographic stationary phases which could withstand elevated temperatures and condensed mobile phases; Designed and constructed instrumentation for single and series split-flow thin (SPLITT) cells; High-resolution separations of 1- to 10-μm model systems based on sedimentation rates were performed; Developed techniques for generating low-temperature plasmas inside capillary gas-chromatography columns; Applicability of these techniques for several column fabrication steps, including cleaning, deactivation, cross-linking, and polarity modification was explored; Made basic improvements on existing commercial instruments to extend the limits of quantitation for SO_x and NO_x.
Selected Publications	Springston, S. R., Myers, M. N., and Giddings, J. C. Continuous particle fractionation based on gravitational sedimentation in split-flow thin cells. Anal. Chem. 59, 344-50 (1987).
	Roberts, J. M., Fajer, R. W., and Springston, S. R. The capillary gas chromatographic separation of alkyl nitrates and peroxycarboxylic nitric anhydrides. Anal. Chem. 61, 771-2 (1989).
	Springston, S. R. and Dezaro, D. A. Nonextractable stationary phases for gas chromatography cross-linked by exposure to low-temperature plasmas. J. Chromatog. 473, 79-92 (1989).

IGNATIUS N. TANG Chemical Engineer

Education	National Taiwan University (B.S., Chemical Engineering, 1955); University of North Dakota (M.S., Chemical Engineering, 1960); New York University (Graduate Studies, Chemical Engineering, 1961-64); State University of New York at Stony Brook (M.S., Applied Mathematics, 1975; Ph.D., Applied Mathematics, 1982).
Research Interests	Aerosol chemistry; Laser light scattering; Solution thermodynamics; Gas-phase reaction kinetics; High-temperature chemistry; Applied inverse problems.
Professional Affiliations	American Chemical Society; American Association for Aerosol Research; The New York Academy of Sciences; Listed in American Men and Women in Science, and Who's Who in Frontier of Science and Technology.
Summary of Experience	Current research activities include deliquescence properties of hygroscopic aerosols, thermodynamics of concentrated electrolyte solutions, chemical and phase equilibria for atmospheric trace gases, elastic and inelastic light scattering from suspended aerosol particles; Performed research in areas including theoretical and experimental studies of molecular clustering about atmospheric ions, gas-phase kinetics, nucleation phenomenon, radiation chemistry, nuclear reactor safety studies, and hazardous chemical spills in water and on land.
Selected Publications	Tang, I. N., Munkelwitz, H. R., and Lee, J. H. Vapor-liquid equilibrium measurements for dilute nitric acid solutions. Atmos. Environ. 22, 2579-85 (1988). Tang, I. N. and Munkelwitz, H. R. Evaporation kinetics of ammonium chloride solution droplets in water vapor. J. Colloid Interface Sci. 128, 289-95 (1989). Tang, I. N. and Fung K. H. Characterization of inorganic salt particles by Raman spectroscopy. J. Aerosol Sci. 20, 609-17 (1989).

ROGER L. TANNER Chemist

Education	Pennsylvania State University (B.S., Chemistry, 1964); University of Illinois (Ph.D., Analytical Chemistry, 1969; Postdoctoral Fellow, 1972-73).
Research Interests	Analytical chemistry of trace substances in the environment; Chemical and physical transformations of atmospheric aerosols and their gaseous precursors; Chemical instrumentation for *in situ* measurements and air pollutant source allocation.
Professional Affiliations	American Chemical Society and its Environmental Chemistry Division and New York Section; American Association for the Advancement of Science.
Committees	EPA Science Review Panel for Air Chemistry and Physics; EPRI Health Effects Research Advisory Committee.
Summary of Experience	Analytical chemistry of trace organic and inorganic species in the atmospheric environment especially aerosol carbon, sulfur and nitrogen compounds; studies of the processes leading temporal and spatial variability of these species in the ambient atmosphere; participation in several major field studies relating to atmospheric sulfur, nitrogen, and carbon compounds including MAP3S and MAP3S/RAINE programs (1976-1982), the New York Aerosol Study (1976-1979), the Southern California Air Quality Study (1987) and the DOE PRECP program (1984-1989) and (Field Manager, PRECP I Field Study, April 1985); participation in development of instrumentation for airborne studies in clear air and clouds.
Selected Publications	Tanner, R. L. and Miguel, A. H. Carbonaceous aerosol sources in Rio de Janeiro. Aerosol Sci. Technol. 10, 213-23 (1989).
	Daum, P. H., Kelly, T. J., Tanner, R. L., Tang, X., Anlauf, K., Bottenheim, J., Brice, K. A., and Wiebe, H. A. Winter measurements of trace gas and aerosol composition at a rural site in southern Ontario. Atmos. Environ. 23, 161-73 (1989).
	Tanner, R. L., Kelly, T. J., Dezaro, D. A., and Forrest, J. A comparison of filter denuder and real-time chemiluminescence techniques for nitric acid determination in ambient air. Atmos. Environ. 23, in press.

ROBERT G. WILSON Chemistry Associate I

Education	Long Island University (B.S., Chemistry, 1951).
Research Interests	Analytical chemistry; Inorganic and gas analysis.
Professional Affiliations	American Association for the Advancement of Science
Summary of Experience	Analyzed a variety of samples by atomic absorption spectrophotometry and emission spectroscopy; Pure gases and gas mixtures were analyzed for contaminants or composition by mass spectrometry; Occasionally required to perform volumetric or gravimetric analyses; Have had some experience in neutron activation and gamma pulse height analysis; Recently calibrated instruments used for real-time measurements of oxides of sulfur and nitrogen in field studies; Have participated in collecting, preparation and analysis of samples in the atmospheric diagnostic programs; Involved with the Tracer Technology Center in the preparation and analysis by gas chromatography of perfluorocarbon tracers used in subsurface tagging; Recently built and operated a vacuum system for the Radionuclide and Radiopharmaceutical Research Division to cryogenically purify ^{127}Xe produced in the Medical research reactor.

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