AP42 Section:	9.2.1
Title:	Industry comments from early '90s to 1999.

Note: This material is related to a section in *AP42, Compilation of Air Pollutant Emission Factors, Volume I Stationary Point and Area Sources.* AP42 is located on the EPA web site at www.epa.gov/ttn/chief/ap42/

The file name refers to the file number, the AP42 chapter and then the section. The file name "rel01_c01s02.pdf" would mean the file relates to AP42 chapter 1 section 2. The document may be out of date and related to a previous version of the section. The document has been saved for archival and historical purposes. The primary source should always be checked. If current related information is available, it will be posted on the AP42 webpage with the current version of the section.

The Fertilizer Institute

Jim Skillen
Director
Environmental Programs

May 5, 1999

Mr. Dallas W. Safriet
Emission Factor And Inventory Group (MD-14)
Office of Air Quality Planning and Standards
U. S. Environmental Protection Agency
Research Triangle Park, NC 27711

Re: Comments on Draft AP-42 Emission Factor for Fertilizer Application

Dear Mr. Safriet:

The Fertilizer Institute (TFI), on behalf of its member companies, submits these comments in response to the draft U.S. Environmental Protection Agency ("EPA") report entitled "Emission Factor Documentation for AP-42 Section 9.2.1: Fertilizer Application" (hereinafter referred to as "Draft Report").

Statement Of Interest

TFI is a voluntary, non-profit trade association of the fertilizer industry. TFI's nearly 250 member companies manufacture over 90 percent of the domestically produced fertilizer. TFI's membership includes producers, manufacturers, distributors, transporters and retail farm suppliers of fertilizer and fertilizer materials. Because the Draft Report seeks to quantify and qualify emissions from fertilizer application, and because that quantification could be the predicate for the adoption of fertilizer application regulations applicable to TFI members, TFI and its members have an interest in ensuring that any final report be based only on sound science and accurate information.

Comments

TFI's comments fall into four categories: (1) specific comments about the background information in the Draft Report; (2) specific comments about the emission factors in the Draft Report; (3) general policy questions and concerns; and (4) editorial comments on the Draft Report. For EPA's convenience, the editorial comments are included as a separate attachment (in blue-line). The other three types of comments follow.

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A. Emission Factor Documentation for AP-42: Section 9.2.1 Fertilizer Application

1. Emission Control Technology (Section 2.4)

Section 2.4 of the Draft Report discusses several "control technologies" based on emissions data reported in literature discovered by EPA during the preparation of the Draft Report. As presented in greater detail below, the underlying data are too crop-specific or otherwise insufficient for use in suggesting "control technologies" at this time.

a. Fertilizer Additives and Encapsulation

The Draft Report discusses fertilizer additives that reduce the denitrification potential, as well as encapsulation, as potential means of inhibiting nitrogen loss from the soil:

> Because a substantial quantity of emissions from fertilizer applications is related to the denitrification process, management techniques that reduce denitrification potential also will increase nitrogen utilization and decrease emissions. Additives to fertilizer nitrogen sources that reduce or inhibit nitrification or urea hydrolysis (N-Serve, DCD, and others) may reduce the potential for gaseous nitrogen emissions. Use of encapsulated calcium carbide (ECC) has been shown to be effective in the inhibition of nitrification and the reduction of N_2O and N_2 emissions from irrigated corn and wheat fields as well as flooded rice fields. It was not effective for dry land wheat fields. Details on these studies can be found in References 24, 25, and 26. Encapsulation of the fertilizer nitrogen also may significantly reduce emission losses. Considerable more research is required to identify the most effective inhibitors.

Draft Report, 2-13. The Draft Report suggests that additives to fertilizer nitrogen sources should be considered that would reduce or inhibit nitrification or urea hydrolysis and, therefore, may reduce the potential for gaseous nitrogen emissions. The Draft Report states that encapsulated calcium carbide may be one such effective additive. TFI cautions EPA that the agronomic and environmental effects of any such additive must first be evaluated. We see no mention of such a consideration in the Draft Report. Further, the costs to the industry of using such an additive must be considered.

Even in the data cited in the Draft Report, the use of fertilizer additives is not uniformly helpful for all agronomic contexts. For example, the method was not effective on dry land wheat fields. It is possible that further research would determine that the method is affirmatively adverse to a crop in some contexts. Thus, it is premature at this time to suggest this approach as a control technology.

b. Application of Nitrogen in Conjunction with Maximum Nitrogen Demand

The Draft Report suggests a "nutrient management" control strategy whereby nitrogen fertilizers would be applied as close as possible to the time that the crop requires the nitrogen.

> Appropriate nutrient management requires not only appropriate quantities of fertilizer but also timing of the application. Maximizing the quantity of nitrogen recovered by the plant requires that the nitrogen be applied as close to the time of maximum nitrogen demand as is possible. Therefore, split applications (part of the nitrogen is applied before planting and part is applied during an early crop growth stage) will maximize crop recovery and minimize gaseous emissions of the applied nitrogen.

Draft Report, 2-13. This position is unsupported as a general statement because there are many instances where, for example, a single, pre-plant application of nitrogen fertilizer is more efficient than a split application of nitrogen fertilizer. The use of general statements, across all soil conditions and crops, is not supported.

c. Spatially Varied Fertilizer Application

The Draft Report also prefigures a future control technology based on varying the application of nitrogen-based fertilizers to target higher nitrogen application rates to the areas of a field with the higher crop yield potential:

> Currently, uniform nitrogen recommendations are provided for a crop grown on a given field, and nitrogen is applied at a uniform rate over the entire field. Since crop yield potential varies spatially over a field, varied nitrogen application rates would also increase nitrogen utilization. However, the technologies that facilitate variable nitrogen application to improve nitrogen use efficiency

> and minimize the environmental impact of nitrogen use are not generally available at this time.

Draft Report, 2-13.

This characterization of industry practice is incorrect in two respects. First, uniform nitrogen recommendations are not provided for a given field. With the advent of Global Positioning Systems (GPS), certified crop advisors work with farmers to target nitrogen-deficient acreage to ensure that the proper balance of nitrogen is added to the soils. Even in areas where GPS is unavailable, or the financial profile of the crop/farm precludes its use, crop advisors recommend area-specific nitrogen application based on soil conditions. Second, the application of additional fertilizer is targeted to the areas where the soil requires the additional nutrients to increase production of crops, not to the areas of theoretically highest crop yield potential. Total yields may drop considerably if field areas with relatively lower crop yield potential were under-fertilized in favor of the portions of the same field with a higher crop yield potential.

2. Review of Specific Data Sets (Section 4.1)

In addition to the criticisms EPA itself raised on the reliability of the data from the literature that EPA reviewed (Draft Report, 4-1, 4-11, 4-12), TFI's specific comments regarding the reported emissions studies are listed below.

a. Reference Number 2

These data were generated on fields that received 168 pounds of nitrogen per acre as beef manure. Next, 13 pounds of nitrogen per acre as ammonium nitrate were applied as starter fertilizer in a 2 inch by 2 inch band beside and below the corn seed. Field 2 had an additional 56 pounds of nitrogen per acre applied as urea. The authors concluded "Manure applied at the sites was the major source of N for N_2O production." This study, at most, shows the emissions of nitrogen gases from fields as a result of beef manure application.

b. Reference Number 4

Both calcium nitrate and sodium nitrate are not typical nitrogen fertilizers.

c. Reference Number 5

Both ammonium chloride and sodium nitrate are not typical nitrogen fertilizers.

d. Reference Numbers 7 and 8

This is a flawed study to determine if the reported losses are typical losses of ammonia after application of anhydrous ammonia to fields. This study was done in New South Wales, Australia. The soil was heavy clay with a very high pH of 8.2. The soil was too wet when the ammonia was applied and the authors state that the soil did not readily cover the injection slit. "All of these factors could be conducive to large losses of ammonia" according to the authors. The ammonia was injected to a depth of only 12.4 cm (4.9 inches) and this shallow depth is typically less than the 6 to 8 inches recommended by U.S. University Cooperative Extension Services. The study seems to have been selected to show an extreme situation where relatively large losses of ammonia occurred due to poor execution of the research work.

e. Reference Number 11

This is study done in Canada where urea was topdressed on a Kentucky bluegrass/fesaue turf. This is again a situation where a researcher would expect relatively large losses of ammonia from volatilization.

f. Reference Number 12

This study reported ammonia volatilization rates of "nil" for all of the values that are marked <1.21. The detection limit of the equipment was 0.1% so anything with less than 0.1% was reported as nil. EPA appears to have assumed a loss of 0.05% (half way between 0 and 0.1%), which may overstate actual emissions.

g. Reference Number 41

The study was done on no-till corn in western Tennessee. This was, over-all, a good study and a well documented study. The soil was no-till with a high bulk density that was recorded at 1.61 g/cc. This density suggests a compacted soil since typical soil values are 1.3 g/cc. No-till and high bulk density soil would lead to higher denitrification rates and higher emissions of nitrogen gases.

B. Draft AP-42: Section 9.2.1 Fertilizer Application

The Draft Report notes the data in the studies reviewed in preparing the draft emission factors are highly variable.

> Note that the studies that were used to develop these emission factors indicate that emissions can exhibit substantial temporal and

> spatial variability. Factors that affect this variability include soil type and composition, soil properties such as moisture content and pH, and ambient temperature. These *factors result in wide differences in emissions from site-to-site as well as day-to-day variations and diurnal emission variation at a given site.* Consequently, the emissions factors shown in *Table 9.2.1-2 should be used with caution because data from the 15 studies used to develop them were extremely variable.*

Draft Report, at 9.2.1-3 (emphasis added). This variability reflects an even lower standard of reliability than the "E rating" that EPA has given the draft emission factors. For the present, EPA should de-emphasize the fertilizer form and, instead, should show the great variation in emissions. For example, the table could be re-ordered to show the "reference," the "form of fertilizer applied," and the "measured emissions." Such a chart would not suggest, as does the current chart, that the use of solid ammonium nitrate has nearly ten times the emissions of fluid surface-applied ammonium nitrate. The data underlying the draft chart is too weak to support the inferences that it raises in its current form.

C. Policy Considerations

1. AP-42 Emission Factors Should Avoid or Address Overlap With Other AP-42 Sections

The Draft Report indicates that the industry includes the Standard Industrial Classification (SIC) Code for pesticides and other agricultural chemicals (SIC 2879). This SIC code is also included in the background document for AP-42 Section 9.2.2 (Pesticide Application). (Emission Factor Documentation for AP-42 Section 9.2.2, Pesticide Application: Final Report, 2-1 (Sept. 1994)). EPA should clarify the application of Section 9.2.1 (fertilizer application) and Section 9.2.1 (pesticide application) for SIC code 2879.

The Draft Report does not discuss the relationship, if any, between the fertilizer application emission factor data in Section 9.2.1 and the emission factor for N_2O from fertilized soils in AP-42 Section 14.1, Emissions from Soils-Greenhouse Gases. There is some overlap because the draft Section 9.2.1 applies not only to the emissions from the application of fertilizer (as its title suggests), but also to the increased soil emissions resulting from the fertilizer in the soil.

The Draft Report calls emissions resulting from reactions in the soil after application of the fertilizer "latent emissions" and emissions from the application of fertilizer "immediate emissions." TFI believes that the immediate emissions are capable of general quantification, in the manner proposed by the Draft Report. However, latent emissions are not adequately

characterized in the Draft Report and significant work remains before this type of emissions can be characterized.

2. Insufficient Detail on Variations Between Crops, Climates, and Soil Chemistry

Quantifying latent emissions from agricultural fertilizer application is a very complex process that requires not only better data than are cited in the Draft Report, but also data across the spectrum of parameters (such as crops, geography, climates, and soil chemistry) intended to be covered by the emission factors. The data cited in the Draft Report do not cover a wide spectrum of crops, climates, or geographies.

By comparison, AP-42 Section 1 includes subsections on eleven different categories of external combustion sources: Bituminous and Sub-bituminous Coal Combustion; Anthracite Coal Combustion; Fuel Oil Combustion; Natural Gas Combustion; Liquefied Petroleum Gas Combustion; Wood Waste Combustion in Boilers; Lignite Combustion; Bagasse Combustion in Sugar Mills; Residential Fireplaces; Residential Wood Stoves; and Waste Oil Combustion. Most of these subsections include emission factors for multiple configurations of sources and/or fuels within a source. Without even considering the various permutations of emission controls, there are 28 different types of coal combustion sources (AP-42 Volume V, Table 1.1-3, Table 1.2-1) and 20 different types of oil and gas combustion sources (AP-42 Volume V, Table 1.3-1, Table 1.4-1, Table 1.5-1).

Just as EPA distinguishes between five different types of oil in its emission factors for fuel oil combustion (AP-42 Volume V, Table 1.3-1), it may need to distinguish between several different soil-climatic-geographic permutations of growing wheat. Similar distinctions need to be addressed across types of crops (e.g., rice, corn, celery). The data cited in the Draft Report are also not representative of the sources that the Draft Report endeavors to cover.

3. Emission Factor Should Quantify Background Biogenic Emissions

For pollutants such as NO_x that occur biogenically, as well as via anthropogenic application of fertilizer, AP-42 should provide a "biogenic background" emission baseline. The AP-42 emission factor for N_2O emissions from soils included emission factors of fertilized soils as well as a variety of natural ecosystems (coniferous and deciduous temperate forests, tropical forests, savanna, grassland, and shrubs/woodlands). AP-42 Volume V, Table 12.1-2.

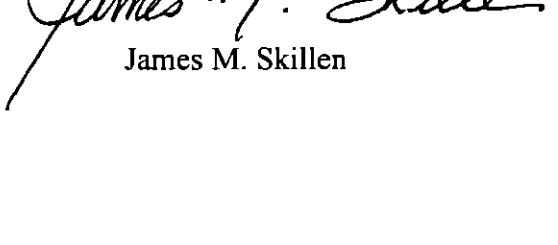
This is important because, while both biogenic and anthropocentric emissions are included in the baseline emission inventory (57 Fed. Reg. 13498, 13502 (Apr. 16, 1992)), only

anthropogenic emissions are used in meeting certain Clean Air Act regulatory requirements. *E.g.*, 42 U.S.C. § 7511a(b)(1)(B). The legislative history of the Clean Air Act makes clear that anthropogenic emissions include the marginal increase in emissions from an otherwise "natural" process, if that marginal increase is caused by human intervention. *See* H.R. Rep. No. 101-490, 265-66 (1990) (dust storms from dry lakebeds made more severe by diversion of water from the lakes to Los Angeles). Thus, the emissions caused by farming that are over the biogenic baseline for a particular ecosystem may be of regulatory concern.

* * * *

TFI has been pleased to submit these comments on EPA's Draft Report. Should you have any questions concerning our comments, please call me at (202) 608-5910.

Sincerely,



James M. Skillen

JMS/gcm
Enclosures a/s

cc: TFI's Agronomy Task Force

Editorial Comments on AP-42 Section 9.2.1 (Fertilizer Application)

I. AP-42: SECTION 9.2.1 FERTILIZER APPLICATION

A. Section 9.2.1.1

The role of fertilizers in the agriculture industry is to supply essential plant nutrients to improve crop production. There are ~~16~~ 17 essential elements or nutrients necessary for plant growth, three of which (carbon, hydrogen, and oxygen) are supplied from the atmosphere or water. The other ~~13~~ 14 elements (nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, copper, zinc, boron, manganese, iron, nickel, chlorine, and molybdenum) are principally supplied through the soil medium. Concentrations of some of these elements are limited in most soils and must be supplemented by fertilizers. (Page 9.2.1-1)

Fertilizers are produced by the following types of industries: fertilizer plant foods; nitrogen and organic fertilizers; and phosphate, potash and other fertilizers. Fertilizers are distributed through agricultural supply retailers, farmers' cooperatives, and fertilizer dealers. Application is performed by farmers and by fertilizer dealers using specialized application equipment. (Page 9.2.1-1)

B. Section 9.2.1.2

Anhydrous ammonia, which supplies nitrogen, is the only gaseous fertilizer used. Farmers ~~usually hire trained specialists to~~ apply ~~the~~ approximately 5.7 million tons of ammonia ~~used~~ annually in the United States... The ammonia quickly vaporizes, but is captured by several components in the soil including water, organic matter, clay, and other minerals. (Page 9.2.1-1)

The equipment for surface spraying of fertilizers consists of the vehicle, a tank holding the fluid, a metering system, manifolds, and spray nozzles. The manifolds are mounted inside long booms (20 to ~~40~~ 90 feet) having no more than 20 nozzles. Fluid fertilizers are most commonly sprayed onto the surface of freshly tilled soils. Figure 9.2.1-2 shows a side view and rear view of a typical spray nozzle system. By ~~varying the height of the~~ changing nozzles ~~above the ground~~ and the flow of the fluid fertilizer, the applicator can apply the fertilizer in discreet bands

(band and row) or as overlapping coverage (broadcast). (Page 9.2.1-2)

Solid Fertilizers — In the United States, solid fertilizers are typically either straight nitrogen fertilizers (urea or ammonium nitrate) or mixed fertilizers containing nitrogen and ~~phosphate,~~ phosphorous, potassium, and other nutrients... The application rate of solid fertilizer is controlled by a gate and the opening and closing of that gate. The distribution pattern on the field is controlled by ~~is dependent on~~ the position of the spinner blades, the position where the fertilizer drops on the spinner blades, the spinner speed, and the particle size of the fertilizer. Figure 9.2.1-3 shows an example of a centrifugal spreader. (Page 9.2.1-2)

C. **Section 9.2.1.3**

These sources are:... (2) volatilization of the fertilizer immediately behind the vehicle generating gaseous emissions, potentially including NH_3 and/or the fertilizer itself, (3) soil disturbance creating PM emissions with constituents that become airborne, and (4) volatilization of the fertilizer immediately above the solid fertilizer trailer, generating gaseous emissions potentially including NH_3 and/or the fertilizer. (Page 9.2.1-3)

Emission factors are not presently available for PM. A number of heavy elements listed as Hazardous Air Pollutants in the 1990 Clean Air Act Amendments have been identified in soils treated with phosphate, nitrogen, and manure fertilizers, and could become airborne with fugitive dust. These elements are: cadmium, mercury, nickel, selenium, chromium, manganese, lead, and cobalt. ~~Some~~ All of these elements also occur naturally in some soils. Research is needed to quantify fertilizer and manure contributions to airborne heavy metals. (Page 9.2.1-3)

Figure 9.2.1-4: Make "Believed to be negligible" bold under bullet 2 and bullet 4. (Page 9.2.1-6)

Table 9.2.1-1: In footnote b: "For ~~fliud~~ fluid fertilizers..." (Page 9.2.1-7)

Table 9.2.1-1: In footnote c, change the formula to divide the pounds of nitrogen by the nitrogen content (weight percent) that is derived in footnote b (*e.g.*, 934 lb. N / (0.823 lb. N/lb. ammonia) = 1134.9 lb. ammonia). (Page 9.2.1-7)

II. EMISSION FACTOR DOCUMENTATION FOR AP-42: SECTION 9.2.1 FERTILIZER APPLICATION

A. Section 2.2 Method of Application

The NH_3 application system generally consists of an exit line from the pressurized tank (nurse tank) to the manifold, which feed the applicator tubes located immediately behind the applicator knives in the ~~tilling trailer~~ tool bar... The spacing between application rows is between 30 and 45 cm (12 and 18 in), depending on the ~~tilling trailer~~ tool bar. (Page 2-3)

In band application, ~~the height of~~ the nozzles are changed to produce a narrow spray pattern ~~is reduced~~ and the band width of the resultant spray is narrowed so the fluid fertilizers can be applied between rows of growing crops. A recent trend has been to use a rolling coulter with a solid stream nozzle to place a fluid fertilizer in shallow slits in the soil between the rows of growing crops. Figure 2-5 shows a typical band application. (Page 2-4)

Solid fertilizers can be applied using a broadcast technique by aircraft or by high flotation applicator. Because no emission data were found for aerial application, the discussion focuses on high flotation application. Note however, that irrespective of application method, solid fertilizers are ~~frequently~~ infrequently mixed with herbicides in order to reduce the expense of a second application.[1] (Page 2-5)

B. Section 2.3 Emissions

Emissions from the application of fertilizer generally are attributed to four different mechanisms:... (2) volatilization of

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[1] The sentence should probably be stricken. The practice of mixing herbicides with solid fertilizers is no longer practiced extensively because it resulted in too much contamination of the fertilizer blending equipment and applicators.

the fertilizer immediately behind the vehicle generating gaseous emissions, potentially of NH_3 and/or the fertilizer itself, (3) soil disturbance generating PM emissions where soil particles and other materials in the soil become airborne, and (4) volatilization of the fertilizer immediately above the solid fertilizer trailer generating gaseous emissions, potentially of NH_3 and/or other fertilizers. (Page 2-6)

Particulate matter emissions from fertilizers or manures have not been characterized in the literature. ~~However, heavy~~ Heavy elements listed as Hazardous Air Pollutants (HAP's) in the 1990 Clean Air Act Amendments have been identified in soils treated with various types of fertilizers. However, these heavy elements can also be found in soils that have never been treated with fertilizers. Table 2-2 provides a summary of data obtained from a variety of investigators and compiled by Kabata-Pendias and Pendias for trace elements in fertilizer-treated soil. A number of these elements are listed HAP's. (Page 2-7)

Gaseous air emissions from fertilizer application can occur either immediately, as a result of the volatilization of the fertilizer itself, or after a period of time, as a result of the biological/chemical transformation of the fertilizer and subsequent release of gases to the atmosphere. The transformation products are generally oxidized forms of either nitrogen or, sulfur~~, or phosphorus~~...[2] (Page 2-7)

Because of the complexity of the emission mechanisms and the interaction of many of the factors, data are insufficient to estimate the magnitude of the effects of most of the factors... For most fertilizers, it is believed that emissions increase significantly if the soil becomes wet from ~~as moisture contents are raised via~~ rainfall or irrigation prior to application of the fertilizer. Also, emissions are directly related to ambient temperatures... (Page 2-7)

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[2] Phosphorous is not converted into a form that volatilizes into the air, but remains as phosphate in the soil. It is converted into less soluble forms in the soil by chemical reactions with soil iron, aluminum, calcium, and magnesium.

Ammonia Volatilization — Ammonium is normally stored in soil as part of the cation exchange complex. It is absorbed onto the surfaces of clay and organic matter particles due to the attraction of the negatively charged clay and organic matter particles for the positively charged ammonium ions. It is readily absorbed by plant roots~~a complex with carbonate ions or sulfate ions and is readily absorbed by plant roots. Ammonia volatilizes more readily when the soil lacks these anions~~. Ammonia volatilization may increase with high soil pH, the presence of high levels of calcium carbonate, and high or elevated temperatures~~also increases with flooding, high soil pH, the presence of high levels of calcium, and high or elevated temperatures. Flooding mobilizes the NH_3 and carries it to the surface where it is readily volatilized into the atmosphere~~. Soils with high pH (basic soils) shift the equilibrium of the chemical balance between ammonia and ammonium to favor higher concentrations of ammonia in the soil. Any ammonia molecules near the soil surface may volatilize into the atmosphere. Ammonia emissions may also increase with increases in soil temperature~~react with ammonium ions to generate water and NH_3 gas. Calcium forms insoluble precipitates with sulfates and carbonates, thus reducing the anions available for complexing with ammonium ions. Ammonia emissions also increase with temperature~~. Under drying conditions, especially with increasing wind speed, soils with high moisture content enhance NH_3 volatilization, especially with urea-containing materials that are applied on the soil surface. (Page 2-9)

Reduction of Nitrates — Generally, nitrate is a soluble anion found in the soil solution and is readily absorbed by plant roots. However, these nitrate compounds can undergo reduction reactions to produce ~~less soluble~~ gaseous oxides of nitrogen and increase emissions of NO_x. The magnitude and rate of nitrate reduction in soils is increased with increasing quantities of decomposable organic matter, soil moisture content (decreasing soil aeration), soil pH, soil temperature, and soil nitrate content. (Page 2-9)

Climatic conditions that affect emission rates through their influence on biological and chemical reaction rates include moisture, temperature and wind speed... Also, daily peak emissions will increase throughout the summer season as compared to the other three seasons if fertilizers containing urea

are broadcast on the soil during this time period. Denitrification also increases with rising temperature. Additional information may be found in References 7 and 23. (Page 2-11)

C. **Section 2.4 Emission Control Technology**

Appropriate nutrient management requires not only appropriate quantities of fertilizer but also timing of the application. Maximizing the quantity of nitrogen recovered by the plant requires that the nitrogen be ~~applied~~ made available to plant roots as close to the time of maximum nitrogen demand as is possible. (Page 2-13)

Figure 2-2. Label the metal frame to which the applicator knives are mounted as the "Tool Bar." (Page 2-19)

Figure 2-5. Change the illustration to a tool bar with rolling coulters and solid stream nozzles mounted on the back of the rolling coulters. (Page 2-23)

Figure 2-7d. Make the text "Believed to be negligible" bold text. (Page 2-25)

Figure 2-8. Add a label showing "NH_3 Volatilization from Plant Leaves" from the corn leaves. (Page 2-27)

D. **Section 3.4 Emission Testing Methods for Fertilizer Application**

The integral on page 3-4 should be from 0 to Z. The Draft Report shows it from 0 to an undefined symbol (⊥). (Page 3-4)

Data Sources
Commercial Fertilizers 1998

Commercial Fertilizers 1998 is based on fertilizer consumption information submitted by state fertilizer control offices. The consumption data include total fertilizer sales or shipments for farm and non-farm use. Liming materials, soil amendments, soil additives, and soil conditioners are excluded. Materials used for the manufacture or blending of reported fertilizer grades or for use in other fertilizers are excluded to avoid duplicate reporting. Some states do not report final grades; therefore, basic materials including both single-nutrient and multiple-nutrient are reported. Significant effort was exerted to check the accuracy of and faithfully summarize each state's data; however, AAPFCO is not responsible for the accuracy of the data.

Comments on the 1998 data from certain specific states follow (See *Commercial Fertilizers 1997* for comments on the 1997 data sources). Some states' 1997 data have been updated as noted below.

Alaska-In the absence of any report from Alaska the 1998 tonnage was set equal to the 1997 tonnage. The tonnage of the individual materials and grades was carried forward from 1997.

Arkansas-The 1997 data have been updated.

California-The grade of the non-farm tonnage that was used for calculating the nutrient data was estimated as 10-3-3. All NPK fertilizers of unknown analyses were assigned a grade of 12-11-8 and 12-18-6 for July-December and January-June periods, respectively. These estimated grades were excluded from Tables 15-17.

Georgia-The GA Department of Agriculture does not report the grades of mixed fertilizers. The estimated grades of dry mixed and liquid mixed fertilizers that were used for calculating nutrient data were 8-12-18 and 7-9-15, respectively. These estimated grades were excluded from Tables 15-17.

Hawaii-In the absence of any report from the HI Department of Agriculture, an estimate of the total tonnage for 1998 was set equal to 103% of the 1997 tonnage based on information provided by industry representatives. The total tonnage was proportioned into the tonnage for the individual materials and grades in the same ratio as in the original TVA estimate. The specific materials and grades reported are based on a TVA estimate from about 1989 that have been carried forward and adjusted each year as above.

Indiana-Additional undifferentiated tonnage of 488,016 was submitted by the IN State Chemist's Office to be added to their original data set. This additional tonnage was proportioned into the tonnage for the individual materials, grades, and counties in the same ratio as in the original data.

Maine-The 1998 data were estimated as 101.7% of the 1997 tonnage which is the weighted average of the change from 1997 to 1998 in the reported tonnage from the surrounding states of CT, MA, NH, RI, and VT.

Nevada-The 1997 data have been updated.

North Dakota-Reported tonnage is for January-December 1997.

Puerto Rico-The total tonnage was received from the Puerto Rico Department of Agriculture and is considered accurate. The total tonnage was proportioned into the tonnage for the individual materials and grades in the same ratio as that in 1997.

South Dakota-SD reports tonnage on a calendar year basis. The data for 1997 were unavailable at publication time because of a computer problem. The SD Department of Agriculture estimated 935,000 tons for calendar year 1997 based on income received. The total tonnage was proportioned into the tonnage for the individual materials and grades in the same ratio as that in 1996.

Texas-Reported tonnage is for the year, September 1-August 31.

Washington-No report was received from the WA Department of Agriculture; however, their estimate was that the 1998 tonnage was 95% of that of 1997. The total tonnage was proportioned into the tonnage for the individual materials and grades in the same ratio as that in 1997.

Wisconsin-The WI Department of Agriculture reported only the total tonnage which is considered accurate. The total tonnage was proportioned into the tonnage for the individual materials and grades in the same ratio as in the 1997 data.

Wyoming-All tonnage was estimated based on tonnage reported in the surrounding states of ID, MT, and UT and in consultation with the Wyoming Department of Agriculture. The 1998 tonnage was estimated as 104.7% of the 1997 tonnage. The individual materials and grades and their distribution by county are based on the last Wyoming tonnage report that was for fertilizer year 1993. The total tonnage was proportioned into the tonnage for the individual materials and grades in the same ratio as that in 1993.

Electronic Data Bases

Complete data sets for fertilizer years 1985-1998 are available in ASCII or Lotus computer file formats on 3.5-inch diskettes at a cost of $150(US) per year. There were 33 states reporting county data for the 1998 fertilizer year. Special analyses of the data are available upon request at an additional cost. Requests should be made to: ***David L. Terry, 103 Regulatory Services Building, University of Kentucky, Lexington, KY 40546-0275, Phone 606/257-2668, FAX 606/257-7351, E-Mail: dterry@ca.uky.edu.*** Some of the data are posted on the internet at:

<http://www.uky.edu/Agriculture/RegulatoryServices/natonnage.htm>

Acknowledgment and Request

Appreciation is expressed to each control official and the workers in their offices for supplying the data for this publication. Without their cooperation this publication would not be possible. Comments and suggestions are invited and should be directed to the address above.

Regions and States

New England

Maine
New Hampshire
Vermont
Massachusetts
Rhode Island
Connecticut

Middle Atlantic

New York
New Jersey
Pennsylvania
Delaware
Maryland
West Virginia

South Atlantic

Virginia
North Carolina
South Carolina
Georgia
Florida

East North Central

Ohio
Indiana
Illinois
Michigan
Wisconsin

West North Central

Minnesota
Iowa
Missouri
North Dakota
South Dakota
Nebraska
Kansas

East South Central

Kentucky
Tennessee
Alabama
Mississippi

West South Central

Arkansas
Louisiana
Oklahoma
Texas

Mountain

Montana
Idaho
Wyoming
Colorado
New Mexico
Arizona
Utah
Nevada

Pacific

Washington
Oregon
California

Other

Alaska
Hawaii
Puerto Rico

1985-1998 COMMERCIAL FERTILIZERS DATA - ASCII FILES BY REGION

Information and Instructions

(Note-This is file-INSTR98.DOC,a MS Word97 file)

Note: You must have a software program that can read ASCII files and do statistical analyses to fully utilize these data.

Commercial Fertilizers data for each fertilizer year have been divided into eight regions and stored in ASCII files (.R extension). The ASCII files were zipped to self-extracting files (.EXE extension) and then copied to three diskettes for each year. The diskettes are labeled with the fertilizer year and disk number. Use Table 1 to locate the data file you need to extract.

To extract a file, follow these steps:

1. Determine the name of file to extract and the disk number where the file is stored using Table 1 (example: NWEMA95).

2. Create a directory on your hard drive where you want to store the CF data (example: C:\cf95data).

3 Insert the diskette into floppy drive (example: A).

3 From your hard drive change directories to the directory you created for the data (C:\cf95data>), type A:NWEMA95 and then press ENTER. If you are using Windows you can do the same thing with File Manager by making C:\cf95data your default directory, then click on 'RUN', type 'A:NWEMA95' in the command line, and click 'OK'.

4 The ASCII file NWEMA95.R will be copied to C:\cf95data

Note: If you are having problems please call D. L. Terry 606/257-2668.

The following tables provide specific information about the CF data:

Table 1: Disk Number, ASCII File Names and States By Region.
Table 2: Number of Records Per File For Each Year.
Table 3: ASCII File Layouts - CF Data Files.
Table 4: ASCII File Layouts-County Name and Fertilizer Code Files.
Table 5: County Data Availability.
Table 6. Fertilizer Code Listing.

Table 1: Disk Number, ASCII File Names and States by Region.
(Note-For 1995, 1996, and 1997: ENCENyy, ESCENyy and MTPACyy are on Disk 1; NWEMAxx, WNCENxx, AND WSCENxx are on Disk 2; and, SOATLyya and SOATLyyb are on the Instruction Disk.)

----------DISK 1---------- ----------DISK 2----------

ENCENyy- EAST NORTH CENTRAL	ESCENyy- EAST SOUTH CENTRAL	MTPACyy- MOUNTAIN, PACIFIC, OTHER	NWEMAyy- NEW ENGLAND AND MIDDLE ATLANTIC	SOATLyyA/ SOATLyyB- SOUTH ATLANTIC	WNCENyy- WEST NORTH CENTRAL	WSCENyy- WEST SOUTH CENTRAL
Illinois	Alabama	Alaska	Connecticut	Florida	Iowa	Arkansas
Indiana	Kentucky	Arizona	Delaware	Georgia	Kansas	Louisiana
Michigan	Mississippi	California	Maine	North Carolina	Minnesota	Oklahoma
Ohio	Tennessee	Colorado	Maryland	South Carolina	Missouri	Texas
Wisconsin		Hawaii	Massachusetts	Virginia	Nebraska	
		Idaho	New Hampshire		North Dakota	
		Montana	New Jersey		South Dakota	
		Nevada	New York			
		New Mexico	Pennsylvania			
		Oregon	Rhode Island			
		Puerto Rico	Vermont			
		Utah	West Virginia			
		Washington				
		Wyoming		***For 1996, 1997 and 1998 there is only one SOATL file:SOATL98.EXE**		

Table 2: Number of Records Per File For Each Year.

yy	NWEMAyy	SOATLyyA	SOATLyyB	ENCENyy	WNCENyy	ESCENyy	WSCENyy	MTPACyy
85	6048	80000	58196	47505	25295	29103	22069	17759
86	8854	60000	53190	58532	30867	31761	44302	14781
87	25625	70000	50903	56298	28346	31147	45316	13521
88	32747	70000	51810	57119	29350	31195	47499	19086
89	34748	70000	57202	55404	31495	35674	19960	19914
90	23516	50000	43984	63559	34709	41932	54718	28057
91	34100	50000	49428	64719	34976	36848	55859	31264
92	38074	80000	31305	65226	34201	43967	55900	16842
93	43751	50000	48303	61165	34788	43269	56801	13800
94	47121	50000	46847	46436	32962	39423	60810	11730
95*	53263	50000	45482	50222	32680	44661	57403	12098
96**	53236	50000	53364	56899	33085	46191	57562	10619
97**	48373	50000	49292	56386	37021	48298	55844	8388
98	44617	50000	36005	49005	34551	46932	59070	7894

NOTE: To ensure validity of data, the number of records extracted from each file should match this table.
*1995 data updated 1/97.
** 1996 and 1997 data updated 4/99.

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Table 3: ASCII File Layout - CF Data Files.

ASCII Data File Layout

Field	Type	Length	Implied Decimals	Description/Example
Fertilizer Year	numeric	2		example: 85=July-June, 1985
Extra County Data	character	1		"X"=extra county data, incomplete
State Abbreviation	character	2		example: "AL"=Alabama
County FIPS Code	numeric	3		for county names, see ASCIICTY.
Reporting Period	numeric	2		6=Jul-Dec 12=Jan-Jun
Quantity (tons)	numeric	9	2	amount shipped in tons
Fertilizer Code	numeric	3		for descriptions, see ASCIIFRT.R
Container	numeric	1		1=bag 2=bulk 3=liquid
Use	numeric	1		1=farm 2=nonfarm
Grade: N	numeric	3	1	% nitrogen
P2O5	numeric	3	1	% phosphate
K2O	numeric	3	1	% potash

Table 4: ASCII File Layouts - County Name (See file: ASCIICTY.R) and Fertilizer Codes (See ASCIIFRT.R) Files.

County Name File Layout (For file: **ASCIICTY.R**)

Field	Type	Length
State Abbreviation	character	2
County FIPS Code	numeric	3
County Name	character	25

Fertilizer Code File Layout (For file: **ASCIIFRT.R**)

Field	Type	Length
Fertilizer Code	numeric	3
Fertilizer Name	character	40
Short Name-Part 1	character	8
Short Name-Part 2	character	8

Table 5: County Data Availability.

A = county data available X = Incomplete county data E=Estimated data

State	85	86	87	88	89	90	91	92	93	94	95	96	97	98
ALABAMA	A	A	A	A	A	A	A	A	A	A	A	A	A	A
ALASKA	.	.	.	.	.	.	.	.	.	.	.	.	.	.
ARIZONA	.	.	.	A	A	A	A	A	A	A	A	A	A	A
ARKANSAS	.	A	A	A	A	A	A	A	A	A	A	A	A	A
CALIFORNIA	.	A	A	A	A	A	A	A	A	A	A	A	A	A
COLORADO	X	X	X	X	X	X	X	X	X	.	.	.	.	.
CONNECTICUT	.	.	.	.	.	.	.	.	.	.	.	.	.	.
DELAWARE	.	.	.	A	A	A	A	A	A	A	A	A	A	A
FLORIDA	A	A	A	A	A	A	A	A	A	A	A	A	A	A
GEORGIA	A	A	A	A	A	.	X	X	.	.	.	.	.	.
HAWAII	.	.	.	.	.	.	.	.	.	.	.	.	.	.
IDAHO	.	.	.	.	.	.	.	.	.	.	.	.	.	.
ILLINOIS	A	A	A	A	A	A	A	A	A	A	A	A	A	A
INDIANA	A	A	A	A	A	A	A	A	A	A	A	A	A	E
IOWA	A	A	A	A	A	A	A	A	A	A	A	A	A	A
KANSAS	X	X	X	X	X	A	A	A	A	A	A	A	A	A
KENTUCKY	A	A	A	A	A	A	A	A	A	A	A	A	A	A
LOUISIANA	A	A	A	A	A	X	X	A	A	A	A	A	A	A
MAINE	.	.	.	A	A	A	A	A	A	A	A	.	E	E
MARYLAND	.	.	A	A	A	A	A	A	A	A	A	A	A	A
MASSACHUSETTS	.	.	.	.	.	.	.	.	.	.	.	.	.	.
MICHIGAN	.	.	.	A	A	A	A	A	A	A	A	A	A	A
MINNESOTA	.	.	.	A	A	A	A	A	A	A	A	A	A	A
MISSISSIPPI	A	A	A	A	A	A	A	A	A	A	A	A	A	A
MISSOURI	A	A	A	A	A	A	A	A	A	A	A	A	A	A
MONTANA	.	.	.	.	.	.	.	.	.	.	.	.	.	.
NEBRASKA	X	X	A	A	A	A	A	A	A	A	A	A	A	A
NEVADA	.	.	.	.	.	.	.	.	.	.	.	.	.	.
NEW HAMPSHIRE	.	.	.	.	.	.	.	.	.	.	.	.	.	.
NEW JERSEY	.	.	.	.	.	.	.	.	.	.	.	.	.	.
NEW MEXICO	A	X	A	A	A	A	A	A	A	A	A	A	A	A
NEW YORK	.	.	.	.	.	A	.	A	A	A	A	A	A	A
NORTH CAROLINA	A	A	A	A	A	A	A	A	A	A	A	A	A	E
NORTH DAKOTA	.	.	.	.	X	A	A	.	.	A	A	A	A	A
OHIO	A	A	A	A	A	A	A	A	A	A	A	A	A	A
OKLAHOMA	X	A	A	A	A	A	A	A	A	A	A	A	A	A
OREGON	.	.	.	.	.	.	.	.	.	.	.	.	.	.
PENNSYLVANIA	.	.	A	A	A	A	A	A	A	A	A	A	A	A
RHODE ISLAND	.	.	.	.	.	.	.	.	.	.	.	.	.	.
SOUTH CAROLINA	A	A	A	A	A	A	A	A	A	A	A	A	A	A
SOUTH DAKOTA	.	.	.	.	.	.	.	.	.	.	.	.	.	.
TENNESSEE	A	A	A	A	A	A	A	A	A	A	A	A	A	A
TEXAS	X	A	A	A	A	A	A	A	A	A	A	A	A	A
UTAH	.	.	.	.	.	.	.	.	.	.	.	.	.	.
VERMONT	.	.	.	.	A	A	A	A	A	A	A	A	A	A
VIRGINIA	A	A	A	A	A	A	A	A	A	A	A	A	A	A
WASHINGTON	.	.	.	.	.	.	.	.	A	A	A	A	.	.
WEST VIRGINIA	.	.	.	X	X	X	X	X	A	A	A	A	A	A
WISCONSIN	.	.	.	.	.	.	.	.	.	.	.	.	.	.
WYOMING	.	.	.	A	A	A	A	A	A	E	E	E	E	E
PUERTO RICO	.	.	.	.	.	.	.	.	.	.	.	.	.	.
TOTALS	23	23	25	32	34	34	34	34	34	34	34	33	33	33

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Table 6: Fertilizer Code Listing.

CODE	NAME	N	P2O5	K2O	RANGE	CONTAINER
0	IDENTIFIED BY GRADE	0.0	0.0	0.0		DRY,LIQ
2	ANHY AMMONIA	82.0	0.0	0.0	80-83% N	LIQ
6	AQUA AMMONIA	20.5	0.0	0.0	10-30% N	LIQ
10	AMMONIUM NITRATE	34.0	0.0	0.0	33-34% N	DRY
12	AMM NIT SOLUTION	20.0	0.0	0.0	18-20% N	LIQ
13	AMM NIT LIME MIX	20.5	0.0	0.0	17-26% N	DRY
16	AMMONIUM NIT-SUL	30.0	0.0	0.0	26-30% N	DRY
20	AMMONIUM POLYSULF	20.0	0.0	0.0	18-23% N	LIQ
24	AMMONIUM SULFATE	21.0	0.0	0.0	20-21% N	DRY
25	AMM SUL SOLUTION	6.0	0.0	0.0		LIQ
27	AMMONIUM SUL-NIT	26.0	0.0	0.0		DRY,LIQ
29	AMMONIUM SUL-UREA	33.5	0.0	0.0	33-34% N	DRY
31	AMMONIUM THIOSUL	12.0	0.0	0.0		LIQ
35	CALCIUM AMM NIT	17.0	0.0	0.0	17-20.5% N	DRY,LIQ
38	CALCIUM CYANAM	20.5	0.0	0.0		DRY,LIQ
43	CALCIUM NITRATE	15.5	0.0	0.0	15-15.5% N	DRY,LIQ
46	CALCIUM NIT-UREA	33.8	0.0	0.0	30-35% N	DRY
50	FERROUS AMM-SUL	7.0	0.0	0.0	14% FE, 16% S	DRY
52	MAGNE- SIUM NIT	7.1	0.0	0.0	6.6% MG	LIQ
54	NITRIC ACID	15.0	0.0	0.0		LIQ
56	NITROGEN SOL <28%	0.0	0.0	0.0	<28% N	LIQ
58	NITROGEN SOL 28%	28.0	0.0	0.0	28-29.9% N	LIQ
59	NITROGEN SOL 30%	30.0	0.0	0.0	30-31.9% N	LIQ
60	NITROGEN SOL 32%	32.0	0.0	0.0	32-32.9% N	LIQ
61	NITROGEN SOL >32%	0.0	0.0	0.0	>32% N	LIQ
62	SODIUM NITRATE	16.0	0.0	0.0		DRY
64	SUL CTD UREA	36.0	0.0	0.0	36-38%N	DRY
66	UREA	46.0	0.0	0.0	45-46% N	DRY
67	UREA SOLUTION	20.0	0.0	0.0		LIQ
68	UREA- FORM	38.0	0.0	0.0	35-40% N	DRY
73	ZINC AMM SUL SOL	10.0	0.0	0.0	10-15% N, 10% Z, 5% S	LIQ
77	ZINC MAN AMM SUL	9.0	0.0	0.0		LIQ,DRY
97	NITROGEN NO CODE	0.0	0.0	0.0	2-44% N	DRY,LIQ
98	NITROGEN NO ID	0.0	0.0	0.0	2-44% N	DRY,LIQ
201	AMMONIUM METAPHOS	12.0	51.0	0.0		DRY
202	AMMONIUM PHOS	11.0	48.0	0.0		DRY
203	DAP	18.0	46.0	0.0	18-21% N, 46-54% P2O5	DRY
204	AMMONIUM POLY	15.0	60.0	0.0		DRY,LIQ
205	LIME PHOS	0.0	0.0	0.0	5-37% P2O5	DRY
206	AMM PHOS NITRATE	27.0	14.0	0.0		DRY
207	AMM PHOS SULFATE	16.0	20.0	0.0		DRY,LIQ
208	BASIC SLAG	0.0	9.0	0.0	8-10% P2O5	DRY
209	MONOAMM PHOS	11.0	52.0	0.0		DRY
212	BONE BLK SPENT	1.0	33.0	0.0		DRY
214	RAW BONE MEAL	3.9	22.0	0.0		DRY
216	STM BONE MEAL	2.2	27.0	0.0		DRY
218	BONE PRECIP	0.0	35.0	0.0	28-45% P2O5	DRY
223	CALCIUM METAPHOS	0.0	60.0	0.0	60-62% P2O5	DRY
228	COLLOID PHOS	0.0	2.0	0.0	2-8% P2O5	DRY
233	PHOS LIMESTNE	0.0	13.0	0.0	13-14% P2O5	DRY
238	MAG PHOS	0.0	18.0	0.0	17-18% P2O5	DRY

Table 6: Fertilizer Code Listing(Continued)

CODE	NAME	N	P2O5	K2O	RANGE	CONTAINER
241	NITRIC PHOS	0.0	0.0	0.0	14-22% N, 10-22% P2O5	DRY
243	PHOS ROCK	0.0	3.0	0.0	2-4% P2O5	DRY
248	PHOS ACID	0.0	54.0	0.0	2-75% P2O5	LIQ
249	LIQ AMM POLY	10.0	34.0	0.0	5-12% N, 17-37% P2O5	LIQ
253	PRECIP PHOS	0.0	35.0	0.0	24-45% P2O5	DRY
263	NORMAL SUPER	0.0	22.0	0.0	18-22% P2O5	DRY
265	ENRICHED SUPER	0.0	23.0	0.0	23-39% P2O5	DRY

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267	TRIPLE SUPER	0.0	46.0	0.0	40-54% P2O5	DRY
273	SUPER PHOS ACD	0.0	68.0	0.0	68-75% P2O5	LIQ
297	PHOS NO CODE	0.0	0.0	0.0	1-75% P2O5	DRY,LIQ
298	PHOS NO ID	0.0	0.0	0.0	1-75% P2O5	DRY,LIQ
408	LIME-POT MIXTURES	0.0	0.0	10.0	5-10% K2O	DRY
413	MANURE SALTS	0.0	0.0	20.0	20-30% K2O	DRY
415	POTASH SUSP	0.0	0.0	0.0		LIQ
423	POT CARBON	0.0	0.0	64.0	52-69% K2O	DRY,LIQ
428	MUR OF POT 60%	0.0	0.0	60.0	59-61% K2O	DRY
430	MUR OF POT 62%	0.0	0.0	62.0		DRY
443	POT-MAG SULFATE	0.0	0.0	22.0	21-28% K2O	DRY
448	POT METAPHOS	0.0	55.0	37.0		DRY
453	POT NITRATE	14.0	0.0	44.0	12-14% N, 44-46% K2O	DRY
458	POT-SOD NITRATE	15.0	0.0	14.0		DRY,LIQ
463	POT SULFATE	0.0	0.0	50.0	48-52% K2O	DRY
478	TOBACCO STEMS	2.0	0.0	6.0		DRY
497	POTASH NO CODE	0.0	0.0	0.0	0-47% K2O	DRY,LIQ
498	POTASH NO ID	0.0	0.0	0.0	0-47% K2O	DRY,LIQ
601	DRIED BLOOD	12.0	0.0	0.0		DRY
604	CASTOR POMACE	5.0	1.0	1.0		DRY
607	COCOA SH MEAL	2.5	1.0	2.0		DRY
610	COCOA TANKAGE	4.0	1.5	2.0		DRY
613	COMPOST	2.0	2.0	1.0		DRY
615	COT SEED MEAL	6.4	2.0	1.0		DRY
617	FISH SCRAP	6.0	6.0	6.0		DRY
629	GUANO	12.0	11.0	2.0		DRY
649	MANURE	0.5	0.5	0.5		DRY
652	PEAT	1.9	0.2	0.2		DRY
661	ACT SEW SLUDGE	6.0	2.0	2.0		DRY,LIQ
663	DIG SEW SLUDGE	10.0	2.0	0.0		DRY
665	HT DRIED SEW SLGE	6.0	2.0	2.0	3-7% N, 1-7% P2O5, 1-2% K2O	DRY
667	OTH SEW SLUDGE	6.0	2.0	1.0		DRY,LIQ
671	SOYBEAN MEAL	6.0	1.0	2.0		DRY
673	ANIMAL TANKAGE	8.1	5.3	5.9		DRY
675	PROCESS TANKAGE	7.8	0.0	0.0		DRY
681	LINSEED MEAL	5.6	2.0	1.0		DRY
685	TUNG PUMACE	8.0	2.0	2.0		DRY
697	NAT ORG NO CODE	0.0	0.0	0.0		DRY
698	NAT ORG NO ID	0.0	0.0	0.0		DRY
702	ALUMINUM SULFATE	0.0	0.0	0.0		DRY
706	BORAX	0.0	0.0	0.0		DRY
710	BRUCITE	0.0	0.0	0.0		DRY
714	COBALT SULFATE	0.0	0.0	0.0		DRY
716	BLK COP OXIDE	0.0	0.0	0.0		DRY
717	RED COP OXIDE	0.0	0.0	0.0		DRY

Table 6: Fertilizer Code Listing(Continued)

CODE	NAME	N	P2O5	K2O	RANGE	CONTAINER
720	COPPER SULFATE	0.0	0.0	0.0		DRY,LIQ
722	COPPER CHELATE	0.0	0.0	0.0		LIQ,DRY
723	COPPER COMPOUND	0.0	0.0	0.0		LIQ,DRY
724	FERRIC OXIDE	0.0	0.0	0.0		DRY
726	FERRIC SULFATE	0.0	0.0	0.0		DRY
728	FERROUS SULFATE	0.0	0.0	0.0		DRY
730	IRON CHELATE	0.0	0.0	0.0		DRY,LIQ
731	IRON COMPOUND	0.0	0.0	0.0		DRY,LIQ
732	GYPSUM	0.0	0.0	0.0		DRY
733	CALCIUM CHELATE	0.0	0.0	0.0		DRY,LIQ
734	CALCIUM SUL (HY)	0.0	0.0	0.0		LIQ,DRY
736	LIME SUL SOLUTION	0.0	0.0	0.0		LIQ
742	MAGNESIA	0.0	0.0	0.0		DRY
744	EPSOM SALT	0.0	0.0	0.0		DRY
745	MAG CHELATE	0.0	0.0	0.0		DRY,LIQ
748	MANGAN AGSTONE	0.0	0.0	0.0		DRY
749	MANGAN CHELATE	0.0	0.0	0.0		DRY,LIQ

750	MANGAN OXIDE	0.0	0.0	0.0	DRY
752	MANGAN SLAG	0.0	0.0	0.0	DRY
754	MANGAN SULFATE	0.0	0.0	0.0	DRY
758	MANGAN OXIDE	0.0	0.0	0.0	DRY
762	MOLY	0.0	0.0	0.0	DRY
764	SOIL AMENDMNT	0.0	0.0	0.0	DRY,LIQ
765	SOIL ADDITIVE	0.0	0.0	0.0	DRY,LIQ
766	SOIL COND	0.0	0.0	0.0	DRY,LIQ
767	POTTING SOIL	0.0	0.0	0.0	DRY
770	SULFUR	0.0	0.0	0.0	DRY,LIQ
773	CALCIUM CHLORIDE	0.0	0.0	0.0	DRY,LIQ
774	SULFURIC ACID	0.0	0.0	0.0	LIQ
778	ZINC OXIDE	0.0	0.0	0.0	DRY
780	ZINC OXY SULFATE	0.0	0.0	0.0	DRY
782	ZINC SULFATE	0.0	0.0	0.0	DRY
783	ZINC SUL SOLUTION	0.0	0.0	0.0	LIQ
784	ZINC CHELATE	0.0	0.0	0.0	DRY,LIQ
797	SEC/MIC NO CODE	0.0	0.0	0.0	DRY,LIQ
798	SEC/MIC NO ID	0.0	0.0	0.0	DRY,LIQ
901	CALCIUM OXIDE	0.0	0.0	0.0	DRY
902	CALCIUM HYDROX	0.0	0.0	0.0	DRY
903	DOLOMITE	0.0	0.0	0.0	DRY
904	DOLOMITE 75% NEUT	0.0	0.0	0.0	DRY,LIQ
905	STD CALCITE	0.0	0.0	0.0	DRY
906	CALCITIC 75% NEUT	0.0	0.0	0.0	DRY,LIQ
907	LIME NO CODE	0.0	0.0	0.0	DRY
908	LIME NO GRADE	0.0	0.0	0.0	DRY,LIQ
910	DOL/CAL BLEND	0.0	0.0	0.0	DRY
912	LIME SUSP	0.0	0.0	0.0	LIQ
915	NON-LIME FILLER	0.0	0.0	0.0	DRY,LIQ
978	FERT NO ID	0.0	0.0	0.0	DRY,LIQ
988	SGLE-NUT NO ID	0.0	0.0	0.0	DRY,LIQ
990	SPCIALTY NO GRADE	0.0	0.0	0.0	DRY,LIQ
998	MULT-NUT NO GRADE	0.0	0.0	0.0	DRY,LIQ

Update: 07/27/99-9:13 AM

North Carolina State University is a land-grant university and a constituent institution of The University of North Carolina

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919.515.3711
919.515.7802 (fax)

April 26, 1999

Mr. Dallas W. Safriet
US EPA
MD-32
Research Triangle Park, NC 27711

Subject: **Workshop on Atmospheric Nitrogen Compounds II: Emissions, Transport, Transformation, Deposition and Assessment, June 7-9 1999, The Friday Center, Chapel Hill, NC**

Web Site: http://www2.ncsu.edu/ncsu/CIL/WRRI/nitrowork.html

Dear Mr. Safriet:

I invite you and your staff to participate in the Workshop on "Atmospheric Nitrogen Compounds II: Emissions, Transport, Transformation, Deposition and Assessment". Enclosed please find the agenda for the workshop. The workshop will begin at 7:30 A.M. on Monday, June 7, 1999, and conclude at 12:00 P.M. on Wednesday, June 9, 1999. The workshop will be held at the Friday Center, Chapel Hill, NC. Additional information may be obtained at the workshop web site provided above.

As you are well aware, the Neuse and other rivers in North Carolina are suffering under increasing loads of nitrogen. While much of the focus has been on direct runoff and overflow, there is evidence that nitrogen compounds are making their way into the watersheds by way of atmospheric deposition. To evaluate the situation, the workshop is planned as an open forum at which investigators and researchers evaluating atmospheric nitrogen deposition can share current knowledge with other North Carolina, national and international researchers and discuss approaches to studying atmospheric nitrogen deposition. Researchers, policy makers, industry representatives and others interested in the technical aspects of evaluating atmospheric nitrogen deposition may find the workshop of interest.

Please complete your registration form and mail it to the address provided along with the registration fee as soon as possible. As part of your registration a continental breakfast will be available each day; and a buffet lunch will be served on Monday and Tuesday, and dinner on Tuesday. We will publish a Proceedings containing 5 to 10 pages extended abstract of the presentation, and a summary of the panel discussions.

We look forward to your participation. If I can be of any further assistance, please feel free to contact me at my office (919-515-7808) or via FAX (919-515-7802).

Sincerely,

Viney Pal Aneja
Research Professor

Enclosure

United States Department of Agriculture | Agricultural Research Service | Beltsville Area Beltsville Agricultural Research Center | Beltsville, Maryland 20705

Mr. Dallas W. Safriet
U.S. Environmental Protection Agency
Emission Factor & Invent. Grp. (MD-14)
Research Triangle Park, NC 27711

March 3, 1999

Dear Mr. Safriet:

Enclosed are my review thoughts for the draft copy of Section 9.2.1 Fertilizer Application Emission Factors being considered for publication in "Compilation of Air Pollutant Emission Factors, AP-42".

The core of the problem is well stated in the draft report: "actual fertilizer emission test reports for NH3, NOx, and N2O do not exit" (p.4-1, sect. 4.1, par. 2), therefore estimates from the scientific literature are needed.

My over-all recommendations are: i.) to revise and restructure the approach for estimating emission factors for fertilizers by using 'expert panels', and ii.) to re-evaluate the relevant literature to obtain 'expert consensus estimates' of fertilizer emission factors. I believe it is important to glean the best fertilizer emission factors possible out of the scientific literature, this difficult task will require the interaction of several knowledgeable scientists with enough experience to identify the most important relevant studies. The specific reasons and justifications for the above general recommendations are contained in the enclosures.

I have also included a short list of references that I consider relevant for estimating ammonia emission factors.

I am willing to interact with you, or others on your staff or in USDA, to discuss the above recommendations further. My telephone number is 301-504-5276, and my e-mail address is jmeising@asrr.arsusda.gov.

Sincerely,

J. J. Meisinger

J. J. Meisinger
Soil Scientist USDA-ARS
Environmental Chemistry Lab.
Beltsville, MD

cc: Elvis Graves USDA (MD-15) Liaison
Richard Amerman, USDA-ARS, Nat. Prog. Staff
Cathleen Hapeman, USDA-ARS, Research Leader ECL

Review of EPA Draft Report

"Emission Factor Documentation for AP-42
Section 9.2.1 Fertilizer Application"
dated June 1998

Detailed Review

1. This reviewer has some fundamental disagreements with the approaches used in developing Emission Factors for Fertilizer Applications contained in the above document. The basic problem is the fact that "actual fertilizer emission test reports for NH3, NOx, and N2O do not exit" (as per p.4-1, sect. 4.1, par. 2). Therefore, it is necessary to estimate emission factors from the technical scientific literature in refereed journals. Under these circumstances the selection criterion for including/excluding a candidate study is critical. The criterion cited in the draft document (p.3-1, sect. 3.1, par. 4) is inadequate, specifically:

"1. The report must be a primary reference:"

'a. Source testing must be from a study that does not reiterate information from previous studies.'

Problem: This puts heavy, almost sole, emphasis on the first studies in a given area. The early studies are typically 'pioneering studies' which usually document the relative size of a process and the conditions contributing to losses. But the best quantitative estimates of these processes usually are done in second- and third-generation studies which use improved instrumentation, optimal experimental conditions, and a more in-depth interpretation of results because the scientific knowledge of the process is better understood by the broader scientific community.

'b. The document must constitute the original source of test data.'

Problem: This again puts sole emphasis on the first studies, which are usually not the most accurate or well-conducted studies, for the same reasons as given above for item 1.a above.

"2. The referenced study must contain test results based on more than one test run."

Problem: In general this is a sound basis for evaluation because it is basically calling for replicated studies in space and/or replications in time. However, some very good studies, by their very nature, do not lend themselves to replication, e.g. watershed studies, micrometeorology studies, and any studies encountering unique environmental conditions that enhance or limit the process under study (hydrologic events, soil conditions, etc.). Therefore, it should be desirable to have replicated studies but it should not be a basis for exclusion.

"3. The report must contain sufficient data to evaluate the testing procedures and source operating conditions."

Problem: Most research scientists perform studies using methods that are: generally accepted by the scientific community at that point in time, or use new and innovative methods that either pass or fail "the test of time", or use methods that are justified for the unique soil and environmental conditions of their study. Thus,

the evaluation of the testing procedures and source operating conditions is usually not a primary objective of environmental research scientists. However, the adequacy of methods used in a given study should meet the criterion that the process under investigation is studied by an unbiased and valid procedure which allows estimation of the appropriate emission factor. Many studies simply employ 'common knowledge best methods' which are understood within the research community, but may appear to be unsubstantiated to non-scientists.

2. The second basis for disagreeing with the approaches used in developing Emission Factors for Fertilizer Applications centers on the fact that any fertilizer emission factors for latent emissions of NH3, NOx, and N2O will be highly dependent on a unique set of physical-chemical-biological-weather conditions that interact with each other and the environment over time. That is, the unique soil conditions (pH, cation exchange capacity, soil water regime, microbial activity, etc.), weather conditions (rainfall and/or irrigation, temperature, evaporative potential, etc.), fertilizer management factors (placement, timing in relation to crop need, use of inhibitors, etc.), and actual N source (gaseous NH3, liquid urea-ammonium-nitrate (UAN), solid urea, etc.) all interact with each other and the environment over time to produce the final NH3, NOx, or N2O losses being studied or being estimated by the proposed emission factor.

There is no clear-cut solution to this problem, except to clearly delineate the major soil-climate-management factors affecting emissions and to produce 'best estimates' of applicable emission factors classified according to (or based upon) important site variables as determined by 'expert knowledge/opinion'.

3. Other disconcerting areas to this reviewer are:

i) the frequent use of non-traditional, or minor use, fertilizers (NaNO3, Ca(NO3)2, NH4Cl) in the development of emission factors (which may/may not relate) to emissions for the major use fertilizers of liquid anhydrous ammonia, or UAN, or solid urea or ammonium nitrate;

ii) the lack of recognition of fertilizer placement/application method (soil injection, irrigation applications) as a major factor in NH3 losses, especially for urea containing fertilizers;

iii) the decided preference for closed flux chambers for quantitative estimates of all gases (p.3-5, sect. 3.4.1.3, par. 1) when there are strong arguments that the best quantitative estimates of 'real world' emissions are micro-meteorology based studies (although there are some emissions which must be studied by chamber methods); and

iv) the lack of recognition of basic soil properties (pH, drainage, CEC) or water management properties (irrigation, flooded rice, dryland, etc) in affecting NH3, NOx, and/or N2O emissions.

Overview

The above points are not intended to be negative. Rather, they are offered to clarify the situation and to point out the fact that simple emission factors will be very difficult parameters to estimate because of they are an over-simplification of a complex and dynamic system.

Fertilizer emission factors for NH3, NOx, and N2O will necessarily have to be evaluated over a wide range of environmental conditions and summarized according to some type of environmental-management loss-ranking system. Most (if not all) of the scientific literature has studied gaseous N cycle losses for the common agricultural conditions of a given (sometimes unique) area using the experimental approaches appropriate for the financial base supporting the project. These circumstances always lead to a wide range in data quality with some studies using sophisticated equipment on very narrowly applicable environments, and other studies using less elegant approaches on problems that are wide-spread and very important. Despite the above problems, society has asked for air quality improvements and the scientific community should contribute to the development of the best emission factors possible.

Therefore, my suggestion is to convene an 'expert panel' of 3-5 experienced and widely knowledgeable scientists to review and evaluate the scientific literature with the required goal of determining the dominant variables affecting emission factors and to produce an 'expert consensus estimate' of appropriate fertilizer emission factors. A separate 'expert panel' should be constructed for NH3, for NOx, and for N2O because each gaseous species is produced from different and unique soil-fertilizer N transformations extending over different time scales. Some type of small grant may have to be offered as "carrots" to attract the best people, because the best people are usually already busy.

A few Ammonia Emission
References Worth Considering
(in no particular order)

J. J. Meisinger

Sherlock, R.R., J. R. Freney, N.P. Smith, and K.C. Cameron. 1989. Evaluation of a sampler for assessing ammonia losses from fertilized fields. Fertilizer Research 21:61-66.

Black, A.S., R.R. Sherlock, K.C. Cameron, N.P. Smith and K. M. Goh. 1985. Comparison of three field methods for measuring ammonia volatilization from urea granules broadcast on to a pasture. J Soil Sci. 36:271-280.

Wilson, J. D., V. R. Catchpoole, O. T. Denmead, and G. W. Thurtell. 1983. Verification of a simple micrometeorological method for estimating the rate of gaseous mass transfer from the ground to the atmosphere. Agric. Meteorology 29:183-189.

Ryden, J. C. and D. R. Lockyer. 1985. Evaluation of a system of wind tunnels for field studies of ammonia loss from grassland through volatilization. J. Sci. Food Agric. 36: 781-788.

Gui-xin, C., Z. Zhao-liang, A.C. F. Trevitt, J. R. Freney and J. R. Simpson. 1986. Nitrogen loss from ammonium bicarbonate and urea fertilizers applied to flooded rice. Fertilizer Res. 10:203-215.

DeDatta, S. K., A. C. F. Trevitt, J. R. Freney, W. N. Obcemea, J. G. Real, and J. R. Simpson. 1989. Measuring nitrogen losses from lowland rice using bulk aerodynamic and nitrogen-15 balance methods. Soil Sc. Soc. Am. J. 53:1275-1281.

Freney, J. R. J. R. Simpson, O. T. Denmead W. A. Muirhead and R. Leuning. 1985. Transformations and transfers of N after irrigating a cracking clay soil with a urea solution. Aust. J Agric. Res. 36:685-694.

Hargrove, W. L., D. E. Kissel and L. B. Fenn. 1977. Field measurements of ammonia volatilization from surface applications of ammonium salts to a calcareous soil. Agron. J. 69:473-476.

Kissel D. E., H.L. Brewer and G. F. Arkin. 1977. Design and test of a field sampler for ammonia volatilization. Soil Sc. Soc. Am. J. 41:1133-1138.

Marshall, V.G. and D.S. DeBell. 1980. Comparison of four methods of measuring volatilization losses of N following urea fertilization of forest soils. Can. J. Soil Sci 60:549-563.

Volk, G.M. 1959. Volatile loss of ammonia following surface application of urea to turf or bare soils. Agron. J. 51:746-749.

Miyamoto, S., J. Ryan and J. L. Stroehlein. 1975.Sulfuric acid for the treatment of ammoniated irrigation water: I. reducing ammonia volatilization. Soil Sc. Soc. Am. J. 39:544-548.

Hansen, C. H., M. M. Mortland and L. S. Robertson. 1957. A technique to determined volatilization losses in the application of fertilizers which contain free ammonia. Mich. Agr Expt. Stn. Quart. Bulletin. 39:495-499.

Mikkelsen, D.S., S. K. DeDatta and W. N. Obcemea. 1978. Ammonia volatilization losses from flooded rice soils. Soil Sc. Soc. Am. J. 42:725-730.

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March 31, 1999

Dallas W. Seifert
Environmental Engineer
US-EPA
Research Triangle Park, NC 27711

Dear Dallas:

Enclosed are review comments pertaining to Section 9.2.1 of the *Compilation of Air Pollutant Factors, AP-42*. Although the document is well organized and provides useful information, several issues need to be addressed. Because of the emerging concerns regarding agriculturally related N emissions to the atmosphere, the research community has increased efforts in the last five years to quantify sources and management impacts. The most recent reference used in this document is dated 1996, which means the research was likely conducted in the early 1990's. I would recommend that US-EPA continually update this document to reflect current literature. I have provided some excellent examples of contemporary research. We would welcome participating with US-EPA on a revision process that would result in improved estimates of agriculturally related N emissions to the atmosphere.

In addition, the document indicates that little research is available on N volatilization and soil and N management effects on volatilization. This area of research was intensely active from 1970 to 1990 and many references are available. I would be happy to provide these references or a review of the current literature if needed. This document could be dramatically improved with inclusion of these data and references.

I also have included a copy of selected pages in the standard soil fertility textbook used throughout the US and Canada that provides pertinent information on the terminology and definitions of nutrient placement options. AP-42 should be changed to reflect this terminology.

Thank you for the opportunity to review AP-42 and I hope my comments are helpful. If you have any questions please do not hesitate to call.

Sincerely:

John L. Havlin
Professor and Head

Comments

Page 2-2; 3rd line:	Sentence does not represent fact. Significant literature exists for volatilization of NH_3 from fertilizers. Gaseous emissions of H_2S, SO_2, etc. from fertilizers is substantially lower than that emitted from global volcanic activity and large animals (incl. humans), that we could/should ignore it.
Page 2-3; 2nd para: Last line	Replace "*....on the tilling trailer*" with "*...applicator*".
Page 2-4; 2nd para:	The description of fertilizer or nutrient placement methods is confusing and should conform to current terminology and definitions. [See Havlin, Beaton, Tisdale, & Nelson (1998), *Soil Fertility and Fertilizers,* pg. 370.] The correct terminology is designed to separate applications *before, at,* and *after* planting into *surface broadcast, surface band,* and *subsurface band*. The term "band: includes with the seed at planting as well as below the seed *before, at,* and *after planting*. Conformation to these definitions will avoid confusion.
Page 2-5; 4th para: 1st line	First sentence should read "Solid fertilizers can be broadcast applied by high flotation applicators or by aircraft".
Page 2-5; 4th para: 3rd & 4th line	Although herbicides can be applied with fertilizers, "frequently" is an overstatement. Most herbicides (>90%) are applied separately.
Page 2-8; 2nd para: 2nd line	Replace "*....determine the soil reaction rates.*" With "*....determine the transformation rates for these elements in soil*".
Page 2-9; 1st para: 1st line	Replace "*...reduces nitrate to nitrogen.....*" with "*...reduces nitrate to nitrogen gas(es).....*".
Page 2-12; 2nd para: 2nd line	Replace "(*e.g. urea, ammonium nitrate*)" with "(*e.g. urea, urea ammonium nitrate*)".
Page 2-12; 4th para: 2nd line	Replace "*..is applied to the subsurface will..*" with "*..is subsurface applied will ...*".
Page 2-13; 1st para:	Substantial literature is available on N management practices to enhance or reduce NH_3 volatilization.
Page 2-13; 3rd para:	In most cases (esp. with urea or urea- or NH_4-based fertilizers), volatilization losses can substantially exceed denitrification losses, except under reducing conditions as described in previous section. The 1st sentence is somewhat misleading in this regard.
Section 4.1	Although several citations received a "D" rating, the data are still considered representative of emission levels. Substantial research has been conducted

since the 1st draft was written (I reviewed 1st draft in 1995 or 1996) and may expand and enhance the reliability of the report. Are there plans for an update? (several important recent data sets are included)

Sect. 9.2.1.2; 2nd para: Majority of NH_3 is applied by the producer/operator, although most dealers offer this service.

Sect. 9.2.1.2; 5th para: Majority of fluid fertilizers are subsurface or surface band applied.

Sect. 9.2.1-2: Section number is identified as 9.6.1-2 and should be 9.2.1-2. Numbering scheme is confusing. Started with 9.2.1 with subsections of 9.2.1.1 through 9.2.1.3. Next section "EMISSION FACTORS" is identified as 9.6.1-4 and should be 9.2.1-2 ?? Was 9.2.1-1 "**Fertilizer Application**" ?? Where does 9.6 come from ??

Sect.9.2.1-4: last para: In the 1st sentence what does fertilizer "type" refer to....liquid, solid, gases??? Fertilizer "type" can be interpreted as "source or form". Fertilizer type, source or form can influence nutrient emission losses. Thus, the remaining nutrient management factors are rate, placement, and timing. Additions to fertilizers (coatings on solids or additives to fluids) can reduce losses. Thus the last sentence should read "In other words, the fertilizer form, rate, timing, and placement is the best available control of emissions of fertilizer nutrients applied to soils."

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
NATIONAL EXPOSURE RESEARCH LABORATORY
Research Triangle Park, NC 27711

Office of
Research and Development

April 6, 1999

MEMORANDUM

SUBJECT: Review of the Draft AP-42 Section, "Fertilizer Application"

FROM: Thomas E. Pierce
Atmospheric Modeling Division (MD-80)

TO: Dallas Safriet (MD-14)
Emission Factor and Inventory Group, OAQPS

Thank you for giving me an opportunity to review the draft AP-42 section on fertilizer application. My perspective is that of an air quality modeler, who is keenly interested in modeling the temporally-varying biogenic fluxes of VOCs, NO, and NH3. Fertilized soils present a special challenge. They are neither anthropogenic nor natural. They are perturbed by human influences, notably the application of nitrogen-based fertilizer that enhances microbial activity. Emissions can be very sporadic, peaking but continuing in a diminishing mode after the application of fertilizer. Emissions vary considerably depending on soil moisture, soil temperature, presence or absence of vegetation, and ambient air concentrations of NO and NH3. Because of these complications, developing tabular values of annual emission rates as a function of fertilizer amounts is a daunting task.

The draft document does a reasonable job performing this task. I found the descriptions of the different types of fertilizer and the equipment to be quite informative. Other comments on the document are given below.

NH3 emissions:

I was surprised that the Batteye report was not referenced nor were there many references from the Batteye report. In my opinion, the Batteye report did a decent job summarizing the literature and its emission factors agree more or less with those assumed by the Global Emissions Inventory Activity (GEIA).

NO emissions:

Reference #19 (Anderson and Levine) probably should not have been rejected, as it includes some information on fertilizer application. Its abstract states "Of the 196.4 kg ha-1 of fertilizer added to the soil site being studied, 0.79% was lost as NO(N), and 1.2% was lost as N2O(N)."

Here are some more references that probably should be added to the literature review:

R. Harrison et al., "Effect on fertilizer application on NO and N2O fluxes from agricultural fields", J. Geophysical Research, vol. 100, pp. 25923-25931, 1995.

It includes measurements from fertilized plots in England.

P. Matson et al., "Fertilization practices and soil variations control nitrogen oxide emissions from tropical sugar cane", J. Geophysical Research, vol. 101, pp. 18533-18545, 1996.

It includes measurements from fertilized fields in Hawaii.

F. Thornton et al., "NO emissions from soil in the southeastern United States", J. Geophysical Research, vol. 102, pp. 21189-21195, 1997.

This is probably a more complete reference than the other Thornton papers referenced in the AP-42 document.

V. Aneja et al., "Contribution of biogenic nitric oxide in urban ozone: Raleigh, NC, as a case study", Atmospheric Environment, vol. 31, pp. 1531-1537, 1997.

It includes measurements made over fertilized lawns and golf courses.

General comments:

The emission of NO, N2O, and NH3 from fertilized soils is very dynamic, depending not only on the amount and type of nitrogen-based fertilizer but also on environmental factors such as soil temperature, water filled pore space, soil texture, vegetation, and ambient concentrations of NH3 and NO. Fluxes of NH3 and NO can be bidirectional and it is dangerous to assign a "one size fits all" emission factor based on the amount of applied fertilizer. Because current emission algorithms do not adequately incorporate environmental factors, the emission factors

of NO and NH3 for fertilized soils should be assigned a high degree of uncertainty.

The AP-42 guidance should advise readers to be wary of double counting if they are also using a biogenic emission algorithm, such as BEIS2. BEIS2 computes emissions from fertilized and uncultivated soils, with most NO emissions coming from fertilized soils.

If you have any questions regarding this review, please give me a holler. You may reach me at pierce.tom@epa.gov or 919/541-1375.

July 29, 1993

TO: Dallas Safriet

FROM: Roy Neulicht RN

RE: Trip Report for Soil NOx Workshop

Attached is John Kinsey's trip report for the Soil NOx workshop. The "additional data" that John is referring to as possibly available is the data mentioned on page 14 of the SOS summary report. On page 14, Ray Valente and Frank Thornton of TVA indicate they have a database of up to 3500 chamber measurements; they are suggesting collaborative work by the SOS group using this database to refine NOx emission models. Some folks at TVA commented on the draft fertilizer report back in Decmeber, but I did not find any reference to available data in their comments.

cc
Joe McSorley

INTEROFFICE COMMUNICATION

MIDWEST RESEARCH INSTITUTE

July 27, 1993

To: Roy Neulicht and Margie Wickham-St. Germain

From: John Kinsey

Subject: Trip Report for Soil NO_x Workshop

On May 10, 1993, I attended a workshop sponsored by the Southern Oxidants Study (SOS) on the emissions of nitrogen oxides (NO_x) from soil. I was present for the first day of this two day workshop held in Denver, Colorado. During the workshop, I acted as an unofficial observer with the intent of gathering information on current research activities to support our emission factor work for the Emissions Inventory Branch (EIB) of EPA's Office of Air Quality Planning and Standards. Except for myself, the workshop was attended by representatives of various governmental agencies and laboratories as well as members of the academic community.

SOS sponsored the workshop in order to further their understanding of biogenic emissions, especially volatile organics and NO_x, which contribute to the formation of photochemical oxidants. The stated objectives of the workshop are summarized as follows:

(1) To develop a general consensus about the current state of knowledge relative to the contribution of soil-generated NO_x to the total emissions inventory in the southern U. S.;

(2) To discuss current measurement techniques used to estimate soil NO_x emissions, uncertainties associated with these measurements, and suggest research programs to improve emission estimates for use in atmospheric photochemical models;

(3) To identify funding needs and set priorities for future research; and

(4) To coordinate and, to the extent possible, collaborate on future research and modeling efforts.

During the first morning, formal presentations were made by various investigators on chamber and micrometeorological measurement methods, mechanisms of NO_x formation, the status of inventory and model development, and descriptions of current research programs. After lunch, each participant was asked to present a "If I Were King" statement which recommended future research directions and priorities. A copy of our "If I Were King" contribution is attached. This handout was prepared by Margie and I based on our work for EIB in the development of NO_x emission factors for nitrogen fertilizers.

On the second day of the workshop (which I did not attend), the participants prepared a summary of the proceedings as well as recommendations for future research. A copy of the final report from the workshop is also attached for your information.

A number of general observations were made from the portion of the SOS workshop which I attended. First, in the past there was not a great deal of coordination in the various research programs being conducted. Each agency had its own agenda with the Forest Service looking strictly at forest ecosystems, the Agriculture Research Service investigating croplands, etc. Most of these efforts were fundamental studies directed toward global climate change issues with some later interest in tropospheric ozone formation.

Another observation from the workshop is that soil NO_x emissions appear to be a significant contributor to the total emissions inventory in some parts of the U. S. There is, however, a substantial amount of uncertainty associated with the current emissions estimates, especially with respect to time-resolved pollutant generation. To date, only selected pollutants, soils, and environmental parameters have been investigated. Future research should be directed toward looking at all parameters and pollutants of interest.

Third, emission measurements made with chambers and micrometeorological systems have inherent limitations with respect to resolution and spatial extent. It was recommended in the final workshop report that these techniques be combined in the future and <u>all</u> atmospheric constituents, including reactive hydrocarbons and hydrogen peroxide, be monitored. However, long path instruments (e.g., FTIR, LIDAR, etc.) which are capable of directly measuring multiple species over large areas have <u>not</u> been traditionally used. Long path techniques offer a powerful tool to substantially improve emission estimates which should not be ignored in the future. (Note that the use of long path instruments is given only minor mention in the workshop recommendations.)

Finally, it appears that a substantial body of data may exist in the various agencies conducting the research which was not considered during our recent emission factor development effort for EIB. If such is indeed the case, it may be worthwhile to obtain and review this information to potentially improve the emission estimates. Also, due to the low quality of these emission factors, a decision should be made by EIB whether to publish the current estimates or to wait until better data become available.

In conclusion, I would recommend that EIB at least monitor the progress of the research program proposed as a result of the SOS workshop and provide input whenever and wherever possible. If the program is actually implemented, it might be at least 3 to 5 years before the results become available.

I would also recommend that a collaborative study be conducted involving all agencies involved in the research, including EIB, which would combine chamber, micrometeorological, and long path measurements. This could be done in conjunction with the National Center for Atmospheric Research's ASTER facility as proposed in the workshop report. If EIB were to become actively involved, I believe that the data could be converted to useful emission factors much more quickly than waiting for the other organizations to provide final results. MRI would, of course, be pleased to support EIB in this effort utilizing our expertise in long path FTIR and other related instrumentation.

If you have any questions regarding the above workshop, please give me a call.

SUMMARY
OF A
WORKSHOP ON EMISSIONS OF NO_X FROM SOILS

Held on
May 10 - 11, 1993
in
Denver, Colorado

Organized by

Southern Oxidants Research Program on Emissions and Effects
of the
Southern Oxidants Study

and

Atmospheric Research and Exposure Assessment Laboratory
of the
U.S. Environmental Protection Agency

INTRODUCTION

A Workshop on Emissions of NO_X From Soils, was held in Denver, Colorado on May 10-11, 1993. The workshop was sponsored by the Southern Oxidants Research Program on Emissions and Effects (SORP-EE), a part of the Southern Oxidants Study (SOS), in collaboration with the Atmospheric Research and Exposure Assessment Laboratory of the U.S. Environmental Protection Agency.

Interest by the Southern Oxidants Study, as well as other groups within EPA, in sponsoring this workshop has been stimulated by a growing scientific belief that emissions of NO_X from natural sources are not negligible, as has often been assumed in the past. Although natural sources of NO_X can be divided into two categories, lightning and soils, this workshop was planned to focus on soil NO_X. In order to better set priorities for research to investigate emissions of NO_X from soils, a better understanding of current research activities and assessment of the major uncertainties in scientific understanding of these emissions was deemed necessary. As a result, financial and personnel resources might also be used more efficiently, and duplication of effort avoided.

The workshop was organized to meet the following specific objectives:

1) To develop a general consensus about the current state of knowledge about emissions of NO_X from soils, especially from soils of land use types that contribute significantly, because of relatively high flux rates and/or relatively large land areas, to the total NO_X emissions inventory in the southern United States;

2) To discuss current methods used to estimate soil NO_X fluxes, assess the uncertainties associated with those measurement methods, and determine measurement programs that would most effectively improve the NO_X emission estimates that are used in atmospheric photochemical grid models;

3) To identify current and proposed funding needs and to set priorities for future research on NO_X emissions from soils in the southern United States; and

4) To coordinate and, to the extent possible, collaborate on current and future research and modeling efforts.

Invitations were extended to individuals from various universities, federal agencies, and private research organizations who are considered leading research scientists in the area of measurement or modeling of emissions of NO_X from soils and/or who represent a major sponsoring organization that has an ongoing interest in understanding soil NO_X emissions. The workshop was designed to allow exchange of information about research programs that are currently being funded or will be funded by major sponsors, research activities currently being undertaken by scientists with funding from other sources, and perceived priorities for research by both scientists and sponsors. The interchange was intended to foster collaboration among workshop attendees and enable organizations such as USDA, NOAA, EPRI, NASA, and EPA to assess priorities for their own research programs. The memorandum of invitation to workshop participants with tentative agenda and the list of workshop invitees with addresses are included as Appendix 1 and Appendix 2, respectively.

Several workshop participants agreed to make short presentations to encourage discussion of selected topics related to soil NO_X emissions, measurement, and modeling (see agenda included in Appendix 1). Copies of the overheads used by each presenter are included as Appendix 3.

MAJOR CONCLUSIONS FROM THE WORKSHOP

A number of general conclusions emerged as a result of the very productive discussions that took place during the workshop. The following statements attempt to summarize the consensus judgments of the scientific experts who participated.

(1) Current estimates of soil NO (nitric oxide) emissions indicate that soils contribute substantially to the total NO_x (NO and NO_2 [nitrogen dioxide]) budget, especially in rural areas and/or over fertilized lands during summer months. Globally, biogenic NO_x emissions are reported to be similar in magnitude to emissions from combustion sources; but in the highly industrialized U.S. the combustion source is by far the largest except in fertilized agricultural regions during the summer, when soil emissions may contribute 15% of the total NO_x flux to the atmosphere..

(2) Soil chamber methods are useful tools for performing both surveys and process-level studies of gross soil NO emissions important for model development. Comparisons among various soil chamber techniques show reasonable agreement. However, soil chamber measurements do not represent the net NO_x flux from the biosphere to the atmosphere, which is more appropriately determined by micrometeorological techniques.

(3) Current NO emission and atmospheric photochemical models incorporate an overly simplistic picture of the processes contributing to net NO_x flux to the atmosphere. Atmospheric models should incorporate the linked system of NO emissions, photochemistry of the lower atmosphere, and NO_2 and O_3 deposition (with the role of plants in those processes fully represented).

(4) NO emissions from soils are driven by many biological, chemical, and physical processes. The most robust parameters controlling those processes over many temporal and spatial scales are: soil N availability, soil O_2 availability, and soil temperature. In current emissions modeling, these factors have been represented by N fertilizer application rates, soil water content, and air temperature.

(5) Soils that have been dried and then wetted often yield a burst of NO emissions. In some ecosystems, the sum of these relatively brief pulses can be larger than the sum of the remaining long-term NO emission rates on an annual basis. Saturated soils emit negligible amounts of NO.

(6) Current evidence suggests that autotrophic microbial populations involved in nitrification processes are responsible for most of the soil NO emissions from soils in the South. The processes responsible for NO and nitrous oxide (N_2O) emission from soil are so tightly coupled that neither should be studied without simultaneous consideration of the possibility for interaction with the other.

(7) Although gaps currently exist in our knowledge of NO emissions from soils, understanding is sufficient to proceed with the use of mechanistic models of soil processes controlling NO emissions.

"IF I WERE KING OR QUEEN" STATEMENTS

To facilitate discussions during the workshop, participants were requested to prepare a one-page statement which outlined the research that each scientist (personally or collaboratively) would most like to accomplish or see accomplished during the next few years in an area of research related to emissions of NO_x from soils. It has proven both fun and productive in previous planning meetings of this sort to use these "If I were King or Queen" statements and the discussions they evoke as a means by which to assess priorities for research and to potentially identify a cadre of scientists that will be needed to get this research done in a timely way and at reasonable cost. Each one-page statement was requested to indicate the objectives, approach, approximate cost, and estimated time-frame for delivery of useful research results.

A few individuals who were unable to attend the workshop provided input by conveying a statement for consideration. The text of all of the submitted statements are included here.

Peter S. Bakwin – University of Colorado

The net atmosphere/surface exchange of NO_x is the difference between emissions (mostly NO) and deposition (mostly NO_2). Studies of atmosphere/surface exchange of NO_x have typically focused on only one of these processes at a time, and have been of two types: (1) observations of NO emissions from the surface using chambers or mass balance approaches, or (2) enclosure measurements of NO_2 uptake by various vegetative or abiotic surfaces. Neither type of work addresses directly the question of greatest interest to atmospheric chemists, which is quantification of the *net* flux of NO_x. For example, if a forest is cleared for agriculture the net flux of NO_x may change due to changes in soil emissions of NO and surface uptake of NO_2.

A few studies have attempted to approach this problem using eddy correlation (e.g. Delany et al., 1986), gradient/flux relationships (Bakwin et al., 1992), or atmosphere/biosphere exchange models (Jacob and Bakwin, 1991). However, direct observations of the net surface flux of NO_x over spatial (hectares) and time (days) scales that can be addressed with photochemical models have proven difficult because of the difficulty of making accurate and specific measurements of NO and NO_2 with sufficient time resolution for eddy correlation (i.e. several Hz). Furthermore, it has been shown that, since photochemical cycles interconvert NO and NO_2 on a time scale shorter than or comparable to the mixing time of the atmospheric surface layer, the flux of either NO or NO_2 at some height above the surface can be independent of the surface flux, while the flux of NO_x is conserved (Lenschow and Delany, 1987).

Recent developments have improved the situation with regard to direct observations of the atmosphere/exchange exchange of NO_x. In particular, conditional sampling, a micrometeorological method proposed by Businger and Oncley (1990) and developed by the NCAR/ASTER group, may be well suited to direct, continuous observations of NO_x exchange on a spatial scale of hectares. This method utilizes the difference in trace gas (NO_x) concentration carried by updrafts and downdrafts to derive the flux at the measurement height (e.g. several m above the local plant canopy). Fast response instruments are not required. Ambient NO would be converted to NO_2 by ambient or added O_3 within a continuous flow

conditional sampler, and total NO_X would be quantified as NO_2 using standard methods (photofragmentation to NO, detection of NO using O_3-chemiluminescence). Vertical profiles of NO, NO_2 and O_3 concentrations through the local plant canopy should be measured simultaneously to investigate surface uptake, and to quantify changes in NO_X and O_3 storage within the surface layer below the height of the flux measurement. The observations would be automated and could therefore be made continuously for an arbitrary period, to provide diurnal and seasonal fluxes of NO_X.

(References cited are available from the author)

Eric Davidson – Woods Hole Research Center

Starting from a global perspective, the biggest gap in our knowledge about soil emissions of NO is the sketchiness, and in some cases complete absence, of data from important biomes of the world. The highest emissions of NO from soil are from tropical savannas of Venezuela, but no other data have been published from other savanna regions, although a few studies have been conducted very recently and manuscripts are presumably being prepared. No studies have been published to my knowledge for deserts and semi-deserts, yet these arid ecosystems are likely candidates for large emissions of NO during brief rainy periods.

On a regional scale (such as the southeastern US upon which this workshop is focused), we lack means of relating spatial variation of ecosystems and their nutrient cycling characteristics with mechanistic models of N gas emissions. Most successful mechanistic models rely on two factors: (1) rates of N cycling (N availability) and (2) soil moisture. We know a lot about how soil moisture affects the ratios of emissions of NO, N_2O, and N_2 from soils and we can probably model soil moisture on a regional scale. But finding appropriate indicators of N availability or measures of N cycling that are robust and can be applied across widely varying soil types and ecosystem types remains problematic. I suggest an effort to create a GIS database on ecosystem types, soil types, N inputs from atmospheric deposition, N fertilization, agricultural and silvicultural management regimes, and rates of N mineralization and nitrification. Databases already exist for the southeastern US for all of these parameters but the rates of N mineralization and nitrification. New research would be needed to learn how to assign estimates of N cycling dynamics to the pixels created from the combinations of other factors in the GIS database. As a first cut, it might be sufficient to extract estimates of net nitrification from representative sites from the agronomy, forestry, and ecology literature. A small team of modelers and with field experience and GIS experts would conduct this work. The databases could be acquired and a crude model run within two years for about $300 K/yr. Model improvement and validation would continue for two to four years thereafter.

Predictions of NO emissions from a regional scale model would need validation for a carefully designed field sampling scheme. The sampling would need sufficient frequency (temporal) and replication (spatial) to characterize annual emissions of NO from representative sites. This work would be carried out by numerous independent investigators throughout the region. To make their work more interesting and to take advantage of their innovations, these investigators would also be encouraged to design their work to address controlling factors at both the field scale and the landscape scale within their study locations. Five to ten teams might be assembled, and each team granted $150 K/yr for 3 years. Finally, if numerous investigators are involved in field flux measurements, an intercomparison would need to be

organized in order to assure that the data generated are free of biases that result from artifacts of individual measurement designs. This project would be organized by one PI at a cost of $100 K and would be conducted towards the end of the first year of the other grants.

Anthony Delany – National Center for Atmospheric Research

To understand the relationship between the actual NO_x surface flux and the effective NO_x flux to the atmosphere, it is necessary to understand the interaction between the turbulent transport and the atmospheric chemistry of NO and NO_2. I propose that we undertake a comprehensive study to determine this interaction. The profiles of the fluxes and the means of NO, NO_2, and O_3, together with the necessary additional atmospheric chemistry measurements to define the local atmospheric chemical environment need to be determined for a fertilized crop. The project will need full micrometeorological support and I propose that the study be based on the NCAR ASTER facility. The facility can provide the micrometeorological sensors and can support all the chemical sensors.

Weigang Gao and Marvin L. Wesely – Argonne National Laboratory

1. **Background.** Our numerical studies show that NO emitted from soil can be quickly converted to NO_2, which in turn deposits at the Earth's surface. The two-way transport modulated by rapid in-air chemistry near the NO sources appears to lead to a reduction in net upward NO_x transport. This flux change due to chemistry in the lower atmosphere above the surface is not currently considered in large scale models and should be parameterized to estimate the net NO_x flux into the lower atmosphere. We have conducted numerical simulations of flux profiles in the atmospheric boundary layer and in a forest canopy by using a coupled turbulence-chemistry model. In the forest, photochemical processes are substantially weakened, and the NO to NO_2 conversion rate is enhanced. The upward NO flux at the canopy top is much smaller than at the forest floor. To estimate the magnitude of NO_x flux that actually enters the atmosphere, it is necessary to combine measurements at the surface and modeling of chemical modification in near-surface atmosphere.

2. **Objectives**: To estimate vertical changes of NO_x flux in the region from soil surface to the lower atmosphere above the soil or canopy surfaces using numerical models and field measurements at representative land use types.

3. **Approaches**:

Measurements: Three sets of simultaneous measurements would be needed: soil chamber measurement of NO flux from soil; measurements of NO_x fluxes at one or two heights within 10 m above the surface, and the mean concentrations of NO, NO_2, O_3, at a flux measurement height above the surface and basic micrometeorological conditions.

Modeling: Two types of numerical modeling would be carried out: (1) modeling with a simplified NO-NO_2-O_3 chemical cycle, and (2) modeling with more complete chemistry including potential influences of biogenic nonmethane hydrocarbons that might be present. Simulations would use field data as inputs and as diagnostic variables to evaluate changes of NO_x fluxes above the surface.

Scenarios: We need to carry out this research for representative types of chemical conditions and land use. Initially, studies for grassland and deciduous forest would be feasible at the Argonne experimental site and the Oak Ridge Environmental Research Park.

4. **Estimated Cost and Time Frame:** Field measurements could be kept simple because much of results would be derived from numerical modeling. Approximately 12 months of effort would be needed for field measurements at the Argonne grassland site and for associated modeling study. For the forest site, approximately 18 months of effort would be needed. Existing instrumentation and models could be used.

5. **Deliverable Results:** The proposed research would provide a good estimate of changes of NO_x fluxes in the lower atmosphere above the surface in addition to NO flux at soil surfaces. The results are applicable to estimating chemical influences for grassland and deciduous forest, and methods developed from this research could be used for studies of other land use types. In this way, parameterizations for large scale models could be developed.

D. Alan Hansen – Electric Power Research Institute

EPRI has funded the development by Dr. David Cooper at SRI International of an eddy correlation flux measurement system. We refer to it as the FMS FCS for "frequency modulated spectroscopic fast chemical sensor." It is the culmination of an investment of approximately $2.5 million. It uses lead-salt diode lasers to generate the narrow-band IR radiation in conjunction with folded path optics to measure IR absorbing small molecules down to parts per trillion levels. In the flux measurement mode it samples at a faster rate than that used for making ambient concentration measurements, say ten hertz, coincident with a 3-D sonic anemometer and appropriate signal processing and software to measure fluxes of materials present at one to two orders of magnitude higher concentrations. In field tests in the San Joaquin Valley, it successfully measured fluxes of N_2O and NH_3 over a cotton field. With modification, it could measure simultaneously NO and NO_2 fluxes from soil. In fact, such a proposal has been made to EPA in response to AREAL's recent cooperative agreement solicitation. EPA's decision on the proposal has not been announced. I had hoped to fund, irrespective of EPA's decision, the modification and use of the system to measure NO and NO_2 fluxes in concert with and to corroborate Jim Meagher's enclosure technique measurements this summer, but was unsuccessful in securing funds.

The advantage of the FMS FCS, of course, is that it is non-invasive, not perturbing in any way the local environment of the surface to and from which fluxes are being measured. Further, being a spectroscope technique, it is not subject to many of the sampling artifacts or other problems associated with sample collection and analysis. Being relatively portable, it could be used to measure fluxes over a wide variety of surfaces over an extended time and space frame.

My primary objective therefore for the workshop is to bring to the attention of attendees the availability of this unique measurement capability and to seek opportunities for collaboratively funding its application to NO and NO_2 flux measurements. Another objective is to have the subject of the influence of flux divergence caused by rapid reaction of NO with ambient O_3 or photolysis of NO_2 on the FMS FCS measurement, the detectors for which are some 10s to 100s of meters from the actual area of air-surface exchange, and how to correct for it.

Elisabeth A. Holland – National Center for Atmospheric Research

Interactions between carbon and nitrogen cycling are central to understanding fluxes of reactive species from the biosphere to the atmosphere. Atmospheric nitrogen is fixed and

incorporated into vegetative biomass and soil organic matter. In most terrestrial ecosystems, the rate of nitrogen conversion from these organic components into mineral NH_4 (called *mineralization*) or from NH_4 into NO_3 (*nitrification*), limits the production of new plant biomass. Thus, the rate of N cycling determines an ecosystem's ability to store carbon. Because N limitation of plant production is so ubiquitous, undisturbed natural ecosystems tend to conserve N, losing little to the atmosphere via volatilization or to groundwater and rivers via nitrate leaching. Out current understanding is that N losses from an ecosystem are proportional to the rate of N turnover within a system and that any disturbance which disrupts the partitioning of N between plants and soil microbes will increase the rate of N loss dramatically. Natural disturbances, grazing, fire, hurricanes, and disease, and anthropogenic disturbances, clear cutting, cropping, irrigation, and N deposition, disrupt this balance and greatly increase the potential for N loss from ecosystems.

Volatile nitrogen losses from ecosystems include NO and N_2O production in soils as well as NH_3 volatilization from plants and soils. NO and N_2O are by-products and/or intermediates of two different N transformation pathways: *nitrification*, the conversion of NH_4 into NO_3 and *denitrification*, the reduction of NO_3 to NO, N_2O, and N_2 which are used as alternative electron acceptors when $[O_2]$ declines. As N losses from ecosystems accrue, via volatilization or nitrate leaching, an ecosystem loses its ability to fix carbon and produce new plant biomass. Substrate supply, $[NH_4]$ for nitrification and $[NO_3]$ for denitrification, controls the rate of processing and interacts with the physical and chemical environment, soil temperature and water content, $[O_2]$, pH, and carbon availability, to moderate the rates of both nitrification and denitrification. A number of distal factors regulate N turnover and affect substrate supply including net primary production, the distribution of carbon and nitrogen among the various plant components of an ecosystem: wood, leaves, roots, stems, and reproductive biomass, as well as the partitioning of carbon and nitrogen within each of these components.

I propose a series of experiments which will address both the proximal controls of substrate supply and environment as well as the broader distal controls over NO production. The study will have three interacting dimensions: a laboratory component to quantify the relationship between the proximal controls outlined above and NO production, a modeling component to incorporate information from the laboratory studies into a broader framework which includes the distal controls as well as providing a means of extrapolating in both space and time, and a field component to validate the model. The field studies proposed here, if done in conjunction with measurements of natural hydrocarbon emission studies will also address the role of nitrogen availability in determining isoprene and terpene emissions.

Laboratory Studies:

I propose to use chlorate slurries to screen for a soil's potential to produce nitrate, a nitrification intermediate. Chlorate inhibits the conversion of nitrite to nitrate and allows quantification of nitrate accumulation instead of measuring nitrate which is simultaneously being produced and consumed. These slurries will be done at a range of temperatures as well to determine if the temperature relationship used to describe general microbial activity (soil respiration) are appropriate for nitrification as well. Soil respiration does not follow traditional enzyme kinetics because CO_2 is a ubiquitous metabolic by-product and does not follow traditional single enzyme kinetics. Because nitrification relies on a specific set of enzymes, the relationship with temperature may have a clear optimum like that of simple enzyme processes (e.g. photosynthesis).

Incubating soils in flasks with different headspace concentrations of acetylene allows differentiation of NO production from nitrification and denitrification. Nitrifiers are much more sensitive to acetylene than are denitrifiers and nitrifier activity halts with 10 kPa of acetylene while denitrifier activity doesn't halt until headspace concentrations reach 100 Pa. Using this technique, I will examine how NO production from the two pathways differ with changing [NH_4], [NO_3], temperature, pH, and [O_2].

Potential net N mineralization assays will be used to directly examine the links between N turnover and NO production.

New instrumentation required for these assays includes a spectrophotometer for nitrite analyses as well as a chemiluminescence detector for NO measurements.

Modeling Studies:

CENTURY is a biogeochemical model which couples plant production to soil organic matter production, simulating rates of nitrogen turnover which, in turn, control plant production. CENTURY was originally developed for grassland and agricultural sites and has been used for regional analysis of soil organic matter and trace gas dynamics. CENTURY explicitly represents external N inputs through fixation and N deposition, volatile N losses as well as nitrate leaching, and disturbances which disrupt the balance between plant and microbial uptake of N tremendously increasing the potential for N losses. More recently, it has been revised to include forest, shrubland, and tundra simulations. I propose to build an additional NO module which will represent the proximal controls of NO production while the existing portion of the model handles the distal controls. Presently, CENTURY groups NO fluxes with other nitrogen oxides ($NO+N_2O+N_2$)and simulates the flux as a proportion of gross N mineralization. I will refine this representation and partition the flux into that which is associated with nitrification and that associated with denitrification. Adequate simulation of the flux will require a more detailed representation of soil structure and some information about the diffusion properties of the soil and how they change with changing soil texture and moisture.

Field Studies:

I propose measurement of NO fluxes along gradients of N and water availability in disturbed ecosystems to explicitly test whether NO fluxes are linked to rates of N turnover. These measurements will be done in conjunction with a suite of other measurements which characterize the physical and chemical environment as well as N availability. To adequately test the model, measurements will need to be made over at least one entire seasonal cycle, extension of the measurements over more than one seasonal cycle would permit testing the model during different weather years. The field studies will be conducted opportunistically and build on sites where many of the auxiliary measurements are already underway.

Execution of this plan will require internal NCAR funds as well as solicitations from EPA and possibly NASA.

Gordon L. Hutchinson – Agricultural Research Service, U.S. Department of Agriculture

Eric Davidson recently estimated the global soil NO_x source to be about 20 Tg N yr^{-1}, which is more than double the previously accepted value. His estimate, computed by summing the products of the mean measured NO emission rate, area, and length of the growing season for each of the Earth's major biomes, was dominated by emissions from three savanna sites all in the same Latin American country (7.7 Tg N yr^{-1}), so it may be revised downward once

more savanna sites are studied, but is also subject to certain upward revision because nearly half the Earth's surface is covered by biomes for which no NO exchange estimates were available, including deserts, semi-deserts, polar deserts, peatland, mixed forests, tiaga, and tundra. *Understanding the contribution of biogenic sources to the global atmospheric NO_x budget requires more measurements from those biomes with uncertain or unknown emission rates.* Although they may have little interest to SOS scientists, deserts (especially semi-deserts) may be particularly important, because of the large burst of NO_x emissions that typically follows wetting of very dry soil.

Although the value of improved budgets is unequivocal, such calculations are hopelessly inadequate for achieving a predictive understanding of the immense spatial and temporal variability characteristic of soil NO_x exchange rates at local, field, and landscape scales. Accordingly, the long-range goal of additional measurements should be to capture the exchange rates in terms of their basic physical, chemical, and biological controllers, so that dependence of the flux on these controllers can be described using simulation models parameterized by variables observable at the scale of interest. The available data suggest that soil NO_x emission is strongly dependent on the type of vegetative cover, fertilization, burning, grazing, precipitation amount/intensity/duration, etc., but the importance of most of these factors can be explained by their effect on the three major environmental controllers – soil temperature, N availability, and O_2 availability, which is regulated primarily by soil water content. Correspondingly, NO_x emission from the small plots I have been monitoring at Akron, Colorado is best and most simply simulated by the product of a constant that (somehow) reflects soil N availability, an exponential function of soil temperature (equivalent to assuming $Q_{10}=2$), and a dual-slope linear function of water-filled soil pore space (WFPS) that captures the dependence of microbial activity on this parameter outlined by Skopp et al. (SSSAJ 54:1619-1625, 1990), thereby accounting for all three of these major environmental controls. Order-of-magnitude differences between two sets of fluxes measured on sampling dates with widely divergent conditions were reduced to less than a factor of 2 after normalization to the same temperature and percentage WFPS, and the remaining differences between the two data sets were correlated with measured changes in various soil N availability indices. *Understanding dependence of the model constant on the sizes and/or transformation rates of identifiable soil N pools, confirming the usefulness of our soil temperature and soil water parameterization schemes in other soils and climates, and developing an effective method of adjusting the effect of precipitation for soil water content prior to the wetting event are needed* before this approach can be extended over the much larger areal and temporal domains to which we think it may apply.

Sub-questions for which answers would facilitate addressing these needs include: (1) *What are the reasons for the unusually large burst of soil NO_x emissions following wetting of very dry soil?* My lab (and others) have shown that autotrophic nitrifiers are directly involved (or indirectly involved as a source of nitrite), but the mechanism for such copious release of NO_x remains unclear. (2) *Do microbial processes other than autotrophic nitrification and heterotrophic denitrification contribute significantly to soil NO_x emission in some situations?* In my lab, small aerobic soil NO_x emission rates that continue in the presence of autotrophic nitrification inhibitors are correlated with soil respiration, indicating a C-dependent source such as heterotrophic nitrification or any of several other microbial processes resulting in oxidation or reduction of N through the +2 oxidation state. (3) *What is the relation of soil NO_x to N_2O emissions?* Biotic and abiotic processes involved in the production, consumption,

and transport of these two gases in soil are so tightly coupled that soil exchange of either gas should not be considered without simultaneous consideration of the possibility for interactions with the other.

John Kinsey – Midwest Research Institute

AP-42 STUDY:

- Developed emission factors for NH_3, NO, N_2O, NO_2 for nitrogen fertilizers.
- Based emission factors on published data from academic investigators (foreign and domestic).
- Used mostly flux chambers at selected times after application (i.e., "snapshots").
- Temporal resolution poor with incomplete speciation of nitrogen gases from soil surface (i.e., only selected pollutants determined in most studies).

Testing Needs:

- Common fertilizer types, multiple crop types, and different soil conditions should be evaluated for *all* nitrogenous pollutants of concern following an approved statistical design.
- "Whole-field" sampling should be performed in lieu of chambers over relatively small areas.
- Soil properties should be thoroughly characterized, both chemically and biologically (i.e., Cation Exchange Capacity, etc.).
- EPA and agrichemical industry should be involved throughout the study.

Possible Approaches:

- Profile pollutant concentrations from test plot spatially and temporally using open path instruments, such as the FTIR.
- Couple concentration measurements with on-site meteorology to determine mass flux (i.e., similar to MRI exposure profiling method for particulate matter).
- Characterize soil gases frequently over study period using buried probes, etc.
- Determine types and quantities of soil organics and chemical constituents by grab sampling throughout period.
- Conduct intensive sample and analysis during 2-week maximum emission period.
- Collect air and soil samples before, during, and after fertilizer application to determine background emission and the effects of the application (i.e., natural vs. manmade emissions).

Bill Massman and Karl Zeller – Forest Service, U.S. Department of Agriculture

Measuring NO_x emissions from soils can be accomplished by micrometeorological means using eddy covariance or conditional sampling methods. However, since ozone is also present the purely aerodynamic approach may yield biased results depending on the ozone concentration because of the photoreactions of NO, NO_2, and O_3. Nevertheless, we suggest the following experiment to address the question of NO_x emissions from soils.

(1) Fluxes and ambient concentrations of NO, NO_2, and O_3 be measured at two or more heights above a surface (a fertilized field for example). At least two measurement heights are necessary to evaluate the surface layer flux divergences caused by the photoreaction of NO, NO_2, and O_3. Similar and concurrent measurements of isoprenes and/or terpenes

would also be made. Several simultaneous leaf level gas exchange systems for hydrocarbon emissions from plants and chamber systems for NO emissions from soil would also be made.

(2) Measurements of light intensity in the spectral wavebands which drive the photolytic reactions. For modeling purposes measurements of atmospheric aerosols, water vapor and cloudiness should also be made.

(3) To assess whether pressure pumping plays any role in the release of NO from the soils simultaneous measurements of the high frequency fluctuations of pressure in both the soil and ambient atmosphere should also be made. Profiles of soil temperatures and soil water content are also needed because these are important factors regulating microbial activity and the concomitant NO emissions from the soils.

(4) Lastly, a model that incorporates (a) NO emissions from soils, (b) the photolytic reactions between the O_3, NO_2, and NO and hydrocarbons, OH and NO_2, (c) atmospheric turbulent exchange between the surface and the atmosphere and (d) any plant influenced effects would also be required.

Estimated cost:

Eddy covariance instrumentation and equipment..	$250,000.00
Chamber instrument and equipment.....	$250,000.00
Salaries per year	$600,000.00
Travel (relocation of eddy covariance system)	$100,000.00
Laboratory and Misc.	$ 50,000.00

Duration of experiment: At least two years with eddy covariance data being taken at three or more sites of interest.

Bill Munger -- Harvard University

Given unlimited time, personnel, and resources our group would pursue the following overall research objectives:

(1) Determine seasonal cycle of soil NO emissions from a mixed deciduous forest.

(2) Quantify aerial nitrogen inputs from wet and dry deposition and in particular, evaluate the role of NO_2 deposition within the canopy and to the soil surface.

(3) Assess the role, if any, of heterogeneous reactions that convert NO_2 to NO on organic matter.

(4) Compare NO fluxes made at the canopy level to NO fluxes measured in chambers during selected periods.

As part of the Harvard Forest Long-Term Ecological Research site our group has established an Environmental Measurement Station for measuring trace-gas concentration profiles and eddy correlation fluxes. A 30 m tower was erected in a 23 m mixed hardwood forest that is dominated by oaks. In particular measurements of CO_2, O_3, NO and NO_2 concentration profiles allow estimation of NO soil emission and NO_2 deposition within the canopy. Total nitrogen deposition is determined by precipitation collection and analysis and NOy eddy correlation flux measurements.

Elevated concentrations of NO beneath the canopy at night indicate a persistent source of NO at the forest floor. We will continue the measurements and augment them to obtain better temporal and vertical resolution. Fluxes of NO are calculated from integrating the chemical mass balance. In addition we will construct a model of vertical mixing, surface reaction and chemical reaction for the forest. Simultaneous measurements of CO_2 and O_3 fluxes and concentration gradients can be used to constrain the mixing rates and surface

interactions. Direct estimation of the flux by ratio to the soil CO_2 flux and gradient is not possible because the reaction with O_3 is rapid.

In light of Nishimura et al.'s [1986] observations of NO_2 reduction on various plant material we propose to investigate the relationship between measured NO fluxes and ambient NO_2 concentrations. In addition laboratory experiments to test this reaction on other substrates and at environmentally realistic concentrations are needed.

The facilities at Harvard Forest provide an ideal site for making chamber flux measurements of NO emission by soils. Direct measurements of soil fluxes are needed to verify the canopy level estimates. In addition we would seek to arrange with Melillo et al. to make NO flux measurements within their nitrogen fertilization and soil-warming plots located nearby.

Thomas E. Pierce – Atmospheric Research and Exposure Assessment Laboratory, U.S. EPA

For several years, we have recognized that biogenic VOC emissions play an important role in photochemical ozone production and the selection of appropriate emission control strategies. Until recently, it was thought that "biogenic" NO_x emissions from soils were negligible. However, Williams et al. have shown that soil NO could be a significant portion of the total NO_x emissions budget. As "king" of ozone modeling at EPA, it is important that we properly model the soil NO flux into the atmosphere and examine how soil NO_x emission might affect emissions control strategies. Such a research program might entail soil chamber measurements, micrometeorological field verification, emission model development, atmospheric model improvements, and model uncertainty analysis.

(1) Soil Chamber Measurements. A number of soil chamber measurements have already been made. More measurements are needed over the heavily-fertilized soils, which appear to be the areas where NO emissions are appreciable and could significantly influence the overall NO_x emissions budget. The additional chamber measurements would also enable better emission models to be constructed that include factors such a as soil moisture, soil nutrient levels, and soil types.

(2) Micrometeorological Field Verification. Soil chamber measurements may not provide a complete picture of the NO emission flux into the atmosphere. Recognizing that NO emissions is tightly coupled to the NO-NO_2-O_3 photochemical system, micrometeorological verification of the soil NO emission factors is needed.

(3) Emission Model Development. Using data from (1) and (2), the algorithm for computing soil NO emissions could be updated. It could include other factors, such as soil moisture and soil nutrient status. Such a model should be consistent with available data bases.

(4) Atmospheric Model Improvements. Most current photochemical models use a stand-alone processor for estimating NO emissions. It is apparent from the literature that NO emissions are strongly coupled with NO-NO_2-O_3 concentrations in the ambient air. The emissions module then should be made a part of the atmospheric model.

(5) Model Uncertainty. The issue with biogenic emission uncertainty is how does it affect the way we manage air quality. For example, an overprediction of soil NO emissions could change preference from a NO_x to a VOC control strategy. Ozone production is very non-linear and depends on VOC and NO_x emissions. Model simulations are needed to see how uncertainties in emission factors affect ozone concentrations and emission control strategy

selection. Model simulations are also needed to establish the required accuracy of the soil NO emission factors.

Mark Poth – Forest Service. U.S. Department of Agriculture

The practices currently used to manage productive forest lands, as with agricultural lands, may promote the production of NO_x from soils. The amounts produced may be significant given the enduring nature of NO_x production observed from some other forest systems and that the southern U.S. has the greatest percentage of area in forest production of any region in the U.S. Forest soil NO_x emission rates in the South are virtually unknown.

Currently the Forest Service is conducting a study of forest management practices on long term site productivity (LTSP). This nation wide, approximately $10 million, study includes several sites (20 plus) in the south. Each site includes treatments for soil compaction, harvesting and plant community diversity. The data base being produced includes information on climatology, soil physical and chemical properties, plant survival, growth and nutrition, insect and disease outbreaks, and forest biomass modeling. These data can be made available to cooperators at no cost.

Objective

Obtain preliminary measurements of soil NO_x production from managed forest stands in the south, taking advantage of the LTSP study.

Approach

A combination of chamber studies for mechanistic evaluation of emissions and micrometeorological methods for flux measurements.

Approximate Cost

No cost for the land treatments and the site data. Costs would be for teams to measure NO_x emissions using the two methods, concomitantly.

Time Frame

With the sites already prepared, measurements could be made this summer and results analyzed and reports/papers produced by this fall. This information would provide an assessment of forest soils as a source of NO_x. Additionally, it may provide information on management practices to mitigate such emissions.

Additional Advantages

There is the potential to link with similar studies in other regions of the country at other LTSP sites.

Ray Valente and Frank Thornton – Tennessee Valley Authority

Model Validation and Improvement

Over the past three years TVA has collected a database of soil NO_x emissions from several fertilized and unfertilized sights in the mid-south. This database now includes over 3500 individual chamber measurements (2500 from fertilized soils and 1000 from unfertilized soils) along with soil temperature, soil moisture, and soil chemistry information. We propose collaborative work to use this database to validate and help refine the soil NO_x emissions models currently being developed for application in SOS. (Cost: $25K)

Spatial Variability Experiment

Spatial variability is the nemesis of accurate regional soil NO_x emissions estimates. Spatial variability as high as of a factor of 100 has sometimes been observed, even on a very

small spatial scale (adjacent chamber plots on a fertilized cotton field, e.g.). In order to develop an understanding of the influence of spatial variability on the accuracy of regional emissions we propose a soil NO_x spatial variability study. In this field study soil NO_x emissions measurements will be made at many locations within a single model grid cell in order to document the spatial variability and to develop an understanding of the uncertainty in extrapolating from a few sites to grid-scale and regional estimates. The study would be done during the warm season and would utilize the mobile capabilities of current measurement systems. The emphasis of this study would be to perform measurements at as many sites (20-30 seems practical for a month long study) within the grid cell as possible rather than to focus in detail on any particular location. The grid cell and sites selected for the study would include fertilized agricultural areas, pasture lands, urban lawns, parks, truck crop areas, residential plantings, etc. The results of this study would, for the first time, permit a statistical estimate of the uncertainty involved in regional soil NO_x estimates. (Cost: $30K, assuming the work could be done at a grid cell near the home office of the investigators)

Is Reabsorption of NO or NO_2 Reducing the Emissions to the Boundary Layer?

Because of the uncertainty in the amount of NO that originates from biogenic sources, chiefly soil, TVA has been attempting to inventory soils in the mid-south. These estimates suggest that soil NO_x emissions in the region are clearly non-negligible, especially during the photochemical ozone season. Questions have been raised as to how much of the NO released at the surface is reabsorbed by plant canopies before it can reach the boundary layer. We propose a collaborative study in which comparisons between chamber and diode laser or other micrometeorological technique could answer the question posed above. (Cost: $50K, but could vary depending on the micrometeorological technique chosen)

RESEARCH PRIORITIES

Considerable discussion among workshop participants centered around specific research programs that should be undertaken to most effectively enhance current understanding of NO_x emissions from soils. It was generally agreed that the highest research priority of the Southern Oxidants Study in the short-term should be survey work using soil chambers. The focus of the survey work should be specific land-use or ecosystem types common to the Southeast for which NO_x flux estimates are either unknown or very uncertain. This especially includes fertilized urban areas such as golf courses and lawns.

Research projects that could be pursued on a longer-term basis are described below.

(1) **Full Characterization of the Net NO_x Flux to the Atmosphere From Soils**

The objectives of this study would be to:

(a) fully characterize and quantify the processes that contribute to the net biosphere-atmosphere exchange of NO_x, including emission of NO as a result of microbial activity in soils, photochemical conversion of NO to NO_2, and deposition of NO_2 to soils and plants; and

(b) demonstrate the applicability of micrometeorological techniques for measuring fluxes of NO, NO_2, and O_3.

This study that would utilize both soil chamber methods and micrometeorological techniques to provide information on the vertical exchange of nitrogen oxides between the

atmosphere and the biosphere. Soil chambers can provide process-level information on soil emissions of NO and uptake of NO_2 and O_3. Use of micrometeorological methods may provide some insight into how to resolve the spatial and temporal variability inherent in chamber data with estimates of larger-scale fluxes.

The proposed study would require coordinated efforts in soil characterization, soil chamber measurements, and micrometeorological measurements. It is desirable that a variety of micrometeorological techniques be employed, including gradient techniques, conditional sampling, and eddy correlation. It was suggested that NCAR's ASTER facility could be used as a micrometeorological platform. "Remote sensing" techniques, such as FMS FCS and FTIR, were also mentioned as having some long-term promise. It was strongly recommended that the micrometeorological measurements include flux profiles because of the NO flux divergence that occurs in this highly reactive chemical system. To fully characterize the NO_x flux interaction with the local atmospheric composition it will be necessary to make sufficient additional chemistry measurements to characterize this chemical environment. Thus measurements of reactive hydrocarbons, hydrogen peroxide, and other species should be considered. Likewise it will be necessary to undertake appropriate meteorological and measurements; for example, the need for continuous measurement of boundary layer height should be considered. Several soil chamber measurement groups would be encouraged to participate. Substantial up-front work would be needed to carefully design the experiment, to locate the best field site, to characterize the site, and to enhance the chemical instrumentation needed to make the micrometeorological measurements.

Important characteristics for an experimental site for the study were identified as: a flat, well-drained, fertilized, agricultural field with a fetch of 2 km and having available irrigation. Ideally, the site should be available for the entire growing season and not be influenced by anthropogenic pollution sources. Sources of isoprene should also be considered because of the role that this hydrocarbon plays in photochemistry. The working group felt that the experiment should consist of brief intensive operating periods (~2 weeks each) over the course of a growing season.

Because of the scale of such an intensive experiment, it was suggested that 1993 be used for planning purposes, 1994 be used for further planning and perhaps pilot studies, and the summer of 1995 be the implementation of the full-scale study.

(2) **Emissions model development**

While models currently exist to relate soil NO emissions to land use class and soil temperature, the workshop participants concluded that sufficient information is available to refine these algorithms to include fertilizer application and soil water content. Short-term research is needed to assimilate this information, to construct an algorithm, and to test it against field measurements. It is important during this developmental process to recognize the limited availability of input data bases and to identify the measurements and data bases that will be needed to drive future emission models. It was suggested that GIS data bases are available from the Soil Conservation Service (SCS) that might improve modeling efforts.

(3) **Field chamber measurements**

Field chamber measurements have been rather limited. Furthermore, much experimental work has not included measurements of important process-related variables. Ideally, future studies should report soil temperature, rates of nitrogen mineralization or some other measure of soil nitrogen status, soil texture, water-filled pore space, antecedent soil

water content, and climatic variables (such as precipitation history). Additional studies are needed to expand the data base to other sites, especially fertilized sites; to examine spatial and temporal variability; and to better establish the processes dominating soil NO_x emission. Special attention should be given to the role of N cycling. For example, chamber measurement programs should include N_2O fluxes because comparing fluxes of NO relative to N_2O yields important information about the mechanisms controlling emissions of both gases. Field studies should be designed to support the development of improved NO_x emission models.

(4) **Atmospheric model development and uncertainty analysis**

Most current photochemical ozone models use stand-alone processors for estimating NO_x emission and deposition. Future models should integrate the emission and deposition processes into the chemical-meteorological core model. The model should incorporate (a) NO emission from soils, (b) the important chemical and photochemical reactions of NO_x, (c) atmospheric turbulent exchange between the surface and the atmosphere, and (d) any plant-influenced effects that might be important. A significant but often unrealized facet of model development is the need for experimental verification of these modeled processes.

Another issue that needs to be explored is that of emission uncertainty. How does the uncertainty in NO_x fluxes affect the way that air quality is managed? Model simulations are needed to see how these uncertainties affect predicted ozone concentrations and emission control strategy selection. Model simulations are also needed to determine the required accuracy of the soil NO emission factors.

APPENDIX 1. Memorandum of Invitation and Agenda for Workshop on Emissions of NO_x from Soils.

North Carolina State University

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22 April 1993

MEMORANDUM

To: Peter Bakwin, NOAA CMDL
Ellis Cowling, North Carolina State University
Eric Davidson, Woods Hole Research Center
Anthony Delany, National Center for Atmospheric Research
Fred Fehsenfeld, NOAA Aeronomy Laboratory
Weigang Gao, Argonne National Laboratory
Chris Geron, EPA Air and Energy Engineering Research Laboratory
Alex Guenther, National Center for Atmospheric Research
Alan Hansen, Electric Power Research Institute
Gordon Hutchinson, USDA Agricultural Research Service
Joel Levine, The NASA Langley Research Center
William Massman, USDA Forest Service
Pamela Matson, NASA/Ames
William Parton, Colorado State University
Mark Poth, USDA Forest Service
Brian Templeman, NOAA
Ralph Valente, Tennessee Valley Authority
Eric Williams, NOAA Aeronomy Laboratory
Steven Wofsy, Harvard University
Karl Zeller, USDA Forest Service
Patrick Zimmerman, National Center for Atmospheric Research

From: Cari Furiness, North Carolina State University C.F.
Tom Pierce, EPA Atmospheric Research and Exposure Assessment Laboratory T.P.

Subject: Workshop on Emissions of NO_x From Soils

The purpose of this memorandum is to invite you to participate in a 1-1/2-day Workshop on Emissions of NO_x From Soils, which will be held in Denver, Colorado on May 10-11, 1993. This workshop is being sponsored by the Southern Oxidants Research Program on Emissions and Effects (SORP-EE), a part of the Southern Oxidants Study (SOS), in collaboration with the Atmospheric Research and Exposure Assessment Laboratory of the Environmental Protection Agency.

Your participation in the workshop is sought because you are a leading research scientist in this area and/or you represent a major sponsoring organization that has an ongoing interest in understanding soil NOx emissions. This workshop will allow a fruitful exchange of information

North Carolina State University is a land-grant university and a constituent institution of The University of North Carolina.

about research programs that are currently being funded or will be funded by major sponsors, research activities currently being undertaken by scientists with funding from other sources, and perceived priorities for research by both scientists and sponsors. The interchange should foster collaboration among workshop attendees and enable organizations such as USDA, NOAA, EPRI, NASA, and EPA to assess priorities for their own research programs.

The objectives of the workshop are as follows:

1) To develop a general consensus about the current state of knowledge about emissions of NO_X from soils, especially from soils of land use types that contribute significantly, because of relatively high flux rates and/or relatively large land areas, to the total NO_X emissions inventory in the southern United States;

2) To discuss current methods used to estimate soil NOx fluxes, assess the uncertainties associated with those measurement methods, and determine measurement programs that would most effectively improve the NO_X emission estimates that are used in atmospheric photochemical grid models;

3) To identify current and proposed funding needs and to set priorities for future research on NO_X emissions from soils in the southern United States; and

4) To coordinate and, to the extent possible, collaborate on current and future research and modeling efforts.

To facilitate our discussions on May 10 and 11, we request that you prepare a one-page statement which outlines the research you (personally or collaboratively) would most like to accomplish or see accomplished during the next few years in the area of research related to emissions of NO_X from soils. It has been both fun and productive in previous planning meetings of this sort to use these "If I were King or Queen Statements" and the discussions they evoke as a means by which to assess priorities for research and to potentially identify a cadre of scientists that will be needed to get this research done in a timely way and at reasonable cost. Each one-page statement ideally should indicate the objectives, approach, approximate cost, and estimated time-frame for delivery of useful research results. Please send your statements to either of us by May 5, or if that is impossible, please bring 20 copies with you to the meeting.

The Southern Oxidants Study is keenly interested in sponsoring this workshop. This interest is a result of a growing scientific consensus that emissions of NOx from natural sources are not negligible as often has been assume in the past. It is generally accepted that there are two different natural sources of NOx: 1) soil microorganisms and 2) lightning. We will not deal with lightning as a NOx source in this workshop. But we intend to explore thoroughly, the possibility that emissions of NOx by microorganisms growing in well fertilized soils in both rural and urban areas may be significantly larger than has previously been assumed. Present estimates of the magnitude of soil NOx emissions are especially uncertain in:

1) well-fertilized rural pasture lands and row-crop lands, and
2) in well-fertilized urban lawns, parks, truck crop areas, and in lands devoted to residential ornamental plantings.

The Emissions and Effects Taskgroup of SOS, as well as other groups within EPA, are interested to sponsor further study in the area of soil NO_X emissions. In order to better set priorities for such research, a better understanding of current research activities and assessment of

the major uncertainties in scientific understanding of these biogenic emissions are necessary; in this way, financial and personnel resources can be used more efficiently, and duplication of effort can be avoided.

A tentative agenda for the workshop and an information sheet about the hotel are enclosed. Your suggestions for improvement of the agenda are welcome both prior to and during the workshop.

The workshop is scheduled to last from 8:30 am on Monday, May 10 through 12:00 noon on Tuesday, May 11 at the Radisson Graystone Castle, conveniently located in Thornton, a northern suburb of Denver. The hotel offers complimentary shuttle bus service from Stapelton International Airport. A block of rooms has been reserved at a $49 per room rate. To receive this rate, call 1/800/422-7699 and request a reservation at the Radisson Graystone Castle, making sure to mention it is for the Southern Oxidants Study (or SOS) meeting.

As many of you are aware, an SOS Data Analysis Workshop will begin on Tuesday morning at the same location, so that there will be an unavoidable overlap with the morning session of that workshop. Although we regret the conflict, planning this Soil NOx Workshop at the same time should allow greater participation and smaller travel costs. Some funds are available for participant travel; please contact Cari Furiness with requests.

If you have suggestions for the agenda, need further information about the workshop, or have questions about travel or accommodations, please call Cari Furiness at (919) 515-4653 or Tom Pierce at (919) 541-1375.

Tentative Agenda

Workshop on Emissions of NOx From Soils
May 10-11, 1993

Radisson Graystone Motel
Denver, Colorado

Monday, May 10			
8:30 am	Introduction, Charge to Attendees		Tom Pierce Cari Furiness Ellis Cowling
8:40 am	Introductions, Bias Statements		All Participants
	Overviews of the Current State of the Science:		
9:00 am	Chamber Measurement Methodology		Eric Williams
9:30 am	Micrometeorological Measurement Methodology		Anthony Delany
10:00 am	**Break**		
10:15 am	Mechanisms and Predictors of Soil NOx Emissions		Eric Davidson
10:45 am	NOx Emissions Modeling, and Inventory Development		Eric Williams and Weigang Gao
	Descriptions of Research Currently Being Funded:		
	(10 minutes per agency)		
11:15 am	EPA	NOAA	
	EPRI	USDA-FS	
	USDA-ARS	TVA	
	NASA	NSF	
12:30 pm	**Lunch**		
1:30 pm	Presentation and Discussion of "If I Were King" Statements		All Participants
5:00 pm	**Adjourn**		
Tuesday, May 11			
8:30 am	Discussion of Research Priorities and Recommendations for Research		All Participants
11:30 am	Summary of Workshop		Tom Pierce Cari Furiness Ellis Cowling
12 noon	**Adjourn**		

APPENDIX 2. List of Invitees to Workshop on Emissions of NO_x from Soils (names marked with an asterisk indicate attendance at the workshop).

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AP-42 Study:

- Developed emission factors for NH_3, NO, N_2O, NO_2 for nitrogen fertilizers (see attached).
- Based emission factors on published data from academic investigators (foreign and domestic).
- Used mostly flux chambers at selected times after application (i.e., "snapshots").
- Temporal resolution poor with incomplete speciation of nitrogen gases from soil surface (i.e., only selected pollutants determined in most studies).

Testing Needs:

- Common fertilizer types, multiple crop types, and different soil conditions should be evaluated for *all* nitrogenous pollutants of concern following an approved statistical design.
- "Whole-field" sampling should be performed in lieu of chambers over relatively small areas.
- Soil properties should be thoroughly characterized, both chemically and biologically (i.e., Cation Exchange Capacity, etc.).
- EPA and agrichemical industry should be involved throughout the study.

Possible Approaches:

- Profile pollutant concentrations from test plot spatially and temporally using open path instruments, such as the FTIR.
- Couple concentration measurements with on-site meteorology to determine mass flux (i.e., similar to MRI exposure profiling method for particulate matter).
- Characterize soil gases frequently over study period using buried probes, etc.
- Determine types and quantities of soil organics and chemical constituents by grab sampling throughout period.
- Conduct intensive sample and analysis during 2-week maximum emission period.
- Collect air and soil samples before, during, and after fertilizer application to determine background emission and the effects of the application (i.e., natural vs. manmade emissions).

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December 21, 1992

Mr. Dallas W. Safriet
Environmental Engineer
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Agency
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Standards
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Dear Mr. Safriet:

As requested in your November 19, 1992, letter we have reviewed the draft version of a proposed new section 6.2.1, *Fertilizer Application*, of AP-42, *Compilation of Air Pollutant Emission Factors*. As you requested we reviewed only Section 5 of the background documentation.

Our staff members reviewed draft Section 6.2.1. The reviewers found the draft section to be not well written, quite inaccurate, and apparently inadequately researched. In our opinion the draft section should be rewritten after a more extensive literature review is performed. We have enclosed an example of a possible rewrite that we believe more accurately describes the information you are attempting to document. However, the rewrite does not include additional data other than that already incorporated into the draft version. According to our staff there is much more reliable data and information available than that referenced in the draft section.

We have also collaborated with staff members from the Tennessee Valley Authority on the draft section and understand they were also requested to review the document. We have reviewed their comments that were sent to you and fully agree with them.

Please note that we did not review the data included in Table 6.2.1-1. The data would have demanded an extensive review of all the references included in the background documentation. We could undertake this task but only under a reimbursable agreement due to the magnitude of such an effort.

We hope this information is helpful to the EPA in developing appropriate and accurate emission factors for AP-42.

Sincerely yours,

James J. Schultz
Director
Outreach Division

Enclosure

IFDC
December 21, 1992

Example of Suggested Rewrite of Section 6.2.1

6.2.1 Fertilizer Application

6.2.1.1 General. The role of fertilizers in the agricultural industry is to supply essential plant nutrients to improve crop production. It has long been recognized that there are 16 essential elements or nutrients necessary for plant growth, three of which are supplied from the atmosphere or water (carbon, hydrogen, and oxygen). The other 13 elements (nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, copper, zinc, boron, manganese, iron, chlorine, and molybdenum) are principally supplied through the soil medium. Some of these elements are limited in the soil medium and must be supplemented by fertilizers. Fertilizers are distributed through agricultural supply retailers, farmers' cooperatives, and fertilizer dealers. Application is typically performed by farmers and by fertilizer dealers using specialized application equipment.

6.2.1.2 Process Description. Based on the physical form of the fertilizer, there are three basic types of fertilizer application. The basic method of application is determined according to whether the fertilizer is in a gaseous, fluid, or solid form.

6.2.1.2.1 Gaseous fertilizer. Anhydrous ammonia is the only gaseous fertilizer used, and supplies nitrogen. Typically, about 6 million tons of ammonia is applied annually in the United States. Farmers generally apply ammonia thenselves. Anhydrous ammonia is typically stored in a liquid form: most commonly, under pressure; and to a lesser degree, by refrigeration. Anhydrous ammonia is actually injected as a liquid/gaseous mixture into the soil where it vaporizes into a gas and then is captured by several components in the soil, including water, clay, and other minerals.

Because it is a gas at atmospheric pressure, anhydrous ammonia must be injected from 4 to 10 inches (10 to 25 cm) below the soil surface, depending upon the soil type, soil conditions, and spacing. Generally, typical equipment for anhydrous ammonia application consists of a tractor, a pressurized tank containing the anhydrous ammonia, a metering system, manifolds, and injection knives. Figure _____ (not the one shown) is a typical example of application equipment for anhydrous ammonia.

The only calibration done during the application of ammonia is a tracking of pounds applied versus acres covered. Precise orifice calibration for metering the flow of liquid ammonia is done at the factory, and farmer dials in the orifice setting according to speed, desired rate, and tool bar width.

6.2.1.2.2 Fluid fertilizer. Fluid fertilizers are typically classified as either solutions or suspensions. Solution fertilizers are free of solid particles. Suspension fertilizers are two-phase fertilizers in which solid particles are maintained in suspension in the aqueous phase. The equipment used in the application of fluid fertilizers typically

consists of a vehicle (truck or tractor), a tank holding the fluid, a metering system, manifolds, and spray nozzles. The manifolds are mounted inside long booms (20-40 ft) with the nozzles spaced along the manifold so that the spray patterns overlap. Fluid fertilizers are most commonly sprayed onto the surface of freshly tilled soils.

Figure _____ (not the one shown) is an example of a typical applicator for fluid fertilizers.

6.2.1.2.3 Solid fertilizers. In the United States, solid fertilizers are typically applied as straight nitrogen fertilizers (urea or ammonium nitrate) or as mixed fertilizers containing not only nitrogen but also phosphate, potassium, and other nutrients. Application of solid fertilizers is done predominantly either by fan-type spreaders (Figure _____) or by boomed (pneumatic- or auger-type) spreaders (Figure _____).

6.2.1.3 Emission and Controls. Both solid-phase (particulate matter) and vapor-phase air pollutants can be generated from the application of fertilizers. In both cases, two general classes of emissions are noted: "immediate" pollutant emissions which can occur either during or shortly after application; and "latent" pollutant emissions which can be generated days or weeks following application.

Wind-blown dust can be created immediately during the application of dry fertilizers and later from disturbances caused by mechanical operations (e.g., tilling) and/or wind erosion. Vapor-phase emissions can be generated after application by the immediate volatilization of gaseous fertilizers (i.e., anhydrous ammonia) or after some period of time by the chemical/biological transformation of N added as fertilizers to the soil.

At the current time, vapor-phase emission factors are available only for nitrogen fertilizers. These emission factors are shown in Table 6.2.1-1 on the basis of equivalent nitrogen applied to the soil. Finally, where more specific data are not available, Table 6.2.1-2 provides equivalent nitrogen contents of common chemical fertilizers for use with the emission factors shown in Table 6.2.1-1. (Refer to TVA comments regarding questionable validity of vapor-phase emission factors.)

Table 6.2.1-1. Candidate Emission Factors for the Application of Nitrogen Fertilizers[a]

IFDC did not attempt to verify the data included in this table. This could be done on a reimbursable basis.

Table 6.2.1-2. Equivalent Nitrogen Content of Common Chemical Fertilizers[a]

Type of Fertilizer	Chemical Formula	Nitrogen Content (Weight Percent)	Amount of Fertilizer Applied per Hectare to Produce 1 kg N/ha Equivalent Application (kg)
Anhydrous ammonia	NH_3	82.3	1.22
Urea	$CO(NH_2)_2$	46.7	2.14
Ammonium sulfate	$(NH_4)_2SO_4$	21.2	4.72
Calcium nitrate	$Ca(NO_3)_2$	17.1	5.85
Ammonium nitrate	NH_4NO_3	35.0	2.86
Ammonium chloride	NH_4Cl	26.2	3.82
Sodium nitrate	$NaNO_3$	16.5	6.06
Diammonium phosphate (DAP)	$(NH_4)_2HPO_4$	21.2	4.72
Potassium nitrate	KNO_3	13.9	7.19

a. For pure chemicals. 1 kg = 1,000 g = 2.2 lb; 1 ha = $10^4 m^2$ = 2.471 acres. From Table 4-5 of Reference 7.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
ATMOSPHERIC RESEARCH AND EXPOSURE ASSESSMENT LABORATORY
RESEARCH TRIANGLE PARK
NORTH CAROLINA 27711

December 28, 1993

MEMORANDUM

SUBJECT: Review of the Revised Draft Report, "Emission Factor for AP-42, Section 6.2.1: Fertilizer Application"

FROM: Thomas E. Pierce (MD-80)
MSAB/ACMD/AREAL/ORD

TO: Dallas W. Safriet (MD-14)
EIB/OAQPS

As you requested, I have reviewed the revised draft report on emission factors from fertilizer application. I will restrict my review comments to those areas that I have some degree of familiarity: NO_x emissions from soils. I believe the authors of the report have done a credible job, considering the paucity of information on the subject and the inter-disciplinary range of the references (compared to other AP-42 emission factor studies). I further appreciate that considerable efforts were made to develop emission factors that could be clearly expressed in tabular form for AP-42. However, I have two major recommendations concerning the proposed values for NO and NO_2.

(1) Most scientific papers discussing biological mechanisms of NO_x emissions from soils note that most (>90%) if not all of the emissions are in the form of nitric oxide (NO). According to Hutchinson and Brahms (J. of Geophysical Research, pp. 9889-9896, 1992), there is no evidence to suggest that NO_2 is directly emitted from soils. Other scientists support this statement (references available on request). Admittedly, the emission factors were based on chamber experiments that measured increased levels of NO_2, which would lead one to infer emissions of NO_2. This probably occurs because NO emitted from the soil into the chamber is quickly converted to NO_2 in the presence of ozone. In fact, the revised AP-42 draft report on page 4-3 notes: "Because any NO emitted is likely to be converted quickly to NO_2 in the atmosphere, the NO_x emissions were estimated as NO_2." However, EPA's air quality simulation models supposedly handle the chemical transformations that occur when a gas is directly emitted in the air, even in the case of NO when this transformation occurs rapidly near the soil/air interface. For this reason, **I recommend that the emission factors for NO and NO_2 be expressed only as NO.**

(2) The authors correctly noted that substantial variability of NO_x emissions occur both within and among sites. Because of this and the shortage of experimental data, I do not think sufficient data exist to divide emission factors according to the type of fertilizer application. I am worried that a policy maker, who is looking into NO_x emission abatement strategies, might review the proposed AP-42 emission factor table and conclude that different types of fertilizers could be

used for NO_x emission reductions. While this may in fact be true, I do not think sufficient experimental data currently exist to differentiate NO emissions between fertilizer types. Therefore, **I recommend that only one NO emission factor (applicable to all nitrogen-based fertilizers) be reported in the draft AP-42 table.**

I wanted to let you know that the Regional Oxidant Model (ROM) employs an algorithm from Williams et al. (Global Biogeochemical cycles, pp. 351-388, 1992) that allows NO emissions to vary as a function of temperature and land use type. The Williams et al. work was mentioned in the draft report, but understandably it was not used in the emission factor table because fertilizer rates were not reported. Out of curiosity, I have compared the emission factors from AP-42 with the emissions estimated from the ROM. In the ROM, an NO emissions flux from fertilized corn fields of 586 $\mu g\ m^{-2}\ h^{-1}$ is assumed at a temperature of 30 C. If we assume a fertilizer application of 100 kg N/ha and that NO emissions occur a period of 120 days, then the percentage loss of N in the form of NO is 8%. This compares to the AP-42 values of 6% for urea, 1% for ammonium nitrate (fluid), and 11% ammonium nitrate (as a solid). So it would appear that we are both in the same ballpark, but neither one of us really knows the size of the ballpark.

I appreciate the effort that your branch is making to improve emission factors for ozone precursors. As indicated in my comments and as reflected in the draft report, there is still much work left to be done. If I can be of any further assistance, please call me at extension 1-1375.

cc: J. Novak
C. Geron (AEERL)

Tennessee Valley Authority, Post Office Box 1010, Muscle Shoals, Alabama 35660

January 13, 1994

Mr. Dallas W. Safriet
USEPA
Emission Inventory Branch MD-14
Research Triangle Park, North Carolina 27711

Dear Mr. Safriet:

I am writing you in response to your request that our organization, TVA, respond to your report entitled "Emission Factor Documentation for AP-42, Section 6.2.1, Fertilizer Application." John Culp forwarded the document to me and asked that I be the future contact on this work since I and members of our research section are actively involved in measuring soil emissions of NO and N_2O. Our efforts in this area are chiefly driven by the need to better characterize the biogenic soil source of NO due to its role in rural ozone formation. As you may know, TVA is actively involved in the Southern Oxidant Study (SOS), which seeks to better understand the factors involved in ozone formation and transport in the Southeast. As a part of this effort, TVA has been measuring soil emissions of NO for the past several years in various locations throughout the Tennessee Valley. The intent of these studies is to provide data that can be used in building an emission inventory for soil of varying land use in the Tennessee Valley. To date, we have visited 13 sites and measured emissions in forests, pastures, and a variety of agricultural crops. This past field season, we conducted an experiment at Jackson, Tennessee, looking at both NO and N_2O emissions from a no-till corn experiment fertilized at three different N rates. We are currently analyzing the data from this study in order to prepare a journal manuscript. I have included our recent paper published in the Journal of Geophysical Research that deals with our finding from the summer of 1991. I will also send you another article dealing with soil NO emissions from cotton that has been accepted by the journal as soon as we make the suggested changes made by the reviewers.

I think it will also be of interest for you to know that we will be undertaking a number of projects in collaboration with TVA's Agricultural Research and Practices Section over the next several years that deal with NO and N_2O emissions from agricultural soils. In addition to our work on mineral fertilizers, we plan to investigate NO and N_2O emissions associated with applications of animal waste (either dairy and/or poultry litter). Denitrification losses associated with manure applications are not well characterized and it is thought that losses from animal waste land applications may equal or exceed those from mineral fertilizers. Furthermore, these studies will likely have a component to look at volatilization losses as well. In short, TVA is very actively involved in characterizing soil emissions of both NO and N_2O and will

continue to do so in the next several years. Given our past involvement and our future plans, we would be receptive to try and incorporate some of your agency's needs in our work, as it is apparent that we both are attempting to decrease the uncertainty associated with building regional inventories of these trace gases.

In regard to my comments on the document, I would make the following:

1. A significant shortfall of this document is the omission of many current literature citations that deal with the subject matter. It would be advised that the authors refer to the recent review article of Williams et al. (1992) which is an excellent review of NO and N_2O emissions from soils. Some of the following articles are cited in the afore mentioned article, but the authors sorely need to update their literature source. For example, the TVA data base on fertilizer usage for 1989/198 is used. Why not use the 1992/1993 TVA published report? A brief listing of some of these articles are:

   I. Ammonium related

   Whitehead, D. C. and N. Raistrick, J. Agric. Sc. (Cambridge) 121:73-81, 1993.
   Sommers, S. G. et al., J. Agric. Sc.(Cambridge) 121:63-71, 1993.
   Oenema, O. and G. L. Velthof, Neth. J. Agric. Sc. 41:63-80, 1993.
   Burton, C. H. et al., Bioresource Tech. 45:233-235, 1993.
   Sibbesen, E. and A. M. Lind, Acta Agric. Scanda. Ect. B. Soil and Plant Sci.43:16-20.

   II. NO and N_2O related

   Hansen, S. et al., Soil Biol. Biochem 25:621-630, 1993.
   Skiba, U. et al., Atmos. Environ. 26A:2477-2488, 1992.
   Bronson, K. F. and A. R. Mosier, ASA Publ. 55, pp. 133-144, Madison, WI.
   Bronson, K. F. et al., Soil Sci Soc Am. J. 56:161-165, 1992.
   Bronson, K. F. and A. R. Mosier, Biol Fertil. Soils 11:116-120, 1991.
   Jarvis, S. C. et al., Plant and Soil 131:77-88, 1991.
   Lindau, C. W. et al., Plant and Soil 129:269-276, 1990.
   Brumme, R. and F. Beese, J. Geophy. Res. 97:12,851-12,858, 1992.
   Nugroho, S. G. and S. Kuwatsuka, Soil Sci. Plant Nutr. 38:593-600 1992.

Aulakh, M. S. et al., Soil Sci Soc Am. J. 48:790-794, 1984.
Schloenmer, S., Z. Pflanzenernahr. Bodenk. 153:439-444, 1990.
Valente, R. J. and F. C. Thornton, J. Geophy. Res. 98:16,745-16,753, 1993.
Skiba, U. et al., Soil Biol. Biochem 25:1527-1536, 1993.

2. A fertilizer is "any substance that is added to the soil to supply elements required for plant nutrition" (Tisdale and Nelson, Soil Fertility and Fertilizers, 2nd ed., 1975), why then do you not address animal waste and green manures. I suggest you change the title to indicate you are only referring to mineral fertilizers. I also realize there is very little information on this related to NO and N_2O but a fair bit of information is available for dairy and swine waste, particularly related to loss of NH_3 and N_2O in storage prior to land application.

3. Pages 2-28 through 2-29. There is some work by Bronson et al. on the used of nitrification inhibitors to reduce N_2O emissions. I think this work needs to be incorporated into the document.

4. Page 4-3. I am unclear why in lines 21-23 you state that "NO_x emissions were estimated as NO_2." Earlier on the same page, lines 3-5 you note that the study indicated that the emissions "were primarily" NO not NO_2. Our work and the published work of most all researchers studying soil NO emissions have found that NO is the dominant species, thus I do not understand why you calculate emissions as NO_2. Even the author of the paper you cite states that it is mostly NO that is emitted, not NO_2.

5. Page 4-20, lines 12-15. Admittedly, the fertilizers you chose not to include do not represent a significant tonnage but I would argue that regardless of fertilizer form there is an addition of NO_3 or NH_4 that is ultimately available for soil processes, whether it be denitrification or any other soil process, i.e., leaching. I think that these data should be used. Soil microorganism do not discriminate among NO_3 or NH_4 ions provided by a particular fertilizer formulation.

6. Page 4-12. I question your approach of taking the arithmetic mean of the calculated emission factors in the papers you selected for inclusion in this work. The soil emissions of NO and N_2O are typically lognormally distributed. I would suggest you refer to the work of Parkin (Soil Sc. Soc. Am. J. 52: 323-329, 1988;

also 54: 321-326; Agronomy J. 1993--I'm not sure of the issue, I have a copy of a galley proof). Why do some and not all of the emission factor estimates listed in tables 4.2 and 4.3 include standard deviation estimates? Due to the large temporal and spatial variability I think these should be included for all entries. I might also add that while you do acknowledge the limitations of the data set used, you do not point out fact that in all cases the data used are from limited point estimates throughout the growing season. In our work this past year we have seen tremendous variability from day to day in N_2O emissions. In studies were measurements are taken on a weekly basis you may miss the majority of the emission events. The recent comments of Auluka (1992) are well taken; he contends that weekly or biweekly measurements are not adequate to estimate seasonal or annual trace gas emissions. He suggests that "annual denitrification loss estimates may require daily measurements." I concur with that statement and we have established a protocol in our studies where we make measurements eight times a day on replicates for the entire growing season.

Should you have questions concerning my comments, please do not hesitate to contact me by phone at 205-386-3642 or fax at 205-386-2499. I would be happy to discuss the comments I have made or discuss in further detail our research on soil trace gas emissions.

Sincerely,

Frank C. Thornton /les

Frank C. Thornton
Senior Soil Scientist
Atmospheric Sciences

Enclosure

Tennessee Valley Authority, Post Office Box 1010, Muscle Shoals, Alabama 35660

December 14, 1992

Mr. Dallas W. Safriet
Environmental Engineer
Emission Inventory Branch
United States Environmental
Protection Agency
Office of Air Quality Planning
and Standards
Research Triangle Park, North Carolina 27711

Dear Mr. Safriet:

John Culp and I enjoyed our phone conversation with you this morning and the discussion describing our concerns about the draft AP-42 document you sent for review. Enclosed are comments from Roland Hauck, Michael Broder, and me. In general, because of the inaccuracies, dated information, and errors we feel that a complete rewrite is necessary to make this information accurate and current. Our comments are not necessarily complete because of the quick turn around you indicated was necessary. After you have an opportunity to review our comments, we would welcome further discussions on how the revisions could be made.

Thank you for giving us the opportunity to review this draft.

Sincerely,

Horace C. Mann

Horace C. Mann
Projects Manager
Field Programs Department
National Fertilizer and
Environmental Research Center

Enclosure

Suggestions for improving EPA AP-42 Draft Report from Michael Broder

In the interest of time I have limited my suggestions to Section 5 which I believe is the only part that will appear in AP-42. In summary, the descriptions of the application processes are inaccurate and misleading. Anyone remotely familiar with the use of fertilizers in crop production in the U.S. would find the information suspect. A couple of references are available which adequately describe application processes; chapter 9 of TVA Bulletin Y-185 Fluid Fertilizers, or chapter 31 of Nitrogen in Crop Production edited by Roland D. Hauck. Section 5 should be completely rewritten and then resubmitted for review. The gross errors in the application process descriptions and in fertilizer formulas would cause any informed reader to question the emission factors.

Section 6.2.1.1 General

SIC codes don't seem to be relevant to this discussion. The adjective "custom" is not normally used to describe fertilizer dealers. Application is performed by custom applicators in addition to farmers and fertilizer dealers. In Florida, for example, nearly all fertilizer applied commercially is done by custom applicators who do not sell the fertilizer.

Section 6.2.1.2 Process Description

This paragraph could be made much less awkward as follows:

Fertilizer is applied by three basic methods depending on its physical state; solid (granular), fluid, or gaseous.

Section 6.2.1.2.1 Gaseous Fertilizer

Trucks are never used to apply anhydrous ammonia. They don't have the pulling power at the low speeds required. Plowing discs/plates is not a recognized term. The American Society of Agricultural Engineers Standards lists terminology of tillage devices. Injection knives or chisels are the proper term. The tube holders are an insignificant part of the system. Metering application rate) is controlled by three methods; 1) a calibrated orifice is preset to release a constant amount of ammonia per hour while applicator speed is held constant (orifice calibration is accurate for tank pressures between 50 and 150 psig), 2) a heat exchanger is used to provide liquid ammonia to a flow meter installed in line with an orifice which is controlled electronically to adjust ammonia flow according to speeds indicated by a radar speed sensor, 3) a piston pump driven by a chain from a ground driven wheel is used to deliver ammonia. The latter two systems are more accurate than the first because the ammonia flow is synchronized with ground speed.

Because of the difficulty and danger associated with collecting and measuring anhydrous ammonia these machines are only calibrated by researchers and at the manufacturing site. Metering systems have precisely machined orifices which normally do not require calibration.

Most anhydrous ammonia is applied by farmers. The service is not profitable for dealers and custom applicators because the area that can be treated in a given time is 3 to 6 times less than what can be achieved by broadcast application. The margin, consequently, is not large enough to offset the higher labor cost.

The planting of seed and anhydrous ammonia application is never done simultaneously.

Figure 6.2.1-1-should be replaced with a sketch depicting only anhydrous application. Dual systems are not the norm. Also, the ammonia supply tank is generally a nurse tank which trails behind the tillage (incorporation) implement.

Section 6.2.1.2.2 Fluid Fertilizer

The application of fluid fertilizer and anhydrous is not at all similar. Fluid fertilizers are generally not diluted. Economics dictate that they be shipped and applied as concentrated as physical properties allow. Manifolds are not composed of booms. Manifolds are plumbing devices which split the flow of fluid into two or more equal flows which are further divided along the booms which are generally 20 to 40 feet long.

The figure 6.2.1-2 depicts a spray system on a tillage device. Though this is a common practice, a much greater volume of product is applied using truck mounted sprayers and specially build high flotation vehicles. Though fluid can be applied in discreet bands by lowering broadcast nozzles, generally, nozzles which produce a solid stream are used for banding. Most custom application equipment has booms mounted at a fixed height to facilitate operating at high speeds.

The proper overlap varies according to nozzle design. Flooding and hollow cone nozzle patterns should be overlapped 100 percent, flat fan nozzles should be overlapped 30 percent. Since most commercial rigs have booms 3 to 4 feet above the ground and nozzles spaced 5 feet, the actual overlap of nozzle sprays is as high as 200 to 300 percent.

Section 6.2.1.2.3. Solid fertilizers

About two-thirds of the fertilizer applied in the U.S. is in solid form. I don't believe timed release fertilizer technology has caused broadcast application to grow. If broadcast application is growing it is due to its low cost and efficiency relative to other methods.

The most common method for applying solid fertilizer is by centrifugal spreaders. Centrifugal spreaders have one disc or two counter-rotating discs, mounted

horizontally, which broadcast material falling from a belt or mesh-chain conveyor. An adjustable gate in the hopper above the conveyor is used to set application rates. Output is synchronized with ground speed either electronically or mechanically.

Among the boomed applicators, three different pneumatic designs and one auger metered system are most popular. The impetus for using boomed spreaders is for uniform application of dry fertilizer impregnated with herbicide. This practice and boomed solid applicator are described in detail in chapter 13 of the monograph, Methods of Applying Herbicides, edited by C. G. McWhorter and M. R. Gebhardt.

The description of equipment in this section is atrocious. ; Deflectors and not nozzles are used to direct pneumatically conveyed material to the ground. there are no orifices at the discharge end and there are no fan blades that spin. The authors appear to have combined parts of both, centrifugal and pneumatic applicators.

6.2.1.3 Emission and Controls

I don't believe there is enough data to support mentioning the heavy metals which may become airborne with fugitive dust.

Table 6.2.2-1

This table needs to be reviewed by Roland Hauck or someone in his department.

Table 6.2.2-2

The chemical formulas for urea, ammonium sulfate, and calcium nitrate are wrong. The nitrogen contents are incorrect for three of the materials (see Don Kachelman's attached corrections).

N:\Broder.EPA.corrections

Comments on the draft report "Background Documentation for AP-42 Section 6.2.1, Fertilizer Application, MRI Paper No. 6500-K(35) Roland D. Hauck

General Comment

Section 2 of the subject draft report can be greatly improved by: (i) correcting many inaccuracies and misinterpretations of information, and (ii) tightening up the discussion to make it more directly relevant to the objectives of the study. Regardless of the criteria used for selecting data and the care taken in calculating emission factors, the value of the emission factors given in section 5 is suspect because the discussion in section 2 indicates only an elementary and incomplete knowledge of the process dynamics leading to gaseous nitrogen emissions.

Specific Comments

2-7 The term fluid fertilizer rather than liquid fertilizer should be used. The information about liquid fertilizers is not entirely correct. They usually are concentrated rather than dilute solutions (lower handling, transport, and distribution costs). They may be injected or dribbled on as well as sprayed.

2-7 para.4. The paragraph assumes that time-release fertilizers use is growing and that such fertilizers comprise or will comprise a significant amount of total fertilizer use. This assumption is incorrect.

2-10 The contaminants listed in Table 2-1 also are present in soils to which no fertilizer has been added.

sec. 2.3.1.1 The discussion of ammonia/ammonium reactions in soils reflects a poor understanding of soil chemistry. Although several statements made are essentially correct, they are presented neither clearly nor accurately.. For example, there is no clear distinction between the dissolution of ammonia in or absorption by water and adsorption of ammonium ion on inorganic and organic exchange surfaces. .

sec. 2.3.1.2 The term, (NO)x, most generally is used when referring to the N oxide gases. NO, NO2, N2O, and N2O4, although the most rigid use would restrict it to NO and NO2. Nitrite and nitrate normally are not included in this group, as indicated in this section. There is little evidence that nitrification leads to significant loss of gaseous nitrogen.

Sec.2.3.1.2 This section also reflects only rudimentary understanding of the subject. For example, the discussion relating to ammonium nitrate is incorrect; equation 2-1 is for the reaction of ammonium with nitrite rather than nitrate. Nitrite usually is not present in appreciable quantities in soils except in microsites of high pH. The reaction shown by equation

2.1 occurs appreciably only at low pH (below 5).

Sec.2.3.1.3 One of the main sulfur sources supplied in fluid fertilizers, ammonium thiosulfate, is not listed. Sulfur dioxide (listed) is not a common source. The amount supplied as sulfur-coated urea is negligible when compared to the whole. During the period when fertilizer use was increasing in the United States, there was a corresponding increase in the total nutrient content of fertilizer materials and a decrease in the level of impurities, including heavy metals and sulfur. The amount of nitrogen added as ammonium sulfate, therefore the amount of sulfur added from this material, also will not increase (ammonium sulfate is mainly a by-product rather than made primarily for fertilizer use).

2-21, para.2 Fluid fertilizers, rather than solid ones, can be applied more rapidly per unit of nutrient. There is no evidence that emissions from solid fertilizers generally exceed those from fluids with the exception of surface-applied, un-incorporated urea or diammonium phosphate from which ammonia may be liberated to the atmosphere. Other comments could be made to point out the fallacy of making generalizations from an extensive literature without a solid understanding of that literature.. This lack of understanding is reflected further in the discussion on page 2-2. For example, the definition of CEC given in the footnote would almost be correct only if the parenthetical phrase were deleted.

4-1, para.3 The data given in the references cited may be considered accurate. What may be questionable is the use of the data for extrapolating to dimensions several magnitudes larger than the system from which the data sets were collected.

4-10, para.1 A rating of D is given for the data from references 15a and 15b because a nonstandard and unproven method was used. The method used, however, is the only one of all methods cited in the accepted references that makes measurements in the unconfined atmosphere over an entire field. Extrapolating data obtained in this manner to large dimensions is more justifiable than a similar extrapolation of data collected from chamber studies.

Table 6.2.1-1 The weak basis for the numbers given in this table was adequately discussed in the previous section. However, once data are published in an official document they may assume an undeserved validity. For example, the emission factor for ammonia from solid fertilizers is based on ammonia volatilization from surface-applied, un-incorporated urea, which does not represent the bulk of solid nitrogen fertilizers nor the manner in which they are used. The emission factor for nitrous oxide is based on studies that measured nitrous oxide formed during nitrification, whereas most nitrous oxide released to the atmosphere from soils probably is the result of denitrification. Also, where nitrification is involved, the type, physical state, and, if solid, the particle size are among the factors affecting the rate of nitrification and course of its reaction products. These factors were not considered in the studies cited nor in the

evaluation of data.

To construct a table of emission factors for fertilizers from an admittedly extremely limited and weak data base is not justifiable. To present the information in terms of 0.1g/kg or 0.1 lb./ton implies a precision not warranted by the data.

Table 6.2.1-2 This table lists calcium nitrate and ammonium chloride as common fertilizers used in the United States, which they are not, and omits such materials as monoammonium and diammonium phosphates, which are common components of mixed fertilizers.

Additional comments on Sections 2, 4, and 5 -Proposed AP-42 - Specific and general--H. C. Mann

Page 2-1, 2-2 - "Liquid fertilizer" should be "fluid fertilizer."

Page 2-2 - Suggest 20-30% NH_3 instead of 30-40% or put temperatures where vapor pressure is 0 psig.

Page 2-4 (Figure 2-1) - No pump on NH_3 applicator.

2.2.2 - "Fluid" instead of liquid on title and first word in 1.

Last sentence is wrong, needs to include injection

2nd and 3rd paragraphs need rewriting to include injection, remove "liquid" and replace with fluid where appropriate.

2.2.3 - Whole section needs rewriting to reflect both current equipment available and application practices.

Figure 2-5 - Do not normally spray on a " young" plant. Banding is normally to the side and below and by injection.

Table 2-1 - Sources of phosphate and nitrogen fertilizer need to be identified to not cause misconceptions - i.e., NH_3 does not contain a number of the elements listed. All phosphate fertilizers do not contain 200 ppm of Ba, 20 ppm Ce, etc.

Paragraph 2.3 - First sentence is <u>too</u> absolute. Needs to be qualified significantly.

Section 5, paragraph 6.2.1.2.2 - "Liquid" should be changed to fluid and the entire section rewritten to reflect current commercial practices.

Section 5, paragraph 6.2.1.2.3 - Section needs to be rewritten to reflect current commercial practices.

Section 5, paragraph 6.2.1.3 - Too absolute, needs to be qualified significantly.

Tables 4-5 and 6.2.1-2 - Urea formula wrong, should be $(NH_2)_2$ CO.

Ammonium sulfate wrong, should be $(NH_4)_2$ SO_4.
Calcium nitrate wrong, should be Ca $(NO_3)_2$.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
ATMOSPHERIC RESEARCH AND EXPOSURE ASSESSMENT LABORATORY
RESEARCH TRIANGLE PARK
NORTH CAROLINA 27711

November 9, 1992

MEMORANDUM

SUBJECT: Review of "Background Documentation for AP-42, Section 6.2.1: Fertilizer Application"

FROM: Thomas E. Pierce (MD-80) Thomas E. Pierce
MSAB, ACMD

TO: Dallas Safriet (MD-14)
EIB, TSD, OAQPS

I appreciate the opportunity to review the draft AP-42 report on fertilizer application. The Atmospheric Research and Exposure Assessment Laboratory (AREAL) is keenly interested in the study of photochemical oxidant pollution and in ensuring that all anthropogenic and biogenic sources of nitrogen oxide emissions, which play a critical role in ozone production, are included in the modeling emissions inventories. Because of my limited knowledge on nitrogen-based emissions, my comments are restricted to those areas that I have some experience: emissions of NO and NO_2.

Before discussing the report, allow me to offer a perspective from an ozone modeler and a biogenic emissions algorithm developer. As a atmospheric modeler, I view the atmosphere as having a closely-linked system of nitrogen sources and sinks. The draft AP-42 report and other scientific literature make it clear that NO and NO_y can be both emitted from the soil and deposited to the soil and vegetation. This highly-dynamic phenomenon makes it difficult to develop generic emission factors. In our attempt to develop biogenic emission algorithms, we are modeling nitric oxide (NO) emissions from soils as a function of land use type and soil temperature. Admittedly, the amount of nitrogen-based fertilizer can significantly affect the amount of NO_x emitted into the air. However, other factors such as soil moisture, soil type, and ambient conditions confound the relationship making it very difficult to develop general emission factors (for further background, see the recent article by Williams et al, 1992, *Journal of Geophysical Research*, vol. 97, pp. 7511-7520).

I have several specific concerns regarding the emission factors noted in the publication. Scientific literature indicate that almost all NO_x from the soil is emitted in the form of NO, not NO_2. Reference 1 in the AP-42 report states specifically that >98% of the NO_x emissions are in the form of NO. Therefore, **the NO_2 emission factor should be reexamined and probably computed as an NO emission factor.**

Regarding the NO emission factor, I was somewhat disappointed that some recent work was not included. Specifically, articles by Williams et al. (1992) and Slemr and Seiler (1991, *Journal of Geophysical Research*, vol. 96, pp. 13017-13031) are relevant. The Williams article lists NO emission rates as a function of crop type and fertilizer application. We are investigating the possible use of the Williams algorithm with the Biogenic Emissions Inventory System (BEIS), which is a preprocessor for EPA's Regional Oxidant Model. BEIS already uses a simplified version of the algorithm, but it does not yet assume the high emission rates from fertilized fields. The Williams article is also important because it clearly demonstrates that NO emissions depend strongly on soil temperature and moisture. In my opinion, **any published hourly emission rate should include a formula for converting a normalized emission factor by an environmental adjustment factor.**

The Slemr and Seiler work is important for two reasons. First, it updates their 1984 work, which was referred to extensively in the AP-42 document. Second, the Slemr and Seiler work shows that:

(1) NO_y emissions are usually lower than NO emissions.
(2) Emissions are strongly dependent on whether vegetation is present. In the presence of vegetation, NO and NO_y emissions are reduced.
(3) Deposition (negative emissions) is commonly observed and appears to be linked to vegetation coverage and ambient concentrations of NO_y.

The article further demonstrates to me that NO emissions from soils should be simulated with an atmospheric model that properly accounts for soil properties, meteorological conditions, and ambient concentrations of NO_y.

In summary, while I think the published NO emission rates are useful information, it is very important that appropriate caveats on their uncertainty be given in the report.

Please keep me informed on the status of this document and its possible inclusion in AP-42. Since both of us are working on emissions from soils (from an anthropogenic and biogenic perspective), it is important that we avoid double-counting NO emissions from soils in future air quality modeling work. If you would like to discuss this review with me, please call me at 541-1375.

cc: C. Geron
W. Benjey

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February 17, 1995

To: Dallas Safriet
OAQPS/EMAD/EFIG (MD-14)
U. S. Environmental Protection Agency
Research Triangle Park, NC 27711

From: Tom Lapp

Subject: Response to TVA and EPA/AREAL Comments on AP-42 Section 9.2.1
EPA Contract No. 68-D2-0159, Work Assignment II-03
MRI Project No. 4602-03

Review comments were received from Mr. Frank C. Thornton of the Tennessee Valley Authority and Mr. Thomas Pierce of EPA/ORD/AREAL on the November 30, 1993 draft background report and AP-42 Section 9.2.1, Fertilizer Application. The comments will help improve the background report and the AP-42 section. Responses to each of the comments are tabulated below. Copies of the comments are attached.

I. Frank Thornton; TVA

Comment 1. Seventeen of the 18 references were obtained and reviewed; one could not be found. Of the 17, 5 of the papers were incorporated into the background report, 7 were cited in Section 4 of the background report but were not used, and 5 pertained to emissions from the storage or treatment of animal wastes. Of the 5 papers incorporated, 2 contained data for emission factors and 3 were concerned with inhibition of nitrification; these were cited in Section 2 of the background report. The 7 papers cited in Section 4, Table 4-1, were not used because they either were not applicable or did not contain sufficient information for calculation of emission factors. The 5 papers containing emission information from the storage or treatment of animal wastes will be reviewed for use in Section 9.5.4, Manure Processing, or other applicable sections. The review article by Williams, et al (1992) was obtained and cited in Section 4 and the AP-42 section.

Comment 2. Added a sentence in AP-42 Section 9.2.1.3 referring the reader to AP-42 Section 9.5.4, Manure Processing, for emissions from animal waste and green manure in storage prior to land application.

Comment 3. This refers to the 3 papers cited under Comment 1 concerning inhibition of nitrification; the work was cited in Section 2 of the background report.

Comment 4. Emissions of NO_x were changed to NO instead of NO_2 as requested. The emission factors were also changed to reflect emissions as NO and not as NO_2. This same comment was also provided by Tom Pierce. A discussion of NO emissions versus NO_2 emissions was provided in Section 4.2.1 of the background report and appropriate references were cited.

Comment 5. This comment may have some validity regarding the microorganisms in the soil not being able to distinguish the source of nitrate and ammonium ions. However, there seems to be little added value by including rarely used fertilizers of very low tonnage in the AP-42 tables. There are few available emission factors for the most common fertilizers; most of the columns in Tables 4-5, 4-6, 9.2.1-2, and 9.2.1-3 contain ND (no data) entries. There is little to be gained by including a couple of factors for these low tonnage fertilizers and significantly increasing the number of ND entries. As additional data become available, it may be realistic to add these fertilizers in the next edition. The data are provided in Table 4-3 of the background report for the interested reader.

Comment 6. The average emission factors are based on averaging either 2 or a maximum of 3 factors. There is no rationale for suggesting the use of an average other than arithmetic. Soil emissions may be lognormally distributed but that has no impact on averaging 2 or 3 numbers to obtain an average factor. Based on Mr. Thornton's further comments, he may be misinterpreting the source of the average emission factors and think they are based on individual data points taken from the cited studies. The discussion of temporal and spatial variability as well as weekly (or biweekly) versus hourly measurements may be true but it has no relevance to the calculation of average emission factors and is primarily irrelevant information.

II. Thomas E. Pierce; EPA/ORD/AREAL

Comment 1. The cited article was obtained, reviewed, and cited in Section 4.2.1 of the background report. Emission factors for NO_2 were recalculated and reported as NO emissions, as requested. This request was also made in Comment 4 by Mr. Thornton.

Comment 2. MRI understands Mr. Pierce's concern but disagrees that the emission factors in Tables 4-5, 4-6, 9.2.1-2, and 9.2.1-3 should be condensed as requested. A caveat was added at the end of Section 4.2.2 of the background report and in AP-42 Section 9.2.3 stating this concern and advising the reader that

the data used to develop the emission factors are sparse and cautioning against any thoughts for emission reduction strategies using these factors.

Rec'd from Dallas
1/19/94 TR

Tennessee Valley Authority, Post Office Box 1010, Muscle Shoals, Alabama 35660

January 13, 1994

Mr. Dallas W. Safriet
USEPA
Emission Inventory Branch MD-14
Research Triangle Park, North Carolina 27711

Dear Mr. Safriet:

I am writing you in response to your request that our organization, TVA, respond to your report entitled "Emission Factor Documentation for AP-42, Section 6.2.1, Fertilizer Application." John Culp forwarded the document to me and asked that I be the future contact on this work since I and members of our research section are actively involved in measuring soil emissions of NO and N_2O. Our efforts in this area are chiefly driven by the need to better characterize the biogenic soil source of NO due to its role in rural ozone formation. As you may know, TVA is actively involved in the Southern Oxidant Study (SOS), which seeks to better understand the factors involved in ozone formation and transport in the Southeast. As a part of this effort, TVA has been measuring soil emissions of NO for the past several years in various locations throughout the Tennessee Valley. The intent of these studies is to provide data that can be used in building an emission inventory for soil of varying land use in the Tennessee Valley. To date, we have visited 13 sites and measured emissions in forests, pastures, and a variety of agricultural crops. This past field season, we conducted an experiment at Jackson, Tennessee, looking at both NO and N_2O emissions from a no-till corn experiment fertilized at three different N rates. We are currently analyzing the data from this study in order to prepare a journal manuscript. I have included our recent paper published in the Journal of Geophysical Research that deals with our finding from the summer of 1991. I will also send you another article dealing with soil NO emissions from cotton that has been accepted by the journal as soon as we make the suggested changes made by the reviewers.

I think it will also be of interest for you to know that we will be undertaking a number of projects in collaboration with TVA's Agricultural Research and Practices Section over the next several years that deal with NO and N_2O emissions from agricultural soils. In addition to our work on mineral fertilizers, we plan to investigate NO and N_2O emissions associated with applications of animal waste (either dairy and/or poultry litter). Denitrification losses associated with manure applications are not well characterized and it is thought that losses from animal waste land applications may equal or exceed those from mineral fertilizers. Furthermore, these studies will likely have a component to look at volatilization losses as well. In short, TVA is very actively involved in characterizing soil emissions of both NO and N_2O and will

continue to do so in the next several years. Given our past involvement and our future plans, we would be receptive to try and incorporate some of your agency's needs in our work, as it is apparent that we both are attempting to decrease the uncertainty associated with building regional inventories of these trace gases.

In regard to my comments on the document, I would make the following:

1. A significant shortfall of this document is the omission of many current literature citations that deal with the subject matter. It would be advised that the authors refer to the recent review article of Williams et al. (1992) which is an excellent review of NO and N_2O emissions from soils. Some of the following articles are cited in the afore mentioned article, but the authors sorely need to update their literature source. For example, the TVA data base on fertilizer usage for 1989/198 is used. Why not use the 1992/1993 TVA published report? A brief listing of some of these articles are:

   I. Ammonium related

   Whitehead, D. C. and N. Raistrick, J. Agric. Sc. (Cambridge) 121:73-81, 1993.
   Sommers, S. G. et al., J. Agric. Sc.(Cambridge) 121:63-71, 1993.
   Oenema, O. and G. L. Velthof, Neth. J. Agric. Sc. 41:63-80, 1993.
   Burton, C. H. et al., Bioresource Tech. 45:233-235, 1993.
   Sibbesen, E. and A. M. Lind, Acta Agric. Scanda. Ect. B. Soil and Plant Sci.43:16-20.

   II. NO and N_2O related

   Hansen, S. et al., Soil Biol. Biochem 25:621-630, 1993.
   Skiba, U. et al., Atmos. Environ. 26A:2477-2488, 1992.
   Bronson, K. F. and A. R. Mosier, ASA Publ. 55, pp. 133-144, Madison, WI.
   Bronson, K. F. et al., Soil Sci Soc Am. J. 56:161-165, 1992.
   Bronson, K. F. and A. R. Mosier, Biol Fertil. Soils 11:116-120, 1991.
   Jarvis, S. C. et al., Plant and Soil 131:77-88, 1991.
   Lindau, C. W. et al., Plant and Soil 129:269-276, 1990.
   Brumme, R. and F. Beese, J. Geophy. Res. 97:12,851-12,858, 1992.
   Nugroho, S. G. and S. Kuwatsuka, Soil Sci. Plant Nutr. 38:593-600 1992.

Aulakh, M. S. et al., Soil Sci Soc Am. J. 48:790-794, 1984.
Schloenmer, S., Z. Pflanzenernahr. Bodenk. 153:439-444, 1990.
Valente, R. J. and F. C. Thornton, J. Geophy. Res. 98:16,745-16,753, 1993.
Skiba, U. et al., Soil Biol. Biochem 25:1527-1536, 1993.

2. A fertilizer is "any substance that is added to the soil to supply elements required for plant nutrition" (Tisdale and Nelson, Soil Fertility and Fertilizers, 2nd ed., 1975), why then do you not address animal waste and green manures. I suggest you change the title to indicate you are only referring to mineral fertilizers. I also realize there is very little information on this related to NO and N_2O but a fair bit of information is available for dairy and swine waste, particularly related to loss of NH_3 and N_2O in storage prior to land application.

3. Pages 2-28 through 2-29. There is some work by Bronson et al. on the used of nitrification inhibitors to reduce N_2O emissions. I think this work needs to be incorporated into the document.

4. Page 4-3. I am unclear why in lines 21-23 you state that "NO_x emissions were estimated as NO_2." Earlier on the same page, lines 3-5 you note that the study indicated that the emissions "were primarily" NO not NO_2. Our work and the published work of most all researchers studying soil NO emissions have found that NO is the dominant species, thus I do not understand why you calculate emissions as NO_2. Even the author of the paper you cite states that it is mostly NO that is emitted, not NO_2.

5. Page 4-20, lines 12-15. Admittedly, the fertilizers you chose not to include do not represent a significant tonnage but I would argue that regardless of fertilizer form there is an addition of NO_3 or NH_4 that is ultimately available for soil processes, whether it be denitrification or any other soil process, i.e., leaching. I think that these data should be used. Soil microorganism do not discriminate among NO_3 or NH_4 ions provided by a particular fertilizer formulation.

6. Page 4-12. I question your approach of taking the arithmetic mean of the calculated emission factors in the papers you selected for inclusion in this work. The soil emissions of NO and N_2O are typically lognormally distributed. I would suggest you refer to the work of Parkin (Soil Sc. Soc. Am. J. 52: 323-329, 1988;

also 54: 321-326; Agronomy J. 1993--I'm not sure of the issue, I have a copy of a galley proof). Why do some and not all of the emission factor estimates listed in tables 4.2 and 4.3 include standard deviation estimates? Due to the large temporal and spatial variability I think these should be included for all entries. I might also add that while you do acknowledge the limitations of the data set used, you do not point out fact that in all cases the data used are from limited point estimates throughout the growing season. In our work this past year we have seen tremendous variability from day to day in N_2O emissions. In studies were measurements are taken on a weekly basis you may miss the majority of the emission events. The recent comments of Auluka (1992) are well taken; he contends that weekly or biweekly measurements are not adequate to estimate seasonal or annual trace gas emissions. He suggests that "annual denitrification loss estimates may require daily measurements." I concur with that statement and we have established a protocol in our studies where we make measurements eight times a day on replicates for the entire growing season.

Should you have questions concerning my comments, please do not hesitate to contact me by phone at 205-386-3642 or fax at 205-386-2499. I would be happy to discuss the comments I have made or discuss in further detail our research on soil trace gas emissions.

Sincerely,

Frank C. Thornton

Frank C. Thornton
Senior Soil Scientist
Atmospheric Sciences

Enclosure

Recd 1/5/94
TC

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
ATMOSPHERIC RESEARCH AND EXPOSURE ASSESSMENT LABORATORY
RESEARCH TRIANGLE PARK
NORTH CAROLINA 27711

December 28, 1993

MEMORANDUM

SUBJECT: Review of the Revised Draft Report, "Emission Factor for AP-42, Section 6.2.1: Fertilizer Application"

FROM: Thomas E. Pierce (MD-80)
MSAB/ACMD/AREAL/ORD

TO: Dallas W. Safriet (MD-14)
EIB/OAQPS

As you requested, I have reviewed the revised draft report on emission factors from fertilizer application. I will restrict my review comments to those areas that I have some degree of familiarity: NO_x emissions from soils. I believe the authors of the report have done a credible job, considering the paucity of information on the subject and the inter-disciplinary range of the references (compared to other AP-42 emission factor studies). I further appreciate that considerable efforts were made to develop emission factors that could be clearly expressed in tabular form for AP-42. However, I have two major recommendations concerning the proposed values for NO and NO_2.

(1) Most scientific papers discussing biological mechanisms of NO_x emissions from soils note that most (>90%) if not all of the emissions are in the form of nitric oxide (NO). According to Hutchinson and Brahms (J. of Geophysical Research, pp. 9889-9896, 1992), there is no evidence to suggest that NO_2 is directly emitted from soils. Other scientists support this statement (references available on request). Admittedly, the emission factors were based on chamber experiments that measured increased levels of NO_2, which would lead one to infer emissions of NO_2. This probably occurs because NO emitted from the soil into the chamber is quickly converted to NO_2 in the presence of ozone. In fact, the revised AP-42 draft report on page 4-3 notes: "Because any NO emitted is likely to be converted quickly to NO_2 in the atmosphere, the NO_x emissions were estimated as NO_2." However, EPA's air quality simulation models supposedly handle the chemical transformations that occur when a gas is directly emitted in the air, even in the case of NO when this transformation occurs rapidly near the soil/air interface. For this reason, **I recommend that the emission factors for NO and NO_2 be expressed only as NO.**

(2) The authors correctly noted that substantial variability of NO_x emissions occur both within and among sites. Because of this and the shortage of experimental data, I do not think sufficient data exist to divide emission factors according to the type of fertilizer application. I am worried that a policy maker, who is looking into NO_x emission abatement strategies, might review the proposed AP-42 emission factor table and conclude that different types of fertilizers could be

used for NO_x emission reductions. While this may in fact be true, I do not think sufficient experimental data currently exist to differentiate NO emissions between fertilizer types. Therefore, **I recommend that only one NO emission factor (applicable to all nitrogen-based fertilizers) be reported in the draft AP-42 table.**

I wanted to let you know that the Regional Oxidant Model (ROM) employs an algorithm from Williams et al. (Global Biogeochemical cycles, pp. 351-388, 1992) that allows NO emissions to vary as a function of temperature and land use type. The Williams et al. work was mentioned in the draft report, but understandably it was not used in the emission factor table because fertilizer rates were not reported. Out of curiosity, I have compared the emission factors from AP-42 with the emissions estimated from the ROM. In the ROM, an NO emissions flux from fertilized corn fields of 586 $\mu g\ m^{-2}\ h^{-1}$ is assumed at a temperature of 30 C. If we assume a fertilizer application of 100 kg N/ha and that NO emissions occur a period of 120 days, then the percentage loss of N in the form of NO is 8%. This compares to the AP-42 values of 6% for urea, 1% for ammonium nitrate (fluid), and 11% ammonium nitrate (as a solid). So it would appear that we are both in the same ballpark, but neither one of us really knows the size of the ballpark.

I appreciate the effort that your branch is making to improve emission factors for ozone precursors. As indicated in my comments and as reflected in the draft report, there is still much work left to be done. If I can be of any further assistance, please call me at extension 1-1375.

cc: J. Novak
C. Geron (AEERL)

Rec'd 1/5/94
TC

IFDC INTERNATIONAL FERTILIZER DEVELOPMENT CENTER • MUSCLE SHOALS, ALABAMA 35662 USA
P.O. BOX 2040 • 205-381-6600
TWX-810-731-3970 IFDEC MCHL
TELEFAX NO. 205-381-7408

December 17, 1993

Mr. Dallas W. Safriet
Environmental Engineer
Emission Inventory Branch
United States Environmental Protection
Agency (EPA)
Office of Air Quality Planning and
Standards
Research Triangle Park, North Carolina 27711

Dear Mr. Safriet:

We recently received your December 3, 1993, letter and the second draft version of a proposed new section 6.2.1, "Fertilizer Application," of AP-42, "Compilation of Air Pollutant Emission Factors." The text of Section 5 of the second draft appears to be a much improved version of the draft which you asked us to review in November 1992. However, we still detected several errors and questionable statements in Section 5 of the background document.

We only superficially reviewed the text, tables, and figures in Section 5. We did not check the accuracy or reliability of the data in the tables. As we indicated to you last year, the data would have demanded an extensive review of all the references included in the background document. In addition, we feel it would be necessary to do a literature search for other pertinent data which may have been inadvertently overlooked in this report. We would be willing to undertake this task, but we would need to do it under a reimbursable cost agreement due to the level of such an effort. If you are interested in IFDC performing this type of service for EPA, please contact us and we will be happy to provide you with a scope of work, budget, and timetable.

I am sorry that we cannot be more helpful. We believe that for IFDC to properly review this document, we would need to invest a considerable amount of staff time. Unfortunately, as a public, nonprofit international organization, we cannot spend this time without reimbursement.

Sincerely,

James J. Schultz
Director
Outreach Division

SOUTHERN OXIDANTS STUDY

3 June 1993

MEMORANDUM

To: Viney Aneja, North Carolina State University
Peter Bakwin, NOAA CMDL
Ellis Cowling, North Carolina State University
Eric Davidson, Woods Hole Research Center
Anthony Delany, National Center for Atmospheric Research
Fred Fehsenfeld, NOAA Aeronomy Laboratory
Weigang Gao, Argonne National Laboratory
Gordon Hutchinson, USDA Agricultural Research Service
John Kinsey, Midwest Research Institute
William Massman, USDA Forest Service
William Munger, Harvard University
Thomas Pierce, EPA Atmospheric Research and Exposure Assessment Laboratory
Mark Poth, USDA Forest Service
Wayne Robarge, North Carolina State University
Ralph Valente, Tennessee Valley Authority
Eric Williams, NOAA Aeronomy Laboratory
Karl Zeller, USDA Forest Service
Patrick Zimmerman, National Center for Atmospheric Research

From: Cari Furiness, North Carolina State University Cari

Subject: Draft Summary of a Workshop on Emissions of NO_x From Soils

Thank you once again for your participation in our recent Workshop on Emissions of NO_x From Soils, which was held in Denver, Colorado on May 10-11, 1993. We are very excited about the productive results of the group's collective thinking.

Please find enclosed a draft version of a Summary of a Workshop on Emissions of NO_x From Soils. The draft attempts to provide a general summary of the workshop activities, as well as the conclusion statements and research priorities you have already seen in previous draft form. This version incorporates changes that several of you suggested in those documents.

Please review this draft for accuracy and completeness. We are eager to have any suggestions for further changes in the summary or for additions of information that would add to its completeness. Your willingness to contribute to this process is appreciated. We would like to have comments by June 18 if possible. We will then develop a final version of the Summary for distribution to those who were invited but unable to attend and to other interested individuals. If you know of someone who might be interested to receive it, we would be happy to send it to them.

SUMMARY
OF A
WORKSHOP ON EMISSIONS OF NO_X FROM SOILS

Held on
May 10 - 11, 1993

in
Denver, Colorado

Organized by

Southern Oxidants Research Program on Emissions and Effects
of the
Southern Oxidants Study

and

Atmospheric Research and Exposure Assessment Laboratory
of the
U.S. Environmental Protection Agency

INTRODUCTION

A Workshop on Emissions of NO_X From Soils, was held in Denver, Colorado on May 10-11, 1993. The workshop was sponsored by the Southern Oxidants Research Program on Emissions and Effects (SORP-EE), a part of the Southern Oxidants Study (SOS), in collaboration with the Atmospheric Research and Exposure Assessment Laboratory of the U.S. Environmental Protection Agency.

Interest by the Southern Oxidants Study, as well as other groups within EPA, in sponsoring this workshop has been stimulated by a growing scientific belief that emissions of NOx from natural sources are not negligible, as has often been assumed in the past. Although natural sources of NO_X can be divided into two categories, lightning and soils, this workshop was planned to focus on soil NO_X. In order to better set priorities for research to investigate emissions of NO_X from soils, a better understanding of current research activities and assessment of the major uncertainties in scientific understanding of these emissions was deemed necessary. As a result, financial and personnel resources might also be used more efficiently, and duplication of effort avoided.

The workshop was organized to meet the following specific objectives:

1) To develop a general consensus about the current state of knowledge about emissions of NO_X from soils, especially from soils of land use types that contribute significantly, because of relatively high flux rates and/or relatively large land areas, to the total NO_X emissions inventory in the southern United States;

2) To discuss current methods used to estimate soil NO_X fluxes, assess the uncertainties associated with those measurement methods, and determine measurement programs that would most effectively improve the NO_X emission estimates that are used in atmospheric photochemical grid models;

3) To identify current and proposed funding needs and to set priorities for future research on NO_X emissions from soils in the southern United States; and

4) To coordinate and, to the extent possible, collaborate on current and future research and modeling efforts.

Invitations were extended to individuals from various universities, federal agencies, and private research organizations who are considered leading research scientists in the area of measurement or modeling of emissions of NO_X from soils and/or who represent a major sponsoring organization that has an ongoing interest in understanding soil NO_X emissions. The workshop was designed to allow exchange of information about research programs that are currently being funded or will be funded by major sponsors, research activities currently being undertaken by scientists with funding from other sources, and perceived priorities for research by both scientists and sponsors. The interchange was intended to foster collaboration among workshop attendees and enable organizations such as USDA, NOAA, EPRI, NASA, and EPA to assess priorities for their own research programs. The memorandum of invitation to workshop participants with tentative agenda and list of workshop invitees are included as Appendix 1 and Appendix 2, respectively.

Several workshop participants agreed to make short presentations to encourage discussion of selected topics related to soil NO_X emissions, measurement, and modeling (see agenda included in Appendix 1) Copies of the overheads used by each presenter are included as Appendix 3.

MAJOR CONCLUSIONS FROM THE WORKSHOP

A number of general conclusions emerged as a result of the very productive discussions that took place during the workshop. The following statements attempt to summarize the consensus judgments of the scientific experts who participated.

(1) Current estimates of soil NO (nitric oxide) emissions indicate that soils can contribute substantially to the total NO_X (NO and NO_2 [nitrogen dioxide]) budget, especially in rural areas and/or over fertilized lands during summer months. For North America, estimates of annual soil biogenic NO_X emissions are approximately an order of magnitude less than urban anthropogenic sources; however, during the summertime, soil emissions may constitute 15% of the total NO_X flux to the atmosphere.

(2) Soil chamber methods are useful tools for performing surveys of soil NO emissions. Comparisons among various soil chamber techniques are necessary to assure that data from different research groups are comparable. A few such comparisons have been completed and show reasonable agreement. However, soil chamber measurements do not accurately represent the net NO_X flux from the biosphere to the atmosphere.

(3) With continuing development of chemical sensors, micrometeorological approaches can be used to measure the atmosphere/surface exchange of NO_X.

(4) Current NO emission and atmospheric photochemical models incorporate an overly simplistic picture of the processes contributing to net NO_X flux to the atmosphere. Atmospheric models need to incorporate the linked system of NO emissions, photochemistry of the lower atmosphere, and NO_2 and O_3 deposition (with the role of plants in those processes fully represented).

(5) NO emissions from soils are driven by many biological, chemical, and physical processes. The most robust parameters controlling those processes over many temporal and spatial scales are: soil N availability, soil O_2 availability, and soil temperature. In current emissions modeling, these factors have been represented by N fertilizer application rates, soil moisture, and air temperature. NO emissions approximately double for a 10_ C increase in soil temperature

(6) Soils that have been dried and then wetted exhibit high pulses of NO emissions. In some ecosystems, the sum of these relatively brief pulses can be larger than the sum of the remaining long-term NO emission rates on an annual basis. Saturated soils emit negligible amounts of NO.

(7) Current evidence suggests that autotrophic microbial populations involved in nitrification processes are responsible for most of the soil NO emissions.

(8) Although gaps currently exist in our knowledge of NO emissions from soils, understanding is sufficient to proceed with the use of mechanistic models of soil processes controlling NO emissions.

"IF I WERE KING OR QUEEN" STATEMENTS

To facilitate discussions during the workshop, participants were requested to prepare a one-page statement which outlined the research that each scientist (personally or collaboratively) would most like to accomplish or see accomplished during the next few years in an area of research related to emissions of NO_X from soils. It has proven both fun and productive in previous planning meetings of this sort to use these "If I were King or Queen Statements" and the discussions they evoke as a means by which to assess priorities for research and to potentially identify a cadre of scientists that will be needed to get this research done in a timely way and at reasonable cost. Each one-page statement was requested to indicate the objectives, approach, approximate cost, and estimated time-frame for delivery of useful research results.

A few individuals who were unable to attend the workshop provided input by conveying a statement for consideration. The text of all of the submitted statements are included here.

Peter S. Bakwin -- University of Colorado

The net atmosphere/surface exchange of NO_X is the difference between emissions (mostly NO) and deposition (mostly NO_2). Studies of atmosphere/surface exchange of NO_X have typically focused on only one of these processes at a time, and have been of two types: (1) observations of NO emissions from the surface using chambers or mass balance approaches, or (2) enclosure measurements of NO_2 uptake by various vegetative or abiotic surfaces. Neither type of work addresses directly the question of greatest interest to atmospheric chemists, which is quantification of the *net* flux of NO_X. For example, if a forest is cleared for agriculture the net flux of NO_X may change due to changes in soil emissions of NO and surface uptake of NO_2.

A few studies have attempted to approach this problem using eddy correlation (e.g. Delany et al., 1986), gradient/flux relationships (Bakwin et al., 1992), or atmosphere/biosphere exchange models (Jacob and Bakwin, 1991). However, direct observations of the net surface flux of NO_X over spatial (hectares) and time (days) scales that can be addressed with photochemical models have proven difficult because of the difficulty of making accurate and specific measurements of NO and NO_2 with sufficient time resolution for eddy correlation (i.e. several Hz). Furthermore, it has been shown that, since photochemical cycles interconvert NO and NO_2 on a time scale shorter than or comparable to the mixing time of the atmospheric surface layer, the flux of either NO or NO_2 at some height above the surface can be independent of the surface flux, while the flux of NO_X is conserved (Lenschow and Delany, 1987).

Recent developments have improved the situation with regard to direct observations of the atmosphere/exchange exchange of NO_X. In particular, conditional sampling, a micrometeorological method proposed by Businger and Oncley (1990) and developed by the NCAR/ASTER group, may be well suited to direct, continuous observations of NO_X exchange on a spatial scale of hectares. This method utilizes the difference in trace gas (NO_X) concentration carried by updrafts and downdrafts to derive the flux at the measurement height

(e.g. several m above the local plant canopy). Fast response instruments are not required. Ambient NO would be converted to NO_2 by ambient or added O_3 within a continuous flow conditional sampler, and total NO_x would be quantified as NO_2 using standard methods (photofragmentation to NO, detection of NO using O_3-chemiluminescence). Vertical profiles of NO, NO_2 and O_3 concentrations through the local plant canopy should be measured simultaneously to investigate surface uptake, and to quantify changes in NO_x and O_3 storage within the surface layer below the height of the flux measurement. The observations would be automated and could therefore be made continuously for an arbitrary period, to provide diurnal and seasonal fluxes of NO_x.

(References cited are available from the author)

Eric Davidson -- Woods Hole Research Center

Starting from a global perspective, the biggest gap in our knowledge about soil emissions of NO is the sketchiness, and in some cases complete absence, of data from important biomes of the world. The highest emissions of NO from soil are from tropical savannas of Venezuela, but no other data have been published from other savanna regions, although a few studies have been conducted very recently and manuscripts are presumably being prepared. No studies have been published to my knowledge for deserts and semi-deserts, yet these arid ecosystems are likely candidates for large emissions of NO during brief rainy periods.

On a regional scale (such as the southeastern US upon which this workshop is focused), we lack means of relating spatial variation of ecosystems and their nutrient cycling characteristics with mechanistic models of N gas emissions. Most successful mechanistic models rely on two factors: (1) rates of N cycling (N availability) and (2) soil moisture. We know a lot about how soil moisture affects the ratios of emissions of NO, N_2O, and N_2 from soils and we can probably model soil moisture on a regional scale. But finding appropriate indicators of N availability or measures of N cycling that are robust and can be applied across widely varying soil types and ecosystem types remains problematic. I suggest an effort to create a GIS database on ecosystem types, soil types, N inputs from atmospheric deposition, N fertilization, agricultural and silvicultural management regimes, and rates of N mineralization and nitrification. Databases already exist for the southeastern US for all of these parameters but the rates of N mineralization and nitrification. New research would be needed to learn how to assign estimates of N cycling dynamics to the pixels created from the combinations of other factors in the GIS database. As a first cut, it might be sufficient to extract estimates of net nitrification from representative sites from the agronomy, forestry, and ecology literature. A small team of modelers and with field experience and GIS experts would conduct this work. The databases could be acquired and a crude model run within two years for about $300 K/yr. Model improvement and validation would continue for two to four years thereafter.

Predictions of NO emissions from a regional scale model would need validation for a carefully designed field sampling scheme. The sampling would need sufficient frequency (temporal) and replication (spatial) to characterize annual emissions of NO from representative sites. This work would be carried out by numerous independent investigators throughout the region. To make their work more interesting and to take advantage of their innovations, these investigators would also be encouraged to design their work to address controlling factors at both the field scale and the landscape scale within their study locations. Five to ten teams

might be assembled, and each team granted $150 K/yr for 3 years. Finally, if numerous investigators are involved in field flux measurements, an intercomparison would need to be organized in order to assure that the data generated are free of biases that result from artifacts of individual measurement designs. This project would be organized by one PI at a cost of $100 K and would be conducted towards the end of the first year of the other grants.

Anthony Delany -- National Center for Atmospheric Research

In order to explore the relationship between NO/NO_2 soil emission/deposition and flux of NO/NO_2 to the above canopy atmosphere, we need to fully characterize profiles of $NO/NO_2/O_3$ fluxes and means above a canopy and $NO/NO_2/O_3$ means within the canopy. This should be done in coordination with measurements of N_2O (and CO_2/H_2O) fluxes and means. Also H_2O and other relevant species should be measured. This research should be planned at a fertilized crop field with full micrometeorological support. In addition, the study should be carried out day and night for one month using ASTER. A high canopy site in a forest could also be used.

Weigang Gao and Marvin L. Wesely -- Argonne National Laboratory

1. **Background.** Our numerical studies show that NO emitted from soil can be quickly converted to NO_2, which in turn deposits at the Earth's surface. The two-way transport modulated by rapid in-air chemistry near the NO sources appears to lead to a reduction in net upward NO_X transport. This flux change due to chemistry in the lower atmosphere above the surface is not currently considered in large scale models and should be parameterized to estimate the net NO_X flux into the lower atmosphere. We have conducted numerical simulations of flux profiles in the atmospheric boundary layer and in a forest canopy by using a coupled turbulence-chemistry model. In the forest, photochemical processes are substantially weakened, and the NO to NO_2 conversion rate is enhanced. The upward NO flux at the canopy top is much smaller than at the forest floor. To estimate the magnitude of NO_X flux that actually enters the atmosphere, it is necessary to combine measurements at the surface and modeling of chemical modification in near-surface atmosphere.

2. **Objectives**: To estimate vertical changes of NO_X flux in the region from soil surface to the lower atmosphere above the soil or canopy surfaces using numerical models and field measurements at representative land use types.

3. **Approaches**:

Measurements: Three sets of simultaneous measurements would be needed: soil chamber measurement of NO flux from soil; measurements of NO_X fluxes at one or two heights within 10 m above the surface, and the mean concentrations of NO, NO_2, O_3, at a flux measurement height above the surface and basic micrometeorological conditions.

Modeling: Two types of numerical modeling would be carried out: (1) modeling with a simplified $NO\text{-}NO_2\text{-}O_3$ chemical cycle, and (2) modeling with more complete chemistry including potential influences of biogenic nonmethane hydrocarbons that might be present. Simulations would use field data as inputs and as diagnostic variables to evaluate changes of NO_X fluxes above the surface.

Scenarios: We need to carry out this research for representative types of chemical conditions and land use. Initially, studies for grassland and deciduous forest would be feasible at the Argonne experimental site and the Oak Ridge Environmental Research Park.

4. **Estimated Cost and Time Frame**: Field measurements could be kept simple because much of results would be derived from numerical modeling. Approximately 12 months of effort would be needed for field measurements at the Argonne grassland site and for associated modeling study. For the forest site, approximately 18 months of effort would be needed. Existing instrumentation and models could be used.

5. **Deliverable Results**: The proposed research would provide a good estimate of changes of NO_X fluxes in the lower atmosphere above the surface in addition to NO flux at soil surfaces. The results are applicable to estimating chemical influences for grassland and deciduous forest, and methods developed from this research could be used for studies of other land use types. In this way, parameterizations for large scale models could be developed.

D. Alan Hansen -- Electric Power Research Institute

EPRI has funded the development by Dr. David Cooper at SRI International of an eddy correlation flux measurement system. We refer to it as the FMS FCS for "frequency modulated spectroscopic fast chemical sensor." It is the culmination of an investment of approximately $2.5 million. It uses lead-salt diode lasers to generate the narrow-band IR radiation in conjunction with folded path optics to measure IR absorbing small molecules down to parts per trillion levels. In the flux measurement mode it samples at a faster rate than that used for making ambient concentration measurements, say ten hertz, coincident with a 3-D sonic anemometer and appropriate signal processing and software to measure fluxes of materials present at one to two orders of magnitude higher concentrations. In field tests in the San Joaquin Valley, it successfully measured fluxes of N_2O and NH_3 over a cotton field. With modification, it could measure simultaneously NO and NO_2 fluxes from soil. In fact, such a proposal has been made to EPA in response to AREAL's recent cooperative agreement solicitation. EPA's decision on the proposal has not been announced. I had hoped to fund, irrespective of EPA's decision, the modification and use of the system to measure NO and NO_2 fluxes in concert with and to corroborate Jim Meagher's enclosure technique measurements this summer, but was unsuccessful in securing funds.

The advantage of the FMS FCS, of course, is that it is non-invasive, not perturbing in any way the local environment of the surface to and from which fluxes are being measured. Further, being a spectroscope technique, it is not subject to many of the sampling artifacts or other problems associated with sample collection and analysis. Being relatively portable, it could be used to measure fluxes over a wide variety of surfaces over an extended time and space frame.

My primary objective therefore for the workshop is to bring to the attention of attendees the availability of this unique measurement capability and to seek opportunities for collaboratively funding its application to NO and NO_2 flux measurements. Another objective is to have the subject of the influence of flux divergence caused by rapid reaction of NO with ambient O_3 or photolysis of NO_2 on the FMS FCS measurement, the detectors for which are some 10s to 100s of meters from the actual area of air-surface exchange, and how to correct for it.

Elisabeth A. Holland -- National Center for Atmospheric Research

Interactions between carbon and nitrogen cycling are central to understanding fluxes of reactive species from the biosphere to the atmosphere. Atmospheric nitrogen is fixed and

incorporated into vegetative biomass and soil organic matter. In most terrestrial ecosystems, the rate of nitrogen conversion from these organic components into mineral NH_4 (called mineralization) or from NH_4 into NO_3 (nitrification), limits the production of new plant biomass. Thus, the rate of N cycling determines an ecosystem's ability to store carbon. Because N limitation of plant production is so ubiquitous, undisturbed natural ecosystems tend to conserve N, losing little to the atmosphere via volatilization or to groundwater and rivers via nitrate leaching. Out current understanding is that N losses from an ecosystem are proportional to the rate of N turnover within a system and that any disturbance which disrupts the partitioning of N between plants and soil microbes will increase the rate of N loss dramatically. Natural disturbances, grazing, fire, hurricanes, and disease, and anthropogenic disturbances, clear cutting, cropping, irrigation, and N deposition, disrupt this balance and greatly increase the potential for N loss from ecosystems.

Volatile nitrogen losses from ecosystems include NO and N_2O production in soils as well as NH_3 volatilization from plants and soils. NO and N_2O are by-products and/or intermediates of two different N transformation pathways: *nitrification*, the conversion of NH_4 into NO_3 and *denitrification*, the reduction of NO_3 to NO, N_2O, and N_2 which are used as alternative electron acceptors when $[O_2]$ declines. As N losses from ecosystems accrue, via volatilization or nitrate leaching, an ecosystem loses its ability to fix carbon and produce new plant biomass. Substrate supply, $[NH_4]$ for nitrification and $[NO_3]$ for denitrification, controls the rate of processing and interacts with the physical and chemical environment, soil temperature and water content, $[O_2]$, pH, and carbon availability, to moderate the rates of both nitrification and denitrification. A number of distal factors regulate N turnover and affect substrate supply including net primary production, the distribution of carbon and nitrogen among the various plant components of an ecosystem: wood, leaves, roots, stems, and reproductive biomass, as well as the partitioning of carbon and nitrogen within each of these components.

I propose a series of experiments which will address both the proximal controls of substrate supply and environment as well as the broader distal controls over NO production. The study will have three interacting dimensions: a laboratory component to quantify the relationship between the proximal controls outlined above and NO production, a modeling component to incorporate information from the laboratory studies into a broader framework which includes the distal controls as well as providing a means of extrapolating in both space and time, and a field component to validate the model. The field studies proposed here, if done in conjunction with measurements of natural hydrocarbon emission studies will also address the role of nitrogen availability in determining isoprene and terpene emissions.

Laboratory Studies:

I propose to use chlorate slurries to screen for a soil's potential to produce nitrate, a nitrification intermediate. Chlorate inhibits the conversion of nitrite to nitrate and allows quantification of nitrate accumulation instead of measuring nitrate which is simultaneously being produced and consumed. These slurries will be done at a range of temperatures as well to determine if the temperature relationship used to describe general microbial activity (soil respiration) are appropriate for nitrification as well. Soil respiration does not follow traditional enzyme kinetics because CO_2 is a ubiquitous metabolic by-product and does not follow traditional single enzyme kinetics. Because nitrification relies on a specific set of enzymes, the relationship with temperature may have a clear optimum like that of simple enzyme processes (e.g. photosynthesis).

Incubating soils in flasks with different headspace concentrations of acetylene allows differentiation of NO production from nitrification and denitrification. Nitrifiers are much more sensitive to acetylene than are denitrifiers and nitrifier activity halts with 10kPa of acetylene while denitrifier activity doesn't halt until headspace concentrations reach 100 Pa. Using this technique, I will examine how NO production from the two pathways differ with changing [NH_4], [NO_3], temperature, pH, and [O_2].

Potential net N mineralization assays will be used to directly examine the links between N turnover and NO production.

New instrumentation required for these assays includes a spectrophotometer for nitrite analyses as well as a chemiluminescence detector for NO measurements.

Modeling Studies:

CENTURY is a biogeochemical model which couples plant production to soil organic matter production, simulating rates of nitrogen turnover which, in turn, control plant production. CENTURY was originally developed for grassland and agricultural sites and has been used for regional analysis of soil organic matter and trace gas dynamics. CENTURY explicitly represents external N inputs through fixation and N deposition, volatile N losses as well as nitrate leaching, and disturbances which disrupt the balance between plant and microbial uptake of N tremendously increasing the potential for N losses. More recently, it has been revised to include forest, shrubland, and tundra simulations. I propose to build an additional NO module which will represent the proximal controls of NO production while the existing portion of the model handles the distal controls. Presently, CENTURY groups NO fluxes with other nitrogen oxides ($NO+N_2O+N_2$)and simulates the flux as a proportion of gross N mineralization. I will refine this representation and partition the flux into that which is associated with nitrification and that associated with denitrification. Adequate simulation of the flux will require a more detailed representation of soil structure and some information about the diffusion properties of the soil and how they change with changing soil texture and moisture.

Field Studies:

I propose measurement of NO fluxes along gradients of N and water availability in disturbed ecosystems to explicitly test whether NO fluxes are linked to rates of N turnover. These measurements will be done in conjunction with a suite of other measurements which characterize the physical and chemical environment as well as N availability. To adequately test the model, measurements will need to be made over at least one entire seasonal cycle, extension of the measurements over more than one seasonal cycle would permit testing the model during different weather years. The field studies will be conducted opportunistically and build on sites where many of the auxiliary measurements are already underway.

Execution of this plan will require internal NCAR funds as well as solicitations from EPA and possibly NASA.

Gordon L. Hutchinson -- Agricultural Research Service, U.S. Department of Agriculture

Eric Davidson recently estimated the global soil NO_x source to be about 20 Tg N yr^1, which is more than double the previously accepted value. His estimate, computed by summing the products of the mean measured by NO emission rate, area, and length of the growing season for each of the Earth's major biomes, was dominated by emissions from three savanna sites all in the same Latin American country (7.7 Tg N yr^1), so it may be revised downward

once more savanna sites are studied, but is also subject to certain upward revision because nearly half the Earth's surface is covered by biomes for which no NO exchange estimates were available, including deserts, semi-deserts, polar deserts, peatland, mixed forests, tiaga, and tundra. ***Understanding the contribution of biogenic sources to the global atmospheric NO_x budget requires more measurements from those biomes with uncertain or unknown emission rates.*** Although they may have little interest to SOS scientists, deserts (especially semi-deserts) may be particularly important, because of the large burst of NO_x emissions that typically follows wetting of very dry soil.

Although the value of improved budgets is unequivocal, such calculations are hopelessly inadequate for achieving a predictive understanding of the immense spatial and temporal variability characteristic of soil NO_x exchange rates at local, field, and landscape scales. Accordingly, the long-range goal of additional measurements should be to capture the exchange rates in terms of their basic physical, chemical, and biological controllers, so that dependence of the flux on these controllers can be described using simulation models parameterized by variables observable at the scale of interest. The available data suggest that soil NO_x emission is strongly dependent on the type of vegetative cover, fertilization, burning, grazing, precipitation amount/intensity/duration, etc., but the importance of most of these factors can be explained by their effect on the three major environmental controllers -- soil temperature, N availability, and O_2 availability, which is regulated primarily by soil water content. Correspondingly, NO_x emission from the small plots I have been monitoring at Akron, Colorado is best and most simply simulated by the product of a constant that (somehow) reflects soil N availability, an exponential function of soil temperature (equivalent to assuming $Q_{10}=2$), and a dual-slope linear function of water-filled soil pore space (WFPS) that captures the dependence of microbial activity on this parameter outlined by Skopp et al. (SSSAJ 54:1619-1625, 1990), thereby accounting for all three of these major environmental controls. Order-of-magnitude differences between two sets of fluxes measured on sampling dates with widely divergent conditions were reduced to less than a factor of 2 after normalization to the same temperature and percentage WFPS, and the remaining differences between the two data sets were correlated with measured changes in various soil N availability indices. ***Understanding dependence of the model constant on the sizes and/or transformation rates of identifiable soil N pools, confirming the usefulness of our soil temperature and soil water parameterization schemes in other soils and climates, and developing an effective method of adjusting the effect of precipitation for soil water content prior to the wetting event are needed*** before this approach can be extended over the much larger areal and temporal domains to which we think it may apply.

Sub-questions for which answers would facilitate addressing these needs include: (1) ***What are the reasons for the unusually large burst of soil NO_x emissions following wetting of very dry soil?*** My lab (and others) have shown that autotrophic nitrifiers are directly involved (or indirectly involved as a source of NO_2), but the mechanism for such copious release of NO_x remains unclear. (2) ***Do microbial processes other than autotrophic nitrification and heterotrophic denitrification contribute significantly to soil NO_x emission in some situations?*** In my lab, small aerobic soil NO_x emission rates that continue in the presence of autotrophic nitrification inhibitors are correlated with soil respiration, indicating a C-dependent source such as heterotrophic nitrification or any of several other microbial processes resulting in oxidation or reduction of N through the +2 oxidation state. (3) ***What is the relation of soil NO_x to N_2O emissions?*** Biotic and abiotic processes involved in the

production, consumption, and transport of these two gases in soil are so tightly coupled that soil exchange of either gas should not be considered without simultaneous consideration of the possibility for interactions with the other.

John Kinsey -- Midwest Research Institute

AP-42 STUDY:

- Developed emission factors for NH_3, NO, N_2O, NO_2 for nitrogen fertilizers.
- Based emission factors on published data from academic investigators (foreign and domestic).
- Used mostly flux chambers at selected times after application (i.e., "snapshots").
- Temporal resolution poor with incomplete speciation of nitrogen gases from soil surface (i.e., only selected pollutants determined in most studies).

Testing Needs:

- Common fertilizer types, multiple crop types, and different soil conditions should be evaluated for *all* nitrogenous pollutants of concern following an approved statistical design.
- "Whole-field" sampling should be performed in lieu of chambers over relatively small areas.
- Soil properties should be thoroughly characterized, both chemically and biologically (i.e., Cation Exchange Capacity, etc.).
- EPA and agrichemical industry should be involved throughout the study.

Possible Approaches:

- Profile pollutant concentrations from test plot spatially and temporally using open path instruments, such as the FTIR.
- Couple concentration measurements with on-site meteorology to determine mass flux (i.e., similar to MRI exposure profiling method for particulate matter).
- Characterize soil gases frequently over study period using buried probes, etc.
- Determine types and quantities of soil organics and chemical constituents by grab sampling throughout period.
- Conduct intensive sample and analysis during 2-week maximum emission period.
- Collect air and soil samples before, during, and after fertilizer application to determine background emission and the effects of the application (i.e., natural vs. manmade emissions).

Bill Massman and Karl Zeller -- Forest Service, US Department of Agriculture

Measuring NO_x emissions from soils can be accomplished by micrometeorological means using eddy covariance or conditional sampling methods. However, since ozone is also present the purely aerodynamic approach may yield biased results depending on the ozone concentration because of the photoreactions of NO, NO_2, and O_3. Nevertheless, we suggest the following experiment to address the question of NO_x emissions from soils.

(1) Fluxes and ambient concentrations of NO, NO_2, and O_3 be measured at two or more heights above a surface (a fertilized field for example). At least two measurement heights are necessary to evaluate the surface layer flux divergences caused by the photoreaction of NO, NO_2, and O_3. Similar and concurrent measurements of isoprenes and/or terpenes

would also be made. Several simultaneous leaf level gas exchange systems for hydrocarbon emissions from plants and chamber systems for NO emissions from soil would also be made.

(2) Measurements of light intensity in the spectral wavebands which drive the photolytic reactions. For modeling purposes measurements of atmospheric aerosols, water vapor and cloudiness should also be made.

(3) To assess whether pressure pumping plays any role in the release of NO from the soils simultaneous measurements of the high frequency fluctuations of pressure in both the soil and ambient atmosphere should also be made. Profiles of soil temperatures and soil water content are also needed because these are important factors regulating microbial activity and the concomitant NO emissions from the soils.

(4) Lastly, a model that incorporates (a) NO emissions from soils, (b) the photolytic reactions between the O_3, NO_2, and NO and hydrocarbons, OH and NO_2, (c) atmospheric turbulent exchange between the surface and the atmosphere and (d) any plant influenced effects would also be required.

Estimated cost:

Eddy covariance instrumentation and equipment..	$250,000.00
Chamber instrument and equipment.....	$250,000.00
Salaries per year	$600,000.00
Travel (relocation of eddy covariance system)	$100,000.00
Laboratory and Misc.	$ 50,000.00

Duration of experiment: At least two years with eddy covariance data being taken at three or more sites of interest.

Bill Munger -- Harvard University

Given unlimited time, personnel, and resources our group would pursue the following overall research objectives:

(1) Determine seasonal cycle of soil NO emissions from a mixed deciduous forest.

(2) Quantify aerial nitrogen inputs from wet and dry deposition and in particular, evaluate the role of NO_2 deposition within the canopy and to the soil surface.

(3) Assess the role, if any, of heterogeneous reactions that convert NO_2 to NO on organic matter.

(4) Compare NO fluxes made at the canopy level to NO fluxes measured in chambers during selected periods.

As part of the Harvard Forest Long-Term Ecological Research site our group has established an Environmental Measurement Station for measuring trace-gas concentration profiles and eddy correlation fluxes. A 30 m tower was erected in a 23 m mixed hardwood forest that is dominated by oaks. In particular measurements of CO_2, O_3, NO and NO_2 concentration profiles allow estimation of NO soil emission and NO_2 deposition within the canopy. Total nitrogen deposition is determined by precipitation collection and analysis and NOy eddy correlation flux measurements.

Elevated concentrations of NO beneath the canopy at night indicate a persistent source of NO at the forest floor. We will continue the measurements and augment them to obtain better temporal and vertical resolution. Fluxes of NO are calculated from integrating the chemical mass balance. In addition we will construct a model of vertical mixing, surface reaction and chemical reaction for the forest. Simultaneous measurements of CO_2 and O_3 fluxes and concentration gradients can be used to constrain the mixing rates and surface

interactions. Direct estimation of the flux by ratio to the soil CO_2 flux and gradient is not possible because the reaction with 0# is rapid.

In light of Nishimura et al.'s [1986] observations of NO_2 reduction on various plant material we propose to investigate the relationship between measured NO fluxes and ambient NO_2 concentrations. In addition laboratory experiments to test this reaction on other substrates and at environmentally realistic concentrations are needed.

The facilities at Harvard Forest provide an ideal site for making chamber flux measurements of NO emission by soils. Direct measurements of soil fluxes are needed to verify the canopy level estimates. In addition we would seek to arrange with Melillo et al. to make NO flux measurements within their nitrogen fertilization and soil-warming plots located nearby.

Thomas E. Pierce -- Atmospheric Research and Exposure Assessment Laboratory, U.S. EPA

For several years, we have recognized that biogenic VOC emissions play an important role in photochemical ozone production and the selection of appropriate emission control strategies. Until recently, it was thought that "biogenic" NO_X emissions from soils were negligible. However, Williams et al. have shown that soil NO could be a significant portion of the total NO_X emissions budget. As "king" of ozone modeling at EPA, it is important that we properly model the soil NO flux into the atmosphere and examine how soil NO_X emission might affect emissions control strategies. Such a research program might entail soil chamber measurements, micrometeorological field verification, emission model development, atmospheric model improvements, and model uncertainty analysis.

(1) Soil Chamber Measurements. A number of soil chamber measurements have already been made. More measurements are needed over the heavily-fertilized soils, which appear to be the areas where NO emissions are appreciable and could significantly influence the overall NO_X emissions budget. The additional chamber measurements would also enable better emission models to be constructed that include factors such a as soil moisture, soil nutrient levels, and soil types.

(2) Micrometeorological Field Verification. Soil chamber measurements may not provide a complete picture of the NO emission flux into the atmosphere. Recognizing that NO emissions is tightly coupled to the NO-NO_2-O_3 photochemical system, micrometeorological verification of the soil NO emission factors is needed.

(3) Emission Model Development. Using data from (1) and (2), the algorithm for computing soil NO emissions could be updated. It could include other factors, such as soil moisture and soil nutrient status. Such a model should be consistent with available data bases.

(4) Atmospheric Model Improvements. Most current photochemical models use a stand-alone processor for estimating NO emissions. It is apparent from the literature that NO emissions are strongly coupled with NO-NO_2-O_3 concentrations in the ambient air. The emissions module then should be made a part of the atmospheric model.

(5) Model Uncertainty. The issue with biogenic emission uncertainty is how does it affect the way we manage air quality. For example, an overprediction of soil NO emissions could change preference from a NO_X to a VOC control strategy. Ozone production is very non-linear and depends on VOC and NO_X emissions. Model simulations are needed to see how uncertainties in emission factors affect ozone concentrations and emission control strategy

selection. Model simulations are also needed to establish the required accuracy of the soil NO emission factors.

Mark Poth – U.S. Department of Agriculture Forest Service

The practices currently used to manage productive forest lands, as with agricultural lands, may promote the production of NO_X from soils. The amounts produced may be significant given the enduring nature of NO_X production observed from some other forest systems and that the southern U.S. has the greatest percentage of area in forest production of any region in the U.S. Forest soil NO_X emission rates in the South are virtually unknown.

Currently the Forest Service is conducting a study of forest management practices on long term site productivity (LTSP). This nation wide, approximately $10 million, study includes several sites (20 plus) in the south. Each site includes treatments for soil compaction, harvesting and plant community diversity. The data base being produced includes information on climatology, soil physical and chemical properties, plant survival, growth and nutrition, insect and disease outbreaks, and forest biomass modeling. These data can be made available to cooperators at no cost.

Objective

Obtain preliminary measurements of soil NO_X production from managed forest stands in the south, taking advantage of the LTSP study.

Approach

A combination of chamber studies for mechanistic evaluation of emissions and micrometeorological methods for flux measurements.

Approximate Cost

No cost for the land treatments and the site data. Costs would be for teams to measure NO_X emissions using the two methods, concomitantly.

Time Frame

With the sites already prepared, measurements could be made this summer and results analyzed and reports/papers produced by this fall. This information would provide an assessment of forest soils as a source of NO_X. Additionally, it may provide information on management practices to mitigate such emissions.

Additional Advantages

There is the potential to link with similar studies in other regions of the country at other LTSP sites.

Ray Valente and Frank Thornton -- Tennessee Valley Authority

Model Validation and Improvement

Over the past three years TVA has collected a database of soil NO_X emissions from several fertilized and unfertilized sights in the mid-south. This database now includes over 3500 individual chamber measurements (2500 from fertilized soils and 1000 from unfertilized soils) along with soil temperature, soil moisture, and soil chemistry information. We propose collaborative work to use this database to validate and help refine the soil NO_X emissions models currently being developed for application in SOS. (Cost: $25K)

Spatial Variability Experiment

Spatial variability is the nemesis of accurate regional soil NO_X emissions estimates. Spatial variability as high as of a factor of 100 has sometimes been observed, even on a very small spatial scale (adjacent chamber plots on a fertilized cotton field, e.g.). In order to develop an understanding of the influence of spatial variability on the accuracy of regional emissions we propose a soil NO_X spatial variability study. In this field study soil NO_X emissions measurements will be made at many locations within a single model grid cell in order to document the spatial variability and to develop an understanding of the uncertainty in extrapolating from a few sites to grid-scale and regional estimates. The study would be done during the warm season and would utilize the mobile capabilities of current measurement systems. The emphasis of this study would be to perform measurements at as many sites (20-30 seems practical for a month long study) within the grid cell as possible rather than to focus in detail on any particular location. The grid cell and sites selected for the study would include fertilized agricultural areas, pasture lands, urban lawns, parks, truck crop areas, residential plantings, etc. The results of this study would, for the first time, permit a statistical estimate of the uncertainty involved in regional soil NO_X estimates. (Cost: $30K, assuming the work could be done at a grid cell near the home office of the investigators)

Is Reabsorption of NO or NO_2 Reducing the Emissions to the Boundary Layer?

Because of the uncertainty in the amount of NO that originates from biogenic sources, chiefly soil, TVA has been attempting to inventory soils in the mid-south. These estimates suggest that soil NO_X emissions in the region are clearly non-negligible, especially during the photochemical ozone season. Questions have been raised as to how much of the NO released at the surface is reabsorbed by plant canopies before it can reach the boundary layer. We propose a collaborative study in which comparisons between chamber and diode laser or other micrometeorological technique could answer the question posed above. (Cost: $50K, but could vary depending on the micrometeorological technique chosen)

RESEARCH PRIORITIES

Considerable discussion among workshop participants centered around specific research programs that should be undertaken to most effectively enhance current understanding of NO_X emissions from soils. It was generally agreed that the highest research priority of the Southern Oxidants Study in the short-term should be survey work using soil chambers. The focus of the survey work should be specific land-use or ecosystem types common to the Southeast for which NO_X flux estimates are either unknown or very uncertain. This especially includes fertilized urban areas such as golf courses and lawns.

Research projects that could be pursued on a longer-term basis are described below.

(1) **Full Characterization of the Net NO_X Flux to the Atmosphere From Soils**

The objectives of this study would be to:

(a) fully characterize the processes which contribute to the net flux of NO_X into the atmosphere from soil sources, including emission of NO as a result of microbial activity in soils, photochemical conversion of NO to NO_2, and deposition of NO_2 to soils and plants; and

(b) demonstrate the applicability of micrometeorological techniques for measuring fluxes of NO, NO_2, and O_3.

Soil chamber measurements have historically been used to provide emission factors for biogenic NO_x inventories. They are a useful means for measuring NO emissions for a large number of samples at many sites. However, the workshop participants recognized that chamber measurements do not provide a complete picture of the net NO_x flux between the soil and the atmosphere, mainly because of the chemical transformations that occur when NO is emitted into a highly reactive photochemical system and because the net NO_x flux is the result of both emission and deposition. The participants strongly advocated a study that would measure NO_x fluxes using both micrometeorological techniques and soil chamber methods.

This experiment would provide information on the vertical exchange of nitrogen oxides between the atmosphere and the biosphere and may provide some insight into how to resolve the spatial and temporal variability inherent in chamber data with estimates of larger scale fluxes.

The proposed study would require coordinated efforts in soil characterization, soil chamber measurements, and micrometeorological measurements. It is desirable that a variety of micrometeorological techniques be employed, including gradient techniques, conditional sampling, and eddy correlation. It was suggested that NCAR's ASTER facility could be used as a micrometeorological platform. "Remote sensing" techniques, such as FMSFCS and FTIR, were also mentioned as having some long-term promise. It was strongly recommended that the micrometeorological measurements include flux profiles because of the NO flux divergence that occurs in this highly reactive chemical system. Several soil chamber measurement groups would be encouraged to participate. Substantial up-front work would be needed to carefully design the experiment, to locate the best field site, to characterize the site, and to enhance the chemical instrumentation needed to make the micrometeorological measurements.

Important characteristics for an experimental site for the study would be: a flat, well-drained, fertilized, agricultural field with a fetch of 2 km and having available irrigation. Ideally, the site should be available for the entire growing season and not be influenced by anthropogenic pollution sources. Sources of isoprene should also be considered because of the role that this hydrocarbon plays in photochemistry. The working group felt that the experiment should consist of brief intensive operating periods (~2 weeks each) over the course of a growing season. Because of the scale of such an intensive experiment, it was suggested that 1993 be used for planning purposes, 1994 be used for further planning and perhaps pilot studies, and the summer of 1995 be the implementation of the full-scale study.

(2) **Emissions model development**

While models currently exist to relate soil NO emissions to land use class and soil temperature, the workshop participants concluded that sufficient information is available to refine these algorithms to include fertilizer application and soil moisture. Short-term research is needed to assimilate this information, to construct an algorithm, and to test it against field measurements. It is important during this developmental process to recognize the limited availability of input data bases and to identify the measurements and data bases that will be needed to drive future emission models. It was suggested that GIS data bases are available from the Soil Conservation Service (SCS) that might improve modeling efforts.

(3) **Field chamber measurements**

Field chamber measurements have been rather limited. Furthermore, much experimental work has not included measurements of important process-related variables. Ideally, future studies should report soil temperature, rates of nitrogen mineralization or some other measure of soil nitrogen status, soil texture, water-filled pore space, antecedent soil moisture, and climatic variables (such as precipitation history). Additional studies are needed to expand the data base to other sites, especially fertilized sites; to examine spatial and temporal variability; and to better establish the processes dominating soil NO_X emission. Special attention should be given to the role of N cycling. For example, chamber measurement programs should include N_2O fluxes because comparing fluxes on NO relative to N_2O yields important information about the mechanisms controlling emissions of both gases. Field studies should be designed to support the development of improved NO_X emission models.

(4) **Atmospheric model development and uncertainty analysis**

Most current photochemical ozone models use stand-alone processors for estimating NO_X emission and deposition into the atmosphere. Future models should integrate the emission and deposition processes into the chemical-meteorological core model. The model should incorporate (a) NO emission from soils, (b) the important chemical and photochemical reactions of NO_X, (c) atmospheric turbulent exchange between the surface and the atmosphere, and (d) any plant influenced effects that might be required. An important but often unrealized facet of model development is the need for experimental verification of these modeled processes.

Another important issue that needs to be explored is that of emission uncertainty. How does the uncertainty in NO_X fluxes affect the way that air quality is managed? Model simulations are needed to see how these uncertainties affect predicted ozone concentrations and emission control strategy selection. Model simulations are also needed to establish the required accuracy of the soil NO emission factors.

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March 31, 1993

Mr. Horace Mann
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Muscle Shoals, AL 35660

Dear Mr. Mann:

Thank you for your prompt response to my request for literature. The publication, "Fluid Fertilizers," that you sent will be helpful as I complete the fertilizer section for AP-42. I have enclosed your invoice and a check for $6.00 for the publication.

I enjoyed talking to you last week about the fertilizer application and would certainly appreciate your sending me any additional literature that you think would be useful in preparing Section 6.2.1 on fertilizer application. I hope I might call you again if there are other issues about which I need further information.

Also, I have recently learned that it is possible to enlist consultant assistance under this contract. I would be interested to know if you would be available for a day to review our revised draft in mid-April. Could you let me know if that would be possible and what your daily consultant rate would be?

Thank you for your assistance.

Sincerely,

Margaret E. St. Germain

Margaret E. Wickham St. Germain,
Senior Chemist

MIDWEST RESEARCH INSTITUTE
425 Volker Boulevard
Kansas City, Missouri 64110
Telephone (816) 753-7600
Telefax (816) 753-8420

March 31, 1993

Mr. Bernard Byrnes
International Fertilizer Developement Center (IFDC)
P. O. Box 2040
Muscle Shoals, AL 35662

Dear Mr. Byrnes:

Thank you for talking to me last week about fertilizer application, and for providing me information for the final report, "Estimation of Greenhouse Gas Emissions and Sinks" that you referenced from your review of the fertilizer section for AP-42.

I understand that IFDC is a non-profit organization, and that costs would be incurred if I require any extensive assitance. I hope I might call you again if there are other brief issues about which I need further information.

Thank you for your assistance.

Sincerely,

Margaret E. Wickham St. Germain,
Senior Chemist

MIDWEST RESEARCH INSTITUTE
425 Volker Boulevard
Kansas City, Missouri 64110
Telephone (816) 753-7600
Telefax (816) 753-8420

March 31, 1993

Mr. David Rutledge
International Fertilizer Developement Center (IFDC)
P. O. Box 2040
Muscle Shoals, AL 35662

Dear Mr. Rutledge:

Thank you for talking to me last week about fertilizer application. The references you supplied have proven helpful as I complete the fertilizer section for AP-42. As you recommended, I will contact Michael Broder at Tennessee Valley Authority (TVA) about the figures that we discussed.

I enjoyed talking to you last week and learning about the purpose of IFDC and TVA. I understand that IFDC is a non-profit organization, and that costs would be incurred if I require any extensive assitance. I hope I might call you again if there are other brief issues about which I need further information.

Thank you for your assistance.

Sincerely,

Margaret E. Wickham St. Germain,
Senior Chemist

Margaret Thomas

MIDWEST RESEARCH INSTITUTE
425 Volker Boulevard
Kansas City, Missouri 64110
Telephone (816) 753-7600
Telefax (816) 753-8420

April 28, 1993

Mr. Horace Mann
Tennessee Valley Authority
Post Office Box 1010
Muscle Shoals, AL 35660

Dear Mr. Mann:

As you know, in our last conversation we talked about your serving as a consultant on the AP-42 Section 6.2.1 on Fertilizer Application. Unfortunately, I was informed by our Contracts Department today that hiring an employee of TVA as a consultant would be a conflict of interest. I apologize for any inconvenience that I may have caused you.

Thank you for the information that you and other staff at TVA provided me for the fertilizer application section. It certainly was helpful, and I appreciate your cooperation and assistance.

Sincerely,

Margaret E. St Germain

Margaret E. Wickham St. Germain,
Senior Chemist

Margaret Thomas
MIDWEST RESEARCH INSTITUTE
425 Volker Boulevard
Kansas City, Missouri 64110
Telephone (816) 753-7600
Telefax (816) 753-8420

May 11, 1993

Dr. John Havlin
Kansas State University
Department of Agronomy
Manhattan, KS 66506

Dear Dr. Havlin:

It was a pleasure talking to you about enlisting consultant assistance for the AP-42 Section 6.2.1 on Fertilizer Application.

As Margaret and I discussed with you on Monday, we would like to hire you as a consultant who would act as an adjunct staff member. Specifically, you will receive the background document and Section 6.2.1 by Friday. We will expect you to read the document for accuracy, traceability, concurrence with our grading of the published articles, and determination of any major deficiencies. We will also expect you to resolve any difficulties with the current version of the document and provide new text where deficiencies are observed. We hope to send the final draft to EPA by the end of May.

As we also discussed, we would like you to provide us with an initial reading of the document. This will allow you to more accurately assess the time needed to complete the steps outlined above. After you have estimated your hours, MRI will either provide you with a purchase order specifying a fixed price quote or negotiate a different scope of work.

I look forward to working with you on this section.

Sincerely,

Margaret E. Wickham St. Germain,
Senior Chemist

JOHN L. HAVLIN

BUSINESS ADDRESS

Kansas State University
Department of Agronomy
Throckmorton Hall
Manhattan, KS 66506-5501
(913) 532-7211

HOME ADDRESS

3608 Brenda Ct.
Manhattan, KS 66502
(913) 776-8438

EDUCATION

Ph.D. Soil Fertility/Soil Chemistry	1983	Colorado State University
M.S. Soil Testing/Soil Chemistry	1980	Colorado State University
B.S. Chemistry	1973	Illinois State University

EMPLOYMENT

ASSOCIATE PROFESSOR, Department of Agronomy, Kansas State University, Manhattan, KS 66506 July 1990-present, (60% research-40% teaching)

ASSISTANT PROFESSOR, Department of Agronomy, Kansas State University, Manhattan, KS 66506 Nov. 1985-June 1990, (70% research-30% teaching)

ASSISTANT PROFESSOR, Department of Agronomy, University of Nebraska Panhandle Research and Extension Center, Scottsbluff, NE 69361 Nov. 1983-Nov. 1985 (50% research-50% extension)

ASSISTANT PROFESSOR, Extension Coordinator, Department of Land Resource Science University of Guelph, Guelph, Ontario, Canada. Feb. 1983-Nov. 1983 (70% extension-30% research)

AREA OF RESEARCH

Soil Fertility/Chemistry, Soil Management, Soil Testing, Dryland Crop Management

TEACHING/ADVISING

Soil Fertility, Soil Fertility Laboratory, Soil Conservation and Management, Graduate Seminar. Advising - 15 Undergraduate, 13 M.S., 4 Ph.D.

HONORS AND AWARDS

Gamma Sigma Delta Teaching Award of Merit	1992
National Fertilizer Association - Werner L. Nelson Award	1991
Fluid Fertilizer Foundation Researcher of the Year Award	1989
College of Agriculture Faculty of the Semester Award	1988
Epsilon Sigma Phi Award	1985
Honor Society of Phi Kappa Phi	1983
Colorado State University Alumni Assoc. Student Service Award.	1983
Colorado Graduate Fellowship	1981,1982
Potash and Phosphate Institute Fellowship	1981

PROFESSIONAL AFFILIATIONS

American Society of Agronomy
Soil Science Society of America
Council for Agricultural Science and Technology
Soil and Water Conservation Society
International Soil Tillage Research Organization
Sigma Xi Gamma Sigma Delta Phi Kappa Phi

LEADERSHIP

State, Regional, National, International

North Central Region Committee on Sustainable Agriculture - Chairman (1991-92)
North Central Region Committee on Sustainable Agriculture - Secretary (1990-91)
Great Plains Agric. Task Force on Sustainable Agriculture - Chairman (1991-92)
ESCOP Leadership Development Program - 1991-93)
Central Great Plains Wheat Management Conf. Program Planning Committee (1987)
Great Plains Soil Fertility Conference - Chairman (1988)
Great Plains Soil Fertility Conference Program Planning Committee (1985-present)
Proceedings Great Plains Soil Fertility Conference - Editor (1986-present)
Proceedings Central Great Plains Wheat Management Conf. - Editor (1987)
Agronomy Journal - Associate Editor (1991-present)
Journal of Fertilizer Issues - Editorial Board (1988-present)
USDA-ARS Central Great Plains Research Station Advisory Board (1987-present)
Farmland Industries Advisory Board (1988-present)
MEY Wheat Management Conference Program Planning Committee (1989)
Kansas Agricultural Education Foundation Scientific Review Board (1990-present)
Cooperating Scientist US-INDIA Dryland Agric. Research Project (1989-present)

Kansas State University

Presidential Lecturer (1987-present)
Faculty Salaries and Fringe Benefits Committee, Chairman (1991-92)
College of Agriculture Committee on Effective Instruction (1987-present)
Higher Education Challenge Grant Steering Committee, Chairman (1991-94)
College of Ag Student and Faculty Awards Committee (1989-90).

Dept. of Agronomy

Student Recruitment Committee, Chairman (1991-present)
Greenhouse Committee (1986-present)
Graduate Committee (1988-present)
Undergraduate Research Associate Selection Committee (1990-present)
Seminar Committee (1986-1988)
Sandyland Experiment Field Advisory Committee (1986-87)
Powhattan Experiment Field Advisory Committee (1988-89)
Southcentral Experiment Field Advisory Committee (1990-present)

Community

American Red Cross Board of Directors - Riley Co. KS (1988-present)

PUBLICATIONS (research)

Havlin, J.L., and P.N. Soltanpour. 1980. A nitric acid plant tissue digest method for use with inductively coupled plasma spectrometry. Comm. Soil Sci. and Plant Anal. 11:969-980.

Havlin, J.L., and P.N. Soltanpour. 1981. Evaluation of the NH_4HCO_3-DTPA soil test for Fe and Zn. Soil Sci. Soc. Amer. J. 45:70-75.

Havlin, J.L., and P.N. Soltanpour. 1982. Greenhouse and field evaluation of the NH_4HCO_3-DTPA soil test for Fe. J. of Plant Nutrition. 5:769-783.

Havlin, J.L., and P.N. Soltanpour. 1984. Changes in NH_4HCO_3-DTPA extractable Zn and Fe as affected by various soil properties. Soil Sci. 137:188-193.

Havlin, J.L., D.G. Westfall, and H.M. Golus. 1984. Six years of phosphorus and potassium fertilization of irrigated alfalfa on calcareous soils. Soil Sci. Soc. Am. J. 48:331-336.

Havlin, J.L., and D.G. Westfall. 1984. Soil test P and solubility relationships in calcareous soils. Soil Sci. Soc. Am. J. 48:327-330.

Battison L., P. Groenevelt, J.L. Havlin and R.L. Thomas. 1984. Barriors to sustained agricultural production on Ontario soils. *In* Sustainable Soil Productivity ... Barriors and Solutions. J.W. Ketchson (ED). Notes on Agric., Univ. of Guelph. 19:9-14.

Havlin, J.L., D.G. Westfall, and S.R. Olson. 1985. Mathematical models for potassium release kinetics in calcareous soils. Soil Sci. Soc. Am. J. 49:366-370.

Havlin, J.L., and D.G. Westfall. 1985. Potassium release kinetics and plant response in calcareous soils. Soil Sci. Soc. Am. J. 49:371-376.

Havlin, J.L. 1986. Comparison of statistical methods for separating iron deficient from nondeficient soils. J. of Plant Nutrition. 9:241-249.

Havlin, J.L. 1987. Fertilizer management for no-till irrigated and dryland corn. J. Fert. Issues. 4:60-67.

Sullivan, D.M., and J.L. Havlin. 1988. Agronomic use of ammonium thiosulfate to improve nitrogen fertilizer efficiency. J. Fert. Issues. 5:37-44.

Varvel, G.E., J.L. Havlin, and T.A. Peterson. 1989. Nitrogen placement evaluation for winter wheat in three fallow tillage systems. Soil Sci. Soc. Am. J. 53:288-292.

Sun, Y., J.L. Havlin, and G.M. Paulsen. 1989. Evaluation of nutrient deficiencies in wheat seedlings by chlorophyll fluorescence. J. Plant Nutrition. 12:769-782.

Havlin, J.L., and F.R. Lamm. 1989. Management of dryland corn for the central Great Plains. p.836-838. International Dryland Farming Conf. Proc. Amarillo, TX, Aug. 15-17, 1988.

Sisson, J.B., and J.L. Havlin. 1990. Soil factors affecting yield variance in dryland wheat. p.406-408. International Dryland Farming Conf. Proc. Amarillo, TX

Havlin, J.L., D.E. Kissel, L.D. Maddux, M.M. Claassen, and J.H. Long. 1990. Crop rotation and tillage effects on soil organic carbon and nitrogen. Soil Sci. Soc. Am. J. 54:448-452.

Kitchen, N.R., J.L. Havlin, and D.G. Westfall. 1990. Soil sampling under no-till banded phosphorus. Soil Sci. Soc. Am. J. 54:1661-1665.

Sullivan, D.M., and J.L. Havlin. 1991. Flow injection analysis of urea in soil extracts. Soil Sci. Soc. Am. J. 55:109-113.

Sullivan, D.M., and J.L. Havlin. 1992. Field microplot and laboratory evaluation of urea hydrolysis inhibition by ammonium thiosulfate. Soil Sci. 153:373-381.

Sullivan, D.M., and J.L. Havlin. 1992. Soil and environmental effects on urease inhibition by ammonium thiosulfate. Soil Sci. Soc. Am. J. 56:950-956.

Sullivan, D.M., and J.L. Havlin. 1992. Mechanism of thiosulfate inhibition of urea hydrolysis in soils: tetrathioate as a urease inhibitor. Soil Scl. Soc. Am. J. 957-960.

PUBLICATIONS (teaching)

Havlin, J.L. 1989. Soils. p. 39-54. In D.P. Price (ed.) Modern Agriculture. Southwest Scientific Publishing Co., University Park, NM.

Havlin, J.L. 1989. Soil Fertility Management. p. 55-74. In D.P. Price (ed.) Modern Agriculture. Southwest Scientific Publishing Co., University Park, NM.

Havlin, J.L. 1989. Dryland Agriculture. p. 89-112. In D.P. Price (ed.) Modern Agriculture. Southwest Scientific Publishing Co., University Park, NM.

Havlin J.L., 1986. Dryland Conservation Technology Workshop: A Field Approach. Agron. Abst. p. 23.

Tisdale, S, W. Nelson, J. Beaton, and J. Havlin. Soil fertility and fertilizers. 5th Edition. Macmillon Publishing Co. (In press).

PUBLICATIONS (extension)

Havlin, J.L. 1986. Optimizing wheat inputs for profit. Solutions Magazine. 30(7):50-60.

Havlin, J.L., R.E. Lamond, and D.A. Whitney, 1987. Improving wheat and grain sorghum profits with starter phosphorus. Better Crops. 71:17-19.

Reinsch, W., J.L. Havlin, and E.C. Dickey. 1985. Estimating crop residue - using residue to help control wind and water erosion. USDA-SCS. NE Leaflet No. 3. 6 p.

Paulsen, G., and J. Havlin. 1987. Managing wheat for maximum economic yields in Kansas. State Recommendations for Maximum Economic Wheat Yields. National Assoc. of Wheat Growers Foundation, Wash. D.C.

Havlin, J.L. 1989. Soil and crop management effects on soil organic matter. Solutions Magazine 33:34-36.

Havlin, J.L., and A.J. Schlegel. 1989. Increasing soil organic matter with soil/crop management. Better Crops. 74:7-9.

Havlin, J.L., and J.P. Shroyer. 1990. Establishing on-farm demonstration plots. Kansas State Univ. Coop. Ext. Ser. MF-966.

25 additional local and regional extension publications (list available on request)

PAPERS PRESENTED

105 research and extension papers presented at local, regional, and national meetings (list available on request).

REFERENCES

Dr. David J. Mugler
Director, Academic Programs
College of Agriculture
Kansas State University
Manhattan, KS 66506

Dr. Gerry Posler, Head
Department of Agronomy
Kansas State University
Manhattan, KS 66506

Dr. George E. Ham
Associate Director
Kansas Agricultural Experiment Station
Kansas State University
Manhattan, KS 66506

MIDWEST RESEARCH INSTITUTE
425 Volker Boulevard
Kansas City, Missouri 64110
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May 25, 1993

Mr. Dallas Safriet (MD-14)
Emission Factor and Methodology
U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Emission Inventory Branch
Research Triangle Park, NC 27711

Dear Dallas:

Enclosed for your advance technical review is one copy of the draft background document for Section 6.2.1 Fertilizer Application, the comments log, and a memo on changes made to the previous draft of this report.

In the past we have been providing a set of draft copies for EPA and industry review, but in the interest of time and efficiency it is our intention that you circulate this review copy for the EPA technical review prior to our providing you with copies for industry review. We discussed this with you in our meeting last week, and you were in agreement that this should save the project time and money.

In the case of the fertilizer application report, we would like you to provide us with any EPA review comments within a week so that we still have access to Dr. Havlin. We hope this will be possible.

Advance review copies of the grain report should be coming soon.

Both the cotton ginning and the yeast production reports are ready to be sent in final form, but we are still awaiting final clarification on format requirements to put the AP-42 section on CD-ROM. Deep fat frying can be finalized as soon as we hear back from you. We are also awaiting your findings on fish processing; have you received any industry comments yet? As we discussed, cotton ginning, deep fat frying, and fish processing are our first priority and are nearest final form.

Please let us hear from you as soon as possible about this fertilizer report.

Thank you.

Sincerely,

MIDWEST RESEARCH INSTITUTE

Margaret Thomas

Margaret G. Thomas
Senior Resource Planner

MGT/arc

Margaret Thomas

KSU
KANSAS
STATE
UNIVERSITY

Department of Agronomy

Crop, Soil, and Range Sciences
Throckmorton Hall
Manhattan, Kansas 66506-5501
913-532-6101

June 3, 1993

Ms. M.E.W. St. Germain
Senior Chemist
Midwest Research Institute
425 Volker Boulevard
Kansas City, MO 64110

Dear M. St. Germain:

The enclosed document (AP-42, Section 6.2.1) on fertilizer application has been reviewed and my recommended changes appear directly on the manuscript. Several section have been completely rewritten and also are attached. The following itemized list of concerns and suggested changes should be considered.

General Comments

1. The manuscript leaves the impression that fertilizers are the only source of gaseous emissions of nitrogen. Manure and legume nitrogen also be denitrified and nitrogen gas released during nitrification. I have made several changes to reflect this oversight.

2. The descriptions of soil biological and chemical processes are somewhat inaccurate and I have made substantial changes in these sections.

3. The data obtained from the references provided appear to be accurately interpreted and reported. However, the data quality rating eliminates some valuable data collected from studies that use a micro-meteorological approach which have clearly demonstrated that they may estimate the quantity of gaseous emissions more accurately than small microplot chamber methods.

4. The arithmetic means listed in Table 6.2.1-2 are suspect when the specific gases are compared. For example, research has shown that primarily NO and not NO_2 is emitted from soils. I can't see how NO_2 could be greater than NO. This problem illuminates the numerous problems in the limited data set used, and perhaps more importantly, the criteria used in the data quality rating system.

5. Many of the references used unincorporated nitrogen. Thus, gaseous emission would be over estimated.

6. In general, the data (Table 4-2 and 4-3) used in obtaining the arithmetic means are seriously insufficient to formulate conclusive evidence for fertilizer nitrogen contribution to atmospheric nitrogen gases.

Specific Comments

Section 2.2.1 (pg 2-3): Aqua ammonia can be soil applied. "It" refers to Anhydrous ammonia not aqua ammonia.

Section 2.2.1 (pg 2-4): Depth of NH_3 application most always is deeper than 1 inch. You have used 4 to 10 inches in a subsequent section, thus, you should be consistent.

Section 2.2.2 (pg 2-9): Application rates are determined by the intended crop and expected crop yield potential. "Fallow land" implies no crop, thus, why would fertilizer rates be higher here than under a cropped field? Fertilizers are not usually applied to fallow land, but if it is applied the application will be made close to planting time. I suggest deleting this sentence.

Section 2.2.2 (pg 2-9): Dry fertilizer also can be band applied.

Section 2.3.1 (pg 2-15): In Section 6.2.1.3 manures are mentioned and should be mentioned here.

Section 2.3.2.1 (pg 2-17): Probably need to identify the chemical formula here.

Section 2.3.2.1 (pg 2-17): "photosynthetic" probably works better here.

Section 2.3.2.1 (pg 2-20): Several changes/corrections have been made to these sections.

Section 2.3.2.2 (pg 2-21): This section is poorly written and somewhat inaccurate. The attached page 2-21a should be inserted.

Section 2.3.2.3 (pg 2-21): This section also has numerous inaccuracies and is not well organized. Many of the sentences and paragraphs have been rewritten. One paragraph (pg. 2-22) needs to be moved to Section 2.3.2.4.

Section 2.3.2.4 (pg 2-22): This section has been rewritten.

Section 2.3.2.5 (pg 2-23): This section has been rewritten. Replace with attached pages 2-23a-b.

Section 2.4 (pg 2-23/24): This section has been rewritten. Replace with attached page 2-23b.

Section 3.5.1 (pg 3-11): Standard soil moisture content is always defined on an oven dry weight basis.

Section 4.2.1 (pg 4-15): The last sentence on this page is extremely important and should be highlighted by using a **boldface** font.

Section 4.3.2 (pg 4-18): Table 4-5 should incorporate the range of values contained in the mean. See Table 6.2.1-2 for specific change.

Section 6.2.1.3 (pg 3): The implication that fertilizer represent the only source of emissions is not correct. Thus, I have added the word nutrients an manures at appropriate places.

The Table numbers stated in the 3rd paragraph should be changed.

Statement concerning the need for addition research on heavy metal particulates from fertilizers and manures should be added.

The document needs a precautionary statement regarding the extremely limited and highly variable data found in Tables 6.2.1-2 and 6.2.1-3, and how this affects the usefulness and reliability of the data.

Section 6.2.1.3 (pg 7): The data for N_2O emission of for urea should be 3.98.

To give the reader the appropriate perspective on the high variance in the data, I suggest including the range in the data and the number of data points included in the mean. See page 6.2.1-7a for example change.

Thank you for the opportunity to review this document. Please don't hesitate to call me for more information.

Sincerely,

John Havlin

John L. Havlin
Associate Professor

Recd 1/5/94
TZ

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
ATMOSPHERIC RESEARCH AND EXPOSURE ASSESSMENT LABORATORY
RESEARCH TRIANGLE PARK
NORTH CAROLINA 27711

December 28, 1993

MEMORANDUM

SUBJECT: Review of the Revised Draft Report, "Emission Factor for AP-42, Section 6.2.1: Fertilizer Application"

FROM: Thomas E. Pierce (MD-80)
MSAB/ACMD/AREAL/ORD

TO: Dallas W. Safriet (MD-14)
EIB/OAQPS

As you requested, I have reviewed the revised draft report on emission factors from fertilizer application. I will restrict my review comments to those areas that I have some degree of familiarity: NO_x emissions from soils. I believe the authors of the report have done a credible job, considering the paucity of information on the subject and the inter-disciplinary range of the references (compared to other AP-42 emission factor studies). I further appreciate that considerable efforts were made to develop emission factors that could be clearly expressed in tabular form for AP-42. However, I have two major recommendations concerning the proposed values for NO and NO_2.

97; D9 (9890-9891)

(1) Most scientific papers discussing biological mechanisms of NO_x emissions from soils note that most (>90%) if not all of the emissions are in the form of nitric oxide (NO). According to Hutchinson and Brahms (J. of Geophysical Research, pp. 9889-9896, 1992), there is no evidence to suggest that NO_2 is directly emitted from soils. Other scientists support this statement (references available on request). Admittedly, the emission factors were based on chamber experiments that measured increased levels of NO_2, which would lead one to infer emissions of NO_2. This probably occurs because NO emitted from the soil into the chamber is quickly converted to NO_2 in the presence of ozone. In fact, the revised AP-42 draft report on page 4-3 notes: "Because any NO emitted is likely to be converted quickly to NO_2 in the atmosphere, the NO_x emissions were estimated as NO_2." However, EPA's air quality simulation models supposedly handle the chemical transformations that occur when a gas is directly emitted in the air, even in the case of NO when this transformation occurs rapidly near the soil/air interface. For this reason, **I recommend that the emission factors for NO and NO_2 be expressed only as NO.**

OK

(2) The authors correctly noted that substantial variability of NO_x emissions occur both within and among sites. Because of this and the shortage of experimental data, I do not think sufficient data exist to divide emission factors according to the type of fertilizer application. I am worried that a policy maker, who is looking into NO_x emission abatement strategies, might review the proposed AP-42 emission factor table and conclude that different types of fertilizers could be

wrote a sentence to address this point

used for NO_x emission reductions. While this may in fact be true, I do not think sufficient experimental data currently exist to differentiate NO emissions between fertilizer types. Therefore, **I recommend that only one NO emission factor (applicable to all nitrogen-based fertilizers) be reported in the draft AP-42 table.**

I wanted to let you know that the Regional Oxidant Model (ROM) employs an algorithm from Williams et al. (Global Biogeochemical cycles, pp. 351-388, 1992) that allows NO emissions to vary as a function of temperature and land use type. The Williams et al. work was mentioned in the draft report, but understandably it was not used in the emission factor table because fertilizer rates were not reported. Out of curiosity, I have compared the emission factors from AP-42 with the emissions estimated from the ROM. In the ROM, an NO emissions flux from fertilized corn fields of 586 $\mu g\ m^{-2}\ h^{-1}$ is assumed at a temperature of 30 C. If we assume a fertilizer application of 100 kg N/ha and that NO emissions occur a period of 120 days, then the percentage loss of N in the form of NO is 8%. This compares to the AP-42 values of 6% for urea, 1% for ammonium nitrate (fluid), and 11% ammonium nitrate (as a solid). So it would appear that we are both in the same ballpark, but neither one of us really knows the size of the ballpark.

I appreciate the effort that your branch is making to improve emission factors for ozone precursors. As indicated in my comments and as reflected in the draft report, there is still much work left to be done. If I can be of any further assistance, please call me at extension 1-1375.

541-1375

cc: J. Novak
C. Geron (AEERL)

continue to do so in the next several years. Given our past involvement and our future plans, we would be receptive to try and incorporate some of your agency's needs in our work, as it is apparent that we both are attempting to decrease the uncertainty associated with building regional inventories of these trace gases.

In regard to my comments on the document, I would make the following:

1. A significant shortfall of this document is the omission of many current literature citations that deal with the subject matter. It would be advised that the authors refer to the recent review article of Williams et al. (1992) which is an excellent review of NO and N_2O emissions from soils. Some of the following articles are cited in the afore mentioned article, but the authors sorely need to update their literature source. For example, the TVA data base on fertilizer usage for 1989/198 is used. Why not use the 1992/1993 TVA published report? A brief listing of some of these articles are:

I. Ammonium related

- Whitehead, D. C. and N. Raistrick, J. Agric. Sc. (Cambridge) 121:73-81, 1993.
- Sommers, S. G. et al., J. Agric. Sc.(Cambridge) 121:63-71, 1993.
- Oenema, O. and G. L. Velthof, Neth. J. Agric. Sc. 41:63-80, 1993.
- Burton, C. H. et al., Bioresource Tech. 45:233-235, 1993.
- Sibbesen, E. and A. M. Lind, Acta Agric. Scanda. Sct. B. Soil and Plant Sci. 43:16-20.

II. NO and N_2O related

- Hansen, S. et al., Soil Biol. Biochem 25:621-630, 1993.
- Skiba, U. et al., Atmos. Environ. 26A:2477-2488, 1992.
- Bronson, K. F. and A. R. Mosier, ASA Publ. 55, pp. 133-144, Madison, WI.
- Bronson, K. F. et al., Soil Sci Soc Am. J. 56:161-165, 1992.
- Bronson, K. F. and A. R. Mosier, Biol Fertil. Soils 11:116-120, 1991.
- Jarvis, S. C. et al., Plant and Soil 131:77-88, 1991.
- Lindau, C. W. et al., Plant and Soil 129:269-276, 1990.
- Brumme, R. and F. Beese, J. Geophy. Res. 97:12,851-12,858, 1992.
- Nugroho, S. G. and S. Kuwatsuka, Soil Sci. Plant Nutr. 38:593-600 1992.

Review Article
Eichner → J. Environ. Quality 1990

Interested person: Robert Jackson
EPA, Athens Lab.

Aulakh, M. S. et al., Soil Sci Soc Am. J. 48:790-794, 1984.
Schloenmer, S., Z. Pflanzenernahr. Bodenk. 153:439-444, 1990.
Valente, R. J. and F. C. Thornton, J. Geophy. Res. 98:16,745-16,753, 1993.
Skiba, U. et al., Soil Biol. Biochem 25:1527-1536, 1993.

2. A fertilizer is "any substance that is added to the soil to supply elements required for plant nutrition" (Tisdale and Nelson, Soil Fertility and Fertilizers, 2nd ed., 1975), why then do you not address animal waste and green manures. I suggest you change the title to indicate you are only referring to mineral fertilizers. I also realize there is very little information on this related to NO and N_2O but a fair bit of information is available for dairy and swine waste, particularly related to loss of NH_3 and N_2O in storage prior to land application.

3. Pages 2-28 through 2-29. There is some work by Bronson et al. on the used of nitrification inhibitors to reduce N_2O emissions. I think this work needs to be incorporated into the document.

4. Page 4-3. I am unclear why in lines 21-23 you state that "NO_x emissions were estimated as NO_2." Earlier on the same page, lines 3-5 you note that the study indicated that the emissions "were primarily" NO not NO_2. Our work and the published work of most all researchers studying soil NO emissions have found that NO is the dominant species, thus I do not understand why you calculate emissions as NO_2. Even the author of the paper you cite states that it is mostly NO that is emitted, not NO_2.

5. Page 4-20, lines 12-15. Admittedly, the fertilizers you chose not to include do not represent a significant tonnage but I would argue that regardless of fertilizer form there is an addition of NO_3 or NH_4 that is ultimately available for soil processes, whether it be denitrification or any other soil process, i.e., leaching. I think that these data should be used. Soil microorganism do not discriminate among NO_3 or NH_4 ions provided by a particular fertilizer formulation.

6. Page 4-12. I question your approach of taking the arithmetic mean of the calculated emission factors in the papers you selected for inclusion in this work. The soil emissions of NO and N_2O are typically lognormally distributed. I would suggest you refer to the work of Parkin (Soil Sc. Soc. Am. J. 52: 323-329, 1988;

MIDWEST RESEARCH INSTITUTE

INTEROFFICE COMMUNICATION

To: Margaret Thomas and Chat Cowherd **Date**: May 25, 1993

From: Margie St. Germain

Subject: Synopsis of Improvements to Chapter 6.2.1, Fertilizer Application

Below you will find a listing of the improvements made to AP-42, Chapter 6.2.1 on Fertilizer Application.

In summary, the following changes were made:

1. The terminology was changed to reflect the proper uses of fluid and liquid.

2. A literature search was performed to identify the most frequently used fertilizers. As a result, Section 2.1 discusses the top 13 fertilizers used in the field and compares that list to the fertilizers for which test data are available. Although the test data for nontypical fertilizers were discussed, the emission factors were not incorporated into the background document. The calculated emission factors for typical fertilizers remain unchanged.

3. Additional references were reviewed to improve the discussion of application techniques. Changes were made to Section 2.2 to better summarize the equipment. The figures were changed and some figures added.

4. Additional references were reviewed for the soil chemistry discussion. As a result, Section 2.3 was significantly condensed. This section discusses only the key chemical reactions with references directing the reader to more detailed discussion of soil chemistry references.

The current version is being reviewed by Dr. John Havlin, a consultant.

Accompanying this memo is the comments log.

Comments of James Shultz and Bernard Byrnes
International Fertilizer Development Center (IFDC)

Comment	Action taken
General	
1. Use fluid instead of liquid. Use correct terminology.	1. The terminology was changed to better reflect the technology; specifically, fluid was used instead of liquid where applicable. Additional literature was obtained which described the application of fertilizer.
2. Inaccurate descriptions of application devices, and fertilizers.	2. Catalogs from current fertilizer dealers were obtained initially, and were used for the diagrams and pictures of applicators. The additional references were reviewed for better figures and diagrams. The reviewers were contacted for the literature cited.
3a. Inaccurate information concerning the most frequently used fertilizer.	3. A search on fertilizer application was performed and broken into categories. These categories were compared to the literature available on emission data. Discussion was added on high-use fertilizers as compared to test data fertilizers.
3b. (Section 5) N_2O emissions are much more a soil phenomenon than a fertilizer-related phenomenon.	
3c. (Section 5) Table needs to be revised completely to reflect differences between the various types of fertilizers and also their use.	
Section 5	
1. Supplied a copy of a potential rewrite of Chapter 6.2.1.	
2. All solid (ammonia-based) fertilizers cannot volatilize ammonia at a rate as high as urea—greatly overestimates losses.	2. Reviewed the original data tables from the first draft. The original tables were broken into more precise categories, including physical type, chemical type, and soil type. Changed table to reflect specific fertilizers that were among the top ten used.
3. Recent research has shown that NO, not NO_2, is emitted from soils.	3. Obtained cited literature from Hans Sperling in France. Obtained other references cited. Reviewed new references as compared to original document.

Comments of Horace Mann, Roland Hauck, and Michael Broder
Tennessee Valley Authority

Comment	Action taken
General	
1. Use fluid instead of liquid. Use correct terminology.	1. The terminology was changed to better reflect the technology; specifically, fluid was used instead of liquid where applicable. Additional literature was obtained which described the application of fertilizer.
1a. (Section 2) The term fluid fertilizer should be used rather than liquid fertilizer. Fluid fertilizers are usually concentrated. Need to include injection in Section 2.2.2.	
1b. (Section 2) The term $(NO)_x$ most generally is used when referring to the N oxide gases. Little evidence that nitrification leads to significant loss of gaseous nitrogen.	
1c. (Section 2) Discussion relating to ammonium nitrate is incorrect—nitrite usually is not present in appreciable quantities in soils except in microsites of high pH.	
2. Inaccurate descriptions of application devices, and fertilizers.	2. Catalogs from current fertilizer dealers were obtained initially, and were used for the diagrams and pictures of applicators. The additional references were reviewed for better figures and diagrams. The reviewers were contacted for the literature cited.
2a. (Section 2) Suggest 20%-30% ammonia instead of 30%-40% or put temperatures where vapor pressure is 0 psig.	
2b. (Section 2) Needs rewriting to reflect current practices and equipment.	
3. Inaccurate information concerning the most frequently used fertilizer.	3. A search on fertilizer application was performed and broken into categories. These categories were compared to the literature available on emission data. Discussion was added on high-use fertilizers as compared to test data fertilizers.
3a. (Section 2) Assumes that time-release fertilizer use is growing—this assumption is incorrect.	
3b. (Section 2) One of the main sulfur sources in fluid fertilizers, ammonium thiosulfate, is not listed. The amount supplied as sulfur-coated urea is negligible.	

Comments of Horace Mann, Roland Hauck, and Michael Broder (Continued)
Tennessee Valley Authority

Comment	Action taken
General (Continued)	
3c. (Section 2) Sources of phosphate and nitrogen fertilizers need to be identified. All phosphate fertilizers do not contain 100 ppm of Ba, 20 ppm Ca, etc.	
3d. (Section 5) Table 2 lists calcium nitrate and ammonium chloride as common fertilizers used in the U.S., which they are not, and omits such materials as monoammonium and diammonium phosphates, which are common components of mixed fertilizers.	
Section 2	
1. The contaminants listed in Table 2-1 are also present in soils to which no fertilizer has been added.	1. True; however, by increasing the concentration with fertilizers, man is affecting the natural equilibrium.
2. The discussion of ammonia/ammonium reactions in soils reflects poor understanding of soil chemistry. No clear distinction between dissolution of ammonia in or adsorption by water and adsorption of ammonium ion on inorganic and organic exchange surfaces.	2. Additional data were provided with the comment. These data were reviewed with the original references, and the additional references on soil chemistry, and modified as needed.
3. Formulas are wrong for urea, ammonium sulfate, and calcium nitrate.	3. Corrected formulas and percent nitrogen content.
Section 4	
1a. Fluid fertilizers, rather than solid ones, can be applied more rapidly per unit of nutrient. There is no evidence that emissions from solid fertilizers generally exceed those from fluids, with the exception of surface-applied, unincorporated urea or diammonium phosphate, from which ammonia may be liberated to the atmosphere.	1. The test data available for emissions from applied fertilizers were limited. Unless additional data could be provided by the reviewers, the emission factors remain unchanged. Final tables were changed to reflect the most frequently used fertilizers.
1b. The data given in references cited may be considered accurate. What may be questionable is the use of the data for extrapolating to dimensions several magnitudes larger than the system from which they were collected. References 15a and 15b. . . . is more justifiable than a similar extrapolation of data collected from chamber studies.	

Comments of Horace Mann, Roland Hauck, and Michael Broder (Continued)
Tennessee Valley Authority

Comment	Action taken
Section 4 (Continued)	
1c. The weak basis for the number given . . . once the data are published . . . assume an undeserved validity.	
AP-42 Chapter 6.2.1	
1a. Emission factor for ammonia from solid fertilizer is based on ammonia volatilization from surface applied, unincorporated urea, which does not represent the bulk of solid nitrogen fertilizers nor the manner in which they are used.	1. Reviewed the original data tables from the first draft. The original tables were broken into more precise categories, including physical type, chemical type, and soil type. Changed table to reflect specific fertilizers that were among the top ten used.
1b. Emission factor for nitrous oxide is based on studies that measured nitrous oxide formed during nitrification, whereas most nitrous oxide released to the atmosphere from soils probably is the result of denitrification. Also, where nitrification is involved, the type, physical state, and if solid, the particle size are among the factors affecting the rate of nitrification and course of its reaction products.	
1c. To construct a table of emission factors for fertilizers from an admittedly extremely limited and weak data base is not justifiable. To present the information in terms of 0.1 g/kg or 0.1 lb/ton implies a precision not warranted by the data.	

AP-42 FINAL SUMMARY CHECKLIST

Fertilizer Application, 6.2.1

- OK ① Emission factors provided for each emitting process and pollutant with ratings. Get the line item into table even if no data.

✗ _____ SCCs identified/specified for each emitting process and coordinated/ verified with EFMS.

discussed - no data PM clearly specified in terms of Total (PM), PM-10 including condensibles for organics and solids, plus particle size data available presented and explained, correct symbols and terms used.

OK ② Data presented in Background Document in form of histograms when more than 4 to 6 data points.

- Not Applicable (NA) Process and other flow diagrams completed and consistently labeled and showing all emission points. Add any information on control technology. ✓
  Added discussion

YES ✓ Tables and text laid out so as to minimize "white space on page."

NA ③ Separate attachment summarizing nature, significance, and impact of changes from previously published AP-42 sections. Helps to identify what is important.

✗ TBC ⑥ Separate one-page memo or summary of uncertainties, Importance of source categories, and recommendations for future testing.

YES Are references properly cited and formatted, stressing use of primary references and peer-reviewed summaries.

✓ metals / NO_x, N_2O / SO_2 + H_2SO_4 List of HAPS and identified (after evaluation/validation for reasonableness/completeness) any factors presented when "reasonable." Cross-checked with latest and ongoing work in FIRE and AP-42 with feedback on new data unearthed (e.g., hexane is a HAP, ethanol is a HAP [yeast]).

YES All terms and acronyms defined, especially those unique to the industry.
↳ also diagrammed

NA ⑤ All factors and data internally consistent (by PM always greater than PM-10, VOC HAPS always less than TOC).

~~Not Applicable~~ Not Available Best efforts made to include global warming gases, particularly CO_2 which can often be estimated with stoichiometric calculations. (F factors for combustion source?)

NA ④ Explain why if controlled emissions are greater than uncontrolled emissions. not perfectly clear that ALL emissions are uncontrolled.

Meeting 5/25/95

① N_2O, NO, and NO_2 are product emissions and are ~~not~~ specific to nitrogen fertilizers.

② Three or less references for each emission

③ AP-42, chapter 6.2.1 did not exist previously

④ No controlled emissions currently exist

⑤ All factors were generated to the same final units for comparison.

⑥ TBC - to be completed with final submission

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TELEFAX NO. 205-381-7408

December 21, 1992

Mr. Dallas W. Safriet
Environmental Engineer
Emission Inventory Branch
United States Environmental Protection Agency
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

Dear Mr. Safriet:

As requested in your November 19, 1992, letter we have reviewed the draft version of a proposed new section 6.2.1, *Fertilizer Application*, of AP-42, *Compilation of Air Pollutant Emission Factors*. As you requested we reviewed only Section 5 of the background documentation.

Our staff members reviewed draft Section 6.2.1. The reviewers found the draft section to be not well written, quite inaccurate, and apparently inadequately researched. In our opinion the draft section should be rewritten after a more extensive literature review is performed. We have enclosed an example of a possible rewrite that we believe more accurately describes the information you are attempting to document. However, the rewrite does not include additional data other than that already incorporated into the draft version. According to our staff there is much more reliable data and information available than that referenced in the draft section.

We have also collaborated with staff members from the Tennessee Valley Authority on the draft section and understand they were also requested to review the document. We have reviewed their comments that were sent to you and fully agree with them.

Please note that we did not review the data included in Table 6.2.1-1. The data would have demanded an extensive review of all the references included in the background documentation. We could undertake this task but only under a reimbursable agreement due to the magnitude of such an effort.

We hope this information is helpful to the EPA in developing appropriate and accurate emission factors for AP-42.

Sincerely yours,

James J. Schultz
Director
Outreach Division

Enclosure

Example of Suggested Rewrite of Section 6.2.1

6.2.1 Fertilizer Application

6.2.1.1 General. The role of fertilizers in the agricultural industry is to supply essential plant nutrients to improve crop production. It has long been recognized that there are 16 essential elements or nutrients necessary for plant growth, three of which are supplied from the atmosphere or water (carbon, hydrogen, and oxygen). The other 13 elements (nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, copper, zinc, boron, manganese, iron, chlorine, and molybdenum) are principally supplied through the soil medium. Some of these elements are limited in the soil medium and must be supplemented by fertilizers. Fertilizers are distributed through agricultural supply retailers, farmers' cooperatives, and fertilizer dealers. Application is typically performed by farmers and by fertilizer dealers using specialized application equipment.

6.2.1.2 Process Description. Based on the physical form of the fertilizer, there are three basic types of fertilizer application. The basic method of application is determined according to whether the fertilizer is in a gaseous, fluid, or solid form.

6.2.1.2.1 Gaseous fertilizer. Anhydrous ammonia is the only gaseous fertilizer used, and supplies nitrogen. Typically, about 6 million tons of ammonia is applied annually in the United States. Farmers generally apply ammonia thenselves. Anhydrous ammonia is typically stored in a liquid form: most commonly, under pressure; and to a lesser degree, by refrigeration. Anhydrous ammonia is actually injected as a liquid/gaseous mixture into the soil where it vaporizes into a gas and then is captured by several components in the soil, including water, clay, and other minerals.

Because it is a gas at atmospheric pressure, anhydrous ammonia must be injected from 4 to 10 inches (10 to 25 cm) below the soil surface, depending upon the soil type, soil conditions, and spacing. Generally, typical equipment for anhydrous ammonia application consists of a tractor, a pressurized tank containing the anhydrous ammonia, a metering system, manifolds, and injection knives. Figure _____ (not the one shown) is a typical example of application equipment for anhydrous ammonia.

The only calibration done during the application of ammonia is a tracking of pounds applied versus acres covered. Precise orifice calibration for metering the flow of liquid ammonia is done at the factory, and farmer dials in the orifice setting according to speed, desired rate, and tool bar width.

6.2.1.2.2 Fluid fertilizer. Fluid fertilizers are typically classified as either solutions or suspensions. Solution fertilizers are free of solid particles. Suspension fertilizers are two-phase fertilizers in which solid particles are maintained in suspension in the aqueous phase. The equipment used in the application of fluid fertilizers typically

consists of a vehicle (truck or tractor), a tank holding the fluid, a metering system, manifolds, and spray nozzles. The manifolds are mounted inside long booms (20-40 ft) with the nozzles spaced along the manifold so that the spray patterns overlap. Fluid fertilizers are most commonly sprayed onto the surface of freshly tilled soils.

Figure _____ (not the one shown) is an example of a typical applicator for fluid fertilizers.

6.2.1.2.3 Solid fertilizers. In the United States, solid fertilizers are typically applied as straight nitrogen fertilizers (urea or ammonium nitrate) or as mixed fertilizers containing not only nitrogen but also phosphate, potassium, and other nutrients. Application of solid fertilizers is done predominantly either by fan-type spreaders (Figure _____) or by boomed (pneumatic- or auger-type) spreaders (Figure _____).

6.2.1.3 Emission and Controls. Both solid-phase (particulate matter) and vapor-phase air pollutants can be generated from the application of fertilizers. In both cases, two general classes of emissions are noted: "immediate" pollutant emissions which can occur either during or shortly after application; and "latent" pollutant emissions which can be generated days or weeks following application.

Wind-blown dust can be created immediately during the application of dry fertilizers and later from disturbances caused by mechanical operations (e.g., tilling) and/or wind erosion. Vapor-phase emissions can be generated after application by the immediate volatilization of gaseous fertilizers (i.e., anhydrous ammonia) or after some period of time by the chemical/biological transformation of N added as fertilizers to the soil.

At the current time, vapor-phase emission factors are available only for nitrogen fertilizers. These emission factors are shown in Table 6.2.1-1 on the basis of equivalent nitrogen applied to the soil. Finally, where more specific data are not available, Table 6.2.1-2 provides equivalent nitrogen contents of common chemical fertilizers for use with the emission factors shown in Table 6.2.1-1. (Refer to TVA comments regarding questionable validity of vapor-phase emission factors.)

Table 6.2.1-1. Candidate Emission Factors for the Application of Nitrogen Fertilizers[a]

IFDC did not attempt to verify the data included in this table. This could be done on a reimbursable basis.

Table 6.2.1-2. Equivalent Nitrogen Content of Common Chemical Fertilizers[a]

Type of Fertilizer	Chemical Formula	Nitrogen Content (Weight Percent)	Amount of Fertilizer Applied per Hectare to Produce 1 kg N/ha Equivalent Application (kg)
Anhydrous ammonia	NH_3	82.3	1.22
Urea	$CO(NH_2)_2$	46.7	2.14
Ammonium sulfate	$(NH_4)_2SO_4$	21.2	4.72
Calcium nitrate	$Ca(NO_3)_2$	17.1	5.85
Ammonium nitrate	NH_4NO_3	35.0	2.86
Ammonium chloride	NH_4Cl	26.2	3.82
Sodium nitrate	$NaNO_3$	16.5	6.06
Diammonium phosphate (DAP)	$(NH_4)_2HPO_4$	21.2	4.72
Potassium nitrate	KNO_3	13.9	7.19

a. For pure chemicals. 1 kg = 1,000 g = 2.2 lb; 1 ha = $10^4 m^2$ = 2.471 acres. From Table 4-5 of Reference 7.

Memorandum

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To: David W. Rutland, Physical Properties Specialist, Outreach Division

From: Bernard H. Byrnes, Soil Scientist, Resources Management Research and Development Division

Date: December 16, 1992

Subject: COMMENTS ON "ESTIMATION OF GREENHOUSE GAS EMISSIONS AND SINKS"--FINAL REPORT

Table 6.2.1-1 is the essence of the entire report, since it lists emission factors for N gases derived from N fertilizers.

1. NH_3--All solid fertilizers cannot volatilize ammonia at a rate as high as urea for the obvious reasons that many contain nitrate as a component and do not produce alkalinity to support volatilization. This emission rate, based on unincorporated application, greatly overestimates losses.

2. NO, NO_2--Recent research (see page A-5 in references) has shown that NO, not NO_2, is emitted from soils. To have a larger emission factor for NO_2 than NO makes no sense. Why would NO come from liquid fertilizers but not others?

3. N_2O--N_2O emissions are much more a soil phenomenon (nitrification rates and denitrification rates as influenced by water dynamics) than a fertilizer-related phenomenon. Bouwman (1990) compiled data from recent literature and failed to see a relationship to fertilizer type and came up with a factor of 4.17 g/kg N or, if poorly drained soils were excluded, 7.50 g/kg N. The attached tables appear to be more valid estimates.

The table needs to be revised completely to reflect differences between the various types of fertilizers and also their use.

BHB:daf
Attachment
cc: C. A. Baanante
J. J. Schultz

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**********TELEFAX COMMUNICATION**********

To: Mr. Dallas W. Safriet
Environmental Engineer
Emission Inventory Branch
United States Environmental Protection Agency
Research Triangle Park, North Carolina 27711

December 23, 1992

From: James J. Schultz

Fax 919-541-0684

MESSAGE:

RE: SECTION 6.2.1, FERTILIZER APPLICATION DRAFT REPORT, AP-42

You may find the attached comments by Dr. B. H. Byrnes of our staff to be useful. I should have included them with my letter to you dated December 21, 1992. Please let me know if you need any additional information.

Dr. Byrnes can be reached at (205) 381-6600, extension 289.

Regards,

James J. Schultz
Director
Outreach Division

Attachment

OECD / OCDE

ESTIMATION OF GREENHOUSE GAS EMISSIONS AND SINKS

FINAL REPORT

From
OECD Experts Meeting, 18-21 February 1991

Prepared For

Intergovernmental Panel on Climate Change

Revised August 1991

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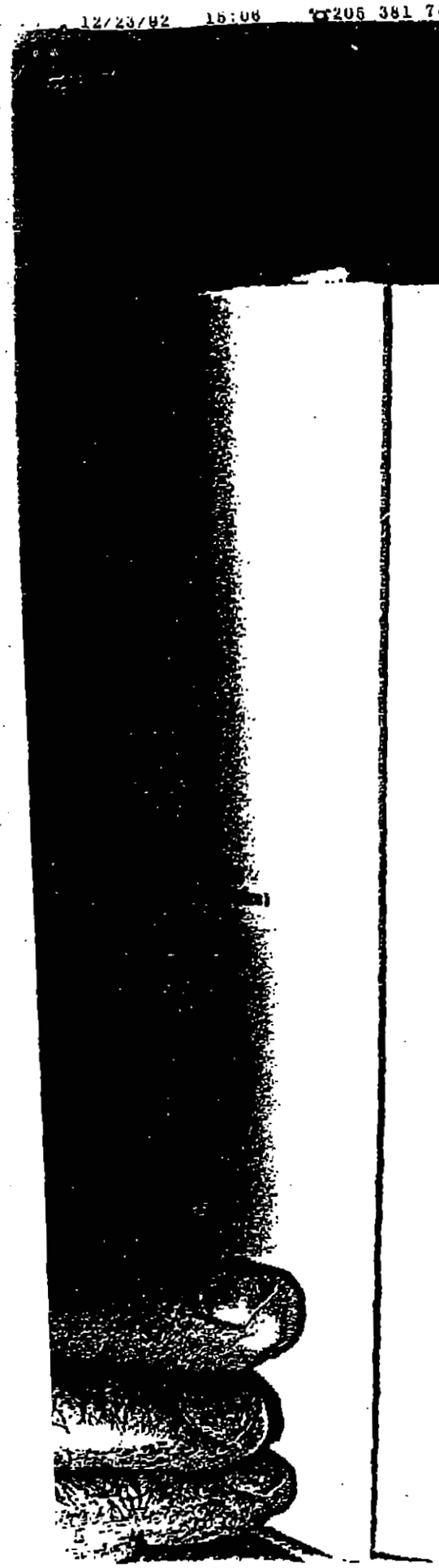

Soils and the Greenhouse Effect

The Present Status and Future Trends
Concerning the Effect of Soils and their Cover
on the Fluxes of Greenhouse Gases,
the Surface Energy Balance and the Water Balance

Edited by A.F. Bouwman

Proceedings of the International Conference
Soils and the Greenhouse Effect

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Tennessee Valley Authority, Post Office Box 1010, Muscle Shoals, Alabama 35660

December 14, 1992

Mr. Dallas W. Safriet
Environmental Engineer
Emission Inventory Branch
United States Environmental
Protection Agency
Office of Air Quality Planning
and Standards
Research Triangle Park, North Carolina 27711

Dear Mr. Safriet:

John Culp and I enjoyed our phone conversation with you this morning and the discussion describing our concerns about the draft AP-42 document you sent for review. Enclosed are comments from Roland Hauck, Michael Broder, and me. In general, because of the inaccuracies, dated information, and errors we feel that a complete rewrite is necessary to make this information accurate and current. Our comments are not necessarily complete because of the quick turn around you indicated was necessary. After you have an opportunity to review our comments, we would welcome further discussions on how the revisions could be made.

Thank you for giving us the opportunity to review this draft.

Sincerely,

Horace C. Mann

Horace C. Mann
Projects Manager
Field Programs Department
National Fertilizer and
Environmental Research Center

Enclosure

Comments on the draft report "Background Documentation for AP-42 Section 6.2.1, Fertilizer Application, MRI Paper No. 6500-K(35) Roland D. Hauck

General Comment

Section 2 of the subject draft report can be greatly improved by: (i) correcting many inaccuracies and misinterpretations of information, and (ii) tightening up the discussion to make it more directly relevant to the objectives of the study. Regardless of the criteria used for selecting data and the care taken in calculating emission factors, the value of the emission factors given in section 5 is suspect because the discussion in section 2 indicates only an elementary and incomplete knowledge of the process dynamics leading to gaseous nitrogen emissions.

Specific Comments

2-7 The term fluid fertilizer rather than liquid fertilizer should be used. The information about liquid fertilizers is not entirely correct. They usually are concentrated rather than dilute solutions (lower handling, transport, and distribution costs). They may be injected or dribbled on as well as sprayed.

2-7 para.4. The paragraph assumes that time-release fertilizers use is growing and that such fertilizers comprise or will comprise a significant amount of total fertilizer use. This assumption is incorrect.

2-10 The contaminants listed in Table 2-1 also are present in soils to which no fertilizer has been added.

sec. 2.3.1.1 The discussion of ammonia/ammonium reactions in soils reflects a poor understanding of soil chemistry. Although several statements made are essentially correct, they are presented neither clearly nor accurately.. For example, there is no clear distinction between the dissolution of ammonia in or absorption by water and adsorption of ammonium ion on inorganic and organic exchange surfaces. .

sec. 2.3.1.2 The term, (NO)x, most generally is used when referring to the N oxide gases. NO, NO2, N2O, and N2O4, although the most rigid use would restrict it to NO and NO2. Nitrite and nitrate normally are not included in this group, as indicated in this section. There is little evidence that nitrification leads to significant loss of gaseous nitrogen.

Sec.2.3.1.2 This section also reflects only rudimentary understanding of the subject. For example, the discussion relating to ammonium nitrate is incorrect; equation 2-1 is for the reaction of ammonium with nitrite rather than nitrate. Nitrite usually is not present in appreciable quantities in soils except in microsites of high pH. The reaction shown by equation

2.1 occurs appreciably only at low pH (below 5).

Sec.2.3.1.3 One of the main sulfur sources supplied in fluid fertilizers, ammonium thiosulfate, is not listed. Sulfur dioxide (listed) is not a common source. The amount supplied as sulfur-coated urea is negligible when compared to the whole. During the period when fertilizer use was increasing in the United States, there was a corresponding increase in the total nutrient content of fertilizer materials and a decrease in the level of impurities, including heavy metals and sulfur. The amount of nitrogen added as ammonium sulfate, therefore the amount of sulfur added from this material, also will not increase (ammonium sulfate is mainly a by-product rather than made primarily for fertilizer use).

2-21, para.2 Fluid fertilizers, rather than solid ones, can be applied more rapidly per unit of nutrient. There is no evidence that emissions from solid fertilizers generally exceed those from fluids with the exception of surface-applied, un-incorporated urea or diammonium phosphate from which ammonia may be liberated to the atmosphere. Other comments could be made to point out the fallacy of making generalizations from an extensive literature without a solid understanding of that literature.. This lack of understanding is reflected further in the discussion on page 2-2. For example, the definition of CEC given in the footnote would almost be correct only if the parenthetical phrase were deleted.

4-1, para.3 The data given in the references cited may be considered accurate. What may be questionable is the use of the data for extrapolating to dimensions several magnitudes larger than the system from which the data sets were collected.

4-10, para.1 A rating of D is given for the data from references 15a and 15b because a nonstandard and unproven method was used. The method used, however, is the only one of all methods cited in the accepted references that makes measurements in the unconfined atmosphere over an entire field. Extrapolating data obtained in this manner to large dimensions is more justifiable than a similar extrapolation of data collected from chamber studies.

Table 6.2.1-1 The weak basis for the numbers given in this table was adequately discussed in the previous section. However, once data are published in an official document they may assume an undeserved validity. For example, the emission factor for ammonia from solid fertilizers is based on ammonia volatilization from surface-applied, un-incorporated urea, which does not represent the bulk of solid nitrogen fertilizers nor the manner in which they are used. The emission factor for nitrous oxide is based on studies that measured nitrous oxide formed during nitrification, whereas most nitrous oxide released to the atmosphere from soils probably is the result of denitrification. Also, where nitrification is involved, the type, physical state, and, if solid, the particle size are among the factors affecting the rate of nitrification and course of its reaction products. These factors were not considered in the studies cited nor in the

evaluation of data.

To construct a table of emission factors for fertilizers from an admittedly extremely limited and weak data base is not justifiable. To present the information in terms of 0.1g/kg or 0.1 lb./ton implies a precision not warranted by the data.

Table 6.2.1-2 This table lists calcium nitrate and ammonium chloride as common fertilizers used in the United States, which they are not, and omits such materials as monoammonium and diammonium phosphates, which are common components of mixed fertilizers.

Additional comments on Sections 2, 4, and 5 -Proposed AP-42 - Specific and general--H. C. Mann

Page 2-1, 2-2 - "Liquid fertilizer" should be "fluid fertilizer."

Page 2-2 - Suggest 20-30% NH_3 instead of 30-40% or put temperatures where vapor pressure is 0 psig.

Page 2-4 (Figure 2-1) - No pump on NH_3 applicator.

2.2.2 - "Fluid" instead of liquid on title and first word in 1.

Last sentence is wrong, needs to include injection

2nd and 3rd paragraphs need rewriting to include injection, remove "liquid" and replace with fluid where appropriate.

2.2.3 - Whole section needs rewriting to reflect both current equipment available and application practices.

Figure 2-5 - Do not normally spray on a " young" plant. Banding is normally to the side and below and by injection.

Table 2-1 - Sources of phosphate and nitrogen fertilizer need to be identified to not cause misconceptions - i.e., NH_3 does not contain a number of the elements listed. All phosphate fertilizers do not contain 200 ppm of Ba, 20 ppm Ce, etc.

Paragraph 2.3 - First sentence is <u>too</u> absolute. Needs to be qualified significantly.

Section 5, paragraph 6.2.1.2.2 - "Liquid" should be changed to fluid and the entire section rewritten to reflect current commercial practices.

Section 5, paragraph 6.2.1.2.3 - Section needs to be rewritten to reflect current commercial practices.

Section 5, paragraph 6.2.1.3 - Too absolute, needs to be qualified significantly.

Tables 4-5 and 6.2.1-2 - Urea formula wrong, should be $(NH_2)_2$ CO.

Ammonium sulfate wrong, should be $(NH_4)_2$ SO_4.
Calcium nitrate wrong, should be Ca $(NO_3)_2$.

Suggestions for improving EPA AP-42 Draft Report from Michael Broder.

In the interest of time I have limited my suggestions to Section 5 which I believe is the only part that will appear in AP-42. In summary, the descriptions of the application processes are inaccurate and misleading. Anyone remotely familiar with the use of fertilizers in crop production in the U.S. would find the information suspect. A couple of references are available which adequately describe application processes; chapter 9 of TVA Bulletin Y-185 Fluid Fertilizers, or chapter 31 of Nitrogen in Crop Production edited by Roland D. Hauck. Section 5 should be completely rewritten and then resubmitted for review. The gross errors in the application process descriptions and in fertilizer formulas would cause any informed reader to question the emission factors.

Section 6.2.1.1 General

SIC codes don't seem to be relevant to this discussion. The adjective "custom" is not normally used to describe fertilizer dealers. Application is performed by custom applicators in addition to farmers and fertilizer dealers. In Florida, for example, nearly all fertilizer applied commercially is done by custom applicators who do not sell the fertilizer.

Section 6.2.1.2 Process Description

This paragraph could be made much less awkward as follows:

Fertilizer is applied by three basic methods depending on its physical state; solid (granular), fluid, or gaseous.

Section 6.2.1.2.1 Gaseous Fertilizer

Trucks are never used to apply anhydrous ammonia. They don't have the pulling power at the low speeds required. Plowing discs/plates is not a recognized term. The American Society of Agricultural Engineers Standards lists terminology of tillage devices. Injection knives or chisels are the proper term. The tube holders are an insignificant part of the system. Metering application rate) is controlled by three methods; 1) a calibrated orifice is preset to release a constant amount of ammonia per hour while applicator speed is held constant (orifice calibration is accurate for tank pressures between 50 and 150 psig), 2) a heat exchanger is used to provide liquid ammonia to a flow meter installed in line with an orifice which is controlled electronically to adjust ammonia flow according to speeds indicated by a radar speed sensor, 3) a piston pump driven by a chain from a ground driven wheel is used to deliver ammonia. The latter two systems are more accurate than the first because the ammonia flow is synchronized with ground speed.

Because of the difficulty and danger associated with collecting and measuring anhydrous ammonia these machines are only calibrated by researchers and at the manufacturing site. Metering systems have precisely machined orifices which normally do not require calibration.

Most anhydrous ammonia is applied by farmers. The service is not profitable for dealers and custom applicators because the area that can be treated in a given time is 3 to 6 times less than what can be achieved by broadcast application. The margin, consequently, is not large enough to offset the higher labor cost.

The planting of seed and anhydrous ammonia application is never done simultaneously.

Figure 6.2.1-1-should be replaced with a sketch depicting only anhydrous application. Dual systems are not the norm. Also, the ammonia supply tank is generally a nurse tank which trails behind the tillage (incorporation) implement.

Section 6.2.1.2.2 Fluid Fertilizer

The application of fluid fertilizer and anhydrous is not at all similar. Fluid fertilizers are generally not diluted. Economics dictate that they be shipped and applied as concentrated as physical properties allow. Manifolds are not composed of booms. Manifolds are plumbing devices which split the flow of fluid into two or more equal flows which are further divided along the booms which are generally 20 to 40 feet long.

The figure 6.2.1-2 depicts a spray system on a tillage device. Though this is a common practice, a much greater volume of product is applied using truck mounted sprayers and specially build high flotation vehicles. Though fluid can be applied in discreet bands by lowering broadcast nozzles, generally, nozzles which produce a solid stream are used for banding. Most custom application equipment has booms mounted at a fixed height to facilitate operating at high speeds.

The proper overlap varies according to nozzle design. Flooding and hollow cone nozzle patterns should be overlapped 100 percent, flat fan nozzles should be overlapped 30 percent. Since most commercial rigs have booms 3 to 4 feet above the ground and nozzles spaced 5 feet, the actual overlap of nozzle sprays is as high as 200 to 300 percent.

Section 6.2.1.2.3. Solid fertilizers

About two-thirds of the fertilizer applied in the U.S. is in solid form. I don't believe timed release fertilizer technology has caused broadcast application to grow. If broadcast application is growing it is due to its low cost and efficiency relative to other methods.

The most common method for applying solid fertilizer is by centrifugal spreaders. Centrifugal spreaders have one disc or two counter-rotating discs, mounted

horizontally, which broadcast material falling from a belt or mesh-chain conveyor. An adjustable gate in the hopper above the conveyor is used to set application rates. Output is synchronized with ground speed either electronically or mechanically.

Among the boomed applicators, three different pneumatic designs and one auger metered system are most popular. The impetus for using boomed spreaders is for uniform application of dry fertilizer impregnated with herbicide. This practice and boomed solid applicator are described in detail in chapter 13 of the monograph, Methods of Applying Herbicides, edited by C. G. McWhorter and M. R. Gebhardt.

The description of equipment in this section is atrocious. ; Deflectors and not nozzles are used to direct pneumatically conveyed material to the ground. there are no orifices at the discharge end and there are no fan blades that spin. The authors appear to have combined parts of both, centrifugal and pneumatic applicators.

6.2.1.3 Emission and Controls

I don't believe there is enough data to support mentioning the heavy metals which may become airborne with fugitive dust.

Table 6.2.2-1

This table needs to be reviewed by Roland Hauck or someone in his department.

Table 6.2.2-2

The chemical formulas for urea, ammonium sulfate, and calcium nitrate are wrong. The nitrogen contents are incorrect for three of the materials (see Don Kachelman's attached corrections).

N:\Broder.EPA.corrections

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December 21, 1992

Mr. Dallas W. Safriet
Environmental Engineer
Emission Inventory Branch
United States Environmental Protection Agency
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

Dear Mr. Safriet:

As requested in your November 19, 1992, letter we have reviewed the draft version of a proposed new section 6.2.1, *Fertilizer Application*, of AP-42, *Compilation of Air Pollutant Emission Factors*. As you requested we reviewed only Section 5 of the background documentation.

Our staff members reviewed draft Section 6.2.1. The reviewers found the draft section to be not well written, quite inaccurate, and apparently inadequately researched. In our opinion the draft section should be rewritten after a more extensive literature review is performed. We have enclosed an example of a possible rewrite that we believe more accurately describes the information you are attempting to document. However, the rewrite does not include additional data other than that already incorporated into the draft version. According to our staff there is much more reliable data and information available than that referenced in the draft section.

We have also collaborated with staff members from the Tennessee Valley Authority on the draft section and understand they were also requested to review the document. We have reviewed their comments that were sent to you and fully agree with them.

Please note that we did not review the data included in Table 6.2.1-1. The data would have demanded an extensive review of all the references included in the background documentation. We could undertake this task but only under a reimbursable agreement due to the magnitude of such an effort.

We hope this information is helpful to the EPA in developing appropriate and accurate emission factors for AP-42.

Sincerely yours,

James J. Schultz
Director
Outreach Division

Enclosure

IFDC
December 21, 1992

Example of Suggested Rewrite of Section 6.2.1

6.2.1 Fertilizer Application

6.2.1.1 General. The role of fertilizers in the agricultural industry is to supply essential plant nutrients to improve crop production. It has long been recognized that there are 16 essential elements or nutrients necessary for plant growth, three of which are supplied from the atmosphere or water (carbon, hydrogen, and oxygen). The other 13 elements (nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, copper, zinc, boron, manganese, iron, chlorine, and molybdenum) are principally supplied through the soil medium. Some of these elements are limited in the soil medium and must be supplemented by fertilizers. Fertilizers are distributed through agricultural supply retailers, farmers' cooperatives, and fertilizer dealers. Application is typically performed by farmers and by fertilizer dealers using specialized application equipment.

6.2.1.2 Process Description. Based on the physical form of the fertilizer, there are three basic types of fertilizer application. The basic method of application is determined according to whether the fertilizer is in a gaseous, fluid, or solid form.

6.2.1.2.1 Gaseous fertilizer. Anhydrous ammonia is the only gaseous fertilizer used, and supplies nitrogen. Typically, about 6 million tons of ammonia is applied annually in the United States. Farmers generally apply ammonia thenselves. Anhydrous ammonia is typically stored in a liquid form: most commonly, under pressure; and to a lesser degree, by refrigeration. Anhydrous ammonia is actually injected as a liquid/gaseous mixture into the soil where it vaporizes into a gas and then is captured by several components in the soil, including water, clay, and other minerals.

Because it is a gas at atmospheric pressure, anhydrous ammonia must be injected from 4 to 10 inches (10 to 25 cm) below the soil surface, depending upon the soil type, soil conditions, and spacing. Generally, typical equipment for anhydrous ammonia application consists of a tractor, a pressurized tank containing the anhydrous ammonia, a metering system, manifolds, and injection knives. Figure _____ (not the one shown) is a typical example of application equipment for anhydrous ammonia.

The only calibration done during the application of ammonia is a tracking of pounds applied versus acres covered. Precise orifice calibration for metering the flow of liquid ammonia is done at the factory, and farmer dials in the orifice setting according to speed, desired rate, and tool bar width.

6.2.1.2.2 Fluid fertilizer. Fluid fertilizers are typically classified as either solutions or suspensions. Solution fertilizers are free of solid particles. Suspension fertilizers are two-phase fertilizers in which solid particles are maintained in suspension in the aqueous phase. The equipment used in the application of fluid fertilizers typically

consists of a vehicle (truck or tractor), a tank holding the fluid, a metering system, manifolds, and spray nozzles. The manifolds are mounted inside long booms (20-40 ft) with the nozzles spaced along the manifold so that the spray patterns overlap. Fluid fertilizers are most commonly sprayed onto the surface of freshly tilled soils.

Figure _____ (not the one shown) is an example of a typical applicator for fluid fertilizers.

6.2.1.2.3 Solid fertilizers. In the United States, solid fertilizers are typically applied as straight nitrogen fertilizers (urea or ammonium nitrate) or as mixed fertilizers containing not only nitrogen but also phosphate, potassium, and other nutrients. Application of solid fertilizers is done predominantly either by fan-type spreaders (Figure _____) or by boomed (pneumatic- or auger-type) spreaders (Figure _____).

6.2.1.3 Emission and Controls. Both solid-phase (particulate matter) and vapor-phase air pollutants can be generated from the application of fertilizers. In both cases, two general classes of emissions are noted: "immediate" pollutant emissions which can occur either during or shortly after application; and "latent" pollutant emissions which can be generated days or weeks following application.

Wind-blown dust can be created immediately during the application of dry fertilizers and later from disturbances caused by mechanical operations (e.g., tilling) and/or wind erosion. Vapor-phase emissions can be generated after application by the immediate volatilization of gaseous fertilizers (i.e., anhydrous ammonia) or after some period of time by the chemical/biological transformation of N added as fertilizers to the soil.

At the current time, vapor-phase emission factors are available only for nitrogen fertilizers. These emission factors are shown in Table 6.2.1-1 on the basis of equivalent nitrogen applied to the soil. Finally, where more specific data are not available, Table 6.2.1-2 provides equivalent nitrogen contents of common chemical fertilizers for use with the emission factors shown in Table 6.2.1-1. (Refer to TVA comments regarding questionable validity of vapor-phase emission factors.)

Table 6.2.1-1. Candidate Emission Factors for the Application of Nitrogen Fertilizers[a]

IFDC did not attempt to verify the data included in this table. This could be done on a reimbursable basis.

Table 6.2.1-2. Equivalent Nitrogen Content of Common Chemical Fertilizers[a]

Type of Fertilizer	Chemical Formula	Nitrogen Content (Weight Percent)	Amount of Fertilizer Applied per Hectare to Produce 1 kg N/ha Equivalent Application (kg)
Anhydrous ammonia	NH_3	82.3	1.22
Urea	$CO(NH_2)_2$	46.7	2.14
Ammonium sulfate	$(NH_4)_2SO_4$	21.2	4.72
Calcium nitrate	$Ca(NO_3)_2$	17.1	5.85
Ammonium nitrate	NH_4NO_3	35.0	2.86
Ammonium chloride	NH_4Cl	26.2	3.82
Sodium nitrate	$NaNO_3$	16.5	6.06
Diammonium phosphate (DAP)	$(NH_4)_2HPO_4$	21.2	4.72
Potassium nitrate	KNO_3	13.9	7.19

a. For pure chemicals. 1 kg = 1,000 g = 2.2 lb; 1 ha = $10^4 m^2$ = 2.471 acres. From Table 4-5 of Reference 7.

Memorandum

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To: David W. Rutland, Physical Properties Specialist, Outreach Division

From: Bernard H. Byrnes, Soil Scientist, Resources Management Research and Development Division

Date: December 16, 1992

Subject: COMMENTS ON "ESTIMATION OF GREENHOUSE GAS EMISSIONS AND SINKS"--FINAL REPORT

Table 6.2.1-1 is the essence of the entire report, since it lists emission factors for N gases derived from N fertilizers.

1. NH_3--All solid fertilizers cannot volatilize ammonia at a rate as high as urea for the obvious reasons that many contain nitrate as a component and do not produce alkalinity to support volatilization. This emission rate, based on unincorporated application, greatly overestimates losses.

2. NO, NO_2--Recent research (see page A-5 in references) has shown that NO, not NO_2, is emitted from soils. To have a larger emission factor for NO_2 than NO makes no sense. Why would NO come from liquid fertilizers but not others?

3. N_2O--N_2O emissions are much more a soil phenomenon (nitrification rates and denitrification rates as influenced by water dynamics) than a fertilizer-related phenomenon. Bouwman (1990) compiled data from recent literature and failed to see a relationship to fertilizer type and came up with a factor of 4.17 g/kg N or, if poorly drained soils were excluded, 7.50 g/kg N. The attached tables appear to be more valid estimates.

The table needs to be revised completely to reflect differences between the various types of fertilizers and also their use.

BHB:daf
Attachment
cc: C. A. Baanante
J. J. Schultz

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**********TELEFAX COMMUNICATION**********

To: Mr. Dallas W. Safriet
Environmental Engineer
Emission Inventory Branch
United States Environmental Protection Agency
Research Triangle Park, North Carolina 27711

December 23, 1992

From: James J. Schultz

Fax 919-541-0684

Page 1 of 4

MESSAGE:

RE: SECTION 6.2.1, FERTILIZER APPLICATION DRAFT REPORT, AP-42

You may find the attached comments by Dr. B. H. Byrnes of our staff to be useful. I should have included them with my letter to you dated December 21, 1992. Please let me know if you need any additional information.

Dr. Byrnes can be reached at (205) 381-6600, extension 289.

Regards,

James J. Schultz
Director
Outreach Division

Attachment

OECD / OCDE

ESTIMATION OF GREENHOUSE GAS EMISSIONS AND SINKS

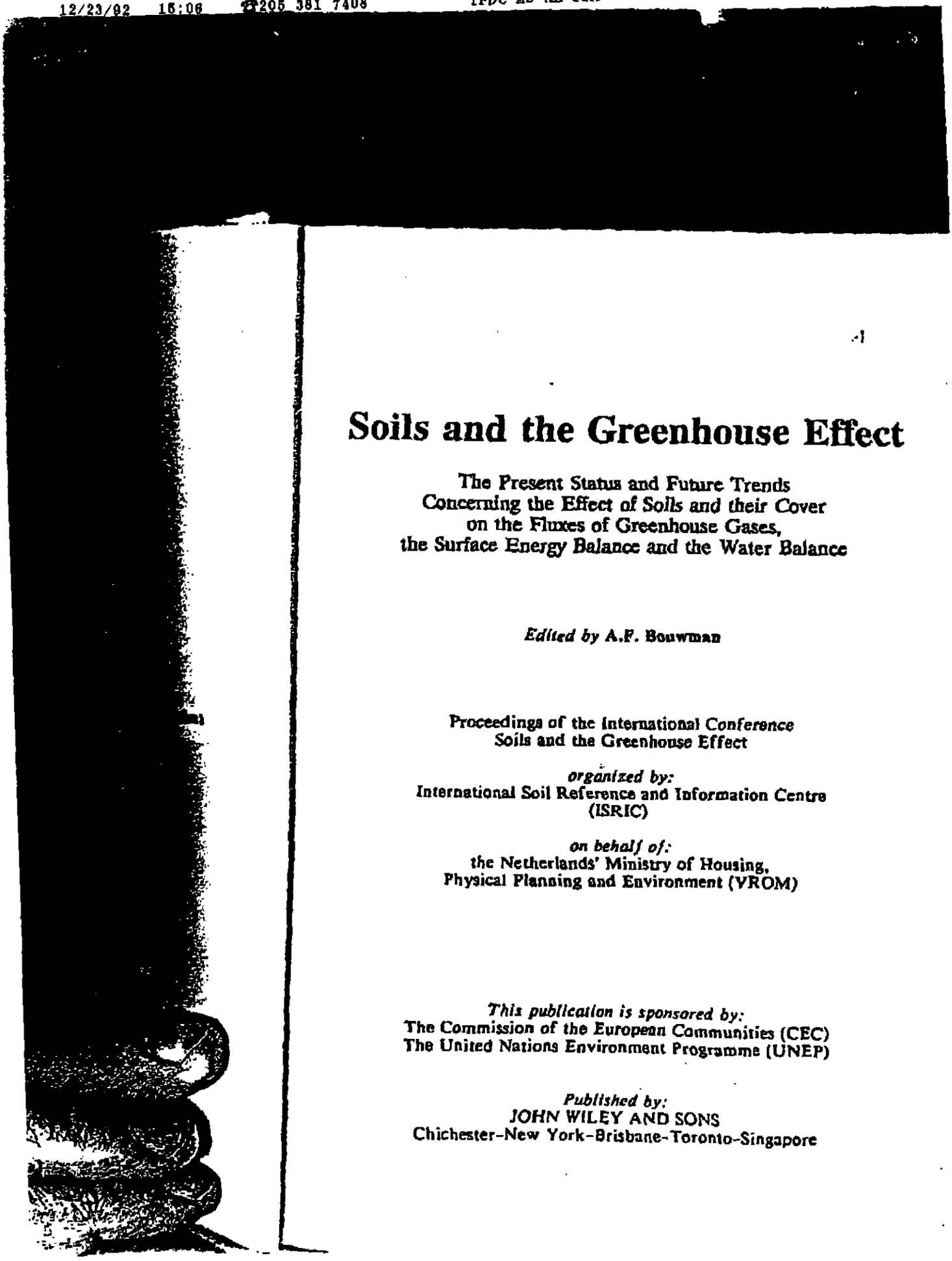
FINAL REPORT

From
OECD Experts Meeting, 18-21 February 1991

Prepared For

Intergovernmental Panel on Climate Change

Revised August 1991



Soils and the Greenhouse Effect

The Present Status and Future Trends
Concerning the Effect of Soils and their Cover
on the Fluxes of Greenhouse Gases,
the Surface Energy Balance and the Water Balance

Edited by A.F. Bouwman

Proceedings of the International Conference
Soils and the Greenhouse Effect

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913-532-6101

June 3, 1993

Ms. M.E.W. St. Germain
Senior Chemist
Midwest Research Institute
425 Volker Boulevard
Kansas City, MO 64110

Dear M. St. Germain:

The enclosed document (AP-42, Section 6.2.1) on fertilizer application has been reviewed and my recommended changes appear directly on the manuscript. Several section have been completely rewritten and also are attached. The following itemized list of concerns and suggested changes should be considered.

General Comments

1. The manuscript leaves the impression that fertilizers are the only source of gaseous emissions of nitrogen. Manure and legume nitrogen also be denitrified and nitrogen gas released during nitrification. I have made several changes to reflect this oversight.

2. The descriptions of soil biological and chemical processes are somewhat inaccurate and I have made substantial changes in these sections.

3. The data obtained from the references provided appear to be accurately interpreted and reported. However, the data quality rating eliminates some valuable data collected from studies that use a micro-meteorological approach which have clearly demonstrated that they may estimate the quantity of gaseous emissions more accurately than small microplot chamber methods.

4. The arithmetic means listed in Table 6.2.1-2 are suspect when the specific gases are compared. For example, research has shown that primarily NO and not NO_2 is emitted from soils. I can't see how NO_2 could be greater than NO. This problem illuminates the numerous problems in the limited data set used, and perhaps more importantly, the criteria used in the data quality rating system.

5. Many of the references used unincorporated nitrogen. Thus, gaseous emission would be over estimated.

6. In general, the data (Table 4-2 and 4-3) used in obtaining the arithmetic means are seriously insufficient to formulate conclusive evidence for fertilizer nitrogen contribution to atmospheric nitrogen gases.

Specific Comments

Section 2.2.1 (pg 2-3): Aqua ammonia can be soil applied. "It" refers to Anhydrous ammonia not aqua ammonia.

Section 2.2.1 (pg 2-4): Depth of NH_3 application most always is deeper than 1 inch. You have used 4 to 10 inches in a subsequent section, thus, you should be consistent.

Section 2.2.2 (pg 2-9): Application rates are determined by the intended crop and expected crop yield potential. "Fallow land" implies no crop, thus, why would fertilizer rates be higher here than under a cropped field? Fertilizers are not usually applied to fallow land, but if it is applied the application will be made close to planting time. I suggest deleting this sentence.

Section 2.2.2 (pg 2-9): Dry fertilizer also can be band applied.

Section 2.3.1 (pg 2-15): In Section 6.2.1.3 manures are mentioned and should be mentioned here.

Section 2.3.2.1 (pg 2-17): Probably need to identify the chemical formula here.

Section 2.3.2.1 (pg 2-17): "photosynthetic" probably works better here.

Section 2.3.2.1 (pg 2-20): Several changes/corrections have been made to these sections.

Section 2.3.2.2 (pg 2-21): This section is poorly written and somewhat inaccurate. The attached page 2-21a should be inserted.

Section 2.3.2.3 (pg 2-21): This section also has numerous inaccuracies and is not well organized. Many of the sentences and paragraphs have been rewritten. One paragraph (pg. 2-22) needs to be moved to Section 2.3.2.4.

Section 2.3.2.4 (pg 2-22): This section has been rewritten.

Section 2.3.2.5 (pg 2-23): This section has been rewritten. Replace with attached pages 2-23a-b.

Section 2.4 (pg 2-23/24): This section has been rewritten. Replace with attached page 2-23b.

Section 3.5.1 (pg 3-11): Standard soil moisture content is always defined on an oven dry weight basis.

Section 4.2.1 (pg 4-15): The last sentence on this page is extremely important and should be highlighted by using a **boldface** font.

Section 4.3.2 (pg 4-18): Table 4-5 should incorporate the range of values contained in the mean. See Table 6.2.1-2 for specific change.

Section 6.2.1.3 (pg 3): The implication that fertilizer represent the only source of emissions is not correct. Thus, I have added the word nutrients an manures at appropriate places.

The Table numbers stated in the 3rd paragraph should be changed.

Statement concerning the need for addition research on heavy metal particulates from fertilizers and manures should be added.

The document needs a precautionary statement regarding the extremely limited and highly variable data found in Tables 6.2.1-2 and 6.2.1-3, and how this affects the usefulness and reliability of the data.

Section 6.2.1.3 (pg 7): The data for N_2O emission of for urea should be 3.98.

To give the reader the appropriate perspective on the high variance in the data, I suggest including the range in the data and the number of data points included in the mean. See page 6.2.1-7a for example change.

Thank you for the opportunity to review this document. Please don't hesitate to call me for more information.

Sincerely,

John L. Havlin
Associate Professor

John Kinsey

Tennessee Valley Authority, Post Office Box 1010, Muscle Shoals, Alabama 35660

December 14, 1992

Mr. Dallas W. Safriet
Environmental Engineer
Emission Inventory Branch
United States Environmental
Protection Agency
Office of Air Quality Planning
and Standards
Research Triangle Park, North Carolina 27711

Dear Mr. Safriet:

John Culp and I enjoyed our phone conversation with you this morning and the discussion describing our concerns about the draft AP-42 document you sent for review. Enclosed are comments from Roland Hauck, Michael Broder, and me. In general, because of the inaccuracies, dated information, and errors we feel that a complete rewrite is necessary to make this information accurate and current. Our comments are not necessarily complete because of the quick turn around you indicated was necessary. After you have an opportunity to review our comments, we would welcome further discussions on how the revisions could be made.

Thank you for giving us the opportunity to review this draft.

Sincerely,

Horace C. Mann

Horace C. Mann
Projects Manager
Field Programs Department
National Fertilizer and
Environmental Research Center

Enclosure

Comments on the draft report "Background Documentation for AP-42 Section 6.2.1, Fertilizer Application, MRI Paper No. 6500-K(35) Roland D. Hauck

General Comment

Section 2 of the subject draft report can be greatly improved by: (i) correcting many inaccuracies and misinterpretations of information, and (ii) tightening up the discussion to make it more directly relevant to the objectives of the study. Regardless of the criteria used for selecting data and the care taken in calculating emission factors, the value of the emission factors given in section 5 is suspect because the discussion in section 2 indicates only an elementary and incomplete knowledge of the process dynamics leading to gaseous nitrogen emissions.

Specific Comments

2-7 The term fluid fertilizer rather than liquid fertilizer should be used. The information about liquid fertilizers is not entirely correct. They usually are concentrated rather than dilute solutions (lower handling, transport, and distribution costs). They may be injected or dribbled on as well as sprayed.

2-7 para.4. The paragraph assumes that time-release fertilizers use is growing and that such fertilizers comprise or will comprise a significant amount of total fertilizer use. This assumption is incorrect.

2-10 The contaminants listed in Table 2-1 also are present in soils to which no fertilizer has been added.

sec. 2.3.1.1 The discussion of ammonia/ammonium reactions in soils reflects a poor understanding of soil chemistry. Although several statements made are essentially correct, they are presented neither clearly nor accurately.. For example, there is no clear distinction between the dissolution of ammonia in or absorption by water and adsorption of ammonium ion on inorganic and organic exchange surfaces. .

sec. 2.3.1.2 The term, (NO)x, most generally is used when referring to the N oxide gases. NO, NO2, N2O, and N2O4, although the most rigid use would restrict it to NO and NO2. Nitrite and nitrate normally are not included in this group, as indicated in this section. There is little evidence that nitrification leads to significant loss of gaseous nitrogen.

Sec.2.3.1.2 This section also reflects only rudimentary understanding of the subject. For example, the discussion relating to ammonium nitrate is incorrect; equation 2-1 is for the reaction of ammonium with nitrite rather than nitrate. Nitrite usually is not present in appreciable quantities in soils except in microsites of high pH. The reaction shown by equation

2.1 occurs appreciably only at low pH (below 5).

Sec.2.3.1.3 One of the main sulfur sources supplied in fluid fertilizers, ammonium thiosulfate, is not listed. Sulfur dioxide (listed) is not a common source. The amount supplied as sulfur-coated urea is negligible when compared to the whole. During the period when fertilizer use was increasing in the United States, there was a corresponding increase in the total nutrient content of fertilizer materials and a decrease in the level of impurities, including heavy metals and sulfur. The amount of nitrogen added as ammonium sulfate, therefore the amount of sulfur added from this material, also will not increase (ammonium sulfate is mainly a by-product rather than made primarily for fertilizer use).

2-21, para.2 Fluid fertilizers, rather than solid ones, can be applied more rapidly per unit of nutrient. There is no evidence that emissions from solid fertilizers generally exceed those from fluids with the exception of surface-applied, un-incorporated urea or diammonium phosphate from which ammonia may be liberated to the atmosphere. Other comments could be made to point out the fallacy of making generalizations from an extensive literature without a solid understanding of that literature.. This lack of understanding is reflected further in the discussion on page 2-2. For example, the definition of CEC given in the footnote would almost be correct only if the parenthetical phrase were deleted.

4-1, para.3 The data given in the references cited may be considered accurate. What may be questionable is the use of the data for extrapolating to dimensions several magnitudes larger than the system from which the data sets were collected.

4-10, para.1 A rating of D is given for the data from references 15a and 15b because a nonstandard and unproven method was used. The method used, however, is the only one of all methods cited in the accepted references that makes measurements in the unconfined atmosphere over an entire field. Extrapolating data obtained in this manner to large dimensions is more justifiable than a similar extrapolation of data collected from chamber studies.

Table 6.2.1-1 The weak basis for the numbers given in this table was adequately discussed in the previous section. However, once data are published in an official document they may assume an undeserved validity. For example, the emission factor for ammonia from solid fertilizers is based on ammonia volatilization from surface-applied, un-incorporated urea, which does not represent the bulk of solid nitrogen fertilizers nor the manner in which they are used. The emission factor for nitrous oxide is based on studies that measured nitrous oxide formed during nitrification, whereas most nitrous oxide released to the atmosphere from soils probably is the result of denitrification. Also, where nitrification is involved, the type, physical state, and, if solid, the particle size are among the factors affecting the rate of nitrification and course of its reaction products. These factors were not considered in the studies cited nor in the

evaluation of data.

To construct a table of emission factors for fertilizers from an admittedly extremely limited and weak data base is not justifiable. To present the information in terms of 0.1g/kg or 0.1 lb./ton implies a precision not warranted by the data.

Table 6.2.1-2 This table lists calcium nitrate and ammonium chloride as common fertilizers used in the United States, which they are not, and omits such materials as monoammonium and diammonium phosphates, which are common components of mixed fertilizers.

Additional comments on Sections 2, 4, and 5 -Proposed AP-42 - Specific and general--H. C. Mann

Page 2-1, 2-2 - "Liquid fertilizer" should be "fluid fertilizer."

Page 2-2 - Suggest 20-30% NH_3 instead of 30-40% or put temperatures where vapor pressure is 0 psig.

Page 2-4 (Figure 2-1) - No pump on NH_3 applicator.

2.2.2 - "Fluid" instead of liquid on title and first word in 1.

Last sentence is wrong, needs to include injection

2nd and 3rd paragraphs need rewriting to include injection, remove "liquid" and replace with fluid where appropriate.

2.2.3 - Whole section needs rewriting to reflect both current equipment available and application practices.

Figure 2-5 - Do not normally spray on a " young" plant. Banding is normally to the side and below and by injection.

Table 2-1 - Sources of phosphate and nitrogen fertilizer need to be identified to not cause misconceptions - i.e., NH_3 does not contain a number of the elements listed. All phosphate fertilizers do not contain 200 ppm of Ba, 20 ppm Ce, etc.

Paragraph 2.3 - First sentence is <u>too</u> absolute. Needs to be qualified significantly.

Section 5, paragraph 6.2.1.2.2 - "Liquid" should be changed to fluid and the entire section rewritten to reflect current commercial practices.

Section 5, paragraph 6.2.1.2.3 - Section needs to be rewritten to reflect current commercial practices.

Section 5, paragraph 6.2.1.3 - Too absolute, needs to be qualified significantly.

Tables 4-5 and 6.2.1-2 - Urea formula wrong, should be $(NH_2)_2$ CO.

Ammonium sulfate wrong, should be $(NH_4)_2$ SO_4.
Calcium nitrate wrong, should be Ca $(NO_3)_2$.

Suggestions for improving EPA AP-42 Draft Report from Michael Broder.

In the interest of time I have limited my suggestions to Section 5 which I believe is the only part that will appear in AP-42. In summary, the descriptions of the application processes are inaccurate and misleading. Anyone remotely familiar with the use of fertilizers in crop production in the U.S. would find the information suspect. A couple of references are available which adequately describe application processes; chapter 9 of TVA Bulletin Y-185 Fluid Fertilizers, or chapter 31 of Nitrogen in Crop Production edited by Roland D. Hauck. Section 5 should be completely rewritten and then resubmitted for review. The gross errors in the application process descriptions and in fertilizer formulas would cause any informed reader to question the emission factors.

Section 6.2.1.1 General

SIC codes don't seem to be relevant to this discussion. The adjective "custom" is not normally used to describe fertilizer dealers. Application is performed by custom applicators in addition to farmers and fertilizer dealers. In Florida, for example, nearly all fertilizer applied commercially is done by custom applicators who do not sell the fertilizer.

Section 6.2.1.2 Process Description

This paragraph could be made much less awkward as follows:

Fertilizer is applied by three basic methods depending on its physical state; solid (granular), fluid, or gaseous.

Section 6.2.1.2.1 Gaseous Fertilizer

Trucks are never used to apply anhydrous ammonia. They don't have the pulling power at the low speeds required. Plowing discs/plates is not a recognized term. The American Society of Agricultural Engineers Standards lists terminology of tillage devices. Injection knives or chisels are the proper term. The tube holders are an insignificant part of the system. Metering application rate) is controlled by three methods; 1) a calibrated orifice is preset to release a constant amount of ammonia per hour while applicator speed is held constant (orifice calibration is accurate for tank pressures between 50 and 150 psig), 2) a heat exchanger is used to provide liquid ammonia to a flow meter installed in line with an orifice which is controlled electronically to adjust ammonia flow according to speeds indicated by a radar speed sensor, 3) a piston pump driven by a chain from a ground driven wheel is used to deliver ammonia. The latter two systems are more accurate than the first because the ammonia flow is synchronized with ground speed.

Because of the difficulty and danger associated with collecting and measuring anhydrous ammonia these machines are only calibrated by researchers and at the manufacturing site. Metering systems have precisely machined orifices which normally do not require calibration.

Most anhydrous ammonia is applied by farmers. The service is not profitable for dealers and custom applicators because the area that can be treated in a given time is 3 to 6 times less than what can be achieved by broadcast application. The margin, consequently, is not large enough to offset the higher labor cost.

The planting of seed and anhydrous ammonia application is never done simultaneously.

Figure 6.2.1-1-should be replaced with a sketch depicting only anhydrous application. Dual systems are not the norm. Also, the ammonia supply tank is generally a nurse tank which trails behind the tillage (incorporation) implement.

Section 6.2.1.2.2 Fluid Fertilizer

The application of fluid fertilizer and anhydrous is not at all similar. Fluid fertilizers are generally not diluted. Economics dictate that they be shipped and applied as concentrated as physical properties allow. Manifolds are not composed of booms. Manifolds are plumbing devices which split the flow of fluid into two or more equal flows which are further divided along the booms which are generally 20 to 40 feet long.

The figure 6.2.1-2 depicts a spray system on a tillage device. Though this is a common practice, a much greater volume of product is applied using truck mounted sprayers and specially build high flotation vehicles. Though fluid can be applied in discreet bands by lowering broadcast nozzles, generally, nozzles which produce a solid stream are used for banding. Most custom application equipment has booms mounted at a fixed height to facilitate operating at high speeds.

The proper overlap varies according to nozzle design. Flooding and hollow cone nozzle patterns should be overlapped 100 percent, flat fan nozzles should be overlapped 30 percent. Since most commercial rigs have booms 3 to 4 feet above the ground and nozzles spaced 5 feet, the actual overlap of nozzle sprays is as high as 200 to 300 percent.

Section 6.2.1.2.3. Solid fertilizers

About two-thirds of the fertilizer applied in the U.S. is in solid form. I don't believe timed release fertilizer technology has caused broadcast application to grow. If broadcast application is growing it is due to its low cost and efficiency relative to other methods.

The most common method for applying solid fertilizer is by centrifugal spreaders. Centrifugal spreaders have one disc or two counter-rotating discs, mounted

horizontally, which broadcast material falling from a belt or mesh-chain conveyor. An adjustable gate in the hopper above the conveyor is used to set application rates. Output is synchronized with ground speed either electronically or mechanically.

Among the boomed applicators, three different pneumatic designs and one auger metered system are most popular. The impetus for using boomed spreaders is for uniform application of dry fertilizer impregnated with herbicide. This practice and boomed solid applicator are described in detail in chapter 13 of the monograph, Methods of Applying Herbicides, edited by C. G. McWhorter and M. R. Gebhardt.

The description of equipment in this section is atrocious. ; Deflectors and not nozzles are used to direct pneumatically conveyed material to the ground. there are no orifices at the discharge end and there are no fan blades that spin. The authors appear to have combined parts of both, centrifugal and pneumatic applicators.

6.2.1.3 Emission and Controls

I don't believe there is enough data to support mentioning the heavy metals which may become airborne with fugitive dust.

Table 6.2.2-1

This table needs to be reviewed by Roland Hauck or someone in his department.

Table 6.2.2-2

The chemical formulas for urea, ammonium sulfate, and calcium nitrate are wrong. The nitrogen contents are incorrect for three of the materials (see Don Kachelman's attached corrections).

N:\Broder.EPA.corrections

MIDWEST RESEARCH INSTITUTE
425 Volker Boulevard
Kansas City, Missouri 64110
Telephone (816) 753-7600
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March 25, 1993

Dr. Hans Sperling
Organization for Economic Cooperation
and Development (OECD)
Environmental Directorate, Pollution
Prevention Control Division
2, rue Andre-Pascal
75016 Paris
FRANCE

Dear Dr. Sperling:

I am in the process of preparing a new chapter, Section 6.2.1, Fertilizer Application, for "Compilation of Air Pollutant Emission Factors," commonly called AP-42, which is published by the U.S. Environmental Protection Agency (EPA). EPA has contracted with Midwest Research Institute to produce background documents and revise and prepare AP-42 chapters.

As part of the required technical review process, I recently talked with Dr. Bernard Byrnes from the International Fertilizer Development Center in Muscle Shoals, Alabama. Dr. Byrnes recommended that I contact you to ask for a copy of the (OECD) report, "Estimation of Greenhouse Gas Emissions and Sinks," dated August 1991. He felt that this document would greatly enhance the completion of the chapter.

I would appreciate you sending me a copy of the report and any follow-up reports on this same topic that might be available. If there is a cost to obtain these reports, please let me know. My telephone is 1-816-753-7600, Ext. 563. My fax number is 1-816-753-8240.

Thank you for your assistance.

Sincerely,

Margaret E. Wickham St. Germain
Senior Chemist

MEWSG/sp

cc: Chat Cowherd
Margaret Thomas

OECD

ORGANISATION DE COOPERATION ET
DE DEVELOPPEMENT ECONOMIQUES

OCDE

ORGANISATION FOR ECONOMIC
CO-OPERATION AND DEVELOPMENT

DIRECTION DE L'ENVIRONNEMENT / ENVIRONMENT DIRECTORATE
2, rue Andre-Pascal 75016 Paris

Pollution Prevention and Control Division

Tel: (33-1) 45 24 98 70
Fax: (33-1) 45 24 78 76

April 26, 1993

Dear Dr. St. Germain:

Thank you for your interest in the IPCC/OECD Climate Change Programme. Please find enclosed a copy of the document *Estimation of Greenhouse Gas Emissions and Sinks* last revised in August 1991. I apologize for the delay in getting to you. Thank you.

Sincerely,

Hans Sperling

KSU
KANSAS STATE UNIVERSITY

Department of Agronomy

Crop, Soil, and Range Sciences
Throckmorton Hall
Manhattan, Kansas 66506-5501
913-532-6101

June 3, 1993

Ms. M.E.W. St. Germain
Senior Chemist
Midwest Research Institute
425 Volker Boulevard
Kansas City, MO 64110

Dear M. St. Germain:

The enclosed document (AP-42, Section 6.2.1) on fertilizer application has been reviewed and my recommended changes appear directly on the manuscript. Several section have been completely rewritten and also are attached. The following itemized list of concerns and suggested changes should be considered.

General Comments

1. The manuscript leaves the impression that fertilizers are the only source of gaseous emissions of nitrogen. Manure and legume nitrogen also be denitrified and nitrogen gas released during nitrification. I have made several changes to reflect this oversight.

2. The descriptions of soil biological and chemical processes are somewhat inaccurate and I have made substantial changes in these sections.

3. The data obtained from the references provided appear to be accurately interpreted and reported. However, the data quality rating eliminates some valuable data collected from studies that use a micro-meteorological approach which have clearly demonstrated that they may estimate the quantity of gaseous emissions more accurately than small microplot chamber methods.

4. The arithmetic means listed in Table 6.2.1-2 are suspect when the specific gases are compared. For example, research has shown that primarily NO and not NO_2 is emitted from soils. I can't see how NO_2 could be greater than NO. This problem illuminates the numerous problems in the limited data set used, and perhaps more importantly, the criteria used in the data quality rating system.

5. Many of the references used unincorporated nitrogen. Thus, gaseous emission would be over estimated.

6. In general, the data (Table 4-2 and 4-3) used in obtaining the arithmetic means are seriously insufficient to formulate conclusive evidence for fertilizer nitrogen contribution to atmospheric nitrogen gases.

Specific Comments

Section 2.2.1 (pg 2-3): Aqua ammonia can be soil applied. "It" refers to Anhydrous ammonia not aqua ammonia.

Section 2.2.1 (pg 2-4): Depth of NH_3 application most always is deeper than 1 inch. You have used 4 to 10 inches in a subsequent section, thus, you should be consistent.

Section 2.2.2 (pg 2-9): Application rates are determined by the intended crop and expected crop yield potential. "Fallow land" implies no crop, thus, why would fertilizer rates be higher here than under a cropped field? Fertilizers are not usually applied to fallow land, but if it is applied the application will be made close to planting time. I suggest deleting this sentence.

Section 2.2.2 (pg 2-9): Dry fertilizer also can be band applied.

Section 2.3.1 (pg 2-15): In Section 6.2.1.3 manures are mentioned and should be mentioned here.

Section 2.3.2.1 (pg 2-17): Probably need to identify the chemical formula here.

Section 2.3.2.1 (pg 2-17): "photosynthetic" probably works better here.

Section 2.3.2.1 (pg 2-20): Several changes/corrections have been made to these sections.

Section 2.3.2.2 (pg 2-21): This section is poorly written and somewhat inaccurate. The attached page 2-21a should be inserted.

Section 2.3.2.3 (pg 2-21): This section also has numerous inaccuracies and is not well organized. Many of the sentences and paragraphs have been rewritten. One paragraph (pg. 2-22) needs to be moved to Section 2.3.2.4.

Section 2.3.2.4 (pg 2-22): This section has been rewritten.

Section 2.3.2.5 (pg 2-23): This section has been rewritten. Replace with attached pages 2-23a-b.

Section 2.4 (pg 2-23/24): This section has been rewritten. Replace with attached page 2-23b.

Section 3.5.1 (pg 3-11): Standard soil moisture content is always defined on an oven dry weight basis.

Section 4.2.1 (pg 4-15): The last sentence on this page is extremely important and should be highlighted by using a **boldface** font.

Section 4.3.2 (pg 4-18): Table 4-5 should incorporate the range of values contained in the mean. See Table 6.2.1-2 for specific change.

Section 6.2.1.3 (pg 3): The implication that fertilizer represent the only source of emissions is not correct. Thus, I have added the word nutrients an manures at appropriate places.

The Table numbers stated in the 3rd paragraph should be changed.

Statement concerning the need for addition research on heavy metal particulates from fertilizers and manures should be added.

The document needs a precautionary statement regarding the extremely limited and highly variable data found in Tables 6.2.1-2 and 6.2.1-3, and how this affects the usefulness and reliability of the data.

Section 6.2.1.3 (pg 7): The data for N_2O emission of for urea should be 3.98.

To give the reader the appropriate perspective on the high variance in the data, I suggest including the range in the data and the number of data points included in the mean. See page 6.2.1-7a for example change.

Thank you for the opportunity to review this document. Please don't hesitate to call me for more information.

Sincerely,

John L. Havlin
Associate Professor

Chat Cawthorn

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March 31, 1993

Mr. Horace Mann
Tennessee Valley Authority
Post Office Box 1010
Muscle Shoals, AL 35660

Dear Mr. Mann:

Thank you for your prompt response to my request for literature. The publication, "Fluid Fertilizers," that you sent will be helpful as I complete the fertilizer section for AP-42. I have enclosed your invoice and a check for $6.00 for the publication.

I enjoyed talking to you last week about the fertilizer application and would certainly appreciate your sending me any additional literature that you think would be useful in preparing Section 6.2.1 on fertilizer application. I hope I might call you again if there are other issues about which I need further information.

Also, I have recently learned that it is possible to enlist consultant assistance under this contract. I would be interested to know if you would be available for a day to review our revised draft in mid-April. Could you let me know if that would be possible and what your daily consultant rate would be?

Thank you for your assistance.

Sincerely,

Margaret E. Wickham St. Germain

Margaret E. Wickham St. Germain,
Senior Chemist

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March 31, 1993

Mr. Bernard Byrnes
International Fertilizer Developement Center (IFDC)
P. O. Box 2040
Muscle Shoals, AL 35662

Dear Mr. Byrnes:

Thank you for talking to me last week about fertilizer application, and for providing me information for the final report, "Estimation of Greenhouse Gas Emissions and Sinks" that you referenced from your review of the fertilizer section for AP-42.

I understand that IFDC is a non-profit organization, and that costs would be incurred if I require any extensive assitance. I hope I might call you again if there are other brief issues about which I need further information.

Thank you for your assistance.

Sincerely,

Margaret E. Wickham St. Germain,
Senior Chemist

MIDWEST RESEARCH INSTITUTE
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Telephone (816) 753-7600
Telefax (816) 753-8420

March 31, 1993

Mr. David Rutledge
International Fertilizer Developement Center (IFDC)
P. O. Box 2040
Muscle Shoals, AL 35662

Dear Mr. Rutledge:

Thank you for talking to me last week about fertilizer application. The references you supplied have proven helpful as I complete the fertilizer section for AP-42. As you recommended, I will contact Michael Broder at Tennessee Valley Authority (TVA) about the figures that we discussed.

I enjoyed talking to you last week and learning about the purpose of IFDC and TVA. I understand that IFDC is a non-profit organization, and that costs would be incurred if I require any extensive assitance. I hope I might call you again if there are other brief issues about which I need further information.

Thank you for your assistance.

Sincerely,

Margaret E. Wickham St. Germain

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AP-42 Study:

- Developed emission factors for NH_3, NO, N_2O, NO_2 for nitrogen fertilizers (see attached).
- Based emission factors on published data from academic investigators (foreign and domestic).
- Used mostly flux chambers at selected times after application (i.e., "snapshots").
- Temporal resolution poor with incomplete speciation of nitrogen gases from soil surface (i.e., only selected pollutants determined in most studies).

Testing Needs:

- Common fertilizer types, multiple crop types, and different soil conditions should be evaluated for *all* nitrogenous pollutants of concern following an approved statistical design.
- "Whole-field" sampling should be performed in lieu of chambers over relatively small areas.
- Soil properties should be thoroughly characterized, both chemically and biologically (i.e., Cation Exchange Capacity, etc.).
- EPA and agrichemical industry should be involved throughout the study.

Possible Approaches:

- Profile pollutant concentrations from test plot spatially and temporally using open path instruments, such as the FTIR.
- Couple concentration measurements with on-site meteorology to determine mass flux (i.e., similar to MRI exposure profiling method for particulate matter).
- Characterize soil gases frequently over study period using buried probes, etc.
- Determine types and quantities of soil organics and chemical constituents by grab sampling throughout period.
- Conduct intensive sample and analysis during 2-week maximum emission period.
- Collect air and soil samples before, during, and after fertilizer application to determine background emission and the effects of the application (i.e., natural vs. manmade emissions).

DRAFT

6.2.1 FERTILIZER APPLICATION

6.2.1.1 General[1-4]

The role of fertilizers in the agriculture industry is to supply essential plant nutrients to improve crop production. It has long been recognized that there are 16 essential elements or nutrients necessary for plant growth, three of which (carbon, hydrogen, and oxygen) are supplied from the atmosphere or water. The other 13 elements (nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, copper, zinc, boron, manganese, iron, chlorine, and molybdenum) are principally supplied through the soil medium. Concentrations of some of these elements are limited in most soils and must be supplemented by fertilizers.

Fertilizers are produced by industries in standard industrial classification (SIC) codes 2871 Fertilizer Plant Food, 2873 Nitrogen and Organic Fertilizers, 2874 Phosphate Potash and other Fertilizers, and 2879 Pesticides and other Agricultural Chemicals. Fertilizers are distributed through agricultural supply retailers, farmers' cooperatives, and fertilizer dealers. Application is performed by farmers and by fertilizer dealers using specialized application equipment.

6.2.1.2 Process Description[3-6]

Fertilizer application is based on the physical form of the fertilizer, i.e., a gaseous, fluid, or solid form.

Gaseous Fertilizer — Anhydrous ammonia, which supplies nitrogen, is the only gaseous fertilizer used. Farmers usually hire trained specialists to apply the 5.7 million tons of ammonia used annually in the United States. Anhydrous ammonia is typically stored in a liquid form, most commonly under pressure, and to a lesser degree, by refrigeration. Anhydrous ammonia is applied by subsurface injection. The ammonia quickly vaporizes, but is captured by several components in the soil including water, clay, and other minerals.

The equipment for the injection of anhydrous ammonia consists of a vehicle (truck or tractor), a pressurized tank containing anhydrous ammonia, a metering system, manifolds, and injection knives. The critical components of the injection system are the metering assembly and injection knives. The meter assembly controls release of the fertilizer in direct proportion to the speed of the vehicle. Generally, the depth settings for injection are from 4 to 10 inches (10 to 25 centimeters) below the surface, depending on soil type, soil conditions, and spacing of injection knives. Figure 6.2.1-1 shows a simplified trailer used to apply anhydrous ammonia and liquid fertilizers.

The only calibration during the application of ammonia is to track the pounds applied versus acres covered. Precise orifice calibration for metering the flow of liquid ammonia is done at the factory. The applicator selects the orifice setting according to expected vehicle speed, desired application rate, and number of injectors or bar width.

Fluid Fertilizer — Fluid fertilizers are typically classified as either solutions or suspensions. Solution fertilizers are free of solid particles. Suspension fertilizers are two-phase fertilizers in which solid particles are maintained in suspension in the aqueous phase.

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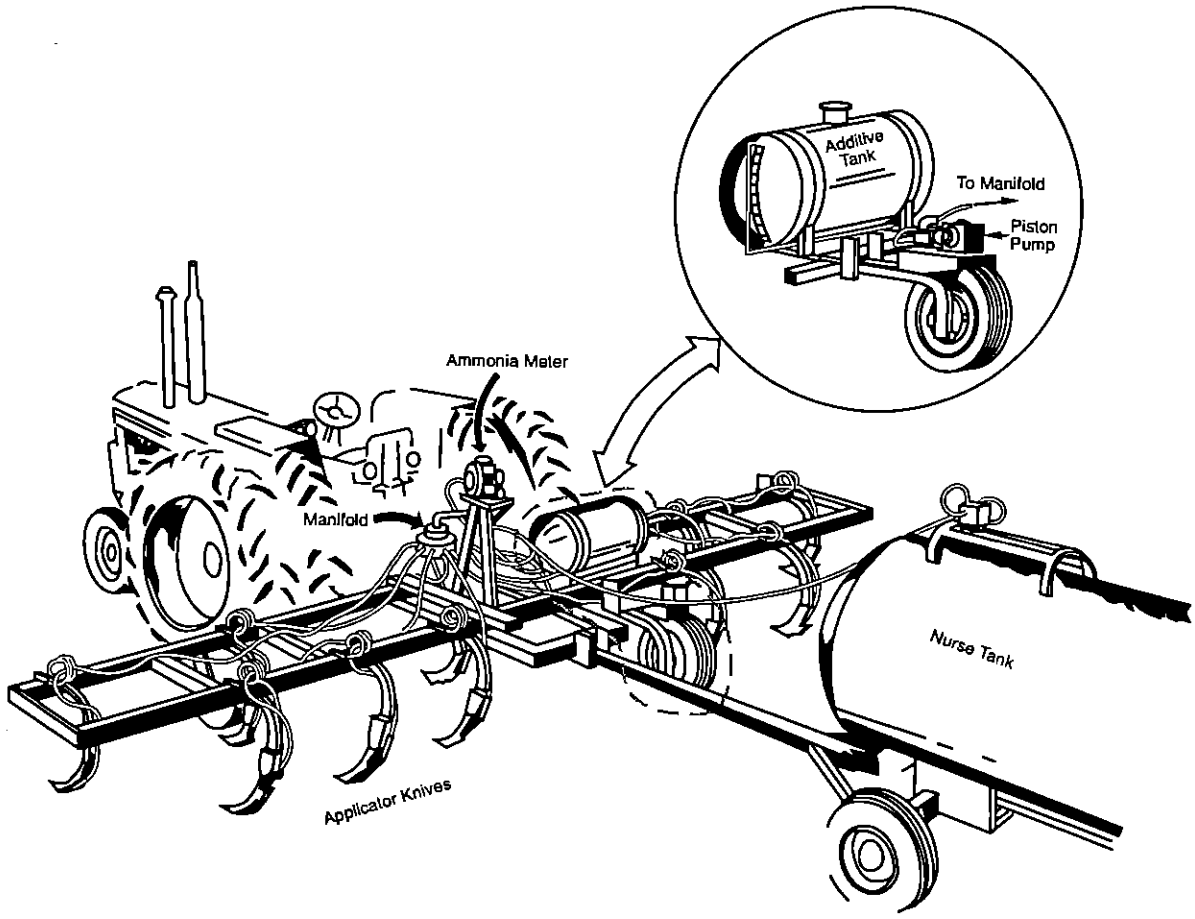

Figure 6.2.1-1. Typical trailer for application of anhydrous ammonia and liquid fertilizers.

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The equipment for surface spraying of fertilizers consists of the vehicle, a tank holding the fluid, a metering system, manifolds, and spray nozzles. The manifolds are mounted inside long booms (20 to 40 feet) having no more than 20 nozzles. Fluid fertilizers are most commonly sprayed onto the surface of freshly tilled soils. Figure 6.2.1-2 shows a side view and rear view of a typical spray nozzle system. By varying the height of the nozzles above the ground and the flow of the liquid fertilizer, the applicator can apply the fertilizer in discreet bands or as overlapping coverage.

Solid Fertilizers — In the United States, solid fertilizers are typically either straight nitrogen fertilizers (urea or ammonium nitrate) or mixed fertilizers containing nitrogen and phosphate, potassium, and other nutrients. The equipment for broadcast application of fertilizers consists of the vehicle, a dry hopper containing solid fertilizer, a metering system, and either fan-type spreaders or boomed spreaders. The flow is controlled by a sprocket-driven belt that feeds the dry fertilizer into the spreader. The application rate is dependent on the position of the spinner blades, the position where the fertilizer drops on the spinner blades, the spinner speed, and the particle size of the fertilizer. Figure 6.2.1-3 shows an example of a centrifugal spreader.

6.2.1.3 Emission And Controls[3,5,6,7,8]

Both particulate matter and gaseous air emissions are generated from the application of fertilizers. In both cases, emissions may be immediate (occurring during or shortly after application), and latent (occurring days or weeks following application).

Wind-blown dust is created immediately during the application of dry fertilizers and later from disturbances caused by mechanical operations (e.g., tilling) and/or wind erosion. Gaseous air emissions can be generated after application by the immediate volatilization of gaseous fertilizers (i.e., anhydrous ammonia) or after some period of time by the chemical/biological transformation of nitrogen (N) added as fertilizers to the soil.

At present, only gaseous air emission factors have been developed for nitrogen fertilizers. These emission factors, which are shown in Tables 6.2.1-1 and 6.2.1-2, are based on equivalent nitrogen applied to the soil.

Emission factors are not presently available for particulate matter. A number of heavy elements listed as Hazardous Air Pollutants in the 1990 Clean Air Act Amendments have been identified in soils treated with phosphate, nitrogen, and manure fertilizers, and could become airborne with fugitive dust. These elements are: cadmium, mercury, nickel, selenium, chromium, manganese, lead, and cobalt.

Some of these element also occur naturally in some soils. Finally, where more specific data are not available, Table 6.2.1-1 provides equivalent nitrogen contents of common chemical fertilizers for use with the emission factors shown in Tables 6.2.1-2 and 6.2.1-3.

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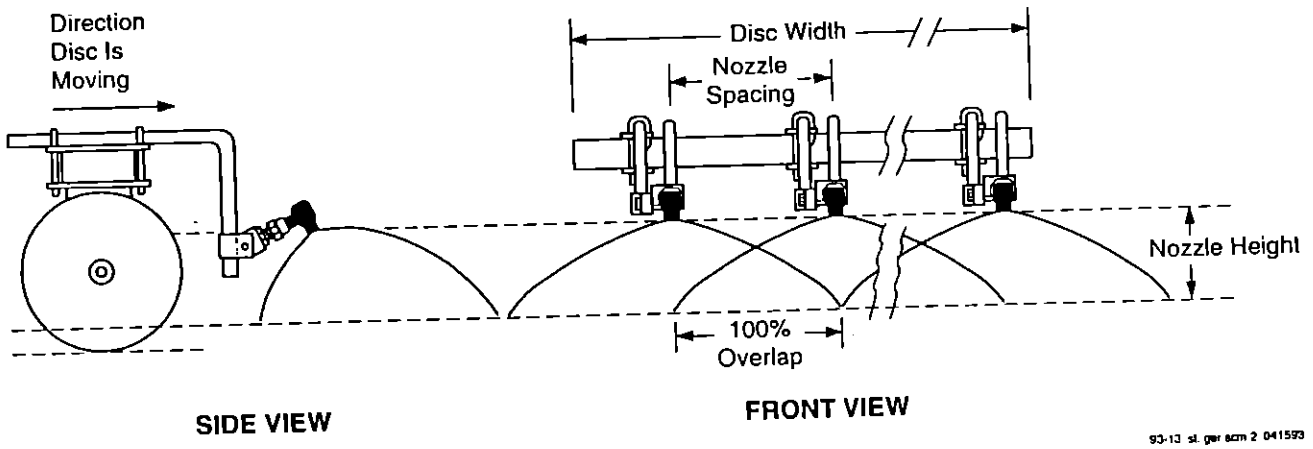

Figure 6.2.1-2. Side view and rear view of a typical spray nozzle system used for application of liquid fertilizers.

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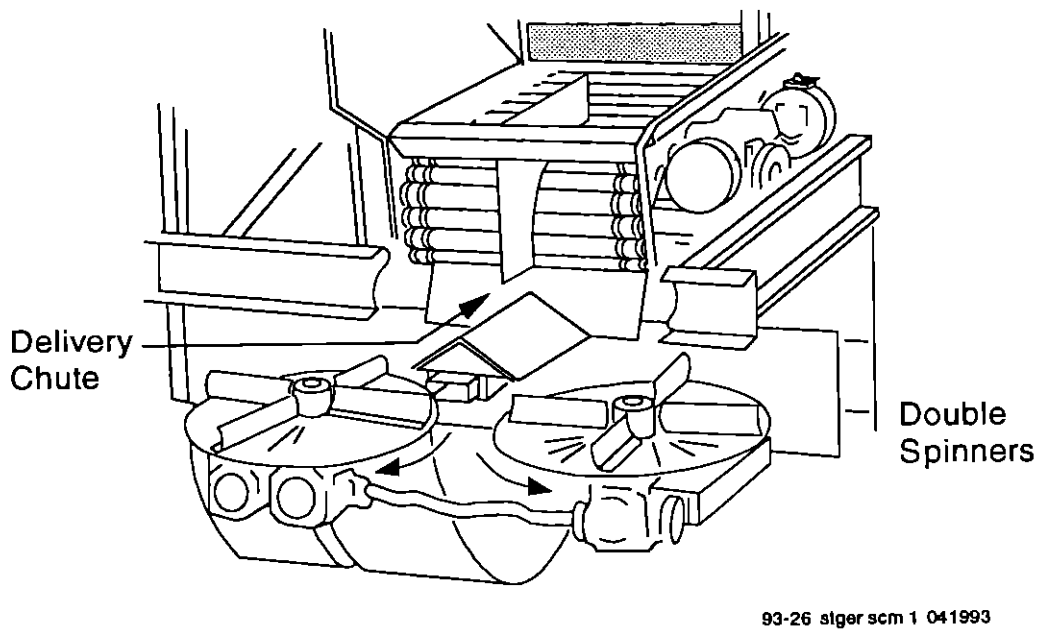

Figure 6.2.1-3. Example of centrifugal spreader.

DRAFT

Table 6.2.1-1.
EQUIVALENT NITROGEN CONTENT OF COMMON CHEMICAL FERTILIZERS[a]

Type of fertilizer	Chemical formula	Nitrogen content (weight percent)	Amount of fertilizer applied per hectare to produce 1 kg N/ha equivalent application[b]
Anhydrous ammonia	NH_3	82.3	1.21 kg
Urea	$CO(NH_2)_2$	46.7	2.14 kg
Ammonium nitrate	NH_4NO_3	35.0	2.86 kg

[a]Nitrogen content calculated for pure chemicals.
[b]1 kg = 1,000 g = 2.2 lb; 1 ha = 10^4 m^2 = 2.471 acres. From reference 7.

DRAFT

Table 6.2.1-2 (Metric Units).
CANDIDATE EMISSION FACTORS FOR THE APPLICATION OF NITROGEN FERTILIZERS[a]

EMISSION FACTOR RATING: E

Pollutant[b]	Type of fertilizer[c]	Total mass emission factor[d] g/kg N applied	Emission time scale[e]
NH_3	ℓ-NH_3 [f]	1.94	Immediate
	Solid N fertilizer[g]	132	Latent
N_2O	NH_4NO_3	96.0	Latent
	Urea	3.48	Latent
NO	NH_4NO_3	14.4	Latent
	Urea	69.7	Latent
NO_2	Solid and liquid N fertilizers[h]	118	Latent

[a]Reference 7. Applies to all nitrogen-based fertilizer regardless of chemical composition.
[b]NH_3 = ammonia; N_2O = nitrous oxide; NO = nitric oxide; and NO_2 = nitrogen dioxide.
[c]Fertilizer can be applied in solid, liquid, or gaseous form by dry broadcasting, spraying, or injection.
[d]Mass of pollutant per equivalent amount of nitrogen applied. See Table 6.2.1-3 for nitrogen content of common chemical fertilizers. 1 kg = 1,000 g = 2.2 lb; 1 ton = 2,000 lb.
[e]Immediate = 2 to 9 hr after application; latent = up to 1 year after application.
[f]Liquid anhydrous ammonia injected as a gas at a depth of at least 4 in (10 cm).
[g]Data for dry application of urea.
[h]NH_4NO_3 and urea—dry and fluid.

DRAFT

Table 6.2.1-3 (English Units).
CANDIDATE EMISSION FACTORS FOR THE APPLICATION OF NITROGEN FERTILIZERS[a]

EMISSION FACTOR RATING: E

Pollutant[b]	Type of fertilizer[c]	Total mass emission factor[d] lb/ton N applied	Emission time scale[e]
NH_3	ℓ-NH_3 [f]	3.88	Immediate
	Solid N fertilizer[g]	264	Latent
N_2O	NH_4NO_3	192	Latent
	Urea	7.95	Latent
NO	NH_4NO_3	28.8	Latent
	Urea	139	Latent
NO_2	Solid and liquid N fertilizers[h]	236	Latent

[a]Reference 7. Applies to all nitrogen-based fertilizer regardless of chemical composition.
[b]NH_3 = ammonia; N_2O = nitrous oxide; NO = nitric oxide; and NO_2 = nitrogen dioxide.
[c]Fertilizer can be applied in solid, liquid, or gaseous form by dry broadcasting, spraying, or injection.
[d]Mass of pollutant per equivalent amount of nitrogen applied. See Table 6.2.1-3 for nitrogen content of common chemical fertilizers. 1 kg = 1,000 g = 2.2 lb; 1 ton = 2,000 lb.
[e]Immediate = 2 to 9 hr after application; latent = up to 1 year after application.
[f]Liquid anhydrous ammonia injected as a gas at a depth of at least 4 in (10 cm).
[g]Data for dry application of urea.
[h]NH_4NO_3 and urea—dry and fluid.

DRAFT

References for Section 6.2.1

1. H. L. Hargett, *et al.*, *Fertilizer Use By Class*, National Fertilizer Development Center, Muscle Shoals, AL, 1989.

2. H. L. Hargett and J. T. Berry, *Today's Retail Fertilizer Industry*, National Fertilizer Development Center, Muscle Shoals, AL, July 1988.

3. O. P. Engelstad, editor, *Fertilizer Technology And Use*, Third Edition, Soil Science Society of America Inc., Madison, WI, 1985.

4. *Standard Industrial Classification Manual*, Fertilizer Application (p. 31-33), National Technical Information Service, Springfield, VA, 1987.

5. R. J. Haynes and R. R. Sherlock, "Gaseous Losses Of Nitrogen", In *Mineral Nitrogen And The Plant-Soil System*, Academic Press, San Diego, CA, 1986.

6. K. Simpson, *Fertilizers And Manures*, Longman Inc., New York, 1986.

7. *Emission Factor Documentation For AP-42 Section 6.2.1, Fertilizer Application*, EPA Contract No. 68-D2-0159, Midwest Research Institute, Kansas City, MO, April 1993.

8. A. Kabata-Pendias and H. Pendias, *Trace Elements In Soils And Plants*, CRC Press, Boca Raton, FL, 1984.

John Kinsey

TVA

Tennessee Valley Authority, Post Office Box 1010, Muscle Shoals, Alabama 35660

December 14, 1992

Mr. Dallas W. Safriet
Environmental Engineer
Emission Inventory Branch
United States Environmental
Protection Agency
Office of Air Quality Planning
and Standards
Research Triangle Park, North Carolina 27711

Dear Mr. Safriet:

John Culp and I enjoyed our phone conversation with you this morning and the discussion describing our concerns about the draft AP-42 document you sent for review. Enclosed are comments from Roland Hauck, Michael Broder, and me. In general, because of the inaccuracies, dated information, and errors we feel that a complete rewrite is necessary to make this information accurate and current. Our comments are not necessarily complete because of the quick turn around you indicated was necessary. After you have an opportunity to review our comments, we would welcome further discussions on how the revisions could be made.

Thank you for giving us the opportunity to review this draft.

Sincerely,

Horace C. Mann

Horace C. Mann
Projects Manager
Field Programs Department
National Fertilizer and
Environmental Research Center

Enclosure

Comments on the draft report "Background Documentation for AP-42 Section 6.2.1, Fertilizer Application, MRI Paper No. 6500-K(35)
Roland D. Hauck

General Comment

Section 2 of the subject draft report can be greatly improved by: (i) correcting many inaccuracies and misinterpretations of information, and (ii) tightening up the discussion to make it more directly relevant to the objectives of the study. Regardless of the criteria used for selecting data and the care taken in calculating emission factors, the value of the emission factors given in section 5 is suspect because the discussion in section 2 indicates only an elementary and incomplete knowledge of the process dynamics leading to gaseous nitrogen emissions.

Specific Comments

2-7 The term fluid fertilizer rather than liquid fertilizer should be used. The information about liquid fertilizers is not entirely correct. They usually are concentrated rather than dilute solutions (lower handling, transport, and distribution costs). They may be injected or dribbled on as well as sprayed.

2-7 para.4. The paragraph assumes that time-release fertilizers use is growing and that such fertilizers comprise or will comprise a significant amount of total fertilizer use. This assumption is incorrect.

2-10 The contaminants listed in Table 2-1 also are present in soils to which no fertilizer has been added.

sec. 2.3.1.1 The discussion of ammonia/ammonium reactions in soils reflects a poor understanding of soil chemistry. Although several statements made are essentially correct, they are presented neither clearly nor accurately.. For example, there is no clear distinction between the dissolution of ammonia in or absorption by water and adsorption of ammonium ion on inorganic and organic exchange surfaces. .

sec. 2.3.1.2 The term, (NO)x, most generally is used when referring to the N oxide gases. NO, NO2, N2O, and N2O4, although the most rigid use would restrict it to NO and NO2. Nitrite and nitrate normally are not included in this group, as indicated in this section. There is little evidence that nitrification leads to significant loss of gaseous nitrogen.

Sec.2.3.1.2 This section also reflects only rudimentary understanding of the subject. For example, the discussion relating to ammonium nitrate is incorrect; equation 2-1 is for the reaction of ammonium with nitrite rather than nitrate. Nitrite usually is not present in appreciable quantities in soils except in microsites of high pH. The reaction shown by equation

2.1 occurs appreciably only at low pH (below 5).

Sec.2.3.1.3 One of the main sulfur sources supplied in fluid fertilizers, ammonium thiosulfate, is not listed. Sulfur dioxide (listed) is not a common source. The amount supplied as sulfur-coated urea is negligible when compared to the whole. During the period when fertilizer use was increasing in the United States, there was a corresponding increase in the total nutrient content of fertilizer materials and a decrease in the level of impurities, including heavy metals and sulfur. The amount of nitrogen added as ammonium sulfate, therefore the amount of sulfur added from this material, also will not increase (ammonium sulfate is mainly a by-product rather than made primarily for fertilizer use).

2-21, para.2 Fluid fertilizers, rather than solid ones, can be applied more rapidly per unit of nutrient. There is no evidence that emissions from solid fertilizers generally exceed those from fluids with the exception of surface-applied, un-incorporated urea or diammonium phosphate from which ammonia may be liberated to the atmosphere. Other comments could be made to point out the fallacy of making generalizations from an extensive literature without a solid understanding of that literature.. This lack of understanding is reflected further in the discussion on page 2-2. For example, the definition of CEC given in the footnote would almost be correct only if the parenthetical phrase were deleted.

4-1, para.3 The data given in the references cited may be considered accurate. What may be questionable is the use of the data for extrapolating to dimensions several magnitudes larger than the system from which the data sets were collected.

4-10, para.1 A rating of D is given for the data from references 15a and 15b because a nonstandard and unproven method was used. The method used, however, is the only one of all methods cited in the accepted references that makes measurements in the unconfined atmosphere over an entire field. Extrapolating data obtained in this manner to large dimensions is more justifiable than a similar extrapolation of data collected from chamber studies.

Table 6.2.1-1 The weak basis for the numbers given in this table was adequately discussed in the previous section. However, once data are published in an official document they may assume an undeserved validity. For example, the emission factor for ammonia from solid fertilizers is based on ammonia volatilization from surface-applied, un-incorporated urea, which does not represent the bulk of solid nitrogen fertilizers nor the manner in which they are used. The emission factor for nitrous oxide is based on studies that measured nitrous oxide formed during nitrification, whereas most nitrous oxide released to the atmosphere from soils probably is the result of denitrification. Also, where nitrification is involved, the type, physical state, and, if solid, the particle size are among the factors affecting the rate of nitrification and course of its reaction products. These factors were not considered in the studies cited nor in the

evaluation of data.

To construct a table of emission factors for fertilizers from an admittedly extremely limited and weak data base is not justifiable. To present the information in terms of 0.1g/kg or 0.1 lb./ton implies a precision not warranted by the data.

Table 6.2.1-2 This table lists calcium nitrate and ammonium chloride as common fertilizers used in the United States, which they are not, and omits such materials as monoammonium and diammonium phosphates, which are common components of mixed fertilizers.

Additional comments on Sections 2, 4, and 5 -Proposed AP-42 - Specific and general--H. C. Mann

Page 2-1, 2-2 - "Liquid fertilizer" should be "fluid fertilizer."

Page 2-2 - Suggest 20-30% NH_3 instead of 30-40% or put temperatures where vapor pressure is 0 psig.

Page 2-4 (Figure 2-1) - No pump on NH_3 applicator.

2.2.2 - "Fluid" instead of liquid on title and first word in 1.

Last sentence is wrong, needs to include injection

2nd and 3rd paragraphs need rewriting to include injection, remove "liquid" and replace with fluid where appropriate.

2.2.3 - Whole section needs rewriting to reflect both current equipment available and application practices.

Figure 2-5 - Do not normally spray on a " young" plant. Banding is normally to the side and below and by injection.

Table 2-1 - Sources of phosphate and nitrogen fertilizer need to be identified to not cause misconceptions - i.e., NH_3 does not contain a number of the elements listed. All phosphate fertilizers do not contain 200 ppm of Ba, 20 ppm Ce, etc.

Paragraph 2.3 - First sentence is <u>too</u> absolute. Needs to be qualified significantly.

Section 5, paragraph 6.2.1.2.2 - "Liquid" should be changed to fluid and the entire section rewritten to reflect current commercial practices.

Section 5, paragraph 6.2.1.2.3 - Section needs to be rewritten to reflect current commercial practices.

Section 5, paragraph 6.2.1.3 - Too absolute, needs to be qualified significantly.

Tables 4-5 and 6.2.1-2 - Urea formula wrong, should be $(NH_2)_2$ CO.

Ammonium sulfate wrong, should be $(NH_4)_2$ SO_4.
Calcium nitrate wrong, should be Ca $(NO_3)_2$.

Suggestions for improving EPA AP-42 Draft Report from Michael Broder.

In the interest of time I have limited my suggestions to Section 5 which I believe is the only part that will appear in AP-42. In summary, the descriptions of the application processes are inaccurate and misleading. Anyone remotely familiar with the use of fertilizers in crop production in the U.S. would find the information suspect. A couple of references are available which adequately describe application processes; chapter 9 of TVA Bulletin Y-185 Fluid Fertilizers, or chapter 31 of Nitrogen in Crop Production edited by Roland D. Hauck. Section 5 should be completely rewritten and then resubmitted for review. The gross errors in the application process descriptions and in fertilizer formulas would cause any informed reader to question the emission factors.

Section 6.2.1.1 General

SIC codes don't seem to be relevant to this discussion. The adjective "custom" is not normally used to describe fertilizer dealers. Application is performed by custom applicators in addition to farmers and fertilizer dealers. In Florida, for example, nearly all fertilizer applied commercially is done by custom applicators who do not sell the fertilizer.

Section 6.2.1.2 Process Description

This paragraph could be made much less awkward as follows:

Fertilizer is applied by three basic methods depending on its physical state; solid (granular), fluid, or gaseous.

Section 6.2.1.2.1 Gaseous Fertilizer

Trucks are never used to apply anhydrous ammonia. They don't have the pulling power at the low speeds required. Plowing discs/plates is not a recognized term. The American Society of Agricultural Engineers Standards lists terminology of tillage devices. Injection knives or chisels are the proper term. The tube holders are an insignificant part of the system. Metering application rate) is controlled by three methods; 1) a calibrated orifice is preset to release a constant amount of ammonia per hour while applicator speed is held constant (orifice calibration is accurate for tank pressures between 50 and 150 psig), 2) a heat exchanger is used to provide liquid ammonia to a flow meter installed in line with an orifice which is controlled electronically to adjust ammonia flow according to speeds indicated by a radar speed sensor, 3) a piston pump driven by a chain from a ground driven wheel is used to deliver ammonia. The latter two systems are more accurate than the first because the ammonia flow is synchronized with ground speed.

Because of the difficulty and danger associated with collecting and measuring anhydrous ammonia these machines are only calibrated by researchers and at the manufacturing site. Metering systems have precisely machined orifices which normally do not require calibration.

Most anhydrous ammonia is applied by farmers. The service is not profitable for dealers and custom applicators because the area that can be treated in a given time is 3 to 6 times less than what can be achieved by broadcast application. The margin, consequently, is not large enough to offset the higher labor cost.

The planting of seed and anhydrous ammonia application is never done simultaneously.

Figure 6.2.1-1-should be replaced with a sketch depicting only anhydrous application. Dual systems are not the norm. Also, the ammonia supply tank is generally a nurse tank which trails behind the tillage (incorporation) implement.

Section 6.2.1.2.2 Fluid Fertilizer

The application of fluid fertilizer and anhydrous is not at all similar. Fluid fertilizers are generally not diluted. Economics dictate that they be shipped and applied as concentrated as physical properties allow. Manifolds are not composed of booms. Manifolds are plumbing devices which split the flow of fluid into two or more equal flows which are further divided along the booms which are generally 20 to 40 feet long.

The figure 6.2.1-2 depicts a spray system on a tillage device. Though this is a common practice, a much greater volume of product is applied using truck mounted sprayers and specially build high flotation vehicles. Though fluid can be applied in discreet bands by lowering broadcast nozzles, generally, nozzles which produce a solid stream are used for banding. Most custom application equipment has booms mounted at a fixed height to facilitate operating at high speeds.

The proper overlap varies according to nozzle design. Flooding and hollow cone nozzle patterns should be overlapped 100 percent, flat fan nozzles should be overlapped 30 percent. Since most commercial rigs have booms 3 to 4 feet above the ground and nozzles spaced 5 feet, the actual overlap of nozzle sprays is as high as 200 to 300 percent.

Section 6.2.1.2.3. Solid fertilizers

About two-thirds of the fertilizer applied in the U.S. is in solid form. I don't believe timed release fertilizer technology has caused broadcast application to grow. If broadcast application is growing it is due to its low cost and efficiency relative to other methods.

The most common method for applying solid fertilizer is by centrifugal spreaders. Centrifugal spreaders have one disc or two counter-rotating discs, mounted

horizontally, which broadcast material falling from a belt or mesh-chain conveyor. An adjustable gate in the hopper above the conveyor is used to set application rates. Output is synchronized with ground speed either electronically or mechanically.

Among the boomed applicators, three different pneumatic designs and one auger metered system are most popular. The impetus for using boomed spreaders is for uniform application of dry fertilizer impregnated with herbicide. This practice and boomed solid applicator are described in detail in chapter 13 of the monograph, Methods of Applying Herbicides, edited by C. G. McWhorter and M. R. Gebhardt.

The description of equipment in this section is atrocious. ; Deflectors and not nozzles are used to direct pneumatically conveyed material to the ground. there are no orifices at the discharge end and there are no fan blades that spin. The authors appear to have combined parts of both, centrifugal and pneumatic applicators.

6.2.1.3 Emission and Controls

I don't believe there is enough data to support mentioning the heavy metals which may become airborne with fugitive dust.

Table 6.2.2-1

This table needs to be reviewed by Roland Hauck or someone in his department.

Table 6.2.2-2

The chemical formulas for urea, ammonium sulfate, and calcium nitrate are wrong. The nitrogen contents are incorrect for three of the materials (see Don Kachelman's attached corrections).

N:\Broder.EPA.corrections

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December 21, 1992

Mr. Dallas W. Safriet
Environmental Engineer
Emission Inventory Branch
United States Environmental Protection
Agency
Office of Air Quality Planning and
Standards
Research Triangle Park, North Carolina 27711

Dear Mr. Safriet:

As requested in your November 19, 1992, letter we have reviewed the draft version of a proposed new section 6.2.1, *Fertilizer Application*, of AP-42, *Compilation of Air Pollutant Emission Factors*. As you requested we reviewed only Section 5 of the background documentation.

Our staff members reviewed draft Section 6.2.1. The reviewers found the draft section to be not well written, quite inaccurate, and apparently inadequately researched. In our opinion the draft section should be rewritten after a more extensive literature review is performed. We have enclosed an example of a possible rewrite that we believe more accurately describes the information you are attempting to document. However, the rewrite does not include additional data other than that already incorporated into the draft version. According to our staff there is much more reliable data and information available than that referenced in the draft section.

We have also collaborated with staff members from the Tennessee Valley Authority on the draft section and understand they were also requested to review the document. We have reviewed their comments that were sent to you and fully agree with them.

Please note that we did not review the data included in Table 6.2.1-1. The data would have demanded an extensive review of all the references included in the background documentation. We could undertake this task but only under a reimbursable agreement due to the magnitude of such an effort.

We hope this information is helpful to the EPA in developing appropriate and accurate emission factors for AP-42.

Sincerely yours,

James J. Schultz
Director
Outreach Division

Enclosure

IFDC
December 21, 1992

Example of Suggested Rewrite of Section 6.2.1

6.2.1 Fertilizer Application

6.2.1.1 General. The role of fertilizers in the agricultural industry is to supply essential plant nutrients to improve crop production. It has long been recognized that there are 16 essential elements or nutrients necessary for plant growth, three of which are supplied from the atmosphere or water (carbon, hydrogen, and oxygen). The other 13 elements (nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, copper, zinc, boron, manganese, iron, chlorine, and molybdenum) are principally supplied through the soil medium. Some of these elements are limited in the soil medium and must be supplemented by fertilizers. Fertilizers are distributed through agricultural supply retailers, farmers' cooperatives, and fertilizer dealers. Application is typically performed by farmers and by fertilizer dealers using specialized application equipment.

6.2.1.2 Process Description. Based on the physical form of the fertilizer, there are three basic types of fertilizer application. The basic method of application is determined according to whether the fertilizer is in a gaseous, fluid, or solid form.

6.2.1.2.1 Gaseous fertilizer. Anhydrous ammonia is the only gaseous fertilizer used, and supplies nitrogen. Typically, about 6 million tons of ammonia is applied annually in the United States. Farmers generally apply ammonia thenselves. Anhydrous ammonia is typically stored in a liquid form: most commonly, under pressure; and to a lesser degree, by refrigeration. Anhydrous ammonia is actually injected as a liquid/gaseous mixture into the soil where it vaporizes into a gas and then is captured by several components in the soil, including water, clay, and other minerals.

Because it is a gas at atmospheric pressure, anhydrous ammonia must be injected from 4 to 10 inches (10 to 25 cm) below the soil surface, depending upon the soil type, soil conditions, and spacing. Generally, typical equipment for anhydrous ammonia application consists of a tractor, a pressurized tank containing the anhydrous ammonia, a metering system, manifolds, and injection knives. Figure _____ (not the one shown) is a typical example of application equipment for anhydrous ammonia.

The only calibration done during the application of ammonia is a tracking of pounds applied versus acres covered. Precise orifice calibration for metering the flow of liquid ammonia is done at the factory, and farmer dials in the orifice setting according to speed, desired rate, and tool bar width.

6.2.1.2.2 Fluid fertilizer. Fluid fertilizers are typically classified as either solutions or suspensions. Solution fertilizers are free of solid particles. Suspension fertilizers are two-phase fertilizers in which solid particles are maintained in suspension in the aqueous phase. The equipment used in the application of fluid fertilizers typically

consists of a vehicle (truck or tractor), a tank holding the fluid, a metering system, manifolds, and spray nozzles. The manifolds are mounted inside long booms (20-40 ft) with the nozzles spaced along the manifold so that the spray patterns overlap. Fluid fertilizers are most commonly sprayed onto the surface of freshly tilled soils.

Figure _____ (not the one shown) is an example of a typical applicator for fluid fertilizers.

6.2.1.2.3 Solid fertilizers. In the United States, solid fertilizers are typically applied as straight nitrogen fertilizers (urea or ammonium nitrate) or as mixed fertilizers containing not only nitrogen but also phosphate, potassium, and other nutrients. Application of solid fertilizers is done predominantly either by fan-type spreaders (Figure _____) or by boomed (pneumatic- or auger-type) spreaders (Figure _____).

6.2.1.3 Emission and Controls. Both solid-phase (particulate matter) and vapor-phase air pollutants can be generated from the application of fertilizers. In both cases, two general classes of emissions are noted: "immediate" pollutant emissions which can occur either during or shortly after application; and "latent" pollutant emissions which can be generated days or weeks following application.

Wind-blown dust can be created immediately during the application of dry fertilizers and later from disturbances caused by mechanical operations (e.g., tilling) and/or wind erosion. Vapor-phase emissions can be generated after application by the immediate volatilization of gaseous fertilizers (i.e., anhydrous ammonia) or after some period of time by the chemical/biological transformation of N added as fertilizers to the soil.

At the current time, vapor-phase emission factors are available only for nitrogen fertilizers. These emission factors are shown in Table 6.2.1-1 on the basis of equivalent nitrogen applied to the soil. Finally, where more specific data are not available, Table 6.2.1-2 provides equivalent nitrogen contents of common chemical fertilizers for use with the emission factors shown in Table 6.2.1-1. (Refer to TVA comments regarding questionable validity of vapor-phase emission factors.)

Table 6.2.1-1. Candidate Emission Factors for the Application of Nitrogen Fertilizers[a]

IFDC did not attempt to verify the data included in this table. This could be done on a reimbursable basis.

Table 6.2.1-2. Equivalent Nitrogen Content of Common Chemical Fertilizers[a]

Type of Fertilizer	Chemical Formula	Nitrogen Content (Weight Percent)	Amount of Fertilizer Applied per Hectare to Produce 1 kg N/ha Equivalent Application (kg)
Anhydrous ammonia	NH_3	82.3	1.22
Urea	$CO(NH_2)_2$	46.7	2.14
Ammonium sulfate	$(NH_4)_2SO_4$	21.2	4.72
Calcium nitrate	$Ca(NO_3)_2$	17.1	5.85
Ammonium nitrate	NH_4NO_3	35.0	2.86
Ammonium chloride	NH_4Cl	26.2	3.82
Sodium nitrate	$NaNO_3$	16.5	6.06
Diammonium phosphate (DAP)	$(NH_4)_2HPO_4$	21.2	4.72
Potassium nitrate	KNO_3	13.9	7.19

a. For pure chemicals. 1 kg = 1,000 g = 2.2 lb; 1 ha = $10^4 m^2$ = 2.471 acres. From Table 4-5 of Reference 7.

Memorandum

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To: David W. Rutland, Physical Properties Specialist, Outreach Division

From: Bernard H. Byrnes, Soil Scientist, Resources Management Research and Development Division

Date: December 16, 1992 B213

Subject: COMMENTS ON "ESTIMATION OF GREENHOUSE GAS EMISSIONS AND SINKS"--FINAL REPORT

Table 6.2.1-1 is the essence of the entire report, since it lists emission factors for N gases derived from N fertilizers.

1. NH_3--All solid fertilizers cannot volatilize ammonia at a rate as high as urea for the obvious reasons that many contain nitrate as a component and do not produce alkalinity to support volatilization. This emission rate, based on unincorporated application, greatly overestimates losses.

2. NO, NO_2--Recent research (see page A-5 in references) has shown that NO, not NO_2, is emitted from soils. To have a larger emission factor for NO_2 than NO makes no sense. Why would NO come from liquid fertilizers but not others?

3. N_2O--N_2O emissions are much more a soil phenomenon (nitrification rates and denitrification rates as influenced by water dynamics) than a fertilizer-related phenomenon. Bouwman (1990) compiled data from recent literature and failed to see a relationship to fertilizer type and came up with a factor of 4.17 g/kg N or, if poorly drained soils were excluded, 7.50 g/kg N. The attached tables appear to be more valid estimates.

The table needs to be revised completely to reflect differences between the various types of fertilizers and also their use.

BHB:daf
Attachment
cc: C. A. Baanante
J. J. Schultz

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**********TELEFAX COMMUNICATION**********

To: Mr. Dallas W. Safriet
Environmental Engineer
Emission Inventory Branch
United States Environmental Protection Agency
Research Triangle Park, North Carolina 27711

December 23, 1992

From: James J. Schultz

Fax 919-541-0684

Page 1 of 4

MESSAGE:

RE: SECTION 6.2.1, FERTILIZER APPLICATION DRAFT REPORT, AP-42

You may find the attached comments by Dr. B. H. Byrnes of our staff to be useful. I should have included them with my letter to you dated December 21, 1992. Please let me know if you need any additional information.

Dr. Byrnes can be reached at (205) 381-6600, extension 289.

Regards,

James J. Schultz
Director
Outreach Division

Attachment

OECD / OCDE

ESTIMATION OF GREENHOUSE GAS EMISSIONS AND SINKS

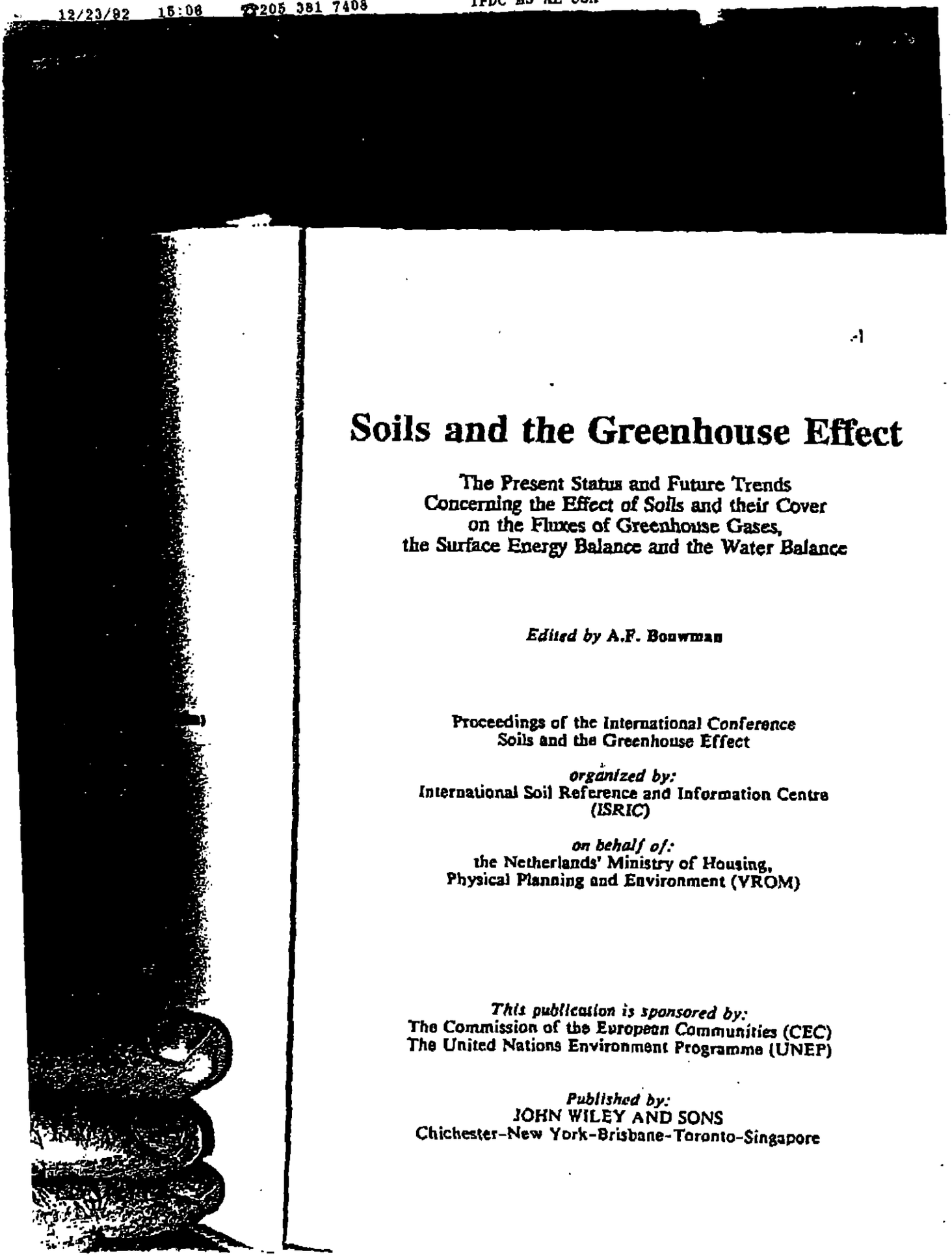
FINAL REPORT

From
OECD Experts Meeting, 18-21 February 1991

Prepared For

Intergovernmental Panel on Climate Change

Revised August 1991



Soils and the Greenhouse Effect

The Present Status and Future Trends Concerning the Effect of Soils and their Cover on the Fluxes of Greenhouse Gases, the Surface Energy Balance and the Water Balance

Edited by **A.F. Bouwman**

Proceedings of the International Conference
Soils and the Greenhouse Effect

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June 3, 1993

Ms. M.E.W. St. Germain
Senior Chemist
Midwest Research Institute
425 Volker Boulevard
Kansas City, MO 64110

Dear M. St. Germain:

The enclosed document (AP-42, Section 6.2.1) on fertilizer application has been reviewed and my recommended changes appear directly on the manuscript. Several section have been completely rewritten and also are attached. The following itemized list of concerns and suggested changes should be considered.

General Comments

1. The manuscript leaves the impression that fertilizers are the only source of gaseous emissions of nitrogen. Manure and legume nitrogen also be denitrified and nitrogen gas released during nitrification. I have made several changes to reflect this oversight.

2. The descriptions of soil biological and chemical processes are somewhat inaccurate and I have made substantial changes in these sections.

3. The data obtained from the references provided appear to be accurately interpreted and reported. However, the data quality rating eliminates some valuable data collected from studies that use a micro-meteorological approach which have clearly demonstrated that they may estimate the quantity of gaseous emissions more accurately than small microplot chamber methods.

4. The arithmetic means listed in Table 6.2.1-2 are suspect when the specific gases are compared. For example, research has shown that primarily NO and not NO_2 is emitted from soils. I can't see how NO_2 could be greater than NO. This problem illuminates the numerous problems in the limited data set used, and perhaps more importantly, the criteria used in the data quality rating system.

5. Many of the references used unincorporated nitrogen. Thus, gaseous emission would be over estimated.

6. In general, the data (Table 4-2 and 4-3) used in obtaining the arithmetic means are seriously insufficient to formulate conclusive evidence for fertilizer nitrogen contribution to atmospheric nitrogen gases.

Specific Comments

Section 2.2.1 (pg 2-3): Aqua ammonia can be soil applied. "It" refers to Anhydrous ammonia not aqua ammonia.

Section 2.2.1 (pg 2-4): Depth of NH_3 application most always is deeper than 1 inch. You have used 4 to 10 inches in a subsequent section, thus, you should be consistent.

Section 2.2.2 (pg 2-9): Application rates are determined by the intended crop and expected crop yield potential. "Fallow land" implies no crop, thus, why would fertilizer rates be higher here than under a cropped field? Fertilizers are not usually applied to fallow land, but if it is applied the application will be made close to planting time. I suggest deleting this sentence.

Section 2.2.2 (pg 2-9): Dry fertilizer also can be band applied.

Section 2.3.1 (pg 2-15): In Section 6.2.1.3 manures are mentioned and should be mentioned here.

Section 2.3.2.1 (pg 2-17): Probably need to identify the chemical formula here.

Section 2.3.2.1 (pg 2-17): "photosynthetic" probably works better here.

Section 2.3.2.1 (pg 2-20): Several changes/corrections have been made to these sections.

Section 2.3.2.2 (pg 2-21): This section is poorly written and somewhat inaccurate. The attached page 2-21a should be inserted.

Section 2.3.2.3 (pg 2-21): This section also has numerous inaccuracies and is not well organized. Many of the sentences and paragraphs have been rewritten. One paragraph (pg. 2-22) needs to be moved to Section 2.3.2.4.

Section 2.3.2.4 (pg 2-22): This section has been rewritten.

Section 2.3.2.5 (pg 2-23): This section has been rewritten. Replace with attached pages 2-23a-b.

Section 2.4 (pg 2-23/24): This section has been rewritten. Replace with attached page 2-23b.

Section 3.5.1 (pg 3-11): Standard soil moisture content is always defined on an oven dry weight basis.

Section 4.2.1 (pg 4-15): The last sentence on this page is extremely important and should be highlighted by using a **boldface** font.

Section 4.3.2 (pg 4-18): Table 4-5 should incorporate the range of values contained in the mean. See Table 6.2.1-2 for specific change.

Section 6.2.1.3 (pg 3): The implication that fertilizer represent the only source of emissions is not correct. Thus, I have added the word nutrients an manures at appropriate places.

The Table numbers stated in the 3rd paragraph should be changed.

Statement concerning the need for addition research on heavy metal particulates from fertilizers and manures should be added.

The document needs a precautionary statement regarding the extremely limited and highly variable data found in Tables 6.2.1-2 and 6.2.1-3, and how this affects the usefulness and reliability of the data.

Section 6.2.1.3 (pg 7): The data for N_2O emission of for urea should be 3.98.

To give the reader the appropriate perspective on the high variance in the data, I suggest including the range in the data and the number of data points included in the mean. See page 6.2.1-7a for example change.

Thank you for the opportunity to review this document. Please don't hesitate to call me for more information.

Sincerely,

John Havlin

John L. Havlin
Associate Professor