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NO_x AND N_2O EMISSIONS FROM SOIL

E. J. Williams[1]

Aeronomy Laboratory, National Atmospheric and Oceanic Administration, Boulder, Colorado

G. L. Hutchinson

U.S. Department of Agriculture, Agricultural Research Service, Fort Collins, Colorado

F. C. Fehsenfeld[1]

Aeronomy Laboratory, National Atmospheric and Oceanic Administration, Boulder, Colorado

Abstract. Emission of NO_x (principally NO) and N_2O from soils is reviewed with particular emphasis placed on the atmospheric and ecological implications of this source. The photochemistry of these species in the atmosphere is summarized as well as the methods available for the determination of fluxes. Processes which produce and consume both NO and N_2O in soils are principally microbiological in nature and are linked directly and indirectly with the chemical and physical factors that control gaseous transport through the soil medium. Linkages among these processes occur over many different temporal and spatial scales which makes interpretation of the available data difficult. A summary of results from laboratory and field studies shows that considerable spatial and temporal variability exists in the emissions. This variability can be related to factors such as temperature, water content, soil composition, nutrient availability, vegetation, disturbances (e.g., burning, agricultural practices), and others. Because NO_x and N_2O play central roles in many important environmental problems, there is a need for accurate estimates of the magnitude of the soil source, but the large degree of variability in the existing data makes extrapolation highly uncertain. To overcome this uncertainty, models are required which can simulate the processes responsible for production, consumption, and transport of these species at all relevant temporal and spatial scales. Integrated field studies will also be required to validate the model results.

[1]Also at Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder.

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1. INTRODUCTION

Numerous articles in both the popular and technical press reflect increasing public and scientific concern regarding not only the prospect for global climate change but also additional potential health and environmental effects of changing atmospheric trace gas concentrations. Among the trace gases of greatest concern, nitrous oxide (N_2O) and nitric oxide/nitrogen dioxide ($NO + NO_2 = NO_x$) are directly or indirectly involved in atmospheric warming, as well as the production and consumption of atmospheric oxidants such as ozone (O_3) and hydroxyl radical (OH), and the photochemical formation of nitric acid (HNO_3), which is the fastest-growing component of acidic deposition. Natural sources of N_2O and NO_x established the background atmospheric concentrations of these two gases that anthropogenic activities are now perturbing.

For NO_x, five natural sources have been identified, lightning, microbial processes in soil, oxidation of atmospheric ammonia (NH_3), stratospheric injection, and photolytic processes in the oceans. The characteristics and magnitudes of each of these sources have been summarized in several recent review articles [Crutzen, 1983; Ehhalt and Drummond, 1982; Homolya and Robinson, 1984; Logan, 1983; Placet and Streets, 1987; Stedman and Shetter, 1983]. Despite considerable disagreement regarding the magnitude of biogenic production of NO in soil, all these reviews agree that the process represents a significant source of global atmospheric NO_x. For example, Logan [1983] calculated that microbial activity in soil contributes 4 to 16 Tg N (teragram (Tg) = 10^{12} g) to the global NO_x budget, equal to and perhaps greater than the lightning source, and much larger than the other three natural sources listed above. Using additional, more recent data, Davidson [1991] estimated the global soil NO source to be ~20 Tg N yr^{-1}. He noted that his estimate was dominated by emissions from three savanna sites all in the same country; thus it is not only subject to downward

revision once more savanna sites are studied but also subject to upward revision because arid regions and deserts have not been sampled and were not included in the calculation. This more current estimate is comparable to the 21 Tg N yr^{-1} estimated for global energy-related combustion emissions quoted by Logan [1983] and is much larger than the 12 Tg N yr^{-1} estimate of emissions from biomass burning. Thus the soil source of NO_x may represent as much as 40% of the global NO_x budget (range: 25-99 Tg N yr^{-1}) [Logan, 1983]. Conrad [1990] recently discussed these points in a review of soil NO_x flux.

Clearly, soil NO emissions contribute substantially to atmospheric NO_x; yet characterization of the soil source has been difficult because of the extreme variability of the emissions in space and time. Further, because of the reactivity of NO_x the impact of the soil source on tropospheric photochemistry (e.g., enhanced oxidant formation) tends to be more local or regional, thus estimates of large-scale source strengths may not accurately reflect smaller-scale impacts. For example, a recent inventory of soil NO emissions for the United States [Williams et al., 1992] indicated that, during summer, the soil source is at most 14% of total combustion sources. However, for some rural agricultural areas in the United States, the soil source can be much greater than combustion-related emissions. This level of variability is also present at smaller scales and represents a significant challenge to understanding and predicting soil NO_x exchange. A major objective of this review is to describe the progress that has been made in the characterization of the soil source of NO and to underscore the uncertainties that remain.

The relatively long atmospheric lifetime of N_2O (150 years [Hao et al., 1987] 110 years [Ko et al., 1991]) and the smaller number of important natural sources of this gas, has made it possible to establish with somewhat greater certainty both the magnitude of the total global source of this gas, as well as the fraction of the total represented by microbial activity in soil. McElroy and Wofsy [1986] estimated the former to be about 15 Tg N yr^{-1} and the latter to be greater than one half. The estimated 4 Tg N_2O-N that is produced each year by combustion of fossil fuels nearly matched the amount required to support the observed 0.2-0.3% annual growth rate of atmospheric N_2O over the past few decades [Prinn et al., 1990; Rasmussen and Khalil, 1986], so a cause-and-effect relationship was generally assumed. Recently, though, the magnitude of the combustion source was reduced by more than a factor of 10 due to discovery of an artifact in flask sampling procedures [Muzio and Kramlich, 1988], thus renewing interest in the possibility of an enhanced biogenic source. However, based on a comprehensive analysis of recent measurements from tropical terrestrial ecosystems, Matson and Vitousek [1990] found that the estimated magnitude of this biogenic N_2O source must also be reduced 3-4 Tg from the 7.4 Tg N yr^{-1} reported by McElroy and Wofsy [1986], further upsetting the near balance between known sources and sinks. Finally, if the more recent shorter lifetime estimate of 110 years is indeed correct, then the total source strength for N_2O must be increased [Ko et al., 1991].

Eichner [1990] recently compared the N_2O emission rates of N-fertilized and unfertilized agricultural soils across the United States; Sahrawat and Keeney [1986] and Yoshinari [1990] gave more general reviews of soil N_2O emission rates and processes; and the Intergovernmental Panel on Climate Change (IPCC) report [1990] summarized the present state of knowledge regarding the relative importance of all terrestrial, aquatic, and atmospheric N_2O sources and sinks. Because these reviews are current, soil N_2O emissions will not be covered here with the same rigor as soil NO_x emissions; nevertheless, the topic is included to facilitate discussion of the many similarities between the biogenic sources of these trace gases. When NO_x emissions were reviewed by the authors cited earlier, the literature contained few soil NO emissions data, but since then soil emission of NO_x has been measured from several different ecosystem types under a variety of soil and climatic conditions around the world (cf. references associated with Table 1, below). The results of these studies will be critically reviewed and incorporated into revised estimates of the importance of soil NO_x exchange to current issues involving atmospheric trace gases.

In the first section below we place soil NO_x and N_2O emissions in perspective by providing a brief summary of the chemistry of these compounds in the atmosphere. So that available field and laboratory soil NO_x and N_2O exchange data can be discussed at the process level, we then describe present understanding of the basic chemical and biological processes responsible for production and consumption of the two gases in soil, as well as techniques for measuring their exchange with the atmosphere. Then, after summarizing the available data and analyzing the influence of known soil and environmental controllers on the exchange rates, we discuss approaches to modeling the emission of these trace gases from soil. Finally, we present some speculation regarding the ecological implications of these processes.

2. ATMOSPHERIC CHEMISTRY OF NO_x AND N_2O

2.1. *Nitric Oxide/Nitrogen Dioxide (NO_x)*

Nitric oxide participates actively in atmospheric chemistry. The principal end product of this chemistry, HNO_3, is incorporated rapidly by aerosols, cloud water, and rain and then lost from the atmosphere by wet and dry deposition. For this reason the lifetime of the oxides of nitrogen (NO_x = NO + NO_2) in the atmosphere is short; consequently, NO_x emitted at the surface does not reach the stratosphere. However, within the troposphere NO_x (1) is important in regulating the concentration of the principal oxidizing agent in the atmosphere, the hydroxyl radical (OH); (2) is central in the photochemical production of O_3, which not only is a radiatively important trace species but also is an important secondary pollutant and a precursor of OH; and (3) is the precursor of HNO_3, which is one of the principal components of acid deposition [Chameides and Walker, 1973; Cox, 1988; Crutzen, 1973, 1988; Fishman and Crutzen, 1978; Liu et al., 1987].

When NO enters the atmosphere it reacts rapidly with ozone to form nitrogen dioxide,

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (1)$$

Although O_3 is lost when it reacts with NO, the NO_2 that is formed photodissociates during the daytime to reform O_3,

TABLE 1. Comparison of NO Emissions From a Variety of Land Areas

Land Use Category	Flux, ngN/m²/s Mean	Range	Reference
Agricultural Fields			
Recently fertilized			
Bermuda grass (Texas, 0-9 weeks)	44	13-186	Hutchinson and Brams [1992]
Beans (Canada, 0-5 mos.)	25	0.42-162	Shepherd et al. [1991]
Corn (Pennsylvania, one month)	94	1.6-338	Williams et al. [1988]
Corn (Virginia, 5-30 days)	25	6-67	Anderson and Levine [1987]
Barley/grass ley (Sweden, 0-14 days)	10	0.1-62	Johansson and Granat [1984]
Unplanted field (Spain, 0-20 days)	52.6	2.2-203	Slemr and Seiler [1984]
Not recently fertilized			
Bermuda grass (Texas)	13	1-71	Hutchinson and Brams [1992]
Beans (Canada, 19 years)	---	0.42-11.6	Shepherd et al. [1991]
Wheat (Pennsylvania, one year)	1.2	0.21-3.8	Williams et al. [1988]
Soybeans (Virginia, three months)	4	0.7-9.4	Anderson and Levine [1987]
Wheat (Colorado, July, one year)	2	0.001-6.1	Anderson and Levine [1987]
Wheat (Colorado, July, irrigated, one year)	10	2.4-16.0	Anderson and Levine [1987]
Wheat (Colorado, May, one year)	2.8	0.8-5.0	Anderson and Levine [1987]
Barley/lucerne (Sweden)	3.5	0.1-17	Johansson and Granat [1984]
Bare soil (Spain, ten months)	8.8	-2.2-107	Slemr and Seiler [1984]
Unforested Areas			
Grassland, pastures, meadows			
Pasture (Mexico, upland, dry season)	0.25	---	Davidson et al. [1991]
Pasture (Mexico, floodplain, dry season)	9.9	---	Davidson et al. [1991]
Pasture (Mexico, upland, wet season)	28.6	---	Davidson et al. [1991]
Pasture (Mexico, floodplain, wet season)	25.6	---	Davidson et al. [1991]
Grassland (Colorado, grazed)	10.0	1.15-52.9	Williams and Fehsenfeld [1991]
Grass (Illinois)	---	1.4-4.2	Wesely et al. [1989]
Grass (Virginia)	3	0.003-9.0	Anderson and Levine [1987]
Pasture (United Kingdom, urine-treated)	12	0.53	Colbourne et al. [1987]
Pasture (United Kingdom, untreated)	0.5	neg.-7.2	Colbourne et al. [1987]
Grassland (Colorado, Aug.-Nov.)	3.0	0.028-65	Williams et al. [1987]
Crested wheat grass (Colorado)	9	-9-26	Delany et al. (1986)
Grassland (Australia, grazed)	---	0.6-124	Galbally et al. [1985]
Bare soil (Germany)	2.2	-5.8-14.2	Slemr and Seiler [1984]
Pasture (Australia)	1.6	0.6-2.6	Galbally and Roy [1978]
Pasture (Australia, grazed)	3.5	1.5-7.3	Galbally and Roy [1978]
Savanna/chaparral (arid/semi-arid)			
Savanna (Venezuela, rainy season)	0.64	0.07-0.70	Sanhueza et al. [1990]
Savanna (Venezuela, dry season)	8	3-15	Johansson et al. [1988]
Savanna (Venezuela, rainy season)	56	2-250	Johansson and Sanhueza [1988]
Chaparral (California, burned, wet/dry)	31	6-101	Anderson et al. [1988]
Chaparral (California, burned, wet/dry)	27	---	Levine et al. [1988]
Chaparral (California, unburned, wet/dry)	13	0-35	Anderson et al. [1988]
Chaparral (California, unburned, wet/dry)	13	---	Levine et al. [1988]
Forests			
Temperate forests			
Deciduous forest (Tennessee)	0.28	0.056-1.12	Williams and Fehsenfeld [1991]
Forest clearing (Pennsylvania)	1.2	0.18-4.1	Williams et al. [1988]
Coniferous forest (Sweden)	0.4	0.1-0.8	Johansson [1984]
Tropical forests			
Forest (Mexico, upland, dry season)	0.92	---	Davidson et al. [1991]
Forest (Mexico, upland, wet season)	2.78	---	Davidson et al. [1991]
Semideciduous forest (Venezuela)	0.51	---	Sanhueza et al. [1990]
Tropical rain forest (Brazil)	2.1 (clay)	---	Bakwin et al. [1990a]
Tropical rain forest (Brazil)	7.8 (sand)	---	Bakwin et al. [1990a]
Tropical evergreen rain forest (Brazil)	10.2	9.2-16	Kaplan et al. [1988]
Tropical cloud forest (Venezuela)	---	0.1-2	Johansson et al. [1988]

TABLE 1. (continued)

Land Use Category	Flux, ngN/m²/s Mean	Range	Reference
	Other		
Tidal marsh (South Carolina)	0.034	0-0.085	Williams and Fehsenfeld [1991]
Wetlands (florida, 3 sites, unburned)	0.12	---	Levine et al. [1990]
Wetlands (Florida, 3 sites, burned)	0.58	---	Levine et al. [1990]
Temperate flooded rice field (Australia)	---	0.2-0.95	Galbally et al. [1987]

$$NO_2 + h\nu \rightarrow O(^3P) + NO \quad (2)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \quad (3)$$

These reactions typically proceed rapidly during daytime and, after a few minutes of exposure to sunlight, atmospheric NO, NO_2, and O_3 concentrations equilibrate yielding a photostationary state. Consequently, in the absence of other processes, the continued occurrence of reactions (1)-(3) leads to no further net ozone production or loss for a given sunlight intensity. Because of this close coupling of NO and NO_2, it is useful to consider NO and NO_2 as a single entity with the sum of the two species referred to as NO_x.

2.1.1. *Ozone production.* Compounds other than ozone are also capable of oxidizing NO to NO_2. The most important of these [Cox, 1988; Crutzen, 1988] is the hydroperoxy radical, HO_2,

$$HO_2 + NO \rightarrow OH + NO_2 \quad (4)$$

In the troposphere, HO_2 is formed principally by the oxidation of CO

$$OH + CO \rightarrow H + CO_2 \quad (5)$$

$$H + O_2 + M \rightarrow HO_2 + M \quad (6)$$

In the presence of NO_x, the combination of reactions (2) through (6) will lead to O_3 production [Chameides and Walker, 1973; Crutzen, 1973; Levy, 1971, 1972]:

$$\text{net: } CO + 2O_2 \rightarrow CO_2 + O_3 \quad (7)$$

Thus oxidation of CO in the troposphere in the presence of NO_x produces O_3. It is important to note that, overall, odd hydrogen ($HO_x = OH + HO_2$) and NO_x are neither produced nor lost in these coupled reactions but simply catalyze photochemical ozone production at rates proportional to their abundances.

A similar catalytic reaction sequence for oxidation of methane (CH_4) is shown diagrammatically in Figure 1 [Logan et al., 1981]. The process is initiated by reaction of CH_4 with OH, and this leads to a complex series of reactions. In Figure 1 boxes indicate those compounds that are stable enough to be present at reasonable concentrations in the

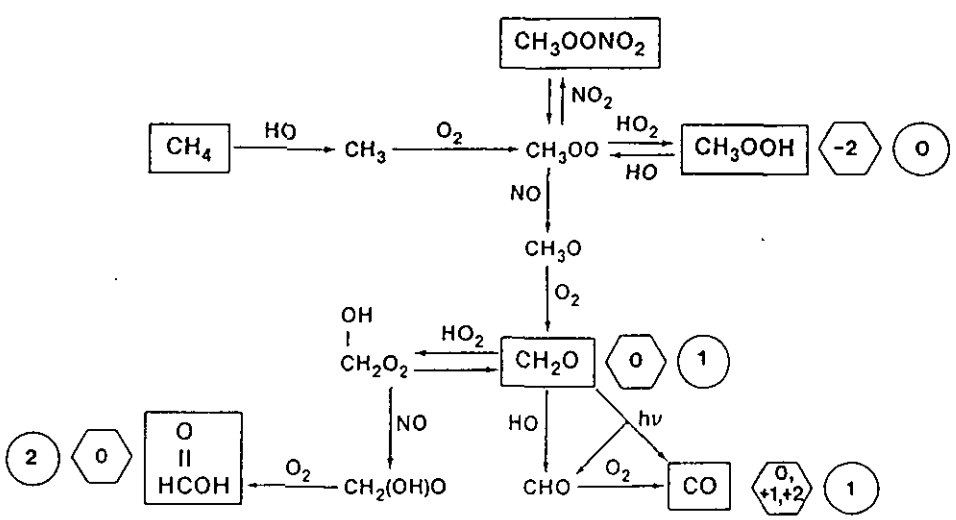

Fig. 1. A simple block diagram indicating the oxidation of methane in the troposphere.

atmosphere, and which may terminate the photochemistry. Numbers enclosed in circles adjacent to each box indicate the number of O_3 molecules produced or destroyed in forming the boxed-in compound. Numbers enclosed in hexagons indicate the number of odd-hydrogen free radicals that are generated or lost in forming each of these terminal compounds. Note that if reactions destroy the odd-hydrogen radicals, then O_3 photolysis, which produces these radicals, also becomes an O_3 destruction process. Destruction of odd-hydrogen radicals occurs when NO levels are low. With an adequate supply of NO, reaction of methyl peroxide radical (CH_3OO) with NO will dominate, and, during daytime, will lead to products that form O_3 and free radicals, which speed tropospheric oxidation. On the other hand, in the absence of NO the radical-radical reactions will dominate and lead to products without producing O_3. Overall, free radicals will be destroyed and O_3-forming oxidation will slow, which results in net O_3 destruction when ozone photolysis is considered.

In the continental boundary layer the oxidation of CH_4 or CO is not expected to be the most important factor controlling the photochemical production or loss of ozone. There are ample concentrations of nonmethane hydrocarbons (NMHC) which, when coupled with their higher photochemical reactivities, can dominate O_3 production. Nonetheless, in the case of NMHC, as with CH_4, the level of NO is expected to determine whether oxidation leads to O_3 production or loss. This process can be represented approximately by the following simplified scheme [Liu et al., 1987]:

$$NMHC + OH + O_2 \rightarrow RO_2 \quad (8)$$

$$RO_2 + NO + O_2 \rightarrow NO_2 + HO_2 + CARB \quad (9)$$

$$HO_2 + NO \rightarrow NO_2 + OH \quad (10)$$

$$2(NO_2 + h\nu + O_2 \rightarrow NO + O_3) \quad (11)$$

$$\text{net: } NMHC + 4O_2 + 2h\nu \rightarrow 2O_3 + CARB \quad (12)$$

where R stands for a hydrocarbon radical and CARB denotes a carbonyl compound. Reaction (12) shows that two O_3 molecules are produced for every NMHC molecule oxidized. In addition, the carbonyl compounds may undergo further photochemical reactions which will result in a significant gain of hydrogen free radicals and, in turn, produce more ozone.

The preceding reactions show how tropospheric oxidation of CO, CH_4, and NMHC in the presence of NO can lead to O_3 production. However, this odd-hydrogen free radical chemistry can also consume ozone. The most important of these O_3-destroying reactions is

$$HO_2 + O_3 \rightarrow OH + 2O_2 \quad (13)$$

Consequently, when NO concentrations are small, and reaction (13) is favored over reaction (4), the oxidation of CO, CH_4, and NMHC can lead to O_3 destruction.

2.1.2. *Oxidation of nitrogen oxides.* In addition to catalyzing the formation of O_3 during tropospheric oxidation, NO and NO_2 are chemically processed, as illustrated in Figure 2. The oxides of nitrogen enter the troposphere from a variety of natural and anthropogenic sources, usually in the form of NO. During the day rapid interconversion of NO and NO_2 produces O_3, but this NO_x can be further oxidized to a variety of other organic and inorganic compounds, collectively referred to as NO_y ($NO_y = NO_x$ + organic nitrates + inorganic nitrates + nitrites). The conversion of NO_x to the other members of the NO_y family takes place within a few hours during photochemically active summer days but requires a few days during winter.

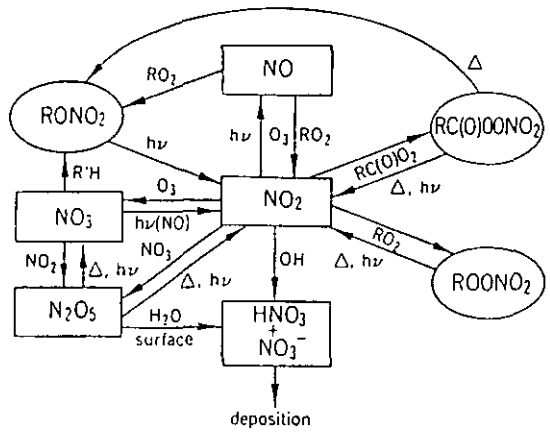

Fig. 2. A block diagram indicating the oxidation of the oxides of nitrogen in the troposphere.

The oxidation of organic compounds in the presence of NO_x usually leads to the formation of organic nitrates [Atherton and Penner, 1988; Atkinson and Lloyd, 1984; Calvert and Mandronich, 1987; Crutzen, 1979; Shepson et al., 1985; Stockwell, 1986; Trainer et al., 1991], listed as $ROONO_2$, $RC(O)OONO_2$, and $RONO_2$ in Figure 2. Although the oxidation of volatile organic compounds can form a large variety of organic nitrates, the most abundant, and by far the most studied of these compounds, is peroxyacetic nitric anhydride, also called peroxyacetyl nitrate (PAN, $CH_3C(O)OONO_2$). This compound was first observed in the atmosphere as a component of urban photochemical smog [Scott et al., 1957]. Since that time, surface and aircraft observations have confirmed its ubiquity in the atmosphere [Bottenheim et al., 1986; Buhr et al., 1990; Ridley et al., 1990; Rudolph et al., 1987; Singh et al., 1985, 1990]. The organic nitrates, such as PAN, act to temporarily preserve nitrogen oxides in the troposphere, especially at low temperatures, and release them at high temperatures or by photochemical reactions. Since the lifetimes of the organic nitrates depend strongly on temperature and sunlight intensity, the lifetime for a given organic nitrate can range from less than an hour to several weeks [Roberts, 1990]. Hence the importance of organic nitrates, and in particular PAN, relative to NO_x increases rapidly at the lower temperatures characteristic of winter, high latitudes, and high altitudes. Under these conditions, PAN levels may substantially exceed NO_x levels, thus implying a significant role for PAN and the other organic nitrates in the long range transport of NO_x through the atmosphere.

The principal inorganic nitrate is HNO_3 formed mainly by the reaction

$$OH + NO_2 + M \rightarrow HNO_3 + M \quad (14)$$

In addition, at night the reaction of NO_2 with O_3 forms the nitrate radical (NO_3) and nitrogen pentoxide (N_2O_5), which can further react through homogeneous and heterogeneous chemistry to form HNO_3 and NO_3^- [Liu et al., 1987].

Nitric acid and nitrate ions are relatively stable against photochemical destruction and in the absence of precipitation they can persist for extended periods (weeks) in the free troposphere. Hence wet and dry deposition of these species represent the principal mechanisms for removal of NO_y from the troposphere. This HNO_3 and NO_3^- represents a component (and in locations with large emissions of NO_x, an important component) of acid deposition and a mechanism for the redistribution of biospheric N. However, since NO is rapidly converted to NO_2 and other reactive N oxides once it enters the atmosphere and these species are more rapidly deposited to the surface than is NO, it is not certain how much of the NO that is emitted from the soil survives in the atmosphere sufficiently long to influence the atmospheric chemistry or to participate in long-range redistribution of biospheric N. Therefore it is important to make measurements to determine the net flux of soil-emitted NO_x from the near-surface boundary layer.

2.1.3. *Control of the tropospheric oxidation rate.* The principal process for the formation of the odd-hydrogen free radicals is initiated with the absorption of sunlight by O_3 [Chameides and Walker, 1973; Crutzen, 1973; Levy, 1971, 1972; Liu et al., 1987],

$$O_3 + h\nu\ (< 305\ nm) \rightarrow O(^1D) + O_2 \quad (15)$$

The electronically excited oxygen atom $O(^1D)$ is highly reactive toward water vapor, and unless it is quenched to a ground state oxygen atom $O(^3P)$ by reaction with N_2 or O_2 before it collides with a water molecule, it creates two OH radicals,

$$O(^1D) + H_2O \rightarrow 2OH \quad (16)$$

Thus as NO_x influences the production of O_3, it also establishes the rate that odd-hydrogen free radicals can be produced in the atmosphere.

Additionally, in the course of the chemistry outlined for the formation of O_3, it can be seen that the concentration of NO also directly mediates the relative amounts of peroxy radicals, HO_2 and RO_2, to that of OH. During the sunlight hours and at relatively low NO_x mixing ratios ($NO_x < 1$ part per billion by volume (1:10^9), ppbv) the amount of OH present in the atmosphere will depend directly on the level of NO through reactions (4) and (9). Since OH is responsible for initiating the oxidation of CH_4 and NMHC and for the conversion of CO to CO_2, under these conditions the concentration of NO also determines the rate of oxidation in the troposphere. However, at elevated NO_x mixing ratios ($NO_x > 10$ ppbv) the rapid reaction of NO_2 and OH to form HNO_3 will serve to reduce the amount of odd-hydrogen free radicals in the atmosphere and thus slow the oxidation process.

2.2. *Nitrous Oxide*

Nitrous oxide has two important impacts on the chemistry and physics of the atmosphere in that it contributes to global atmospheric warming and it influences the chemistry of the stratospheric ozone layer. In the troposphere N_2O absorbs long-wave terrestrial radiation and thus contributes to greenhouse warming of the atmosphere. Because N_2O is inert to chemical reaction in the troposphere, the lifetime of this compound is substantial, perhaps as long as 110 [Ko et al., 1991] to 150 years [Watson et al., 1990]. The only known sinks for N_2O at the surface of the earth are uptake by soils [Blackmer and Bremner, 1976] and by the oceans [Elkins et al., 1978]. However, McElroy and Wofsy [1986] noted that these are not significant loss processes compared to photochemical destruction in the stratosphere. On a per molecule basis, N_2O is approximately 200 times more potent than CO_2 with respect to atmospheric warming. However, because of a much lower atmospheric concentration than CO_2 (N_2O: 310 ppbv ; CO_2: 353 parts per million by volume (1:10^6), ppmv) and a much smaller rate of increase (N_2O: 0.25% yr^{-1}; CO_2: 0.5% yr^{-1}), N_2O contributes only a few percent (~6%) to total warming and may not contribute significantly to global warming over a time scale of up to a century [IPCC, 1990].

In the stratosphere the principal destruction mechanism for N_2O is by photolysis at wavelengths shorter than 240 nm [cf. Brasseur and Solomon, 1984],

$$N_2O + h\nu \rightarrow N_2 + O(^1D). \quad (17)$$

In addition, N_2O is destroyed by reaction with excited oxygen atoms. The reaction has three possible channels:

$$N_2O + O(^1D) \rightarrow 2NO \quad (18)$$

$$N_2O + O(^1D) \rightarrow N_2 + O_2 \quad (19)$$

$$N_2O + O(^1D) \rightarrow N_2O + O(^3P) \quad (20)$$

[Davidson et al., 1979; Wine and Ravishankara, 1982], and has a profound impact on stratospheric chemistry. While reaction (19) is the dominant channel, reaction (18) is also significant, being the largest source of NO in the stratosphere [Crutzen, 1971; Jackman et al., 1980; Nicolet, 1971]. The production of NO in the stratosphere initiates a complex set of gas-phase and heterogeneous reactions that play a key role in the chemical production and destruction of O_3 in the stratosphere [cf. World Meteorological Organization (WMO), 1992, and the references therein).

3. BIOCHEMICAL PROCESSES FOR NO_x AND N_2O PRODUCTION AND CONSUMPTION

Both biotic and abiotic processes are involved in the production of NO and N_2O in soils. Among the biotic sources, numerous groups of soil microorganisms contribute to the production of these two N gases through a variety of biochemical reactions. The bacterial processes of nitrification and denitrification are generally accepted to be the principal sources of NO and N_2O in soil, but most all microbial processes that involve oxidation or reduction of N through the

+1 or +2 oxidation state probably yield at least trace amounts of the two gases [Conrad, 1990; Firestone and Davidson, 1989; Focht and Verstraete, 1977; Haynes, 1986, and references therein; Knowles, 1985]. For example, N_2O production by processes other than nitrification or denitrification has been observed in acid forest soils [Robertson and Tiedje, 1987] and in pure cultures of some fungi [Bollag and Tung, 1972; Burth and Ottow, 1983], so a fungal source seems likely. Nitrous oxide loss also occurs during assimilatory nitrate reduction by some yeasts [Bleakley and Tiedje, 1982], and both NO and N_2O are reportedly produced in varying amounts by nondenitrifying nitrate-reducing bacteria [Anderson and Levine, 1986; Smith and Zimmerman, 1981]. The importance of these and other nonnitrifying/nondenitrifying processes to total biogenic NO and N_2O production is uncertain; this topic was recently reviewed by Tiedje [1988].

Abiotic production of N_2O, and particularly NO, occurs primarily through a set of reactions collectively termed chemodenitrification. The most important of these reactions is the disproportionation of nitrous acid (HNO_2) known to occur in acid soils [Nelson, 1982], especially those high in organic matter content [Blackmer and Cerrato, 1986]. Although this reaction has not been demonstrated in neutral or alkaline soils in the laboratory, its occurrence in the natural environment cannot be discounted because of the possible existence in undisturbed soils of microsites where the required accumulation of nitrite (NO_2^-) and low pH can occur as a result of solute concentration in thin water films during freezing or drying, or because of proximity to a colony of NH_4^+ oxidizers [Davidson, 1992a]. Other abiological processes for NO and N_2O production in soil include decomposition of hydroxylamine (NH_2OH) and reaction of NO_2^- with the phenolic constituents of soil organic matter, among others [Nelson, 1982]. The contribution of the latter reactions to soil emission of NO and N_2O is apparently surpassed by that of HNO_2 disproportionation, which itself makes at least an order of magnitude smaller contribution [Johansson and Galbally, 1984; Remde et al., 1989] than the biological processes of nitrification and denitrification discussed below.

3.1. *Nitrification*

Nitrification is defined as the biological oxidation of NH_4^+ to NO_2^- and NO_3^-, or a biologically induced increase in the oxidation state of N [Soil Science Society of America, 1987]. Numerous studies have indicated that the process is a quantitatively important component of the N cycle in most cultivated agricultural soils. Contrary to earlier literature [Bormann and Likens, 1979; Melillo, 1981] nitrification also plays a significant role in the N cycle of mature natural ecosystems, with the exception of wetlands and many coniferous forest systems [Robertson, 1982]. For example, Davidson et al. [1990] recently reported that despite the previously hypothesized poor ability of nitrifiers to compete with plants and heterotrophic microorganisms for available NH_4^+, between 12 and 46 percent of the N mineralized in an undisturbed N-limited California grassland was oxidized to NO_3^-, even during seasons when plant uptake and microbial immobilization were both active. They speculated that microsite heterogeneity in NH_4^+ mineralization rates and in the distributions of organisms and roots was at least partially responsible for the high net nitrification rates.

The process of nitrification is associated with the metabolism of chemoautotrophic bacteria of the family *Nitrobacteraceae*, as well as several species of heterotrophic microorganisms. Heterotrophs such as *Aspergillus flavus* and *Alcaligenes sp.*, among many others, have been reported to form NO_2^- or NO_3^- from NH_4^+ or other reduced forms of N when grown in culture media [Castignetti and Gunner, 1980; Schmidt, 1982]. Convincing evidence that relates the occurrence of a particular heterotroph in its natural environment to the progression of nitrification in that environment is limited to forest soils [Schimel et al., 1984] and soils with pH too low or temperature too high to support the growth of chemoautotrophic nitrifiers [Stroo et al., 1986]. However, Anderson et al. [1991] and Papen et al. [1991] have recently provided evidence that heterotrophic nitrification may have greater significance than is commonly believed.

The conventional wisdom is that the preponderance of nitrification in soil is accomplished by a few genera of chemoautotrophic bacteria: *Nitrosomonas* and *Nitrosospira*, which oxidize NH_4^+ to NO_2^-; and *Nitrobacter*, which converts NO_2^- to NO_3^-. Although low numbers of a few other NH_4^+-oxidizing chemoautotrophs are also present in many soils, *Nitrobacter* is the only genus known to be involved in the oxidation of NO_2^-, so it is surprising that this ion is promptly oxidized and rarely accumulates in soil. Notable exceptions include tropical savannah [Johansson and Sanhueza, 1988] and seasonally dry tropical forest soils [Davidson et al., 1991] that accumulate NO_2^- during the dry season. Oxygen is obligatory for the chemoautotrophic oxidation of either NH_4^+ or NO_2^-, and both reactions are coupled to electron transport phosphorylation, thereby providing the energy required for growth and regeneration of the responsible organisms. All members of the family *Nitrobacteraceae* are aerobes that synthesize their cell constituents from CO_2 by way of the Calvin reductive pentose phosphate cycle. The relatively narrow species diversity of the chemoautotrophs responsible for nitrification in soil is thought to render the process unusually susceptible to external influences [Haynes, 1986].

The biochemical pathway of chemoautotrophic nitrification remains a subject of much debate. There is good evidence that NH_2OH (N oxidation state -1) is the first intermediate product of NH_4^+ oxidation [Dua et al., 1979], but subsequent intermediates with N oxidation states +1 and +2 are not known with any certainty [Hooper, 1984]. All intermediates formed during the conversion of NH_2OH to NO_2^- are believed to remain bound to the complex enzyme hydroxylamine oxidoreductase. The oxidation of NO_2^- to NO_3^- by *Nitrobacter* is a simple two-electron shift in N oxidation state from +3 to +5 and involves no intermediates [Schmidt, 1982].

There is abundant evidence that both NO and N_2O are usually included among the products of chemoautotrophic nitrification. More than half a century ago, Corbet [1935] observed N_2O formation by cultures of nitrifiers supplied with NH_4^+ or NH_2OH, while Ritchie and Nicholas [1972] first reported reduction of NO_2^- to N_2O by dissimilatory nitrite reductase synthesized by *Nitrosomonas europaea* in pure culture. Several years later, Bremner and Blackmer

[1978] recognized that nitrifying microorganisms were responsible for production of a fraction of the soil-emitted N_2O formerly attributed entirely to denitrification. Likewise, it has long been known that NO is produced by chemoautotrophic nitrifiers in culture, but much more recently recognized that this process serves as a significant source of NO emitted from soil. Studies using acetylene or nitrapyrin [2-chloro-6-(trichloromethyl)-pyridine] to inhibit NH_4^+ oxidation and chlorate to inhibit NO_2^- oxidation have demonstrated that both the N_2O [Aulakh et al., 1984a; Blackmer et al., 1980; Hynes and Knowles, 1984] and NO [Davidson, 1992a; Tortoso and Hutchinson, 1990] produced during chemoautotrophic nitrification are a direct result of the activity of those organisms responsible for oxidation of NH_4^+ to NO_2^-.

Recent evidence suggests that production of N_2O by autotrophic NH_4^+ oxidizers results from a reductive process in which the organisms use NO_2^- as an electron acceptor, especially when O_2 is limiting [Poth and Focht, 1985]. This mechanism not only allows the organisms to conserve limited O_2 for the oxidation of NH_4^+ (from which they gain energy for growth and regeneration), but also avoids the potential for accumulation of toxic levels of NO_2^-. Our knowledge of nitrifier physiology is not sufficient to predict whether the in situ production of NO also results from NO_2^- reduction, as proposed from studies of cell-free extracts by Hooper [1968] and work with intact cells by Remde and Conrad [1990] and Anderson et al. [1991], or if it represents decomposition of an intermediate in the oxidation pathway from NH_4^+ to NO_2^-, as proposed from cell-free extract studies by Hooper and Terry [1979]. Some evidence indicates that NO production during nitrification also increases as O_2 availability decreases [Lipschultz et al., 1981], but Anderson and Levine [1986] and Remde and Conrad [1990] observed no dependence on the partial pressure of O_2, and it is generally accepted that N_2O production by nitrifiers is more sensitive to this condition. As a result, the NO:N_2O ratio of nitrification products, normally of the order of 10 to 20 in fully aerobic environments [Tortoso and Hutchinson, 1990], decreases along with O_2 partial pressure.

The amounts of nitrification-induced NO and N_2O evolved from soil are regulated by two separate, but interdependent, sets of controllers: those that establish the overall rate of the nitrification process and those that determine the NO:NO_3^- and N_2O:NO_3^- ratios of nitrification products [Firestone and Davidson, 1989]. Chemoautotrophic NH_4^+-oxidizing bacteria are widely distributed in soil and require only CO_2, O_2, and NH_4^+ to proliferate. Carbon dioxide is essentially never absent, and O_2 is usually adequate (except for brief intermittent periods) in all but a few very anaerobic environments (e.g., sediments, bogs, sludge), so NH_4^+ availability is the factor that most frequently limits the overall rate of nitrification. Other less important factors that limit nitrifier activity in certain environments include NO_2^- toxicity, phosphate availability, temperature extremes, low water potential, and allelopathic compounds [Haynes, 1986]. Low pH is also commonly listed among the factors that limit nitrifier activity, but DeBoer et al. [1991] showed that

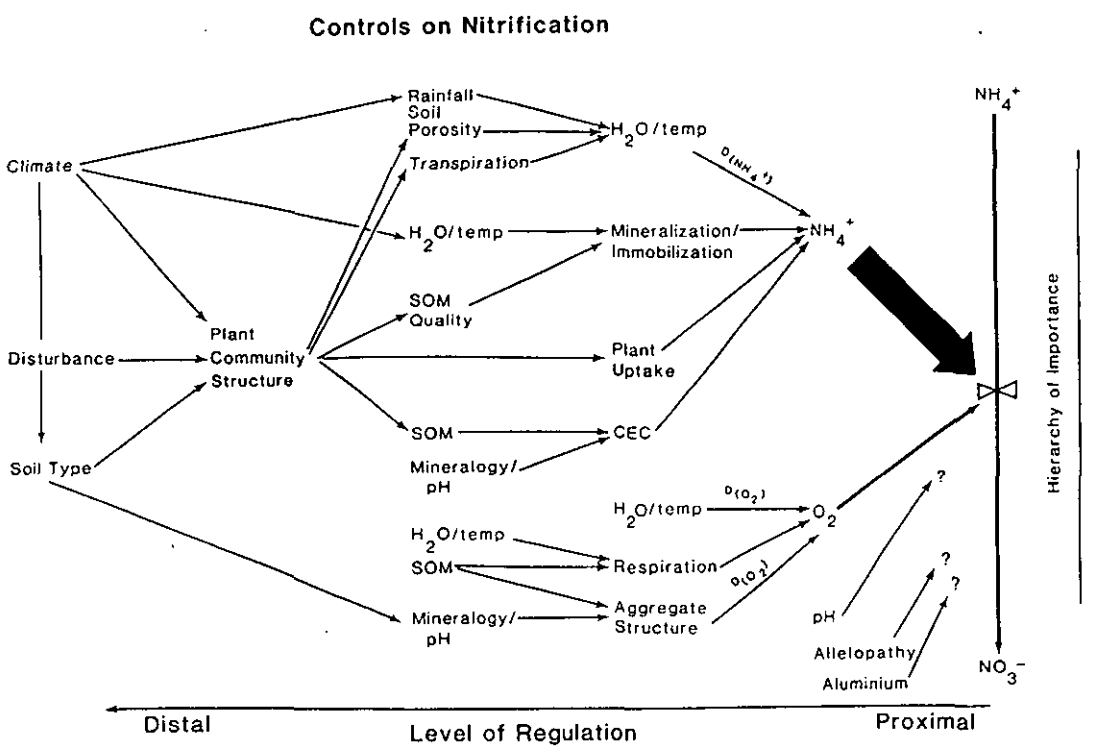

Fig. 3. A conceptual model of controls on nitrification [Robertson, 1989]. This diagram labels as "proximal" controllers those factors that exert influence at the cellular level.

aggregated cells were able to nitrify at pH 4, whereas single cells did not. The importance of NH_4^+ availability is illustrated in Figure 3, a conceptual model of controls on nitrification reproduced from Robertson [1989]. This diagram labels as "proximal" controllers those factors that exert influence at the cellular level and shows pictorially how these are, in turn, regulated by increasingly remote "distal" controllers (mostly soil and environmental parameters). In addition to being essential for all microbial life processes, water is shown to exert an additional important influence on nitrification by controlling the diffusive supply of O_2 and NH_4^+. Similarly, temperature has a modifying influence on both proximal and distal controllers, as well as on the process itself.

Many of the controllers shown in Figure 3 influence not only the overall rate of the nitrification process, but also the $NO:NO_3^-$ and $N_2O:NO_3^-$ ratios of its products. Although control of these ratios is much less well understood, certain relationships are evident. For example, because N_2O apparently results from a reductive process, its importance as a product of nitrification should increase as O_2 availability decreases, but whether that increased importance translates into higher total N_2O production depends on how much the overall process rate is reduced by the limited availability of O_2. The NO and N_2O yields of nitrification are normally relatively small. For N_2O the highest reported value was 20 percent of the NH_4^+ oxidized in an acid forest soil fertilized with urea [Martikainen, 1985]. Such high yields are unusual, and chemical formation of N_2O from NO_2^- may have been involved. The next highest reported yield of N_2O was 6.8 percent of the urea-N added to a poorly drained Iowa soil [Bremner et al., 1981]. The N_2O yield is typically less than 1 percent, often much less. The NO yield of nitrification in well-aerated soil is more constant, most commonly falling in the range 1 to 4 percent of the NH_4^+ oxidized [Hutchinson and Brams, 1992; Hutchinson et al., 1992, 1993], but values as high as 10 percent [Hutchinson and Follett, 1986; Shepherd et al., 1991] and as low as 0.1 percent [Davidson et al., 1993] have been reported.

3.2. *Denitrification*

For the purposes of this review, denitrification is defined as respiratory reduction of NO_3^- or NO_2^- to gaseous NO, N_2O, or N_2 that is coupled to electron transport phosphorylation. Other anaerobic processes often included in the definition of this term (but excluded here) were described briefly at the beginning of this section. Denitrification occupies a position of pivotal importance in the N cycle of the biosphere. In its absence, all biologically available N that has been released from igneous rocks of the Earth's original crust and mantle would have been converted long ago to its more thermodynamically stable form of NO_3^- in the oceans [Lindsay et al., 1981]. Therefore this process, which is often viewed by biologists as a mechanism for loss of plant-available N, also represents the first step in the recovery of excess oxidized N by replenishing the supply of atmospheric N_2 available to symbiotic and nonsymbiotic N-fixing microorganisms. Denitrification also represents the only biological process for consumption of N_2O [Firestone and Davidson, 1989], but biological uptake and reduction of atmospheric N_2O has been demonstrated outside the laboratory only for wetlands [Ryden, 1981].

Unlike the narrow species diversity of organisms responsible for nitrification in soil, denitrification capacity is common to several taxonomically and physiologically different bacterial groups [Focht and Verstraete, 1977; Payne, 1985]. Denitrifiers, which are basically aerobic bacteria with the alternative capacity to reduce N oxides when O_2 becomes limiting, are so widely distributed in nature that any restriction of the denitrifying activity in a given habitat can usually be assumed not to result from lack of enzyme but rather from limited substrate availability or the environmental conditions that regulate the process [Firestone and Davidson, 1989]. One possible exception to this generalization is the short-term response to a very large and sudden change in resource availability, but even this exception is likely to be brief. Denitrifying enzyme activity persists for months, even in very dry soil [Smith and Parsons, 1985], and the activation of these enzymes, as well as their de novo synthesis, begins almost immediately following soil wetting by precipitation or irrigation [Rudaz et al., 1991]. Hence, when abrupt changes in soil water content create conditions that favor denitrification, its rate is unlikely to be enzyme-limited for more than a few hours.

Included among the denitrifiers are phototrophs, lithotrophs, and organotrophs that derive energy for growth and regeneration from light, inorganic substrates, and organic substrates, respectively. The latter group dominates the denitrifying populations of natural soil and water environments. Within this group species of *Pseudomonas* predominate, probably because of their versatility and competitiveness for C substrates, and except in special or unusual environments most of the remaining denitrifying organisms are species of the closely related *Alcaligenes* [Tiedje, 1988]. The resulting similarity in the characteristics of numerically dominant populations in a wide range of natural habitats suggests that the controllers of NO and N_2O production (or consumption) by denitrification should also be similar across major global environments [Firestone and Davidson, 1989].

Although the identity of N compounds involved in the biochemical pathway of denitrification is well established [Fillery, 1983; Payne, 1981; Wijler and Delwiche, 1954], the nature of the participation by NO in this process and the exact mechanism for formation of the N-N bond during reduction of NO_2^- to N_2O remain the subjects of current research [Averill and Tiedje, 1982; Goretski et al., 1990; Goretski and Hollocher, 1990; Heiss et al., 1989; Hoglen and Hollocher, 1989; Weeg-Aerssens et al., 1988; Zafiriou et al., 1989]. The complex biochemistry of denitrification is beyond the scope of this paper, and for our purposes it is sufficient to know that the pathway includes NO and N_2O as intermediates and that both gases can be produced or consumed by denitrifying bacteria.

Having already established the near omnipresence of denitrifying enzyme, remaining requirements for this process to occur are availability of suitable reductant (usually organic C), restricted O_2 availability, and presence of N oxides (NO_3^-, NO_2^-, NO, or N_2O). The relative importances of these three denitrification controllers varies among habitats, but for soil and other habitats exposed to the atmosphere, O_2 availability

is nearly always the most critical; Tiedje [1988] discussed this topic in detail. Although controls on denitrification at the cellular level are easy to itemize and visualize, environmental factors that regulate these cellular controllers are numerous, interactive, and difficult to conceptualize and model [Chalamet, 1985; Focht and Verstraete, 1977; Haynes, 1986]. To illustrate this point, Firestone and Davidson [1989] used the example that in nonflooded terrestrial ecosystems, plant roots can (1) reduce O_2 availability through root respiration and stimulation of microbial respiration by root exudates, (2) increase O_2 availability by enhancing gas diffusion rates through removal of soil water, (3) increase C availability by root exudation, and (4) decrease N oxide availability through NO_3^- uptake. Robertson's [1989] ordering of the factors regulating denitrification into proximal and increasingly distal classes with a hierarchy of importance established within each class (Figure 4) is probably the most useful and informative conceptual model available for understanding and potentially developing simulation models that encompass the many complex interactions that are possible. Figure 4 emphasizes the importance of O_2 availability and shows pictorially how this factor is strongly influenced, for example, by the diffusional constraints imposed by soil water, which is in turn regulated by precipitation, infiltration, and evapotranspiration, which are in turn governed by climate, soil type, plant community structure, etc.

As was the case for nitrification, the total amounts of NO and N_2O produced by denitrification in soil depend not only on factors that determine the overall rate of the process, but also on parameters that control the ratios of its potential products [Firestone and Davidson, 1989]. Dinitrogen and N_2O are considered to be the usual end products of denitrification, and that fraction of the process interrupted at N_2O ranges from almost none to the preponderance of N reduced, depending on such factors as N oxide concentration, O_2 availability, organic C availability, soil gas diffusion rates, pH, temperature, sulfide concentration, enzyme activity ratios, and time since initiation of denitrification activity [Tiedje, 1988, and references therein]. The regulation imposed by most of these parameters can be explained by considering their influence on the relative availability of oxidant versus reductant. When the availability of oxidant overshadows the supply of reductant, then substrate N oxide may be incompletely reduced resulting in a larger $N_2O:N_2$ ratio of end products. Conversely, when the overall rate of denitrification is limited by the supply of oxidant, most of the N oxide is converted to N_2. An analysis of the denitrification sequence based on the Michaelis-Menton model of enzyme kinetics predicts that the proportion of N_2O should increase whenever any of the other controllers listed above slows the overall rate of reduction below the maximum that can be supported by existing enzyme [Betlach and Tiedje, 1981].

Nitric oxide is not usually considered to be a major end

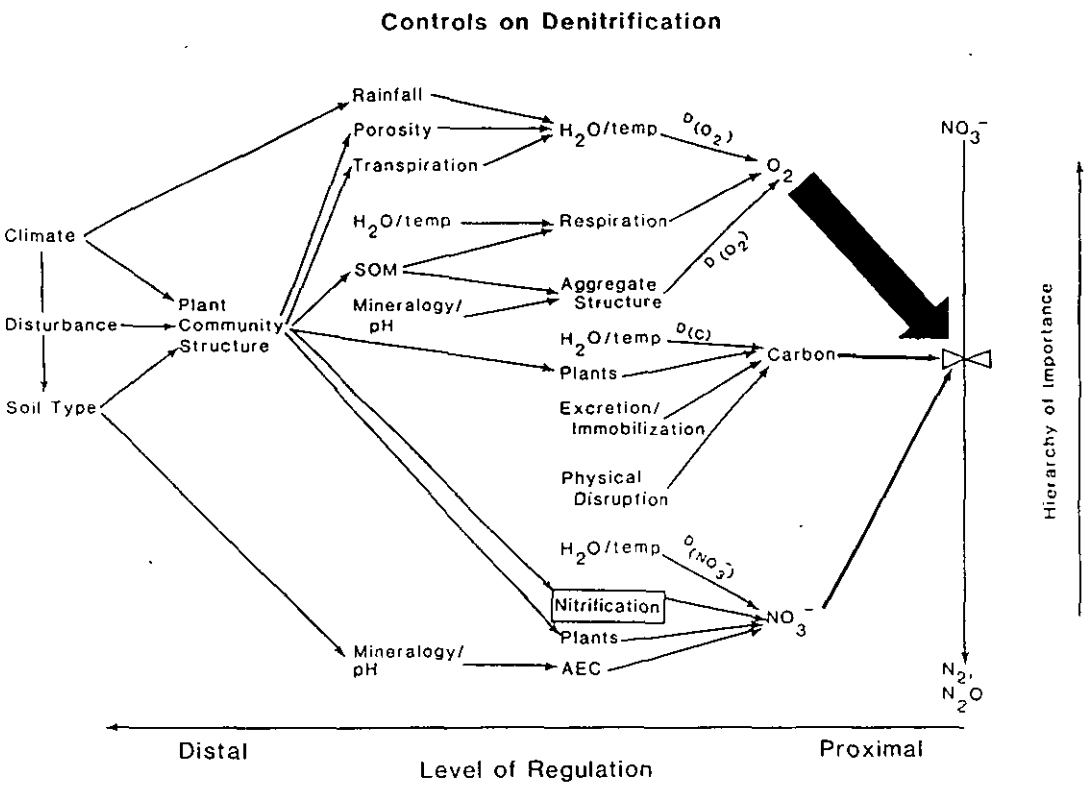

Fig. 4. A conceptual model of controls on denitrification [Robertson, 1989]. This diagram shows an ordering of the factors regulate denitrification at the cellular level into proximal and increasing distal classes with a hierarchy of importance established within each class.

product of denitrification in soil or water. Although this belief may partially reflect that sensitive methodology for NO analysis has been widely available for only the last decade, mass balance experiments long ago confirmed the absence of a major unknown denitrification product. Nevertheless, Tortoso et al. [1986] reported that NO was the principal denitrification product when they initiated the process in laboratory-incubated soil (100-kPa water potential) by removing O_2 from the airstream sweeping the incubation jar headspace. Johansson and Galbally [1984] and McKenney et al. [1982] also found NO to be a major product of denitrification in soil columns incubated under anaerobic flow conditions, and Zafiriou et al. [1989] demonstrated that this gas was the dominant product of denitrification by *Pseudomonas perfectomarina* when grown in low-density cell suspensions that were highly sparged to remove gaseous products. The condition common to these three data sets that separates them from the body of denitrification literature is that the process was initiated without restricting rapid equilibration of gaseous intermediates and products with the ambient atmosphere. In the natural soil environment, denitrification generally occurs only when the soil's water content is high enough to restrict O_2 availability, which also restricts the diffusion rates of other gases in soil. The resulting increase in time required for NO diffusion to the soil surface, combined with its instability toward further reduction, allows very little of this gas to escape.

4. TECHNIQUES FOR MEASURING NO_x AND N_2O EXCHANGE

4.1. *Atmospheric NO_x Concentration Measurement*

Most atmospheric NO_x concentration measurements made during the past decade were performed using one of two types of chemiluminescence detectors. Before that time, studies of NO_x exchange between soil-plant systems and the atmosphere depended on a variety of gas chromatographic (GC) techniques using thermal conductivity [Bailey and Beauchamp, 1973], ultrasonic [Blackmer and Bremner, 1977], or electron capture detection [Kaspar and Tiedje, 1980], or a wet chemical technique involving absorption of NO and NO_2 in alkaline or acidic permanganate solution followed by analysis of the solution for NO_2^- and NO_3^- [Nelson and Bremner, 1970; Smith and Chalk, 1979; Kim, 1973]. Both the GC and absorption techniques suffered from lack of adequate sensitivity and were subject to multiple interferences. The principles of operation and present capabilities of the two chemiluminescence detectors are summarized below.

4.1.1. *NO/O_3 chemiluminescence.* During the past two decades a sensitive, specific chemiluminescence detector for determining the NO and NO_x contents of complex air samples has been developed by Fontijn et al. [1970], Ridley and Howlett [1974], Steffenson and Stedman [1974], Kley and McFarland [1980], and Bollinger [1982]. The system employs a red-sensitive photomultiplier tube to collect and count photons emitted during the decay of excited NO_2 molecules produced by the reaction of NO with excess O_3 in a chamber with infrared-reflective walls. Ridley and Howlett [1974] showed that this photon flux, which has a wavelength range from 600 nm well into the infrared, is proportional to the ambient NO mixing ratio. A detection limit better than 10 parts per trillion by volume ($1:10^{12}$; pptv) at a signal-to-noise ratio of 2 can be achieved using a 10 s averaging time. At slightly higher concentrations, the instrument is adaptable to fast response detection of NO and NO_2 [Delany et al., 1986].

Specificity of the detector is enhanced by using a red filter to prevent light with wavelengths shorter than 620 nm from reaching the photomultiplier and by adjusting the sample residence time in the reaction chamber to minimize interference from competing chemiluminescent reactions with different kinetics. The red filter specifically avoids interference from the blue photon flux resulting from O_3-hydrocarbon reactions, as well as any other chemiluminescence outside the red spectral region. Because the reaction of NO with O_3 is very rapid compared to most interfering chemiluminescent reactions, residence time of the sample in the reaction chamber is kept quite short by adjusting the chamber's volume and pressure within limits imposed by additional effects of these two parameters on sensitivity and quenching [Delany et al., 1982]. Good agreement between soil NO emissions measured simultaneously by enclosure and gradient techniques (section 4.3) indicates that there is no significant interference from other compounds that collect in enclosures placed over the soil surface.

The detection of NO_2 by this technique depends on its prior conversion to NO, which is accomplished in most commercial instruments by thermal and catalytic conversion processes that are simple, efficient, and reliable, but lack the specificity required for some applications. To avoid the potential for interference from other reactive N oxides (NO_y compounds), photolysis of NO_2 by ultraviolet light can be utilized [Kley and McFarland, 1980]. This reaction is understood on a more fundamental basis, so products of the conversion process can be more accurately predicted. Regardless of what process is used to reduce NO_2 to NO, the NO_2 mixing ratio is estimated from the increase in the NO signal following conversion, after adjusting for conversion efficiency as determined with an NO_2 calibration source.

4.1.2. *Luminol chemiluminescence.* The 1980s witnessed development of a second chemiluminescence detector for gas-phase NO_x determination [Maeda et al., 1980; Schiff et al., 1986; Wendel et al., 1983], but unlike the one just described, it responds to NO_2 directly without prior conversion to NO. The detector is based on the chemiluminescent oxidation by NO_2 of luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) in alkaline solution. Sample air (at atmospheric pressure) is drawn past the surface of a wick wetted with a specially formulated luminol solution in a small chamber viewed by a photomultiplier tube. The strong chemiluminescence produced during luminol oxidation is directly proportional to NO_2 mixing ratios above about 1 ppbv. At lower levels the rate controlling step of the reaction is second order in NO_2, causing photomultiplier output to become nonlinear with NO_2 mixing ratio. Drummond et al. [1989] generated an algorithm for estimating NO_2 mixing ratio from the signal obtained under these conditions. It should be noted that the nonlinearity at low NO_2 mixing ratios is a function of the reaction history during the previous 3 to 5 min, a limitation

that must be recognized when using the instrument in fast response applications.

Unlike most atmospheric oxidants that produce chemiluminescence with luminol only in the presence of metal ion catalysts in the liquid phase, luminol oxidation by NO_2 appears to be a surface reaction not requiring the presence of metal ions [Schiff et al., 1986]. The only known exceptions to this generalization (on which specificity of the luminol chemiluminescence detector is based) are that O_3 and PAN cause positive interference equal to about 0.6% and up to 100%, respectively, of an equivalent mixing ratio of NO_2. Interference by O_3 is reduced by adding methanol and Na_2SO_3 to the luminol solution and that due to PAN, by adding any of several alcohols [Schiff et al., 1986].

The only commercially available instrument utilizing this detector is operationally simple, compact, rugged, lightweight, portable, operates from rechargeable batteries, and provides real time measurements with good time resolution, making it well suited to measurements in the field. Its detection limit is approximately 5 pptv calculated as the signal equivalent to noise measured with a clean air sample. Response time (0 to 95%) for a step change of 10 ppbv NO_2 is about 1 s. The instrument has been adapted to also measure NO following oxidation to NO_2 by 10% (w/w) CrO_3 on silica gel [Wendel et al., 1983]. Levaggi et al. [1974] reported 100% efficiency for conversion of NO to NO_2 by CrO_3 at intermediate relative humidities, but the water contents of very wet and very dry samples required adjustment to obtain acceptable conversion efficiency. Methyl nitrite (CH_3ONO) is also converted by CrO_3 to NO_2 and is therefore measured as NO; other potential interferences to the measurement of NO using this converter/detector combination have not yet been investigated. In a ground-based intercomparison, Fehsenfeld et al. [1990] tested the photolysis/chemiluminescence and luminol techniques. The results indicated that PAN and ozone interfered with NO_2 measurements made using the luminol technique. However, those interferences were sufficiently consistent that, for NO_2 levels above 0.3 ppbv, corrections could be made using simultaneously measured values of O_3 and PAN [Fehsenfeld et al., 1990].

4.1.3. *Recent developments in NO_x measurement technology.* Newer technology is emerging to measure NO_2 mixing ratios. Two of the newer techniques which show considerable promise are photofragmentation/two-photon laser induced fluorescence (LIF) [Bradshaw and Davis, 1982; Bradshaw et al., 1985; Davis et al., 1987; Sandholm et al., 1990] and tunable diode laser absorption spectrometry (TDLAS) [Hastie et al., 1983; Schiff et al., 1983, 1990]. The LIF and TDLAS techniques provide specific spectroscopic methods to determine NO_2 mixing ratios. TDLAS, which uses a long-path absorption cell to improve sensitivity, combines the wide applicability of infrared absorption for molecular detection with the spectral resolution of tunable laser diodes needed to discriminate among molecules. The most successful LIF approach uses photofragmentation to convert NO_2 to NO that is subsequently uniquely detected by two-photon laser induced fluorescence (TP/LIF).

In a ground-based intercomparison, Fehsenfeld et al. [1990] tested the TDLAS and photolysis/chemiluminescence techniques. For NO_2 levels greater than about 0.2 ppbv no interferences were found for either technique. However, in the interpretation of data from the TDLAS technique it was determined that a high-correlation coefficient, which is used as a quantitative measure of the overall overlap of the measured spectrum to that of the NO_2 reference spectrum, should not be used as the criterion to evaluate data which are near the detection limit [Fehsenfeld et al., 1990]. At these levels the background noise will be normally distributed about the reference NO_2 spectrum, thus selection of data with high correlation coefficients leads to inferred NO_2 levels that are too high.

Recently, an airborne intercomparison of the TDLAS, LIF, and photolytic converter/chemiluminescence techniques was conducted by Gregory et al. [1990]. In ambient air at NO_2 mixing ratios greater than 0.1 ppbv the level of agreement among the instruments was observed to be of the order of 30-40%. For NO_2 less than about 0.05 ppbv the TDLAS system overestimated the NO_2 mixing ratio, presumably as a result of the reliance on correlation coefficients as the data selection criterion. At these low levels the agreement between LIF and the photolysis/chemiluminescence measurements was within 0.02 ppbv with an equal tendency for one to be high or low compared to the other. This 0.02 ppbv agreement is typically within the stated uncertainties of the two techniques at NO_2 mixing ratios less than 0.05 ppbv.

Presently, it is believed that the LIF and TDLAS techniques are capable of the measurement of NO_2 to levels well below 0.1 ppbv and free of significant artifact or interference, which indicates adequate capability for measuring NO_2 levels in the troposphere. To date, however, these advanced spectroscopic methods have not been applied to the measurement of NO_2 fluxes.

4.1.4. *Total reactive odd-nitrogen oxides (NO_y).* The development of very sensitive methods to measure NO has also provided the basis for the measurement of total reactive N oxides, NO_y ($NO_y = NO_x$ + organic nitrates + inorganic nitrates). Several NO_y measurement techniques have been proposed. In general, all these techniques rely on the reduction of NO_y species to NO followed by the detection of the NO. A ground-based intercomparison of two of these techniques, the Au-catalyzed conversion of NO_y to NO in the presence of CO and the reduction of NO_y to NO on a heated molybdenum oxide surface, has been done [Fehsenfeld et al., 1987]. These instruments were found to give similar results for the measurement of NO_y in ambient air under conditions that varied from clean continental background air to typical urban air, with NO_y levels between 0.4 and 100 ppbv.

4.2. *Atmospheric N_2O Concentration Measurement*

Although several methods have been proposed for gas phase N_2O determination (including mass spectrometry, nondispersive infrared spectroscopy, gas filter correlation analysis, and tunable diode laser systems), GC methods have been used almost exclusively to measure soil emission of this gas. The limited sensitivity of most GC detectors requires concentration of N_2O in ambient air samples prior to analysis, so most investigators have adopted the heated (350°C) ^{63}Ni electron capture (EC) detector [Bremner and Blackmer, 1982; Mosier and Mack, 1980; Rasmussen et al.,

1976], which has adequate sensitivity for direct N_2O analysis of as little as 1 mL of air. Disadvantages of the EC detector are its radioactivity, requirement for frequent calibration, susceptibility to interference from chlorofluorocarbons, CO_2, and water vapor, and extreme sensitivity to the temperature of its environment. The latter problem can be at least partially overcome by operating the GC only in a temperature-controlled laboratory, and interferences can be minimized by using the two-part column described by Mosier and Mack [1980]. Their precolumn is backflushed to remove chlorofluorocarbons and water vapor after N_2O moves onto the analytical column; CO_2 is removed by an Ascarite trap on the GC inlet. When sufficient sample volume is available to overcome the limited N_2O sensitivity of the ultrasonic detector, some researchers prefer the GC method proposed by Blackmer and Bremner [1978] that avoids the problems associated with the GC-EC detector and has the additional important advantage that it permits use of the Xe in air as an internal standard.

4.3. *Approaches to NO_x and N_2O Exchange Rate Estimation*

Several techniques are available for determining the exchange of NO and N_2O between soil and the atmosphere. Enclosure techniques are by far the most commonly used even though they necessarily interfere with production, consumption, and transfer processes normally operating in the field by creating artificial environmental conditions over the study area. The popularity of enclosure methods (also called chamber or soil cover methods) is based primarily on their simplicity, convenience, low equipment cost, and adaptability to small plots, which allows for multiple sampling sites and for research requiring replicate measurements coincident in space or time [Hutchinson and Livingston, 1992]. In addition, the technique has high sensitivity, because elevated NO or N_2O concentrations are measured; it can be used both day and night; it is relatively unaffected by changing concentrations of atmospheric constituents outside the enclosure; and it permits systematically and independently varying the concentrations of atmospheric constituents within the chamber to test their influence on the measured flux.

Two different approaches to determination of flux with a chamber have been used; these are known as open and closed chambers. Open chamber techniques employ a constant gas flow to flush the chamber volume, where, after a few minutes, a steady state mixing ratio is established from which the flux is calculated [Slemr and Seiler, 1984; Williams et al., 1988]. Closed chamber techniques have no forced air exchange or recirculating, closed-loop gas flow, and the flux is calculated from the rate of increase in gas mixing ratio during the first few minutes after a chamber has been in place over the soil surface [Galbally et al., 1985; Johansson et al., 1988]. The relative advantages and disadvantages of open versus closed covers have been discussed by Denmead [1979], Hutchinson and Mosier [1981], Johansson and Granat [1984], and Hutchinson and Livingston [1992]. Hutchinson and Mosier [1981] also presented formulae for estimating optimum closed cover vent dimensions and developed a logarithmic equation for computing flux that compensates for transport-related nonlinearity that often occurs in the rate of NO or N_2O accumulation beneath a closed soil cover, especially when measuring small exchange rates over porous soils. Anthony and Hutchinson [1990] confirmed the importance of employing a nonlinear flux model in these situations from statistical analysis of a large set of N_2O flux measurements performed in a Bermuda grass (*Cynodon dactylon*) pasture on sandy soil in a humid subtropical region of southern Texas. Although only 441 of their 2224 measurements met criteria they established for using the logarithmic equation, this group included 73% of the 255 fluxes greater than 10 g N ha^{-1} d^{-1}, and the resulting estimate of annual N_2O emissions from this site was 27% larger than was computed under the traditional assumption of linear N_2O accumulation.

The net recovery of NO from both open and closed soil covers depends strongly on factors such as the presence of vegetation, wetness of the enclosed soil and vegetation, NO to NO_2 emissions ratio, O_3 concentration of the enclosed air, etc. To correct NO_x emissions estimates for deposition processes (see section 5.2.5), several methods have been developed to adjust for reabsorption of NO and/or NO_2 during their residence in the enclosure [Galbally and Roy, 1980; Galbally et al., 1985; Williams et al., 1988]. In those instances where ambient air is used to sweep an open enclosure [cf. Slemr and Seiler, 1984] significant quantities of NO_2 may be introduced into the chamber. Moreover, emitted NO may be converted to NO_2 within the chamber by reaction with ambient O_3 contained in the sweep gas. Because NO_2 is much more rapidly deposited than NO, correcting for deposition is difficult and imprecise [Galbally et al., 1985]. For this reason, more reliable and consistent measurements of the gross flux of NO from soil can be obtained using a closed soil cover [Johansson et al., 1988] or an open cover swept by a synthetic zero air mixture [Kaplan et al., 1988; Williams et al., 1987, 1988]. Hutchinson and Brams [1992] recirculated sample air from their closed covers to supply the 1.4 L min^{-1} sample required by the luminol-based NO_x detector without creating the problems associated with (1) replacing sample air with ambient air containing NO_2 and O_3, or (2) carrying cylinders of compressed zero air into the field. Residual NO, NO_2, and water vapor were scrubbed from the sample air before returning it to the enclosure, and the measured NO accumulation rate was adjusted accordingly.

Several other methods have been used to determine the flux of NO and N_2O from soil. Rolston et al. [1976] measured in situ N_2O concentrations within the soil matrix and calculated the flux from diffusion theory. In addition to the problems associated with sampling the soil atmosphere, this approach presents other difficulties (e.g., determination of the N_2O diffusion coefficient in soil air) and yields a flux characteristic of a much smaller soil area (typically ~10^{-3} m^2) than enclosures (typically ~1 m^2). Micrometeorological techniques for the measurement of trace gas exchange, which were recently reviewed by Fowler and Duyzer [1989], are attractive because they integrate the flux over an even larger area (typically ~10^3 m^2), and because they do not disturb the aerial and soil environments under study. On the other hand, they require a much larger investment in time and equipment, and, as a result, they have been used principally in intercomparison studies conducted to validate a particular enclosure technique. For example, Hutchinson and Mosier [1979] used a traditional aerodynamic approach to determine

the eddy diffusivity required to compute the vertical flux of N_2O from its measured concentration gradient above an irrigated field of corn (*Zea mays*). Parrish et al. [1987], Kaplan et al. [1988], and Johansson et al. [1988] measured nighttime fluxes of NO from soil using a technique that relies on the measured NO concentration gradient with height above the ground to define the vertical mixing and, thus, avoids the usual requirement for simultaneous measurement of meteorological parameters. This technique, described in detail by Parrish et al. [1987], is based on the premise that during the night when photochemical production of NO from NO_2 is inoperative, net soil emission of NO is equal to its integrated loss in the lower atmosphere due to reaction with O_3. Steady state NO and O_3 concentration profiles and negligible horizontal divergence are assumed.

Kramm et al. [1991] presented a modified profile method for determination of the flux of ozone and reactive N species (NO, NO_2, HNO_3). Numerical solution of a set of coupled nonlinear ordinary differential equations using data on the vertical profiles of wind, temperature, humidity, and trace gas concentrations yields the flux of O_3 and HNO_3. These fluxes are required as input data into a set of budget equations describing the NO-NO_2-O_3-HNO_3 system from which the flux of the other species is computed. An interesting aspect of this technique is that it accounts for vertical flux divergence due to chemical reactions by combining reactive species into groups which are chemically conservative.

The eddy correlation technique has also been used to determine flux of reactive N oxides [Delany et al., 1986; Hicks et al., 1986; Hicks and Matt, 1988; Wesely et al., 1982, 1989; Zeller et al., 1989]. This technique relies on the fast (1-10 Hz) measurement of vertical wind, temperature, humidity, and trace gas concentrations. The flux is calculated by averaging the deviations of the product of the vertical air motion and gas concentration from a mean value over some time interval that is long enough to provide statistical significance. The eddy correlation method can be used both from ground-based as well as aircraft platforms to measure flux of trace species over large areas [Desjardins and MacPherson, 1989]. Application of this method to determination of fluxes of NO_x and N_2O has been limited because of the lack of sensitive, fast-response chemical sensors, particularly for N_2O. However, as spectroscopic detection techniques become more powerful, flux determinations via eddy correlation will be possible (C. Kolb, personal communication, 1991).

4.4. *Techniques for Measuring Ancillary Soil Parameters*

Process-level understanding of both small-scale and large-scale temporal and spatial variability in soil NO and N_2O exchange rates frequently requires simultaneous determination of soil physical, chemical, and biological properties such as (1) activities of various microbial groups responsible for mediating the processes involved in production of the two gases (section 2), (2) pool sizes and transformation rates of several soil organic and inorganic N-containing compounds and ions that represent substrates, intermediates, or products of those processes, and (3) soil physical and environmental parameters that determine not only the suitability of a given habitat to a particular microbial group but also the diffusive transport of substrates and products to and from that habitat.

Temperature is one of the principal factors that controls both production and transport of trace gases in soil and thus is routinely measured during field experiments. However, the magnitude and variability of soil temperature changes substantially with depth below the surface. For example, Arya [1988, pp. 37-46] noted that the amplitude of the diel change of soil temperature decreases exponentially with depth. Depending on whether nitrification or denitrification serves as the source of soil-emitted NO or N_2O, the depth of the primary production zone in the soil may also vary. Thus determination of the appropriate depth for measuring soil temperature is not straightforward and may influence its correlation with the measured flux. Generally soil temperature is determined at depths of 1 to 10 cm with a sheathed thermocouple or thermistor probe [e.g., Anderson and Levine, 1987; Williams et al., 1987], although soil water content/temperature block combination probes [Hutchinson et al., 1992] and soil temperature plates [Slemr and Seiler, 1984] have also been employed.

Soil water content is commonly measured because of the multiplicity of its effects on both biotic and abiotic processes in soil. Direct gravimetric measurement is the simplest, least expensive, and most commonly used approach, but it is time consuming and involves destructive sampling, so several nondestructive instrumental techniques have also been employed (e.g., gamma ray or neutron attenuation, neutron thermalization, and techniques based on water-dependent changes in the electrical properties of soil). Gardner [1986] provided a comprehensive overview of all direct and indirect methods for measuring soil water content except time domain reflectometry, a relatively new and promising technique that yields a measure of volumetric soil water content that is reported to be largely independent of soil texture, density, and salt content, thus indicating little need for calibration [Dalton and van Genuchten, 1986; Topp et al., 1980; Topp, 1987; Zegelin et al., 1989]. Regardless of what approach is used to determine soil water content, the multiple effects of this parameter on emission of NO and N_2O from soil are more easily interpreted when the data are combined with measurements of soil bulk density to yield estimates of water-filled pore space (WFPS), which is the ratio of volumetric soil water content to total soil porosity [Linn and Doran, 1984] (see section 5.2.3).

In addition to soil temperature and water content the most useful and common soil analyses performed to explain and predict variation in soil NO or N_2O exchange rates are various assays intended to measure soil N availability. Soil core samples of 1 to 10 cm depth are taken and either subsampled according to depth or homogenized into a bulk sample. Concentrations of the inorganic ions NH_4^+, NO_2^-, and NO_3^- are generally determined by colorimetric analysis of 1M or 2M KCl extracts of fresh soil samples, while the rates of such processes as mineralization and nitrification are usually inferred from changes in the concentrations of these same ions during long-term incubation of unamended soil. Activities of various microbial groups may be expressed as the result of any of several counting techniques or in terms of their rates of product formation in the presence of unlimited substrate. Procedures for measuring soil chemical and microbiological properties were summarized by Page et al.

[1982] and soil physical properties by Klute [1986]. The procedures described in these two volumes are widely used and generally appropriate, except that modifications proposed by Yadvinder-Singh and Beauchamp [1985] were recently shown to vastly improve the sensitivity and reproducibility of the previously accepted method for determining short-term nitrifier activity in soil, which is known to be an important indicator of the potential for NO and N_2O emission from well-oxygenated soil (G. L. Hutchinson and A. C. Tortoso, unpublished data, 1991).

5. FIELD AND LABORATORY RESULTS

5.1. *Summary of Soil NO_x and N_2O Exchange Measurements*

In the following sections we will summarize the current soil NO_x and N_2O emissions data and then briefly describe some of the features and patterns that can be discerned in these data.

5.1.1. *Nitric oxide and nitrogen dioxide.* Table 1 presents a summary of available field measurements of soil NO emissions. There is general agreement among the authors cited in the table that the preponderance of NO_x emitted by soil is NO, with direct soil emission of NO_2 accounting for less than 10% of the total. Instances where a larger fraction was reported as NO_2 can probably be attributed either to postemission oxidation of NO in the chamber atmosphere or to nonspecificity of the technique chosen for determining the NO_2 fraction of NO_x. Only NO and NO_2 have been unambiguously identified among soil-emitted NO_y compounds, but recent evidence suggests that others may be included [Slemr and Seiler, 1991]. Emission of NO and NO_2 from plants has been reported [Klepper, 1979], although plants are normally considered to represent a sink for both gases [Wetselaar and Farquhar, 1980].

Most of the measurements in Table 1 were made using a variation of the enclosure technique, but a few authors [Kaplan et al., 1988; Johansson et al., 1988; Parrish et al., 1987; Williams et al., 1988; Williams and Fehsenfeld, 1991] compared their enclosure measurements with flux estimates obtained using the nighttime gradient technique outlined in section 4.3. In every case the two techniques agreed within 30% and showed no systematic overall differences. Considering the characteristically high temporal and spatial variability in soil NO emissions, the agreement is remarkably good and indicates that no serious bias is involved in using the somewhat more invasive enclosure technique. Only two of the data sets in Table 1 [Delany et al., 1986; Wesely et al., 1989] were obtained by eddy correlation, which is probably the most fundamentally sound approach to flux estimation. Although results from these experiments were not compared simultaneously with data obtained by one of the other techniques, there was reasonable agreement with averaged chamber data from soils under similar conditions.

There is immense variability in NO emissions from soil, especially across different ecosystem types. The field-measured NO fluxes in Table 1 vary over 4 orders of magnitude, from less than 0.1 up to 231 ng N m^{-2} s^{-1}. Slemr and Seiler [1984] reported even higher variability, with their derived fluxes ranging from less than zero (i.e., deposition) to greater than 250 ng N m^{-2} s^{-1} on unfertilized soils, and from less than zero to more than 2000 ng N m^{-2} s^{-1} on fertilized soils. Mean values reported by the various investigators vary almost as much, ranging from 0.034 ng N m^{-2} s^{-1} for a tidal marsh [Williams and Fehsenfeld, 1991] to 94 ng N m^{-2} s^{-1} for a recently fertilized corn field [Williams et al., 1988]. There are more than fifty different sets of measurements listed in Table 1 with an arithmetic mean emission rate of 12.6 ng N m^{-2} s^{-1} and standard deviation 18.4 ng N m^{-2} s^{-1}. Some of this variability may be due to differences in measurement techniques, especially in the methods used to separate emission from deposition (see section 5.2.5 below), but the greater part probably reflects differences among sites in the nature and rates of the predominant processes for NO production, consumption, and transport. Large temporal variability is also apparent in soil NO emissions. For example, Williams and Fehsenfeld [1991] measured a nearly 10-fold increase in the rate of NO emission from hot, dry grassland soil within an hour following a brief rain shower (<0.03 cm).

5.1.2 *Nitrous oxide.* Table 2 presents a summary of field measurements of soil N_2O emissions from different areas around the globe. Several reviews of N_2O sources and sinks have been published in the last ten years [Bowden, 1986; Davidson, 1991; Eichner, 1990; Hahn and Crutzen, 1982; Schlesinger, 1991, pp. 329-331; Sahrawat and Keeney, 1986; Stedman and Shetter, 1983; IPCC, 1990], so we present here only some recent examples from the large and growing soil N_2O emission data base. As was the case with NO, the majority of these measurements were obtained with enclosure methods because of the convenience and high sensitivity that this technique affords. Because of the need for fast response, high sensitivity detection systems, N_2O flux determinations via micrometeorological methods are rare. However, Mosier and Hutchinson [1981] compared soil N_2O emission rates measured by chamber and micrometeorological (gradient) techniques and found approximately 30% agreement, similar to that noted for NO flux method intercomparisons. Spatial variability in soil N_2O exchange is even greater than that noted for NO. For example, Folorunso and Rolston [1984] calculated coefficients of variation as high as 282-379% for N_2O fluxes measured within a small area of apparently uniform soil, and the data in Table 2 indicate the high level of variability encountered across different land use types.

5.1.3. *Features common to NO and N_2O emissions.* Some investigators have attempted to identify the processes responsible for their reported NO and N_2O exchange rates. For example, based on observed correlations of their measured emission rates of the two gases with soil temperature, soil NO_3^- concentration, and soil water content, Anderson and Levine [1987] concluded that most of the NO was produced by nitrifiers, and most of the N_2O by denitrifiers. Similar evidence was presented by Levine et al. [1988]. Several laboratory soil incubation studies employing acetylene [Davidson et al., 1993] or nitrapyrin [Tortoso and Hutchinson, 1990] to inhibit chemoautotrophic nitrifiers have provided additional strong evidence that this microbial group is responsible for NO production, an interpretation that is also consistent with most results from pure culture studies of *Nitrosomonas europae* [Anderson and Levine, 1986; Lipschultz et al., 1981]. However, at higher concentrations

TABLE 2. Comparison of N_2O Emissions From a Variety of Land Areas

Land Use Category	Flux, $ngN/m^2/s$ Mean	Range	Reference
Agricultural Fields			
Recently fertilized			
Bermuda grass (Texas, 0-9 weeks)	6.5	0-14	Hutchinson and Brams [1992]
Beans (Canada, 0-5 mos.)	--	0-124	Shepherd et al. [1991]
Corn (Virginia, 5-30 days)	85	28-241	Anderson and Levine [1987]
Not recently fertilized			
Bermuda grass (Texas)	2.8	0-4	Hutchinson and Brams [1992]
Beans (Canada, 19 years)	---	0-17.2	Shepherd et al. [1991]
Soybeans (Virginia, three months)	88	66-109	Anderson and Levine [1987]
Wheat (Colorado, July, one year)	21	16-25	Anderson and Levine [1987]
Wheat (Colorado, May, one year)	157	9.7-234	Anderson and Levine [1987]
Barley/lucerne (Sweden)	3.5	0.1-17	Johansson and Granat [1984]
Bare soil (Spain, ten months)	8.8	-2.2-107	Slemr and Seiler [1984]
Unforested Areas			
Grassland, pastures, meadows			
Pasture (Mexico, upland, dry season)	0.39	---	Davidson et al. [1991]
Pasture (Mexico, floodplain, dry season)	1.5	---	Davidson et al. [1991]
Pasture (Mexico, upland, wet season)	0.94	---	Davidson et al. [1991]
Pasture (Mexico, floodplain, wet season)	2.9	---	Davidson et al. [1991]
Pasture (Colorado)	2.9	---	Mosier et al. [1991]
Pasture (Brazil)	28.6	---	Mosier et al. [1990]
Savanna/chaparral (arid/semi-arid)			
Savanna (Venezuela, rainy season)	---	2.0-4.7	Sanhueza et al. [1990]
Savanna (Venezuela, dry season)	1.2	0.42-2.5	Hao et al. [1988]
Chaparral (California, burned, wet/dry)	62	---	Anderson et al. [1988]
Chaparral (California, burned, wet/dry)	13	---	Levine et al. [1988]
Chaparral (California, unburned, wet/dry)	<2	---	Levine et al. [1988]
Forests			
Temperate forests			
Red pine forest (Mass., annual average)	0.032	---	Bowden et al. [1990]
Hardwood forest (Mass., annual average)	0.054	---	Bowden et al. [1990]
Tropical forests			
Forest (Mexico, upland [2 sites], dry season)	0.48	---	Davidson et al. [1991]
Forest (Mexico, upland [2 sites], wet season)	1.4	---	Davidson et al. [1991]
Semideciduous forest (Venezuela)	6.3	2.7-12	Sanhueza et al. [1990]
Tropical upland forest (Brazil)	6.4	---	Keller et al. [1988]
Upland/woodland forest (Brazil, average)	3.6	---	Livingston et al. [1988]
Other			
Rice fields (China, average)	-0.97	-4.4-4.8	Khalil et al. [1990]
Undrained marsh (Wisconsin, average)	0.13	---	Goodroad and Keeney [1984]
Drained marsh (Wisconsin, average)	15	---	Goodroad and Keeney [1984]
Wet meadow (Wisconsin, average)	3.9	---	Goodroad and Keeney [1984]

acetylene is also known to block N_2O reductase activity in denitrifying bacteria [Davidson et al., 1986; Ryden et al., 1979] and may react with NO; thus results from field studies, where control of the acetylene level may not be as accurate as in the laboratory, should be interpreted with caution.

Several recent field and laboratory studies are contradictory to the attractively simple hypothesis that NO arises primarily from the activity of nitrifying bacteria and N_2O primarily from denitrifiers. For example, based on studies with pure cultures, Anderson and Levine [1986] concluded that both nitrifiers and denitrifiers may be involved in the production of N_2O in anaerobic soils or anaerobic microsites in aerobic soils. Davidson et al. [1993] concluded from acetylene inhibition experiments in a seasonally dry Mexican tropical forest that nitrification was the dominant source of both gases during the dry season and during initial soil wetting that marked the beginning of the wet season but that denitrification may be the most important N_2O source during the remainder of the wet season. Similarly, Hutchinson and Brams [1992] found that nitrifiers were responsible for production of both NO and N_2O in a grass pasture on a sandy loam in humid, subtropical southern Texas. Colbourn et al. [1987] also indicated that nitrification may have contributed to N_2O emission from urine-treated pasture, but denitrification seemed to be the principal source; they further indicated that, although nitrification appeared primarily responsible for the sizable observed emission of NO_x, a denitrification NO source could not be ruled out. Laboratory studies [e.g., Johansson and Galbally, 1984; Remde et al., 1989] usually indicate much larger NO emission rates under anaerobic than aerobic conditions, but Galbally and Johansson [1989] showed that NO emission rates observed in the laboratory match those measured from the same soils under similar conditions in the field only in the aerobic case. The latter observation is likely explained by the transport dependence of the NO and N_2O yields of denitrification described in section 3.2.

Despite the intimidating variability of soil NO_x and N_2O emission rates and the diversity of biotic and abiotic processes involved in the production, consumption, and transport of these N gases, various patterns emerge immediately from inspection of Tables 1 and 2. Warmer, dryer soils are more copious sources of NO per unit area than wetter, cooler soils. For this reason, grassland and savannah soils tend to be stronger sources than forest soils at the same latitude. For example, Johansson et al. [1988] observed larger average NO emission from savannah areas than forested areas in Venezuela. They also noted that the NO fluxes measured from both areas were a factor of 3 to 30 larger than the fluxes from analogous ecosystems in temperate regions. The greater importance of tropical versus temperate and boreal biogenic sources also holds for N_2O [IPCC, 1990], but because denitrification has more significance as a source of this gas, the C-rich and usually wetter forest soils at each latitude typically support larger N_2O fluxes than their grassland or savannah counterparts. Further inspection of Tables 1 and 2 suggests that fertilized and burned-over soils are stronger emitters of both gases than unfertilized and unburned soils at similar locations. These and other patterns in the available data indicate that both NO and N_2O exchange across the soil-atmosphere boundary are strong functions of soil temperature, soil water content, vegetative cover, site history (fertilization, burning, domestic animal grazing, etc.), and other factors.

5.2. *Environmental Controls of NO_x and N_2O Exchange*

In the following sections we will discuss in detail several of the environmental factors that control the exchange of NO_x and N_2O between the soil and the atmosphere.

5.2.1 *Soil temperature.* Several field studies have shown a strong temperature dependence in measured NO_x emissions from soil [Anderson and Levine, 1987; Johansson, 1984; Johansson and Granat, 1984; Shepherd et al., 1991; Slemr and Seiler, 1984; Williams et al., 1987, 1988; Williams and Fehsenfeld, 1991]. This dependence is illustrated in Figure 5 taken from Williams and Fehsenfeld [1991]. Although the emission rates shown in the figure vary substantially from one location to another, their dependence on soil temperature over the range 15° to 35°C is similar at all locations. The approximate doubling of the NO emission rate for each 10°C rise in temperature over this range matches the temperature dependence of soil N_2O emissions [Blackmer et al., 1982] as well as most microbial processes, including nitrification [Focht and Verstraete, 1977] and denitrification [Galbally, 1989].

Because the rates of microbial processes generally peak at moderate temperatures, biogenic NO_x and N_2O production in soil declines near the extremes of the normal range of soil temperatures that occur in the field. For example, data from the Pawnee National Grassland in northern Colorado (Figure 5) indicate a decrease in the soil NO release rate at temperatures greater than about 35°C. Lower NO emissions at high temperature may result partially from soil desiccation and its consequent reduction in the mobility of available nutrients but is probably due primarily to the failure of autotrophic nitrifiers to grow above 40°C [Focht and Verstraete, 1977]. The possible quantitative significance of heterotrophic nitrification in high-temperature environments such as desert soils and composting systems was noted in section 3.1; the responsible heterotrophic microorganisms have much greater tolerance to high temperature. Because the heterotrophs responsible for denitrification have similar tolerance to high temperature, and because this process has greater significance as a source of N_2O, soil emission of this gas does not exhibit the same sensitivity to elevated temperature characteristic of NO emissions. In fact, the Arrhenius equation that describes this exponential temperature dependence generally applies only over the range 15° to 35°C for nitrification but applies over the much broader range 15° to 75°C for denitrification [Focht and Verstraete, 1977].

At the other temperature extreme, low but nonzero NO emission rates have been reported at near-freezing soil temperatures at a grassland site near Boulder, CO (Figure 5) and several agricultural fields in Virginia [Anderson and Levine, 1987]. Changes in temperature below about 15°C typically have much greater effect on the rates of all biochemical processes than changes above this threshold and are not well characterized by the Arrhenius equation [Ingraham, 1962]. However, the potential for important soil emission of NO and N_2O at low temperature cannot be discounted because the organisms responsible for both nitrification and denitrification are known to possess a

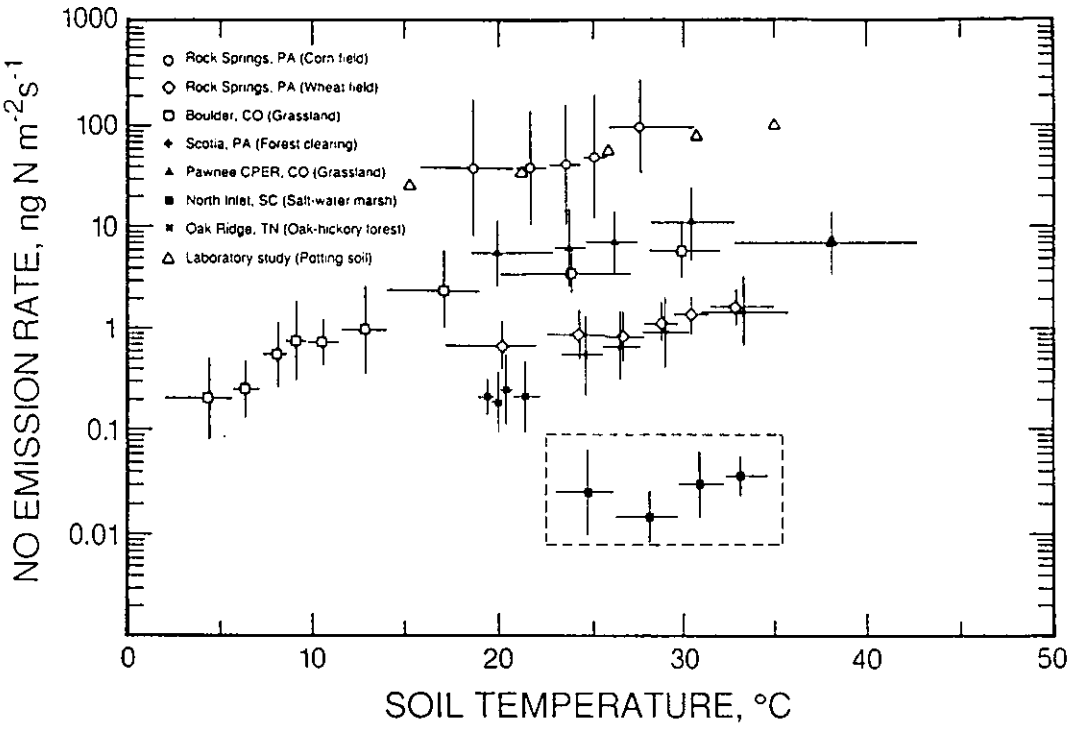

Fig. 5. The flux of NO versus soil temperature. The vertical lines represent the standard deviations of the average NO flux measured over the soil temperature range spanned by the horizontal bars. Heavy crosses, which represent laboratory data, are single data points [Williams and Fehsenfeld, 1991].

significant capacity for adaptation to extreme climates [Focht and Verstraete, 1977; Haynes and Sherlock, 1986].

In addition to its effect on the microbial production of NO and N_2O in soil, temperature also has a strong influence on the physical and chemical parameters that regulate gaseous transport rates through soil and subsequent exchange with the atmosphere (see Figures 3 and 4). Unfortunately, these parameters (e.g., diffusion coefficients, solubilities) also depend on soil texture, soil water content, the composition of aqueous and nonaqueous soil phases, etc., which significantly complicates achieving a predictive understanding of the net effect of temperature on soil NO and N_2O exchange processes. For example, Anderson and Poth [1989] noted that the relationship between flux and temperature observed at higher soil water contents disappeared at low soil water contents. Empirical relationships (cf. Figure 5) that integrate the temperature dependence of all physical, chemical, and biological factors have been used to describe the effect of this environmental controller in the soil NO emissions inventory presented in section 6.2.

5.2.2. *Soil nitrogen availability.* There is abundant evidence that the availability of organic and inorganic N in soils strongly influences rates of NO and N_2O emission. For example, Robertson and Tiedje [1984] found that a net nitrification assay correlated well with N_2O production in intact cores of forest soils from Michigan, while Matson and Vitousek [1987] reported a good correlation between a net mineralization assay and N_2O flux from tropical forest soils, but not from nearby pastures. In NO emission studies, Williams and Fehsenfeld [1991] found that soil NO_3^- concentration was a good predictor of the differences in emission rates of widely-varying ecosystem types across the United States, but Hutchinson et al. [1993] reported that emissions from a grass pasture on sandy loam in humid subtropical southern Texas were much more strongly related to soil NH_4^+ than soil NO_3^- concentration. Unfortunately, all these correlations and others [e.g., Aulakh et al., 1984b; Davidson and Swank, 1986; Rolston et al., 1984] tend to be site-specific or study-specific, and no single predictive parameter or suite of parameters has emerged that accurately reflects the effect of N availability on soil NO_x and N_2O emissions across all sites and studies.

Because biogenic production of NO and N_2O arises principally from the microbial processes of nitrification and denitrification, the measured rate of the predominant process between these two should serve as the best index of the influence of soil N availability on emission rates. Indeed, recent field studies have documented that nitrification rates were strongly correlated with emission of NO from a dry tropical forest soil [Davidson et al., 1993] and with emission of both NO and N_2O from a well-drained subtropical grassland [Hutchinson et al., 1993]. However, nitrification and denitrification rates are difficult and time consuming to estimate, and the relative importances of the two processes, as well as their yields of NO and N_2O, vary across small distances and short times, thus limiting the usefulness of measured mean process rates in many cases.

Alternatively, because both nitrification and denitrification

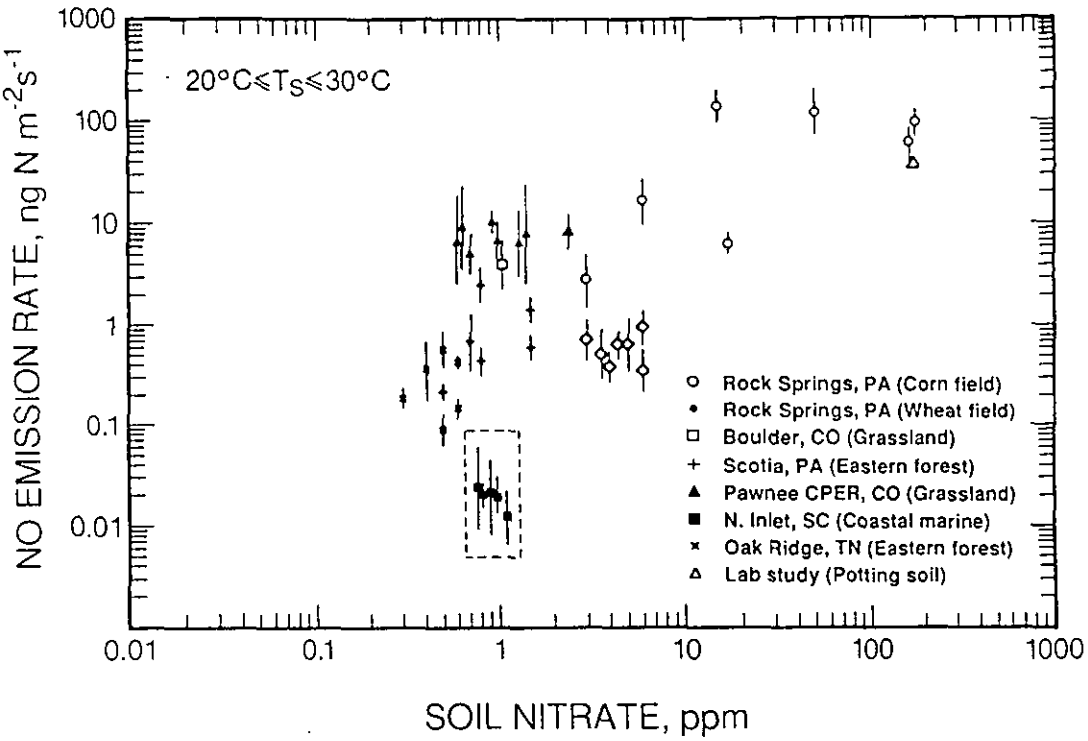

Fig. 6. The flux of NO versus the nitrate content of soil [cf. Williams and Fehsenfeld, 1991]. The NO flux is an average over a temperature range of 20°C to 30°C.

are often substrate-limited (Figures 3 and 4), soil NH_4^+ or soil NO_3^- pool sizes might be expected to serve as useful indicators of the rate of N transformation, and thus to forecast NO_x and N_2O exchange rates. Examples supporting this concept include the correlations of NO fluxes with soil NH_4^+ levels reported by Slemr and Seiler [1984], Anderson et al. [1988], and Levine et al. [1988], as well as similar correlations of N_2O fluxes with soil NH_4^+ concentrations reported by Mosier et al. [1982, 1983]. However, because the turnover rates of soil inorganic N pools are sometimes very rapid, pool sizes may not accurately reflect the prevailing rate of N cycling or, more specifically, the rate of substrate supply to nitrifying or denitrifying bacteria. For example, Davidson et al. [1990] estimated that turnover time of the soil NH_4^+ pool in a dry California grassland was about one day, so low measured NH_4^+ concentrations were a poor indicator of the rate of NH_4^+ supply.

All this complexity makes it extremely difficult to parameterize the dependence on soil N availability of the soil source of NO and N_2O in atmospheric photochemical models, soil emission inventories, or other similar applications. That dependence in the inventory presented in section 6.2 is based on the linear correlation reported by Williams and Fehsenfeld [1991] between soil NO_3^- levels and emission of NO measured from different ecosystems and agricultural areas at soil temperatures between 20° and 30°C (Figure 6). Modeling studies using data from both agricultural and grassland soils showed that NO_3^- pool size is also an important predictor of soil N_2O emission rates [Mosier et al., 1983]. It is not clear whether these correlations reflect the importance of NO_3^- as a substrate for denitrification or as a product of nitrification or simply that NO_3^- tends to accumulate in soils where N is abundant compared to the availability of readily oxidizable C, which generally results in a leaky N cycle.

Several investigators have demonstrated that soil NO and N_2O emissions may be substantially enhanced by addition of NO_3^- fertilizer, thus supporting the use of NO_3^- pool size as an index for gauging dependence of the emission rates on N availability. For NO, this effect was noted in agricultural soils by Shepherd et al. [1991] and Johansson and Granat [1984], in forest soils by Johansson [1984] and Kaplan et al. [1988], and in savannah soils by Johansson et al. [1988] and Sanhueza et al. [1990]. For N_2O, a similar effect was noted by Conrad et al. [1983], Keller et al. [1988], Livingston et al. [1988], and Rolston et al. [1982], as well as by Sahrawat and Keeney [1986, and references therein]. On the other hand, there is little agreement among various authors regarding the fraction of applied fertilizer lost as NO or N_2O, which could be interpreted as arguing against the use of an inorganic N pool size to forecast emission rates of the two gases. For example, Johansson and Granat [1984] reported that about 0.2% of the NO_3^- applied to an agricultural field was lost as NO, not too dissimilar from the 0.35% loss as NO observed for a fertilized forest [Johansson, 1984], but Slemr and Seiler [1984] found that the amount of applied N lost as NO_x depended strongly on the fertilizer source. Their estimates ranged from 0.1% for $NaNO_3$ to 5.4% for urea. In contrast, measurements by Galbally et al. [1987] indicated that only

about 0.002% of the urea applied to a flooded rice field added was lost as NO_x, and Colbourn et al. [1987] found that total NO_x emission amounted to only 0.03% of the N in cattle urine (principally urea) in the two weeks following its application to a field. In fertilized fields in Virginia, Anderson and Levine [1987] determined that in one year 0.79% of fertilizer N was lost as NO, while 1.2% was lost as N_2O in only three months. After just 9 weeks, Hutchinson et al. [1993] measured 3.2% loss as NO and 0.3% loss as N_2O from NH_4SO_4 applied to a well-drained subtropical grassland. Finally, Shepherd et al. [1991] observed even higher losses in a 5-month study in Canada, where 11% of NH_4NO_3 fertilizer was volatilized as NO, and 5% as N_2O. It is important to realize that although these fractional losses of applied fertilizer are small enough that they have little agronomic or economic significance, they are large enough to have considerable importance to the chemistry of the atmosphere, especially on a local or regional basis.

5.2.3. *Soil water content.* The dependence of soil NO_x and N_2O emissions on temperature and N availability described above is further confounded by the effects of soil water content on the biotic and abiotic processes involved in the production, consumption, and transport of the two gases. As noted by Davidson [1992b], because of the multiplicity and complexity of these effects, soil water content is one of the most important, but least well-defined, environmental controllers of soil NO and N_2O emission rates. Part of the confusion results from differences in the way soil water content is expressed by various investigators. Gravimetric soil water content (g H_2O/g dry soil) or volumetric soil water content (cm^3 H_2O/cm^3 soil) are most commonly reported, but both fail to account for textural variation among soils. For example, a value of 0.15 for either parameter is very dry for a fine-textured soil (e.g., clay), but very wet for a coarse-textured soil (e.g., sand). Nevertheless, one of these two parameters is usually employed in the definition of field capacity, which is the water content remaining after free drainage from saturated soil becomes negligible. In contrast, soil water potential, which is a measure of the energy of soil water compared to that of free water (usually expressed in pressure units), effectively accounts for differences in soil texture. Water potential is more useful as an indicator of water availability to living organisms than as a measure of the effect on diffusion rates in either soil gas or liquid phases [Skopp et al., 1990]. Probably the most promising parameter for predicting the effects of soil water content on emission of NO and N_2O via nitrification and denitrification is percentage water-filled pore space (WFPS), which is defined as the ratio of volumetric soil water content to total soil porosity [Linn and Doran, 1984].

Except for its universal requirement by all life processes, the most important effect of water on NO and N_2O production in soil results from its strong influence on the rate of O_2 supply. For example, denitrification occurs only when the O_2 supply is limited, most commonly by high soil water content, while nitrification is dependent on a plentiful supply of O_2, which usually exists only at low or moderate soil water contents. Besides governing which of these processes dominates, soil water content also influences the rates and product ratios of both processes through its effects on the diffusive transport of both gaseous and dissolved reactants and products. Higher water contents increase the ratio of water-filled to air-filled soil pore space and result in thicker water films lining the remaining air-filled pores, thus enhancing the transport of species in the solution phase, but retarding that of species in the gas phase.

These two opposing effects and their relation to WFPS are illustrated in the conceptual diagram (Figure 7) taken from

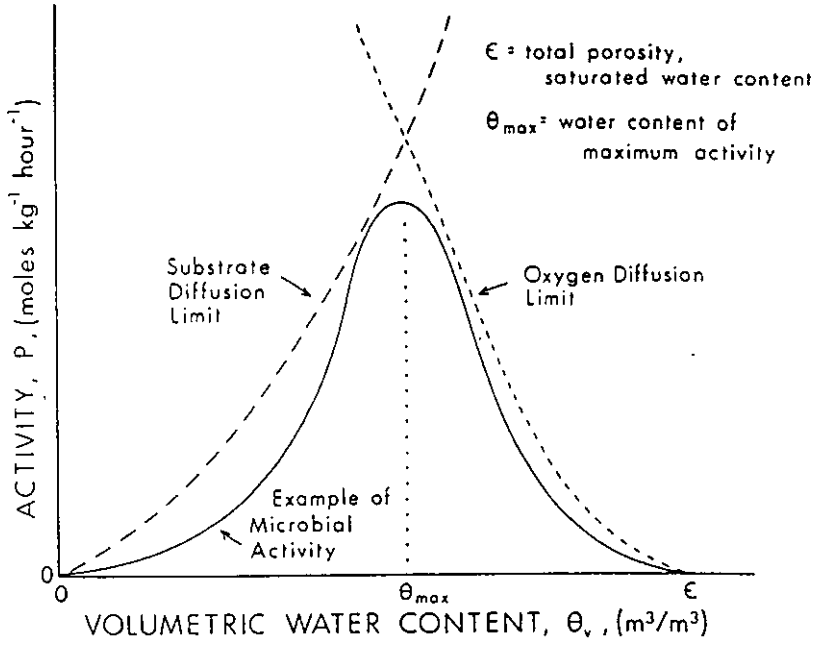

Fig. 7. Conceptual representation of the dependence of microbial activity on soil water content. From Skopp et al. [1990].

Skopp et al. [1990]. The diagram suggests, for example, that heterotrophic microbial activity in dry soil is probably limited by solution-phase diffusion of C substrate, while gas-phase O_2 diffusion rates likely limit microbial respiration in wet soil. Chemoautotrophic nitrification may be similarly limited by slow diffusion of NH_4^+ substrate through thin water films in dry soil, and by restricted gaseous O_2 transport in wet soil [Davidson, 1992b]. The optimum soil water content for these two aerobic processes is about 60% WFPS, but for anaerobic processes such as denitrification, it exceeds this value. Limitation by high WFPS of the transport rates of gases other than O_2 has additional ramifications for the microbial production of NO and N_2O in soil; for example, Remde et al. [1989] and Zafiriou et al. [1989] reported that the NO yields of nitrification and denitrification, respectively, increased with the ease of its escape from the site of production.

Figure 8 confirms the robustness of the 60% WFPS threshold for several microbial processes across a variety of soils [Linn and Doran, 1984]. However, it is important to realize that Figure 8 characterizes the dependence on WFPS of overall process rates, rather than the production of specific end products, so it must be interpreted accordingly [Davidson, 1992b]. For example, the optimal WFPS for N_2O production by nitrifiers may be somewhat higher than for NH_4^+ oxidation, because N_2O is produced by these bacteria only when NO_2^- is used as an electron acceptor apparently in response to incipient O_2 deficiency. Conversely, maximum production of N_2O by denitrifying bacteria may occur at a WFPS that is somewhat lower than the optimal value for the denitrification process in general, because the N_2O:N_2 ratio of denitrification products is determined by the relative availabilities of oxidant versus reductant [Davidson, 1992b].

In addition to these transport-related effects of a soil's water content on its NO_x and N_2O evolution rates, several authors have reported a large burst of emissions concurrent with the flush of CO_2 that typically follows wetting of very dry soil [e.g., Anderson and Levine, 1987; Davidson, 1992a; Hao et al., 1988; Slemr and Seiler, 1984; Williams et al., 1987]. Soil NO and N_2O evolution rates measured during one of these emission bursts may be one, two, or even three orders of magnitude higher than the prevailing rates preceding or following the burst. As a result, the quantity of soil N lost during the few hours or days duration of such an event often approaches, or even exceeds, the total amount emitted during the relatively long periods between times that the soil dries enough to support another emissions burst following the next addition of water. Interestingly, subsequent additions of water by irrigation or rainfall may produce further significant increases in emissions above the levels measured from dry soil, but the amount of increase is small compared to that observed for a single watering of a very dry soil [Johansson et al., 1988; Williams et al., 1987]. Hutchinson et al. [1992] demonstrated in a laboratory soil incubation study that a

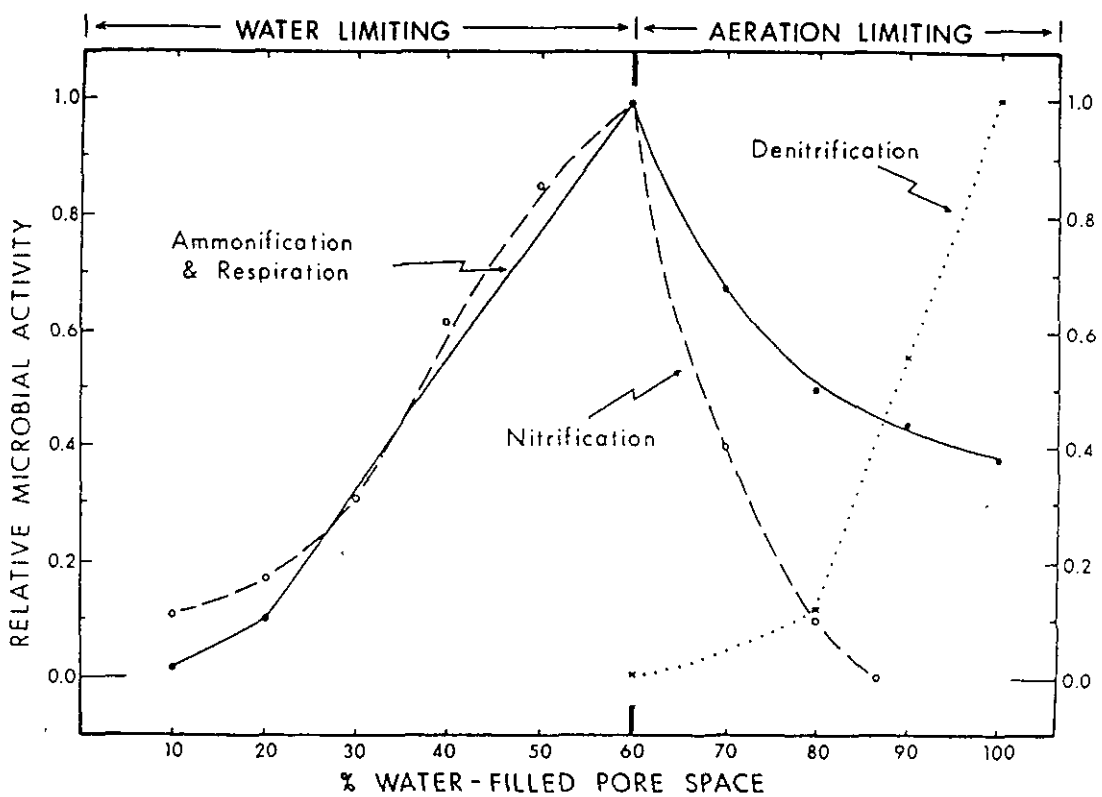

Fig. 8. Relative rates of nitrification, denitrification, respiratory microbial CO_2 production, and respiratory microbial O_2 consumption as functions of percentage WFPS. From Linn and Doran [1984, and references therein].

second NO and N_2O emissions burst similar to the one that followed initial wetting of air-dry soil occurred only where desiccation had reduced both NO and CO_2 evolution to near zero prior to rewetting. Reasons for the unusually large response of N oxide emissions to wetting of dry soil remain unclear. Davidson [1992a] suggested that the wetting response may be due to chemodenitrification of NO_2^- produced by chemoautotrophic NH_4^+ oxidizers, but this conclusion is not entirely consistent with data of other authors [e.g., Tortoso and Hutchinson, 1990].

Existing literature contains many empirical relationships that integrate the multiple and complex effects of soil water content on soil NO_x and N_2O exchange. One particular example is shown in Figure 9, and is taken from Williams and Fehsenfeld [1991]. In this figure, mean NO fluxes (normalized to 30°C) measured from a sandy loam in the Pawnee National Grassland in semiarid northern Colorado are plotted as a function of gravimetric soil water content. Although the data exhibit considerable scatter, a positive correlation over the range 1.4 to 13% is readily apparent. Unfortunately, the difficulty inherent in extrapolating this relation to soils with different particle size distribution limits its usefulness for parameterizing the dependence on soil water content of the soil source of NO_x and N_2O in atmospheric photochemical models, soil emission inventories, or other similar applications. Similar relations reported by Johansson et al. [1988] and other authors suffer the same limitation, and we urge future investigators to measure soil bulk density from which more useful WFPS percentages can be computed.

5.2.4. *Burning.* Although it applies to a smaller fraction of the global land area than the three previously-described environmental controllers, burning the vegetative cover is yet another factor with significant influence on soil NO_x and N_2O exchange. For example, Johansson et al. [1988] noted a tenfold increase in NO emissions following burning of tropical savanna in Venezuela, and Anderson et al. [1988] and Levine et al. [1988] observed that enhanced emissions of both NO and N_2O persisted for at least six months following burning of chaparral. The latter authors reported an average threefold increase in soil NO fluxes both immediately following burning and again six months later on both dry and irrigated sites. They attributed the enhanced emissions to an increase in soil inorganic N due either to enhanced biological activity or to N release from soil minerals by the extreme heat. Similar results were reported by Levine et al. [1990] following burning of a Florida wetland, but Luizão et al. [1989] found no increase in N_2O emissions from lowland tropical forest soil that was cleared and burned five months prior to sampling. Nevertheless, most authors agree that biomass burning, which has previously been shown to contribute directly to NO_x and N_2O loading of the atmosphere, also makes a secondary contribution via enhanced soil emission of both gases long after the flames have subsided.

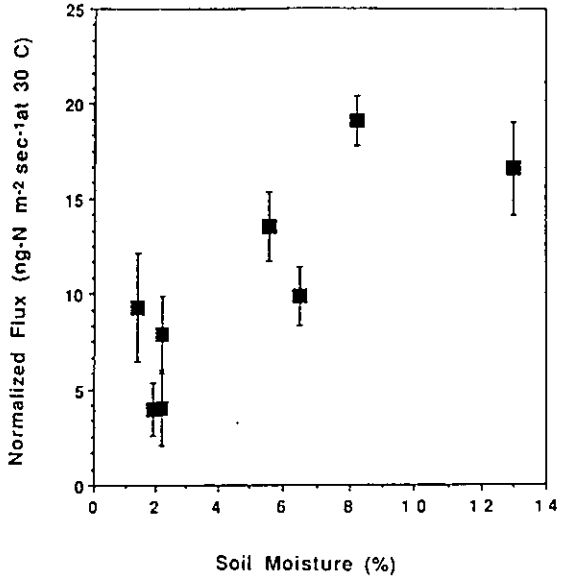

Fig. 9. Average NO emissions are plotted against the percent [dry weight] soil moisture for a site in the western United States [cf. Williams and Fehsenfeld, 1991]. The NO emissions were normalized to 30°C, assuming the NO flux from the soil varies as $\exp(0.071*T_{soil})$.

5.2.5. *Atmospheric concentration effects and deposition.* An effect of atmospheric NO concentration on the exchange rate of this gas across the soil-atmosphere boundary was first reported by Galbally and Roy [1978], who noted that the NO concentration within their closed chambers increased only until NO consumption processes apparently achieved balance with production processes, following which there was no further net exchange. Other authors have reported similar steady state NO mixing ratios varying from 0 to more than 75 ppbv in field studies [Johansson and Granat, 1984; Slemr and Seiler, 1984, 1991] and from 50 ppbv to 600 ppbv in laboratory studies of aerobic soils [Johansson and Galbally, 1984; Remde et al., 1989]. Under anaerobic conditions the steady state levels were even higher (1600-2200 ppbv), presumably due to greater enhancement of NO production than consumption processes [Remde et al., 1989]. The emission of N_2O from soil does not exhibit an analogous steady state mixing ratio, presumably because the only known soil sink for this gas, i.e., reduction to N_2 by denitrifiers, occurs only where the soil is so strongly reduced that the simultaneous production of N_2O by any process is unlikely. Instead, the declining rate of N_2O accumulation often observed beneath a closed chamber results from transient effects of the elevated surface N_2O concentration on the gradient which drives diffusion of this gas through the soil [Hutchinson and Livingston, 1992].

By analogy to the atmospheric CO_2 compensation point, at which the rates of photosynthesis and respiration in higher plants are equal, the steady state mixing ratio at which soil NO production and consumption are balanced is generally referred to as the NO compensation point. Unlike the photosynthesis/respiration couple, however, a combination of biotic and abiotic processes may be involved in NO production/consumption, and the products of NO consumption processes are not likely to be reactants for NO production processes. Because of this imperfect parallelism we suggest that use of the term compensation point is not appropriate in this case because it may foster misconceptions,

particularly in the biological community where a very specific connotation is attached to the term.

Johansson and Granat [1984] discussed the two possible mechanisms that might account for the steady state mixing ratios observed within closed chambers: (1) in soil an equilibrium level of NO may exist that causes the flux to be directed either upward or downward, depending on the magnitude and sign of the difference between that level and the NO mixing ratio in the chamber, and (2) the production of NO in soil may be independent of uptake, which increases with the NO mixing ratio in the chamber until deposition equals emission. Eddy correlation measurements of the net NO flux [Delany et al., 1986] were better explained by the latter mechanism. Galbally et al. [1985] reported good agreement when their soil flux data were simulated by a mathematical model that included competing emission and deposition processes. In another study that related laboratory data to field measurements of NO flux from the same soil, Galbally and Johansson [1989] showed that the data were best fit with a similar model that incorporated a soil NO production term independent of NO uptake. The uptake was modeled as a deposition rate with first-order dependence on NO concentration in the soil atmosphere, and the steady state mixing ratios calculated from the model compared favorably with those measured in laboratory soil column flux determinations.

Laboratory studies have shown that virtually no uptake of NO occurs in autoclaved soils [Johansson and Galbally, 1984; Remde et al., 1989]. Therefore, unlike the case for ozone, chemical and/or physical destruction of NO on soil surfaces apparently are not significant loss processes. When autoclaved soil is reinoculated by exposure to the atmosphere, NO uptake is reestablished which confirms that consumption is a microbially mediated process. However, it is not clear whether nitrifying or denitrifying bacteria are responsible. On the basis of involvement as an intermediate in the denitrification pathway [Firestone et al., 1979], there seems to be no question that denitrifiers can consume NO [Firestone and Davidson, 1989; Weeg-Aerssens et al., 1988; Zafiriou et al., 1989]. The nitrification pathway is much less clearly understood, and no direct evidence exists for consumption of NO by nitrifying bacteria.

Although the influence of environmental variables on NO uptake by soil has not been studied systematically, some reports indicate that the steady state mixing ratios observed in chambers are increased by N fertilization [Johansson, 1984; Johansson and Granat, 1984]. In studies of soil NO flux in Spain and Germany, Slemr and Seiler [1984] noted additional effects of soil temperature, water content, and organic C content. In a later paper, Slemr and Seiler [1991] confirmed these results and speculated that higher steady state concentrations observed over fertilized soil were due to enhanced NO production combined with unchanged soil uptake. They further suggested that uptake of NO by soils at this site is nonnegligible and could result in erroneous estimates of the soil source strength since ambient NO levels and measured steady state levels in the chambers typically have similar magnitudes.

In contrast to the conclusions of Slemr and Seiler [1984, 1991] several field studies have indicated relatively small importance for soil uptake of NO. For example, deposition velocities of the order of 0.1-0.2 cm s^{-1} have been reported for pasture [Galbally and Roy, 1980], 0.02 cm s^{-1} for soil [Gravenhorst and Böttger, 1983], 0.19 cm s^{-1} for a sandy loam [Judeikes and Wren, 1978], 0.35 cm s^{-1} over crested wheat grass [Delany et al., 1986], and 0.06 and 0.04 cm s^{-1} for a corn field and harvested wheat field, respectively [Williams et al., 1988]. Data from a laboratory study by Remde et al. [1989] can be used to calculate uptake rate constants of 0.005-0.04 cm s^{-1}. From these data a median deposition velocity for NO to soil is estimated to be 0.05 - 0.1 cm s^{-1}.

Deposition of NO to vegetation is also relatively unimportant [Hanson and Lindberg, 1991; Hill, 1971; Wesely, 1989]. In a study of pollutant uptake by an alfalfa canopy, Bennett and Hill [1973] found almost no gradient in NO mixing ratio through the canopy, although at the same time strong gradients were observed for more readily deposited species such as O_3 and NO_2. These authors attributed the lack of a gradient in NO principally to minimal uptake by vegetation due to the low solubility of this compound, but emission of NO from the soil may have influenced the concentrations within the canopy. Granat and Johansson [1983] and Johansson [1987] have determined that conductance of NO to pine needles is of the order 0.01-0.03 cm s^{-1}. Similar values were reported by Skärby et al. [1981]. Wesely [1989] indicates that NO has a very high surface resistance to vegetative uptake due to low solubility and reactivity. This conclusion was affirmed by Hanson and Lindberg [1991], who also pointed out that NO concentrations greater than 50 ppbv will lead to deposition to vegetation. Thus it appears that deposition of NO to vegetation is not as important as to soils.

Related to the uptake of NO is the oxidation of emitted NO to NO_2 and higher oxides followed by deposition to soils or vegetation. Such cycling of nitrogen oxides is expected to occur for all ecosystems, although the effects for some (e.g., forests) should be more pronounced than for others. Oxidation of the emitted NO occurs rapidly due to the presence of O_3 and other oxidants in the atmosphere (see section 2). The immediate product is NO_2, but further oxidation can produce NO_3, PAN, HNO_3, and other species, many of which are readily deposited to surfaces. Wesely [1989] has compiled surface resistance values for a large number of compounds, land use types, and environmental conditions. Very high resistances for NO are noted (also see above), and at the other extreme is HNO_3 with a suggested surface resistance value of 10 s m^{-1}. Hanson and Lindberg [1991] reviewed dry deposition of trace N species to vegetation and list canopy-averaged deposition velocities of 0.3-26 cm s^{-1} (median about 3.3 cm s^{-1}) for HNO_3 and 0.07-2.8 cm s^{-1} (median about 1.3 cm s^{-1}) for NO_2. The deposition of HNO_3 can be a major source of N and acidity in some cases. In order to assess properly the impact of soil emissions of NO to the atmosphere, it is imperative that such deposition processes be taken into account [Johansson, 1989; Jacob and Bakwin, 1991]. Toward this end, Johansson et al. [1988] found that the measured emission of NO exceeded the estimated deposition of NO_2 and HNO_3 by a factor of 2 in the tropical savanna region of Venezuela and concluded that substantial net export of NO_x from this region was occurring. Bakwin et al. [1990b] concluded from measurements of soil NO

emissions and NO_y flux at the top of a forest canopy in Brazil that the forest was a net sink for N oxides. Uptake of NO_y was controlled either via plant processes (stomatal control) or by ambient NO_y imported from external sources during the day. An excellent review of the results from the Brazil study is given by Jacob and Bakwin [1991]. This is an important area for future research not only for forests but for all ecosystems.

5.3. *NO_x:N_2O Emissions Ratio*

Information presented in the previous sections indicates that the NO:N_2O emissions ratio of any soil is probably most influenced by its water content. Certainly, soil temperature must be in the range that supports microbial growth, substrate NH_4^+ or oxidizable C and NO_3^- must be available, and the responsible microorganisms must be present, but because it governs O_2 availability, soil water content will usually determine whether a more oxidized (NO) or more reduced (N_2O) product is favored. Field measured NO:N_2O emission ratios are generally consistent with this hypothesis. For example, using the N_2O measurements of Hao et al. [1988], Johansson et al. [1988] reported NO:N_2O emission ratios in the range 6-7 for dry tropical savannah, and Hutchinson and Brams [1992] measured NO emissions nearly an order of magnitude greater than N_2O emissions from an NH_4^+-fertilized humid subtropical grass pasture on well-drained sandy loam. During laboratory incubation of intact soil cores from a dry annual grassland in central California, the NO:N_2O emissions ratio was greater than 1 when soil water content remained below field capacity, but decreased to 0.1 when soil water contents exceeded field capacity [Davidson, 1992a]. Highest NO production occurred at 56% WFPS and highest N_2O production at 75% WFPS, which is consistent with the analysis of Figure 7 presented in section 5.2.3. In addition, acetylene inhibition experiments confirmed that denitrification was the dominant source of N_2O at the higher water content, while nitrifiers produced both gases at lower water contents.

Pure culture studies of nitrifying and denitrifying bacteria have been consistent with the above hypotheses in some cases and in other cases have not. Lipschultz et al. [1981] reported the molar ratio of NO to N_2O produced by *Nitrosomonas europeae* to be 5 at low O_2 concentration (0.5%) and 1 at higher O_2 levels (21%). In a later study, Anderson and Levine [1986] found the opposite result for *N. europeae* with NO:N_2O ratios of 0.9 at 0.5% O_2 and 3.7 at 10% O_2. However, a different *Nitrosomonas* strain gave results consistent with Lipshultz et al., at least at 0.5% O_2 (NO:N_2O = 5.6). The molar ratio of NO to N_2O produced by denitrifiers in the pure culture studies of Anderson and Levine [1986] was much lower, typically much less than 1.

6. MODELING SOIL EMISSIONS OF NO_x AND N_2O

Because of the importance of NO and N_2O to the chemistry and physics of the atmosphere (section 2), there is an unequivocal need to develop a predictive understanding of biogenic NO and N_2O sources at regional to global space scales and seasonal to annual time scales. Budget calculations, the simplest approach to this need, compare best estimates of the magnitudes and distributions of known sources with known sinks, and then attempt to reconcile the net source of each gas with the magnitude, distribution, and trend in its atmospheric concentration. This approach has improved understanding of the relative importances of known sources and sinks, and established the potential for existence of additional unknown sources and sinks. For example, the revised global/annual N_2O budget presented by Matson and Vitousek [1990] confirmed the importance of biogenic compared to combustion sources and, in fact, implied that additional biogenic sources remain to be identified.

The precision of global NO and N_2O budgets can be improved by employing stratified sampling approaches, i.e., grouping the areas and times to be sampled along gradients in the principal flux controllers so that the resulting flux estimates can be weighted by the spatial and temporal extent over which they apply. For example, the tropical forest source term in the N_2O budget of Matson and Vitousek [1990] was inferred from stratification by soil orders within this vegetation biome, which undoubtedly yields a more accurate estimate of source strength than the often-used product of the mean observed exchange rate and total land area. Despite this and other improvements, however, simple budget calculations can never achieve the spatial and temporal resolution required to explain the immense variability in soil NO and N_2O exchange rates measured on field and landscape scales, for which we must ultimately depend on process-level simulation modeling.

Accordingly, the long-range goal of soil NO and N_2O exchange measurements is to capture the exchange rates in terms of their basic physical, chemical, and biological controllers. Subsequent development of models that relate the flux to its controller variables may be based on cellular-level mechanistic controls on the production, consumption, and transport of the two gases, or the models may parameterize these controls based on empirical relations observed in large data sets. The latter approach is most often followed because our level of mechanistic understanding is inadequate to apply to the former. For example, we know that NH_4^+ availability is an important controller of nitrification (Figure 3), as is NO_3^- availability for denitrification (Figure 4), but we lack a universally applicable assay for soil N availability. Similarly, soil water content is known to exert multiple crucial controls on both biotic and abiotic processes involved in the production, consumption, and transport of NO and N_2O in soil, but there is not universal agreement regarding even the most appropriate means for measuring and expressing this parameter. As a result, process-level models with the required spatial and temporal resolution are very difficult to parameterize [Firestone and Davidson, 1989; Galbally, 1989], and databases containing the information required as input to such models may not be adequate [Stewart et al., 1989]. The attempts to overcome these difficulties by using surrogate variables and other model parameterization approaches are summarized below. The section concludes with a discussion of the uncertainties embodied in these approaches.

6.1. *Models of Soil N_2O Emissions*

Several process-level models for simulating N cycling in soil have been proposed [Focht, 1974; McConnaughey and Bouldin, 1985; McGill et al., 1981; Scholefield et al., 1991;

Smith, 1980], many of which include prediction of N_2O emissions. For example, a model has been described (A. Bouwman, I. Fung, private communication, 1991) that uses as input soil physical and chemical properties and produces as output a monthly mean soil N_2O emission rate. Reasonable correlation between model runs and measured N_2O emission rates was obtained with input parameters that included temperature, C availability, soil fertility (a composite measure of nutrient availabilities), soil water status, and soil O_2 availability. Sensitivity analyses indicated strongest dependence on temperature, followed by soil water status. Parton et al. [1988] developed a model for describing N_2O production in grassland soil. Within this model a submodel uses soil texture, air temperature, and precipitation to derive soil temperature and water content. Inorganic N supply (e.g., atmospheric N deposition, grazing intensity) is then used with the submodel output to calculate N_2O production. They concluded that N_2O flux was correlated with inorganic N turnover rate and that nitrification was a more important N_2O source than denitrification. A recent paper by Li et al. [1992a] described a rainfall-driven model of N_2O, CO_2, and N_2 emission from agricultural land. Nitrification-based N_2O production was computed from a submodel of soil organic matter decomposition and production via denitrification from a separate submodel that included calculations for the growth and maintenance of denitrifying bacteria. The model also allows for consumption of N_2O. Inputs include climate variables, soil properties, and agricultural practices. Output from the model has been compared to data from five field studies of N_2O and CO_2 emissions [Li et al., 1992b]; reasonable agreement was found in all cases.

6.2. *Models of Soil NO Emissions*

In contrast to N_2O, there have been few attempts to model the emission of NO from soil. Galbally et al. [1985] successfully simulated measurements of both gross and net NO flux with a mathematical model that included separate production and uptake terms, but did not incorporate soil parameters known to contribute to the spatial and temporal variability in field-measured soil NO emission rates. Similarly, Galbally and Johansson [1989] were able to reproduce NO fluxes determined in both laboratory and field studies using a model that included soil physical parameters (i.e., bulk density and porosity) but not chemical or biological parameters. Adopting a completely different approach, Williams et al. [1992] proposed a parameterization scheme based on empirical relationships derived from the spatial and temporal variability observed in soil NO emissions across many land use types. Emission algorithms formulated from these relationships were combined with an ecological data base to develop an inventory of NO emissions from soils in the United States. Because it illustrates many of the problems encountered in modeling soil NO and N_2O emissions, an abbreviated description of that inventory is presented here.

The general form of the emission relationship used for the inventory development is

$$\text{NO emission (ng N m}^{-2}\text{ s}^{-1}) = A\ (\text{ng N m}^{-2}\text{ s}^{-1})\ \exp\{0.071\ T_{soil}\ (^{\circ}\text{C})\} \quad (20)$$

where A is a factor that, in principle, is related in a broad way to the NO flux determining physical and chemical properties, such as nutrients and water content, of soil in a given region. These soil parameters, in turn, are characteristic of a given biome, thus an ecosystem or land use classification scheme was used as the basis to differentiate the preexponential A factors. Four land use categories were identified: grasslands, temperate forests, wetlands, and agricultural areas. Preexponential factors for the three undisturbed ecosystem types were calculated from the data of Williams et al. [1987, 1988] and Williams and Fehsenfeld [1991]. Agricultural areas were segregated by crop type (corn, wheat, cotton, and soybeans) and A factors were derived from NO flux [Williams et al., 1988] and fertilizer [Berry and Hargett, 1989] data based on the observed linear relationship between emission of NO and soil NO_3^- (Figure 6) and NO flux and fertilizer usage [Shepherd et al., 1991]. With these procedures seven different land use types were identified and corresponding A factors were calculated (Table 3). An exponential relationship between NO emission and soil temperature (Figure 5) provided the means to capture temporal variability (i.e., diel and seasonal effects) in the soil emission data. The weighted average of the slopes of ln(NO flux) versus soil temperature, restricted to 15°-35°C, from the various measurement sites was calculated and incorporated as a universal factor ($0.071\,^{\circ}C^{-1}$) in equation (20). Empirical relationships observed in the data [Williams et al., 1987, 1988; Williams and Fehsenfeld, 1991] were used to derive the conversion formulae between air and soil temperatures shown in Table 3. The seven algorithms then were used in conjunction with land-use and air temperature data from the Geoecology data base of Olson et al. [1980], and monthly mean emission data were calculated for the 3072 counties in the contiguous United States. The land use types in the data base were combined into the categories of grasslands, temperate forests (including coniferous and deciduous), wetlands (including saltwater and freshwater), and agricultural. Crops in the inventory included corn, cotton, wheat, soybeans, hay, and alfalfa. The average fertilizer application was assumed to maintain the average soil nitrate level throughout the growing season, defined as May through August. During the rest of the year all croplands were assumed to emit at the lowest agricultural rate (soybeans).

The major sources of uncertainty in the inventory arise from formulation of the relation between flux, temperature and land use along with the connection of those parameters to the data in the Geoecology Data Base. Comparison of predicted emissions to results from studies of NO emissions from agricultural and undisturbed land areas (see Table 1) provides an estimate of a factor of 2 uncertainty associated with the A factors. Uncertainty in the temperature relations in Table 3 is estimated at ±50% and uncertainty in the data of the Geoecology Data Base was estimated by Lamb et al. [1987] at ±15%. Overall, the uncertainty is estimated at a factor of 3.

A summary of the soil emissions for the seasons from these soils is presented in Table 4. Annually, approximately 85% of the total NO emissions occurs in the spring and summer while only 15% occurs in fall and winter. This generally reflects the exponential dependence that the emissions have on soil temperature but also includes the seasonal dependence of the application of fertilizer. The relative contributions (on an annual basis) of the various soil

TABLE 3. Preexponential A Factors, Average Fertilizer Application Rates and Air-to-Soil Temperature Conversion Formulae for Land Use Categories

Land Use Type	A Factor, $ngNm^{-2}s^{-1}$	Fertilization Rate, $kgNha^{-1}$	Temperature Function
		Natural Areas	
Grasslands	0.9	----	$0.66\ T_A + 8.8$
Forests	0.07	----	$0.84\ T_A + 3.6$
Wetlands	0.003	----	$0.92\ T_A + 4.4$
		Agricultural Areas	
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 (°C). Numbers in parentheses are standard deviations. Data are from Williams et al. [1992].

categories to total soil emission in the United States are shown in Figure 10. For all inventoried sources approximately 66% of the total annual average emissions is accounted for by agricultural soils while natural or undisturbed land areas contribute about 34% annually. By far the dominant category for emissions is from 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 contrast, grasslands account for 28% of total emissions and are the dominant source with respect to natural or undisturbed land areas. Emissions from forest soils are less than 5% of the total even though forest lands constitute over 40% of the total U.S. land area. Emissions from wetlands account for less than 0.1% of the total. It should be noted that these estimates are probably upper limits for the NO that escapes from soil into the atmosphere because some of the NO emitted will be oxidized to NO_2 and taken up by the vegetation canopy and soil (see section 5.2.6).

This inventory indicates that, in the United States, the soil source of NO is small compared to combustion sources of this gas. Figure 11 compares seasonal total soil NO emissions estimates from Table 4 with the seasonal distribution of combustion sources taken from the National Acid Precipitation Assessment Program emission inventory compiled from 1985 EPA estimates of point and area NO_x sources in the continental United States. On an annual basis, the soil source was only 6% of the combustion emissions, but rose to 14% in summer due to the much stronger seasonality in the soil source than the combustion sources.

TABLE 4. Emission of NO by Category and Season

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. Emissions are in thousands of metric tons of nitrogen. Data are from Williams et al. [1992].

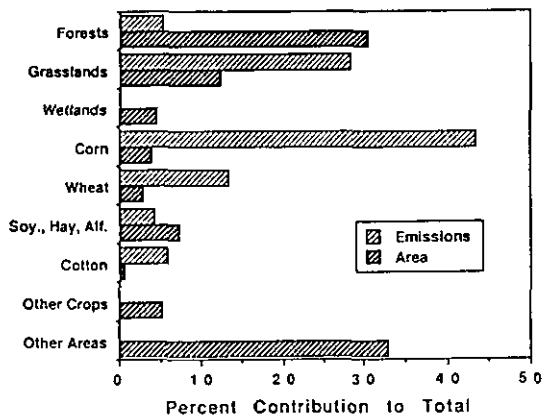

Fig. 10. Percent contribution of each source category to total emission and total area.

The inventory further suggests that in agricultural areas where large amounts of N fertilizers are used (particularly the corn-growing counties of Nebraska, Iowa, and Illinois), soil may become the dominant source of NO_x in spring and summer and thus may have significant impact on local and possibly regional atmospheric NO_x mixing ratios. In addition, the timing of agricultural activities (including N fertilization) generally coincides with the period of maximum photochemical activity in the atmosphere, so regional O_3 production and acid deposition are likely also influenced substantially.

6.3. *Limitations Encountered in Modeling NO_x and N_2O Exchange Rates*

Many of the difficulties encountered in modeling regional to global and seasonal to annual soil NO_x and N_2O exchange are scaling problems associated with the need to draw inferences about these large scale exchanges from fluxes measured over small areas and short times. Techniques for extrapolating local trace gas exchange data to larger time and space scales were recently summarized by Stewart et al. [1989] and Groffman [1991], while Avissar and Verstraete [1990] provided a more general discussion of issues related to representing surface processes in atmospheric models.

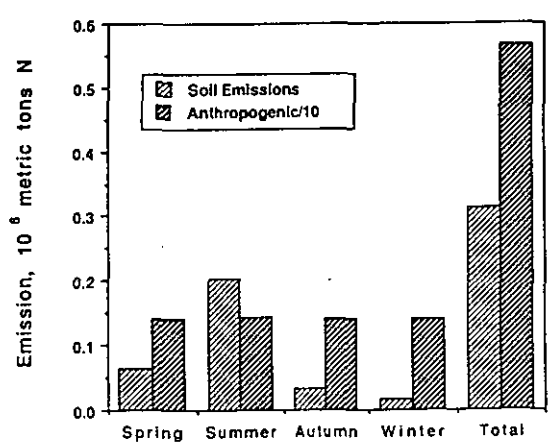

Fig. 11. Comparison of seasonally averaged soil NO emissions to man-made NO emissions in millions of metric tons of nitrogen. Note that the anthropogenic emissions are divided by a factor of 10.

Tables 1 and 2 indicate the immense variability that must be explained by models and budgets for soil NO_x and N_2O exchange. Until recently, most of these efforts have divided the earth's surface into a few major biomes and then characterized each by the product of its area and the mean exchange rate from reasonably well-studied sites assumed to be representative of that biome. However, the criteria for establishing that a particular site (or measurement time) is representative are unknown, and the large variability renders this question so important that the entire approach has questionable value. A statistically valid alternative is to employ random site selection procedures to account for the variability within each biome, but the sampling and logistical requirements of this measurement approach likely would be unmanageable.

Rather than treat the intimidating variability in soil NO_x and N_2O exchange rates as an encumbrance, Matson et al. [1989] proposed to take advantage of it by measuring NO_x and N_2O exchange along gradients of the distal controllers (e.g., climate, soil type, topography, time) of the principal microbial source processes, i.e., nitrification and denitrification (see Figures 3 and 4). Potential uses of the resulting quantitative relationships between flux and controller variables are fourfold: (1) they provide the basis for extrapolating from local to regional/global space scales and seasonal/annual time scales using either ground-based or remotely sensed data, (2) they provide information concerning the timing and distribution of emission events, (3) they provide information about the nature and dynamics of source ecosystems, and (4) they permit predicting how future natural and anthropogenic disturbances might influence the soil source of NO_x and N_2O [Matson et al., 1989]. Limitations of the so-called gradient approach include (1) that our knowledge of source process controllers remains incomplete, (2) that available methods for extrapolating non-normal distributions of flux data are imperfect, and (3) that the resulting extrapolations can only be as good as the climatological and ecological databases on which they are based [Stewart et al., 1989]. Recent examples of modeling efforts that embody the gradient approach are the grassland N cycling model of Parton et al. [1988], the soil NO emissions inventory of Williams et al. [1992], and the global/annual N_2O budget proposed by Matson and Vitousek [1990].

A recent assessment of the climatological and ecological information [Stewart et al., 1989] indicates that improvements are needed. Timely information concerning land use is critical, especially in the light of widespread and rapid man-made alterations. Intercalibration and intercomparison of measurements made to determine interannual and long-term trend analyses is needed. Archiving, improved organization, and better accessibility of this information are required. Despite the need for improvements, however, it is probably true that even existing databases cannot be adequately utilized without additional flux measurements, better simulation models, and greater efforts to validate model parameterization schemes.

Of the techniques available for soil NO_x and N_2O exchange measurement and model verification, chamber systems are the most appropriate for examining fundamental relationships between the flux and its controller variables [Hutchinson and Livingston, 1992]. Tower-based micrometeorological techniques [Fowler and Duyzer, 1989; Hicks, 1989] integrate the flux over a larger area (typically 10^2 to 10^4 m^2) and offer the potential for validating extrapolations of highly variable local scale exchange rates measured by chamber methods (typically <1 m^2). Aircraft eddy correlation measurements [Desjardins and MacPherson, 1989] have special importance because they provide direct exchange measurements over areas with size on the same order as global model grid cells (typically 10^5 to >10^8 m^2). In addition, stable isotope measurements provide tracer information at all spatial scales [Mosier, 1989] and offer the potential to identify the source responsible for absolute and relative changes in atmospheric trace gas concentrations [Stewart et al., 1989]; however, their usefulness for studying the two gases discussed here is limited by inadequate long-term isotope abundance data and the relatively short atmospheric lifetimes of most NO_y species. Matson and Harriss [1988] and Harriss [1989] proposed a framework for studying biosphere-atmosphere trace gas exchange that incorporates measurements across multiple time and space scales, a modeling effort to integrate the results, and prioritization of ecosystems to study based on their sensitivity to climate change and susceptibility to natural and anthropogenic disturbances.

7. SUMMARY, IMPLICATIONS, AND RESEARCH NEEDS

Many major environmental issues facing society today (e.g., acid deposition, global warming, stratospheric O_3 depletion, groundwater contamination, deforestation, biomass burning) are related directly or indirectly to the exchange of NO_x and N_2O across the soil-atmosphere boundary. Because of the high reactivity of NO_x, its exchange strongly influences local and regional atmospheric photochemistry, while the important global atmospheric consequences of N_2O exchange result from the long lifetime and spectral properties of this compound. Despite these vastly different atmospheric chemistries, the processes involved in the production, consumption, and transport of NO and N_2O in soil are similar. Both gases can be produced by biotic or abiotic processes, but the bacterial processes of nitrification and denitrification are by far the most important. Although there is no evidence suggesting competition between NO and N_2O for production by any of these reactions, microbial processes involved in the production and consumption 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.

The available data provide evidence that production of both gases in soil is strongly dependent on temperature, N availability, and O_2 availability, which is governed primarily by soil water content. There appears to be an exponential relationship between soil NO and N_2O exchange and soil temperature, but the dependence of flux on N availability and soil water content is not so clearly defined. Numerous correlations of soil NO or N_2O emission rates with various indices of soil N and water availability have been reported, but these tend to be site-specific or study-specific, and no single predictive parameter or suite of parameters has emerged as being universally applicable. Failure to find common predictors probably arises from several confounding factors. First, two very different processes are involved, i.e., nitrification and denitrification. Second, other process-limiting factors that interact with N availability or soil water content may be more important at some sites than others. In addition, the scale chosen for investigation influences the nature of the predictors likely to be found useful. For example, soil NO_3^- concentration was a good predictor of NO emissions when hardwood forests were compared to fertilized corn fields, but it did not account for substantial variation within each location [Williams and Fehsenfeld, 1991]; at the latter scale, modest topographic gradients or local scale effects of crop residues may be important contributors to the observed variability. The relation of NO emissions to soil NO_3^- concentration at the larger scale reflects that this ion generally accumulates when N availability in the system exceeds C availability, resulting in a leaky N cycle. The rate of N cycling may actually be higher in fertile forest sites than in tilled agricultural fields, but high C availability in temperate forest soils usually results in a conservative N cycle, little NO_3^- accumulation, and low emission of gaseous N oxides.

There is general agreement that microbial processes in soil represent by far the largest source of N_2O in the atmosphere [McElroy and Wofsy, 1986; Matson and Vitousek, 1990]. However, the estimated totality of known sources of this gas (7.9 Tg N yr^{-1}) accounts for little more than half the sum of its stratospheric sink (10.6 Tg N yr^{-1}) and its current rate of accumulation in the atmosphere (3.5 Tg N yr^{-1}), so the relative importance of the biogenic source, as well as its distribution among the earth's major biomes, is subject to change as more data become available and land use patterns are altered [Davidson, 1991].

Similarly, microbial processes in soils are a major source of NO_x. Although he acknowledged the existence of multiple gaps and uncertainties in even the most recent data, Davidson [1991] estimated the global soil NO source to be about 20 Tg N yr^{-1}, comparable to Logan's [1983] estimate of 21 Tg N yr^{-1} from combustion of fossil fuels. Understanding the impact of these NO_x emissions requires definition of the problem being addressed as well as knowledge of both the intensity and the temporal and spatial distributions of the soil source, both on an absolute scale and relative to the distribution and intensity of other NO_x sources. This complexity is illustrated by the role that NO_x plays in the formation of tropospheric O_3 on the regional and global scales and the particular concern surrounding this O_3 (cf. section 2).

Liu et al. [1987] pointed out that throughout much of the troposphere, production of O_3 is NO_x-limited. Because the lifetime of O_3 in the free troposphere (about one month) is large compared to that of NO_x (a few days or less); [Liu et al., 1987], O_3 will be more widely disseminated in the atmosphere that its NO_x precursor. For this reason, NO_x sources have a direct influence on not only the global oxidizing capacity of the troposphere, but also the influence

of O_3 as a radiatively important trace compound ("greenhouse" gas).

Because elevated O_3 levels can be harmful to plants and animals, O_3 is also an important pollutant. Moreover, the lifetime of O_3 is short compared with the large scale tropospheric mixing times, so this pollutant will not be homogeneously distributed in the atmosphere, but instead will reflect the distribution of its sources; i.e., local and regional levels of O_3 will reflect the distribution and strengths of the sources of it photochemical precursor, NO_x. Thus the emission inventory assembled by Williams et al. [1992] indicates that the soil source of NO_x will not be important in determining the O_3 burden in industrialized area such as the eastern United States, because it is small compared to large combustion sources of this gas. In contrast, NO_x emissions from soils in agricultural areas of the midwestern United States or in savanna regions of South America or Africa may be larger than other sources of NO_x and, consequently, may determine the O_3 burden, and potential for ozone damage in these areas.

Wet and dry deposition of atmospheric N oxides has environmental importance equal to that of their emission from soil. Nitrous oxide is relatively inert in the troposphere, so it is not readily deposited to the surface, but the opposite is true of NO_x. Once it enters the atmosphere it is rapidly oxidized to N oxides that are more soluble and more readily redeposited at the surface. For this reason, it is not certain how much of the soil-emitted NO resides in the atmosphere for a sufficient length of time to effectively enter into the photochemical production of ozone. Also, transport distances for N oxides can vary from local to regional scales. An example of the former is plant canopy uptake and metabolism of NO_2 formed via oxidation by O_3 of NO emitted from the underlying soil [Rogers et al., 1979], while regional-scale transport is exemplified by the deposition to northeastern U.S. forests of HNO_3 formed by photochemical oxidation of NO_x emitted from industrial and agricultural sources in the midwestern states. The result of this N transport via the atmosphere is an increasingly significant redistribution of biospheric N with largely unknown ramifications.

Quite complex interactions may result from this redistribution of biospheric N. For example, in its initial stages chronic low-level deposition of gaseous and particulate N oxides to temperate forest ecosystems have been hypothesized to increase their primary productivity without perturbing their relatively conservative N cycles. However, as N availability eventually begins to overwhelm C availability to soil microorganisms and the availability of water and other nutrients to higher plants, the importance of nitrification in the N cycle probably increases [Melillo et al., 1989]. This process contributes directly to net production of NO_x and N_2O and results in accumulation of NO_3^-, which enhances the potential for additional N_2O emissions via denitrification and contributes to leaching losses that enrich groundwater with biologically-available N. Of the six environmental issues listed at the beginning of this section, four were related by this example, and if we had instead chosen an example involving tropical forest converted to agricultural use by burning, all six might have been included.

The transition from a conservative to a leaky temperate forest N cycle described above is but one potential consequence of the chronic deposition of gaseous and particulate oxides of N. Other ecosystem functions are also affected. For example, the capacity of aerobic soils for microbial oxidation of CH_4 was reduced by addition of N to temperate zone forests [Steudler et al., 1989] and grasslands [Mosier et al., 1991]. In addition, chemical oxidation of CH_4 in the troposphere requires hydroxyl radical, the concentration of which is critically dependent on NO_x levels (section 2). Because these two processes represent the largest known biological and chemical sinks for CH_4, respectively, the atmospheric budget of this gas, as well as its contribution to global climate change, are inextricably linked to NO_x emission, transport, and deposition. Similarly, COS and CS_2, which exert important influences on the Earth's heat budget as well as the chemistry of the stratosphere, are produced mainly via soil biological processes that are sensitive to N availability [Melillo et al., 1989]. For example, the sum of COS and CS_2 emissions from both deciduous and coniferous forest soils was enhanced by N fertilization [Melillo and Steudler, 1989].

Because of these and other known and unknown linkages to atmospheric processes and properties that control the habitability of planet Earth, it is imperative that the exchange of NO_x and N_2O across the surface-atmosphere boundary be understood at all scales from cellular to global. An accurate estimate of soil emissions is possible only via process-level models that are driven by variables observed at these scales; extrapolation of a few measurements across continents or throughout the globe is clearly insufficient. Mechanistic models that reproduce basic N cycling processes in the soil would undoubtedly be the most accurate and provide the finest detail, but these models require input data that are not readily available from global ecological data bases. Larger-scale models based on ecosystem-level variables have had some success in predicting emission rates, and parameterizations based on empirical relationships between emission rates and driving variables have also been proposed. There are inadequacies and uncertainties in any of these approaches. In all cases there is a need for emissions data from soils with which to compare the estimates from the models. While results may be 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 models.

Accounting for rapidly changing land use patterns, especially in the tropics, is another of the difficult challenges associated with developing contemporary global NO_x and N_2O models and with comparing current and historical records of the magnitude, distribution, and trend in both gases' atmospheric concentration. Tables 1 and 2 emphasize that soil NO_x and N_2O exchange rates vary substantially not only between the Earth's major biomes, but also with differences in land use within each biome. For example, Matson et al. [1990] reported a substantial increase in soil N_2O emission when tropical forest was converted to pasture. On the basis of the measured impact of N fertilization on soil NO and N_2O emission rates [Hutchinson and Brams, 1992; Shepherd et al., 1991; Williams et al., 1992], it is likely that further increases

in soil NO_x and N_2O emissions will occur as more intensive management practices are adopted to maintain the productivity of tropical forest and savanna soils converted to agricultural use.

Recent recognition of the relationships between the most important cellular controllers (N and O_2 availabilities) and their field, landscape, and global-scale manifestations reflects the progress made in understanding soil NO_x and N_2O exchange [Hutchinson and Davidson, 1993]. The challenge facing future research is to integrate increasing knowledge of process controls at all scales with the rapidly expanding data base of exchange measurements, and then if it is warranted by our enhanced understanding of soil NO and N_2O exchange, to develop control technologies such as alternative land use strategies, alternative soil management practices, or improved fertilizer formulations and application techniques. Toward this end, future research programs must demand explicit clarity in the definition of objectives, sample allocations, measurement techniques, and data analyses used to quantify the exchange rates and exchange mechanisms and to convey the results [Hutchinson and Livingston, 1992]. Failure to acknowledge the requirements and limitations inherent in each aspect of the knowledge-building process can lead to significant error in the resultant conclusions or subsequent adaptations of the data.

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F. C. Fehsenfeld and E. Williams, Aeronomy Laboratory, NOAA, 325 Broadway, Boulder, CO 80303.

G. L. Hutchinson, U.S. Department of Agriculture, Agricultural Research Service, Fort Collins, CO 80522.

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