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Soil-air exchange of nitric oxide: An overview of processes, environmental factors, and modeling studies

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Abstract. Terrestrial ecosystems with their main elements soil and plants may act, in principle, as both source and sink for atmospheric nitric oxide (NO). The net exchange between ecosystems and the atmosphere, however, is globally dominated by biogenic emissions of NO from soils. Consequently the soil–air exchange of NO is the focus of the following overview. Particular emphasis is placed on the major processes that are responsible for NO production in soils (nitrification, denitrification) and their regulation by environmental factors (nitrogen availability, soil water content, soil temperature, ambient NO concentration). It is shown that interactions of these factors are a major reason for the broad range that exists in published data on NO fluxes. This variability makes it difficult to predict the magnitude of NO fluxes on relevant spatial and temporal scales. To overcome the problem various generalization procedures for scaling up in space and time have been developed, and the potential and limitations of the different approaches is discussed.

Introduction

The exchange of nitrogen containing gases between the atmosphere and terrestrial surfaces has been an important issue in agricultural and soil research for a long time. Prominent examples are the fixation of elementary nitrogen by plants and microorganisms, denitrification loss of soil nitrogen in form of molecular nitrogen (N_2) and nitrous oxide (N_2O), and the emission of gaseous ammonia (NH_3) from fertilized soils. Unlike these processes, the exchange of NO between biosphere and atmosphere contributes only a minor part to the nitrogen budget of most terrestrial ecosystems. However, emissions from the soil–plant system are of enormous concern for the NO concentration in the troposphere.

Being a highly reactive trace gas, NO plays a crucial role in tropospheric chemistry (Crutzen 1979; Logan et al. 1981; Warneck 1988). For the fast chemical interconversion with nitrogen dioxide (NO_2), which typically occurs within seconds to minutes, both species are commonly referred to as the single quantity NO_x ($NO_x = NO + NO_2$). Nitrogen oxides (NO_x) are precursors in the photochemical formation of gaseous nitric acid (HNO_3) and thus contribute to the acidity of clouds and precipitation (Liu et al. 1987; Warneck 1988). Probably even more severe is the impact of NO_x on the oxidative capacity of the troposphere. NO_x mediates the production and destruction of ozone and influences the formation of the hydroxyl radical (OH), which in turn regulates the lifetime of numerous compounds in the atmosphere (Liu et al. 1987; Crutzen 1979; Chameides et al. 1992). Sources and sinks of NO_x as well as their temporal and spatial distribution are therefore an essential prerequisite to understand and model atmospheric chemistry.

On a global scale, the primary source of tropospheric NO is anthropogenic emissions from combustion-related processes in industry and transport. According to present knowledge, however, NO is produced in soils nearly ubiquitously; and therefore soil emissions constitute a continuous (but not constant) background flux of NO to the atmosphere. Despite considerable uncertainties, there is substantial evidence that soil emissions make a significant contribution to the tropospheric NO burden even in industrialized regions of the globe (Williams et al. 1992a; Valente & Thornton 1993; Hall et al. 1996; Davidson & Kingerlee 1997). If current and future efforts to reduce NO_x emissions from vehicles and fossil fuel burning are successful, the importance of biogenic emissions will grow considerably in the near future.

Processes involved in NO exchange

Several biotic and abiotic processes in soils and plants are mechanisms for production and consumption of NO (Galbally 1989; Conrad 1996). Although uptake of NO by plants is a common phenomenon, this process is rarely considered to be a major pathway for the NO surface exchange, as the characteristic deposition velocity is extremely low (well below 10^{-3} m/s, c.f. Johansson 1989; Meixner 1994). Abiotic formation of NO in soils may only be of importance in acid soils with high NO_2^- concentrations. However, on a global scale, it seems to be likewise unimportant (Galbally 1989). Among microbial processes, all those that involve oxidative or reductive transformation of N through the +2 valence state carry the potential to act as source or sink for NO (Conrad 1990). Nevertheless it is widely accepted that microbial nitrification and denitrification constitute the principal processes (Williams et al. 1992b).

Denitrification is the respiratory reduction of NO_3^- or NO_2^- to gaseous forms of nitrogen (N_2O, N_2) and is therefore commonly associated with the loss of soil N to the atmosphere. The faculty to reduce NO_X, when O_2 becomes limiting, enables denitrifying bacteria to grow in anaerobic environments. As a broad diversity of bacterial groups is capable of this metabolic pathway (Focht & Verstraete 1977; Conrad 1996), denitrifiers are present almost ubiquitously in natural and cultivated soils. It is generally accepted that NO constitutes an obligatory intermediate in the denitrification sequence (Payne 1981). This involvement as an intermediate provides good reason to assume that denitrifiers can not only produce but also consume NO. Such a dual behaviour has indeed been demonstrated in studies on bacteria cultures and soil samples (Firestone et al. 1979; Johansson & Galbally 1984; Remde & Conrad 1991a). The rate of NO production (or consumption) not only depends on the overall denitrification rate but is also strongly affected by parameters that influence the proportion of NO relative to the terminal products N_2O and N_2 (Firestone & Davidson 1989). Hence, environmental control of NO production and consumption by denitrification is accomplished through complex interactions of numerous relevant parameters (Robertson 1989). Oxygen availability, for instance, which strongly controls the total turnover rate of the denitrification process as well as the relative rate of NO production, is in turn regulated by various other factors (e.g., soil water content, soil texture, activity of plant roots, and microbial respiration).

Nitrification is commonly defined as the biological oxidation of NH_4^+ to NO_3^- with NO_2^- as an intermediate. Although the capacity for nitrification is restricted to a few genera of strictly aerobic, mainly chemoautotrophic bacteria, this process is of major importance for the nitrogen cycling in most cultivated and many natural soils. The exact sequence of the nitrification pathway is still not clarified. Some evidence exists that NO is a (presumably enzyme bound) intermediate in the oxidation step from NH_2OH to NO_2^- (Hooper & Terry 1979). Other research groups (Remde & Conrad 1990), however, suggested that NO formation during nitrification results from the reduction of NO_2^- ('nitrifier denitrification'), a mechanism also shown to be effective for the production of N_2O by nitrifying bacteria (Poth & Focht 1985). The use of NO_2^- as an electron acceptor enables nitrifiers to sustain oxidation of NH_4^+ even at a low partial pressure of O_2. Overall nitrification rates, however, will increase in well-aerated soils, provided that the soil is not very acidic ($pH > 4 – 5$). If these requirements are met, the nitrification rate is predominantly controlled by the availability of NH_4^+ (Robertson 1989).

Despite the fact that most field studies have not explicitly separated nitrification from denitrification contributions to the observed NO flux, there is some evidence that only a small fraction of the nitrogen oxidized by nitrifier activity may be released in form of NO. In well-aerated soils the yield of NO is typically 1% to 4% of the NH_4^+ oxidized (Johansson & Galbally 1984, Hutchinson & Brams 1992). Further studies, however, have demonstrated that the relative NO yield can range from 0.1% (Davidson et al. 1993) to 10% (Shepherd et al. 1991; Veldkamp & Keller 1997).

To assess the importance of nitrification versus denitrification for the exchange of NO is a difficult task. By application of specific inhibitors or by examination of the response to NH_4^+ and NO_3^- based fertilizers, several investigators were able to identify the dominating process for an individual soil; but the results are contradictory. Prevalence of the nitrification pathway has been observed in many soils, including those from temperate (Vos et al. 1994; Skiba et al. 1993; Yamulki et al. 1995) as well as subtropical (Hutchinson & Brams 1992) and tropical (Davidson et al. 1993) ecosystems. On the other hand, production of NO was attributed to denitrifier activity in the experiments of Remde et al. (1993), Cardenas et al. (1993), and Sanhueza et al. (1990). Some indication that the dominant mechanism for the formation of NO is influenced by the soil pH can be taken from a laboratory study of Remde and Conrad (1991b). They found that nitrifiers were responsible for NO production in an alkaline soil (pH 7.8), whereas denitrification was the dominant process in an acidic soil (pH 4.7). In many field situations, however, it is difficult to ascribe NO production to one of both processes as nitrifying and denitrifying bacteria might act simultaneously owing to microsite heterogenities within the same soil profile.

Up to now little attention has been given to the role of transport processes for soil–air exchange of NO. Commonly, molecular diffusion is considered the driving mechanism for gas transport in soil pores (Galbally & Johansson 1989). Laboratory studies, however, have pointed out that convective transfer may not be ignored (Kimball & Lemon 1971; Rudolph et al. 1996; Rudolph & Conrad 1996). Since the NO diffusion coefficient in water is about five orders of magnitude lower than in air, it is obvious that water-filled pores create a strong barrier to the emission of NO into the atmosphere (Galbally 1989). Soil water content also has a strong impact on the diffusion of O_2 into the soil and consequently on the microbial activity (Skopp et al. 1990). Thus a high soil water content favours denitrifier activity but restricts NO transport. This creates a situation where the probability of NO being reconsumed by denitrifiers is largely enhanced; and as a consequence, emission of NO to the atmosphere might deviate significantly from the production of NO in soil. Illustrative for this fact is a laboratory experiment of Skiba et al. (1997), who reported that only 13% of the amount of NO produced in an anaerobic soil was actually emitted from the soil surface.

Unlike many other trace gases, the exchange between vegetation and the atmosphere was considered of little quantitative importance for NO. Emission of NO from plants or plant material has been observed only in a few studies (Klepper 1979; Dean & Harper 1986). Thus the general capability of plants to emit NO remains rather uncertain (Johansson 1989). However, biogenic NO emission from a variety of plant species was recently observed by Wildt et al. (1996) during laboratory fumigation experiments at low ambient NO concentrations. For the plants studied so far (sunflower, sugar cane, soybean, corn, rape, spruce, spinach, and tobacco), the global biogenic NO emission from vegetation was estimated to be approx. 10% of that from soil. However, the nature of plant physiological processes that emit NO is almost unkown. Plants primarily act as a sink for atmospheric NO, but the uptake rate is limited by low solubility of NO (Hill 1971). Deposition velocities observed for different plant species and under various physiological conditions are generally less than 10^{-3} m s^{-1} (Hanson & Lindberg 1991; Meixner 1994). This implies that only at exceptionally high ambient NO concentration, direct deposition to plants might constitute a significant removal mechanism for atmospheric NO.

Major relevance of plant uptake for the net flux of NO, however, results from the close coupling with the surface exchange of NO_2. Once emitted, NO is oxidized rapidly to NO_2 owing to the presence of ozone (O_3), and the uptake by plants is much more effective for NO_2 than for NO (Hill 1971; Hanson & Lindberg 1991; Meixner 1994). Therefore, NO, once emitted from vegetated soils and converted to NO_2 within the plant canopy, may be immediately deposited to the vegetation elements (in form of NO_2), which will then reduce the amount of NO that escapes from the plant canopy. This internal cycling of nitrogen oxides likely occurs in all ecosystems (especially in forests), but adequate quantitative information is currently lacking. On the basis of rough simplifications, Yienger and Levy II (1995; see also Jacob & Bakwin 1991) have computed a global “canopy reduction factor” of about 50%. The “zero-order” approach of Yienger and Levy II, however, should be taken as an indication that in-canopy processes affect the NO exchange substantially rather than as an accurate assessment of this effect. Better understanding and quantification of canopy reduction remains an imperative task for future research on NO (and NO_2) exchange (see, e.g., Andreae et al. 2000).

Factors influencing the NO exchange

Basically, the complete set of environmental factors that regulate the underlying processes of NO production and consumption in soils has the potential to affect the exchange of NO between soil and the atmosphere significantly. The following section will be restricted to the discussion of some factors, which have been encountered as major controllers over a wide range of field situations. Further chemical (soil pH, concentration and composition of organic C), physical (soil texture), and biological (plant cover) variables as well as some cultivation practices (tillage, burning) might be of importance under more specific environmental conditions (see Galbally 1989; Williams et al. 1992b; Meixner 1994). When reviewing the influence of soil properties on the NO exchange, it has to be noted that there is no common agreement with regard to the appropriate depth of soil where these properties should be determined. It is obvious that the correlation of soil parameters with observed NO fluxes depends on the vertical distribution of the relevant processes within the soil. Although the zone of maximum NO productivity most likely varies from soil to soil, there is broad evidence that the primary production zone is located within a very shallow layer at the soil surface (Johansson & Granat 1984, Ludwig et al. 1992; Rudolph et al. 1996; Rudolph & Conrad 1996; Yang & Meixner 1997). Remde et al. (1993), for instance, reported that observed NO fluxes in a marsh soil could be explained by model calculations when applying an effective depth as low as 0.002 m. Soil parameters are typically measured at depths of 0.01 to 0.1 m and thus may, in many cases, only inaccurately reflect the conditions in the shallow topsoil layer, where NO production (or consumption) predominantly occurs.

Nitrogen availability and fertilization

It has been shown by a large number of studies that availability of soil N has a strong impact on NO emission rates. Special interest in this respect is given to the pool size of soil NH_4^+ and NO_3^-, since these compounds serve as substrate for nitrifying and denitrifying bacteria. By examining results from various natural and cultivated sites in North America, Williams and Fehsenfeld (1991) were able to show that differences in the NO_3^- content of the soils accounted for much of the variance in the observed NO emission levels. Similar trends were reported for several European ecosystems (Skiba et al. 1994; Ludwig & Meixner 1994). Therefore it has been argued that the NO_3^- concentration in soils might serve as a useful variable to predict NO emission rates across ecosystems. Further studies, however, have indicated that the relation between soil nitrogen and NO flux is more complex than it appears from these results. Examples for a stronger correlation of NO fluxes with soil NH_4^+ than with NO_3^- concentrations have been reported by Levine et al. (1988), Anderson et al. (1988), Hutchinson et al. (1993), and Steudler (pers. communication). It is also worth to note that typically the spatial variability of NO fluxes within a given field site is not explained by the spatial distribution of soil NO_3^- concentrations (Williams & Fehsenfeld 1991; Ludwig 1994).

One has to keep in mind that observed relationships between NO emission and soil NO_3^- or soil NH_4^+ do not allow to draw simple conclusions concerning the mechanisms of NO production. As pointed out by Williams et al. (1992b), the correlation of soil NO_3^- concentrations and NO emission rates may reflect (a) the status of NO_3^- as a substrate for denitrification, (b) the status of NO_3^- as a product of nitrification, or (c) the fact that accumulation of NO_3^- tends to be a general characteristic of soils that exhibit leaky N cycles. Overall, pool size of available nitrogen may be seen as a rough indicator for the nitrogen turnover rate in a soil, and thus it also provides some indication for microbial production of NO. There are, however, exceptions to this general picture as it is the case in soils where high and rapid turnover rates of nitrifying or denitrifying bacteria lead to low soil NO_3^- or soil NH_4^+ pool sizes (Davidson et al. 1990).

Given the importance of nitrogen availability, it appears logical that application of nitrogen fertilizers has a profound effect on the exchange of NO. A strong stimulation of NO emission by addition of N fertilizers has been noticed at uncultivated (Johansson 1984; Johansson et al. 1988; Cardenas et al. 1993) as well as agricultural sites (Slemr & Seiler 1984; Johansson & Granat 1984; Anderson & Levine 1987; Shepherd et al. 1991; Ludwig 1994; Vermoesen et al. 1996; McKenny & Drury 1997). Likewise, input of N by the excreta of grazing animals results in enhanced levels of the NO release over grasslands (Galbally & Roy 1978; Colbourn et al. 1987; Thornton et al. 1998). Independent of fertilizer type and land use, a rapid increase of NO emissions following fertilizer addition is commonly observed. Maximum emission rates are typically approached within one or two days after fertilization. The period until emission rates drop to prefertilization levels can last for a few days or for several weeks. As an example for various other studies (see e.g. Davidson & Kingerlee 1997 and references therein) we like to present results of a long-term study over a mid-European wheat field (Ludwig 1994) where two variants of fertilizer treatment (88 kg N ha^{-1} yr^{-1} and 218 kg N ha^{-1} yr^{-1}) have been compared. Results are shown in Figure 1. Emissions from those plots that received the higher dose of N fertilizer were elevated throughout the study period. In both variants the seasonal pattern of NO emission was related to the timing of fertilizer applications. The strongest stimulation of NO emissions resulted from fertilizer addition (40 kg N ha^{-1}) to recently harvested plots. As can be seen in Figure 1, emissions from plots

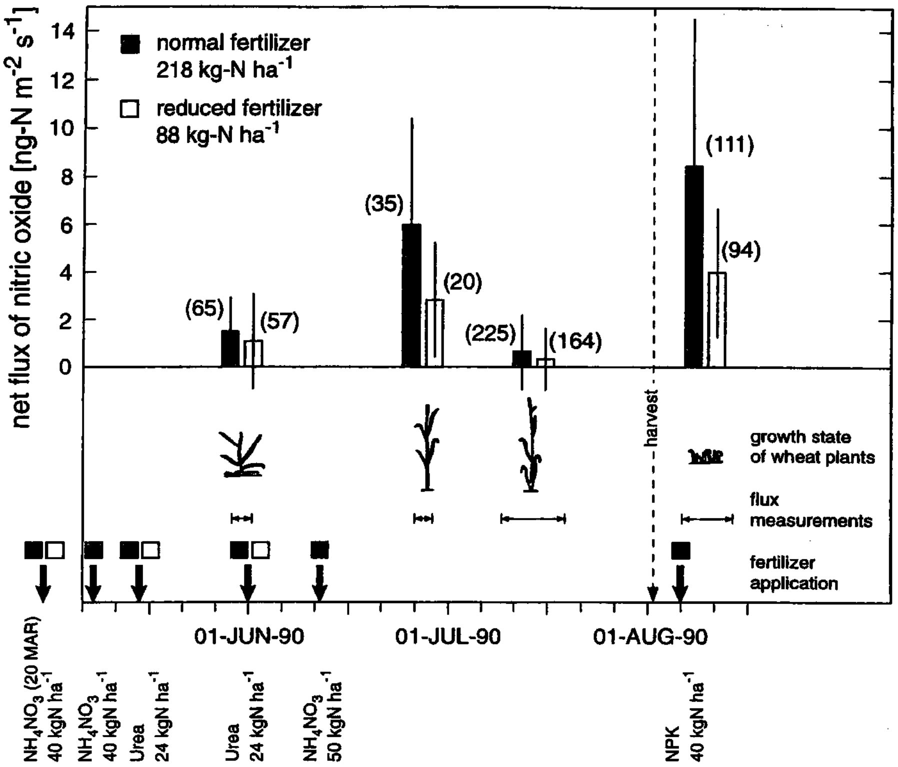

Figure 1. Seasonal variation of the NO net flux over a wheatfield (Manndorf, Germany, 48.708 °N, 12.956 °E). Two variants of N fertilization were applied on the experimental plots. The mean (± standard deviation) over all samples (sample number in parentheses) from the respective plots is given for each of four experimental periods. Date and amount of fertilizer applications for both variants is indicated at the bottom of the figure (adapted from Ludwig 1994).

that received no fertilizer at this time were also stimulated, most likely by the harvest process. Similar observations were made by Hutchinson and Brams (1992), who suggested that the enhancement in post-harvest emissions results from temperature effects and from microbial transformation of N contained in plant residues.

Although numerous observations of elevated NO emissions subsequent to N fertilizer application have been reported in literature, quantification of this effect is difficult. Substantial variability in data prevails with respect to the absolute as well as the relative increase of NO emissions immediately after fertilizer addition. Similar scatter can be found with respect to the persistence of enhanced emissions. For comparison purposes, the fraction of applied nitrogen lost as NO is commonly employed. Reported values of fractional losses range from 0.003% (Slemr & Seiler 1991) to 11% (Shepherd et al. 1991), but a consistent explanation for this wide divergence is lacking. In contrast to earlier assumptions (Galbally 1989), recent compilations of published data (Skiba et al. 1997; Veldkamp & Keller 1997) suggest that a systematic relation between the fractional N loss and fertilizer composition (NO_3^- salts, NH_4^+ salts, urea, manure) does not exist. Veldkamp and Keller (1997) also note that some discrepancy in previous results may be due to the fact that in several studies the fertilizer was applied in dissolved form and thus an additional effect due to water could not be excluded. Their careful evaluation of previous measurements covering a variety of fertilizer types, soils, and climatic conditions indicated that on average approximately 0.5% of applied fertilizer N is released as NO. This is in reasonable agreement with the mean value (0.3%) postulated by Skiba et al. (1997) but a factor of five lower than that derived by Yienger and Levy II (1995). There is clearly a need for systematic investigations to verify and to narrow the range of the fraction of N fertilizer lost as NO.

Soil moisture content

It is widely accepted that soil moisture strongly affects the exchange of NO. Much of our current knowledge originates from observations of the change in NO emission rates subsequent to precipitation events or artificial watering of the soil. Addition of water to very dry soils typically produces a distinct increase of NO emission rates (‘pulsing’). It seems, that ‘pulsing’ is caused by a ‘dormant’ water-stressed microbial community wich consequently ‘wakes up’, feeding of accumulated nutrients as soon as the first water drops are supplied to the desiccated soil. As noted by Williams et al. (1992b), even a slight rain event (0.3 mm) might enhance the emission of NO by a factor of almost 10 compared to that under dry conditions. Commonly the increase of NO fluxes becomes visible within a few minutes after wetting and persists during one or more days. This is of special importance in tropical and subtropical climates with distinct dry and wet seasons, where large bursts of NO emissions at the onset of the rainy season have been encountered (Davidson et al. 1991; Harris et al. 1996; Meixner et al. 1997; Otter et al. 1999). The magnitude of this stimulatory effect appears to be related to the length of the dry period preceeding a rain or irrigation event. This was indicated by experiments of Slemr and Seiler (1984), Johansson et al. (1988), and Davidson et al. (1991), who reported that the irrigation-induced stimulation of NO emissions decreased with repeated watering of the soil. It seems that NO emissions decreasing with successive irrigation are due to the gradual depletion of soil nutrients which have once accumulated prior to the very first watering of the very dry soils. However, several early investigators had to conclude that no clear relation between soil moisture and NO fluxes could be established in their experiments (Johansson & Granat 1984; Williams et al. 1988). Valente and Thornton (1993) reported a tenfold increase of NO emissions subsequent to a light rainfall event, whereas heavy rains eliminated nearly all emissions from the same corn field. Further experiments (Anderson & Levine 1987; Shepherd et al. 1991; Yamulki et al. 1995) have demonstrated that NO emissions decrease drastically as soil moisture approaches saturation.

Clearly, the differences in the observations reflect the multiple regulatory role of soil moisture for many processes controlling the NO exchange. Soil moisture governs whether nitrification or denitrification is the dominant process in a given soil and strongly influences the corresponding turnover as well as the ratio of NO production over NO consumption rates. Soil moisture, moreover, controls transport of microbial substrates and products of microbes. Thus a simple relationship between the flux of NO and the soil water content may not be expected (Davidson 1991, 1993). Surprisingly few workers (Cardenas et al. 1993; Yang & Meixner 1997; Otter et al. 1999) have yet attempted a systematic investigation of this relationship by examining NO emissions as a function of either gravimetric water content or water-filled pore space (WFPS). WFPS defined as the ratio of volumetric soil water content to total porosity of the soil, has proved to be the most suitable among various expressions of soil water, since WFPS is largely comparable among soils of different texture. The uniformity in their findings is, however, encouraging. An example is shown in Figure 2. It indicates the existence of an optimum soil water content (approx. 20% WFPS) for emission of NO and a strong decrease of NO emissions towards extreme values of WFPS (i.e., $<$10% and $>$40% WFPS for very dry and fully saturated soils, respectively). Such a response function is in accordance with conceptual considerations that propose a substrate diffusion limit at low and a gas diffusion limit at high moisture contents (Skopp et al. 1990). An optimal WFPS of about 60% has been noticed for a number of microbial processes (Linn & Doran 1984). The results of Potter et al. (1996), Yang and Meixner (1997), and Otter et al. (1999), however, suggest that this value is not applicable with respect to the emission of NO (Figure 2).

Soil temperature

Considering the dominance of soil microbial processes for the production of NO, one has to expect an influence of soil temperature on NO emission rates. Indeed, the bulk of existing studies (Slemr & Seiler 1984; Johansson & Granat 1984; Johansson 1984; Anderson & Levine 1987; Williams et al. 1987; Williams et al. 1988; Williams & Fehsenfeld 1991; Ludwig et al. 1992; Valente & Thornton 1993; Yang & Meixner 1997; Otter et al. 1999) has

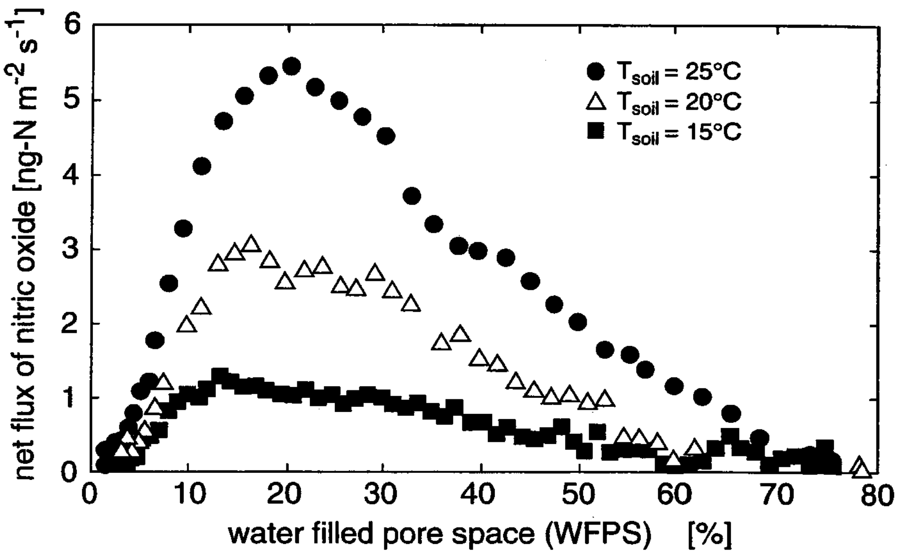

Figure 2. Dependence of NO emission on water-filled pore space (after Yang and Meixner 1997). Data were obtained by a standardized laboratory technique (Yang et al. 1999) applied to soil samples taken from an unfertilized groundnut plot (Grassland Research Station Marondera/Zimbabwe, 18.183 °S, 31.467 °E).

shown an increase of NO emissions with increasing soil temperatures. The response of NO emission to increasing soil temperature, also demonstrated in Figure 2, may serve as an obvious example. This response is due to the fact that rates of enzymatic processes generally increase exponentially with temperature, as long as other factors (substrate or moisture availability) are not limiting. Then, a typical diurnal variation of the NO release, correlating closely with soil temperature, is observed. A convincing example obtained from laboratory studies on actual field samples is presented in Figure 3. Based on observations at eight North American locations Williams and Fehsenfeld (1991) concluded that in a temperature range between 15 °C and 35 °C the response of NO emission to soil temperature will be rather uniform, regardless of the absolute magnitude of emitted NO. According to their finding, each 10 °C rise in temperature results in an approximate doubling of NO emission rates. The general applicability of this relationship, however, appears to be questionable, as can be seen from the results of Valente and Thornton (1993), who reported on average an almost five-fold increase of NO emissions per each 10 °C temperature rise with a considerable variation between different ecosystems. Further restrictions to the validity of an uniform temperature response concern the emission of NO at more extreme temperatures and soil water contents. Some experiments have shown that the relationship between

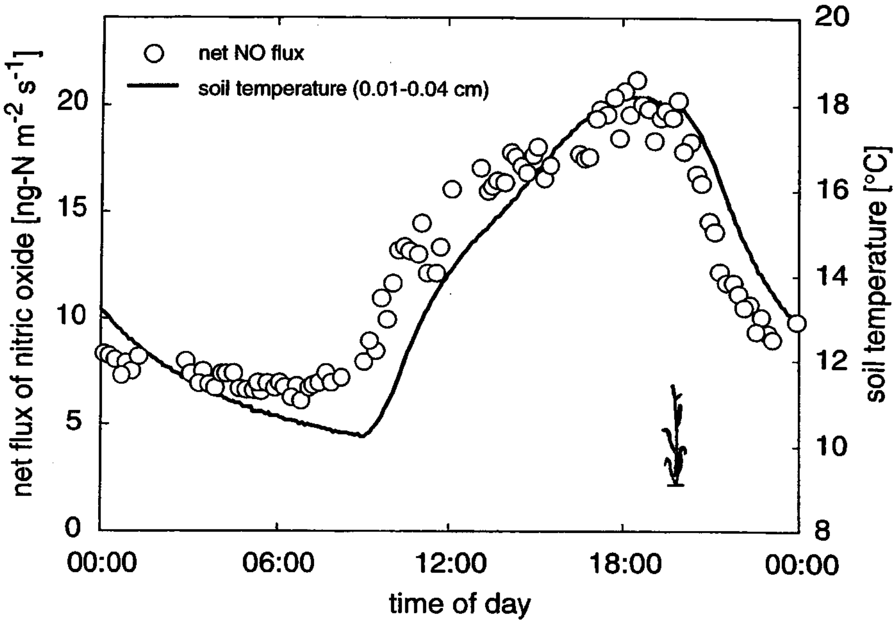

Figure 3. Diurnal variation of the NO emission observed in a laboratory experiment on vegetated soil cores taken from a wheat field near Manndorf, Germany (48.708 °N, 12.956 °E). Measurements were performed by applying an enclosure that was flushed with ambient air of low NO mixing ratio ($<$ 0.5 ppb). Also shown is the diurnal course of soil temperature measured over a depth of 0.01–0.04 m (after Ludwig 1994).

NO emission and soil temperature changes at temperatures higher than about 35 °C and 50 °C, respectively (Valente & Thornton 1993; Yang & Meixner 1997). Other observations even indicate a decline of NO release rates as temperature increases above this value (Williams & Fehsenfeld 1991). No (or only a very weak) relationship between NO flux and temperature could be established in a number of measurements performed over very dry soils (Cardenas et al. 1993; Ludwig 1994; Meixner et al. 1997). Obviously, primary control over the NO flux is accomplished by factors other than soil temperature under dry conditions. Frequently a pronounced positive temperature response becomes visible when moisture is added to these soils (Johansson et al. 1988; Ludwig 1994; Meixner et al. 1997). It should be noted that soil temperature often fails as a variable to account for seasonal variations of NO fluxes (Shepherd et al. 1991; Ludwig 1994). It seems therefore appropriate to regard soil temperature as a factor that mainly modulates short-term variations of the NO exchange, whereas the magnitude of NO emission is predominantly controlled by other factors (see also Otter et al. 1999).

Atmospheric concentration of NO

An influence of ambient NO concentration on the exchange of NO was noticed first by a number of investigators, who used the static (closed) chamber method (Galbally & Roy 1978; Johansson 1984;, Johansson & Granat 1984; Slemr & Seiler 1984). When applying this technique, an enclosure is placed over the surface of interest and the NO emission rate is derived from the increase of NO concentration in the headspace with time. However, in these experiments (in part performed on bare soils), NO mixing ratios increased only until a particular (equilibrium) level was approached. Adjusting the initial NO concentration in the headspace air to a value beyond this level resulted in a concentration decrease to reach the same equilibrium concentration. Evidently, the ambient (headspace) NO concentration determined whether a given soil acted as source or as sink for NO. Such a concentration controlled bi-directional exchange has meanwhile been established for a number of trace gases (Conrad 1994, 1996). The equilibrium concentration at which the rate of NO production equals the rate of NO consumption (i.e., at which the apparent net flux equals zero) is commonly termed NO compensation concentration (or 'compensation point').

More detailed information about the effect of ambient NO concentrations on direction and the magnitude of the rates of the NO exchange has been gained primarily in controlled laboratory experiments. Using dynamic (flow-through) systems, the net NO flux can be determined while the concentration of NO in the gas stream that flushes the enclosure is varied systematically. As an example, results of laboratory measurements on undisturbed (and plant covered) soil cores from a wheat field are presented in Figure 4. At a given soil temperature, the net flux of NO decreases linearly with increasing NO mixing ratio. Positive fluxes (net emission) at low mixing ratios change to negative fluxes (net deposition) at high NO mixing ratios. A similar behaviour was observed in a study with soil columns by Johansson and Galbally (1984). On the basis of their observations, they proposed a model that treats NO production and NO consumption as two autonomous processes that occur simultaneously (Galbally & Johansson 1989). According to this model, the NO production rate is independent of ambient NO concentrations, whereas the uptake process follows a first-order reaction with respect to the atmospheric NO concentration. When plotting NO flux as a function of the NO concentration (as in Figure 4), the NO emission term is represented by the intercept with the y-axis; and the proportionality coefficient between NO uptake and NO concentration is given by the slope of the fitted regression line. The results shown in Figure 4 were obtained under four different soil temperature conditions in the course of a (simulated) day (see Ludwig et al. 1992; Ludwig 1994). Emission rate of NO (y-axis intercept) changed

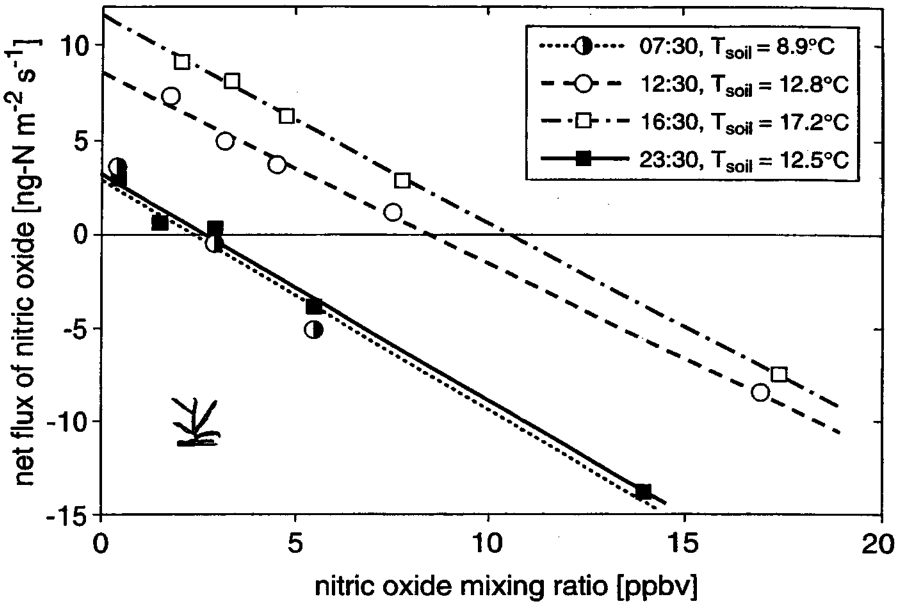

Figure 4. Net flux of NO as a function of NO mixing ratio observed in laboratory experiments on vegetated soil cores taken from a wheat field near Manndorf, Germany (48.708 °N, 12.956 °E). For each of four experiments performed in the course of a (simulated) day, flux data are displayed together with the fitted regression lines. The corresponding soil temperature (depth 0.01–0.04 m) is given in the legend (after Ludwig 1994).

strongly with temperature while the uptake coefficient (slope) remained rather constant. Evidently, environmental control of NO production differs from that of NO consumption.

It remains rather unclear whether the capability of soils to act as a sink for atmospheric NO is of major importance for the exchange of NO on a larger (regional, global) scale. Systematic investigations concerning the uptake of NO and its regulation are scarce and the range of previously observed compensation concentrations is extremely wide. Compensation concentrations of less than 1 ppb have been documented as well as values that exceed several hundred ppb (Johansson & Galbally 1984; Johansson & Granat 1984; Slemr & Seiler 1984; Remde et al. 1989; Slemr & Seiler 1991; Kim et al. 1994). Some of this data indicate that low compensation concentrations are associated with situations that are unfavourable for NO production processes. For example, compensation concentrations as low as 0.2–2 ppb were measured over unfertilized forest soils in Sweden, whereas values up to 170 ppb were found over fertilized soils at the same site (Johansson 1984). In all previous studies, average concentration of NO in the ambient air was found to be less than the compensation concentration; and consequently the mean net flux was directed from the surface to the atmosphere (mean net emission). However, a detailed inspection of published results reveals that a considerable number of field studies has encountered occasional events of net deposition (e.g., Slemr & Seiler 1984; Johansson 1984; Delany et al. 1986; Slemr & Seiler 1991; Ludwig & Meixner 1994). This appears plausible considering that both ambient NO concentrations and compensation points may fluctuate strongly at a given site. It has to be stressed that, even at ambient mixing ratios below the compensation point, the consumption of NO will counterbalance the production to some extent and reduce the actual release of total biogenic NO into the atmosphere.

In this context it is important to note that a lot of research on NO exchange has involved the use of a technique where NO is removed from the ambient air stream that flushes a dynamic enclosure ('zero-air' application; see Williams et al. 1987; Shepherd et al. 1991; Skiba et al. 1993; Yamulki et al. 1995). Application of this technique (a) definitely excludes any uptake of NO and (b) thus may yield the potential (maximal) emission, but never the actual net flux of NO.

NO emission rates from different ecosystems and land-use types

Since the pioneering work of Galbally and Roy (1978), which indicated for the first time the importance of soil emissions for the atmospheric NO budget, field measurements of NO fluxes have been initiated around the globe and thereby have generated a considerable data set covering a variety of terrestrial surfaces under different edaphic and climatic conditions. A recent, comprehensive compilation of available data was provided in tabular form by Davidson and Kingerlee (1997), which is updated in Kramm et al. (2001). This tabular information was transformed to Figure 5, to give a statistically amended summary of the total of 209 measurements which have been reported within the last 20 years. Davidson and Kingerlee's basic classification scheme of ecosystems was retained in Figure 5 (cultivated land, forest, grassland/woodland, others). High emission fluxes of NO have also been reported from cultivated land and from tropical and subtropical grass- and woodland. In contrast, forest soils may be regarded as minor sources of NO, except those forest soils in temperate regions which receive considerable nitrogen inputs (NH_3, HNO_3, NH_4^+, NO_3^-) by wet and dry deposition. Other natural ecosystems, like wetlands and marshes, appear to be negligible with respect to the emission of NO. Some of the patterns in the emission data from different ecosystem classes can be related to characteristic differences in regulatory factors. Thus, the rough ranking of NO emission levels (fertilized

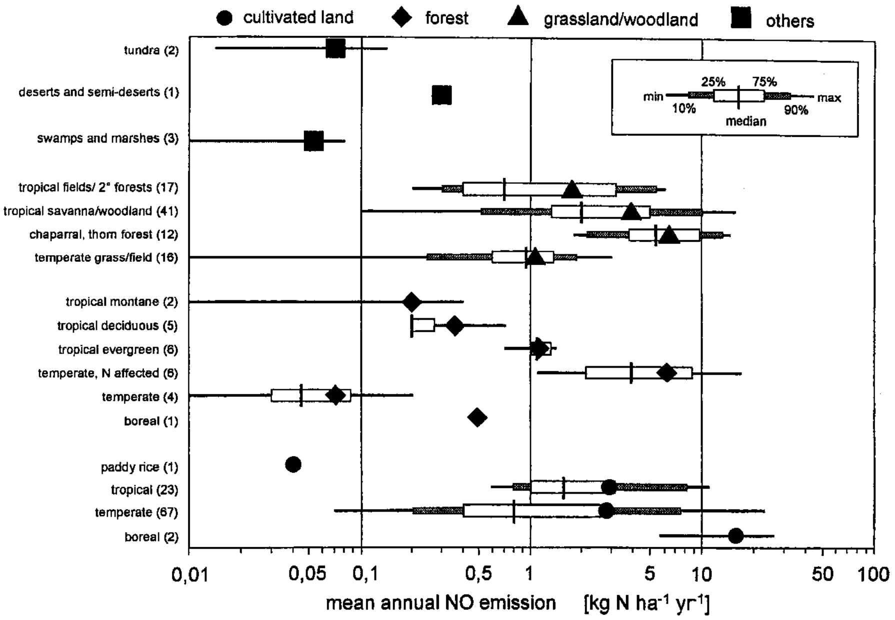

Figure 5. Statistically amended summary of published data of biogenic NO emission from various ecosystems and land-use types, based on a compilation provided by Davidson and Kingerlee (1997) and updated by Kramm et al. (2001). Numbers in parantheses indicate the number of studies performed in each corresponding ecosystem class.

agricultural fields > grasslands > forests > other natural systems) is in broad accordance with the nitrogen status of the corresponding soils (Williams et al. 1992b). Soil water ('pulsing' effect) is a major parameter to explain the high NO emission flux that is indicated for savanna ecosystems. Further inspection of Figure 5 suggests that (sub-)tropical ecosystems release more NO than similar ecosystems in temperate regions. To some extent, this difference mirrors the influence of soil temperature, soil moisture and N availability on NO emission rates.

The general patterns outlined above have to be viewed in consideration of the broad range of variation of the data. Average NO fluxes reported in the literature for similar surfaces deviate by up to two orders of magnitude. For example, the mean value for rainy season emissions at different sites of the Venezuelan savanna region amounted to 0.64 ng N m^{-2} s^{-1} in one study (Sanhueza et al. 1990) but to 56 ng N m^{-2} s^{-1} in another (Johansson & Sanhueza 1988). The span between minimum and maximum values is even much larger and can range for a given ecosystem type from negative NO fluxes to emission rates higher than 100 ng N m^{-2} s^{-1}. Some of this variation may be due to discrepancies in the techniques that were applied for determination of the NO exchange (see reviews in Fowler & Duyzer 1989; Mosier 1989; Williams et al. 1992b; Meixner 1994). However, to a major part, the observed variability in NO flux rates is a consequence of spatial heterogenities and temporal changes in the underlying processes and the environmental factors that control those processes. Even within a few meters of a seemingly uniform field site, the NO emission can differ by as much as a factor of 50 (Williams et al. 1988). Clearly, this variability limits all experimental efforts to derive representative figures for the NO flux at an ecosystem scale. However, micrometeorological techniques, capable to integrate NO net fluxes from a whole ecosystem, are in favour over small-scale enclosure techniques (which are preferred to study controlling mechanisms and influencing factors; see Meixner 1994).

The high level of NO emissions that is associated with the application of N fertilizers to cultivated lands demands some further consideration. As pointed out by Williams et al. (1988, 1992a), soil emissions of NO from heavily fertilized areas can reach the same magnitude as the anthropogenic NO release in urban areas (on a per area and time basis). This is primarily the case for a short period following fertilizer application, otherwise NO emissions are markedly lower during the major part of the season. Only few investigators have attempted to yield long-term information about the emission of NO from agricultural systems. The annual loss of NO derived from such studies was 0.7 kg N ha^{-1} yr^{-1} for a fertilized (218 kg N ha^{-1} yr^{-1}) wheat field in Germany (Ludwig 1994) and 0.6 kg N ha^{-1} yr^{-1} for fertilized (200 kg N ha^{-1} yr^{-1}) arable land in Sweden (Johansson & Granat 1984). The good agreement may be somewhat fortuitous, and one might conclude that those emissions of NO are of little agronomic importance. Recently, Jambert et al. (1997) published NO emissions of 12–52 kg N ha^{-1} yr^{-1} for fertilized (280 kg N ha^{-1} yr^{-1}) and irrigated maize fields in southwestern France. There, the NO emissions correspond to 11.3% of the N input from fertilizer.

In any case, emissions from agricultural sites cannot be ignored as a significant source of atmospheric NO. Williams et al. (1992a) estimated that agricultural land accounts for about 66% of the annual emission of NO from soils in the United States. They also emphasized that NO emissions resulting from agricultural activities are commonly at a maximum when photochemical activity in the troposphere is also at a maximum (‘ozone episodes’). Further concern about fertilizer induced emissions from agricultural soils arises from the fact that a continuous increase of this NO source has to be expected for the future (Matthews 1994). While use of N fertilizer has stabilized in Europe and Northern America, largely increasing consumption rates are reported from

Asia, South America, and Africa. However, experimental data from some of the regions, which are of primary interest in this respect (e.g., the huge agricultural areas of China and the former U.S.S.R), are inadequate or completely lacking (Yienger & Levy II 1995).

Modeling of biogenic NO emissions from soils

Our knowledge about the exchange of NO is primarily based on short-term observations at individual field sites. Assessing the contribution of surface exchange for the atmospheric NO_x budget, however, demands the provision of NO fluxes on larger scales of space (regional, national, global) and time (seasonal, annual). In addition, photochemical models, which are the best tool to study complex chemical processes in the troposphere, require the flux of NO as an input parameter with considerably high temporal and spatial resolutions. Thus the up-scaling of results obtained by individual field experiments by appropriate generalization procedures is a major objective in the research of NO surface exchange.

The most elementary procedure to obtain large-scale fluxes of NO is the extrapolation of individual results within certain biogeographical classes by sheer areal extent of the class. This approach was applied in some early attempts to estimate the global emission of NO from biogenic sources (Stedman & Shetter 1982; Logan 1983; Johansson 1984; Slemr & Seiler 1984). On a global scale, results were typically on the order of 10 Tg N yr^{-1}, which may be compared to a value of 21 Tg N yr^{-1} proposed as the source strength for anthropogenic emissions (Kasibhatla et al. 1993). These early estimates, however, were based on a very limited number of field measurements, and thus the range of uncertainty is enormous (0.2 to 20 Tg N yr^{-1}). Even with increasing availability of field data, such a simplistic approach has inherent limitations since it generally does not account for the influence of environmental variables on the NO exchange. However, the most recent estimate of the global biogenic source strength of NO is 21 Tg N yr^{-1} (± 4–10 Tg N yr^{-1}) (Davidson & Kingerlee 1997), which may be reduced to 13 Tg N yr^{-1} (± 4–10 Tg N yr^{-1}), if a first-order approximation of the ‘canopy reduction factor’ is considered (Davidson & Kingerlee 1997).

The first attempt to apply a more sophisticated up-scaling scheme was made by Williams et al. (1992a). On the basis of their field investigations (Williams et al. 1987; Williams et al. 1988; Williams & Fehsenfeld 1991), they developed an algorithm that relates the biogenic emission of NO to soil temperature and a biome fitting parameter (‘A factor’) which is supposed to be representative of an ecosystem – land-use type. In order to generate an inventory of soil emissions for the United States, four primary biomes (grasslands, forests, wetlands, agricultural managed land) were distinguished with a further breakdown of agricultural areas according to crop type (corn, cotton, wheat, soybeans). The ‘A factor’ for each category was derived from previous field studies or (in the case of agricultural areas) calculated by an empirical relationship between the average fertilization rate and NO emission. Observations at various field sites were used to formulate an exponential temperature response function that was employed universally for all categories. This approach had its merits in providing an estimate for the magnitude of the biogenic NO soil source (6% of U.S. anthropogenic sources) and in localizing those regions of the United States where soil emissions of NO are most significant. However, some substantial deficiencies are obvious. No provision, for example, are taken to account for the spatial heterogeneity within the selected biome classes (cf. Figure 5). Seasonal and interannual variability is modelled only as a function of soil temperature, but the algorithm does not consider temporal effects of changes of soil nutrient (fertilization) and of soil moisture, although these effects often dominate the emission of NO. Furthermore the approach entirely neglects any possibility of a bi-directional NO exchange. Considering potential sources of error, Williams et al. (1992a) estimated the uncertainty of their inventory within a factor of three. Meixner (1997), however, demonstrated that this specification of uncertainty may be far too optimistic as results of (even long-term) field measurements deviated by a factor of up to 15 from the data generated with the algorithm of Williams et al. (1992a).

A similar conceptual framework has been used by Yienger and Levy II (1995) to assess biogenic emissions of NO on a global scale. Substantial extensions to the Williams et al. approach were implemented such as a linear dependency of NO emissions on fertilizer application rates. In addition, the influence of precipitation events on NO emissions was considered, in particular, by applying a ‘pulsing’ term and modifying the temperature response function to reflect the existence of a temperature optimum and the weak temperature dependence in dry soils. Furthermore, Yienger and Levy II introduced a canopy reduction factor to account for that fraction of soil-emitted NO being converted to NO_2 within the canopy. Especially the latter feature had a large effect on the result, as predicted global emission of NO decreased from 10.2 Tg N yr^{-1} at the soil surface to a value of 5.5 Tg N yr^{-1} above canopy.

The obvious improvements of the Yienger and Levy II approach encouraged us to simulate biogenic NO emissions for an area of 120×120 km^2 in south-western part of Germany and adjacent regions. For that, we included the Yienger and Levy II parameterization into the mesoscale model system KAMM/DRAIS (Vogel et al. 1995). This model system is able to simulate the spatial and temporal distributions of meteorological variables (wind, temperature, humidity) and of photooxidant concentrations at the regional scale. The model uses horizontal grid sizes of 2 km and therefore gives the spatial distribution of the surface temperature, which is an important input parameter for the calculation of biogenic NO emissions at that resolution. The soil temperature is available with a temporal resolution of a few seconds. Normally, simulations are carried out for time periods of several days.

Yienger and Levy II (1995) used different functional relationships for the temperature dependence of NO emission in wet and dry soils. On the basis of mean climatological mid-European conditions, we regarded all soils in the given area generally as wet soils. Therefore we applied the suggested relationships for biogenic NO emission and soil temperature: linear for low soil temperatures and exponential for soil temperatures up to 30 °C. The applied parameterization of the biogenic NO emission flux (E_{NO}) is given by eq. (1):

$$E_{NO}(T_S, A) = \begin{cases} c_1 \cdot A \cdot T_S & \text{for } 0\,^\circ C < T_S \leq 10\,^\circ C \\ A \cdot e^{(c_2 \cdot T_S)} & \text{for } 10\,^\circ C < T_S \leq 30\,^\circ C \\ c_3 \cdot A & \text{for } 30\,^\circ C > T_S \end{cases} \qquad (1)$$

where $T_S$is the soil temperature at the individual grid point, A represents the biome- and time-dependent ‘A factor’ (see below), and c_1 to c_3 were set to 0.28, 0.103, and 21.97 $^\circ\mathrm{C}^{-1}$, respectively as in Yienger and Levy II (1995).

According to the available land-use data (see below), five biome-dependent ‘A factors’ were introduced. We classified the area into ‘unfertilized forest’, ‘unfertilized grassland’, fertilized ‘arable land’, ‘vineyards’, and ‘orchards’. For ‘unfertilized forest’ and ‘unfertilized grassland’ we adopted corresponding ‘A factors’ from Yienger and Levy II (0.03 and 0.36 ng N $\mathrm{m}^{-2}\mathrm{s}^{-1}$, respectively). For the total of ‘grassland’ biomes in our model domain, we assumed one half as unfertilized and the other half as fertilized soils. Like Yienger and Levy II, we assumed a linear dependence of biogenic NO emission on fertilizer rate to compute the individual ‘A factors’ of the fertilized soils. But in contrast to Yienger and Levy II, who assumed that all fertilizer is broadcasted uniformly between May and August, we introduced monthly fertilizer rates (FR(month)). Temporally averaging fit procedures were applied to published regional fertilizer rates to obtain individual FR_i(month) for ‘arable land’, ‘vineyards’, and ‘orchards’. The biome- and time-dependent ‘A factors’ (A_i) have been calculated by

$$A_i(\text{fertilized soil}) = A_{i,0} + c_4 \cdot f \cdot FR_i(\text{month}) \qquad (2)$$

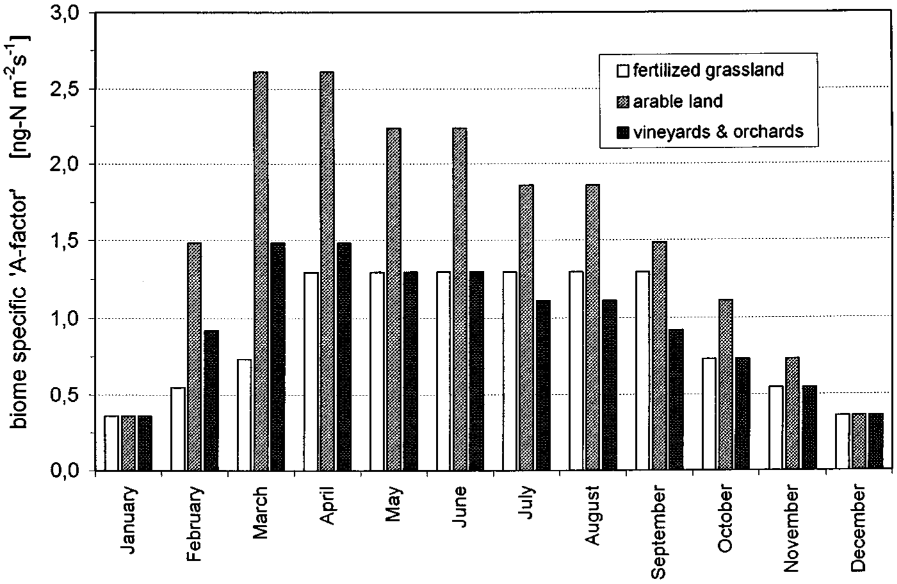

Figure 6. Annual cycles of biome specific “A factors” for different fertilized land-use types in the south-western part of Germany (details, see text).

where $A_{i,0}$ is the ‘A factor’ of ‘unfertilized grassland’, c_4 is the conversion factor to transform monthly fertilizer rates (kg N $ha^{-1}month^{-1}$) into ‘A factor’ units (ng N $m^{-2}s^{-1}$), and f is the fertilizer loss rate (f = 0.1%, see also Veldkamp & Keller 1997). Resulting time-dependent ‘A factors’ are shown in Figure 6. By the described procedure we accounted for regional common farming practices, e.g., highest fertilizer applications at the beginning of the growing season for arable land and a more uniform distribution for grassland.

The use of a special canopy reduction factor was skipped, since this effect is already handled through a complex soil–vegetation parameterization implemented in the mesoscale meteorological model. Land-use data are available for the model domain with a spatial resolution of 30 × 30 m^2. Therefore, for each grid cell, the NO emission factors were determined by integrating the individual contributions of the 30 × 30 m^2 cells to the 2 × 2 km^2 cells. Further details of the parameterization of biogenic NO emissions are given in Förstner (1996) and Obermeier et al. (1997).

The model gives diurnal cycles of biogenic NO emissions. As an example, a map presenting biogenic NO emission rates on 03 August 1990, 1400 LT is shown in Figure 7. As expected, highest emission rates were simulated for areas that are mainly under agricultural use, that is, in the Rhine Valley. The maximum NO emission rates are in the order of 0.6 g N s^{-1} (2 kg N h^{-1}) for a grid cell of 2 × 2 km^2. In contrast, non-cultivated regions like the Black Forest exhibit quite low NO emissions rates ($<$ 13 ng N $m^{-2}s^{-1}$).

Figure 8 is taken from Obermeier et al. (1997) and gives the diel cycles of the biogenic NO emissions together with the anthropogenic NO emissions for the whole model domain. The distinct diel cycle of the biogenic NO emissions is primarily caused by the corresponding diel variation of the surface temperature. It is found that the biogenic emissions contribute 30% to the total NO emissions during the night and about 10% to the total NO emissions during daytime. In some cases, however, the contribution of NO emissions from soil for individual grid cells even exceeds the emissions from anthropogenic sources. The relative importance of the biogenic NO emissions should increase in the future when the anthropogenic NO emissions are expected to decrease (Figure 8). T2005 and M2005 are two different emission scenarios where T2005 includes the already foreseen measures and M2005 includes further possible reduction strategies not yet prescribed by law.

A fundamental constraint in the approaches described above is their strictly empirical character. Undoubtedly, further progress in the development of such empirical relationships will be achieved as more field data become available. However, owing to the enormous variability in NO fluxes, an immense number of observations would be required to keep statistically sound uncertainty ranges within reasonable limits (see Folorunso & Rolston 1984). Most probably, only those generalization procedures that are based more closely on a mechanistic understanding of NO exchange will reflect spatial and temporal variations of NO fluxes in detail (e.g. Hall et al. 1996).

Within recent years, several models have been published which aim to describe nitrogen gas fluxes (mainly N_2O fluxes) towards this direction (CENTURY by Parton et al. 1996; DNDC by Li et al. 1992; NASA-CASA by Potter et al. 1996). Without giving any preference to NASA-CASA, we briefly refer to the model of Potter et al. (1996) as an example of this model type. A mechanistic concept, termed ‘hole in the pipe’ (Firestone & Davidson 1989) was adopted to simulate global biogenic emissions of NO (and N_2O). The basic idea underlying this approach is that the emission of NO can be treated as leaks in the ‘process pipe’ of nitrification and/or denitrification. A major strength of this conception lies in the possibility to implement two levels of regulation, one with regard to the nitrogen turnover rate (‘flow through the pipe’) and one with regard to the quantity of NO escaping from the overall flow (‘size of holes in the pipe’). In the work of Potter et al. (1996) ‘flow through the pipe’ is represented by the gross N mineralization rate, which is computed by means of a complex biosphere model that couples ecosystem production and the cycling of soil carbon and nitrogen (Potter et al. 1993). A relatively simple formulation is then applied to predict NO emission rates as

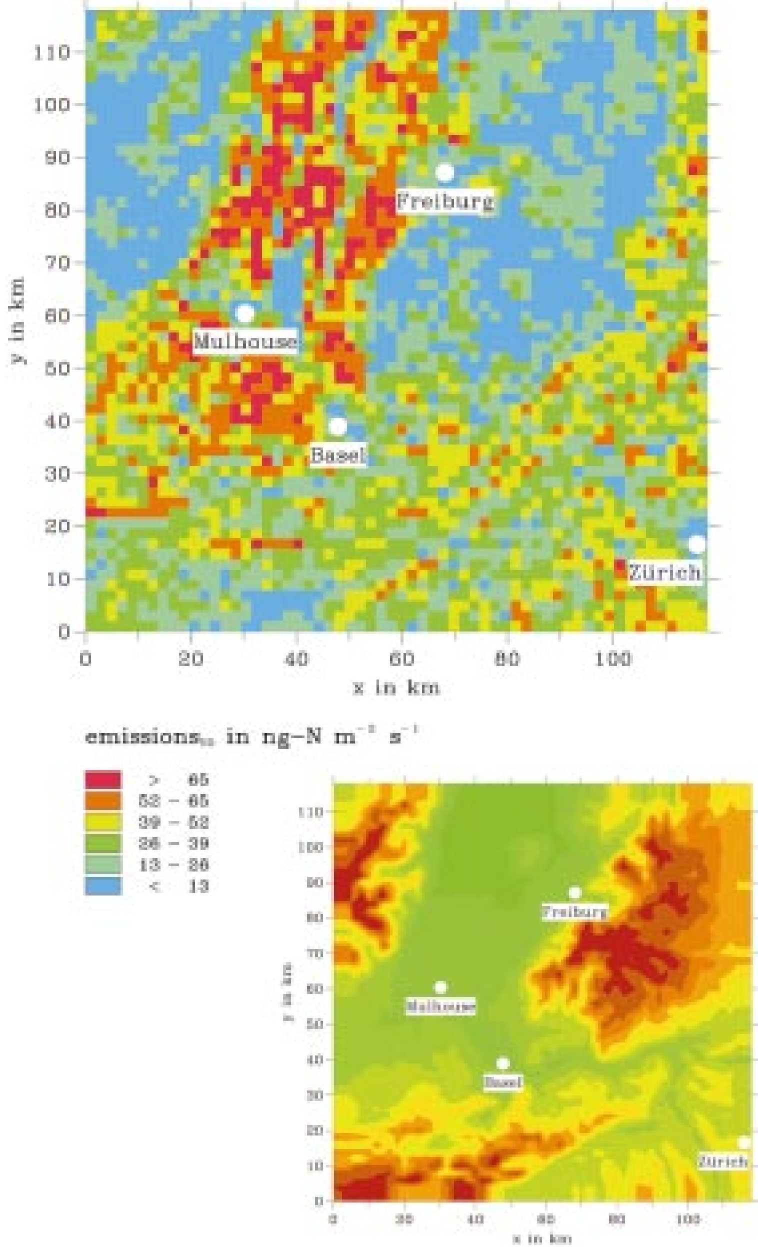

Figure 7. Horizontal distribution of biogenic NO emissions calculated with KAMM/DRAIS for the south-western part of Germany and surrounding areas for 3 August 1990, 1400 LT. The lower right insert shows the topography of the study area, colour coding indicates 10 equidistant elevation steps ranging from 150 m a.s.l. (dark green) to 1500 m a.s.l. (dark brown). Geographical coordinates of the lower left corner of both maps are 47° 12′ N, 06° 58′ E.

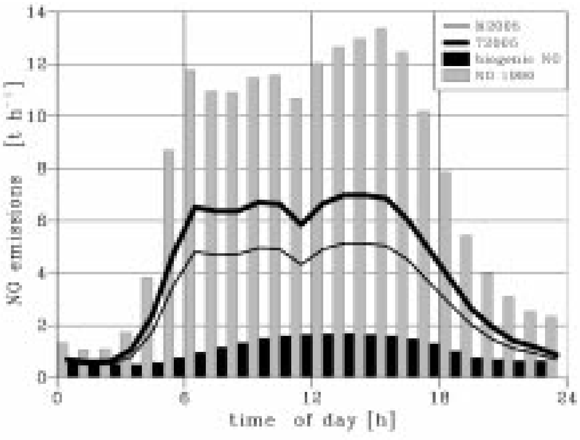

Figure 8. Diurnal cycles of total biogenic (black bars) and anthropogenic NO emissions (grey bars) for the entire model domain for 3 August 1990. In addition, two emission scenarios for anthropogenic NO emissions of the year 2005 are shown (details, see text).

a soil moisture dependent fraction of N mineralization. The global source strength of soil biogenic NO derived in this way amounted to 9.7 Tg N yr^{-1} (Potter et al. 1996). Reliability of this estimate is restricted by the fact that a number of input parameters had to be obtained by educated guesses, since quantitative knowledge on a process level is still rudimentary. Nevertheless, the predicted global NO emission is in remarkable agreement with the estimate of Yienger and Levy II (1995).

A completely different procedure to model NO exchange with respect to basic processes in the soil was provided by Galbally and Johansson (1989). Their approach assumes that the net exchange of NO can be formulated in terms of NO production, NO consumption, and transport of NO through the soil. Production and uptake parameters have to be determined experimentally, while a diffusional model can be applied to describe the transport of NO through the soil. Galbally and Johansson (1989) and Remde et al. (1993) demonstrated that thus calculated fluxes agreed well with measured fluxes. Recently, Yang and Meixner (1997), as well as Otter et al. (1999), refined the approach by developing response functions of both production and uptake rates, with respect to soil temperature and soil moisture. By means of the derived model, they were able to reproduce long-term (Otter et al. 1999), as well as hourly (Yang & Meixner 1997) variations of NO emission rates, which were observed independently in comparative field studies. An example is shown in Figure 9 for the short-term variation of the net NO flux from a subtropical savanna grassland ecosystem. After an extended precipitation-free period, the experimental plot was irrigated with 28-mm de-ionized water

(4 December 1994, 11:30 LT). As observed by a dynamic chamber system (Meixner et al. 1997), the net flux of NO increased from less than 1 ng N $m^{-2}s^{-1}$ (just before irrigation) to 18 ng N $m^{-2}s^{-1}$ (5 hours after irrigation). Corresponding soil temperature and soil moisture response functions were derived from standardized laboratory experiments (Yang et al. 1999) on soil samples which were taken out of the dynamic chambers' steel frames. Thus, using the in situ measured data of soil temperature and moisture, biogenic NO emissions (shown in Figure 9) were calculated. The sudden increase of NO emission after irrigation is only weakly simulated. Allowing the soil system to equilibrate (overnight), the agreement between measured and simulated data on 5 December is excellent. However, a major drawback of this procedure (in its current state) is the fact that it has to be parameterized for each individual soil. The necessary information, however, can be obtained in standardized laboratory experiments. Thus, this method has an attractive potential for the determination of biogenic NO emission by 'scanning' soil samples in the laboratory. Corresponding upscaling to local (regional) estimates may be achieved by emission algorithms similar to those described above.

Conclusions

There is broad consensus that the microscopic level of microorganism metabolism exerts initial control over biogenic NO emission (Conrad 1996). However, microbial processes which are involved in NO production and consumption in soils are numerous and are only partly understood. In case that processes are understood, their effects are complex and can hardly be quantified owing to far reaching feed-back mechanisms. On the other hand, it has been asked, whether microbial diversity and community structure in soil have any consequences at the ecosystem level (Schimel 1995). This may be answered by the considerable progress that has already been achieved in searching for controllers of biogenic NO emissions on a higher (than microscopic) scale of organization and controls.

Since the pioneering work of Galbally and Roy (1978), main controllers/influencing factors were identified. These are the soil water content, the soil temperature, the ambient NO concentration, and the substrate N availability. Coarse-scale models have already incorporated corresponding parameterizations to study the influence, interactions, and dynamics of influencing factors on regional to global and seasonal to interannual scales (Hutchinson et al. 1997). However, these algorithms/models usually fail when small scale, especially temporal effects of biogenic NO emissions are addressed. There is a demand for more appropriate descriptions of the large pulses of biogenic NO emission commonly observed on a time scale

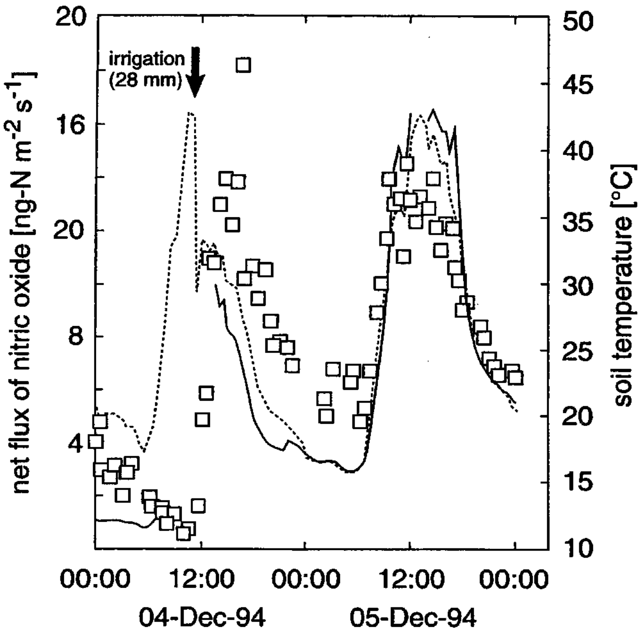

Figure 9. Diel variation of the net NO flux from a subtropical savanna grassland ecosystem (Grassland Research Station Marondera/Zimbabwe, 18.183 °S, 31.467 °E). On 04 December 1994, (11:30 LT), the experimental plot was irrigated with 28-mm de-ionized water. Open squares represent measurements of the net NO flux by a dynamic chamber system, the dashed line indicates the measured soil temperature at –1 cm. The straight line represents results of modelled NO emission (Yang & Meixner 1997); corresponding soil temperature and soil moisture response functions were parameterized by standardized laboratory experiments (Yang et al. 1999) on soil samples which were taken out of the dynamic chambers' steel frames.

of a few hours to a day following (a) wetting of dry soils by precipitation, thawing, and irrigation and (b) agricultural management practices like tilling, fertilization, harvesting, and burning (Hutchinson et al. 1997; Matson 1997). On comparative spatial scales (i.e., a few meters to kilometers), we need better descriptions of (a) the the so-called 'canopy reduction' of soil NO emission (owing to its rapid conversion to NO_2, which is taken up by vegetation elements by an order of magnitude faster than NO) and (b) the consequences of atmospheric deposition of anthropogenic nitrogen on biogenic NO emission from soils (Matson 1997).

In this context, results of some recent models (e.g., Potter et al. 1996) and algorithms (Yang & Meixner 1997; Otter et al. 1999) are encouraging. Since they are based on mechanistic understanding of NO exchange, they enable description of biogenic NO emission (a) on the temporal and spatial dynamics of more general ecosystem variables (like gross mineralization) and (b) on rather short time scales (Figure 9). Amalgamation of such models/algorithms with state-of-the-art (mesoscale-) meteorological models is considered to be the most sophisticated method to solve the up-scaling problem and should be pursued in the near future. It should be mentioned in particular that present mesoscale meteorological – air chemistry models (e.g., Vogel et al. 1995; Ganzeveld & Lelieveld 1995) are already able to tackle the problems of 'canopy reduction' of soil emitted NO, as well as dry and wet deposition of anthropogenic nitrogen by chemistry and small-scale surface exchange modules.

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