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AN INVENTORY OF NITRIC OXIDE EMISSIONS FROM SOILS IN THE UNITED STATES

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Abstract. A national inventory of soil nitric oxide (NO) emissions with county spatial resolution and monthly time resolution has been developed from empirical relationships that were derived from soil NO emissions data. The empirical relationships used to develop the inventory relate the emission of NO to soil temperature and a factor which is representative of an ecosystem or type of land use. Most of the ecosystem/land use factors were derived from analyses of NO emission data from seven different sites in the United States that are representative of three ecosystems and two agricultural land use types. Other agricultural (crop) land use factors were estimated from the two calculated factors based on differences in fertilization associated with the crops. This soil emission inventory exhibits three general features. First, croplands, especially where corn is grown, appear to be significant sources of NO. This has important implications because agricultural activities tend to be localized to certain regions in the United States (i.e., the Midwest) and are highest during the summer, when photochemistry is also most active. Second, undisturbed areas, such as grasslands, forests, and wetlands, do not appear to contribute substantially to atmospheric NO. Third, extensive areas in the western United States have not been included because soil NO emission data are lacking.

1. Introduction

Because ozone photochemistry is inextricably linked to that of the oxides of nitrogen ($\text{NO} + \text{NO}_2 = \text{NO}_x$), it is important to understand the chemistry and the budget of NO_x . With respect to the latter, the sources of these compounds are of much interest. It is well known that the most intense sources of NO_x are those of anthropogenic origin, principally the combustion-related activities of energy production and transportation [Logan, 1983]. These sources, however, are generally confined to small geographic areas and can be reasonably well quantified. On the other hand, natural sources, principally lightning and emission from soils, are more widespread and less intense which makes quantitative estimation much more difficult. However, it is becoming increasingly evident that emission from soils may be a more significant source of atmospheric NO_x than previously thought. Earlier estimates [Logan, 1983] did not indicate seasonal or spatial variability because results were available from only one study from pasture land in Australia [Galbally and Roy, 1978]. More recent measurements at a variety of locations around the globe [Anderson and Levine, 1986; Johansson et al., 1988; Johansson and Sanhueza, 1988; Kaplan et al., 1988; Slemr and Seiler, 1984; Williams et al., 1987, 1988; Williams and Fehsenfeld, 1991] have shown that soil emissions not only can be highly variable on both spatial and temporal scales but also can be quite substantial. Consequently, any estimates of this source which require

extrapolation to large regions, such as continental or global scales, must account for this variability. This is especially true for photochemical modeling of the atmosphere. For example, in rural areas where the man-made source of NO_x is small, emission of the oxides of nitrogen from soil may be the dominant local source of NO_x and thereby have significant impact on local or regional photochemistry since the production rate of ozone is a strong function of the NO_x levels [Liu et al., 1987; Lin et al., 1988]. Atmospheric models which represent the soil source as homogeneous in space and time will not be able to reproduce such effects.

Recently, Williams and Fehsenfeld [1991] have summarized soil emission data from a variety of sources and have noted trends based on land use type. For example, emissions of NO from grassland soils (including temperate grasslands, chaparral, and tropical savannas) are typically an order of magnitude greater than emissions from temperate forest soils, while the variability of emissions within each type of biome is approximately a factor of 3. A similar distinction can be seen in data from forests and wetlands, with the latter emission rate much smaller than the former. Furthermore, it is apparent that emission of NO from agricultural soils can be considerably greater than that of natural or undisturbed soils. Data from Johansson and Granat [1984], Johansson [1984], Slemr and Seiler [1984], Anderson and Levine [1987], Williams et al. [1988], Shepherd et al. [1991], and G. L. Hutchinson and E. A. Brams (NO versus N_2O emissions from an NH_4^+ amended Bermuda grass pasture, submitted to *Journal of Geophysical Research*, 1992) (hereinafter referred to as Hutchinson and Brams, submitted manuscript, 1992) have shown that emissions from highly fertilized soils can approach emission levels of urban areas when compared on a per unit area basis. Also, an exponential dependence of soil NO emissions on soil temperature over the range 15°-35°C has been noted that appears to be reasonably consistent across many land use types [Williams and Fehsenfeld, 1991]. This temperature dependence, approximately a factor of 2 increase in flux per 10° increase in soil temperature, indicates that NO emissions from soils can exhibit considerable diurnal and seasonal variation. Thus the combination of strong spatial and temporal variability can induce large uncertainties in the estimation of soil NO emissions.

While the large spatial and temporal variability in soil emission may appear to be impediments to the estimation of the flux of NO, the apparent "stratification" of flux across land use types can be used to provide data structures from which more accurate estimates of regional or larger-scale emissions can be made. These structures in the soil NO emission data can be used in conjunction with data bases containing ecological and climatological data to provide emission estimates that more accurately reflect spatial and temporal variability. More importantly, these structures are convenient vehicles for incorporation of soil NO emissions into photochemical models since these models already incorporate land use type classification schemes. The temperature dependence of flux as well can be utilized by many atmospheric models since air temperature, if not soil temperature, is a modeled parameter. The purpose of this paper is to describe an inventory of NO emissions from soils in the United States using the above mentioned structures in the data sets that we have obtained from measurements over a 4-year period. This inventory has been developed from emission algorithms that are functions of soil temperature and land use type. The land use scheme is

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based on a coarse-scale segregation of land into natural and agricultural types with further subdivisions based on biome (for natural areas) and fertilizer usage (for agricultural areas). Results from the inventory calculations are in good general agreement not only with our data but also with that of others.

2. Approach

2.1. Emission Parameterization

It is now widely accepted that the emission of NO from soils is a result of the processing of nitrogen-containing nutrients by soil microbes where the principal process pathways are known as nitrification and denitrification. From the stand point of global change or regional air-quality modeling the long-range goal is to capture soil emission of NO_x in terms of the basic bio-physical and biochemical processes that control this emission. Models which are based on these mechanisms would be, of course, capable of providing the most detailed spatial and temporal resolution for the emissions. However, the soil microbial system is quite complex, and our knowledge of these processes is very rudimentary; thus modeling the emission of NO from soil in terms of these processes is beyond the present state of the art [Galbally, 1989; Firestone and Davidson, 1989].

For these reasons, models based on empirical relationships observed in large data sets are alternatives. By their nature these empirical relations, assembled into inventories, should be able to reproduce the observed NO emissions, at least on coarse scales. There are a number of soil parameters, such as temperature, moisture status, carbon and nitrogen availability, pH, composition, etc., that are observed to influence, presumably, the rates of the biological processes and hence the production (and uptake) of NO in soil. These physical and chemical parameters can also influence the emission of NO from soil via changes in physical properties of the soil and hence the ability of gases to diffuse through the soil environment. For example, high water content can cause the pores in soil to fill and prevent the diffusion and availability of gases such as O₂, which in turn regulates the principal soil N cycling processes [Haynes, 1986]. Thus formulation of an adequate empirical relation requires detailed information concerning the physical and chemical composition of the soils. However, input data to be used with these empirical relations to assemble inventories (for example, soil nitrate content or soil moisture level) may not be available for regions of interest or may be too transitory to be assembled into data bases. In this work we have attempted to parameterize the emission of NO from soil in terms of temperature and land use category, quantities that are reasonably well characterized regionally in the United States and at least approximately globally.

Soil temperature is an important controlling element because it can influence biological reaction rates and soil gas diffusion rates. On the basis of our previous measurements we conclude that the relationship between soil temperature and emission of NO is exponential within the soil temperature range 15°–35° C for a variety of measurement sites and corresponds to an approximate doubling of emission per 10° increase in temperature. The temperature relationship noted over the 15°–35° C range is quite similar to that seen in other laboratory and field studies where the so-called Q₁₀ values (change of rate per 10° temperature change) are approximately 2 [Galbally, 1989; Haynes, 1986, and references therein]. This temperature relationship is reasonably consistent over a wide variety of sites and provides the means to capture temporal variability in the soil emission data. The actual value of the factor used to relate the soil temperature to the emission was calculated from a weighted average of the slopes of the regression lines obtained from plots of the logarithm of emission versus soil temperature for the data sets listed in Table 1. This value is 0.071 (± 0.007, 1 sigma) °C⁻¹.

TABLE 1. Summary of Data Used for Algorithm Development

Site (Category)	Number of Data Points	Slope of ln(Flux) Versus Soil Temperature
Boulder, Colo. (grassland)	46	0.068 (0.020)
Nunn, Colo. (grassland)	43	0.056 (0.027)
Scotia, Pa. (forest)	32	0.040 (0.051)
Oak Ridge, Tenn. (forest)	52	0.13 (0.13)
North Inlet, S. C. (coastal marine)	30	0.052 (0.044)
Rock Springs, Pa. (corn field)	89	0.066 (0.051)
Rock Springs, Pa. (wheat field)	119	0.073 (0.011)
Laboratory study	5	0.073 (0.009)

Numbers in parentheses are standard deviations.

The general form of the emission algorithm used for this inventory is

$$\text{NO emission (ngNm}^{-2}\text{s}^{-1}) = A (\text{ngNm}^{-2}\text{s}^{-1}) \exp \{ (0.071 \pm 0.007 \text{ }^{\circ}\text{C}^{-1}) T_{\text{soil}} (^{\circ}\text{C}) \} \quad (1)$$

where A is a factor that is associated with the land use category. In principle, this quantity is related in a broad way to the NO flux determining physical and chemical properties, such as soil nutrient and moisture levels, of the soils in given regions. Calculation of the A factors was accomplished by taking the natural logarithm of both sides of (1) and rearranging to isolate ln(A). Soil temperature and NO flux data from each site were then used to calculate the average of ln(A). If there was more than one site per land use category, the arithmetic mean of the ln(A) values was determined and the antilog of this value reported. The use of logarithms was necessary because the distribution of [ln(NO flux)] is more nearly Gaussian than is [NO flux] (E. J. Williams et al., unpublished manuscript, 1992), and this reduces the influence of extreme values of NO emission on the determination of A.

Because the climatological data base used for compilation of this inventory contains air temperature and not soil temperature, conversion routines were needed. The relationship of air temperature to soil temperature depends on a number of factors. Solar insolation, cloud cover, vegetative canopy cover, and physical and chemical status of the soil all contribute to the manner in which the soil temperature changes to variations in the atmosphere above it [Pikul, 1991]. In some cases, such as grasslands and deserts, there can be substantial deviation between the two temperatures, and in other cases, such as in forests, the temperatures can track each other closely throughout the diurnal cycle [Williams and Fehsenfeld, 1991]. Further, in the case of agricultural areas where the canopy increases substantially over the growing season, there can be sizable changes in the relationship between soil and air

TABLE 2. Emission Algorithm A Factors, Average Fertilizer Application Rates and Air-to-Soil Temperature Conversion Formulae for Land Use Categories

Land Use Type	A Factor, $\text{ngNm}^{-2}\text{s}^{-1}$	Fertilization Rate kgNha^{-1}	Estimated Soil Temperature
<u>Natural Areas</u>			
Grasslands	0.9	-----	$0.66 T_A + 8.8$
Forests	0.07	-----	$0.84 T_A + 3.6$
Wetlands	0.003	-----	$0.92 T_A + 4.4$
<u>Agricultural Areas</u>			
Corn	9	121 (13)	$0.72 T_A + 5.8$
Cotton	4	58 (5)	$1.03 T_A + 2.9$
Wheat	3	40 (9)	$1.03 T_A + 2.9$
Soybeans	0.2	3 (1)	$1.03 T_A + 2.9$

T_A : ambient air temperature ($^{\circ}\text{C}$). Numbers in parentheses are standard deviations.

temperatures over time scales of weeks or months. All of these considerations must be taken into account in order to obtain reasonable estimates of soil temperature from air temperature. In this work, linear least squares fits between air and soil temperature for each of the sites in our data set were calculated. Fits for similar sites were averaged together into the four categories shown in Table 2: grasslands, forests, wetlands, and agricultural areas.

The lack of a comprehensive soil nutrient and moisture data base was considered to be a more serious problem. The NO emissions recorded at the sites we visited are a strong function of these parameters. However, these parameters are essential in determining the ecosystems of an area and are therefore reflected, at least crudely, in the land use. Likewise, the data that were used to derive the algorithms are specific to sites that, in a broad sense, are representative of different ecosystems or land use categories. That there are definable differences among ecosystems is well known and widely accepted; that there are "representative" sites within ecosystems is a concept that is not so widely accepted [Matson et al., 1989]. However, there is no question that similarities exist in emission of NO from soils at sites in different parts of the globe but situated in similar ecosystems. As shown in the work by Williams and Fehsenfeld [1991], emission of NO from soils in grasslands are greater on average by an order of magnitude than emission from temperate forest soils which are greater on average by an order of magnitude than emission from coastal marine sites. Similarities such as these have also been noted for other emitted trace gases [Goodroad and Keeney, 1984]. Thus we employed an ecosystem or land use classification scheme to derive factors that could be used as surrogates to soil nutrient and moisture levels.

As noted above, in this work there are four broad land use categories (grasslands, temperate forests, coastal marine areas, and agricultural areas) for which different A factors and hence algorithms were derived. Algorithms for the undisturbed land use types were derived from data measured at the sites shown in Table 1 and have been broadened in scope to include most of the land use types of the Geocology Data Base [Olson et al., 1980]. Thus grasslands include both shortgrass and tallgrass prairies and steppes, and grazed and ungrazed pastures, but do not include more arid regions such as shrublands and deserts. Forests include all coniferous and deciduous forests regardless of elevation or climatic zone. The wetland category includes freshwater and saltwater areas even

though the algorithm was developed only from data measured at a coastal marine site. The agricultural areas were segregated by crop type and algorithms were developed from fertilizer usage. The 20-year (1970-1989) [Berry and Hargett, 1989] U.S. average level of fertilizer nitrogen applied to a crop regardless of fertilizer type or application method was assumed to be proportional to the average level of nutrients in the soil. Then, using the observed [Williams and Fehsenfeld, 1991] linear relationship between emission and soil nitrate, which was used as a surrogate for total soil nutrients, A factors for different crop types were derived via linear interpolation. A linear relationship between emission and applied fertilizer has also been reported by Shepherd et al. [1991]. Two reference points were initially defined: high emission and fertilizer levels associated with corn and low emission and fertilizer levels associated with soybeans, hay, and alfalfa. Both reference points were derived from data of Williams et al. [1988]. The wheat field data were used to derive an A factor that was used as a surrogate for the soybeans/hay/alfalfa category and not an A factor for wheat because at the time of these measurements the field had been recently harvested and no fertilizer had been applied for about 1 year. These conditions were more typical of soybean, hay, and alfalfa cultivation than of wheat. The A factor derived from the Williams et al. corn field data was associated with the annual average U.S. fertilizer application rate for all corn cultivation even though the actual fertilizer applied was a factor of 4 lower than the U.S. average. This was done because extrapolation of the derived A factor for corn at the lower fertilization rate to the annual U.S. average would have produced unreasonably high estimates of emission rates. Algorithms for four crop categories were derived: corn, cotton, wheat, and soybeans/hay/alfalfa; these were selected because fertilizer use data were available. The A factors derived by the above method and the average fertilizer application rates are shown in Table 2.

Clearly, as more data become available, improved algorithms can be developed. As noted earlier, arid regions, which are quite extensive in the United States (Table 3), are not represented in this inventory nor are many crop types. Not only are algorithms for additional areas possible but also they can be derived for finer-scale distinctions within biomes already represented, such as coniferous versus deciduous forests or saltwater versus fresh water wetlands, as data become available. This approach makes refinement and upgrading of the inventory straightforward.

TABLE 3. Area Coverage of Inventory Categories in the Conterminous United States

Category	Area, 10 ⁶ km ²	Percent
<u>Natural Areas</u>		
Coniferous forest	0.958	12.5
Deciduous forest	1.386	18.0
Grassland	0.937	12.2W
Wetland	0.352	4.6
Other natural*	1.565	20.4
<u>Agricultural Areas</u>		
Corn	0.300	3.9
Wheat	0.214	2.8
Soybean	0.554	7.2
Cotton	0.047	0.6
Other crops	0.406	5.3
<u>Urban Areas</u>		
	0.958	12.5
<u>Totals</u>		
Total land area	7.68	100.0
Total water area	0.15	
Total contiguous area	7.83	

Data are from Olson et al. [1980].

*Arid scrubland and desert.

2.2. Compilation of a U.S. National Emission Inventory

This inventory of NO emissions from soils in the United States was compiled from the algorithms described above and the data contained in the Geoecology Data Base of Olson et al. [1980]. The coupling of the data base and the algorithms was done with a computer software package called SAS (SAS Institute Incorporated, Cary, N.C.), which contains file management, data manipulation, statistical analysis, and graphics routines. The Geoecology Data Base contains

information on many ecological and climatological variables, such as soils, water resources, land use, vegetation, and meteorology, for the 3072 counties in the conterminous United States. The temporal resolution is dependent on the individual data files, and the data are generally current as of 1978. For the purposes of this inventory compilation, monthly mean temperature data were used to calculate mean monthly emission rates. The land use categories in the data base were combined into those described above: grasslands, forests (coniferous and deciduous), wetlands (saltwater and freshwater), and agricultural. For the last category the Geoecology Data Base lists 14 major crop types by yield. Crops in the inventory included corn, cotton, wheat, soybeans, hay, and alfalfa. Noninventoried crops were potatoes, barley, rice, peanuts, tobacco, oats, rye, and sorghum. Table 3 lists the surface area and percent coverage of each source category. The heading "other natural" includes noninventoried biomes, such as scrubland and deserts. We assumed that the average fertilizer application maintained the average soil nutrient level throughout the growing season, defined as May through August. This is a reasonable assumption for those crops, such as corn, that are fertilized more than once during the growing season. The assumption will produce an upper limit on emission from crop soils that are only fertilized once during the growing season. During the rest of the year all croplands were assumed to emit at the lowest agricultural rate (soybeans).

3. Discussion of the Inventory

The preceding sections have explained the approach that was used to develop an inventory of NO emissions from soils for the United States. In this section the inventory is presented. The discussion of the inventory is focused on the following points: (1) the areal coverage and contributions to emissions by land use category, (2) the uncertainties associated with the inventory compilation, and (3) comparison of this natural source to the anthropogenic source on regional scales as a function of season.

3.1. Inventory of Soil Emissions

The spatial coverages of the various soil categories in the United States are listed in Table 3. A summary of the soil emissions for the seasons from these soils is presented in Table 4. No emission algorithms are available for the categories of "other natural, other crops, and urban areas." As a consequence, there are no emissions estimates for these areas presented in Figure 1.

TABLE 4. Emission of NO by Category and Season (Thousands of Metric Tons of Nitrogen)

Source	Spring	Summer	Autumn	Winter	Annual
Grassland	20.2	35.0	22.0	12.1	89.3
Forests	3.71	6.65	4.11	1.83	16.3
Wetlands	0.012	0.021	0.013	0.007	0.053
Corn	26.6	107	1.59	0.338	136
Wheat	7.13	33.0	1.05	0.277	41.5
Soybeans	2.78	6.18	3.17	0.869	13.0
Cotton	3.36	14.1	0.388	0.171	18.0
Total	63.8	202	32.3	15.6	314

Spring: March, April, May; summer: June, July, Aug.; autumn: Sept. Oct., Nov.; winter: Dec., Jan., Feb.

Fig. 1. Percent contribution of each inventory source category to total emission and total area.

As expected, the biogenic emissions from the soils are highly seasonal. Annually approximately 85% of the total NO emissions occur in the spring and summer while only 15% occur in fall and winter. This generally reflects the exponential dependence that this source has on soil temperature. In addition, because the application of fertilizer to the agricultural lands is also seasonal, the seasonality of these emissions is even greater than that of the other categories.

The relative contributions to total emissions for the various land use categories compared to their relative area coverage is shown in Figure 1. The contributions to total emissions (on an annual basis) of the various soil categories in the United States are shown in Figure 1 by the lighter bars. In addition, the spatial coverages, as taken from Table 3, are shown by the darker bars. For all inventoried sources, approximately 66% of the total annual average emissions are accounted for by

agricultural soils, while natural or undisturbed land areas contribute about 34% annually. By far the dominant category for emissions is land cultivated in corn, which comprises only about 4% of the land area but accounts for over 40% of total emission. This is primarily due to the large amount of fertilizer added to this particular crop. In general, agricultural areas contribute a disproportionate amount to emissions in comparison to the areal extent of these lands. It is possible that the other crops not listed in this inventory will also contribute significantly to the total emission.

By contrast, soil emission of NO from nonagricultural areas accounts for only 34% of the total soil-emitted NO. In this category, grasslands account for a sizable percentage (28%) of total emissions and are the dominant source with respect to natural or undisturbed land areas. Forests soils are, at best, weak sources of NO. As indicated in Figure 1, the emissions from forest soils are less than 5% of the total even though forested lands constitute over 30% of the total U.S. land area. In addition, it should be noted that this estimate is an upper limit for the NO_x that escapes the forest. This is because the NO emitted at the surface may be (1) taken up by soils or vegetation and (2) rapidly oxidized to species such as NO₂, which are readily deposited to surfaces. In a modeling study which used data collected in a Brazilian tropical forest, Jacob and Bakwin [1991] determined that, diurnally averaged, only 25% of the NO emitted from the forest floor escaped into the atmosphere above the canopy. More vigorous ventilation of the canopy during the day increased the transported amount to 35%, while at night only 17% of the soil-derived NO escaped into the atmosphere above the canopy. Although most severe for forests, this effect will doubtless hold for all environments. Emissions from wetlands account for less than 0.1% of the total and are not visible on the figure. The category of "other natural" is made up principally of arid lands, such as deserts and scrublands, for which no data exist.

Johansson [1984] provided estimates of median annual emission rates of NO from various ecosystem types in order to estimate the soil emission source strength on a global basis. Using our data to calculate mean values, we find reasonable

Fig. 2. July-averaged emission of nitric oxide from U.S. soils in molecules of NO per square meter per second. The different emission levels are shown in the legend below the figure.

Fig. 3. January-averaged emission of nitric oxide from U.S. soils in molecules of NO per square meter per second. The different emission levels are shown in the legend below the figure.

agreement for temperate forest systems (5 mgNm⁻² [Johansson, 1984] versus 7 mgNm⁻² (this work)), about a factor of 2 difference for temperate grasslands (43 versus 95) and large disagreement for cultivated land (20 versus 187). The disagreement for agricultural land is not too surprising since the Johansson estimate was derived from emissions from unfertilized land. The only estimate of soil NO emissions from the United States is from Logan [1983] in which an average value of about 0.4 million metric tons is provided (range: 0.2 - 0.8). This is in reasonable agreement with the annual average of 0.3 million metric tons from this work.

The emission of NO from inventoried soil sources during a high-emission period, July, and a low-emission period, January, illustrates the variability in the emission distribution with season. The average of soil NO emissions for the month of July in the United States is shown in Figure 2. The emissions in this figure have been placed in bins that increase by an order of magnitude and the units are in molecules per square meter per second. The highest emission levels (in black) are associated with agricultural regions and, in general, correspond to major corn producing regions in Nebraska, Iowa, and Illinois. The cross-hatched regions generally encompass both agricultural areas and grasslands except in the eastern United States where grasslands are not nearly so extensive. Areas of horizontal bars generally correspond to forested regions and lower rates of emission. The regions of vertical bars and those in white are due either to very low emission rates associated with wetlands, principally in the east, or to the presence of a high proportion of noninventoried land, such as scrublands in the west.

The emission of NO from soils in the wintertime is substantially less than in summer, as indicated by Figure 3, which is a map similar to that in Figure 2 but for the month of January. It must be noted that the map of January emissions is somewhat speculative because the emission algorithms are defined for the temperature range 15°-35°C. Williams and Fehsenfeld [1991] note that the emission dependence on soil temperature is different for the range 0°-15°C, but data are available from only one site at these temperatures so a general relationship cannot be calculated. Nevertheless, even for soil temperatures as low as 2°C, emission from soil at the

grassland site near Boulder, Colorado, was almost 8×10^{12} molecules m⁻² s⁻¹ [Williams and Fehsenfeld, 1991]. If we assume that these values are representative (again, data are available from only one site), then the map shown in Figure 3 is probably a reasonable indication of emissions. The most striking differences are in the agricultural areas where the changes are typically from the highest emission levels to the lowest. Most of this effect is due to lower temperatures. However, in the case of agricultural fields there is also an effect from the reduced use of fertilizer after the growing season. This has been accounted for in the inventory by using the lowest emission algorithm (which corresponds to soybeans) for all crop types during the period between September and April. In most cases this assumption regarding fertilization is reasonable. The largest error from this assumption is probably in the case of wheat, which is grown year-round in many areas and may be subject to fertilization during the September to January period.

3.2. Sources of Error and Uncertainty

The major sources of uncertainty in the inventory arise from formulation of the algorithms and the land use and temperature data in the Geoecology Data Base. This includes the uncertainty associated with aggregation of similar, but not identical, land use types with those defined by the algorithms. The smallest source of uncertainty is that due to the uncertainty in the measurements of the NO emissions that were used to derive the algorithms. The error associated with the NO flux measurements is estimated to be approximately $\pm 30\%$. This uncertainty is small compared to either the natural variability in the emissions or the other sources of error listed below.

It is assumed that the temperature relationship in the algorithms for each soil category is universally applicable for each category. This assumption appears to be justified based on available data from field measurements of flux as well as the current understanding of the process gained from laboratory studies of NO production by bacteria. With regard to the temperature term, additional inaccuracy can result from the method used to convert ambient temperature to soil temperature. For the present inventory the uncertainty

associated with the temperature conversion is lowest in summer, the season when the data used to derive the conversion formulae were taken, and highest in winter. Taking these factors into account, we estimate the overall uncertainty resulting from the temperature term to be approximately $\pm 50\%$.

With regard to the preexponential factors (A factors) in the algorithms these were derived from data taken for each of the representative soil categories. These categories are broad generalizations of the many types of soils and soil conditions found in nature and represent a gross simplification of the complexity involved in emission processes. Although the emission rates predicted from these algorithms can reproduce the original data to better than 50% of the mean flux for any given site (and this provides a measure of the uncertainty of the A factors for these data), it is likely that this level of agreement would not be observed between predictions from these algorithms and data obtained at other sites. Clearly, the A factors derived from the measurements made on a soil in one location will introduce error when extrapolated to soils that are only broadly similar. The influence of such highly variable quantities such as soil moisture and nutrient levels which are known to play a direct role in shaping soil emission are not captured. This uncertainty is probably greatest for agricultural areas because of uncertainty associated with the parameterization of fertilization use and variability in fertilizer application rates.

It is apparent that the broad-based classification of the natural or undisturbed land use types can include areas for which a given A factor is not appropriate. For example, the inclusion of freshwater and saltwater wetland areas into a single category is not the most accurate way of representing these biomes and there may be substantial differences in emission rates between them. However, little inaccuracy in regional or larger-scale estimates of emissions will result because the emission rates from wetlands are very low and because wetlands do not account for a large percentage of total land area, at least in the United States (Figure 1). Similarly, while the total area of forests is much greater in extent than wetlands, emission rates from forest soils are low; moreover, it is not clear what percentage of the NO emitted from the soil will escape from the forest canopy into the planetary boundary layer air above. Thus even if emission rates from soils of different types of forests differ substantially, these emissions might not be significant with respect to other sources. On the other hand, grasslands represent a significant source with respect to local or regional NO_x input to the atmosphere because of the extent of these areas (Figure 1) and the magnitude of the emissions. Again, this estimation likely represents an upper limit since it is not known what percentage of NO emissions at the soil surface will be dispersed into the atmosphere above. Although it is possible that differences in emissions from grassland ecosystems (i.e., shortgrass versus tallgrass prairies) might be significant, data compiled by Williams and Fehsenfeld [1991] indicate that the broad-based categorization in this inventory will result in a level of uncertainty of the order of a factor of 3, while differences in emissions between biomes are of the order of a factor of 10. Thus it appears that these distinctions, though somewhat arbitrary, are realistic and can be used as a basis to distinguish among emission levels based on land use categories. For undisturbed land areas we estimate a level of uncertainty in derived A factors of a factor of 2, based on published results from other sites around the globe.

Uncertainty in the A factors for agricultural areas are somewhat more difficult to estimate. In addition to the uncertainty introduced by the interpolation process used to derive some of the factors, there is also uncertainty in the fertilizer application rate data because (1) application rates change from year to year and (2) different levels of nitrogen fertilizer may be applied to the same crop type in different regions of the country. We have made allowance for 1 above by using a 20-year average application rate. The variations in

these rates are indicated by the standard deviations of the average values shown in Table 2. With respect to 2 above we use the annual U.S. average application rates because county-level fertilizer application data are not available. Comparison of predicted values to results from studies of NO emissions from agricultural areas in Canada [Shepherd et al., 1991], Texas [Hutchinson and Brams, submitted manuscript, 1992], Sweden [Johansson and Granat, 1984], and Spain [Slemr and Seiler, 1984] allow us to estimate that the uncertainty associated with the A factors for agricultural areas is of the order of a factor of 2.

Finally, the other major uncertainty in the inventory is in the data from the Geoecology Data Base. The two facets of this are the land use data and the temperature data, and of these it is the former that will be the largest source of error. We use here the $\pm 15\%$ estimate of Lamb et al. [1987], which was based on the internal consistency of the Geoecology Data Base. Estimates [Berry and Hargett, 1989] of total acreage planted for the different crops in the inventory agree with the Geoecology data to about 10%. Overall, then, the uncertainty of the estimates from this inventory are dominated by potential errors in the A factors with smaller contributions from the temperature algorithms and the land use categorizations. Given this information, we estimate the total uncertainty level at a factor of 3. The emission ranges of the maps in Figures 2 and 3 (i.e., order of magnitude graduations) have been selected with this in mind.

3.3. Comparison of Soil and Commercial Industrial Emissions

There is no question that on an annual basis emissions of NO_x into the atmosphere above the United States are dominated by man-made sources. This point is illustrated by Figure 4. In this bar graph the seasonal distribution of anthropogenic NO_x versus soil NO emissions is presented in millions of metric tons of nitrogen. For this comparison the anthropogenic emission inventory of the National Acid Precipitation Assessment Program has been used. The anthropogenic emissions were compiled from the 1985 Environmental Protection Agency (EPA) estimates of point and area sources of NO_x in the continental United States. On an annual basis the soil source is only 6% that of the man-made sources. However, because of the seasonality of emission of NO from soils and the virtual complete lack of such seasonality of the anthropogenic emissions, the soil source becomes more important in summer, amounting to about 14% of anthropogenic sources for the entire United States.

Fig. 4. Comparison of seasonally averaged soil NO emissions to commercial/industrial NO emissions in millions of metric tons of nitrogen. Note that the anthropogenic emissions are divided by a factor of 10.

Fig. 5. Anthropogenic point and area source emissions of NO for an average day in July in molecules of NO per square meter per second. The different emission levels are shown in the legend below the figure.

The soil source can be even more important during the summer when smaller spatial scales in certain regions are considered. Of most significance are the regions shown in black in Figure 2. In these areas, which have high agricultural activities and where large amounts of nitrogen-containing fertilizer are used, the soil emissions of NO may significantly impact local and, possibly, regional levels of atmospheric NO_x mixing ratios. The contrast between the spatial distributions of NO emissions from soil compared with industrial/commercial sources can be seen in the differences between the distributions shown in Figure 2 for the July soil emissions and Figure 5 for the average commercial/industrial emissions, also for July. Most of the eastern portion of the United States is dominated by anthropogenic NO_x emissions. Clearly, though, the agricultural regions of the northern midsection of the country are areas of nonnegligible soil emissions of NO. Specifically, the soil source in a few midwestern states can be a substantial fraction of the anthropogenic source and, in some cases, can even exceed it. This point is illustrated in Table 5, which contrasts the soil emissions and the anthropogenic emissions for summer in several states that have a high level of agricultural activity. Clearly, for states such as Iowa, Nebraska, and South Dakota the emission of NO from soils are an important fraction of total emissions. Since agricultural activities are at a maximum when photochemical activity is at a maximum, this has important consequences in terms of regional ozone production and acid deposition. Finally, since the anthropogenic sources change very little seasonally, the man-made emissions in winter will dominate total NO_x emissions in all areas.

4. Conclusions

The inventory of soil NO emissions presented here is the first to include terms to account for spatial and temporal variability on a large scale. Overall for a given region, the estimated seasonally averaged soil emission provided by the inventory is expected to be reliable within an uncertainty range

of a factor of 3 (lower or higher). In its present form the inventory will be most useful in defining those regions of the United States where soil emissions may represent a significant input of NO into the atmosphere in comparison with anthropogenic sources.

There are some obvious deficiencies. Foremost is the lack of emissions data from soils in the continental United States with which to compare the estimates from the inventory. While results are available from similar sites on other continents, differences in climate, soil types, vegetation, etc. may make realistic comparisons difficult. Ideally, predictions for a specific site should be compared to data from that site and any disagreement between them used to identify other important factors that could be used to refine the algorithms. We have identified soil moisture as one such factor, but more data are needed to determine the systematic effects so that it can be modelled. Doubtless, there are other such factors which

TABLE 5. Comparison of Summertime Soil Versus Commercial/Industrial NO_x Emissions (Thousands of Metric Tons of Nitrogen)

State	Soil	Commercial/ Industrial	Soil: Commercial/ Industrial
Illinois	17.2	66.9	0.26
Indiana	9.2	61.9	0.15
Iowa	18.4	18.6	0.99
Kansas	12.8	29.6	0.43
Minnesota	9.9	24.8	0.40
Nebraska	15.4	11.5	1.34
South Dakota	9.8	5.1	1.92
Texas	16.5	176	0.09

will improve the predictive capacity when incorporated into the algorithms.

The approach that has been presented here also has certain benefits. These algorithms can easily be incorporated into photochemical models of the atmosphere and provide a much more realistic estimate of the soil source of NO than the use of a single estimated value. The algorithms can conveniently be upgraded as other important factors are identified and modeled. Also, the scope of the algorithms can be expanded as soil emission data from other land use types become available. Thus it becomes apparent that this approach can be used not only for a United States inventory but also for one on a global scale.

It is expected that the information presented here will be principally used by the atmospheric chemistry community or those who are concerned with the redistribution of biospheric NO_x. This inventory indicates that soil emissions may play a major role in establishing the atmospheric burden of NO_x in the atmosphere in certain regions or in the redistribution of biospheric fixed nitrogen. In using this inventory, however, it must be recognized that the enclosure measurements, which were used to generate the data base for the algorithm development, measure the gross flux of NO from soils. Once this NO enters the atmosphere, it is rapidly converted to NO₂ and other reactive nitrogen oxides that are more rapidly deposited to the surface than is NO. It is therefore not obvious that the majority of the NO that is emitted from the surface survives in the atmosphere sufficiently long to influence the atmospheric chemistry or to participate in redistribution of biospheric nitrogen. Therefore it is important to make measurements to determine the net flux of soil-emitted NO from the near surface boundary layer.

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References

- Anderson, I. C., and J. S. Levine, Relative rates of nitric oxide and nitrous oxide production by nitrifiers, denitrifiers and nitrate respirers, *Appl. Environ. Microbiol.*, **51**, 938-945, 1986.
- Anderson, I. C., and J. S. Levine, Simultaneous field measurements of biogenic emissions of nitric oxide and nitrous oxide, *J. Geophys. Res.*, **92**, 965-976, 1987.
- Berry, J. T., and N. L. Hargett, *Fertilizer data summary*, *Bull. Y-209* and supplement, Natl. Fertilizer Dev. Cent., Tenn. Valley Authority, Muscle Shoals, Alabama, May, 1989.
- Firestone, M. K., and E. A. Davidson, Microbiological basis of NO and N₂O production and consumption in soil, in *Exchange of Trace Gases Between Terrestrial Ecosystems and the Atmosphere*, edited by M. O. Andreae and D. S. Schimel, pp. 7-21, Wiley-Interscience, New York, 1989.
- Galbally, I. E., Factors controlling NO_x emissions from soils, in *Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere*, edited by M. O. Andreae and D. S. Schimel, pp. 23-38, Wiley-Interscience, New York, 1989.
- Galbally, I. E., and C. R. Roy, Loss of fixed nitrogen from soils by nitric oxide exhalation, *Nature*, **275**, 734-735, 1978.
- Goodroad, L. L., and D. R. Keeney, Nitrous oxide emission from forest, marsh, and prairie ecosystems, *J. Environ. Qual.*, **13**, 448-452, 1984.
- Haynes, R. J. (Ed.), *Mineral Nitrogen and the Plant-Soil System*, pp. 242-302, Academic, San Diego, Calif., 1986.
- Jacob, D. J., and P. S. Bakwin, Cycling of NO_x in tropical forest canopies, in *Microbial Production and Consumption of Greenhouse Gases: Methane, Nitrogen Oxides, and Halomethanes*, edited by J. E. Rogers and W. B. Whitman, pp. 237-253, American Society for Microbiology, Washington, D.C., 1991.
- Johansson, C., Field measurements of emission of nitric oxide from fertilized and unfertilized forest soils in Sweden, *J. Atmos. Chem.*, **1**, 429-442, 1984.
- Johansson, C., and L. Granat, Emission of nitric oxide from arable land, *Tellus*, **36B**, 25-37, 1984.
- Johansson, C., and E. Sanheuz, Emission of NO from savanna soils during rainy season, *J. Geophys. Res.*, **93**, 14,193-14,198, 1988.
- Johansson, C., H. Rodhe, and E. Sanheuz, Emission of NO in a tropical savanna and cloud forest during the dry season, *J. Geophys. Res.*, **93**, 7180-7192, 1988.
- Kaplan, W. A., S. C. Wofsy, M. Keller, and J. M. da Costa, Emission of NO and deposition of O₃ in a tropical forest system, *J. Geophys. Res.*, **93**, 1389-1395, 1988.
- Lamb, B., A. Guenther, D. Gay, and H. Westberg, A national inventory of biogenic hydrocarbon emissions, *Atmos. Environ.*, **21**, 1695-1705, 1987.
- Lin, X., M. Trainer, and S. C. Liu, On the nonlinearity of the tropospheric ozone production, *J. Geophys. Res.*, **93**, 15,879-15,888, 1988.
- Liu, S. C., M. Trainer, F. C. Fehsenfeld, D. D. Parrish, E. J. Williams, D. W. Fahey, G. Hübler, and P. C. Murphy, Ozone production in the rural troposphere and the implications for regional and global ozone distributions, *J. Geophys. Res.*, **92**, 4191-4207, 1987.
- Logan, J. A., Nitrogen oxides in the troposphere: Global and regional budgets, *J. Geophys. Res.*, **88**, 10,785-10,807, 1983.
- Matson, P. A., P. M. Vitousek, and D. S. Schimel, Regional extrapolation of trace gas flux based on soils and ecosystems, in *Exchange of Trace Gases Between Terrestrial Ecosystems and the Atmosphere*, edited by M. O. Andreae and D. S. Schimel, pp. 97-108, Wiley-Interscience, New York, 1989.
- Olson, R. J., C. J. Emerson, and M. K. Nungesser, Geocology: A county-level environmental data base for the conterminous United States, *Rep. ORNL/TM-7351*, 350 pp., Oak Ridge Nat. Lab., Oak Ridge, Tenn., 1980.
- Pikul, J. L., Jr., Estimating soil surface temperature from meteorological data, *Soil Sci.*, **151**, 187-195, 1991.
- Shepherd, M. F., S. Barzetti, and D. R. Hastie, The production of atmospheric NO_x and N₂O from a fertilized agricultural soil, *Atmos. Environ.*, **25A**, 1961-1969, 1991.
- Slemr, F., and W. Seiler, Field measurements of NO and NO₂ emissions from fertilized and unfertilized soils, *J. Atmos. Chem.*, **2**, 1-24, 1984.
- Williams, E. J., and F. C. Fehsenfeld, Measurement of soil nitrogen oxide emissions at three North American ecosystems, *J. Geophys. Res.*, **96**, 1033-1042, 1991.
- Williams, E. J., D. D. Parrish, and F. C. Fehsenfeld, Determination of nitrogen oxide emissions from soils: Results from a grassland site in Colorado, United States, *J. Geophys. Res.*, **92**, 2173-2179, 1987.
- Williams, E. J., D. D. Parrish, M. P. Buhr, and F. C. Fehsenfeld, Measurement of soil NO_x emissions in central Pennsylvania, *J. Geophys. Res.*, **93**, 9539-9546, 1988.
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