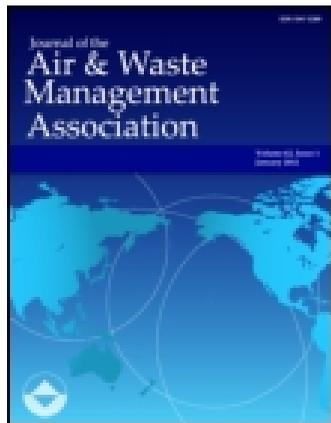


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### Workshop on the Intercomparison of Methodologies for Soil NO<sub>x</sub> Emissions: Summary of Discussion and Research Recommendations

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# Workshop on the Intercomparison of Methodologies for Soil NO<sub>x</sub> Emissions: Summary of Discussion and Research Recommendations

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A workshop on the intercomparison of methodologies for soil NO<sub>x</sub> emissions was held on March 14-15, 1994 at North Carolina State University (NCSU) in Raleigh, North Carolina, in preparation for a field experiment tentatively scheduled for May-June, 1995 involving measurement of rural site NO<sub>x</sub> emissions. The workshop was sponsored jointly by the U.S. Environmental Protection Agency (EPA) and NCSU. Representatives from several agencies will participate in the experiment, including the EPA, NASA, NOAA, DOE, NCAR, Atmospheric Science from the University of Maryland, and Atmospheric Sciences and Soil Sciences from NCSU. Approximately 50 workshop attendees, which included national experts on all aspects of flux measurement technologies, met for a day and a half to discuss techniques for measuring soil NO<sub>x</sub> (= NO + NO<sub>2</sub>) emissions and to suggest how to best incorporate these techniques into a field experiment to compare NO<sub>x</sub> measuring methodologies. The need for more knowledge in the area of soil NO<sub>x</sub> emissions is related to the uncertainty of the relationship between rural NO<sub>x</sub> emissions and the production of tropospheric ozone. In particular, the role of nitrogen-based fertilizers spread over rural agricultural areas in the production or emission of NO<sub>x</sub> is not well documented. To determine the best way to document and model these relationships, a full experimental comparison of NO<sub>x</sub> emission measurement techniques over a rural agricultural area is needed. Thus, it was recommended that a study of the intercomparison of methodologies for soil NO<sub>x</sub> emissions (both intensive field experiments and analysis) should be undertaken. The primary goal of this study will be to relate chamber techniques to micrometeorological flux estimates of NO<sub>x</sub>. The study should include (i) an intensive four-to-six-week experiment for the intercomparison of methodologies for soil NO<sub>x</sub> emissions, (ii) and soil and air quality characterization of the experimental site.

## Introduction and Overview

Introductory and welcoming statements were made by Dr. J. Whitten, dean of the NCSU College of Physical and Mathematical Sciences, and Dr. J. Wynne, dean of the NCSU College of Agriculture And Life Sciences. Dr. Bruce Gay, deputy division director of the EPA, provided the background for the workshop with a discussion that included a brief history of NO<sub>x</sub> emissions and their relation to such pollution problems as photochemical smog and tropospheric ozone. Moving to the present, Dr. Gay discussed the recent National Academy of Sciences report, "Re-thinking the Ozone Problem" (1991), and its finding that efforts to attain the National Ambient Air Quality Standard (NAAQS) for ozone (O<sub>3</sub>) have failed. He then charged the group to develop the best possible plan for the intercomparison of current methodologies for measuring NO<sub>x</sub> emissions, and pointed out that recent changes in EPA funding procedures will mean that a well-thought-out plan will be required to satisfy EPA needs. Dr. Viney P. Aneja, chairman of the workshop, and Dr. Vinod K. Saxena then concluded the introduction with an overview of the project and the flux methodologies, respectively.

Dr. Aneja began by providing a quick review of the nitrogen oxides-ozone cycle in the troposphere. Normally, ultraviolet sunlight energy breaks down nitrogen dioxide (NO<sub>2</sub>) into nitric oxide (NO) and oxygen (O). The single O atom then bonds with O<sub>2</sub> to form O<sub>3</sub>, but the O<sub>3</sub> then combines quickly with the NO to form O<sub>2</sub> and NO<sub>2</sub> again. Thus, O<sub>3</sub> does not accumulate due to the circular photostationary state. It has been noted that the introduction of VOCs (volatile hydrocarbons) disrupts this cycle by reacting with the available NO to produce more NO<sub>2</sub>, leaving the O<sub>3</sub> to accumulate in the atmosphere. Therefore, it is important to determine the sources (both natural and anthropogenic) and the concentrations of NO in the lower atmosphere.

Based on the implications of this interrupted cycle, Dr. Aneja proposed three questions or hypotheses for the workshop attendees to consider:

- 1) Is O<sub>3</sub> production over the rural southeastern United States limited by NO<sub>x</sub>? Is there a need for control of NO<sub>x</sub> emissions from rural sources?

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- 2) Is  $O_3$  a regional phenomenon rather than a local phenomenon (i.e., does transport dominate over emission)? This relates to the following questions, i.e.
- 3) Are natural  $NO_x$  emissions greater than anthropogenic emissions in rural areas?

Dr. Aneja pointed out that past reports attribute only 11 percent of all  $NO_x$  emissions to natural sources. However, his more recent field measurements of  $NO_x$  flux from fertilized agricultural row crops ( $\sim 25 \text{ ng N m}^{-2} \text{ s}^{-1}$ ) and pastures ( $1.8 \text{ ng N m}^{-2} \text{ s}^{-1}$ ) suggest that  $NO_x$  from rural sources may account for more than 20 percent of all known  $NO_x$  emissions. Finally, Dr. Aneja reiterated the primary objective of the workshop: to relate  $NO_x$  flux methodologies - specifically, the gas chamber measurement technique - to micrometeorological measurement techniques. Dr. Aneja then charged the group with determining, before the end of the workshop, the time, place, and complete logistical and operational considerations of the experiment.

## Summaries of Invited Speakers

### Monday Morning Session (March 14, 1994)

The first session was chaired by Dr. Aneja of NCSU

*Presentation 1: Site Selection and Characterization (Dr. Wayne P. Robarge, Soil Sciences, NCSU, Raleigh, North Carolina).* Dr. Robarge provided the group with an overview of agricultural activities in southeastern states such as North Carolina, delineating the top ten counties in North Carolina in farm cash receipts and thus focusing attention on areas that would have heavy fertilizer usage and be worthy of study for  $NO_x$  emissions. These counties are generally along or just east of the fall line in central and eastern North Carolina, and lie in the Coastal Plain physiographic region of the state. For this reason, Dr. Robarge recommended a site located in the Coastal Plain. Focusing on a list of 15 NCSU-North Carolina Department of Agriculture Research Stations that are operated by the North Carolina Agricultural Research Service and therefore would be available for the experiment, Dr. Robarge singled out two sites - one near Kingston, North Carolina and one near Plymouth, North Carolina - as both having adequate facilities, space, and support. He also informed the group that public/state land is not the only choice. If necessary, there are "environmentally aware" private farmers who would be willing to allow the use of their land for the study; however, such facilities and support would be more limited.

During the discussion following Dr. Robarge's presentation, the point was raised that if the soil was thought to produce more  $NO_x$  emissions due to heavy fertilizer usage, then it could possibly be classified as an anthropogenic source. Dr. Aneja stated that for the purposes of this experiment and for EPA modeling, the release of  $NO_x$  from soils is a microbial/nitrification effect and therefore is considered natural. Additional potential sources of  $NO_x$  that were brought to the attention of the group included fertilization of golf courses and home usage of fertilizers.

*Presentation 2: Reactive Nitrogen Measurement Techniques at Low Mixing Ratios (Dr. Russ Dickerson and Dr. Bruce Doddridge, Air Chemistry and Meteorology Group, Department of Meteorology, University of Maryland, College Park, Maryland).* In his portion of the workshop, Dr. Doddridge categorized the experimental requirements of the proposed research and described the  $NO_x$  analytical equipment that he and Dr. Dickerson have available at the University of Maryland to support these requirements.

Dr. Doddridge emphasized that paramount to understanding perturbations in the  $NO_x$ - $O_3$  photostationary state, measurements

of at least one of the constituents must be done on a very short ( $\sim 10 \text{ Hz}$ ) time scale. Dr. Doddridge listed the first requirement in any flux experiment as a fast-response NO detector, which would be used for real-time NO flux measurements across a concentration range typically observed in United States East Coast rural areas (few pptv to 10 ppbv, daytime). He outlined recent improvements in this area, focusing on developments within his research group, and in particular on work done by a graduate student, Kevin Civerolo. Mr. Civerolo produced a custom-built instrument with a detection limit of approximately 2 pptv NO (calculated from a 60-minute averaging of 10-second data) and an "e-folding" response time of about 0.1 to 0.2 seconds. Currently, the instrument acquires data at 5 Hz; however, planned improvements will enable the instrument to sample at 10 Hz, which is a requirement for the proposed experiment.

Moving to the second experimental requirement on his list, that of medium time response  $NO_x$  detectors, Dr. Doddridge discussed a photolytic converter instrument that his group used in boundary layer experiments at various research sites. This instrument's performance characteristics included a  $NO_x$  detection limit of 6 pptv (60-minute averaging of 10-second data) and a  $NO_2$  (to NO) conversion efficiency that ranges from 50 to 65 percent.

Dr. Doddridge then quickly covered calibration procedures used for the above equipment. In particular, a dynamic dilution with zero grade air of a standard NO calibration gas (NIST-traceable) was used to calibrate the fast-response NO detector, while for calibrated measurements of  $NO_x$  and total reactive nitrogen ( $NO_y = NO + NO_2 + NO_3 + HNO_3 + HNO_2 + PAN + \dots$ ), a more complicated gas phase titration technique (to establish conversion efficiencies) was used, in addition to dynamic dilution.

Dr. Doddridge concluded his discussion with a look at some suggested additional trace gas measurements, which might prove most useful in realizing measurement program objectives, and their detectors. In particular, he suggested an investigation of ambient air parcel source contribution and photochemical history from trace gas data, developing a correlation matrix to determine common sources and sinks. Noting that important relationships between  $NO_x$  and  $NO_y$ , and between  $NO_y$  and CO, for example, have been used previously as indicators of photochemical processing, Dr. Doddridge proposed measurement of  $NO_y$  using a three-inlet molybdenum (Mo) converter box in conjunction with a dedicated modified TECo 14B NO analyzer, and measurement of CO with a modified commercial NDIR/GFC TECo 48. The modified 14B setup can provide  $NO_y$  detection to approximately 20 pptv (60-minute averaging of 10-second data) and  $HNO_3$  detection of approximately 50 pptv, with a  $NO_y$  (as determined for  $NO_2$ ) conversion efficiency of 95 to 100 percent under field conditions. The TECo 48 can provide CO detection to approximately 24 ppbv at a 60-second response time; this can be reduced to a 10-second response time.

*Presentation 3: Overview of Nitrogen Oxide Emissions (Dr. Joel S. Levine, Atmospheric Science Division, NASA Langley Research Center, Hampton, Virginia).* Dr. Levine provided a review of current literature containing data on estimated global budgets of  $NO_x$  emissions from various sources. As expected, all published reports agreed on anthropogenic sources as the major contributor, with estimated values averaging approximately 21 Tg (N)  $yr^{-1}$ . Moreover, analysis of various nitrogen budgets begins to show some uncertainty in the natural component of the budget. For example, Dr. Levine noted that some studies indicate that soil emissions of N are comparable with those produced by lightning hypothesized to be about 8 Tg (N)  $yr^{-1}$ , while other sources increase soil emissions to nearly 20 Tg (N)  $yr^{-1}$ , emphasizing that soil emissions are still poorly understood and hence more research is needed.

To provide a better understanding of the role of soil emissions in the total nitrogen and NO budgets, Dr. Levine outlined two major microbial processes: nitrification and denitrification. Nitrification is the process by which microbes in the soil oxidize the ammonium ion ( $\text{NH}_4^+$ ) to produce nitrites and nitrates. During the intermediate stages of this process, NO is formed and subsequently diffuses through the soil into the atmosphere. By contrast, denitrification is an anaerobic process where nitrate ( $\text{NO}_3^-$ ) is converted to  $\text{N}_2$  and  $\text{N}_2\text{O}$ ; but once again, NO is formed in an intermediate stage and diffuses to the atmosphere. Dr. Levine then related research that his group conducted in Africa, which seemed to confirm the importance of the nitrification process in generating NO. In this research, which included measurements of burned fields and vegetation, soil NO emission increased by a factor of 10 to 100 on burned versus nonburned areas. This increase in NO emission most likely was due to an increase in soil  $\text{NH}_4^+$  from the ashes of burned vegetation.

Finally, Dr. Levine summarized comparisons of NO emissions from a variety of land areas, such as grassland, forest, bare soil, and agriculture, and highlighted the large variability and inherent uncertainty of data, even from the same site. However, the figures showed that over various types of vegetation (including the absence of vegetation), recently fertilized soils have a mean flux ( $\text{ng N m}^{-2} \text{s}^{-1}$ ) 10 to 100 times larger than unfertilized soils, again validating the need for more research in this area.

#### Monday Afternoon Session (March 14, 1994)

Mr. Thomas Pierce of EPA chaired the afternoon session, which dealt with specific methodologies for flux measurement and, in particular, techniques that will be available for use in the proposed intercomparison study.

*Presentation 4: NOAA Measurements for  $\text{NO}_x$  Fluxes by Eddy Correlation (Dr. Bruce Hicks, Dr. Winston Luke, and Dr. Tilden Meyers, NOAA, Silver Springs, Maryland, and Oak Ridge, Tennessee).* Dr. Luke began the afternoon flux methodology comparison discussion with a review of the eddy correlation technique. He started with the simplified concept of flux measurement, which states

$$\text{Mean Flux of Species C} = \overline{F_c} = \overline{w'c'}$$

where  $w$  = vertical wind velocity,  $c$  = scalar value of species C, prime denotes fluctuation of  $w$  and  $c$  from their means, and overbar denotes an average value. Dr. Luke then noted that a variety of fluxes can be determined. For example, if  $C$  denotes a chemical concentration, then the above equation derives the flux of this chemical; in contrast, if  $C$  = ambient temperature, then the equation derives the sensible heat flux. Such a simple approximation brings with it some restrictions and requirements as noted by Dr. Luke, most notably the need for aerodynamically clean sensors/platforms (to avoid flow distortion) and fast-response instrumentation (faster than 0.1 second or 10 Hz) to resolve turbulent transfer. Such rapid response times are difficult to achieve with many chemical sensors. Other possible considerations of which Dr. Luke spoke included lag time due to air being ducted through inlets; overall instrument response time; physical separation of the  $w$  and  $c$  probes; chemical corrections that must be applied for reactive trace gases (such as NO and  $\text{NO}_2$ ) during the averaging period for flux determination (typically 30 minutes); and the fact that complex terrain introduces biases and possible flux divergence, so that the technique is best suited for flat, uniform terrain with short vegetation and long fetch.

At this point, Dr. Luke introduced the concept of the Modified Bowen Ratio Technique (MBRT) as a way of measuring chemical

fluxes with slow-response instrumentation to corroborate other measurements in the absence of fast-response instrumentation. In the MBRT, the flux,  $F_c$ , is given by

$$F_c = ([\Delta c] * H) / (\rho * C_p * \Delta T),$$

where

- $[\Delta c]$  = concentration difference of  $c$  between two levels
- $\Delta T$  = temperature difference
- $H$  = sensible heat flux (E/C system)
- $\rho$  = air density
- $C_p$  = heat capacity of air.

This technique measures species of interest (e.g., NO) and a reference quantity (e.g., temperature) at two heights and assumes that the transport of NO mass through the atmosphere is analogous to the transport of the reference quantity (heat). Dr. Luke noted that extreme precision is required to accurately resolve concentration differences, and that the best available approach is to use one chemical sensor that periodically interrogates concentrations at the two levels of interest on a short time scale (less than a few minutes), assuming that mean concentrations do not change significantly over the measurement cycle.

Dr. Meyers followed this discussion on MBRT with some experimental data measuring methane flux from a landfill. In particular, a time series plot of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{CH}_4$  concentrations and the vertical velocity ( $w$ ) show strong similarity in turbulent structure. Dr. Meyers provided an example of a further breakdown of the MBRT for determining fluxes, using the flux of mercury vapor as an example:

$$F_c = -K \left( \frac{\Delta c}{\Delta z} \right) = \chi_c \Delta c$$

1. Measure  $F_{\text{CO}_2}$  and  $(\Delta \text{CO}_2 / \Delta z)$  to get  $K$  for  $\text{CO}_2$ .
2. Measure  $F_{\text{H}_2\text{O}}$  and  $(\Delta \text{H}_2\text{O} / \Delta z)$  to get  $K$  for  $\text{H}_2\text{O}$ .
3. Assume similarity of transfer processes for  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and Hg, and apply to Hg gradients to solve for flux.

Using this technique, Dr. Meyers presented experimental data that closely correlated the  $K$  value for  $\text{CO}_2$  to the  $K$  value for  $\text{H}_2\text{O}$ . In summary, Dr. Meyers warned against trying to measure fluxes with only one instrument, such as measuring for a half hour at one level, then moving the instrument to another level and measuring there, and then trying to calculate fluxes from the data. Such an approach tends to be influenced by transients and misses major shifts in the data. Finally, Dr. Meyers reiterated that 30-minute averaging is "optimum," due to the fact that shorter averaging times lead to more run-to-run variability. Dr. Meyers also reminded the group that longer periods contain inherent problems due to larger-scale transient meteorological phenomena, such as cloud passage.

*Presentation 5: Eddy Correlation Measurements of  $\text{NO}_x$  Flux (Dr. Marvin Wesely, DOE/Argonne National Laboratory, Chicago, Illinois).* Dr. Wesely provided an outline of the eddy correlation technique, including suggested instrumentation and location/height restrictions. In particular, he suggested that the following equipment could be used in eddy correlation measurements at two heights to infer the surface exchange rate of NO:

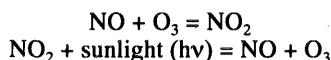
- Two modern 3-D sonic anemometer/thermometers
- Two krypton hygrometers
- One 486 computer data acquisition and analysis system
- Two gas-phase chemiluminescent NO sensors
- Two luminol-chemiluminescent  $\text{NO}_2$  sensors
- Two gas-phase chemiluminescent  $\text{O}_3$  sensors.

Noting that the flux measurements are extremely sensitive to local sources of nitrogen oxides, Dr. Wesely recommended a flat area of uniform surface conditions over distances of 0.5 to 1.0 km, with no vehicular traffic within 1 km upwind of the site. Such a location would be ideal for relating landscape-scale observations made with the eddy correlation to measurements taken with enclosures over relatively small areas. For observation heights, Dr. Wesely stated a minimum height possible for the chemical sensors of 4 to 5 meters. (Using a standard upwind fetch distance/height ratio of 100 to 1 would require a 500-meter fetch for a sensor at a height of 5 meters.) Further, he observed that measuring at a height where fast chemical reactions have a noticeable effect on NO<sub>2</sub> and O<sub>3</sub> fluxes, such as 10 meters, will allow analysis of results with a numerical model to extrapolate NO and NO<sub>2</sub> fluxes to the surface.

Dr. Wesely concluded with a discussion of the hypothesis that NO emitted from the soil is rapidly converted to NO<sub>2</sub> near the surface, and that the NO<sub>2</sub> deposition rates increase correspondingly. He concluded by stating that the task at hand is to apply numerical atmospheric models that describe both rapid in-air chemical reactions and turbulent diffusion to developing parameterizations for NO<sub>2</sub> deposition rates when local emissions rates of NO are substantial.

*Presentation 6: Micrometeorological Measurement Technology (Dr. Anthony Delany, Surface and Sounding Systems Facility, National Center for Atmospheric Research (NCAR), Boulder, Colorado).* Dr. Delany began with a review of the stated function of the proposed program from the viewpoint of "calibrating" the enclosure method of NO<sub>x</sub> flux measurement against micrometeorological methods. He cautioned against expecting a simple "calibration factor" to arise out of the research. Instead, he felt it more likely that agreement would be observed only some of the time, and that many different factors would play a part in the amount of agreement (such as vegetation canopy deposition, temperature, soil moisture, and atmospheric stability). Dr. Delany then reviewed the NO cycle between the soil and the atmosphere, keying in on the difference between the fast photochemical equilibrium control found above a few meters in height and the surface flux, where the biosphere controls the NO cycle.

Evidence is that, in usual circumstances, the soil microbial activity produces NO rather than a mixture of NO and NO<sub>2</sub>. It is this species that moves to the surface and enters the atmosphere. Once in the atmosphere, it immediately begins to participate in atmospheric chemical reactions. The reaction kinetics ensure that within a time of tens to hundreds of seconds, a substantial portion of NO has reacted with atmospheric O<sub>3</sub> to produce NO<sub>2</sub>. The reversible reaction proceeds,



and an equilibrium, dependent upon temperature and sunshine intensity, is attained. (This photostationary state is modified by other reactions, but they occur under considerably longer time scales). Both NO<sub>2</sub> and O<sub>3</sub>, and to a lesser degree NO, undergo interaction with the vegetative surfaces as atmospheric motion carries them through the plant canopy. Turbulent deposition results in the continual modification of the photochemical equilibrium, and photostationarity is not approached until well above the plant canopy. As a consequence of this interaction of emission, deposition, and fast photochemistry, the flux of neither NO nor NO<sub>2</sub> is conserved within the surface layer. However, once above the plant canopy, the flux of the sum of NO and NO<sub>2</sub> (= NO<sub>x</sub>) is conserved.

Showing figures from previous NCAR research, Dr. Delany noted average NO emission fluxes ranging from -6 ng N m<sup>-2</sup> s<sup>-1</sup> to

25 ng N m<sup>-2</sup> s<sup>-1</sup>. In comparison to these values from micrometeorological measurement techniques, Dr. Delany expressed the opinion that enclosure techniques, such as those proposed for this research, have a positive flux bias (allowing for little or no deposition) due to the fact that the very nature of the enclosure modifies the boundary layer turbulence. This may prevent some eddies from transporting reactive oxidants down to the soil where they can react with nitrogen oxides in the soil. Again, Dr. Delany emphasized the need for determining the total environment, i.e., examining as many variables as possible, such as soil temperature and moisture.

To understand the factors controlling the net surface flux of NO and NO<sub>2</sub> (= NO<sub>x</sub>), the suite of measurements recommended by Dr. Wesely should be performed. However, a somewhat less complete suite of flux measurements would suffice if the profile of the means of NO and NO<sub>2</sub> is also determined. Thus, the following are recommended:

- flux measurements of heat, momentum, and moisture at 10 m and at 3 m,
- flux measurements of NO, NO<sub>2</sub>, and O<sub>3</sub> at 10 m,
- flux measurements of NO at 3 m,
- profiles of mean values of NO and NO<sub>2</sub> up to 10 m,
- profiles of mean values of wind speed and direction up to 10 m,
- profiles of mean values of temperature and humidity up to 10 m,
- together with radiation and soil heat flux measurements to enable an energy balance to be determined.

This configuration of sensors can most readily be deployed with the Atmospheric/Surface Turbulent Exchange Research (ASTER) facility. The facility can provide the necessary micrometeorological sensors and infrastructural support. Only the chemical sensors must be provided by other investigators, and ASTER is specifically designed to host other investigators' instruments.

*Presentation 7: Dynamic Chamber Technique for Measurement of NO<sub>x</sub> Flux (Dr. Aneja, NCSU, Raleigh, North Carolina).* In this portion of the workshop, Dr. Aneja covered the concepts and theory behind the dynamic chamber measurement technique, as well as provided preliminary research data from recent experiments by the Air Quality Group at NCSU. Dr. Aneja described the components of the chamber, which included a pump, a flow controller, an input teflon sample bag, the teflon-lined chamber itself (with motor-driven stirrer), and the output teflon-lined bag. By definition, the chamber is a "continuously stirred tank reactor" in which the concentration of the trace gas at the outlet is the same as any point inside the chamber (e.g., there are no concentration gradients). In this situation, the mass balance for NO in the chamber can be written as:

$$\frac{dC}{dt} = \left( \frac{Q[C]_o}{V} + \frac{JA}{V} \right) - \left( \frac{LA[C]_f}{V} + \frac{Q[C]_f}{V} \right) - R$$

where

- A = soil surface area covered by the chamber
- h = height of the chamber
- V = volume of the chamber
- J = emission flux
- C = NO concentration in the chamber
- [C]<sub>o</sub> = NO concentration at the inlet of chamber
- [C]<sub>f</sub> = NO concentration at the outlet of chamber
- L = loss term by chamber wall per unit area assumed first order in [C]
- R = chemical loss in the chamber at steady state,
- h = height of the chamber
- Q = flow rate through the chamber

at steady state,

$$J = h \left\{ \frac{Q}{V} ([C]_f - [C]_o) + \left( \frac{L}{h} + R \right) [C]_f \right\}$$

Dr. Aneja then presented calculations from preliminary research done in Candor, North Carolina, on a fallow field and at the Clayton, North Carolina, Agricultural Research Station. Both sets of data indicated NO flux, but the latter data had one to about two orders of magnitude higher averages and ranges, indicating the significance of the heavily fertilized soil on NO flux. Two other considerations that Dr. Aneja presented to the group through the data were as follows:

- 1) the hypothesis that, since NO emission seemed to increase with increasing temperature until a certain point and then drop off, microbial processes that produce NO emissions reach a critical temperature and then shut down, and
- 2) a reiteration of the "ambient compensation point" in which it is theorized that at less than the compensation point, NO is being both produced by local emissions and transported to the site, but above that critical value (i.e. compensation point) the net NO flux is zero or negative, and therefore ambient NO is being transported into the region.

In conclusion, Dr. Aneja summarized the advantages and disadvantages of the chamber technique by noting that on the positive side the chamber is small, lightweight, portable, and convenient; it encloses a clearly defined area; and it is useful for process studies (i.e., parameterizing the flux). Thus, the overall survey of NO flux is convenient to determine. On the negative side, Dr. Aneja pointed out that the chamber alters the soil/atmosphere environment; it is labor-intensive under some implementations; and it only measures flux from a small area, requiring extrapolation to field-scale processes.

*Presentation 8: Mobile Dry Deposition Measurement System (Mr. Tom Ellestad, Dr. John Clarke, and Dr. Peter Finkelstein, EPA/NOAA, Research Triangle Park, North Carolina).* Mr. Ellestad described a micrometeorological system that his group developed for measuring the dry deposition fluxes of species important to the National Dry Deposition Network (NDDN), a conglomeration of more than 40 sites located mainly in the eastern half of the United States, with a few sites in the Rocky Mountains. The system included a complete set of instrumentation for determining the energy budget. It was developed for testing and improving the NDDN by providing direct measurements of fluxes for comparison with those of the NDDN, which uses an inferential model involving measurement of pollutant concentrations and deposition velocities inferred from simple meteorological measurements and site characteristics. The system will be deployed at NDDN sites in the summer of 1994, with the goal of experiencing a wide variety of site types, seasons, and meteorological conditions.

While the present system does not measure any nitrogen species emitted from the ground, it does monitor a number of parameters important to air-surface exchange, as well as the concentration and deposition of ozone. Mr. Ellestad pointed out that a secondary objective of his group's participation is the comparison of its measurements with those of other experienced micrometeorological research groups.

*Open Discussion.* Mr. Tom Pierce led an open discussion to end the first day of the workshop, beginning with a reminder that the results of this project will be used to make improvements in EPA air quality modeling. During this time a discussion ensued on how the dynamic chamber affected the boundary layer processes, and possible subsequent errors in the parameterization of the chamber output to the real atmospheric results. Changes to the chamber could make it possible to place the chamber on a collar already in the soil for a short time, sample the air, and then remove

the chamber, thereby allowing the surface layer variables to return to normal. Other additional measurements of interest concerning the chamber technique include measuring turbulence inside the chamber by measuring temperature and pressure perturbations. Moreover, the issue of dynamic similarity between an unperturbed atmosphere-biosphere interface and the subsequent placement of a chamber at the interface was discussed. How this perturbation could be minimized or incorporated in the chamber design also was debated.

*Field Trip and Dinner.* The first day of the workshop officially closed with a field trip to the agricultural research station in Clayton (hosted by Mr. G. Clark), where the NCSU Air Quality Group dynamic gas chamber system and NO flux measuring lab was set up for review by the participants. To insure that the trip was worthwhile for the participants, a traditional dinner of North Carolina barbecued pork and chicken awaited everyone at the site when they arrived!

### Tuesday Morning Session (March 15, 1994)

Dr. Aneja of NCSU chaired the Tuesday morning session.

*Presentation 9: Resource Requirements (Dr. Wayne Robarge, NCSU, Raleigh, North Carolina).* Dr. Robarge began the second day's sessions with a review of the resource requirements as indicated by the requirement surveys completed by the participants, including site selection requirements, physical resources (transportation, power requirements, local gas supply, etc.), and supporting data (site characterization, climatology, etc.). In addition to these requirements, the group discussed the crop type, amount of fertilizer, and seasonal timing that would provide adequate yet realistic results for the study. The consensus was that corn or cotton should be used with at least one side-dressing of nitrogen fertilizer in the spring season to limit possible canopy deposition. Armed with this information, Dr. Robarge stated that he would determine which site best fits the experimental needs and begin preparations for the study.

*Presentation 10: Development of Experimental Design (Dr. Aneja, NCSU, Raleigh, North Carolina).* At this point, Dr. Aneja began the long process of assembling all the information gleaned from previous sessions, with the help of the participants. He proposed that the group should prepare a document, to be reviewed by the workshop participants, for publication in a scientific journal. This document would summarize the experimental intent of the study and include an invitation for other researchers, who have both the finances and new technology, to join the project. It was agreed that this document clearly must not be a request for proposals and that participation in the study means agreement to certain protocol in regard to the site, in order to minimize interference among research groups.

Further discussion focused on a number of criteria for the study site. Of these, fetch, emissions footprint, and distance from urban/industrial sources were considered the most important. Dr. Wesely pointed out that for the eddy correlation technique, roughly 100 times the height of the observation point usually is a good guideline for the length of the fetch. He suggested that, for the purposes of this group, fetch should be defined in general terms as the uniformity of the surface in an upwind direction from the meteorological array; however, modifiers could be used when discussing certain types of fetch. For the NO experiments involving eddy correlation at the planned height of 10 m, the fetch for NO emissions must be at least 1 km in order to compare eddy fluxes with the soil chamber results. Acceptance of this guideline necessarily dictates that the fetch for surface roughness must be at least 1 km or greater, if possible. However, the fetch for surface

roughness can include different crop types, as long as the surface roughness is judged uniform across the boundary between the two crop types. This indeed could be the case, especially early in the growing season.

Dr. Delany proposed a working definition of the emissions footprint for the purpose of site selection as the emitting surface within a uniform crop that is sensed by the micrometeorological array. Assuming a fetch of NO emission of 1 km, he estimated that the emissions footprint should be approximately 500 m. Dr. Wesely asked to expand the definition by proposing that the term "footprint" should refer to the sampled area for a given measurement technique, and specific atmospheric and surface conditions. This more general definition would account for fluxes sensed by the array, whether for emissions, deposition, or even momentum flux. A suitable modifier then should be used to discuss the footprint of interest. For example, for the purposes of the intercomparison study, the emissions footprint from the uniform crop must fit within the available fetch for NO emissions. The length of the available emissions footprint will have a direct influence on the measurement heights for the eddy correlation technique. An emissions fetch of less than 500 m would require that some eddy flux measurements be made fairly close to the surface in order to insure that the emissions footprint sensed by the eddy correlation technique does not extend beyond this distance.

All participants agreed that the study site should be isolated from any major urban/industrial areas and from major highways. General guidelines put forth were that the site must be at least 1 km upwind from light traffic areas, at least 3 km upwind from heavy traffic areas (10 km for interstate highways), at least 10 km upwind from small towns or urban areas, and 100 km from any major metropolitan areas. For the planned study period of May through June, 1995, the dominant wind direction will be from the southwest in eastern North Carolina. The final selection of a study site must account for this fact.

The remaining study site criteria listed for consideration included the width of the emissions footprint in front of the meteorological array, fetch for surface roughness behind the array, placement of instrument trailers, and sampling area for soil chamber measurements. The emissions footprint in front of the array should be wide enough to accommodate about a 120-degree field as measured from the center of the array. If the dominant winds fall outside this angle, the individual tower elements within the array will interfere with the measurements. The fetch for surface roughness behind the array should extend at least 50 m, with 100 m being optimal. Ideally, the area behind the array will be the same uniform crop cover as in the emissions footprint, in order to minimize sudden changes in roughness, emission, or deposition patterns. Instrument trailers should be sited approximately 100 to 200 m from the micrometeorological array, and the power trailer can be located within 50 m of the array. The sampling area for the soil chamber measurements must be located nearby and have the same characteristics as the emissions footprint. The optimum location for the sampling area for the soil chamber measurements should be beside the array and downwind of the emissions footprint.

*Additional Items.* Additional items addressed during this session included the following:

- 1) A written draft of the experimental plan will be completed by May 5, 1994.
- 2) A statement of the experimental objective: "Relate chamber techniques to micrometeorological flux estimates of NO<sub>x</sub>."
- 3) (a) The need for two fast-response high-sensitivity (20 pptv) NO instruments (preferably a matched pair) for

measuring the profile of the flux of NO. (Dr. Doddridge's group is one possible source for such instruments.)

- (b) The need for one fast-response ozone instrument for measuring the flux of O<sub>3</sub>. (Mr. Ellestad will be the source of the instrument.)
  - (c) The need for one fast-response NO<sub>2</sub> high-sensitivity instrument for measuring the flux of NO<sub>2</sub>. (Dr. Doddridge's group will be the source of the instrument.)
  - (d) The need for a slow-response high-sensitivity NO and NO<sub>2</sub> (or NO<sub>x</sub>) instrument for measuring the profile of the mean. (Dr. Doddridge's group and/or Dr. Aneja's group will be the source of the instrument.)
- 4) The need for ancillary measurements at the site: soil heat flux, soil heat capacity, CO flux, N<sub>2</sub>O flux, and ambient NMHC analysis.
  - 5) The timing of the study should be coordinated with the availability of the ASTER micrometeorological station. The best time-frame centered around May or June, 1995.
  - 6) The study will require four to six weeks of research and one to two weeks of setup and takedown time.

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