

Evaluating annual nitrous oxide fluxes at the ecosystem scale

Peter M. Groffman,¹ Rainer Brumme,² Klaus Butterbach-Bahl,³ Karen E. Dobbie,⁴ Arvin R. Mosier,⁵ Dennis Ojima,⁶ Hans Papen,³ William J. Parton,⁶ Keith A. Smith,⁴ and Claudia Wagner-Riddle⁷

Abstract. Evaluation of N₂O flux has been one of the most problematic topics in environmental biogeochemistry over the last 10-15 years. Early ideas that we should be able to use the large body of existing research on terrestrial N cycling to predict patterns of N₂O flux at the ecosystem scale have been hard to prove due to extreme temporal and spatial variability in flux. The vast majority of the N₂O flux measurement and modeling activity that has taken place has been process level and field scale, i.e., measurement, analysis and modeling of hourly and daily fluxes with chambers deployed in field plots. It has been very difficult to establish strong predictive relationships between these hourly and daily fluxes and field-scale parameters such as temperature, soil moisture, and soil inorganic N concentrations. In this study, we addressed the question of whether we can increase our predictive understanding of N₂O fluxes by examining relationships between flux and environmental parameters at larger spatial and temporal scales, i.e., to explore relationships between annual rather than hourly or daily fluxes and ecosystem-scale variables such as plant community and soil type and annual climate rather than field-scale variables such as soil moisture and temperature. We addressed this question by examining existing data on annual fluxes from temperate forest, cropland, and rangeland ecosystems, analyzing both multiyear data sets from individual sites as well as cross-site comparison of single annual flux values from multiple sites. Results suggest that there are indeed coherent patterns in annual N₂O flux at the ecosystem scale in forest, cropland, and rangeland ecosystems but that these patterns vary by region and only emerge with continuous (at least daily) flux measurements over multiple years. An ecosystem approach to evaluating N₂O fluxes will be useful for regional and global modeling and for computation of national N₂O flux inventories for regulatory purposes but only if measurement programs are comprehensive and continuous.

1. Introduction

Soil-atmosphere nitrous oxide (N₂O) flux is one of the most difficult to quantify components of the terrestrial N cycle. These fluxes are the product of multiple processes, with complex regulation, and they exhibit extraordinary spatial and temporal variability [Matson and Vitousek, 1990; Bouwman *et al.*, 1995; Brumme *et al.*, 1999]. Uncertainty about the nature and extent of N₂O fluxes is beguiling given that terrestrial N cycling is one of the most extensively studied topics in ecosystem ecology and

biogeochemistry [Schlesinger, 1995]. This uncertainty has great practical importance owing to the fact that N₂O is a "greenhouse" gas which can influence the Earth's radiative budget and plays a role in stratospheric ozone destruction [Mooney *et al.*, 1987; Prather *et al.*, 1995].

Nitrous oxide is a by-product of two nitrogen (N) cycle processes in soil, nitrification (the oxidation of ammonium to nitrate and nitrite) and denitrification (the reduction of nitrate and nitrite to nitric oxide, nitrous oxide, and dinitrogen). This gas is emitted during the intermediate steps in these processes in variable amounts depending on a wide range of soil conditions. A "hole-in-the-pipe" model is commonly used to conceptually depict control of N₂O flux where N is flowing through a pipe and N₂O and NO "leak" out via holes in the pipe [Firestone and Davidson, 1989; Davidson *et al.*, 2000]. The size of the pipe is controlled by the rate of ecosystem N-cycling, and the sizes of the holes are controlled by factors such as soil water content, pH, carbon, and the concentration of N-oxides. Once in the atmosphere, N₂O has a long (~120 years) residence time [Prather *et al.*, 1995].

The vast majority of the N₂O flux measurement and modeling activity that has taken place has been process level and field scale, i.e., measurement, analysis, and modeling of hourly and daily fluxes with chambers deployed in field plots [Davidson, 1991; Smith *et al.*, 1995]. It has been very difficult to establish strong predictive relationships between these hourly and daily fluxes and field-scale parameters such as temperature, soil moisture, and soil inorganic N concentrations [Groffman, 1991; Davidson and Verchot, this issue].

¹Institute of Ecosystem Studies, Millbrook, New York.

²Institute of Soil Science and Forest Nutrition, University of Göttingen, Göttingen, Germany.

³Department of Soil Microbiology, Fraunhofer Institute for Atmospheric Environmental Research, Garmisch-Partenkirchen, Germany.

⁴Institute of Ecology and Resources Management, University of Edinburgh, Edinburgh, United Kingdom.

⁵Agricultural Research Service, U.S. Department of Agriculture, Fort Collins, Colorado.

⁶Natural Resources Ecology Laboratory, Colorado State University, Fort Collins, Colorado.

⁷Department of Land Resources Science, University of Guelph, Guelph, Ontario, Canada.

In this study, we addressed the question of whether we can increase our predictive understanding of N_2O fluxes by examining relationships between flux and environmental parameters at larger spatial and temporal scales, i.e., to explore relationships between annual rather than hourly or daily fluxes and ecosystem-scale variables such as plant community and soil type and annual climate rather than field-scale variables such as soil moisture and temperature. We addressed this question by examining existing data on annual fluxes from temperate forest, cropland, and rangeland ecosystems, analyzing both multiyear data sets from individual sites as well as cross-site comparison of single annual flux values from multiple sites.

Our hypothesis that we can increase our predictive understanding of N_2O fluxes by examining relationships between flux and environmental parameters at larger spatial and temporal scales, i.e., annual fluxes at the ecosystem scale, is based on several preliminary analyses that have found that predictive power was higher in larger-scale analyses [Matson and Vitousek, 1987; Groffman and Tiedje, 1989; Groffman et al., 1992; Brumme et al., 1999]. Conceptually, these studies likely succeeded because much of the spatial and temporal variability in the fluxes and much of the complexity of the controlling factors were integrated or subsumed in the large-scale analyses. More fundamentally, much of our trace gas analysis and modeling is based on the idea that different ecosystem types should exhibit distinctive patterns of trace gas flux [Groffman et al., 1988; Matson et al., 1989; Matson and Vitousek, 1990]. This idea has its origin in the extensive successful body of work that has demonstrated that different ecosystem types exhibit distinctive patterns of N cycling. This work has encompassed a wide range of ecosystems and a wide range of N cycle processes, from N supply to plants, to loss of N following clear cutting [Vitousek et al., 1982; Pastor et al., 1984; Aber et al., 1989]. In a practical sense, efforts to assess and control N_2O fluxes at national, regional, and global scales requires identification of specific ecosystems that are strong sources of N_2O [Intergovernmental Panel on Climate Change (IPCC) 1997].

Although our previous success with ecosystem-scale studies of N cycling suggest that we should be able to identify coherent and practically useful patterns of N_2O flux at the ecosystem scale [Matson et al., 1989; Riley and Vitousek, 1995; Potter et al., 1996], several recent studies have suggested that these patterns may be quite complex. For example, Brumme et al. [1999] were able to stratify N_2O emissions from temperate forest ecosystems into three types of patterns (seasonal, background, and event) but could not discern the factors that influence these patterns in different systems.

In the study presented here, we analyze several cases where an annual flux, ecosystem-scale approach fails and attempt to determine if the failures are due to (1) insufficient data collection, (2) incorrect hypotheses about ecosystem-scale controllers of flux, or (3) the multifactor control and/or chaotic nature of N_2O fluxes, i.e., there may not be coherent patterns of annual N_2O flux at the ecosystem scale.

This paper is a product of the U.S. Trace Gas Network (TRAGNET) and a Trace Gas Fluxes Working Group with international participation sponsored by the U.S. National Center for Ecological Analysis and Synthesis (NCEAS). TRAGNET is centered around a multisite database of trace gas (CO_2 , N_2O , CH_4) fluxes from forest, cropland and rangeland ecosystems. The objectives of the NCEAS working group were to analyze the TRAGNET database and synthesize our understanding of the nature and extent of trace gas fluxes in these ecosystems. This paper is part of a series that addresses different aspects of this understanding by

applying simulation, conceptual and statistical modeling, and analysis of trace gas fluxes at site, ecosystem, regional, and global scales.

2. Materials and Methods

In this study, we conducted two types of analyses: (1) evaluation of multiyear data sets from individual sites and (2) cross-site comparison of single annual flux values from multiple sites. Data were taken from the literature and from the TRAGNET database. We were particularly interested in long-term (multiyear), continuous flux (at least daily sampling) data sets, which are rare. There were separate analyses for temperate forest, cropland, and rangeland ecosystems. This paper presents very little new data. Rather, we attempt a synthetic reanalysis of previously published data, consistent with the mission of our NCEAS working group.

2.1. Forests

2.1.1. Multisite data. Brumme et al. [1999] recently published a comprehensive review of annual N_2O fluxes from temperate forests. Their analysis focused on 11 oak/beech and spruce sites in Germany that receive high rates of N deposition ($20\text{--}40 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) but also included data from other mixed deciduous and coniferous temperate forest studies [Schmidt et al., 1988; Bowden et al., 1990, 1993; Ambus and Christensen, 1995; Klemetsson et al., 1997; MacDonald et al., 1997].

2.1.2. Multiyear data. Papen and Butterbach-Bahl [2000] recently published 3 years of continuous measurements of N_2O flux from spruce and beech forests at the Höglwald, a well-studied site in southern Germany that receives high rates of N deposition ($20\text{--}30 \text{ kg N ha}^{-1} \text{ yr}^{-1}$). Fluxes were measured using an automated chamber (0.25 m^2) system every 2 hours [Butterbach-Bahl et al., 1997] over the 3-year period from 1994 to 1996. While there are many multiyear data sets on N_2O flux from forest ecosystems, this is the only one that we are aware of that is based on continuous (at least daily) measurements.

2.2. Croplands

2.2.1. Multisite data. Bouwman [1996] assembled a comprehensive database of over 250 estimates of direct emissions of N_2O from crop fields. The estimates were based on different temporal and spatial sampling regimes, but the focus of the analysis was on annual fluxes. The analysis evaluated crop type, soil factors, fertilizer type, and fertilizer amount as controllers of annual flux.

2.2.2. Multiyear data. Dobbie et al. [1999] and Clayton et al. [1997] summarized multiyear data on N_2O fluxes from intensively managed grassland and row crop agricultural systems in Scotland. Their analysis focused on systematic differences between cropping systems and on the factors controlling variation in annual flux. Sampling was daily for the first few days after fertilization, then at gradually increasing intervals. There were six to eight 0.125 m^2 flux chambers at each site.

Wagner-Riddle et al. [1997] measured N_2O fluxes over a 3-year period from five crop rotation sequences in southern Canada. Fluxes were measured hourly using micrometeorological techniques and a tunable diode laser trace gas analyzer. We believe that this is the only multiyear data set based on continuous (at least daily) sampling of croplands that is available.

2.3. Rangelands

2.3.1. Multisite data. There have been no multisite evaluations of N_2O fluxes from rangelands.

2.3.2. Multiyear data. Nitrous oxide fluxes have been measured from fertilized and unfertilized rangelands at the Central Plains Experimental Range (CPER) in eastern Colorado, using 0.32 m² chambers since 1990 [Mosier *et al.*, 1996a]. The study site was established in April 1990 within a paired fertilized (PF) and native (PN) pasture. The PF site had been fertilized with 2.2 g N m⁻² yr⁻¹ of ammonium nitrate from 1976 until October 1989. Both pastures were grazed from May through October of each year by cattle (20 head/130 ha). The terrain of the two pastures is essentially flat, and the soil is an Ascalon sandy loam (fine-loamy, mixed, mesic Aridic Argiustolls).

A simulation model for N₂ and N₂O formation from nitrification and denitrification (NGAS) was developed from data at CPER [Parton *et al.*, 1996] and has been used to produce estimates of annual flux that can be compared with estimates of annual flux derived from field measurements. This model is a component of DAYCENT (a daily time-step version of the CENTURY simulation model), which integrates submodels for land surface parameters, soil organic matter and nutrient levels, plant productivity and trace gas fluxes [Parton *et al.*, 1998; Kelly *et al.*, 2000]. We also used the field measurement data set to evaluate the effect of sampling frequency (monthly, twice a month, and weekly) on annual flux estimates.

3. Results and Discussion

3.1. Forests

The analysis of 11 German forest sites conducted by Brumme *et al.* [1999] found very poor relationships between annual N₂O flux and a series of long-term ecosystem-scale "state variables" (soil organic C, annual temperature, annual precipitation, pH, N leaching, N deposition, base saturation, bulk density). Even when the data from Brumme *et al.* [1999] are combined with data from several other forest studies, strong predictive relationships between annual N₂O flux and soil pH, annual precipitation and mean annual temperature do not emerge (Table 1). Combining N₂O flux and soil organic carbon data from several temperate forest studies shows that soil organic carbon is also not a strong predictor of annual N₂O emissions (Figure 1). These data suggest that the multisite approach, i.e., evaluation of single annual flux values from multiple sites, does not produce strong relationships between flux and forest ecosystem properties.

The Brumme *et al.* [1999] analysis, Table 1, and Figure 1, raise several questions about the value of the annual flux/ecosystem-scale approach to evaluating N₂O fluxes. First, we can question the robustness of annual estimates based on a single year of data; that is,

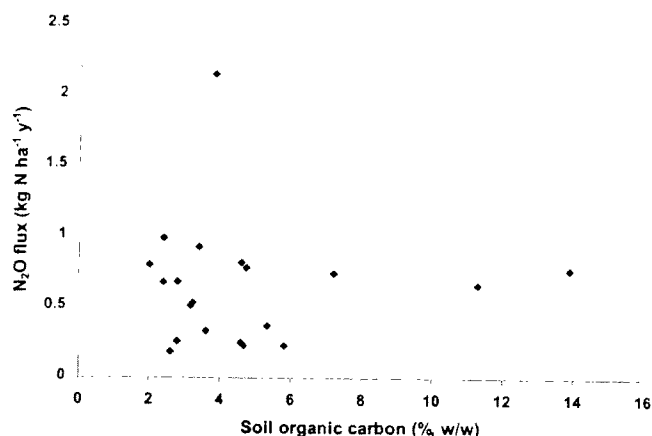


Figure 1. Annual N₂O flux versus soil organic carbon in 21 temperate forest sites. (Data from Schmidt *et al.* [1988], Ambus and Christensen [1995], Borken and Brumme [1997], Goodroad and Keeney [1984], and Goldman *et al.* [1995], TRAGNET database.)

do we know that this is truly a representative year for a given ecosystem type? This question is addressed by our analysis of multiyear data below. Second, we can ask if our concepts about ecosystem-scale control of N₂O flux are correct. While we might expect that soil organic C, N deposition, and N leaching would be strong controllers of annual N₂O flux, perhaps there are other predictors that are more suitable. Brumme *et al.* [1999] point out that physical structures within an ecosystem (plant canopy architecture, forest floor depth, and bulk density) that influence soil aeration may be critical controllers of annual N₂O flux. It is interesting to note that bulk density is the only statistically significant ($p < 0.01$) predictor of flux in Table 1. Brumme *et al.* [1999] also point out the importance of relatively short-term climate events (soil freezing events and summer rainfall patterns) as controllers of annual flux. These ideas suggest that links between ecosystem "type" and N₂O flux may be more complex than the links between ecosystem type and other N cycling processes (e.g., N mineralization, and N loss following clear cutting) and that we need to rethink our concepts about ecosystem-scale control of N₂O flux.

The multiyear data set collected by Papen and Butterbach-Bahl [1999, Table 2] strongly suggests that several years of data and year-round monitoring are required to produce robust estimates of annual N₂O flux. These data show that (1) interannual variability in flux can be quite high, (2) interannual variability is not controlled by mean annual climate, and (3) that it is easier to see consistent differences between ecosystems when we have continuous, multiyear data. Analysis of these data suggests that some of our ideas about ecosystem-scale controls on N₂O flux are sound and that others need reexamination.

The German data (Table 2) show consistent differences between spruce and beech forests that are consistent with well-established ideas about differences in N cycling between deciduous and coniferous forests [Pastor *et al.*, 1984; Hobbie, 1992; Finzi *et al.*, 1998]. Deciduous vegetation generally has higher litter quality (low C:N ratio and low lignin) that fosters high rates of N cycling, availability, and loss than coniferous vegetation.

The German data are also consistent with current ideas about the response of forest ecosystems to high rates of N deposition. These forests can be considered to be N "saturated," a condition that is expected to lead to high rates of N₂O flux [Aber *et al.*, 1989] (note

Table 1. Correlations Between Annual N₂O Flux and Environmental Factors in Temperate Forest Soils

Environmental Variable	Annual N ₂ O Flux
Soil pH	-0.18 ($n = 31$, $p < 0.32$)
Soil bulk density	-0.60 ($n = 18$, $p < 0.01$)
Annual precipitation	0.35 ($n = 21$, $p < 0.11$)
Annual temperature	0.35 ($n = 21$, $p < 0.11$)

Data from Brumme *et al.* [1999], Ambus and Christensen [1995], Bowden *et al.* [1990, 1993], Klemmedsson *et al.* [1997], Schmidt *et al.* [1988], MacDonald *et al.* [1997], Luizao *et al.* [1989], and Keller and Reiners [1994].

Table 2. Annual N₂O Fluxes, Annual Temperature, and Annual Precipitation in Beech, Spruce, and Limed Spruce Stands at the Högwald, Germany in 1994, 1995, and 1996

	N ₂ O Flux, kg N ha ⁻¹ yr ⁻¹	Annual Temperature, °C	Annual Precipitation, mm
<i>Beech</i>			
1994	0.97	6.5	952
1995	3.7	7.4	955
1996	6.6	5.6	936
<i>Spruce</i>			
1994	0.42	8.9	952
1995	0.81	7.6	955
1996	3.1	5.7	936
<i>Spruce (limed)</i>			
1994	0.71	8.9	952
1995	1.1	7.6	955
1996	4.0	5.7	936

Data from Papen and Butterbach-Bahl [1999].

that the N₂O flux rates in Table 2 are quite high). The strong difference between beech and spruce may have been accentuated by the high rates of N deposition at the site. Ecosystems dominated by species with high-quality litter may be much more susceptible to N saturation than ecosystems with low quality litter. In the German studies, 10% of the atmospheric N that was deposited on the beech ecosystem was emitted as N₂O (a very high percentage), while only 0.5% of the atmospheric N that was deposited on the spruce ecosystem was emitted as N₂O. These differences in percent emission were due to higher rates of N deposition and lower rates of N₂O emission in spruce. High rates of N input do not always lead to high N₂O emissions, however. At the Harvard Forest in Massachusetts, large (845 kg N) additions of N over a 6-year period to pine and hardwood forest stands did not lead to increases in emissions [Magill et al., 1997]. Bowden et al. [2000] reported that N additions to an inherently N-rich forest soil did not increase N₂O fluxes.

The responses to liming observed in the German studies are also consistent with generally held ideas about the effects of pH on ecosystem N cycling, i.e., that increasing pH increases rates of N cycling and loss [Nyborg and Hoyt, 1978; Persson et al., 1989; Nagele and Conrad, 1990; Papen et al., 1993; Nodar et al., 1992]. However, consideration of other pH and N₂O flux data shows how links between ecosystem properties and N₂O flux are more complex than links between ecosystem properties and other N-cycling processes. While the German data reported in Table 2 show a clear and coherent response to liming, other German studies show decreases in N₂O flux in response to liming [Borken and Brumme, 1997]. Differences between these studies are likely caused by a complex interaction between soil pH, bioturbation, the structure of the forest floor/litter layer, soil anaerobiosis, and N₂O production by nitrification and denitrification. In acid soils, bioturbation (e.g., earthworm activity) can be eliminated leading to the development of denser soils and litter layers, increases in soil anaerobiosis or microaerophilic conditions, and increases in N₂O flux [Ball et al., 1997]. Liming these soils can thus result in decreases in N₂O flux. An increase in soil pH also influences (negatively) the N₂O:N₂ ratio

of denitrification, which can also contribute to decreases in N₂O flux associated with lime additions [Firestone, 1982]. These contradictory responses to lime show that while we may be able to make predictions about the nature and extent of N₂O flux from forest ecosystems given information on plant community composition, these predictions should be refined with data on soil pH and soil biotic activity. It will be quite challenging to develop data on soil pH and biotic activity at the scales necessary for regional- and global-scale analyses of N₂O flux.

The German forest data also show that we need to think carefully about factors controlling annual variation in flux. There were marked increases in N₂O flux in the German studies in 1996 owing to soil freezing during the winter of 1995-1996. While it has long been known that soil freezing can result in increases in N₂O flux [Goodroad and Keeney, 1984b], these data show that freezing is a critical controller of variation in annual N₂O flux from some forest ecosystems. It will be important to develop approaches to evaluating and predicting the nature and extent of freezing events as we refine methods for producing regional and global estimates of N₂O flux [Groffman et al., 1999].

3.2. Croplands

We expected that ecosystem-scale analysis of N₂O flux from agricultural ecosystems would be especially difficult because of the high diversity and complexity of agricultural management practices. There are multiple management activities that can affect flux (tillage, planting, pesticide use, crop rotation, and fertilizer type), and these vary in space and time. However, analysis of agricultural systems is of great importance to greenhouse gas assessment and mitigation efforts [Mosier et al., 1996b]. There is a great need to know which agricultural ecosystems emit high amounts of N₂O so that these can be accounted for in national N₂O emission inventories and targeted in mitigation efforts.

Bouwman's [1996] analysis of over 250 estimates of direct N₂O emission from agricultural fields was hindered by variation in measurement period and frequency of measurements. As a result, he was able to develop few conclusions about just what type of agricultural systems emit high amounts of N₂O. Bouwman was unable to establish systematic, robust patterns of N₂O flux with soil texture, soil drainage, crop type (grass versus row crop versus legume), residue management, or soil pH. He was able to tentatively verify that different fertilizer types seem to support different amounts of N₂O emissions, building on ideas presented by Eichner [1990]. The analysis also showed that cropping systems on organic soils routinely produce high fluxes.

Using the best data available (i.e., experiments with high frequency, year-round measurements), Bouwman [1996] was able to establish a strong relationship between annual N₂O emission and fertilizer input (Figure 2). This relationship has proven to be very useful for assessment purposes and is the basis for the IPCC National Greenhouse Gas Methodology for N₂O from agriculture [Mosier et al., 1998]. However, the relationship, and the IPCC methodology, is limited in several important regards. Given the complex interactions between cropping system parameters and climate that influence N₂O flux, there are many regions where there will not be strong relationships between fertilizer input and flux (e.g., Figure 3). Nitrous oxide flux is controlled by multiple factors. If any one of them is "limiting," flux will not occur. Given that at least one of the factors is likely to be limiting in multisite analyses, it is very difficult to establish strong predictive

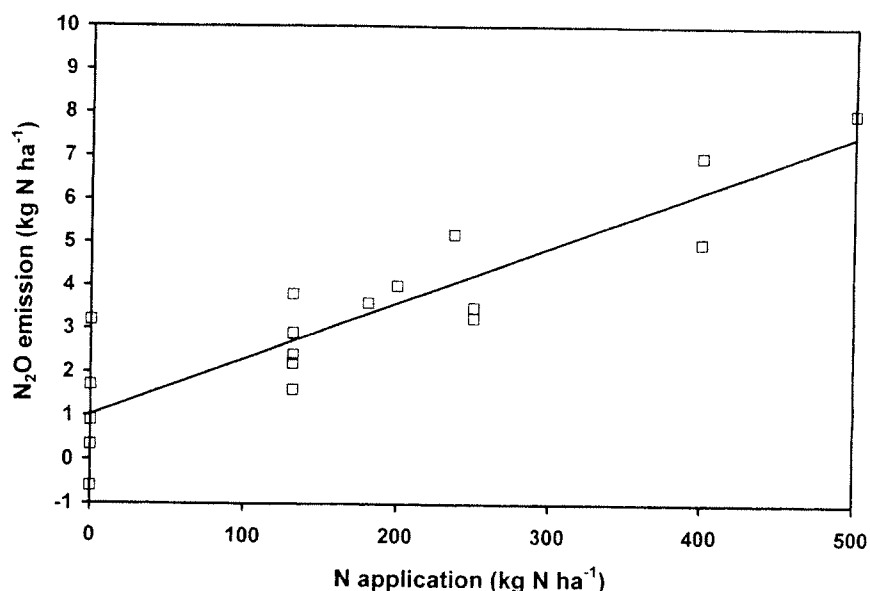


Figure 2. Relationship between N fertilizer application and N_2O emission for mineral soils with N application rates $< 500 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ and a full year of flux measurements. From Bouwman [1996].

relationships between any one factor (e.g., fertilizer input) and flux that are applicable over regional or global scales.

The results reported by Wagner-Riddle *et al.* [1997] amplify the conclusions of Bouwman [1996] and Papen and Butterbach-Bahl [1999] that multi-year continuous flux measurements are necessary for evaluating annual N_2O fluxes at the ecosystem scale. They were able to demonstrate coherent differences between grass and arable cropping systems using micrometeorological techniques that measure fluxes hourly (Table 3). The results reported by Wagner-Riddle *et al.* [1997] also raise questions about some of our ideas about the factors that control annual N_2O fluxes from agricultural ecosystems. The consistent patterns of annual flux in all four plots in 1993 and 1994, despite marked differences in cropping system in some of the plots (i.e., plots 1, 2, and 3), suggest that soil or other "site factor" differences between the plots may be more important as controllers of annual flux than crop type. Their results also support the idea that freezing and thawing events are critical controllers of annual N_2O flux. Fluxes associated with spring thaw accounted for

from 40% to 75% of the annual flux from their plots. The marked reduction in flux in 1995 was attributed to less snow accumulation during the winter and a low number of freeze/thaw periods when compared to 1993 and 1994.

The multiyear data presented by Dobbie *et al.* [in press] have several important implications for evaluating annual N_2O fluxes from agricultural ecosystems. The fact that they were able to observe consistent differences between the major cropping systems in their region (Figure 4) suggests that there is a potential for assessing and mitigating agricultural N_2O sources. The availability of multiyear, continuous flux data allowed them to clearly define consistent differences between grassland, winter cereals, and

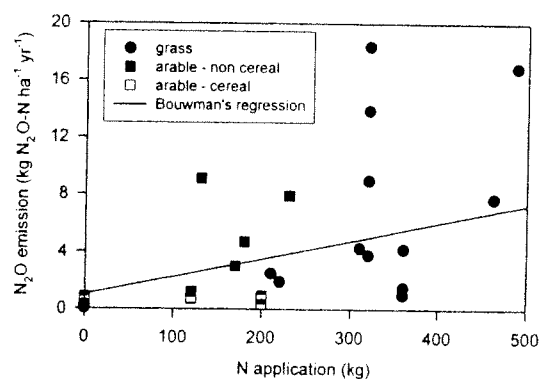


Figure 3. Annual N_2O emission versus N fertilizer application for grassland and arable crops in Scotland, showing "Bouwman's" regression line from Figure 2 [from Dobbie *et al.*, in press].

Table 3. Annual N_2O Fluxes From Cropped Fields in Southern Ontario, Canada from 1993 to 1995

Plot	Year	Crop	N_2O Flux, $\text{kg N ha}^{-1} \text{ yr}^{-1}$
1	1993	fallow	4.0
1	1994	barley	3.7
1	1995	barley	1.8
2	1993	fallow plus manure	5.7
2	1994	soybeans	5.9
2	1995	soybeans	0.9
3	1993	alfalfa	3.7
3	1994	canola	3.8
3	1995	canola	2.8
4	1993	grass	-0.1
4	1994	grass	0.3
4	1995	grass	0.3

Data from 1993 and 1994 from Wagner-Riddle *et al.* [1997].

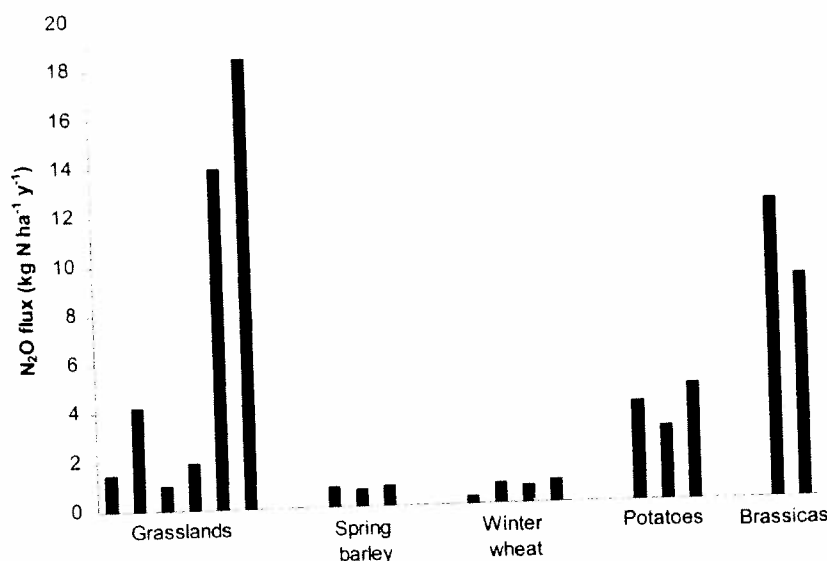


Figure 4. Annual N₂O emissions from the major cropping systems in Scotland, United Kingdom. Each bar represents an annual flux value from a year between 1992 and 1998 (derived from data from *Dobbie et al.* [2000]).

specific vegetable crops. Moreover, multiyear continuous data allowed them to define key controllers of variation in annual flux. For the grassland systems, rainfall in the four-week period around fertilizer application explained 68% of the variation in annual flux (Figure 5). Perhaps most importantly, the data suggest that multiyear, multisite continuous flux data allow for reconciliation of the complex interactions between soil, climate, and specific agricultural management practices that govern patterns of N₂O flux at the regional scale. These results have important implications for assessment and mitigation efforts, suggesting that intensive, region-by-region analysis of this type can produce coherent information on key N₂O sources and the best prospects for mitigation. Another example of this type of analysis is the work by *Kessavalou et al.* [1998] who were able to demonstrate clear differences between sod and row crop systems in Nebraska, with 3 years of weekly flux measurements and were able to evaluate their results relative to C

sequestration and atmospheric chemistry questions in an agricultural policy context. Similarly, *Kaiser et al.* [1998] measured fluxes on a weekly basis for 33 months in Germany and were also able to demonstrate clear differences in emissions from different cropping systems.

3.3. Rangelands

Annual fluxes from unfertilized rangelands at the CPER, produced using the NGAS model, which was developed using data from the site (Figure 6), show that variation in annual flux is much less than variation in daily flux (Figure 7). Moreover, a high percentage (46%) of the variation in annual flux can be explained with annual precipitation (Figure 8), while soil moisture was not a significant predictor of daily flux within a given year (Figure 9).

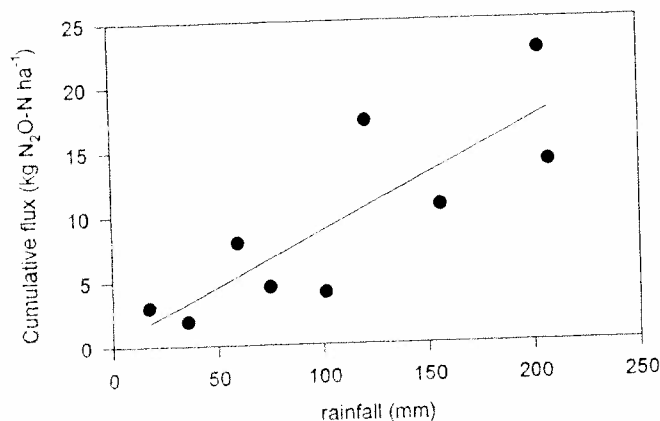


Figure 5. Annual N₂O fluxes from intensively managed grasslands in Scotland, United Kingdom, as a function of summer rainfall around times of fertilizer application (based on data in *Dobbie et al.* [2000]).

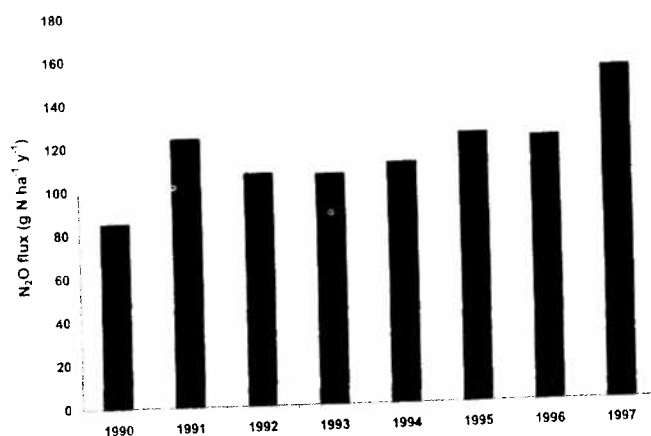


Figure 6. Annual N₂O flux estimates produced using the NGAS simulation model for unfertilized rangelands in eastern Colorado from 1990 to 1997.

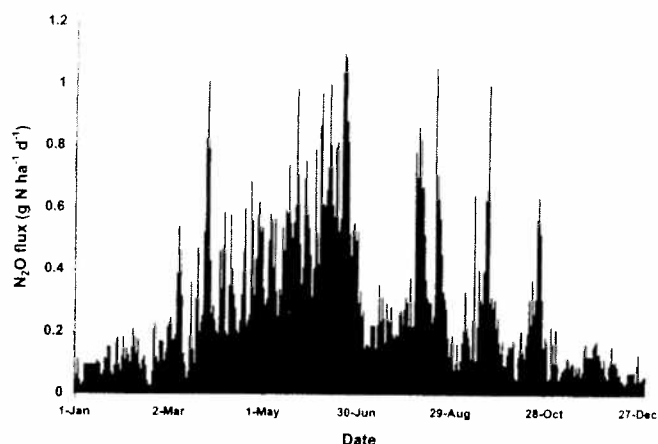


Figure 7. Daily N_2O fluxes produced using the NGAS simulation model for unfertilized rangelands in eastern Colorado in 1993.

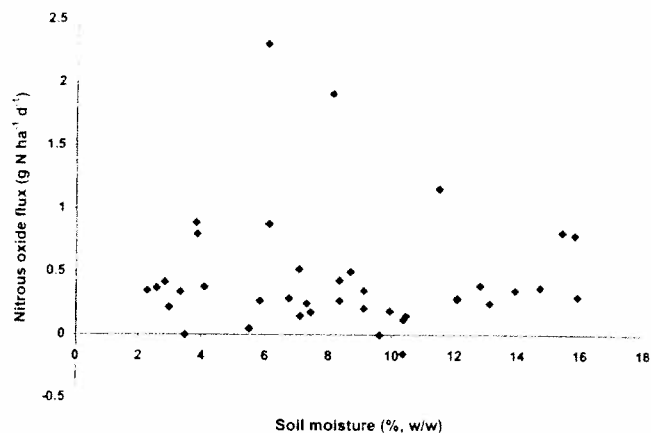


Figure 9. Daily N_2O flux measured in field chambers versus soil moisture in unfertilized rangeland in eastern Colorado in 1993.

The results from CPER amplify the points made above, i.e., that continuous, multiyear data show that there are coherent patterns in annual N_2O flux at the ecosystem scale. It is interesting to note that in this case, annual fluxes were produced using a simulation model that was well calibrated for this specific site [Parton *et al.*, 1996]. It remains to be seen if such models will become accepted as tools for producing annual flux estimates in scientific and regulatory assessments.

The CPER data allow us to evaluate how sampling frequency affects flux estimates and predictive relationships between flux and environmental parameters. Surprisingly, increased sampling frequency did not have consistent effects on estimates of the mean flux (Table 4) and did not increase the strength of relationships between flux and annual precipitation (Table 5). Within any given year, weekly sampling did not give consistently different or less variable estimates of the annual mean flux than twice a month or monthly sampling (Table 4). Increased sampling frequency did not increase the strength of the relationship between annual precipitation and flux (Table 5). These results suggest that coherent patterns in annual flux at the ecosystem scale in these rangelands will only emerge with daily or continuous sampling of the type used in the

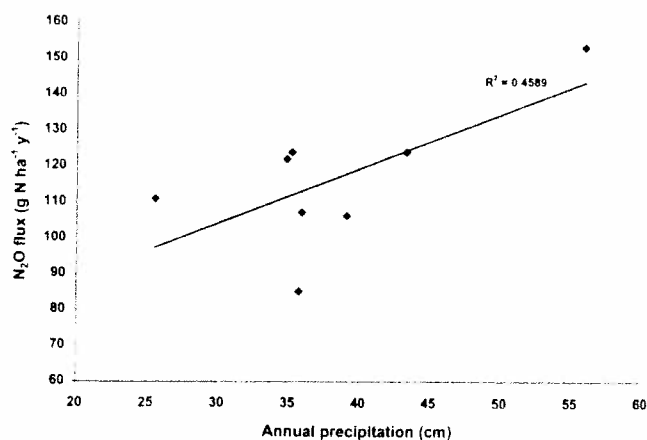


Figure 8. Annual N_2O flux estimated with the NGAS simulation model versus annual precipitation for unfertilized rangeland in eastern Colorado from 1990 to 1997.

forest and cropland studies described above. It is important to consider that increasing sampling frequency from monthly to weekly may be more useful in sites with higher flux than CPER.

4. Conclusions

1. There appear to be coherent patterns in annual N_2O flux at the ecosystem scale in forest, cropland, and rangeland ecosystems, i.e., the "ecosystem approach" can work. As others have found, there is a clear lack of relationship between single annual N_2O emission values and ecosystem properties from forests and croplands, i.e., the multisite approach does not work. However, the few studies where multiyear, continuous flux (at least daily) data are available suggest that different ecosystems do exhibit distinctive patterns of N_2O flux and that these patterns are strongly linked to patterns of C and N flux in these systems. However, the linkages between flux and these patterns are complex and often surprising (see below). Ultimately, an ecosystem approach to evaluating N_2O fluxes should be useful for regional and global modeling and for computation of national N_2O flux inventories for regulatory assessment purposes.

2. Ecosystem-scale controls of N_2O flux are complex and vary within and between regions. For some systems, for example, rangelands, annual precipitation is a strong controller of annual flux, while in other systems, for example, some north temperate forests and croplands, winter freezing is a major factor. Regional assessments must be based in a strong experimental context that addresses the major factors that control flux at the ecosystem scale.

3. In intensively managed (e.g., fertilized grassland) systems, transient factors such as the degree of coincidence of fertilizer timing and the timing of significant amounts of rainfall (or irrigation events) can have a dominant effect on annual flux. This prevents any assessment of an absolute level of flux typical of the ecosystem. However, intensive sampling can be used to characterize when and where relatively higher fluxes occur in different agricultural management systems in some regions. Such characterizations may be very useful for assessing and mitigating N_2O on a regional basis.

4. Continuous (at least daily), multiyear data appear to be required to characterize patterns of annual N_2O flux at the ecosystem scale. Event-based sampling, with daily measurements around large rainfall or fertilization events followed by less frequent

Table 4. Mean annual N₂O flux and annual precipitation in unfertilized rangeland in eastern Colorado

	Weekly	Twice a Month, g N ha ⁻¹ d ⁻¹	Monthly	Annual Precipitation, cm
1991	0.43 (.05)	0.35 (.07)	0.39 (.11)	35
1992	0.29 (.05)	0.28 (.08)	0.16 (.05)	36
1993	0.55 (.12)	0.71 (.22)	0.69 (.21)	39
1994	0.35 (.13)	0.32 (.23)	0.29 (.44)	26
1995	0.49 (.10)	0.36 (.05)	0.36 (.07)	43
1996	0.30 (.06)	0.45 (.11)	0.38 (.18)	35
6-yr mean	0.40 (.04)	0.41 (.06)	0.37 (.07)	

The full data set of weekly flux measurements was subsampled to produce annual flux estimates based on weekly, twice a month, and monthly data. Flux values are mean (standard error).

sampling when there is low activity, may be useful in some systems. Weekly or monthly data may be suitable for some systems, especially for general comparisons of sites and/or treatments. The need for continuous, multiyear data should be strongly considered as national or regional environmental monitoring networks are established.

5. Highly calibrated, site-specific simulation models may be useful tools for ecosystem-based, regional-scale assessments of annual N₂O flux. Such models may be able to substitute for intensive measurement programs in certain systems.

Evaluation of N₂O flux has been one of the most problematic topics in environmental biogeochemistry over the last 10 years. Early ideas that we should be able to use the large body of work on N cycling to predict patterns of N₂O flux at the ecosystem scale [Matson *et al.* 1989] have been hard to prove due to the extreme temporal and spatial variability in flux. However, new intensive measurement campaigns suggest that our early ideas were robust and that we should indeed be able to make sense of landscape, regional, and global patterns in N₂O flux.

Table 5. Correlations (With Significance Values) Between Mean Annual N₂O Flux and Annual Precipitation for Unfertilized Rangelands in Eastern Colorado Between 1991 and 1996 (*n* = 6)

Sampling Frequency	Correlation
Weekly	0.56, <i>p</i> < 0.25
Twice a month	0.33, <i>p</i> < 0.52
Monthly	0.35, <i>p</i> < 0.50

Annual N₂O flux was calculated from actual field measurements at weekly, twice a month, and monthly frequency as in Table 4.

Acknowledgments. The U.S. Trace Gas network (TRAGNET) was begun with financial assistance from the U.S. National Science Foundation (NSF) Long-Term Studies Program (Grant DEB 94-16813) and U.S. Department of Agriculture, Agricultural Research Service. Data archives, constructed by Brian Newkirk and Steven Knox, are housed at the Natural Resource Ecology Laboratory, Colorado State University. Analysis and synthesis of the trace gas data was supported by the National Center for Ecological Analysis and Synthesis, a Center funded by NSF (Grant DEB-94-21535), the University of California at Santa Barbara and the state of California.

References

- Aber, J. D., K. J. Nadelhoffer, P. Steudler, and J. M. Melillo, Nitrogen saturation in northern forest ecosystems, *BioScience*, 39, 378-386, 1989.
- Ambus, P., and S. Christensen, Spatial and seasonal nitrous oxide and methane fluxes in Danish forest-, grassland-, and agroecosystems, *J. Environ. Qual.*, 24, 993-1001, 1995.
- Ball, B. C., K. A. Smith, L. Klemmedtsson, R. Brumme, K. Sitaula, S. Hansen, S. Christensen, A. Prieme, J. MacDonald, and G. W. Horgan, The influence of soil gas transport properties on methane oxidation in a selection of northern European soils, *J. Geophys. Res.*, 102, 23309-23317, 1997.
- Borken, W., and R. Brumme, Liming practice in temperate forest ecosystems and the effects on CO₂, N₂O, and CH₄ fluxes, *Soil Use Manage.*, 13, 251-257, 1997.
- Bouwman, A. F., Direct emission of nitrous oxide from agricultural soils, *Nutrient Cycling in Agroecosystems*, 46, 53-70, 1996.
- Bouwman, A. F., K. W. van der Hock, and J. G. J. Olivier, Uncertainty in the global source distribution of nitrous oxide, *J. Geophys. Res.*, 100, 2785-2800, 1995.
- Bowden, R. D., P. A. Steudler, and J. M. Melillo, Annual nitrous oxide fluxes from temperate forest soils in the northeastern United States, *J. Geophys. Res.*, 95, 13,997-14,005, 1990.
- Bowden, R. D., M. S. Castro, J. M. Melillo, P. A. Steudler, and J. D. Aber, Fluxes of greenhouse gases between soils and the atmosphere in a temperate forest following a simulated hurricane blowdown, *Biogeochemistry*, 23, 61-71, 1993.
- Bowden, R. D., G. Rullo, G. R. Stevens, and P. A. Steudler, Soil fluxes of carbon dioxide, nitrous oxide, and methane at a productive temperate deciduous forest, *J. Environ. Qual.*, 29, 268-276, 2000.

- Brumme, R., W. Borken, and S. Finke, Hierarchical control on nitrous oxide emission in forest ecosystems, *Global Biogeochem. Cycles*, 13, 1137-1148, 1999.
- Butterbach-Bahl, K., R. Gasche, L. Breuer, and H. Papen, Fluxes of NO and N₂O from temperate forest soils: Impact of forest type, N deposition, and liming on the NO and N₂O emissions, *Nutrient Cycling Agroecosystems*, 48, 79-90, 1997.
- Clayton, H., I. P. McTaggart, J. Parker, L. Swan, and K. A. Smith, Nitrous oxide emissions from fertilized grassland: A 2-year study on the effects of N fertilizer form and environmental conditions, *Biol. Fertil. Soils*, 25, 252-260, 1997.
- Davidson, E. A., Fluxes of nitrous oxide and nitric oxide from terrestrial ecosystems, in *Microbial Production and Consumption of Greenhouse Gases: Methane, Nitrogen Oxides and Halomethanes*, edited by W. B. Whitman and J. E. Rogers, pp. 219-235, Am. Soc. for Microbiol., Washington, D. C., 1991.
- Davidson, E. A., M. Keller, H. E. Erickson, L. V. Verchot, and E. Veldkamp, A cross-site test of a conceptual model of nitrous oxide and nitric oxide emissions from soils: Is the hole-in-the-pipe model holistic, holy, or full of holes?, *BioScience*, in press, 2000.
- Davidson, E. A., and L. V. Verchot, Testing the hole-in-the-pipe model of nitric and nitrous oxide emissions from soils using the TRAGNET database, *Global Biogeochem. Cycles*, this issue.
- Dobbie, K. E., I. P. McTaggart, and K. A. Smith, Nitrous oxide emissions from intensive agricultural systems: Variations between crops and seasons; key driving variables; and mean emission factors, *J. Geophys. Res.*, 104, 26,891-26,900, 1999.
- Eichner, M. J., Nitrous oxide emissions from fertilized soils: Summary of available data, *J. Environ. Qual.*, 19, 272-280, 1990.
- Finzi, A. C., N. van Breemen, and C. D. Canham, Canopy tree-soil interactions within temperate forests: Species effects on soil carbon and nitrogen, *Ecol. Appl.*, 8, 440-446, 1998.
- Firestone, M. K., Biological denitrification, in *Nitrogen in Agricultural Soils*, edited by F. J. Stevenson, pp. 289-326, Am. Soc. of Agron., Madison, Wisc., 1982.
- Firestone, M. K., and E. A. Davidson, Microbiological basis of NO and N₂O production and consumption in soil, in *Exchange of Trace Gases Between Terrestrial Ecosystems and the Atmosphere*, edited by M. O. Andreae and D. S. Schimel, pp. 7-22, John Wiley, New York, 1989.
- Goldman, M. B., P. M. Groffman, R. V. Pouyat, M. J. McDonnell, and S. T. A. Pickett, Methane uptake and nitrogen availability in forest soils along an urban to rural gradient, *Soil Biol. Biochem.*, 27, 281-286, 1995.
- Goodroad, L. L., and D. R. Keeney, Nitrous oxide emission from forest, marsh, and prairie ecosystems, *J. Environ. Qual.*, 13, 448-452, 1984a.
- Goodroad, L. L., and D. R. Keeney, Nitrous oxide emissions from soils during thawing, *Can. J. Soil Sci.*, 64, 187-194, 1984b.
- Groffman, P. M., Ecology of nitrification and denitrification in soil evaluated at scales relevant to atmospheric chemistry, in *Microbial Production and Consumption of Greenhouse Gases: Methane, Nitrogen Oxides and Halomethanes*, edited by W. B. Whitman and J. Rogers, pp. 201-217, Am. Soc. of Microbiol., Washington, D. C., 1991.
- Groffman, P. M., and J. M. Tiedje, Denitrification in north temperate forest soils: Relationships between denitrification and environmental factors at the landscape scale, *Soil Biol. Biochem.*, 21, 621-626, 1989.
- Groffman, P. M., J. M. Tiedje, G. P. Robertson, and S. Christensen, Denitrification at different temporal and geographic scales: Proximal and distal controls, in *Advances in Nitrogen Cycling in Agricultural Ecosystems*, edited by J. R. Wilson, pp. 174-192, CAB International, Wallingford, England, U. K., 1988.
- Groffman, P. M., J. M. Tiedje, D. L. Mokma, and S. Simkin, Regional scale estimates of denitrification in north temperate forest soils, *Landscape Ecol.*, 7, 45-53, 1992.
- Groffman, P. M., J. P. Hardy, S. Nolan, C. T. Driscoll, and T. J. Fahey, Snow depth, soil frost and nutrient loss in a northern hardwood forest, *Hydrol. Processes*, 13, 2275-2286, 1999.
- Hobbie, S. E., Effects of plant species on nutrient cycling, *Trends Ecol. Evol.*, 7(10), 336-339, 1992.
- Intergovernmental Panel on Climate Change (IPCC), *Guidelines for National Greenhouse Gas Inventories*, Organization for Economic Cooperation/Organisation de Cooperation et de Développement Economiques, Paris, 1997.
- Kaiser, E.-A., K. Kohrs, M. Kucke, E. Schnug, O. Heinemeyer, and J. C. Munch, Nitrous oxide release from arable soil: Importance of N-fertilization, crops and temporal variation, *Soil Biol. Biochem.*, 30, 1553-1563, 1998.
- Keller, M., and W. A. Reinert, Soil-atmosphere exchange of nitrous oxide and methane under secondary succession of pasture to forest in the Atlantic lowlands of Costa Rica, *Global Biogeochem. Cycles*, 8, 399-409, 1994.
- Kelly, R. H., W. J. Parton, M. D. Hartman, L. K. Stretch, D. S. Ojima, and D. S. Schimel, Intra and interannual variability of ecosystem processes in shortgrass steppe, *J. Geophys. Res.*, in press, 2000.
- Kessavalou, A., A. R. Mosier, J. W. Doran, R. A. Drijber, D. J. Lyon, and O. Heinemeyer, Fluxes of carbon dioxide, nitrous oxide, and methane in grass sod and winter wheat-fallow tillage management, *J. Environ. Qual.*, 27, 1094-1104, 1998.
- Klemetsson, L., A. Kasimir Klemetsson, F. Moldan, and P. Weslien, Nitrous oxide emission from Swedish forest soils in relation to liming and simulated increased N-deposition, *Biol. Fertil. Soils*, 25, 290-295, 1997.
- Luizao, F., P. Matson, G. Livingston, R. Luizao, and P. M. Vitousek, Nitrous oxide flux following tropical land clearing, *Global Biogeochem. Cycles*, 3, 281-285, 1989.
- MacDonald, J. A., U. Skiba, L. J. Sheppard, B. Ball, J. D. Roberts, K. A. Smith, and D. Fowler, The effects of nitrogen deposition and seasonal variability on methane oxidation and nitrous oxide emission rates in an upland spruce plantation and moorland, *Atmos. Environ.*, 31, 3693-3706, 1997.
- Magill, A. H., J. D. Aber, J. J. Hendricks, R. D. Bowden, J. M. Melillo, and P. A. Steudler, Biogeochemical response of forest ecosystems to simulated chronic nitrogen deposition, *Ecol. Appl.*, 7, 402-415, 1997.
- Matson, P. A., and P. M. Vitousek, Cross-system comparisons of soil nitrogen transformations and nitrous oxide flux in tropical forest ecosystems, *Global Biogeochem. Cycles*, 1, 163-170, 1987.
- Matson, P. A., and P. M. Vitousek, Ecosystem approach to a global nitrous oxide budget, *BioScience*, 40, 667-672, 1990.
- Matson, P. A., P. M. Vitousek, and D. S. Schimel, Regional extrapolation of trace gas flux based on soils and ecosystems, in *Exchange of Trace Gases Between Terrestrial Ecosystems and the Atmosphere*, edited by M. O. Andreae and D. S. Schimel, pp. 97-108, John Wiley, New York, 1989.
- Mooney, H. A., P. M. Vitousek, and P. A. Matson, Exchange of materials between terrestrial ecosystems and the atmosphere, *Science*, 238, 926-932, 1987.
- Mosier, A. R., W. J. Parton, D. W. Valentine, D. S. Ojima, D. S. Schimel, and J. A. Delgado, CH₄ and N₂O fluxes in the Colorado shortgrass steppe, 1, Impact of landscape and nitrogen addition, *Global Biogeochem. Cycles*, 10, 387-399, 1996a.
- Mosier, A. R., J. M. Duxbury, J. R. Freney, O. Heinemeyer, and K. Minami, Nitrous oxide emission from agricultural fields: Assessment, measurement, and mitigation, *Plant Soil*, 181, 95-108, 1996b.
- Mosier, A., C. Kroeze, C. Nevison, O. Oenema, S. Seitzinger, and O. van Cleemput, Closing the global atmospheric N₂O budget: Nitrous oxide emissions through the agricultural nitrogen cycle, *Nutrient Cycling Agroecosystems*, 52, 225-248, 1998.
- Nägele, W., and R. Conrad, Influence of soil pH on the nitrate-reducing microbial populations and their potential to reduce nitrate to NO and N₂O, *FEMS Microbiol. Ecol.*, 74, 49-58, 1990.
- Nodar, R., M. J. Acea, and T. Carballas, Microbial response to Ca(OH)₂ treatments in a forest soil, *FEMS Microbiol. Ecol.*, 86, 213-219, 1992.
- Nyborg, M., and P. B. Hoyt, Effects of acidity and liming on mineralization of soil nitrogen, *Can. J. Soil Sci.*, 58, 331-338, 1978.
- Papen, H., and K. Butterbach-Bahl, Three years continuous record of N-trace gas fluxes from untreated and limed soil of a N-saturated spruce and beech forest ecosystem in Germany, 1, N₂O-emissions, *J. Geophys. Res.*, 104(15), 18487-18503, 1999.
- Papen, H., B. Hellmann, H. Papke, and H. Rennenberg, Emission of N-oxides from acid irrigated and limed soils of a coniferous forest in Bavaria, in *Biogeochemistry of Global Change. Radiatively Active*

- Trace Gases*, edited by R. S. Oremland, pp. 245-260, Chapman and Hall, New York, 1993.
- Parton, W. J., A. R. Mosier, D. S. Ojima, D. W. Valentine, D. S. Schimel, K. Weiher, and A. E. Kulmala, Generalized model for N_2 and N_2O production from nitrification and denitrification, *Global Biogeochem. Cycles*, 10, 401-412, 1996.
- Parton, W. J., M. Hartman, D. S. Ojima, and D. S. Schimel, DAYCENT: Its land surface submodel: Description and testing, *Global Planet. Change*, 19, 35-48, 1998.
- Pastor, J., J. B. Aber, C. A. McClaugherty, and J. M. Melillo, Aboveground production and N and P cycling along a nitrogen mineralization gradient on Blackhawk Island, Wisconsin, *Ecology*, 65, 256-268, 1984.
- Persson, T., H. Lundkvist, A. Wiren, R. Hyvonen, and B. Wessen, Effects of acidification and liming on carbon and nitrogen mineralization and soil organisms in mor humus, *Water Air Soil Pollut.*, 45, 77-96, 1989.
- Potter, C. S., P. A. Matson, P. M. Vitousek, and E. A. Davidson, Process modeling of controls on nitrogen trace gas emissions from soils worldwide, *J. Geophys. Res.*, 101, 1361-1377, 1996.
- Prather, M., R. Derwent, D. Ehhalt, P. Fraser, E. Sanhueza, and X. Zhou, Other trace gases and atmospheric chemistry, in *Climate Change 1994: Radiative Forcing of Climate Changes and an Evaluation of the IPCC IS92 Emission Scenarios*, edited by J. Houghton, et al., pp. 77-126, Cambridge Univ. Press, New York, 1995.
- Riley, R. H., and P. M. Vitousek, Nutrient dynamics and nitrogen trace gas flux during ecosystem development in montane rain forest, *Ecology*, 76, 292-304, 1995.
- Schlesinger, W. H., *Biogeochemistry: An Analysis of Global Change*, 2nd ed. Academic, San Diego, Calif., 1995.
- Schmidt, J., W. Seiler, and R. Conrad, Emission of nitrous oxide from temperate forest soils into the atmosphere, *J. Atmos. Chem.*, 1, 95-115, 1988.
- Smith, K. A., H. Clayton, I. P. McTaggart, P. E. Thomsoh, J. R. M. Arah, and A. Scott, The measurement of nitrous oxide emissions from soil by using chambers, *Philosophical Transactions of the Royal Society of London, Series A*, 351, 327-338, 1995.
- Vitousek, P. M., J. R. Gosz, C. C. Grier, J. M. Melillo, W. A. Reiners, and R. I. Todd, A comparative analysis of potential nitrification and nitrate mobility in forest ecosystems, *Ecol. Monog.*, 52, 155-177, 1982.
- Wagner-Riddle, C., G. W. Thurtell, G. K. Kidd, E. G. Beauchamp, and R. Sweetman, Estimates of nitrous oxide emissions from agricultural fields over 28 months, *Can. J. Soil Sci.*, 77, 135-144, 1997.
- R. Brumme, Institute of Soil Science and Forest Nutrition, University of Goettingen, Buesgenweg 2, 37077 Goettingen, Germany. (rbrumme@gwdg.de.)
- K. Butterbach-Bahl and H. Papen, Biosphere/Atmosphere Exchange, Fraunhofer-Institut for Atmospharische Umweltforschung, Kreuzackbahnstrasse 19, Garmisch-Partenkirchen D-82467, Germany. (butterbach@ifu.fhg.de; papen@ifu.fhg.de.)
- K. E. Dobbie and K. A. Smith, Institute of Ecology and Resource Management (IERM), University of Edinburgh, School of Agriculture Building, West Mains Road, Edinburgh EH9 3JG, United Kingdom. (k.e.dobbie@ed.ac.uk; k.a.smith@ed.ac.uk.)
- P. M. Groffman, Institute of Ecosystem Studies, Box AB, Millbrook, New York 12545. (groffmanp@ecostudies.org.)
- A. R. Mosier, U. S. Department of Agriculture/Agricultural Research Service, P. O. Box E, Fort Collins, Colorado 80522. (amosier@lamar.colostate.edu.)
- J. D. Ojima and W. J. Parton, Natural Resource Ecology Lab, Colorado State University, Fort Collins, Colorado 80523. (dennis@nrel.colostate.edu; billp@nrel.colostate.edu.)
- C. Wagner-Riddle, Department of Land Resources Science, University of Guelph, Guelph, Ontario N1G 2W1, Canada. (criddle@lrs.uoguelph.ca.)

(Received September 17, 1999; revised March 1, 2000; accepted March 7, 2000.)