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THE IMPACT OF ATMOSPHERIC OXIDANT ON THE POTATO CROP OF NEW JERSEY, AN HISTORICAL PERSPECTIVE.

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Early in the 1960's a dark stipple was observed on the upper surface of potato foliage in fields in central New Jersey. Because ozone phytotoxicity was a relatively new phenomenon, it had to be established that ozone was in fact the cause of the problem by conducting ozone fumigations with greenhouse-grown potato plants. With those tests it became obvious that potato cultivars showed differential foliar sensitivity to the air pollutant in the following order: Chippewa, Cobbler, Plymouth and Pungo > Katahdin > Green Mountain and Kennebec > Avon. Between 1973 and 1975 tests were conducted in filtered and non-filtered open-top chambers to evaluate the effect of oxidant pollution on biomass or tuber production of various cultivars. In a test comparing Kennebec and Penn 1174 in a non-filtered chamber, Penn 1174 exhibited more foliar symptoms than Kennebec, and biomass was significantly reduced in both cultivars. In a second test, the Superior cultivar also showed a reduction both in total biomass and in tuber production in the non-filtered chamber, whereas Pongo showed no difference.

In 1977 potato tests were taken to the field, Norchip cultivar was grown according to standard commercial practices and every three weeks a soil application of benomyl, EDU (an antioxidant), or an equivalent amount of water was applied. EDU significantly reduced ozone foliar injury, but benomyl did not. Tuber yield, size, and specific gravity were similar in all treatments, however; despite the presence of leaf injury (15%) in the untreated plots. In 1978 and 1980 similar field tests were conducted with Norland, Norchip and Green Mountain cultivars. The order of foliar sensitivity to oxidant was Norland > Norchip > Green Mountain. Oxidant doses of 65 ppm· hr and 110 ppm· hr significantly reduced tuber yield in Norland and Norchip potato respectively. Green Mountain yield was not altered even at the highest oxidant dose.

New Jersey Agricultural Experiment Station No. K-1150-1-82.

THE EFFECT OF A MULTIYEAR POWER PLANT SO_2 EMISSION SIMULATION ON CONCORD GRAPES, P.R. Edmonds, J.A. Maser and C.L. Norton, Energy & Environmental Management, Inc., P. O. Box 71, Murrysville, Pennsylvania 15668.

The response of Concord grape vines (*Vitis labrusca* L.) to sulfur dioxide (SO_2) fumigations which simulated emissions from a proposed 1700 MW Niagara Mohawk Power Corporation coal-burning power plant, located on the eastern shores of Lake Erie was studied. Grape vines, in cylindrical open-top field chambers, were exposed for three consecutive growing seasons to SO_2 concentrations which simulated the ground-level seasonal average dosages, as well as peak hourly dosages, of the proposed power plant. These chronic SO_2 fumigations were applied in addition to ambient ozone and SO_2.

Experimental vines were selected from a 5 acre plot based on location, observed vigor and similar vine size. The selected vines received one of four treatments: chambered ambient air, chambered filtered air, chambered incremental SO_2 and nonchambered ambient air. The incremental SO_2 fumigations were administered as a "step-function" for 2 to 8 hours, with each step lasting one hour. SO_2 concentrations ranged from 0.02 to 0.16 ppm and resulted in a season-long average increment of 0.0012 ppm above ambient. Fumigations were applied typically during mid-day on an average of 4 days per month from May (bud break) to October (post-harvest).

Key biological and meteorological variables were measured to ascertain possible effects on vegetative growth and yield resulting from these incremental changes in air quality. Inferential statistical analyses, both parametric and nonparametric, were conducted to evaluate the differences between treatments. Data were analyzed for single year, as well as cumulative effects at the end of three years of treatment. The vine response variables which were determined included: vine growth and development measured as periderm development, pruning weight, number of clusters, clusters per shoot and number of seeds per berry; leaf injury measured as a visual estimation of the percent chlorotic or necrotic leaf area and the causal agent; vine yield measured as berry count, berry retention, berry weight and sugar content of berries. Vine growth, injury and yield variables showed significant differences between the chambered vines and the nonchambered vines, but no significant response could be attributed to the different SO_2 concentrations. Statistical evaluations strongly support the conclusion that long-term, low level (chronic) doses of SO_2 from the proposed power plant do not result in measureable injury or damage to Concord grapes.

CADMIUM AVAILABILITY IN TERRESTRIAL MICROENVIRONMENTS: RECONCILING AIR POLLUTION STRATEGY AND RCRA WITH RESPECT TO CONTROL AND DISPOSAL OF TOXIC METALS, J. Mika and W.A. Feder, University of Massachusetts Suburban Experiment Station, 240 Beaver Street, Waltham, MA 02254.

Air pollution controls, designed to prevent the dispersion of toxic contaminants into the atmosphere, are merely devices that collect and concentrate the contaminants in the form of fly ash. Incinerator residues, particularly fly ash, contain high concentrations of lead and cadmium. The use of incinerator residues as a resource for construction and/or land reclamation is sharply curtailed by the standards and testing procedures set forth in the Resource Conservation and Recovery Act (RCRA). In order that a potentially valuable resource not be lost to unwarranted regulation, the research described herein, was conducted as part of a continuing program to assess the availability of ash leachate metals in the terrestrial environment. Cadmium availability was monitored by standard chemical analyses of soils and leachate media; cadmium bio-availability was monitored by examining the growth and community stability of the soil algal cultures.

Hutner's medium (diluted 1:4 with deionized H_2O) was contaminated with varying additions of $CdCl_2$, resulting in 8 Cd solutions ranging in Cd concentration from 0 to 850 ppm. Each Cd solution was "leached" (i.e. vacuum filtered) through soil at 25% and 50% soil/liquid ratios. The leachates and Cd solutions thus resulted in 24 treatments, varying in Cd concentration as a function of the Cd retention capacity of the soil. Two g of dried, mixed soil were added to all treatments (3 replicates) to serve as the algal inoculant. Cultures were grown in continuous light at 21°C for 2 weeks. Growth and diversity of the algal communities were determined by observing random fields under the microscope. The results of both chemical and biological analyses indicate that:

1) Soil has a tremendous capacity for removing Cd from waste streams. Cd levels were reduced by nearly 90% (850 ppm to 60 ppm) in the highest treatment.

2) Terrestrial microflora are susceptible to high Cd concentrations. As Cd concentration increased, both abundance and diversity decreased; correlations were -0.527 and -0.798 respectively. Growth was observed in all treatments, though it decreased considerably at higher Cd concentrations (i.e. above 50 ppm).

The results indicate that soils play a significant part in removing cadmium from aquatic and biological cycling and that this factor is severely underestimated in the current RCRA testing procedure (EP Toxicity).

EFFECTS OF LONG TERM SO_2 EMISSIONS ON SOIL ACIDITY IN SOUTH-EASTERN ARIZONA, E. F. Haase, Phelps Dodge Corporation, Drawer 1238, Douglas Arizona 85607.

The pH of surface (0-0.5cm) and subsurface (0.5-15cm) soil samples was determined in early 1979 from 110 sites located near a major copper smelter in southeastern Arizona. The investigation was conducted to evaluate a possible relationship between soil acidification and smelter SO_2 emissions that had been discharged into this semiarid region for 77 years. A random numbers table was used to select the land sections that were sampled from a baseline drawn lengthwise from the smelter north-northwest through the center of the Sulphur Spring Valley outward to 140 km. More soil sampling sites were located closer to the smelter and sampling only included areas with native desert grassland vegetation that had never been known to be cultivated, although in 9% of the sites there was some evidence that large shrubs had been removed sometime in the past to improve forage for cattle grazing.

Results indicate that SO_2 emissions have had no measurable effect on pH of surface soils with a calcium carbonate content of 0.5% or greater. The data also indicate that the pH of less calcareous surface soils within about 10 km of the smelter has at least temporarily been reduced about 0.5 pH units on average. Somewhat greater pH reductions may occur at the air/soil interface during brief periods when SO_2 deposition is actually taking place. The surface soil pH within 10 km of the smelter averaged about 6.7 but was only 6.2 in an area 40 to 80 km up the valley where many soils are derived from acidic igneous parent materials. Surface soils 10 to 40 km and 80 to 140 km from the smelter had an average pH of about 7.1. Subsurface soil pH averaged 7.2 within 10 km of the smelter and was about 7.4 elsewhere, except in the area of acidic parent materials 40 to 80 km up the valley where it was about 6.4. This last area also includes some of the better cropland in the valley. There was no evidence that total plant cover of native shrubs and grasses has been reduced over the years because of smelter emissions, although differential reactions to excess SO_2 and other stresses close to the smelter provide some species with competitive advantages that may result in reduced plant species diversity. It is clear that the composition of soil parent material is more important than 77 years of smelter SO_2 emissions in determining soil pH in this semiarid region, and that extensive field sampling is necessary to properly interpret possible long term effects of emissions on soil acidity. The soils are generally very resistant to permanent changes in pH from smelter emissions, particularly those in which both the surface and subsurface are calcareous.

Various forms of sulfur have been used extensively for their acidifying potential as agricultural soil amendments in the western United States and, under proper management, have been shown to be beneficial since water infiltration, soil tilth, and availability of plant nutrients such as phosphorus and iron may be improved. However, significant long term soil pH reductions resulting from smelter emissions were not found in this investigation. This is true whether the sulfur reaches the soil as dry deposition, as most of it does in the Southwest, or in precipitation, which is a relatively minor component of total atmospheric deposition in this semiarid region.

AIRBORN SALT DRIFT AROUND A SINGLE SOURCE: MEASURING THE RATE OF DEPOSITION AND THE VEGETATION EFFECTS, W.A. Feder, J.S. Mika, and J. Scott-Craig, University of Massachusetts, Suburban Experiment Station, 240 Beaver Street, Waltham, MA 02254.

Windborn saline drift generated by a closed cycle, spray cooling canal using water with salinity values ranging from 7,000-39,000 was measured by impingement on nylon rope collectors, and the values obtained were correlated with wind direction and speed and with vegetation injury. Preliminary laboratory study confirmed the accuracy and reliability of nylon rope pieces as impingement salt collectors. Collection and study sites were selected both up and downwind from the source and measurements were made weekly for 3 years. Vegetation injury observations were taken at monthly intervals during 3 growing seasons. 45.7 cm long pieces of 0.6 cm diameter nylon clothes line rope were hung from trees in a cross configuration from 10 collection sites. Exposed ropes were removed at weekly intervals, and replaced with fresh rope pieces. Exposed ropes were taken to the laboratory, oven dried at 35C for 24 h, soaked in glass distilled water for 24 h, and the Cl^- content of the water was measured with an Orion Specific Ion chloride electrode. Cl^- in moles was converted to grams of NaCl and the salt content impinged on the rope piece was converted to g/m^2 salt deposition/site/week. Salt deposition downwind of the source was found to drop off rapidly as distance from the source increased. Plant injury to trees and shrubs also decreased in severity as distance from the site increased. Vegetation injury ranged from light marginal leaf burn to total defoliation at some sites. Norway maple was found to be an excellent bioindicator for salt drift injury. Reduced plant growth was associated with long term, chronic exposure to low levels of cummulative salt deposition. There was good correlation between the amount of salt collected by the rope impingement collectors and degree of plant injury observed at the various sites. The impingement collector proved to be a reliable, inexpensive tool for making rapid, reproducible field measurements of salt drift from major sources such as spray cooling canals, and natural bodies of salt water.

EFFECT OF WINTER DE-ICING ON ROADSIDE VEGETATION IN NEW JERSEY.

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Salt applied to roads during the winter is detrimental to vegetation growing along roadsides. Sodium chloride and calcium chloride are applied in crystallized form to snow covered streets. Soil sodium and chloride levels are significantly higher in salt run-off areas than in non-run-off areas and are higher during the winter months when the salt is applied. Accumulation in the root zone of adjacent vegetation may result in the absorption of toxic sodium and chloride ions into the roots or a change in the osmotic potential of the soil solution resulting in reduced water and nutrient uptake. Salt is sprayed onto adjacent vegetation by high speed traffic and absorbed by leaves, stems and buds. Decline symptoms include tip and marginal chlorosis and necrosis of broadleaves and tip chlorosis and necrosis of needle-like leaves; branch dieback and deformity of aerial parts; root death; general decline and death of susceptible trees. Tree decline is common along heavily salted roads in New Jersey and other states in the snow belt. Salt sensitivity depends on species, distance from the road, wind direction, amount of salt deposited, speed of traffic, exposure of roots to salt run-off, and soil structure and texture. Red oak, Norway maple and Japanese black pine are relatively tolerant to salt injury, whereas Sugar maple, beech and white pine are relatively sensitive. Vegetation injury is greatest close to the road and decreases as distance from the road increases. Injury is more severe on the downwind side of the highway than on the leeward side. High speed traffic produces more salt spray and consequently more injury to vegetation at greater distances from the road than low speed traffic. Plants growing in heavy, poorly drained soils are much more susceptible to salt injury than plants growing in light, well drained soil.

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OZONE UPTAKE BY CORN: EXPERIMENTAL EVIDENCE OF STOMATAL CONTROL AND A MODEL OF CANOPY FLUXES, CONCENTRATIONS AND CHEMICAL PROTECTANT EFFICIENCY

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Experiments were conducted which show that the uptake of ozone is controlled by the stomatal diffusion resistance. These experiments were part of a larger study (Walker, 1980) of the relationship between ozone uptake and subsequent injury to corn leaves in both greenhouse and field conditions.

A leaf exposure chamber was designed and constructed to enable simultaneous measurements of transpiration, net photosynthesis and ozone uptake. Some degree of stomatal closure was observed during ozone exposure even when there was apparently complete recovery afterwards. Uptakes greater than 15 mg/m^2 caused persisting depression in both transpiration and net photosynthesis.

It was found that the flux of ozone could be calculated from the ozone concentration external to the leaf and the stomatal conductance to water vapour. The conductance to ozone is related to the conductance to water vapour by the ratio of the molecular diffusivities of the gases. Evidence is presented which demonstrates that the concentration of ozone within the substomatal cavity is effectively zero and, conversely, the internal resistance to ozone (analogous to the mesophyll resistance for carbon dioxide) is effectively zero. With clean leaves the cuticular uptake of ozone is negligible. It was observed that contaminants on the leaf surfaces act as resistances in parallel to the stomatal resistance. Their net effect is to decrease the stomatal flux and thereby offer some protection to the leaf.

To examine the degree of protection which might reasonably be expected by the application of reducing materials to the leaf surface, a simple canopy model was developed. A mature corn canopy is assumed to be divided into ten layers of equal height. The layers are linked by an aerodynamic resistance. Within each layer, the resistance to ozone uptake per unit leaf area is the parallel sum of the stomatal resistance and protectant resistance in series with the leaf boundary layer resistance.

J. Wilson (personal communication, 1979) kindly provided leaf area distribution and in-canopy turbulence statistics including momentum fluxes. This permitted the calculation of the aerodynamic and leaf boundary layer resistances using algorithms adapted from Thom (1975) and Leuning et al (1979) respectively. Analysis of the momentum flux data enabled the use of the transfer coefficients of Schuepp (1977) to calculate the diffusion resistance to the soil surface. The remaining required inputs to the model are windspeed at the top of the canopy, the protectant resistance, and the stomatal resistance. The stomatal resistance was assumed to increase exponentially from a maximum at the top of the canopy to a value 10 times greater at the bottom (since typical light intensities at the bottom are 10 percent of the value at the top).

To examine the range of protectant resistances, several readily available materials were applied to glass plates and placed in the leaf exposure chamber. The resistances calculated were: for carbon (paper) 13 s/m; 3-in-1 oil 145 s/m; mineral oil 660 s/m; herbicide oils 200-300 s/m, Benomyl (fungicide) 620 s/m; EDU (Du Pont) 940 s/m (the ideal protectant resistance would be zero).

Assuming that a reasonably efficient protectant might have a resistance of 100 s/m and that the windspeed and stomatal resistance at the top of the canopy are 1.5 m/s and 160 s/m (representative of episode conditions), the model predicts that the protectant would result in a concentration reduction of about 5 percent at the level of maximum productivity and a reduction in leaf uptake of 23 percent.

Graphical solutions for concentrations and fluxes for a complete range of protectant values, stomatal resistances and windspeeds are presented. The results with no protectants agree well with the measured values of Leuning et al (1979).

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OZONE INDUCED FREE RADICALS IN A MODEL PLANT SYSTEM. H. D. Grimes, K. K. Perkins, and W. F . Boss. Dept. of Botany, N. C. State Univ. , Raleigh, N. C. 27650.

To study the interaction of ozone with the plasma membrane in vivo it is imperative to first understand the nature of ozone in solution. Ozone reportedly decomposes into H_2O_2, HO^-, and HO· radicals in solution. We have studied the nature of ozone induced free radicals in solution by forming a stable radical adduct with the spin trap 5,5-dimethyl-pyrolline-N-oxide (DMPO) and measuring the electron spin resonance (esr) signal.

No radicals were detected after blowing ozone (8 ppm) , for up to 3 min, over a simple aqueous solution consisting of only chelexed (Chelex-100) 10mM phosphate buffer at pH 7.2. A small amount of HO· signal was obtained if the ozone was bubbled into this solution for 90 seconds. However, if the phosphate buffer was mixed 1:1 with a 10^{-4}M caffeic acid (or other phenols), HO· radicals were easily detected after blowing ozone (8 ppm) over the solution for only 15 seconds. Extremely strong signals were obtained after 60 sec of blowing over, indicating that phenols enhance ozone-induced HO· radicals. The fact that the observed 1:2:2:1 signal was due to HO·and not a separate chemical reaction was substantiated by forming secondary radicals. When the HO·radical is formed in solution it will react with other compounds such as MeOH, EtOH, and azide to initiate free radicals. These free radicals can also be trapped by DMPO. When either EtOH, MeOH, or azide were added to phosphate/caffeic acid solutions as described, we observed typical carbon-centered or nitrogen-centered DMPO adducts. Superoxide dismutase and catalase had no effect on the HO· signal, indicating that superoxide and H_2O_2 were not intermediates in HO· production.

The acidity of the aqueous environment affected production of HO· radicals. Relative mean peak heights of 14, 90, and 124 units were obtained at pH 4.5, 7.2, and 7.8, respectfully. This decreased signal height at low pH is not due to reduced reactivity of DMPO. Experiments performed with DMPO trapping of HO· from H_2O_2 (3%) and UV light at pH 4.5 showed a strong HO· signal, thus indicating the full reactivity of DMPO. Hence, acidic conditions reduced the number of HO· radicals induced by ozone. This is consistent with water purification data which indicates that ozone is more stable in solution at low pH. These data should be considered when studying the interactions of acid rain and ozone on crop productivity.

The presence of sorbitol or sucrose in the phosphate/caffeic acid solution has been shown to quench the HO· signal. As can be seen from the data below, 0.6 M sorbitol resulted in approximately a 45% reduction in relative HO· peak height.

FIGURE: A) typical HO· signal from O_3 and phosphate/caffeic acid, B) same as A but with 0.6 M sorbitol, note side bands.

Furthermore, as the concentration of sorbitol is increased, a 6-line spectra appears and becomes more prominent at higher sorbitol concentrations. This spectra showed hyperfine splitting of A_N=15.9 gauss and A_H=22.5 gauss. When diethylenetriamine pentoacetic acid (DETAPAC) was added to the phosphate/caffeic acid/sorbitol solution no reduction of the 6-line spectra was noted, suggesting that it was not due to the DMPO-X (Findelstein, et. al., Arch. Biochem. Biophys. 200: 1, 1980). With HCl (pH4.5)/H_2O_2/ sorbitol/DMPO and UV light, the 6-line spectra became more pronounced, further suggesting that it arises from secondary radicals produced by the reaction of HO· with sorbitol. Although the signal is relatively weak the splittings most closely correlate with that of DMPO-EtOH adduct, again suggesting that we are trapping small amounts of C-centered sorbitol radical. The low amounts of this radical trapped can be explained by the large size of the sorbitol molecule which may decrease interaction with the DMPO trap. Attempts to trap this radical with 2-methyl-2-nitrosopropane (MNP) have proven unsuccessful, probably due to the fact that MNP trapping must be done under low pH conditions (4-5) and these pH values suppress HO· production.

Although ozone is toxic to whole plants, snap bean mesophyll protoplasts and carrot suspension culture cells and protoplasts were resistant. Neither protoplasts nor cells showed decreased respiration or viability (fluorescein diacetate) due to ozone (1 ppm) after a 15 min exposure. Further experiments were performed on intact protoplasts in sorbitol where swelling was monitered. Even after extremely harsh conditions (40 ppm O_3-60 min), no change in swelling of the protoplasts was observed, indicating that the plasma membrane is intact. The nature of this O_3 resistance is an extremely interesting phenomenon. Now that we understand ozone degradation in solution, and can manipulate HO· levels, we are studying the interaction of ozone and the plasma membrane. Specifically, the surface glycoproteins and their possible role as free radical scavengers is under investigation.

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Proceedings
75th APCA Annual Meeting
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Table of Contents — Volume 4

82-56.4 **"A Procedure for Determining the Validity of Data Produced by Automatic Continuous Area Monitors"**
H. D. Toy, L. N. Cash

82-56.5 **"Missouri's State Implementation Plan for Lead: The Road to Partial Approval"**
B. W. Reynolds

82-56.6 **"Predicting and Controlling Downwind Concentrations of PCB from Surface Impoundments"**
A. J. Angiola, J. M. Soden

82-56.7 **"Measuring Rates of Volatile Emissions from Non-Point Source Hazardous Waste Facilities"**
S. T. Hwang

82-57.1 **"Application of Chemical Foam Dust Suppressants to Material Processing Operations"**
A. G. Larson, R. M. Burch, K. G. Ori

82-57.3 **"Evaluation of Emissions and Dust Deposition from Coal and Coke Handling at a West Coast Bulk Marine Terminal"**
R. J. Bryan, B. M. Buck

82-57.4 **"A Precipitation/Dust Receptor Model"**
R. G. Steen, J. G. Moldovan

82-58.1 **"Operational Experiences of an Automated Opacity Monitor and Data Reporting System"**
K. E. Dowell, R. W. Devlin, K. MacFarlane

82-58.4 **"An Analysis of the Equal Area Sampling Methodology"**
P. D. Baumann, J. W. Crowder, E. J. Fenyves

82-58.5 **"A General Approach for the Development of an Information Management System for Emissions Sampling"**
L. Titley

82-58.6 **"Validation of EPA Reference Method 25 — Determination of Total Gaseous Nonmethane Organic Emissions as Carbon"**
G. B. Howe, S. K. Gangwal, R. K. M. Jayanty, J. E. Knoll, M. R. Midgett

82-58.7 **"Optical Microscopy as an Enforcement Tool in Air Pollution Complaint Investigations"**
V. L. Fair, C. A. McCauley

82-58.8 **"Simultaneous Fly Ash and Sulfur Dioxide Collection in a Hydro Sonic Systems Scrubber"**
Y. Choung, J. W. Crowder, B. L. Proctor, D. A. Mitchell

82-58.9 **"Measurements of Primary Sulfates with an Acid Condensation System"**
J. L. Cheney, J. T. Chehaske

82-59.2 **"Results of a Baghouse Operation and Maintenance Survey on Industry and Utility Coal-Fired Boilers"**
J. Reynolds, S. Kreidenweis, L. Theodore

82-59.3 **"Alternatives for Energy Conservation in a Baghouse"**
B. J. Bakken, F. A. Horney

82-59.6 **"Performance of a 10MW Fabric Filter Pilot Plant and Comparison to Full-Scale Units"**
W. B. Smith, K. M. Cushing, R. C. Carr

82-59.7 **"A Model for Fabric Filter Cleaning: Single Element and Multiple Compartment Effects"**
P. Farber, L. Theodore, J. Reynolds

82-60.1 **"The Development of a Low NO_x Distributed Mixing Burner for Pulverized Coal-Fired Boilers"**
A. R. Abele, J. L. Reese, B. A. Folsom, J. Vatsky

82-60.2 **"A Low NO_x Burner for Gas-Fired Firetube Boilers"**
J. P. Kesselring, E. B. Merrick, W. V. Krill

82-60.3 **"Formation and Control of NO_x Emissions in Coal-Fired Spreader Stoker Systems"**
J. M. Munro, D. W. Pershing, G. Blair Martin, D. C. Drehmel

82-60.4 **"An Assessment of Environmental Issues Associated with Gasification of Woody Biomass"**
B. Miller, M. W. Glass

82-60.7 **"The Development of Design Criteria for Low NO_x Oil Burners Suitable for Application to TEOR Steamers"**
G. C. England, M. P. Heap, R. Payne, D. W. Pershing, W. S. Lanier

82-61M.1 **"Inhalable Particulate Testing at Cement and Lime Plants"**
F. J. Bergman, H. K. Wilcox

82-61M.2 **"Dilution Sampling for Chemical Receptor Source Fingerprinting"**
J. E. Houck, J. A. Cooper, E. R. Larsen

82-61M.3 **"IP Sampling for Condensible Emissions"**
A. D. Williamson, J. D. McCain, S. C. Parsons

82-62M.1 **"Spatial and Temporal Variation of Hydrocarbon Species Emissions in Houston, Texas"**
A. C. Montz, M. A. Capalongan

82-62M.2 **"Development of an Organic Vapor Emission Inventory for Polyester Resin/Fiberglass Fabrication Processes in California"**

M. B. Rogozen

82-62M.3 **"The Texas Air Control Board's Point Source Emission Inventory Data Collection and Management for 1980"**

C. Snow, J. Panketh

82-62.1 **"The Study of Mesoscale Air Pollution Transport by Routine Applications of Remote Sensors"**

N. D. van Egmond

82-63.2 **"Present and Future Uses of Sodars in Air Quality Studies by Industry and Government"**

J. E. Gaynor

82-63.3 **"Air Quality Applications of Meteorological Satellite Data"**

W. A. Lyons, R. H. Calby

82-63.5 **"Application of Surface-Based and Airborne Lidar Systems for Environmental Monitoring"**

E. E. Uthe

82-64.6 **"Air Pollution Standards, Monitoring, Concentrations and Control in the Republic of China (Taiwan)"**

J. C. Chow, J. G. Watson, C. Y. Chaung

82-65.1 **"Distribution of Selected Gaseous Organic Mutagens and Suspect Carcinogens in Ambient Air"**

H. B. Singh, L. J. Salas, R. E. Stiles

82-65.2 **"Collection and Analysis of Selected Volatile Organic Compounds in Ambient Air"**

B. B. Kebbekus, J. W. Bozzelli

82-65.4 **"Environmental Concentration of Lead in the Area of Secondary Lead Smelters and a Battery Manufacturing Plant in Dallas, Texas"**

E. C. Crosby, V. K. Argento

82-65.5 **"Carbonaceous Aerosol at Urban and Rural Sites in the United States"**

J. J. Shah, R. L. Johnson,
E. K. Heyerdahl, J. J. Huntzicker

82-65.6 **"Ambient Concentrations of Benzene in Harris County, Texas"**

L. R. Roberts

82-65.7 **"Chamber Studies of Formaldehyde Emissions from Wood Products, Urea-Formaldehyde Foam and Carpeting. Effect of Source Combinations"**

T. Godish, B. Kanyer