Testing a Conceptual Model of Soil Emissions of Nitrous and Nitric Oxides

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Investigators from many diverse disciplines—agronomists, atmospheric chemists, ecologists, geochemists, meteorologists, and microbiologists—all study emissions of nitrous oxide (N_2O) and nitric oxide (NO) from soils. Their common interest in soil emissions of nitrogen oxides stems from the attempt to answer the following questions:

- Are emissions of N_2O and NO from soils of sufficient magnitude to significantly affect the regional and global budgets of these gases in the atmosphere,and, if so, do these emissions also significantly affect global warming and the chemical processes of ozone (O_3) production in the troposphere and ozone destruction in the stratosphere?
- Are emissions of N_2O and NO from soils of sufficient magnitude to affect the economic return of nitrogen (N) fertilizer use by farmers,and, to address either economic or environmental concerns, can agricultural practices be modified to reduce gaseous emissions and improve the efficiency of fertilizer use?
- Do changes in land use, particularly deforestation, cattle pasture development, reforestation, and afforestation, significantly affect regional and global budgets of N_2O and NO?
- Can the study of soil emissions of N_2O and NO reveal processes of soil microbial ecology and nutrient cycling that might improve our understanding of the nitrogen cycles of ecosystems?

In this article, we briefly review the disciplinary research on soil emissions of N_2O and NO. We describe a mechanistically based conceptual model—the "hole-in-the-pipe" (HIP) model (Firestone and Davidson 1989)—that integrates the results of these disciplinary studies and that relates emissions of both nitrogen oxides to common soil processes. We then test the model predictions, using data from our recent studies in Costa Rica (Veldkamp et al. 1999), Brazil (Verchot et al.1999),and Puerto Rico (Erickson, etal. in press) and additional data from the literature for forest ecosystems throughout the world.

USING TWO FUNCTIONS BASED ON SOIL NITROGEN AVAILABILITY AND SOIL WATER CONTENT, THE HOLE-IN-THE-PIPE MODEL CHARACTERIZES A LARGE FRACTION OF THE OBSERVED VARIATION OF NITRIC OXIDE AND NITROUS OXIDE EMISSIONS FROM SOILS

Review of disciplinary research

Nitrous and nitric oxides are often studied separately by atmospheric chemists because they play such different roles in the atmosphere. N_2O is a stable greenhouse gas in the lower atmosphere (the troposphere; Ramanathan et al. 1985), but it participates in photochemical reactions in the upper atmosphere (the stratosphere) that destroy ozone (Crutzen 1970). In contrast, NO participates in photochemical reactions in the troposphere that produce ozone.

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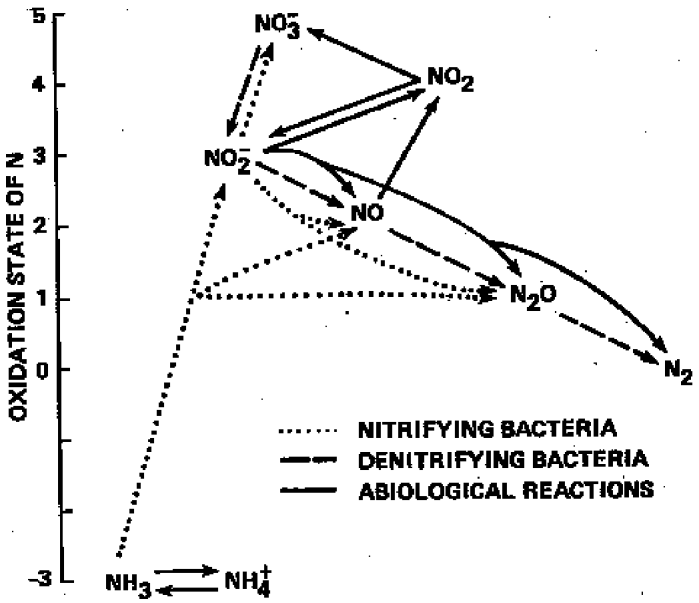

Figure 1. Biological and abiological processes of production and consumption of NO and N_2O as they relate to the oxidation state of nitrogen (from Davidson 1991). Nitrification (dotted line) is the bacterial oxidation of ammonium to nitrite and nitrate, and denitrification (dashed line) is the bacterial reduction of nitrate and other nitrogen oxides to more reduced nitrogen oxides and eventually to molecular dinitrogen. Both nitrifying and denitrifying bacteria can reduce nitrite to N_2O, and denitrifiers can reduce NO to N_2O under low oxygen conditions (Williams et al. 1992, Bollmann and Conrad 1998). Several abiotic reactions (solid lines) in soils can also generate NO and N_2O (Smith and Chalk 1980, Davidson 1992).

Tropospheric ozone, also a greenhouse gas (Lammel and Graßl 1995), is a threat to human health and it decreases crop yield (NAS 1991). Although they have different atmospheric fates and consequences, NO and N_2O are produced in soils primarily by nitrifying and denitrifying bacteria (Figure 1); the same environmental factors affect the production of both nitrogen oxides (see Firestone and Davidson 1989, Davidson 1991, Williams et al. 1992, Granli and Bøckman 1994).

Agronomists studying the production of nitric oxide in soils under laboratory conditions in the 1960s and 1970s generally found that NO production accounted for less than 2% of the fertilizer (nitrogen) applied to soils (Smith and Chalk 1980). While this level of nitric oxide production was of limited interest to agronomists concerned about the efficiency of fertilizer use,it did interest atmospheric chemists concerned about the critical role that even low concentrations of NO can play in photochemical reactions of tropospheric ozone (Thompson 1992). Atmospheric chemists published the first few papers on field measurements of nitric oxide emissions from soils in the late 1970s and early 1980s. Microbiologists, for their part, knew that nitric oxide was produced by nitrifying and denitrifying soil bacteria, but the pathways and enzymatic mechanisms of these processes were not well understood (Firestone 1982, Hooper 1984). As the sensitive chemiluminescence instruments developed by the atmospheric chemists to measure NO began to be used also by agronomists, microbiologists, and ecologists in the mid-1980s and 1990s, the number of publications on soil NO emissions in journals of several disciplines grew rapidly to about 20 in 1990 and 60 in 1996 (see Davidson and Kingerlee 1997).

Research on nitrous oxide followed a much different path. The seminal work of Nõmmik (1956) established the microbiological basis of N_2O and dinitrogen (N_2) production by denitrifying bacteria and identified the effects of most of the environmental factors that are recognized today as controllers of N_2O production. Bremner and Blackmer (1978) showed that nitrous oxide is also produced in soils by nitrifying bacteria. Interest among agronomists in N_2O was stimulated by a report (CAST 1976) suggesting that increased use of nitrogen fertilizers could be one of the main causes of acccumulation of nitrous oxide in the atmosphere, thus contributing to global warming and the stratospheric ozone hole. However, the causes of increasing atmospheric concentrations of nitrous oxide were unknown in the 1970s, and they remain uncertain today (Prather et al. 1995, Kroeze et al. 1999).

As was the case for nitric oxide, the majority of studies on nitrous oxide in temperate regions showed that, on average, only a little more than 1% of nitrogen fertilizer was lost as N_2O, which is economically insignificant from the perspective of farmers (Mosier et al. 1996). Recent studies in tropical agriculture, however, have measured emissions of NO and N_2O that are large enough to matter economically to farmers (Veldkamp and Keller 1997, Matson et al. 1998, Veldkamp et al. 1998).

What is HIP?

The conceptual model offered by Firestone and Davidson in 1989, which has since been dubbed the "hole-in-the-pipe" (HIP) model,synthesized the information known at that time about the microbiological and ecological factors influencing soil emissions of NO and N_2O. Rather than treating each gas separately, the HIP model linked the two gases through their common processes of microbial production and consumption (Figure 1). This linkage was based on several observations. Numerous studies had shown that nitrogen fertilization usually stimulates production of one or both gases (Williams et al. 1992). In unfertilized soils, commonly used indexes of soil-nitrogen availability to plants and microbes, such as net nitrogen mineralization and net nitrification, had been positively correlated with N_2O emissions (Robertson and Tiedje 1984, Matson and Vitousek 1987). Hence, the rate of

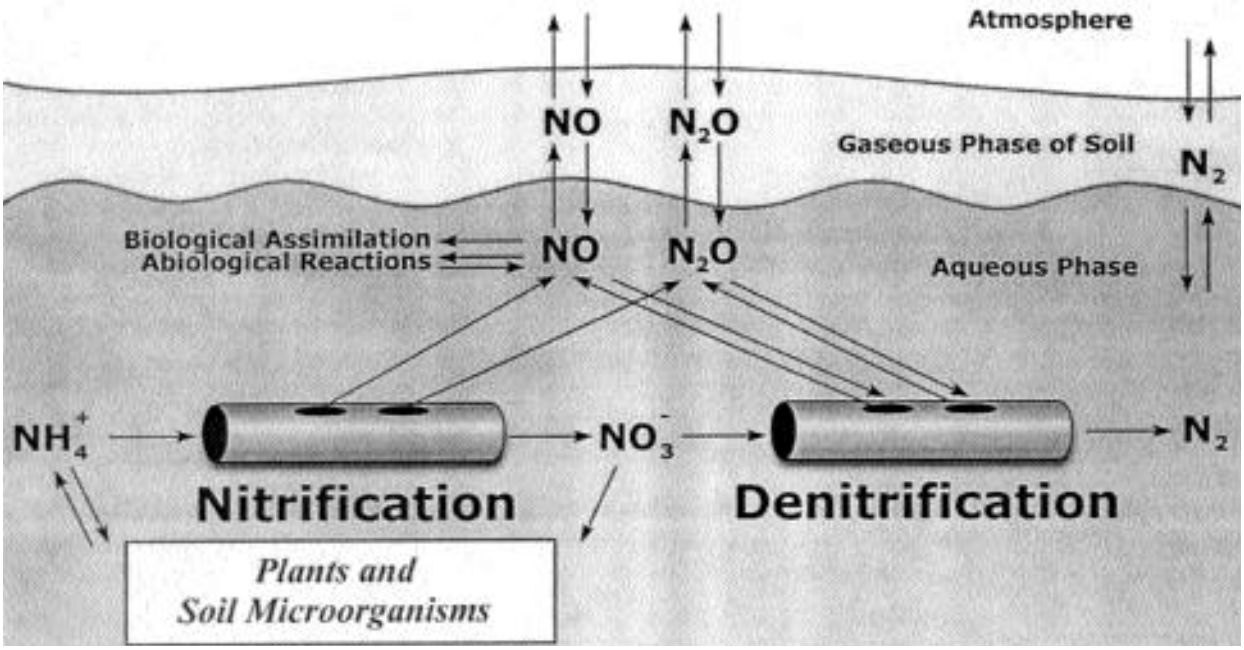

Figure 2. Diagram of the hole-in-the-pipe conceptual model (revised from Davidson 1991). Soil emissions of NO and N_2O are regulated at two levels: First, the rate of nitrogen cycling through ecosystems, which is symbolized by the amount of nitrogen flowing through the pipes,affects total emissions of NO and N_2O; second, soil water content and perhaps other factors affect the ratio of N_2O:NO emissions,symbolized by the relative sizes of the holes through which nitric oxide and nitrous oxide "leak."

nitrogen cycling through the ecosystem is clearly important, and the HIP model relates the sum of production of NO and N_2O as a function of availability of nitrogen in the soil. Virtually every study had also shown a relationship between soil water content and the emissions of either NO or N_2O, but the correlations were sometimes positive and sometimes negative. By combining the observations of emissions of both gases,the HIP model demonstrated that the apparent confusing effects of soil water content could be resolved by describing the ratios of N_2O:NO emissions as a function of soil water content.

These ideas were expressed metaphorically as a fluid flowing through a leaky pipe (Figure 2). The rate of flow of nitrogen through the pipes is analogous to rates of nitrification and denitrification and, more generally, to nitrogen cycling through the ecosystem. The NO and N_2O trace gases "leak" out of holes in the pipe,and the sizes of the holes through which they leak is determined primarily by the soil water content. Soil acidity and relative abundance of electron donors (soil organic carbon) and acceptors (primarily oxygen,nitrate,and sulfate) may also affect the relative proportions of N_2, N_2O, and NO emissions from nitrification and denitrification (Nõmmik 1956, Firestone 1982, Firestone and Davidson 1989), but soil water content appears to be the most common and most robust controller of these ratios (Davidson 1993).

Soil water content is so important because it controls the transport of oxygen into soil and the transport of NO, N_2O, and N_2 out of soil. Emissions of NO, N_2O, and N_2 from soil depend on the balance of production, consumption, and diffusive transport of these gases. In dry, well-aerated soil, the oxidative process of nitrification dominates,and the more oxidized gas, NO (see Figure 1),is the most common nitrogen oxide emitted from the soil. Because the diffusivity of gases is high in dry soils, much of the NO can diffuse out of the soil before it is consumed (Bollmann and Conrad 1998). In wet soils, where gas diffusivity is lower and aeration is poorer, much of the NO is reduced before escaping the soil, and the more reduced oxide, N_2O (Figure 1), is therefore the dominant end product. When the soil is even more water-saturated and mostly anaerobic, much of the N_2O is further reduced to N_2 by denitrifiers before it escapes the soil.

The water holding capacity of clayey soil is far different than that of sandy soil, which precludes using gravimetric or volumetric water contents for comparisons across soils of different textures. Following the model of Linn and Doran (1984), water-filled pore space (WFPS) is the soil water scalar that controls the ratio of N_2O:NO flux in the HIP model. The WFPS is about 60% for many soils at field capacity, which is defined as the soil's water content after excess moisture has drained freely from that soil. At field capacity, soil micropores are water-filled, which permits microbial activity without water stress, and soil macropores are air-filled, which permits relatively good aeration of the bulk of the soil, although anaerobic microsites may

Table 1. Summary of study regions.

Region	Mean annual precipitation ($mm \cdot yr^{-1}$)	Dominant soil types	Forest vegetation	Mature forest litterfall ($mg \cdot ha^{-1} \cdot yr^{-1}$)	Land uses studied
Fazenda Vitória, Paragominas, Pará,Brazil 2°59′S,47°31′W	1800	Haplustox	Evergreen	9.5	Mature forests, 20-year-old secondary forests, active pastures, degraded pastures
La Selva Biological Station and nearby pastures, Heredia Province, Costa Rica 10°12′N,83°32′W	4000	Andic and Oxic Humitropepts	Evergreen	7.8	Mature forest, chrono-sequence of active pastures aged 3–22 years
Luquillo Experimental Forest,Puerto Rico 18°18′N,65°50′W	3000	Tropohumults	Evergreen	8.5	>60-year-old-forests,secondary forests of 25–45 years, pasture abandoned for >10 years, active pastures
Guánica Forest Biosphere Reserve,Puerto Rico 18°00′N,66°55′W	860	Calciustolls	Drought–deciduous	4.8	Secondary forests of 40 years recovering from pasture, and disturbed forests that were "patch-cut" for charcoal about 60 years ago

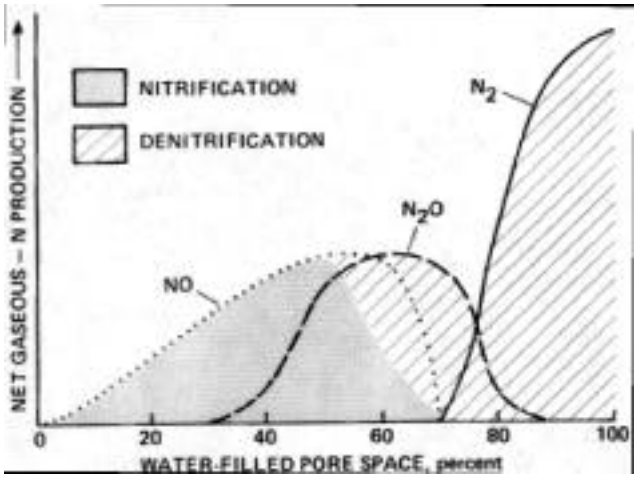

Figure 3. Proposed relative contributions of nitrification (shaded) and denitrification (cross hatched) to emissions of NO and N_2O as a function of soil water-filled pore space (WFPS; from Davidson 1991). The shapes of the curves, the curve heights, WFPS optima, and the inflection points were largely educated guesses based on the limited field and laboratory data available.

exist.Field capacity is the approximate transition in water content at which both oxidative and reductive processes are active in the soil. Based on this assumption and published studies of field and laboratory work, Davidson (1991, 1993) reasoned that the ratio of N_2O:NO flux should be about 1 at 60% WFPS and that the relative contributions of nitrification and denitrification to NO, N_2O, and N_2 emissions could be expressed as a function of WFPS (Figure 3).

Because the atmosphere is mostly N_2, direct study of N_2 production requires costly isotopic approaches or highly controlled laboratory conditions. Acetylene can be used to inhibit N_2O reduction, thereby making it possible to estimate N_2O:N_2 ratios indirectly by comparing N_2O production rates with and without the acetylene inhibitor (Yoshinari et al. 1977). However, this method suffers from artifacts caused by the reaction of acetylene with NO (Bollmann and Conrad 1997). Therefore, because of the paucity of reliable data on N_2 emissions,this article focuses primarily on N_2O:NO ratios.

Considering that rates of nitrogen cycling and water content both strongly affect emissions of NO and N_2O, the advantage of studying these two gases simultaneously becomes apparent. High nitrogen availability, which might be expected to promote high rates of NO production, for example, might instead increase only N_2O production if the water content of the soil favors the production of N_2O. In this example, a researcher who studied both NO and N_2O simultaneously would see that nitrogen availability was indeed related to the sum of NO and N_2O production. In contrast, a researcher who focused solely on NO might mistakenly conclude that nitrogen availability is not important for NO emissions. The HIP model, which conceptualizes the link between NO and N_2O, has proven helpful for the interpretation of results of numerous studies (e.g., Davidson et al. 1993, Keller and Reiners 1994, Riley and Vitousek 1995, Matson et al. 1996, Veldkamp et al.1998),thus conferring further empirical support for the conceptual basis and utility of the HIP model.

One drawback of the HIP model is the difficulty of using it to make comparisons across a range of sites when no universally acceptable and robust measure or index of

nitrogen availability exists. Within a single study, one of the several commonly used indexes of nitrogen availability, such as assays for net nitrogen mineralization,net nitrification, nitrification potential, or extractable ammonium (NH_4^+) and nitrate (NO_3), has usually been found to correlate with emissions of NO or N_2O, or both (Williams et al.1992). Unfortunately, none of these indexes of nitrogen availability has emerged as the best index of "nitrogen flowing through the pipe" for the majority of studies. Some of this inconsistency arises from differences in the way investigators measure nitrogen cycling processes such as net nitrogen mineralization and net nitrification (Hart et al. 1994). Even inorganic nitrogen pools are often measured with different extraction times and ionic strengths of salt solutions. In many studies, only some of the nitrogen-availability indexes or only one of the two nitrogen oxide gases are measured, which further limits comparability across studies.

A field test of the HIP model

We sought to test the HIP model across sites,using consistent methodologies, with two objectives: to demonstrate the usefulness of the HIP model for interpreting measured variation in NO and N_2O emissions under a wide range of climatic conditions and land-use types, and to identify the best measure of nitrogen availability for indicating nitrogen flowing through the pipe.

We chose to conduct this demonstration in tropical forests for several reasons. First, tropical forest soils often emit large amounts of both N_2O (Matson and Vitousek 1990) and NO (Davidson and Kingerlee 1997), because nitrogen is often a relatively abundant nutrient in such ecosystems (where phosphate adsorption onto highly weathered minerals of Oxisols and Ultisols often makes phosphorus more strongly limiting to plant growth [Vitousek and Sanford 1986]). Hence, nitrogen cycling rates (the flows of nitrogen through the pipes) are naturally high in many tropical forests. The N_2O emitted at the soil surface leaves the tropical forest ecosystem and becomes an important source of atmospheric N_2O. In contrast, NO emitted from the soil may be recycled through reactions within the forest canopy (Jacob and Bakwin 1991); its importance to regional and global tropospheric chemistry is therefore less certain, but NO emissions are clearly worthy of study.

A second reason for doing this research in tropical forests is that deforestation is occurring rapidly in tropical regions (Houghton 1993), resulting in land uses, such as active and abandoned cattle pastures, where nitrogen availability and nitrogen oxide emissions may be altered relative to those of the primary forests that were replaced (Matson and Vitousek 1990, Keller and Reiners 1994, Neill et al. 1995). These land use changes may be affecting the global and regional budgets of NO and N_2O, and they also provide wide ranges of nitrogen availability and expected nitrogen oxide emissions for testing the HIP model. Similarly,

Sampling flux chamber headspace gas with a syringe in the drought deciduous forest of Guánica, Puerto Rico. The syringe samples are analyzed in the laboratory for N_2O and CH_4 concentrations by gas chromatography. Photo by H. Erickson

the wide range of climatic regimes within forested areas of the tropics, including mean annual precipitation and length and severity of dry seasons, provides large variation in soil water content for testing the HIP model.

Study design. Four areas spanning a broad range of annual precipitation totals and seasonality were selected (Table 1): the Guánica dry forest in southern Puerto Rico (PR), which has low rainfall and long, severe droughts;the Luquillo evergreen forest in northeastern PR, which has

Making measurements of NO and CO_2 fluxes using a dynamic chamber method in a recently created (less than 1-year-old) cattle pasture near Paragominas, Brazil. The chamber top is held in the air between flux measurements to obtain background atmospheric gas concentration measurements. Photo: E. Davidson.

intermediate rainfall with only slight seasonality; the Fazenda Vitória evergreen forest in the eastern Brazilian Amazon region, which has intermediate rainfall and a long, severe dry season; and the La Selva evergreen forest of eastern Costa Rica, which has high rainfall and a brief, mild dry season.

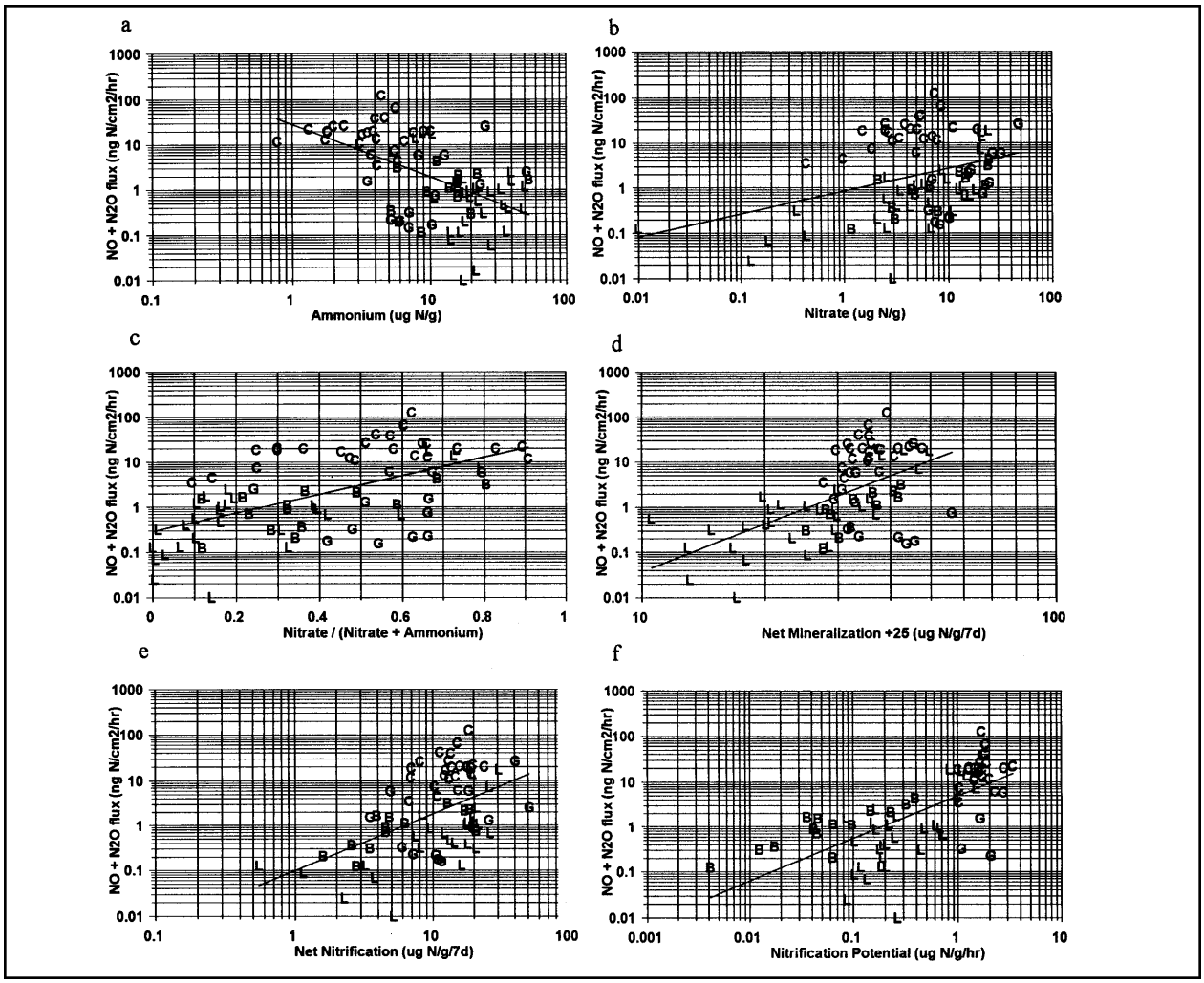

Figure 4. The sum of measured emissions of NO and N_2O as a function of indexes of nitrogen availability (see Hart et al. 1994 for methodological details): (a) Ammonium extracted in 2 M potassium chloride (KCl) (LogY = –1.165LogX + 1.459; R^2 = 0.30; N = 80). (b) Nitrate extracted in 2 M KCl (LogY = 0.504LogX – 0.072; R^2 = 0.12; N = 80). (c) The ratio of extractable nitrate to the sum of extractable nitrate + ammonium (LogY = 2.054X – 0.538; R^2 = 0.34; N = 80). (d) Net nitrogen mineralization determined by the change in extractable inorganic nitrogen during 7-day aerobic laboratory incubations (25 is added to each value in order to render all values positive before logarithmic transformation; negative values had occurred where there was net nitrogen immobilization; LogY = 3.521LogX – 4.952; R^2 = 0.33; N = 78). (e) Net nitrification determined by change in extractable nitrate during the net nitrogen mineralization assays (LogY = 1.326LogX – 1.006; R^2 = 0.26; N = 78).(f) Nitrification potential in a 24-hour laboratory soil slurry assay with excess ammonium (LogY = 0.943LogX + 0.686; R^2 = 0.47; N = 72). All regressions are significant at $\alpha = 0.05$. The plotting symbols indicate study areas: B = Brazil, C = Costa Rica, G = Guánica, L = Luquillo. Each flux estimate is a mean of 4–8 chamber measurements at a study site (a land use such as a forest or pasture of specific age) on a sampling date. Static chambers were used for N_2O fluxes and dynamic chambers for NO fluxes (Davidson et al. 1991, Keller and Reiners 1994). All nitrogen availability indexes are means of 4–32 assays of the top 10 cm of mineral soil for a site and date (the number of replicates varied among regional studies). The data used in this analysis include only those dates where fluxes and nitrogen availability indexes were measured at approximately the same time.

At each of these locations, we identified several land use and land cover types common in those regions. In Costa Rica (seven sites), active cattle pastures of different ages (a chronosequence) and an old forest were studied. In both Luquillo (eight sites) and Brazil (eight sites), we studied active and abandoned cattle pastures, young secondary forests that previously had been pastures, and old forests. Within the Luquillo forest, we also studied fertilized (300 $kg \cdot ha^{-1} \cdot yr^{-1}$ of nitrogen) and unfertilized old forest stands at a site called El Verde. The old forests at Luquillo were determined to be at least 60 years old,based on aerial photography dating back to the 1930s. The Luquillo forests may have experienced varying degrees of human disturbance before 1930, and they also experienced extensive

Table 2. Summary of annual estimates of nitrous oxide and nitric oxide emissons.

Region	Land use study site	Nitrous oxide ($kg \cdot ha^{-1} \cdot yr^{-1}$ of nitrogen)	Nitric oxide ($kg \cdot ha^{-1} \cdot yr^{-1}$ of nitrogen)
Costa Rica	Old-growth forest[a]	5.9	0.9
	3-year-old pasture[b]	6.9	4.4
	6-year-old pasture[b]	11.0	5.4
	7-year-old pasture[b]	10.4	9.2
	9-year-old pasture[b]	32.0	23.0
	14-year-old pasture[b]	13.2	5.5
	22-year-old pasture[b]	3.8	3.7
Puerto Rico–Luquillo[c]	Sabana active pasture	0.7	0.1
	Sabana abandoned pasture	0.2	0.1
	Sabana midsuccessional forest (approximately 25 years)	0.1	0.0
	Sabana old forest (>60 years)	1.7	0.4
	Mameyes active pasture	0.5	0.2
	Mameyes abandoned pasture	0.5	0.1
	Mameyes midsuccessional forest (approximately 45 years)	8.3	0.6
	Mameyes old forest (>60 years)	0.6	0.1
	El Verde control old-growth forest (>60 years)	0.7	0.1
	El Verde N-fertilized old-growth forest (>60 years)	19.2	2.5
Puerto Rico–Guanica[d]	Secondary forest after charcoal production	0.0	0.8
	Secondary forest after charcoal production	0.0	0.5
	Secondary forest after pasturing	0.8	12.0
	Secondary forest after pasturing	0.0	2.5
Brazil–Paragominas[e]	Old-growth forest	2.4	1.5
	Secondary forest (20 years)	0.9	0.3
	Active pasture	0.3	0.5
	Degraded, abandoned pasture	0.1	0.7

[a]Keller and Reiners (1994).
[b]Veldkamp et al. (1999). Fluxes for the same sites three years earlier were reported by Keller et al. (1993).
[c]Erickson, et al. in press.
[d]Heather Erickson, Universidad Metropolitana, unpublished data.
[e]Verchot et al. (1999).

damage from Hurricane Hugo in 1989 (Scatena and Larsen 1991). The old-growth forests of Costa Rica and Brazil have experienced some human influence, but have probably not been cleared during the last few hundred years. In Guánica (4 sites), the study sites were either secondary forests derived from pasture lands or disturbed forests from which trees had been cut in patches for charcoal production about 60 years ago.

The study sites within these four regions provided considerable variation in the two factors most important for the HIP model. First, differences in land use provided variation in nitrogen cycling among forests and pastures, thus providing different flows of nitrogen through the pipe. Second, differences among regions in total annual rainfall and seasonality created variation in soil water content, which regulates the relative sizes of the holes in the pipe and the ratios of N_2O:NO emitted from the soil.

Similar measurement techniques were used for all sites. More information about these sites and details about the methodologies and frequency of measurements are in a series of papers that summarize the results for Puerto Rico (Heather Erickson, et al. in press), Costa Rica (Veldkamp et al. 1999), and Brazil (Verchot et al.1999).

Differences among land uses. The effects of land use change on emissions of N_2O and NO is a timely topic because of concerns about sources of greenhouse gases (Prather et al. 1995). We first offer a few generalizations from our studies:

Old-growth tropical forests have big fluxes. We can reconfirm that lowland old-growth evergreen tropical forests are significant sources of N_2O and NO. In Brazil, the old-growth forest soils emitted 1.5 $kg \cdot N\ ha^{-1} \cdot yr^{-1}$ of NO and 2.4 $kg \cdot N\ ha^{-1} \cdot yr^{-1}$ of N_2O. The Costa Rican old-growth forest soils emitted 0.9 $kg \cdot N\ ha^{-1} \cdot yr^{-1}$ of NO and 5.9 $kg \cdot N\ ha^{-1} \cdot yr^{-1}$ of N_2O (Table 2). These emissions are higher than for most temperate forests (except for those with high rates of atmospheric nitrogen deposition and high nitrogen oxide emissions; Gasche and Papen 1999, Papen and Butterbach-Bahl 1999). The soils of the Costa Rican site are younger and more fertile than those of Brazil, which may explain the very high NO and N_2O emissions there.

Old pastures have little fluxes. Replacement of old-growth lowland tropical forests with cattle pastures changes N_2O and NO emissions (Table 2). In Costa Rica, emissions of NO and N_2O increased in young pastures, but in the 22 year-old pasture emissions of N_2O were lower than in the old forest. In Brazil, both pastures studied were about 20 years old, and the pasture emissions of N_2O and NO were lower than those in the adjacent old-growth

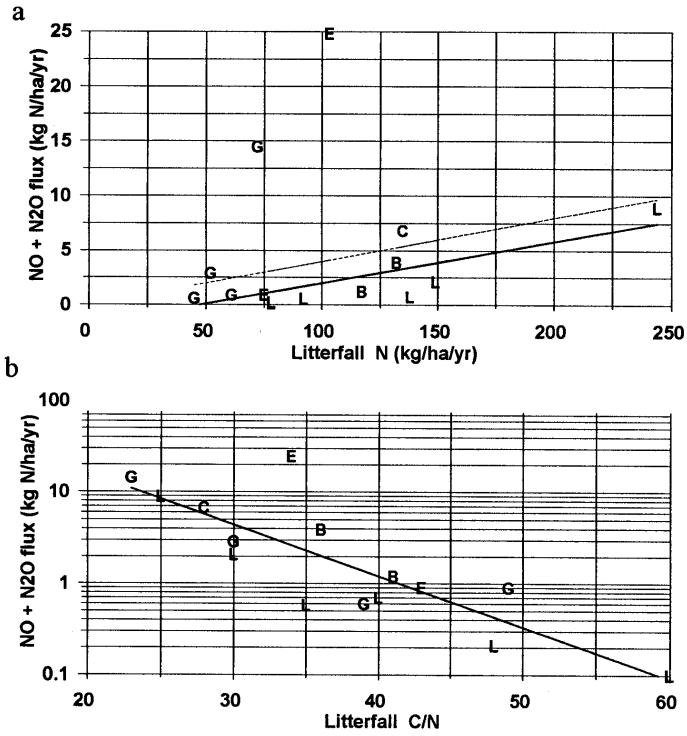

Figure 5. The sum of annual estimates of emissions of NO and N_2O as a function of litterfall characteristics. (a) Annual total fine litterfall nitrogen ($Y = 0.038X - 1.81$; $R^2 = 0.57$; $N = 13$). (b) Litterfall C:N ratios ($LogY = -0.0563X + 2.331$; $R^2 = 0.70$; $N = 15$). Both regressions (solid lines) are significant at $\alpha = 0.05$. The plotting symbols indicate study areas: B = Brazil, C = Costa Rica, G = Guánica, L = Luquillo, E = El Verde. Leaf litterfall nitrogen was estimated by Erickson (in press) for the Guánica, Luquillo, and El Verde sites and adjusted here for total fine litter production (leaf litterfall = 80% of total). Total fine litterfall nitrogen in the same Brazilian forests was estimated by Daniel Markewitz and Eric Davidson (unpublished data). The total fine litterfall nitrogen estimate of Vitousek (1984) was used for La Selva, Costa Rica. Annual estimates of NO and N_2O fluxes were determined from 12 or more monthly measurements at Luquillo and in Brazil,and from 4 seasonal measurements at Guánica and at the Costa Rican pastures. For Costa Rican forests, the annual estimates of Keller and Reiners (1994) were used. The legume-rich Guánica site with high emissions and the fertilized El Verde site with very high emissions were omitted from the regression analysis shown in (a). The dashed line in (a) indicates the predicted emissions based on the assumptions of the CASA model by Potter et al. (1996).

forest. The pastures in Luquillo were more than 60 years old and also had low emissions.

Fluxes from young successional forests are highly variable. In both Brazil and Puerto Rico, abandoned pastures and most of the early to midsuccessional forests had low emissions (Table 2). However, two important exceptions to this generalization were found in Puerto Rico. At Luquillo and Guánica we found one secondary forest in each area that was relatively rich in legume species and that had emissions exceeding those of all other study sites in each respective region (Table 2). We infer from the nitrogen availability data presented below that the presence of nitrogen-fixing leguminous trees, which is linked to land use histories and the resulting successional trajectory of species composition, increased nitrogen availability, thereby also increasing emissions of NO and N_2O (Erickson, et al.in press).

The first HIP metaphor: Nitrogen flowing through the pipe. For the analysis in this article, the most important question is whether these variations in N_2O and NO emissions among regions and among land uses within regions covary with any or all the indexes of nitrogen availability that can be used as proxies for nitrogen flowing through the pipe in the HIP model. For each of the six indexes of nitrogen availability shown in Figure 4, a significant correlation ($\alpha = 0.05$) was found between the sum of NO and N_2O emissions and the nitrogen-availability index.

Extractable NH_4^+ was negatively correlated with nitrogen oxide emissions, whereas extractable NO_3^- and the ratio of NO_3^-:NO_3^- + NH_4^+ were positively correlated with nitrogen oxide emissions (Figures 4a,4b, and 4c). In other words, the sites that had low emissions of NO and N_2O generally also had NH_4^+ as the dominant form of inorganic nitrogen. These low-flux, NH_4^+-dominated sites were mostly the active and abandoned cattle pastures of Puerto Rico and Brazil and the old active cattle pasture of Costa Rica. Where nitrate was the dominant form of soil inorganic nitrogen—such as the primary forests of Costa Rica and Brazil, the young pastures of Costa Rica, and the two legume-rich secondary forests of Puerto Rico—the emissions of NO and N_2O were generally high. A similar distinction between predominance of NH_4^+ in old pastures and NO_3^- in forests and young pastures was found in Rondônia, Brazil (Neill et al. 1995).

Although we recognize that inorganic nitrogen pool sizes are not measures of flow of nitrogen through those pools (Davidson et al. 1990), the pool sizes may be good indicators of whether the nitrogen cycle is conservative (closed) or leaky (open). When NO_3^- accumulates and dominates the inorganic nitrogen pool, then gross rates of nitrification must exceed rates of nitrate uptake by plants and microorganisms. Nitrate accumulation and predominance over NH_4^+ is,therefore, indicative of an open, leaky nitrogen cycle that leaches NO_3^- (Vitousek et al. 1982), and it also appears to be indicative of nitrogen losses as NO and N_2O. In other words, although the NO_3^- pool does not provide a direct measure of nitrogen flux in the soil,it indicates that excess nitrogen is flowing through the pipe relative to the ability of plants and soil microorganisms to assimilate NO_3^-.

The net nitrogen mineralization and net nitrification assays are direct measures of nitrogen flowing through the pipe under laboratory conditions defined by the incubation

methodology (Hart et al.1994). These assays are also good indicators of when nitrogen availability exceeds microbial assimilative demand. The same pasture sites that were dominated by NH_4^+ and had low emissions of NO and N_2O also had net nitrogen immobilization (negative values for net mineralization), low rates of net nitrification, and low nitrification potentials (Figures 4a,4c, 4d,4e,and 4f). Similarly, net nitrogen mineralization, net nitrification, and nitrification potentials were high in the old forests of Costa Rica and Brazil, the young pastures of Costa Rica,and the legume-rich secondary forests of Puerto Rico, where NO_3^- dominated and where the emissions of NO and N_2O were also high.

The nitrification potential assay measures the capacity of the population of nitrifying bacteria in a soil sample to convert added NH_4^+ to NO_3^- under laboratory conditions (Hart et al.1994). Nitrifying bacteria starve and their populations decline when nitrogen availability is low (Davidson et al. 1990). Therefore, low nitrification potentials indicate low population capacities, which result from low nitrogen availability. A high nitrification potential exists only when nitrogen availability remains high enough to support a viable population of nitrifying bacteria, which presumably also means that high rates of nitrification and flow of nitrogen through the nitrification pipe occur frequently enough to sustain a relatively large nitrifier population. Accordingly, this index of nitrogen flowing through the pipe produced the strongest correlation with NO and N_2O emissions (Figure 4f).

To use litterfall nitrogen as an indicator of flow of nitrogen through the pipe, the data were aggregated to annual estimates. Annual total fine litterfall nitrogen is positively correlated with annual NO and N_2O emissions (Figure 5a). The El Verde fertilized site is clearly an outlier and was excluded from the regression analyses. Apparently, this site has become nitrogen saturated (*sensu* Aber et al. 1998), and litterfall nitrogen does not reveal the excess nitrogen availability that remains in the soil (Erickson et al. in press). A legume-rich, secondary dry forest at Guánica is another outlier excluded from regression analyses. Water limits primary productivity in dry forests and litterfall rates are much lower than for evergreen forests (Table 1; Lugo and Murphy 1986), thus making litterfall nitrogen flux an inadequate indicator of excess available nitrogen in the soil of the legume-rich site at Guánica. The old-growth forests of Brazil and Costa Rica and the legume-rich secondary forest of Luquillo registered high rates of litterfall nitrogen and of NO and N_2O emissions .

In addition to the flux of litterfall nitrogen, the carbon (C)-to-nitrogen ratio of litterfall has been used as an indicator of nitrogen availability in ecosystems. This ratio is not a flux that is directly analogous to flow of nitrogen through the pipe, but it may be a reasonable proxy for nitrogen availability in the ecosystem. Litter with a low C:N ratio often produces high rates of net nitrogen mineralization during decomposition. In the Luquillo study, a negative correlation was found between litter C:N ratios and net nitrogen mineralization,and a positive correlation was found between the litter C:N ratio and emissions of carbon dioxide during the nitrogen mineralization assay (Erickson et al. in press). Combining the Luquillo and Guánica data, a negative correlation was found between the litterfall C:N ratio and the logarithm of annual NO and N_2O emissions (Figure 5b; Erickson et al. in press). The fertilized El Verde forest remains an outlier, as it was for the litterfall nitrogen function. Results from the Costa Rican and Brazilian sites are in reasonably good agreement with the Puerto Rico data.

In summary, variation in nitrogen availability among these diverse land uses, as indicated by all the nitrogen availability indexes, corresponded to variation in NO and N_2O emissions. Hence the HIP model's metaphor of nitrogen flowing through a pipe is a useful and mechanistically accurate way of expressing how rates of nitrogen cycling within soils and within ecosystems affect emissions of these two gases.

The second HIP metaphor: The holes in the pipe.

Differences among study regions in amount of precipitation and seasonal patterns (Table 1) provided a large range of soil water contents that could be used to test predictions of the HIP model regarding ratios of N_2O:NO. As expected, we observed a positive correlation between WFPS and the logarithm of the ratio of N_2O:NO (Figure 6). In accordance with the hypothesized transition point at field capacity, which is often about 60% WFPS, the regression line predicts that the ratio of N_2O:NO is 1 when WFPS equals 63%.

The N_2O:NO ratio was usually greater than 1 and the WFPS was usually more than 60% for most of the sites and seasons at Luquillo and Costa Rica, which are at the wet end of the climatic gradient of this study. At Fazenda Vitória, Brazil,the ratio was less than 1 during the dry season and more than 1 during the wet season (Verchot et al. 1999). The Guánica sites always had WFPS under 60%, and NO emissions always exceeded N_2O emissions (ratio less than 1). In order to extend the range as low as 12% WFPS, we also included data from two other Brazilian sites studied by Verchot et al.(1999):a forest at Santana do Araguaia near the transition between Amazonian forest and savanna, and a savanna at the Instituto Brasileiro de Geografia e Estastística (IGBE) Reserve near Brasilia. As expected, the N_2O:NO ratio was also less than 1 at these dry sites.

Caution must be employed when analyzing ratios, because ratios are sensitive to small numbers in the denominator. As the denominator approaches zero, the ratio approaches infinity. For example, if the N_2O flux is consistently 0.50 ng $\cdot$ cm^{-2} $\cdot$ hr^{-1} of nitrogen, and in one case the NO flux is 0.05 ng $\cdot$ cm^{-2} $\cdot$ hr^{-1} of nitrogen and in another case it is 0.01 ng $\cdot$ cm^{-2} $\cdot$ hr^{-1} of nitrogen, then the N_2O:NO ratios will be 10 and 50, respectively. However, both of these NO fluxes are below detection limits,and the

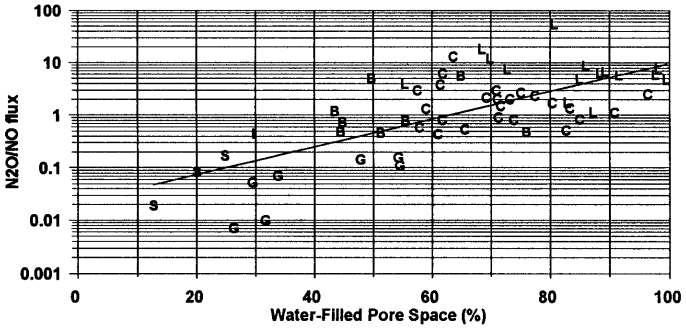

Figure 6. The ratio of N_2O:NO emissions as a function of the percentage of water-filled pore space (WFPS) of the surface mineral soil (LogY = 0.026X – 1.660; R^2 = 0.50; N = 58). The regression is significant at α = 0.05. Plotting symbols and sample sizes are the same as in Figures 4 and 5, except that two additional Brazilian sites, a forest at Santana do Araguaia (S) and a savanna site at the ecological reserve of the Insituto Brasileiro de Geographia e Estatística (I) near Brasilia (Verchot et al. 1999), are also included.

seemingly large difference between the two N_2O:NO ratios is actually not meaningful. Consequently, we found it necessary to exclude all NO fluxes less than 0.1 ng · cm^{-2} · hr^{-1} of nitrogen.

Limitations of the model

The HIP model is a simplification of complex soil biogeochemical processes,including nitrification, denitrification, nitrogen mineralization, competition for inorganic nitrogen, carbon supply, solubility and diffusion of gases, and growth of microbial populations. Like many simplifications,the HIP model can be helpful, but it does have limitations. For example, model predictions will have only broadbrush accuracy; some applications may suffer from signal-to-noise considerations; and some physical, chemical, and biological soil processes that are sometimes important are not included in the HIP model .

Broadbrush accuracy. Although the significant correlations between nitrogen availability indexes and NO and N_2O emissions shown in Figures 4 and 5 clearly support the assertion that nitrogen oxide emissions are related to rates of nitrogen cycling in ecosystems, a model based on these regression parameters will have only order-of-magnitude prediction accuracy.

Big residuals. Residuals of the best-fit lines in Figure 4 show that the measured emissions are frequently more than a factor of 10 different from predicted values. Moreover, there are clear biases among the residuals, such as consistent underestimation of emissions for the Costa Rican sites by nearly all of the indexes. For a given level of net nitrogen mineralization or any of the other indexes of nitrogen availability in Figure 4, more NO and N_2O was produced in the Andic Inceptisols of Costa Rica than in the Oxisols and Ultisols at the other sites. Perhaps carbon availability to denitrifiers, frequently high soil water content, or some other factor causes greater nitrogen oxide gas production per unit of nitrogen cycled in the Costa Rican forest.

A similar conclusion was reached by Reich et al. (1997) with respect to correlations of litterfall nitrogen and net nitrogen mineralization with aboveground net primary productivity (ANPP) across a range of temperate forests: All of the sites Reich and colleagues studied showed strong correlations, indicating the importance of nitrogen availability for ANPP, but other differences among soil types appeared to affect the amount of ANPP per unit of available nitrogen. Future refinements of HIP-style models may include more complex parameterizations involving soil types, total precipitation, or other factors that influence the relationship between nitrogen availability and NO and N_2O emissions. At this point, we can say only that the underlying principle of linkage between nitrogen cycling rates and nitrogen oxide emissions is generally consistent and widely applicable. Water-filled pore space has also been reconfirmed as an effective predictor of the ratio of N_2O:NO emissions, although the large residuals reveal that the measured ratios are also often a factor of 10 different from predicted values (Figure 6).

Application to global models and datasets. Global models that use 1 degree pixels,and even those that can achieve 1 km^2 resolution, must use simplifications to model biogeochemical processes. The broadbrush accuracy demonstrated in this article by the HIP model is appropriate for that use. Annual rates of litterfall nitrogen and litterfall C:N ratios have the greatest promise as drivers of regional and global biogeochemical models that predict NO and N_2O emissions from soils. Litterfall data are more widely available and are less dynamic than are soil assays of inorganic nitrogen pools, nitrogen mineralization, and nitrification. Annual litterfall also integrates over much of the temporal and spatial variation of nitrogen availability in forest stands.

For an additional, independent test of the applicability of litterfall nitrogen as a predictor of NO and N_2O emissions, we identified eight sites for which estimates of NO and N_2O emissions and litterfall nitrogen are available in the literature. These included tropical lowland and montane evergreen forests, a drought–deciduous tropical forest, and temperate forests with modest and high nitrogen deposition rates (Figure 7). We used the regression shown in Figure 5a to predict NO and N_2O emissions from annual litterfall nitrogen. Most of the sites fall near the 1:1 line in Figure 7. The main outliers to this regression are two temperate forests in Germany that receive 20–30 kg · ha^{-1} · yr^{-1} of nitrogen from atmospheric deposition. About 15–16% of that nitrogen was emitted as NO and N_2O from the soil, which is about five times the fraction of nitrogen in litterfall assumed to be lost as nitrogen oxides in our regression model.

Similarly, the El Verde fertilized forest of Puerto Rico lost about 7% of the 300 kg · ha^{-1} · yr^{-1} of fertilizer nitrogen as

NO and N_2O. Hence, in some special situations—when sites are rich in nitrogen—this litterfall nitrogen regression does not work well; this is true for the legume-rich secondary forest of the dry Guánica site, the nitrogen-fertilized El Verde forest, and the nitrogen-deposition-affected temperate forests of Germany. Apparently, for all of these sites, high inputs of nitrogen could not be fully utilized by the trees. We expect that other such exceptions exist but that the majority of the world's forests will conform, within a "broadbrush factor" of about 2, to the emissions predicted by the regression equation in Figure 5a.

Signal-to-noise. Regression analyses are often more successful when the values of the variables span large ranges. This was certainly the case for the analyses of nitrogen-availability indexes in Figure 4. All of the Costa Rica sites, however, had relatively high values of nitrogen availability and nitrogen oxide emissions, and the natural "noise" within this relatively narrow range of values precluded Veldkamp et al. (1999) from finding statistically significant regressions, although they detected the same trends as reported here. When these same data from Costa Rica are added to the very low values from cattle pastures of Luquillo, however, statistically significant regressions are obtained. The pastures and forests of the study site in Brazil had sufficient variability in nitrogen availability and seasonal fluctuation in soil water content that Verchot et al. (1999) found significant correlations for both the nitrogen availability indexes and WFPS.

Why do some availability indexes give good correlations with nitrogen oxide emissions in some studies while others do not? The answer is probably that the range of values being regressed is too narrow for some of the correlations to be statistically significant (i.e.,a type II statistical error). Because of the high spatial and temporal variability in NO and N_2O emissions, each mean flux has a large uncertainty, and large differences among means are often needed to differentiate the regression "signal" from the measurement "noise." Taking advantage of the large range of variability in this analysis allows us to conclude that nitrogen oxide emissions are correlated with all of the indexes of nitrogen availability.

Holes to be filled. Although the simplicity of the HIP model is appealing, further improvements will probably require that physical, chemical,and biological processes be added to the model and that more detailed consideration be given to spatial and temporal variation.

Time scales and wet-up events. Our monthly sampling scheme did not consider the short-term effects of rainfall events, and the HIP model does not explicitly address this type of fine-scale temporal variation. Nevertheless, wet-up events have been considered short-term pulses of increased nitrogen flowing through the pipe (Davidson et al. 1993), and a numerical version of the HIP model was developed with hourly time steps (Potter et al. 1997). The DNDC (DeNitrification DeComposition) model (Li et al. 1992) also uses hourly time steps when the soil is wet enough to promote denitrification, and it models rapid changes in soil inorganic nitrogen and readily decomposable organic carbon. Where modeling this type of short-term variation is important, a blend of these approaches might be advantageous.

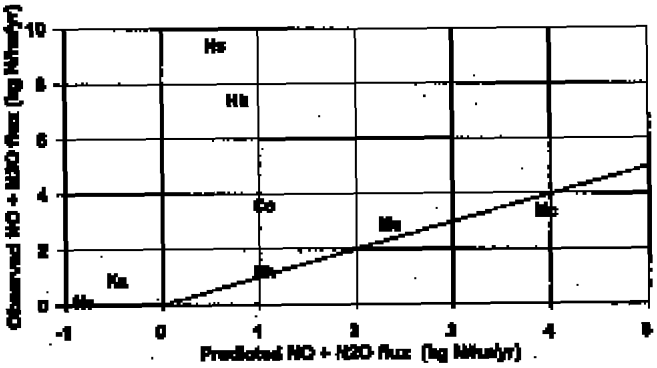

Figure 7. Comparison of predicted and observed annual emissions of NO and N_2O emissions for other forests of the world where data are available in the literature: Co = Congo (Serça et al. 1994); Ch = Chamela, Mexico (Davidson et al. 1991, Garcia-Mendez et al. 1991, Jamarillo and Sanford 1995); Hv = Harvard Forest, Massachusetts, USA (Bowden et al.1990, Munger et al. 1996, Magill et al. 1997); Hb = Höglwald beech and Hs = Höglwald spruce, Bavaria, Germany (Gasche and Papen 1999, Papen and Butterbach-Bahl 1999); Ka = Kauai, Hawaii, USA (Riley and Vitousek 1995); Ms = Manaus sandy soil and Mc = Manaus clayey soil,Brazil (emissions from several references summarized by Davidson 1991, and litterfall from Luizão 1989). Predictions were based on annual litterfall nitrogen, using the regression shown in Figure 5a. The 1:1 line is shown.

Depth of microbial activity. An important limitation of using nitrogen availability indexes based on soil assays is that they assume that the important microbial activity occurs in the top 10 cm of mineral soil, or wherever the soil has been sampled for the assay. Verchot et al. (1999) found that concentrations of N_2O within the soil atmosphere increased to 8 $uL \cdot L^{-1}$ air at 1 m depth in the Brazilian old-growth forest soil during the rainy season,indicating that significant N_2O production had occurred well below the depth of 10 cm. When production occurs deep within the soil, then microbial consumption and gas transport along the long diffusive path to the surface also become important. Perhaps some of the differences among the Costa Rican, Puerto Rican, and Brazilian sites could be explained by the relative importance of microbial activity in the litter layers and in the mineral soils from the surface to variable depths. Indexes of nitrogen availability might be further improved if assays were made at several soil-depth increments and the results expressed as a weighted sum for the entire soil profile on a mass-per-unit-area basis (by multiplying available nitrogen concentrations by the bulk density of each soil-depth increment).

The best index of nitrogen availability. Although we

have demonstrated the importance of nitrogen availability and the effectiveness of using the concept of nitrogen flowing through the pipe for studying soil emissions of NO and N_2O, we have not been completely successful in finding the best parameterization of any of the nitrogen availability indexes. They all seem to work to some extent, but none of the parameterizations of nitrogen availability indexes emerges as the Holy Grail of nitrogen oxide emissions. Nevertheless, some suggestions arise from the analysis of this article. First, the distinction between ammonium-dominated and nitrate-dominated systems should be very useful as a broadbrush approximation of low and high emitting soils. Second, for the design of short-duration plot-scale studies, we recommend that a suite of nitrogen availability measures be used, with due consideration for the range of variability to be expected. Third, for studies lasting a year or longer, we recommend the collection of litterfall data.

How to use litterfall nitrogen. The regression based on aboveground litterfall nitrogen (Figure 5a) ignores root turnover, which contributes to soil nitrogen cycling but is very difficult to measure. Potter et al. (1996) attempted to include root inputs of nitrogen in their implementation of a HIP approach to modeling NO, N_2O, and N_2 in their CASA (Carnegie Ames Stanford Approach) global biogeochemical model. They assumed that root litter nitrogen was equal to aboveground litterfall nitrogen, and that 2% of above- and belowground litter nitrogen (i.e., 4% of aboveground litterfall nitrogen) was used as an initial best guess of the fraction of total litterfall nitrogen lost as NO, N_2O, and N_2 during decomposition and gross nitrogen mineralization. The slope of 0.038 in Figure 5a supports Potter et al.'s (1996) assumption that about 4% of the aboveground litterfall nitrogen would be lost as NO and N_2O. However, a statistically significant nonzero Y intercept (–1.81 in Figure 5a) indicates that this 4% incremental loss applies only when litterfall nitrogen is in excess of about 50 $kg \cdot ha^{-1} \cdot yr^{-1}$ of nitrogen. Therefore, the best guess of Potter et al. (1996)—4%—was reasonably good, although the nonzero Y intercept indicates a threshold effect that they did not consider.

An exponential model has been proposed for the Luquillo forest data, in which the fraction of nitrogen lost as NO and N_2O increases with increasing litterfall nitrogen (Erickson et al. in press). As nitrogen availability and rates of nitrogen cycling increase, plant and microbial sinks for NH_4^+ become nearly satisfied, and the fraction of mineralized nitrogen available to nitrifiers increases. Similarly, as nitrification rates increase, plant and microbial demand for NO_3^- is eventually saturated and the fraction of NO_3^- available for denitrification increases. Hence, a mechanistic basis exists for an exponential relationship between indexes of nitrogen availability and the sum of NO and N_2O production.

If the exponential model is correct, then the CASA model of Potter et al. (1996) and the linear regression shown in Figure 5a may underestimate fluxes at nitrogen-rich sites and overestimate fluxes at nitrogen-poor sites. An exponential model through the origin would also avoid the erroneous prediction of negative fluxes for sites with very low litterfall nitrogen (Figure 7). Although litterfall nitrogen shows promise as a broadbrush predictor of nitrogen oxide emissions, the shape and optimal parameterization of this relationship await further research.

Diffusivity. The WFPS function to predict the ratio of N_2O:NO emissions is robust. The N_2O:NO ratio is commonly equal to 1 at field capacity, which is often about 60% WFPS in many soils. There are exceptions, however, to this generalization. Compacted soils and volcanic soils often have a larger fraction of microporosity than most other soils, resulting in a higher water content at field capacity. Aggregation varies among soils, which also affects the distribution of pore sizes and the water content at field capacity. Although WFPS works reasonably well for predicting ratios of N_2O:NO emissions for most soils, the parameterization shown in Figure 6 will not be universally applicable.

The next advance may be to refine and apply models of diffusivity within soils and use effective diffusivity as the independent variable in lieu of WFPS. Many estimates of diffusivity, however, require information on pore size distribution (Davidson and Trumbore 1995), which is more difficult to estimate than is WFPS. It may also be necessary to evaluate WFPS or diffusivity throughout the soil profile wherever NO and N_2O are produced, rather than relying only on WFPS of the top layer of mineral soil.

Abiotic processes. The HIP model addresses classical nitrification and denitrification as defined by Firestone and Davidson (1989). Chemodenitrification (abiotic reactions involving reduction of nitrite) has been suspected to be an important source of NO emissions from soils following fire, after wetting very dry soil, and in excessively fertilized soils, where nitrite can accumulate (Davidson 1992, Neff et al. 1995, Veldkamp and Keller 1997, Verchot et al. 1999). Production of NO by chemodenitrification may have affected the Y intercept of the regression of WFPS and the N_2O:NO ratio in a heavily fertilized banana plantation (Veldkamp and Keller 1997). Chemodenitrification and perhaps some other processes of NO and N_2O production and consumption that have yet to be adequately described may produce further exceptions to the general applicability of the HIP model.

Production of N_2 during denitrification. In our test of the HIP model, we were unable to quantify the production of N_2 by denitrifiers. Because N_2O is reduced to N_2 at high WFPS, emissions of N_2O might be expected to decrease (Figure 3). In Costa Rican forests, however, Keller and Reiners (1994) found that N_2O emissions increased exponentially with WFPS, even at WFPS greater than 80%. We might also expect poor correlations between NO and N_2O emissions and indexes of nitrogen availability when soils are consistently near saturation, not only because of N_2

production but also because the procedures for three of the indexes (net nitrogen mineralization,net nitrification, and nitrification potential) require aerobic conditions.

Holistic approach

Has the HIP model passed its test? On the broad scale, the answer is a clear yes. Regional and global models of soil emissions of NO and N_2O can capture a large fraction of the variation among land uses and climates. On the finer scale, the HIP model prediction may be less accurate unless parameterized by site-specific data. The HIP model is not meant to preclude further reductionism where warranted. Rather, the HIP model provides a sound ecological and mechanistic basis for interpreting temporal and spatial variation at all scales of study by neatly encapsulating into two functions—nitrogen availability and soil water content—a large fraction of the variability caused by numerous environmental factors that influence the production and consumption of NO and N_2O by nitrifying and denitrifying bacteria.

This concise description of the most important factors affecting emissions permits the HIP model to explain, clearly and simply, how ecosystems are likely to respond to several perturbations. For example, increases in inputs of nitrogen to ecosystems by fertilization,atmospheric deposition, and nitrogen fixation are likely to have similar effects: Soil emissions of NO and N_2O will increase. The model also demonstrates how these emissions might be managed or mitigated. For example, applications of fertilizers will result in less flow of nitrogen through the nitrification and denitrification "pipes" when crop plants are already established as good competitors for the fertilizer nitrogen. Premature fertilization will result in larger gaseous emissions of nitrogen oxides. By understanding how water content affects the relative ratios of NO and N_2O, local and regional concerns about tropospheric ozone could be mitigated by avoiding fertilizer application during dry periods when the ozone precursor, NO, is most likely to leak out of the pipe. Irrigation immediately after fertilization is likely to increase N_2O emissions. Despite the different roles of NO and N_2O in the atmosphere and the many different reasons why scientists from several disciplines study one or the other gas, combining studies of the two gases and linking them mechanistically in conceptual and empirical models makes good biological, ecological, and practical sense.

Acknowledgments

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