

## General model for N<sub>2</sub>O and N<sub>2</sub> gas emissions from soils due to denitrification

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**Abstract.** Observations of N gas loss from incubations of intact and disturbed soil cores

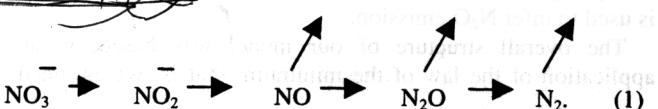
were used to model N<sub>2</sub>O and N<sub>2</sub> emissions from soil as a result of denitrification. The model assumes that denitrification rates are controlled by the availability in soil of NO<sub>3</sub> (*e*<sup>-</sup> acceptor), labile C compounds (*e*<sup>-</sup> donor), and O<sub>2</sub> (competing *e*<sup>-</sup> acceptor). Heterotrophic soil respiration is used as a proxy for labile C availability while O<sub>2</sub> availability is a function of soil physical properties that influence gas diffusivity, soil WFPS, and O<sub>2</sub> demand. The potential for O<sub>2</sub> demand, as indicated by respiration rates, to contribute to soil anoxia varies inversely with a soil gas diffusivity coefficient which is regulated by soil porosity and pore size distribution. Model inputs include soil heterotrophic respiration rate, texture, NO<sub>3</sub> concentration, and WFPS. The model selects the minimum of the NO<sub>3</sub> and CO<sub>2</sub> functions to establish a maximum potential denitrification rate for particular levels of *e*<sup>-</sup> acceptor and C substrate and accounts for limitation of O<sub>2</sub> availability to estimate daily N<sub>2</sub>+N<sub>2</sub>O flux rates. The ratio of soil NO<sub>3</sub> concentration to CO<sub>2</sub> emission was found to reliably ( $r^2=0.5$ ) model the ratio of N<sub>2</sub> to N<sub>2</sub>O gases emitted from the intact cores after accounting for differences in gas diffusivity among the soils. The output of the ratio function is combined with the estimate of total N gas flux rate to infer N<sub>2</sub>O emission. The model performed well when comparing observed and simulated values of N<sub>2</sub>O flux rates with the data used for model building ( $r^2=0.50$ ) and when comparing observed and simulated N<sub>2</sub>O+N<sub>2</sub> gas emission rates from irrigated field soils used for model testing ( $r^2=0.47$ ).

### 1. Introduction

Nitrous oxide (N<sub>2</sub>O) concentration in the atmosphere has increased from a preindustrial level of 275 ppb to a modern level of 314 ppb (National Oceanic and Atmospheric Administration (NOAA), [www.cmdl.noaa.gov/ftpdata.html](http://www.cmdl.noaa.gov/ftpdata.html)). N<sub>2</sub>O is long lived (~ 120 years), and its primary sink is the stratosphere, where it contributes to ozone depletion [Prather *et al.*, 1995]. Although the atmospheric concentration of N<sub>2</sub>O is ~1000-fold smaller than that of CO<sub>2</sub>, an N<sub>2</sub>O molecule has ~310 times the warming potential of a CO<sub>2</sub> molecule [Albritton *et al.*, 1995]. The atmospheric concentrations of well-mixed trace gases (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O) can be accurately measured, but estimates of the fluxes associated with various sources and sinks of these gases are highly uncertain [Matson and Harris, 1995]. Valid trace gas models can be linked with

ecosystem models to calculate global carbon and nitrogen budgets and reduce these uncertainties. Models also test hypothesis regarding the controls of biogeochemical processes such as denitrification and can be used to compare results of laboratory and field experiments.

The major sources of N<sub>2</sub>O are terrestrial soils, aquatic systems, combustion of fossil fuels and biomass, and industrial processes other than combustion [Bouwman, 1994]. Estimates of annual N<sub>2</sub>O emissions from soils range from 5 to 15 TgN and soils are thought to account for over half the total N<sub>2</sub>O inputs to the atmosphere [Prather *et al.*, 1995]. N<sub>2</sub>O is emitted from soils via two biogeochemical pathways, nitrification and denitrification. Nitrifying microbes oxidize ammonium (NH<sub>4</sub><sup>+</sup>) to nitrate (NO<sub>3</sub><sup>-</sup>), but some N is lost as N<sub>2</sub>O and nitric oxide (NO) during the intermediary steps [Firestone and Davidson, 1989]. Peak nitrification rates occur in aerobic soils of moderate water content [Linn and Doran, 1984]. In contrast, denitrification involves N oxides serving as electron acceptors during oxidation of labile carbon when O<sub>2</sub> is not available. Various genera of heterotrophic bacteria contribute to the NO<sub>3</sub> reduction sequence under anaerobic conditions [Paul and Clark, 1989]:



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Nitrification and denitrification are related in that the oxidized N species that are the by products of nitrification ( $\text{NO}$ ,  $\text{N}_2\text{O}$ , and  $\text{NO}_3$ ) may serve as  $e^-$  acceptors for denitrification. Although some  $\text{NO}$  from denitrification may be released from soil, the amounts tend to be very small because  $\text{NO}$  is highly reactive under conditions that facilitate denitrification [Conrad, 1996]. Consequently, our model simulates  $\text{N}_2\text{O}$  and  $\text{N}_2$  but not  $\text{NO}$  emissions from denitrification in soils.

The major controls on denitrification rates are soil  $\text{NO}_3$ ,  $\text{O}_2$ , and labile C levels [Firestone and Davidson, 1989]. As soils become more anoxic, a higher proportion of  $\text{N}_2\text{O}$  produced from denitrification is further reduced to  $\text{N}_2$  before leaving the soil [Davidson and Schimel, 1995]. In addition to water content, soil parameters related to texture (porosity, field capacity) affect  $\text{O}_2$  availability and N gas flux [Groffman, 1991].

Denitrification models simulate processes and use statistical methods to varying degrees. Highly mechanistic models may simulate microbial growth rates [Myrold and Tiedje, 1985] and solute and gas diffusion through the soil profile and through aggregates [Smith, 1980] or may include dynamics of microbial biomass and gas and solute transport [Grant and Pattey, 1999]. Such models usually require detailed data from laboratory experiments. Stochastic models have been developed to simulate the high variability of denitrification rates observed during incubation studies [Parkin and Robinson, 1989]. More general models correlate nitrogen gas flux with estimates of soil N cycling and water content [Potter et al., 1996a]. The presented model is a hybrid. It was developed with data from laboratory incubations, but it is intended to predict denitrification rates in field soils, and commonly measured and modeled field parameters are used as inputs. Also, best-fitting equations were empirically determined, but the equations are based on physical and biological principles. The model was designed to be linked with larger-scale nutrient cycling models (e.g., CENTURY [Parton et al., 1994, 1998]) so that estimates of soil N gas flux through natural and managed systems can be improved.

The denitrification submodel of NGAS, a nitrogen gas flux model developed by Parton et al. [1996], was modified to account for nitrogen gas flux data from incubations of intact soil cores. NGAS was designed to simulate  $\text{N}_2$  and  $\text{N}_2\text{O}$  emissions from soils owing to nitrification and denitrification. The model assumes that denitrification occurs in anoxic microsites when  $\text{NO}_3$  and C are available. Heterotrophic respiration is used to indicate labile C availability, while soil water-filled pore space (WFPS) and physical properties related to gas diffusivity are used to estimate the proportion of soil volume that is sufficiently anoxic for  $\text{NO}_3$  reduction to occur. Model inputs are soil  $\text{NO}_3$  concentration ( $\mu\text{gN gsoil}^{-1}$ ), heterotrophic  $\text{CO}_2$  respiration ( $\mu\text{gC gsoil}^{-1} \text{d}^{-1}$ ), water-filled pore space (WFPS = % relative saturation), bulk density ( $\text{g cm}^{-3}$ ), and field capacity ( $\text{cm}^3\text{H}_2\text{O cm}^{-3}\text{soil}^{-1}$ ). NGAS uses equations relating these inputs to denitrification and assumes that the law of the minimum applies. At daily intervals, total nitrogen gas flux is estimated, then an  $\text{N}_2/\text{N}_2\text{O}$  ratio function is used to infer  $\text{N}_2\text{O}$  emission.

The overall structure of our model was based on an application of the law of the minimum; that is, we assumed

that denitrification is controlled by the molecular species ( $\text{NO}_3$  or labile C) or environmental condition ( $\text{O}_2$  availability) that is most limiting. The law of the minimum also dictated how the data were analyzed. To derive appropriate equations to represent how denitrification responds to changes in one of the major input variables (soil  $\text{NO}_3$  concentration, respiration, or WFPS), data points that were subjected to strong limitation due to levels of the other inputs were eliminated. For example, soil may have sufficient labile C and  $\text{NO}_3$  available to facilitate high rates of denitrification but little denitrification will occur if soil water is below a threshold ranging from ~60 to 70% WFPS [Clayton et al., 1997]. Other researchers have also observed thresholds of soil nutrient levels and environmental conditions that strongly limit denitrification [Luo et al., 1999; de Klein and van Lotestijn, 1996].

The soils used to develop the original denitrification model [Weier et al., 1993] were sieved and repacked to specific bulk densities and treated with various levels of  $\text{NO}_3$ , glucose, and water. Gas flux measurements showed peak N gas emission rates from denitrification occurring at lower WFPS in the sandy soil than in the clay soil [Weier et al., 1993]. However, as an anaerobic process, denitrification is thought to occur at higher rates in poorly aerated fine-textured soils than in coarse-textured soils at an equivalent WFPS. To test the hypothesis that the anomalous interaction between soil water content and texture is related to the disturbance effects of sifting and packing and to generate data for model refinement, we performed incubations similar to Weier et al. [1993] of intact soil cores. The effect of WFPS on N gas flux from denitrification was found to significantly interact with  $\text{CO}_2$  emission in the intact fine-textured soils but not in the repacked fine-textured soils. The ratio of  $e^-$  acceptor ( $\text{NO}_3$ ) to  $\text{CO}_2$  emission (a proxy for  $e^-$  donor availability) was a reliable ( $r^2=0.50\%$ ) predictor of the  $\text{N}_2/\text{N}_2\text{O}$  ratio in the intact soils but not for the disturbed soils ( $r^2=0.18$ ). These results suggest that disturbance alters the response of denitrification rates to soil WFPS and the relative proportions of  $\text{N}_2\text{O}$  and  $\text{N}_2$  released from soil as a result of denitrification.

This paper is a product of the U.S. Trace Gas Network (TRAGNET) and a Trace Gas Fluxes Working Group sponsored by the U.S. Center for Ecological Analysis and Synthesis (NCEAS). TRAGNET was established in 1992 with the goals of documenting contemporary fluxes of  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2\text{O}$ , determining the major controls of trace gas flows, and improving our ability to predict future fluxes in response to ecosystem and climate change. The objectives of the NCEAS Working Group were to analyze the TRAGNET database and enhance our understanding of the controls and magnitudes of  $\text{CH}_4$  and  $\text{N}_2\text{O}$  fluxes in various natural and managed ecosystems by using models and by comparing fluxes at various scales. This paper contributes to this goal by quantifying the primary controls of denitrification, a major contributor to  $\text{N}_2\text{O}$  gas emissions.

## 2. Experiments

To quantify how soil  $\text{NO}_3$ , labile C, and water levels affect N gas emissions from denitrification, Weier et al. [1993] performed 5 day core incubations of four benchmark soils

**Table 1.** Properties of Soils Used for Model Development

| Soil                  | Classification   | PH  | BD        | % sand | % clay | FC<br>(% PS) |
|-----------------------|--|-----|-----------|--------|--------|--------------|
| <i>Repacked Soils</i> |  |     |           |        |        |              |
| Valentine sand        | typic mixed, mesic ustipsamment                                | 7.4 | 1.35      | 90     | 3      | -            |
| Hord silt loam        | cumulic fine-silty, mesic haplustoll                           | 7.3 | 1.15      | 34     | 20     | -            |
| Yolo silt loam        | typic fine silty, mixed xerorthent                             | 7.0 | 1.20      | 22     | 24     | -            |
| Sharpsburg            | typic fine, montmoril-lonitic, mesic argidoll                  | 6.5 | 1.10      | 3      | 34     | -            |
| <i>Intact Soils</i>   |  |     |           |        |        |              |
| HC                    | nunn clay loam (fine otmoril-lonitic) mesic Aridic Argustoll   | 7.6 | 0.9 - 1.6 | 26     | 47     | 86           |
| PC                    | renohill clay loam (fine montmorillonitic) Ustollie Haplargids | 7.0 | 1.1 - 1.4 | 34     | 36     | 76           |
| SCL                   | nunn loam (fine montmoril-lonitic) mesic aridic Argustoll      | 5.7 | 1.1 - 1.5 | 47     | 27     | 68           |
| SL                    | ascolon sandy loam (fine loamy mixed) mesic Argustoll          | 6.5 | 1.0 - 1.5 | 74     | 13     | 40           |

HC, horticultural clay; PC, pasture clay; SCL, sandy clay loam; and SL, sandy loam, repacked soil data from Weier *et al.* [1993].

(Table 1). Nitrate, glucose, and water levels were varied in a full factorial design (Table 2). Soil cores were sieved and repacked to specific bulk densities to obtain precise nutrient concentrations and water contents. To determine if the ratio of N<sub>2</sub>/N<sub>2</sub>O gases emitted from soil due to denitrification could be related to the independent variables, Weier *et al.* [1993] treated half of the cores in each treatment with acetylene to prevent N<sub>2</sub>O reduction. This allowed both N<sub>2</sub> and N<sub>2</sub>O emissions to be inferred for each treatment even though N<sub>2</sub>O was the only N gas species measured.

In 1996 we collected 120 soil core samples (inside diameter=5.7 cm, depth=10 cm) from each of four soils from northern Colorado (Table 1) for gas flux incubations. The horticultural clay (HC) soil was collected from the Colorado State University horticultural farm near Fort Collins and has a history of barley and wheat cultivation. The pasture clay (PC) soil was collected near Fort Collins and has a history of moderate grazing. The sandy clay loam (SCL) and sandy loam (SL) soils were collected from the Central Plains Experimental Range (CPER) and have a history of moderate

grazing. The samples were collected field moist, stored intact in PVC cylinders, and frozen until use for the incubations.

Prior to treatment for incubations, the cores were allowed to equilibrate to ambient temperature. Three cores from each of the four soils were analyzed by KCl extraction for initial NO<sub>3</sub> concentrations and water contents to establish initial WFPS levels. Sets of soil cores were treated by injecting multiple injections into both ends of each soil core, appropriate amounts of solution containing appropriate concentrations of dextrose, and <sup>15</sup>N labeled NO<sub>3</sub>, to achieve the nominal nutrient levels and water contents for the treatments listed in Table 3. Dextrose was added to stimulate microbial activity because most denitrifying bacteria are heterotrophs. NO<sub>3</sub> was labeled with <sup>15</sup>N (99% enrichment) so that N<sub>2</sub> from denitrification could be distinguished from ambient N<sub>2</sub>. Labeling of the added NO<sub>3</sub> also allowed N<sub>2</sub>O gas from denitrification to be distinguished from any N<sub>2</sub>O from nitrification that may have occurred during the incubations. The soil cores, each with a volume of 255 mL, were then placed in 473 mL jars, leaving a headspace volume of 218

**Table 2.** Experimental Treatments

| Soil                                       | Number of Cores | WFPS, %    | Added NO <sub>3</sub> , ugN gsoil <sup>1</sup> | Added Glucose, UgC gsoil <sup>1</sup> |
|--|-----------------|------------|--|---------------------------------------|
| <i>5-Day Incubations of Repacked Cores</i> |                 |            |  |                                       |
| Valentine sand                             | 27              | 60, 75, 90 | 0, 139, 277                                    | 0, 500, 1000                          |
| Hord silt loam                             | 27              | 60, 75, 90 | 0, 139, 277                                    | 0, 500, 1000                          |
| Yolo silt loam                             | 27              | 60, 75, 90 | 0, 139, 277                                    | 0, 500, 1000                          |
| Sharpsburg clay                            | 27              | 60, 75, 90 | 0, 139, 277                                    | 0, 500, 1000                          |
| <i>3-Day Incubations of Intact Cores</i>   |                 |            |  |                                       |
| HC   | 92              | 30 - 100   | 8 - 456  | 0 - 570                               |
| PC   | 124             | 49 - 100   | 9 - 46   | 0 - 123                               |
| SCL  | 88              | 43 - 100   | 8 - 42   | 0 - 107                               |
| SL   | 88              | 41 - 100   | 9 - 48   | 0 - 120                               |

Five-day incubations of repacked cores from Weier *et al.* [1993].

**Table 3.** Nominal Treatment Values of the Independent Variables for Intact Soil Core Incubations

| Soil | WFPS,% | $\text{NO}_3$ , ugN gsoil <sup>1</sup> | Dextrose, ugC gsoil <sup>1</sup> | Reps | Soil | WFPS,% | $\text{NO}_3$ , ugN gsoil <sup>1</sup> | Dextrose, ugC gsoil <sup>1</sup> | Reps |
|------|--------|--|----------------------------------|------|------|--------|--|----------------------------------|------|
| HC   | 40     | 10                                     | 0                                | 3    | PC   | 60     | 40                                     | 100                              | 4    |
| HC   | 40     | 10                                     | 50                               | 3    | PC   | 70     | 40                                     | 100                              | 5    |
| HC   | 40     | 40                                     | 0                                | 3    | PC   | 80     | 40                                     | 100                              | 5    |
| HC   | 40     | 40                                     | 50                               | 4    | PC   | 90     | 40                                     | 100                              | 5    |
| HC   | 50     | 10                                     | 0                                | 4    | PC   | 100    | 40                                     | 100                              | 3    |
| HC   | 50     | 10                                     | 50                               | 4    | SL   | 60     | 10                                     | 0                                | 4    |
| HC   | 50     | 40                                     | 0                                | 4    | SL   | 80     | 10                                     | 0                                | 4    |
| HC   | 50     | 40                                     | 50                               | 4    | SL   | 100    | 10                                     | 0                                | 4    |
| HC   | 50     | 100                                    | 0                                | 4    | SL   | 70     | 10                                     | 25                               | 4    |
| HC   | 50     | 100                                    | 500                              | 4    | SL   | 70     | 10                                     | 50                               | 4    |
| HC   | 50     | 400                                    | 0                                | 4    | SL   | 90     | 10                                     | 50                               | 4    |
| HC   | 50     | 400                                    | 500                              | 4    | SL   | 70     | 25                                     | 0                                | 4    |
| HC   | 70     | 10                                     | 0                                | 4    | SL   | 100    | 25                                     | 0                                | 4    |
| HC   | 70     | 10                                     | 50                               | 4    | SL   | 70     | 20                                     | 25                               | 4    |
| HC   | 70     | 40                                     | 0                                | 4    | SL   | 70     | 20                                     | 50                               | 4    |
| HC   | 70     | 40                                     | 50                               | 4    | SL   | 70     | 20                                     | 100                              | 4    |
| HC   | 70     | 100                                    | 0                                | 4    | SL   | 100    | 20                                     | 100                              | 4    |
| HC   | 70     | 100                                    | 500                              | 4    | SL   | 70     | 40                                     | 0                                | 4    |
| HC   | 70     | 400                                    | 0                                | 4    | SL   | 80     | 40                                     | 0                                | 4    |
| HC   | 70     | 400                                    | 500                              | 4    | SL   | 90     | 40                                     | 0                                | 4    |
| HC   | 90     | 10                                     | 0                                | 4    | SL   | 70     | 40                                     | 25                               | 4    |
| HC   | 90     | 10                                     | 50                               | 4    | SL   | 70     | 40                                     | 50                               | 4    |
| HC   | 90     | 40                                     | 0                                | 4    | SL   | 40     | 40                                     | 100                              | 4    |
| HC   | 90     | 40                                     | 50                               | 4    | SL   | 70     | 40                                     | 100                              | 4    |
| PC   | 50     | 10                                     | 0                                | 5    | SL   | 80     | 40                                     | 100                              | 4    |
| PC   | 70     | 10                                     | 0                                | 5    | SL   | 90     | 40                                     | 100                              | 4    |
| PC   | 90     | 10                                     | 0                                | 5    | SCL  | 70     | 10                                     | 0                                | 3    |
| PC   | 100    | 10                                     | 0                                | 5    | SCL  | 90     | 10                                     | 0                                | 5    |
| PC   | 70     | 10                                     | 25                               | 4    | SCL  | 100    | 10                                     | 0                                | 4    |
| PC   | 60     | 10                                     | 100                              | 4    | SCL  | 70     | 10                                     | 25                               | 4    |
| PC   | 70     | 10                                     | 100                              | 4    | SCL  | 80     | 10                                     | 50                               | 4    |
| PC   | 80     | 10                                     | 100                              | 4    | SCL  | 80     | 10                                     | 100                              | 4    |
| PC   | 100    | 10                                     | 100                              | 4    | SCL  | 100    | 10                                     | 100                              | 4    |
| PC   | 70     | 20                                     | 0                                | 4    | SCL  | 100    | 10                                     | 100                              | 4    |
| PC   | 60     | 20                                     | 0                                | 4    | SCL  | 70     | 20                                     | 0                                | 4    |
| PC   | 80     | 20                                     | 0                                | 4    | SCL  | 70     | 20                                     | 0                                | 4    |
| PC   | 100    | 20                                     | 0                                | 4    | SCL  | 100    | 20                                     | 25                               | 4    |
| PC   | 80     | 20                                     | 25                               | 4    | SCL  | 70     | 20                                     | 50                               | 4    |
| PC   | 80     | 20                                     | 50                               | 4    | SCL  | 70     | 20                                     | 100                              | 4    |
| PC   | 60     | 20                                     | 100                              | 4    | SCL  | 100    | 20                                     | 100                              | 4    |
| PC   | 70     | 20                                     | 100                              | 4    | SCL  | 90     | 40                                     | 0                                | 4    |
| PC   | 100    | 20                                     | 100                              | 4    | SCL  | 80     | 40                                     | 0                                | 4    |
| PC   | 50     | 40                                     | 0                                | 4    | SCL  | 100    | 40                                     | 0                                | 4    |
| PC   | 60     | 40                                     | 0                                | 4    | SCL  | 70     | 40                                     | 25                               | 4    |
| PC   | 80     | 40                                     | 0                                | 4    | SCL  | 70     | 40                                     | 50                               | 4    |
| PC   | 90     | 40                                     | 0                                | 4    | SCL  | 40     | 40                                     | 100                              | 4    |
| PC   | 100    | 40                                     | 0                                | 4    | SCL  | 60     | 40                                     | 100                              | 4    |
| PC   | 70     | 40                                     | 25                               | 4    | SCL  | 80     | 40                                     | 100                              | 4    |
| PC   | 80     | 40                                     | 50                               | 4    | SCL  | 100    | 40                                     | 100                              | 4    |

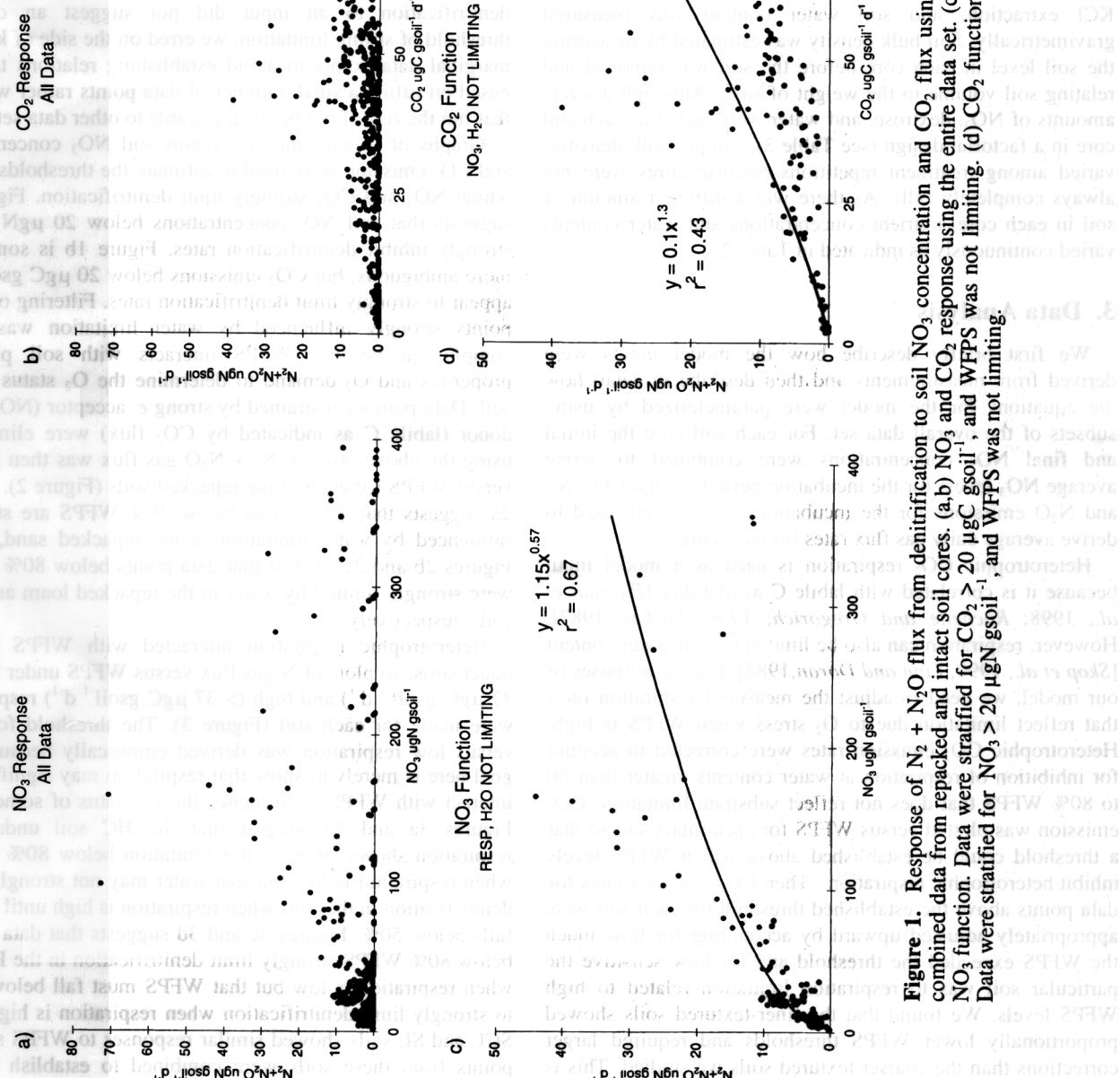
the soil solution. This is consistent with the observation that denitrification rates are often higher in soils with lower concentrations of nitrate (e.g.,  $\text{NO}_3^-$ ) and higher concentrations of oxygen ( $\text{O}_2$ ) [e.g.,  $\text{NO}_3^- + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{NO}_2^- + \text{HNO}_3 + \text{H}_2\text{O}$ ].

The relationship between soil  $\text{NO}_3^-$  concentration and  $\text{N}_2\text{O}$  flux was examined using a linear regression model. The results showed that there was a significant positive correlation between soil  $\text{NO}_3^-$  concentration and  $\text{N}_2\text{O}$  flux ( $R^2 = 0.17$ ,  $p < 0.05$ ). This indicates that as soil  $\text{NO}_3^-$  concentration increased, the rate of denitrification also increased. This is consistent with the observation that denitrification rates are often higher in soils with higher concentrations of nitrate (e.g.,  $\text{NO}_3^-$ ) and lower concentrations of oxygen ( $\text{O}_2$ ) [e.g.,  $\text{NO}_3^- + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{NO}_2^- + \text{HNO}_3 + \text{H}_2\text{O}$ ].

The relationship between soil  $\text{CO}_2$  concentration and  $\text{N}_2\text{O}$  flux was examined using a linear regression model. The results showed that there was a significant negative correlation between soil  $\text{CO}_2$  concentration and  $\text{N}_2\text{O}$  flux ( $R^2 = 0.17$ ,  $p < 0.05$ ). This indicates that as soil  $\text{CO}_2$  concentration increased, the rate of denitrification decreased. This is consistent with the observation that denitrification rates are often higher in soils with lower concentrations of carbon dioxide (e.g.,  $\text{CO}_2$ ) and higher concentrations of oxygen (e.g.,  $\text{O}_2$ ) [e.g.,  $\text{NO}_3^- + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{NO}_2^- + \text{HNO}_3 + \text{H}_2\text{O}$ ].

The relationship between soil  $\text{NO}_3^- + \text{N}_2\text{O}$  concentration and  $\text{N}_2\text{O}$  flux was examined using a linear regression model. The results showed that there was a significant positive correlation between soil  $\text{NO}_3^- + \text{N}_2\text{O}$  concentration and  $\text{N}_2\text{O}$  flux ( $R^2 = 0.17$ ,  $p < 0.05$ ). This indicates that as soil  $\text{NO}_3^- + \text{N}_2\text{O}$  concentration increased, the rate of denitrification also increased. This is consistent with the observation that denitrification rates are often higher in soils with higher concentrations of nitrate (e.g.,  $\text{NO}_3^-$ ) and lower concentrations of oxygen (e.g.,  $\text{O}_2$ ) [e.g.,  $\text{NO}_3^- + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{NO}_2^- + \text{HNO}_3 + \text{H}_2\text{O}$ ].

The relationship between soil  $\text{NO}_3^- + \text{N}_2\text{O}$  concentration and  $\text{CO}_2$  flux was examined using a linear regression model. The results showed that there was a significant positive correlation between soil  $\text{NO}_3^- + \text{N}_2\text{O}$  concentration and  $\text{CO}_2$  flux ( $R^2 = 0.17$ ,  $p < 0.05$ ).



**Figure 1.** Response of  $\text{N}_2 + \text{N}_2\text{O}$  flux from denitrification to soil  $\text{NO}_3^-$  concentration and  $\text{CO}_2$  flux using combined data from repacked and intact soil cores. (a,b)  $\text{NO}_3^-$  and  $\text{CO}_2$  response using the entire data set. (c) Data were stratified for  $\text{CO}_2 > 20 \mu\text{gC gsoil}^{-1}$ , and WFPS was not limiting. (d)  $\text{CO}_2$  function. Data were stratified for  $\text{NO}_3^- > 20 \mu\text{gN gsoil}^{-1}$ , and WFPS was not limiting.

mL. The jars were sealed with a lid that was fitted with a gas sampling septum and incubated at 25°C for 3 days. Forty milliliters of headspace gas were removed by syringe, and the gas samples were analyzed for N<sub>2</sub>O and CO<sub>2</sub> by gas chromatography and for N<sub>2</sub> by isotope ratio mass spectrometry within 6 hours of sampling. After sampling, jar lids were removed, and the jar atmosphere was flushed with air. The jars were then resealed and incubated for another 24 hours. Gas flux rates were calculated from changes in headspace concentration of the gases as described by Mosier and Klemmedsson [1994]. Both N<sub>2</sub>O and N<sub>2</sub> were measured so that the effects of the independent variables on the N<sub>2</sub>/N<sub>2</sub>O ratio could be investigated. At the end of the incubation period, soil NO<sub>3</sub> concentration in each core was measured by KCl extraction, and soil water content was measured gravimetrically. Soil bulk density was estimated by measuring the soil level in each core before the soil was removed and relating soil volume to the weight of soil. Although discrete amounts of NO<sub>3</sub>, dextrose, and water were added to each soil core in a factorial design (see Table 3), sample bulk densities varied among treatment repetitions because cores were not always completely full. As there was a different amount of soil in each core, nutrient concentrations and water contents varied continuously as indicated in Table 2.

### 3. Data Analysis

We first briefly describe how the model inputs were derived from measurements and then describe in detail how the equations for the model were parameterized by using subsets of the overall data set. For each soil core the initial and final NO<sub>3</sub> concentrations were combined to derive average NO<sub>3</sub> levels for the incubation periods. Total CO<sub>2</sub>, N<sub>2</sub>, and N<sub>2</sub>O emissions for the incubation periods were used to derive average daily gas flux rates for each core.

Heterotrophic CO<sub>2</sub> respiration is used as a model input because it is correlated with labile C availability [Pascual et al., 1998; Rochette and Gregorich, 1998; Parkin, 1987]. However, respiration can also be limited by soil water content [Skop et al., 1990; Linn and Doran, 1984]. For the purposes of our model, we need to adjust the measured respiration rates that reflect limitation due to O<sub>2</sub> stress when WFPS is high. Heterotrophic CO<sub>2</sub> emission rates were corrected to account for inhibition of respiration at water contents greater than 60 to 80% WFPS that does not reflect substrate limitation. CO<sub>2</sub> emission was plotted versus WFPS for each intact soil so that a threshold could be established above which WFPS levels inhibit heterotrophic respiration. Then CO<sub>2</sub> emission rates for data points above the established threshold for each soil were appropriately adjusted upward by accounting for how much the WFPS exceeded the threshold and for how sensitive the particular soil was to respiration limitation related to high WFPS levels. We found that the finer-textured soils showed proportionally lower WFPS thresholds and required larger corrections than the coarser textured soils we studied. This is not surprising because the finer-textured soils have lower gas diffusivity at a given WFPS than the coarser textured soils, and thus O<sub>2</sub> diffusion is reduced, and respiration is limited to a greater degree.

Soil volumetric water content at field capacity (FC) for the intact soils was inferred from estimates based on texture analysis [Saxton et al., 1986]. Although FC commonly refers to the water-holding capacity of field soils, we use it to

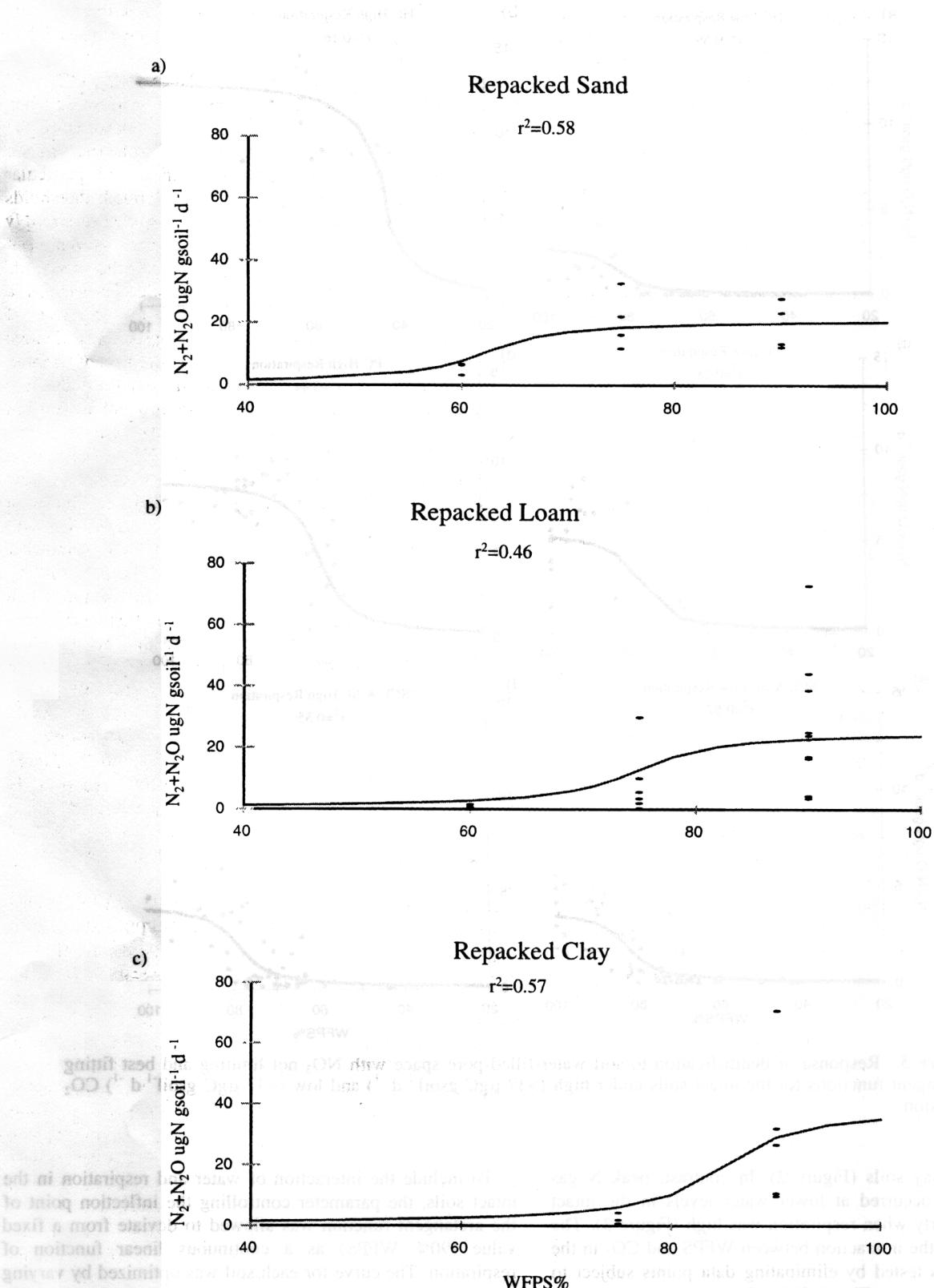
estimate the relative proportions of micropores and macropores and as a driver to calculate soil gas diffusivity in the nondisturbed cores.

The effects of the major input variables (NO<sub>3</sub>, CO<sub>2</sub>, and WFPS) on N<sub>2</sub>+N<sub>2</sub>O flux from denitrification were weak when the entire data set was used (Figures 1a-1b). Presumably, the effects of the other inputs confounded the relationships we wanted to establish between denitrification and particular inputs. To minimize this problem, we defined thresholds below which each of the major inputs is assumed to strongly limit denitrification. The thresholds selected to represent limitation due to a particular input reflect the trade off between selectivity of criteria and statistical power as a function of sample size. In cases where the response of denitrification to an input did not suggest an obvious threshold of strong limitation, we erred on the side of keeping marginal data points to avoid establishing relations that are based on fitting a small number of data points rather well but that run the risk of not being applicable to other data sets.

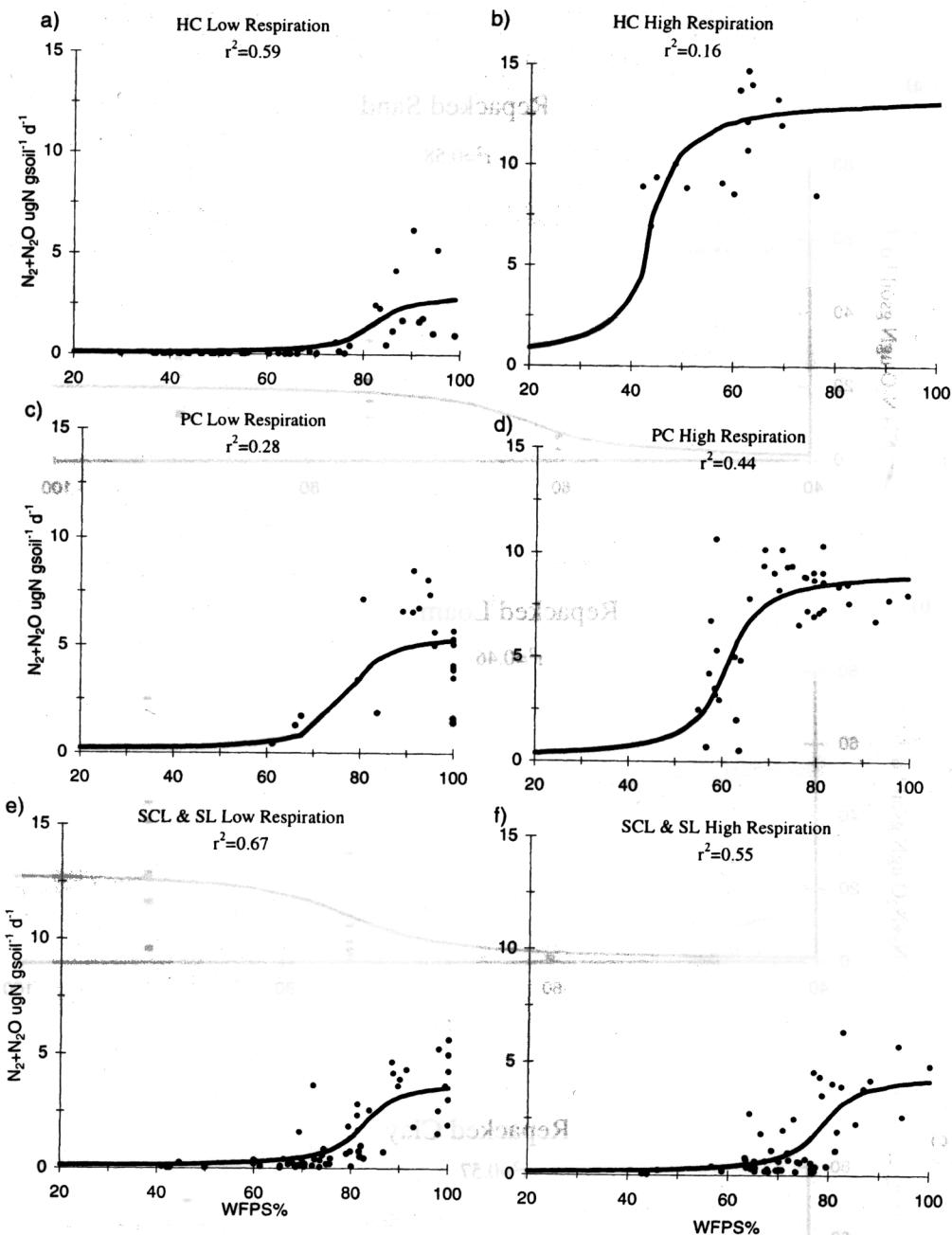
Graphs of N gas emission versus soil NO<sub>3</sub> concentration and CO<sub>2</sub> emission were used to estimate the thresholds below which NO<sub>3</sub> and CO<sub>2</sub> strongly limit denitrification. Figure 1a suggests that soil NO<sub>3</sub> concentrations below 20 µgN gsoil<sup>-1</sup> strongly inhibit denitrification rates. Figure 1b is somewhat more ambiguous, but CO<sub>2</sub> emissions below 20 µgC gsoil<sup>-1</sup> d<sup>-1</sup> appear to strongly limit denitrification rates. Filtering out data points strongly influenced by water limitation was more complicated because WFPS interacts with soil physical properties and O<sub>2</sub> demand to determine the O<sub>2</sub> status of the soil. Data points constrained by strong e<sup>-</sup> acceptor (NO<sub>3</sub>) or e<sup>-</sup> donor (labile C as indicated by CO<sub>2</sub> flux) were eliminated using the above criteria. N<sub>2</sub> + N<sub>2</sub>O gas flux was then plotted versus WFPS for each of the repacked soils (Figure 2). Figure 2a suggests that data points below 70% WFPS are strongly influenced by water limitation in the repacked sand, while Figures 2b and 2c suggest that data points below 80% WFPS were strongly limited by water in the repacked loam and clay soils, respectively.

Heterotrophic respiration interacted with WFPS in the intact soils, so plots of N gas flux versus WFPS under low (< 37 µgC gsoil<sup>-1</sup> d<sup>-1</sup>) and high (> 37 µgC gsoil<sup>-1</sup> d<sup>-1</sup>) respiration were made for each soil (Figure 3). The threshold for high versus low respiration was derived empirically because our goal here is merely to show that respiration may significantly interact with WFPS to influence the O<sub>2</sub> status of some soils. Figures 3a and 3b suggest that the HC soil under low respiration shows strong water limitation below 80% WFPS when respiration is low but that water may not strongly limit denitrification in this soil when respiration is high until WFPS falls below 50%. Figures 3c and 3d suggest that data points below 80% WFPS strongly limit denitrification in the PC soil when respiration is low but that WFPS must fall below 65% to strongly limit denitrification when respiration is high. The SCL and SL soils showed similar responses to WFPS so data points from these soils were combined to establish WFPS thresholds. Figures 3e and 3f suggest that WFPS values below 80% strongly limit denitrification in these soils, regardless of respiration rates. Comparisons of the overall data and stratified data show that the response of denitrification to each input variable was significantly stronger when the other variables were not limiting (Table 4, Figure 1).

To derive a function for the effect of soil NO<sub>3</sub> concentration on denitrification, data points that showed



**Figure 2.** Response of denitrification to soil water-filled pore space with  $\text{NO}_3$  and  $\text{CO}_2$  not limiting and best fitting arctangent functions for (a) coarse (b) medium, and (c) fine-textured soils from incubations of repacked soil cores [Weier et al., 1993].



**Figure 3.** Response of denitrification to soil water-filled pore space with  $\text{NO}_3$  not limiting and best fitting arctangent functions for the intact soils under high ( $>37 \mu\text{gC gsoil}^{-1} \text{d}^{-1}$ ) and low ( $<37 \mu\text{gC gsoil}^{-1} \text{d}^{-1}$ )  $\text{CO}_2$  emission.

compared to clay soils (Figure 2). In contrast, peak N gas emission rates occurred at lower water levels in the intact clays, particularly when respiration was high (Figure 3). The significance of the interaction between WFPS and  $\text{CO}_2$  in the intact soils was tested by eliminating data points subject to strong  $\text{NO}_3$  limitation. The WFPS/ $\text{CO}_2$  interaction was found to be highly significant ( $p<0.0001$ ), whereas the primary effect of water was insignificant ( $p=0.48$ ) in the clay soils (HC and PC). However, the WFPS/ $\text{CO}_2$  interaction was insignificant ( $p>0.1$ ), and the primary effect of water was highly significant ( $p<0.0001$ ) in the coarser textured soils (SCL and SL).

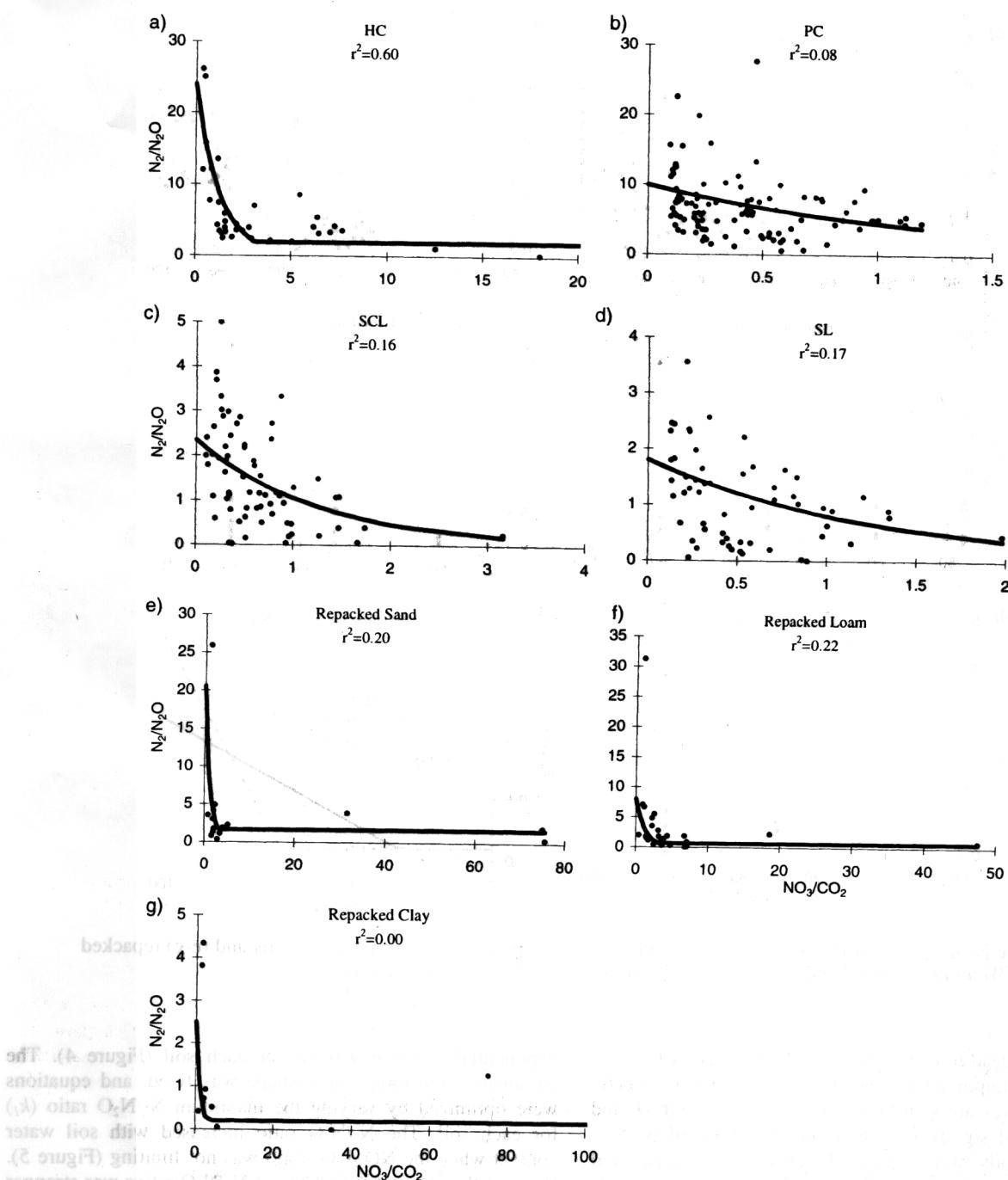
To include the interaction of water and respiration in the intact soils, the parameter controlling the inflection point of the arctangent function was allowed to deviate from a fixed value (90% WFPS) as a continuous linear function of respiration. The curve for each soil was optimized by varying a  $\text{CO}_2$  multiplier ( $M$ ) that represents the magnitude of the WFPS/ $\text{CO}_2$  interaction.

To infer  $\text{N}_2\text{O}$  flux given total N gas emission from denitrification, it is necessary to estimate the  $\text{N}_2/\text{N}_2\text{O}$  ratio. To develop the  $\text{N}_2/\text{N}_2\text{O}$  ratio function, data were stratified to filter out records with very low  $\text{N}_2\text{O}$  emission rates ( $< 0.1 \mu\text{gN gsoil}^{-1} \text{d}^{-1}$ ). This was done because  $\text{N}_2\text{O}$  emission rates

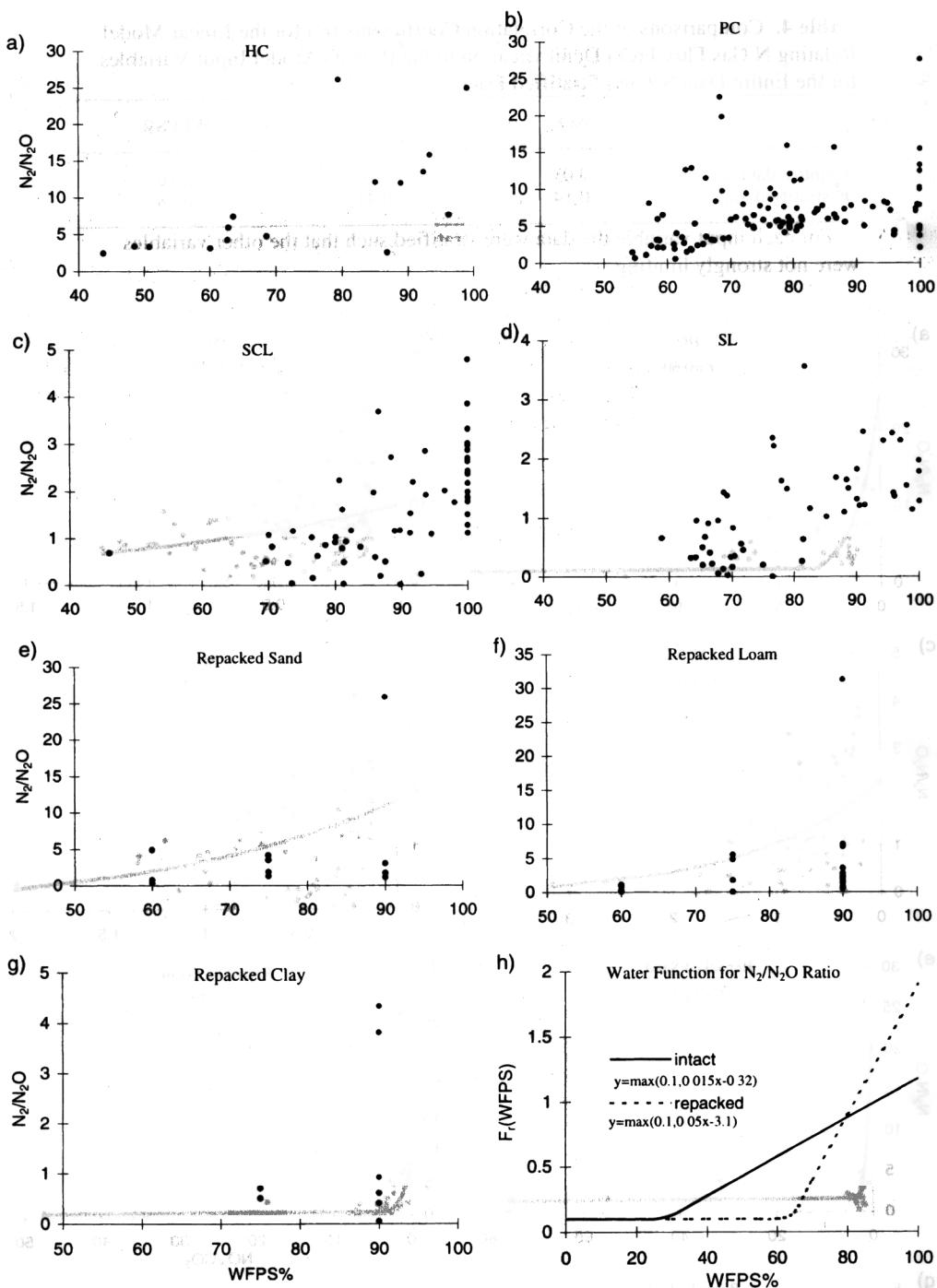
**Table 4.** Comparisons of the Correlation Coefficients ( $r^2$ ) for the Linear Model Relating N Gas Flux From Denitrification to the Primary Model Input Variables for the Entire Data Set and Stratified Data

|                       | NO <sub>3</sub> | CO <sub>2</sub> | WFPS% |
|-----------------------|-----------------|-----------------|-------|
| $r^2$ entire data set | 0.03            | 0.16            | 0.16  |
| $r^2$ stratified data | 0.54            | 0.41            | 0.38  |

For each input variable the data were stratified such that the other variables were not strongly limiting.



**Figure 4.** Response of the N<sub>2</sub>/N<sub>2</sub>O ratio to the ratio of NO<sub>3</sub> ( $\mu\text{gN gsoil}^{-1}$ ) to heterotrophic CO<sub>2</sub> respiration ( $\mu\text{gC gsoil}^{-1} \text{d}^{-1}$ ) and best fitting exponential functions for (a-d) intact soil cores and (e-g) repacked soil cores [Weier et al., 1993].



**Figure 5.** Response of the N<sub>2</sub>/N<sub>2</sub>O ratio to soil water-filled pore space in (a-d) intact soils and (e-g) repacked soils [Weier *et al.*, 1993] and (h) optimized disturbance specific water multipliers.

close to 0 can lead to extremely high (50-200) N<sub>2</sub>/N<sub>2</sub>O ratios and it is more important to predict the N<sub>2</sub>/N<sub>2</sub>O ratio correctly when N<sub>2</sub>O fluxes are significant. The ratio of NO<sub>3</sub>/CO<sub>2</sub> and soil WFPS had significant effects on the observed N<sub>2</sub>/N<sub>2</sub>O ratios. The soils were analyzed separately because soil properties also influence the N<sub>2</sub>/N<sub>2</sub>O ratio. All of the soils showed stable N<sub>2</sub>/N<sub>2</sub>O ratios when NO<sub>3</sub>/CO<sub>2</sub> was high and increasing N<sub>2</sub>/N<sub>2</sub>O ratios as NO<sub>3</sub>/CO<sub>2</sub> approached 0 so an

exponential function was fit for each soil (Figure 4). The parameter controlling curve shape was fixed, and equations were optimized by varying the maximum N<sub>2</sub>/N<sub>2</sub>O ratio ( $k_1$ ) for each soil. The N<sub>2</sub>/N<sub>2</sub>O ratio increased with soil water content when the NO<sub>3</sub>/CO<sub>2</sub> ratio was not limiting (Figure 5). Because the effect of NO<sub>3</sub>/CO<sub>2</sub> on N<sub>2</sub>/N<sub>2</sub>O ratios was stronger than the effect of WFPS ( $r^2=0.50$  versus 0.37), water was included in the model as a multiplier of the estimate from the

$\text{NO}_3/\text{CO}_2$  function. Optimizing the interaction resulted in linear best fitting water functions for the intact and repacked soils (Figure 5h).

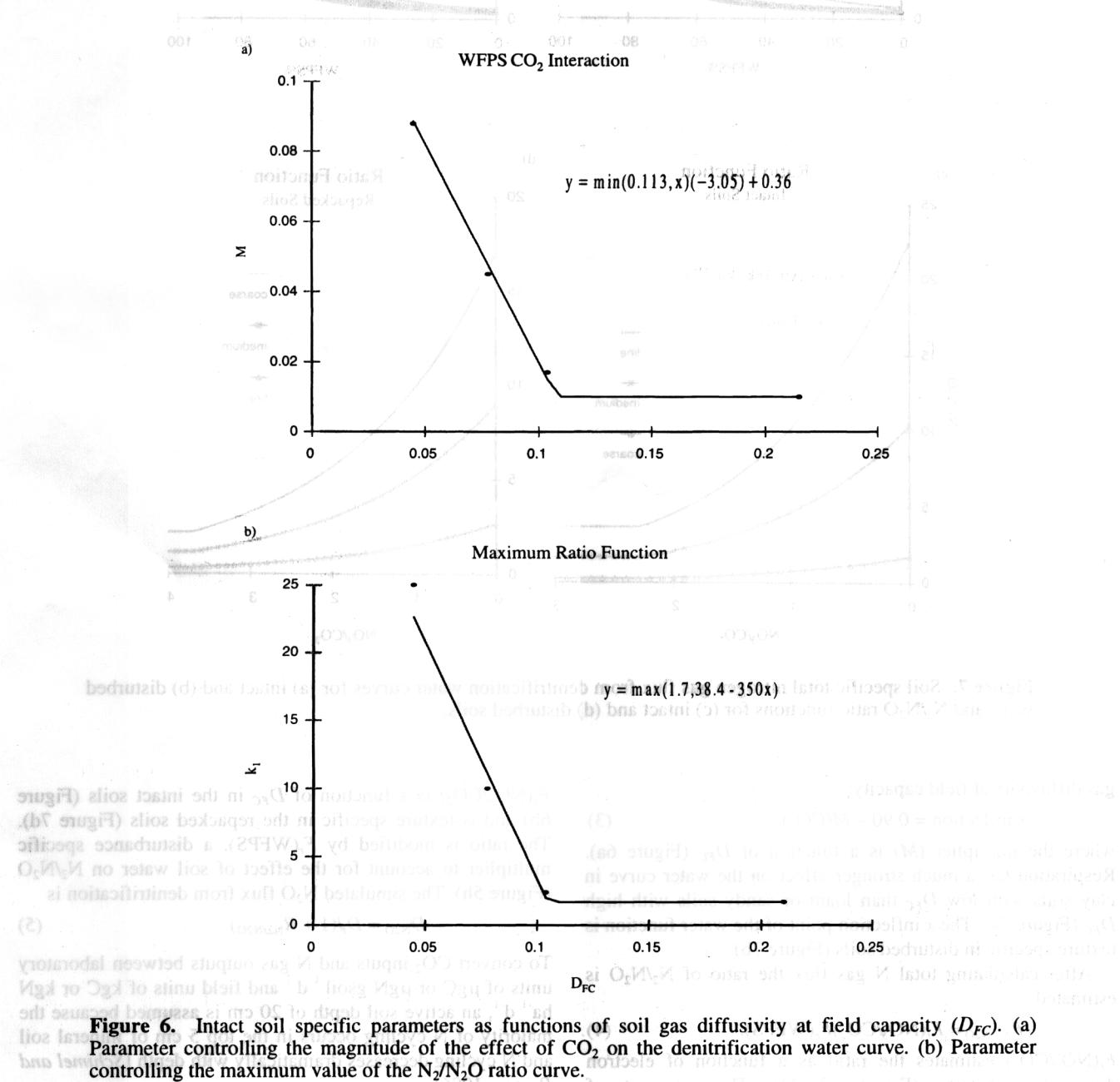
To quantify the differences in soil physical properties that influence the extent to which respiration may contribute to soil anoxia and the maximum  $\text{N}_2/\text{N}_2\text{O}$  ratio, a gas diffusivity coefficient ( $D_{FC}$ ) was calculated for each of the nondisturbed soils.  $D_{FC}$ , a relative index of gas diffusivity through soil assuming a water content of field capacity, was calculated as a function of porosity and FC using the method described by Potter et al., [1996b] for aggregated soils. The parameter controlling the potential for respiration to shift the  $x$  inflection point of the denitrification water curve to lower WFPS values varied inversely with  $D_{FC}$  (Figure 6a). The parameter controlling the maximum value of the  $\text{N}_2/\text{N}_2\text{O}$  ratio function was also correlated with  $D_{FC}$  (Figure 6b).

#### 4. The Model

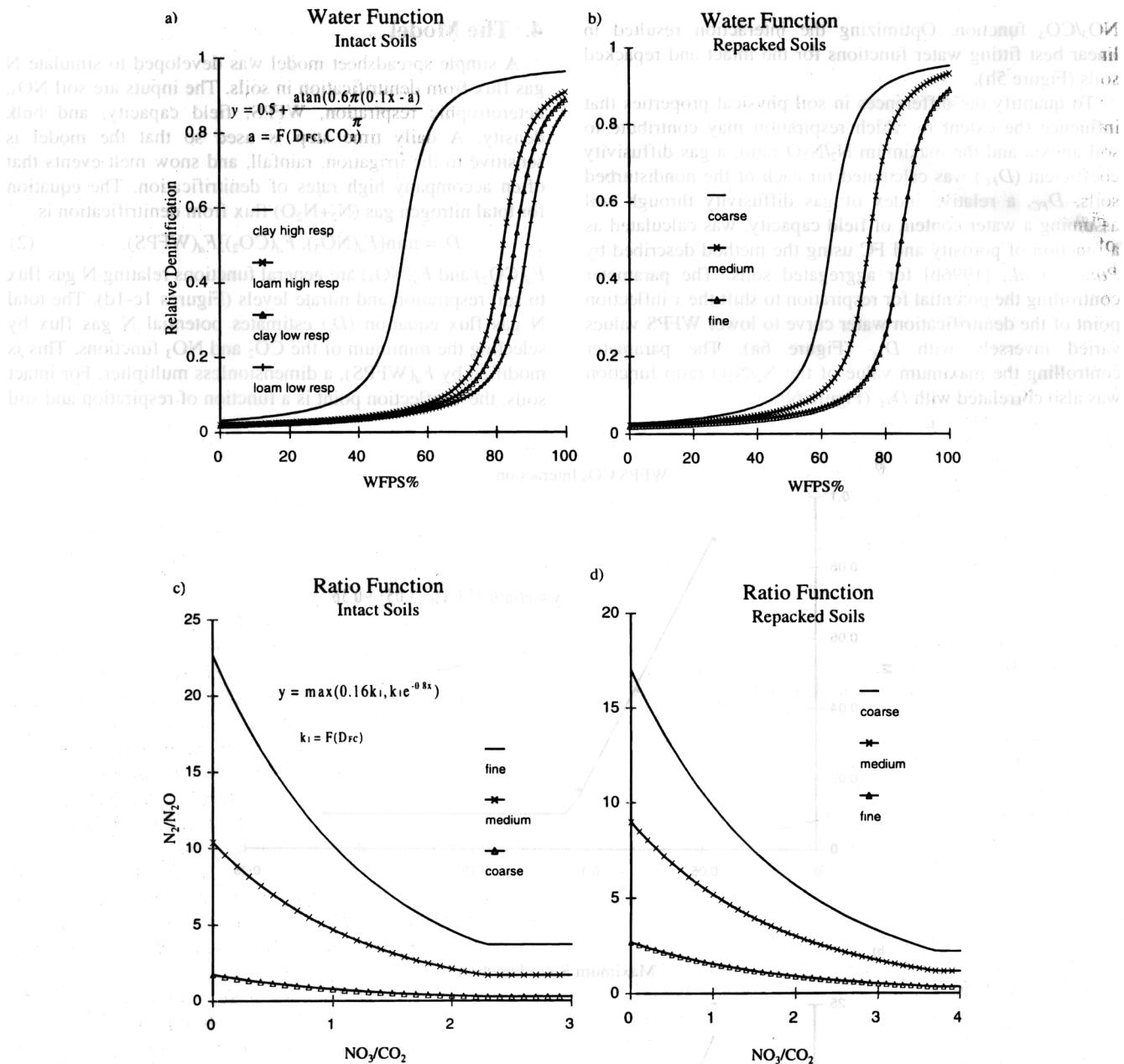
A simple spreadsheet model was developed to simulate N gas flux from denitrification in soils. The inputs are soil  $\text{NO}_3$ , heterotrophic respiration, WFPS, field capacity, and bulk density. A daily time step is used so that the model is sensitive to the irrigation, rainfall, and snow melt events that often accompany high rates of denitrification. The equation for total nitrogen gas ( $\text{N}_2+\text{N}_2\text{O}$ ) flux from denitrification is

$$D_t = \min[F_d(\text{NO}_3), F_d(\text{CO}_2)]F_d(\text{WFPS}). \quad (2)$$

$F_d(\text{CO}_2)$  and  $F_d(\text{NO}_3)$  are general functions relating N gas flux to soil respiration and nitrate levels (Figures 1c-1d). The total N gas flux equation ( $D_t$ ) estimates potential N gas flux by selecting the minimum of the  $\text{CO}_2$  and  $\text{NO}_3$  functions. This is modified by  $F_d(\text{WFPS})$ , a dimensionless multiplier. For intact soils, the  $x$  inflection point is a function of respiration and soil



**Figure 6.** Intact soil specific parameters as functions of soil gas diffusivity at field capacity ( $D_{FC}$ ). (a) Parameter controlling the magnitude of the effect of  $\text{CO}_2$  on the denitrification water curve. (b) Parameter controlling the maximum value of the  $\text{N}_2/\text{N}_2\text{O}$  ratio curve.



**Figure 7.** Soil specific total nitrogen gas flux from denitrification water curves for (a) intact and (b) disturbed soils, and N<sub>2</sub>/N<sub>2</sub>O ratio functions for (c) intact and (d) disturbed soils.

gas diffusivity at field capacity:

$$x \text{ inflection} = 0.90 - M(CO_2), \quad (3)$$

where the multiplier ( $M$ ) is a function of  $D_{FC}$  (Figure 6a). Respiration has a much stronger effect on the water curve in clay soils with low  $D_{FC}$  than loam or sandy soils with high  $D_{FC}$  (Figure 7a). The  $x$  inflection point of the water function is texture specific in disturbed soils (Figure 7b).

After calculating total N gas flux the ratio of N<sub>2</sub>/N<sub>2</sub>O is estimated:

$$R_{N2/N2O} = F_r(NO_3/CO_2)F_r(WFPS). \quad (4)$$

$F_r(NO_3/CO_2)$  estimates the ratio as a function of electron donor to substrate (Figures 7c-7d). The intercept of

$F_r(NO_3/CO_2)$  is a function of  $D_{FC}$  in the intact soils (Figure 6b) and is texture specific in the repacked soils (Figure 7d). The ratio is modified by  $F_r(WFPS)$ , a disturbance specific multiplier to account for the effect of soil water on N<sub>2</sub>/N<sub>2</sub>O (Figure 5h). The simulated N<sub>2</sub>O flux from denitrification is

$$D_{N2O} = D_r / (1 + R_{N2/N2O}). \quad (5)$$

To convert CO<sub>2</sub> inputs and N gas outputs between laboratory units of  $\mu\text{gC}$  or  $\mu\text{gN gsoil}^{-1} \text{d}^{-1}$  and field units of  $\text{kgC}$  or  $\text{kgN ha}^{-1} \text{d}^{-1}$ , an active soil depth of 20 cm is assumed because the majority of N cycling occurs in the top 5 cm of mineral soil and N cycling decreases dramatically with depth [Schimel and Parton, 1986].

## 5. Results and Discussion

The model simulated  $\text{N}_2\text{O} + \text{N}_2$  gas fluxes from denitrification rather well in the intact soils ( $r^2=0.74$ , mean error < 15%), but N gas flux rates in the repacked soils used for model development were underestimated (Figures 8a-8b). The  $\text{N}_2/\text{N}_2\text{O}$  ratio function also performed better in the intact ( $r^2=0.52$ ) soils compared to the disturbed ( $r^2=0.24$ ) soils (Figures 8c-8d). Estimates of  $\text{N}_2\text{O}$  emission include the error of the total N gas function and the error of the ratio function, but the model still achieved  $r^2$  values of 0.53 and 0.41 when comparing simulated and observed  $\text{N}_2\text{O}$  flux rates in the intact and disturbed soils, respectively (Figures 8e-8f). These results support the assumptions that denitrification is a function of labile C,  $\text{NO}_3^-$ , and water levels, and the process is controlled by the factor that is most limiting.

Field data from irrigated agricultural soils in Pakistan [Mahmood, 1997] were used for model validation. The model achieved an  $r^2$  of 0.47 with the independent data set, and the mean error was less than 5% in these soils (Figure 8g). The performance of the model with the field data suggests that labile C,  $\text{NO}_3^-$ , and water levels are significant controls of denitrification, but other factors not accounted for by the model, such as microbial biomass and species composition, may be important controls in field soils. Model error could also result from finer-scale variation in the input parameters than the model is designed to resolve or differences in experimental methodologies among the data sets.

Denitrification rates in the repacked soils were underestimated because these soils showed stronger responses to high labile C and  $\text{NO}_3^-$  additions than the intact soils, but the model is biased toward the intact cores by the sample sizes of the data sets. This bias in favor of the intact soils is justified because the intact cores more closely resemble field soils in that they were less disturbed and they received generally lower additions of C and  $\text{NO}_3^-$  than the repacked soils (Table 2).

The structure of our model and the parameterization of the equations assumed that the law of the minimum applies to denitrification. Evidence showing that the response of N gas flux from denitrification to the input variables was significantly stronger when the other inputs were not limiting (Table 4) supports this assumption. Dobbie *et al.* [1999] showed that WFPS had a significant effect on  $\text{N}_2\text{O}$  emissions from agricultural soils when data points strongly limited by soil  $\text{NO}_3^-$  concentration were removed. Similarly, Luo *et al.* [1999] observed that additions of carbon to a soil that was nitrate limited had little effect on denitrification rates but nitrate additions stimulated denitrification rates.

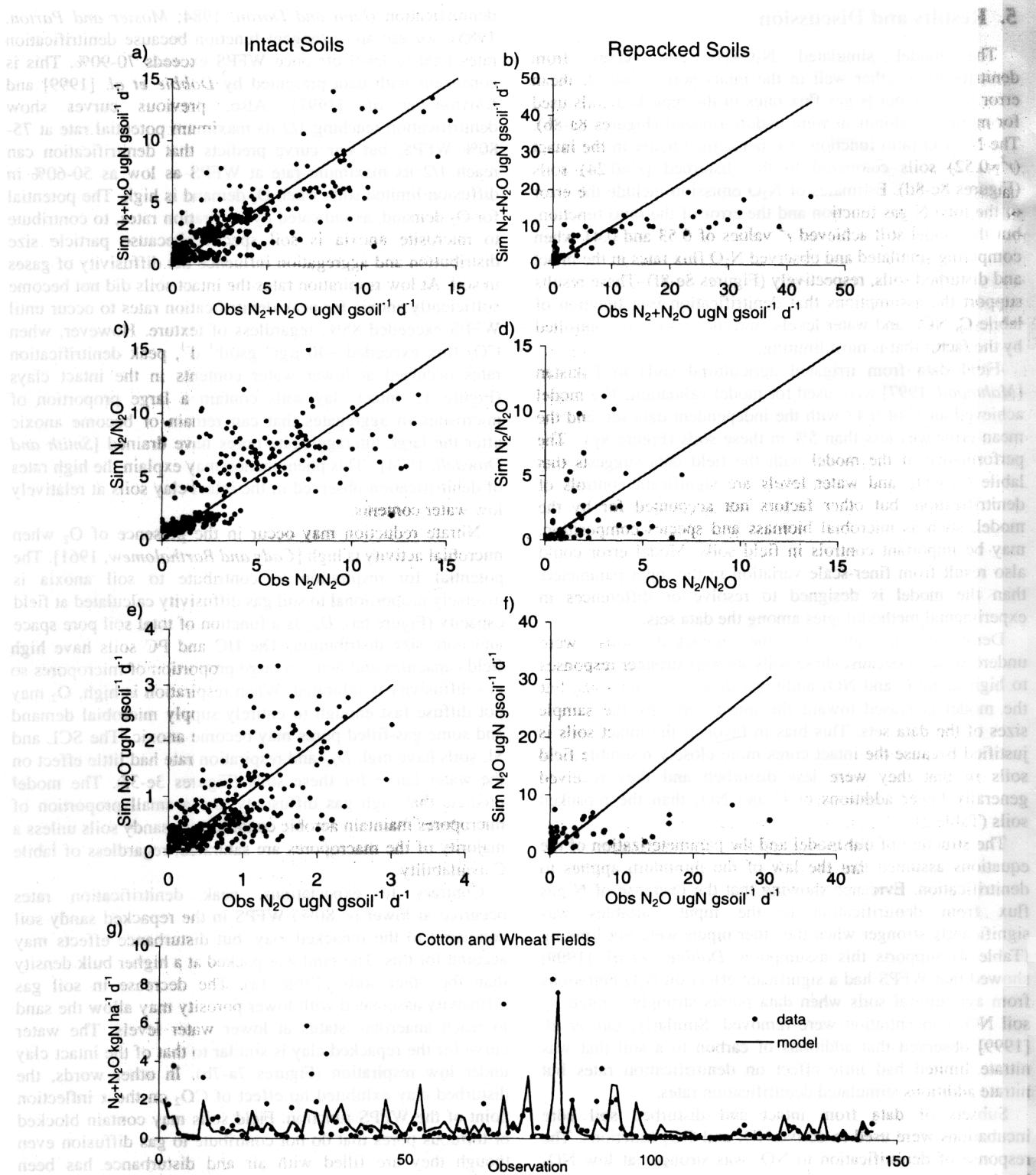
Subsets of data from intact and disturbed soil core incubations were used to derive  $\text{NO}_3^-$  and  $\text{CO}_2$  functions. The response of denitrification to  $\text{NO}_3^-$  was stronger at low  $\text{NO}_3^-$  levels, implying some degree of  $\text{NO}_3^-$  saturation exists (Figure 1a). Other researchers have also observed an N saturation effect [Sholefield and Hawkins, 1997]. The response of denitrification to respiration was fairly linear but increased slightly at high  $\text{CO}_2$  levels (Figure 1b).

The shape of our water curve is consistent with curves developed from different data sets, but our water function is different in two ways. Whereas previous models have used an exponential function to represent the effect of soil WFPS on

denitrification (Linn and Doran, 1984; Mosier and Parton, 1985), we use an arctangent function because denitrification rates tend to level off once WFPS exceeds 70–90%. This is consistent with data presented by Dobbie *et al.* [1999] and Clayton *et al.* [1997]. Also, previous curves show denitrification reaching 1/2 its maximum potential rate at 75–80% WFPS, but our curve predicts that denitrification can reach 1/2 its maximum rate at WFPS as low as 50–60% in diffusion limited soils when  $\text{O}_2$  demand is high. The potential for  $\text{O}_2$  demand, as indicated by respiration rates, to contribute to microsite anoxia is soil specific because particle size distribution and aggregation influence the diffusivity of gases in soil. At low respiration rates the intact soils did not become sufficiently anoxic for peak denitrification rates to occur until WFPS exceeded 85%, regardless of texture. However, when  $\text{CO}_2$  flux exceeded  $\sim 40 \mu\text{gC gsoil}^{-1} \text{ d}^{-1}$ , peak denitrification rates occurred at lower water contents in the intact clays (Figure 3). Intact clay soils contain a large proportion of microsites in aggregates that can remain or become anoxic after the large interaggregate pores have drained [Smith and Dowdell, 1974]. This phenomenon may explain the high rates of denitrification observed in the intact clay soils at relatively low water contents.

Nitrate reduction may occur in the presence of  $\text{O}_2$  when microbial activity is high [Cady and Bartholomew, 1961]. The potential for respiration to contribute to soil anoxia is inversely proportional to soil gas diffusivity calculated at field capacity (Figure 6a).  $D_{FC}$  is a function of total soil pore space and pore size distribution. The HC and PC soils have high field capacities and hence a large proportion of micropores so gas diffusivity is inhibited. When respiration is high,  $\text{O}_2$  may not diffuse fast enough to entirely supply microbial demand and some gas-filled pores may become anoxic. The SCL and SL soils have high  $D_{FC}$  and respiration rate had little effect on the water curve for these soils (Figures 3e-3f). The model predicts that high gas diffusivity and a small proportion of micropores maintain aerobic conditions in sandy soils unless a majority of the macropores are saturated, regardless of labile C availability.

Contrary to expectations, peak denitrification rates occurred at lower (< 80%) WFPS in the repacked sandy soil compared to the repacked clay, but disturbance effects may account for this. The sand was packed at a higher bulk density than the other soils (Table 1a). The decrease in soil gas diffusivity associated with lower porosity may allow the sand to reach anaerobic status at lower water levels. The water curve for the repacked clay is similar to that of the intact clay under low respiration (Figures 7a-7b). In other words, the disturbed clay exhibited no effect of  $\text{CO}_2$  on the  $x$  inflection point of the WFPS function. Field soils may contain blocked or tortuous pores that do not contribute to gas diffusion even though they are filled with air and disturbance has been shown to alter the proportion of these pores, particularly in fine textured soils [Gradwell, 1961]. This may explain why the repacked clay soil showed little evidence of anoxia at WFPS less than 80%. Also, Weier *et al.* [1993] passed soils through a 2 mm sieve. Sexstone *et al.* [1985] measured  $\text{O}_2$  levels in aggregates and found that aggregates of radius larger than 2 mm often harbored anaerobic micropores even though the bulk soil was aerobic. The repacked clays showed high denitrification rates only at high water contents because the



**Figure 8.** Simulated versus observed N gas flux rates and  $\text{N}_2/\text{N}_2\text{O}$  ratios with 1:1 lines: (a,b) Total N gas flux rates in the soils used for model building,  $r^2=0.74$  and 0.75, respectively. (c,d) The  $\text{N}_2/\text{N}_2\text{O}$  ratios in the soils used for model building,  $r^2=0.52$  and 0.24, respectively. (e,f)  $\text{N}_2\text{O}$  flux rates in the soils used for model building  $r^2=0.53$  and 0.41, respectively. (g) Total N gas flux rates from irrigated fields [Mahmood, 1997] and model simulations,  $r^2=0.47$ .

denitrification model. The model was able to predict the denitrification rates in the soils used for model building with a coefficient of determination ( $r^2$ ) of 0.74 and 0.75, respectively, for the total N gas flux rates (Figure 8a and b). The model was also able to predict the  $\text{N}_2/\text{N}_2\text{O}$  ratios in the soils used for model building with  $r^2$  values of 0.52 and 0.24, respectively (Figure 8c and d). The model was also able to predict the  $\text{N}_2\text{O}$  flux rates in the soils used for model building with  $r^2$  values of 0.53 and 0.41, respectively (Figure 8e and f).

The model was also able to predict the total N gas flux rates from irrigated fields with  $r^2=0.47$  (Figure 8g). The model was able to predict the denitrification rates in the soils used for model building with a coefficient of determination ( $r^2$ ) of 0.74 and 0.75, respectively, for the total N gas flux rates (Figure 8a and b). The model was also able to predict the  $\text{N}_2/\text{N}_2\text{O}$  ratios in the soils used for model building with  $r^2$  values of 0.52 and 0.24, respectively (Figure 8c and d). The model was also able to predict the  $\text{N}_2\text{O}$  flux rates in the soils used for model building with  $r^2$  values of 0.53 and 0.41, respectively (Figure 8e and f).

change in soil aggregate structure and pore size distribution induced by disturbance and sieving decreased the proportion of micropores that can become anoxic at moderate water contents.

The ratio of  $N_2/N_2O$  reflects the completeness of nitrogen reduction. It is a function of soil gas diffusivity and the relative proportion of electron acceptor to electron donor.  $N_2/N_2O$  increased with water content, supporting the assertion that as soils become more anoxic more  $N_2O$  will be further reduced to  $N_2$  before being emitted from the soil (Davidson and Schimel, 1995). The data also support the suggestion of Firestone and Davidson [1989] that  $N_2O$  is more likely to be further reduced when substrate (labile C) is in excess compared to the initial electron acceptor,  $NO_3^-$ , (Figure 4).

The magnitude of the  $N_2/N_2O$  ratio was highly variable among soils (Figures 6b, 7c, and 7d). Higher ratios in the intact clays than the intact loams can be explained by gas diffusivity. Lower gas diffusion rates in the intact clays contribute to anoxia and increase the residence time of  $N_2O$  in the soil, thus increasing the probability that  $N_2O$  from denitrification will be reduced to  $N_2$  in the soil. The repacked soils showed higher ratios in sand than clay, and the response of  $N_2/N_2O$  to the model inputs was more variable than in the intact soils, suggesting that disturbance strongly affects soil properties that influence the  $N_2/N_2O$  ratio.

## 6. Conclusions

The denitrification model shows that simple functions based on soil water, nitrate, respiration, and texture can be combined to model nitrogen gas emission from soil. The model performed well with the nondisturbed soils used for model building and testing. However, N gas flux rates were underestimated in the disturbed soils. The model needs to be tested with soils from diverse biomes.

Model results (Figure 8) and comparisons of stratified and unstratified data (Table 4) support the assumption that denitrification rates are controlled by the molecular species ( $NO_3^-$  or labile C) or environmental condition ( $O_2$  availability) that is most limiting. The data used for model building suggest that general  $NO_3^-$  and  $CO_2$  functions apply to diverse soils and that the water curve for N gas emission from denitrification can vary with respiration in nondisturbed soils. High  $CO_2$  respiration not only indicates high labile C availability but also contributes to microsite anoxia in unsaturated fine textured soils. Daily variations in soil  $NO_3^-$ ,  $CO_2$ , and WFPS may adequately explain daily variability of  $N_2/N_2O$  at a given site, but average ratios vary by up to a factor of 10 among soils. Thus a single function cannot be used to model the  $N_2/N_2O$  ratio.

Model parameters related to soil properties that affect gas diffusivity showed opposite trends in response to texture in the intact and repacked soils. The intact clays became anaerobic at lower WFPS and had higher  $N_2/N_2O$  ratios than the intact loams. Both observations suggest that the intact clays contain a higher volume of anoxic microsites at a given water content than the loams. However, the repacked clay required higher WFPS for denitrification and showed lower  $N_2/N_2O$  ratios than the repacked loamy or sandy soils.

Disturbance appears to enhance gas diffusivity in fine textured soils and to decrease aeration in coarse soils. Disturbance also decreases the ability of  $NO_3^-/CO_2$  and WFPS to predict the  $N_2/N_2O$  ratio (Figures 8c-8d). The data show that in nondisturbed soil cores the response of total N gas flux from denitrification and the  $N_2/N_2O$  ratio vary among soils and that differences in response may be explained by soil physical properties related to gas diffusivity. These results support the hypothesis that disturbance significantly alters the effect of soil water content on denitrification. Further work is needed to better predict how soil factors related to particle size distribution and aggregate structure interact with water and respiration to control  $O_2$  availability and potential N gas emission rates from denitrification.

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## References

- Albritton, D.L., R.G. Derwent, I.S.A. Isaksen, M. Lal, and D.J. Wuebles, Trace gas radiative forcing indices, in *Climate Change 1994*, edited by J.T. Houghton et al., pp. 205-231, Cambridge Univ. Press, New York, 1995.
- Bouwman, A.F., Estimated global source distribution of nitrous oxide, in *CH<sub>4</sub> and N<sub>2</sub>O: Global Emissions and Controls from Rice Fields and Other Agricultural and Industrial Sources*, edited by K. Minami, A. Mosier, and R. Sass, pp. 147-159, Yokendo, Tokyo, 1994.
- Cady, F.B., and W.V. Bartholomew, Influence of low  $PO_2$  on denitrification processes and products, *Soil Sci. Soc. Am. Proc.*, 25, 362-365, 1961.
- Clayton, H., I.P. McTaggart, J. Parker, L. Swan, and K.A. Smith, Nitrous oxide emissions from fertilized grassland: A 2-year study of the effects of N fertiliser form and environmental conditions, *Biol. Fertil. Soils*, 25, 252-260, 1997.
- Conrad, R., Soil microorganisms as controllers of atmospheric trace gases ( $H_2$ ,  $CO$ ,  $CH_4$ ,  $OCS$ ,  $N_2O$ , and  $NO$ ), *Microbiol. Rev.*, 60, 609-640, 1996.
- Davidson, E.A., and J.P. Schimel, Microbial processes of production and consumption of nitric oxide, nitrous oxide and methane, in *Biogenic Trace Gases: Measuring Emissions from Soil and Water*, edited by P.A. Matson and R.C. Harriss, pp. 327-357, Blackwell, Malden, Mass., 1995.
- De Klein, C.A., and R.S. Lotjetstijn, Denitrification in grassland soils in the Netherlands in relation to irrigation, N-application rate, soil water content and soil temperature, *Soil Biol. Biochem.*, 28, 231-237, 1996.
- 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**, 26,891-26,899, 1999.
- Firestone, M.K., and E.A. Davidson, Microbial basis of NO and N<sub>2</sub>O production and consumption in soils, in *Exchange of Trace Gases between Terrestrial Ecosystems and the Atmosphere*, edited by M.O. Andreae and D.S. Schimel, pp. 7-21, John Wiley, New York, 1989.
- Gradwell, M.W., A laboratory study of the diffusion of oxygen through pasture soils, *New Zealand J. Sci.*, **4**, 250-270, 1961.
- Grant, R.F., and E. Pattey, Mathematical modeling of nitrous oxide emissions from an agricultural field during spring thaw, *Global Biogeochem. Cycles*, **13**, 679-694, 1999.
- 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 Halomethane*, edited by J.E. Rogers and W.B. Whitman, pp. 201-217, Am. Soc. Microbiol., Washington, D.C., 1991.
- Linn, D.M., and J.W. Doran, Effect of water-filled pore space on carbon dioxide and nitrous oxide production in tilled and nontilled soils, *Soil Sci. Am. J.*, **48**, 1267-1272, 1984.
- Luo, J., R.W. Tillman, and P.R. Baul, Factors regulating denitrification in a soil under pasture, *Soil Biol. Biochem.*, **31**, 913-927, 1999.
- Mahmood, T., *Studies on the Denitrification Loss from Some Irrigated Soil-plant Systems*, Soil Biol. Div., Nucl. Inst. for Agric. and Biol., Faisalabad, Pakistan, 1997.
- Matson, P.A., and R.C. Harriss, Trace gas exchange in an ecosystem context: Multiple approaches to measurement and Analysis, in *Biogenic Trace Gases: Measuring Emissions From Soil and Water*, edited by P.A. Matson and R.C. Harriss, pp. 1-13, Blackwell Sci., Malden, Mass., 1995.
- Mosier, A.R., and L. Klemmedsson, Measuring denitrification in the field, in *Methods of Soil Analysis, Part 2, Microbiological and Biochemical Properties*, pp. 1047-1065, Soil Sci. Soc. of Am., Madison, Wisc., 1994.
- Mosier, A.R., and W.J. Parton, Denitrification in a shortgrass prairie: A modeling approach, in *Planetary Ecology*, edited by D.E. Caldwell, J.A. Brierly, and C.L. Brierly, pp. 441-452, Van Nostrand Rheinhold, New York, 1985.
- Myrold, D.D., and J.M. Tiedje, Diffusional constraints on denitrification in soils, *Soil Sci. Soc. Am. J.*, **49**, 651-657, 1985.
- Partin, T.B., Soil microsites as a source of denitrification variability, *Soil Sci. Soc. Am. J.*, **51**, 1194-1199, 1987.
- Partin, T.B., and J.A. Robinson, Stochastic models of soil denitrification, *Appl. Environ. Microbiol.*, **55**, 72-77, 1989.
- Parton, W.J., A.R. Mosier, and D.S. Schimel, Rates and pathways of nitrous oxide production in a shortgrass steppe, *Biogeochemistry*, **6**, 45-58, 1988.
- Parton, W.J., D.S. Ojima, C.V. Cole, and D.S. Schimel, A general model for soil organic matter dynamics: Sensitivity to litter chemistry, texture and management, in *Quantitative Modeling of Soil Forming Processes*, *Soil Sci. Soc. of Am. Spec. Pub.*, **39**, 147-167, 1994.
- Parton, W.J., A.R. Mosier, D.S. Ojima, D.W. Valentine, D.S. Schimel, K. Weier, and K.E. Kulmala, Generalized model for N<sub>2</sub> and N<sub>2</sub>O 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.
- Pascual, J.A., T. Hernandez, C. Garcia, and M. Ayuso, Carbon mineralization in a arid soil amended with organic wastes of varying degrees of stability, *Commun. Soil Sci. Plant Anal.*, **29**, 835-846, 1998.
- Paul, E.A., and F.E. Clark, *Soil Microbiology and Biochemistry*, Academic, San Diego, Calif., 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, 1996a.
- Potter, C.S., E.A. Davidson, and L.V. Verchot, Estimation of global biogeochemical controls and seasonality in soil methane consumption, *Chemosphere*, **32**, 2219-2245, 1996b.
- Prather, M.J., R. Derwent, D. Ehhalt, P. Fraser, E. Sanhueza, and X. Zhou, Other trace gases and atmospheric chemistry, in *Climate Change 1994*, edited by J.T. Houghton et al., pp. 73-126, Cambridge Univ. Press, New York, 1995.
- Rochette, P., and E.G. Gregorich, Dynamics of soil microbial biomass C, soluble organic C and CO<sub>2</sub> evolution after three years of manure application, *Can. J. Soil Sci.*, **78**, 283-290, 1998.
- SAS Institute Inc., *SAS/STAT User's Guide*, version 6, 4th ed., Cary, N.C., 1990.
- Saxton, K.E., W.J. Rawls, J.S. Romberger, and R. I. Papendick, Estimating generalized soil-water characteristics from texture, *Soil Sci. Soc. Am. J.*, **50**, 1031-1036, 1986.
- Schimel, D.S., and W.J. Parton, Microclimatic controls of nitrogen mineralization and nitrification in shortgrass steppe soils, *Plant Soil*, **93**, 347-357, 1986.
- Scholefield, D., and J.M. Hawkins, Determination of controls over denitrification using a flowing helium atmosphere system, in *Gaseous Nitrogen Emissions From Grasslands*, edited by S.C. Jarvis and B.F. Pain, pp. 27-35, CAB Int., Wallingford, Oxfordshire, U. K., 1997.
- Sexstone, A.J., N.P. Revsbech, T.B. Parkin, and J.M. Tiedje, Direct measurements of oxygen profiles and denitrification rates in soil aggregates, *Soil Sci. Soc. Am. J.*, **49**, 645-657, 1985.
- Skop, J., M.D. Jawson, and J.W. Doran, Steady state aerobic microbial activity as a function of soil water content, *Soil Sci. Soc. Am. J.*, **54**, 1619-1625, 1990.
- Smith, K.A., A model of the extent of anaerobic zones in aggregated soils, and its potential application to estimates of denitrification, *J. Soil Sci.*, **31**, 263-277, 1980.
- Smith, K.A., and R.J. Dowdell, Field studies of the soil atmosphere, I, Relationship between ethylene, oxygen, soil moisture content and temperature, *J. Soil Sci.*, **25**, 219-230, 1974.
- Weier, K.L., J.W. Doran, and D.T. Walks, Denitrification and the dinitrogen/nitrous oxide ratio as affected by soil water, available carbon, and nitrate, *Soil Sci. Soc. Am. J.*, **57**, 66-72, 1993.

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