



## Effects of soil solution on the dynamics of N<sub>2</sub>O emissions: a review

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Received 19 January 1998; accepted in revised form 29 January 1999

**Key words:** nitrous oxide, soil solution, soil air, solubility, nitrogen balance, modeling, leaching

### Abstract

In this review, which consists of two parts, major interactions between nitrous oxide (N<sub>2</sub>O) and soil solution are described. In the first part, as an introduction, concentrations of dissolved N<sub>2</sub>O in different aqueous systems are summarized. An inventory of data on maximal N<sub>2</sub>O concentrations in soil solution (up to 9984 µg N<sub>2</sub>O-N l<sup>-1</sup>) and in soil air (up to 8300 ppm) from literature is presented. The peak N<sub>2</sub>O concentrations represent a N<sub>2</sub>O supersaturation in the soil solution up to 30000 times with respect to ambient air and a soil air N<sub>2</sub>O concentration about 25000 times higher than in the atmosphere. The main physico-chemical parameters (solubility, diffusion) controlling N<sub>2</sub>O distribution between soil solution and soil air are outlined. The influences of cultivation practice, nitrogen turnover, water content and temperature on N<sub>2</sub>O accumulation in soil solution and soil air are reviewed. In the second part some models of N<sub>2</sub>O dynamics in soils are discussed with emphasis on N<sub>2</sub>O transport processes. A simple qualitative scheme is developed to categorize the effects of the soil solution on N<sub>2</sub>O dynamics in soils. In this scheme the temporary, intensive N<sub>2</sub>O oversaturation of the soil solution is interpreted as a result of gas diffusion inhibition by water (barrier function of soil solution) resulting in an accumulation of N<sub>2</sub>O. In addition, N<sub>2</sub>O supersaturation is an indication that transitory much N<sub>2</sub>O can be stored in the soil solution (storage function of soil solution). Where the soil solution flows up-, down- or sideways it can act as a relevant transport medium for dissolved N<sub>2</sub>O (transport function of soil solution). This scheme is applied to examples from the literature.

### Introduction

Nitrous oxide (N<sub>2</sub>O) is one of the important trace gases contributing to climate change. Moreover, N<sub>2</sub>O is the main source of stratospheric NO<sub>x</sub>, which is the major natural catalyst of stratospheric ozone layer depletion (IPCC, 1994).

In order to have caused the recent increase in atmospheric N<sub>2</sub>O concentration (0.3% annually), global sources and sinks for N<sub>2</sub>O must have been as much as 30% off balance (Vitousek, 1994). The main share of world-wide N<sub>2</sub>O emissions originates from natural processes but more than one-third are estimated to stem from human activities (IPCC, 1994). However, this distinction is somewhat artificial since many so-called natural ecosystems are anthropogenically contaminated with nitrogen.

In spite of the extensive efforts undertaken to identify the global N<sub>2</sub>O dynamics there are still many

uncertainties. Probably yet unknown sources or mechanisms which lead to an incomplete budgeting may exist (Bouwman et al., 1995). New approaches improving calculations of total N<sub>2</sub>O emissions caused by agriculture include in addition to the direct N<sub>2</sub>O emissions from soils those from animal production and those indirect ones from atmospheric nitrogen deposition, nitrogen leaching, nitrogen runoff and human sewage (IPCC, 1997).

One attempt to improve the understanding of N<sub>2</sub>O emissions is to explore its distribution between the atmosphere and aquatic systems. As N<sub>2</sub>O is highly soluble in water, large amounts may remain dissolved in eutrophicated waters after having arisen from denitrification or nitrification. Dependent on the microbiological production rate, extensive N<sub>2</sub>O supersaturation with respect to ambient air may result (e.g. Bowden & Bormann, 1986; Harris et al., 1984; Minami & Ohsawa, 1990).

This applies, for example, to oxygen-depleted seas although, in principle, the concentration of dissolved  $\text{N}_2\text{O}$  in oceans is in equilibrium with the atmospheric  $\text{N}_2\text{O}$  concentration (Elkins et al., 1978; Ronen et al., 1988). Especially in coastal areas with high organic carbon input, vast areas can be  $\text{N}_2\text{O}$  oversaturated by up to more than 1000% (Duyzer, 1995; Hahn, 1974; Law & Owens, 1990; Law et al., 1992; Slater & Capone, 1987). Such systems are major global emitters of  $\text{N}_2\text{O}$  (Seitzinger et al., 1983). On the other hand, a consumption of atmospheric  $\text{N}_2\text{O}$  may also take place under anoxic conditions at heavily polluted shores (Cohen, 1978).

Potentially much  $\text{N}_2\text{O}$  might be evolved in shallow aquifers contaminated by nitrogen compounds but often easily available carbon is the limiting factor for denitrification or nitrification (Bradley et al., 1992; Gillham & Cherry, 1978; Obenhuber & Lowrance, 1991). Nevertheless,  $\text{N}_2\text{O}$  supersaturation can also rise up to 1000% in groundwater (Ronen et al., 1988). This  $\text{N}_2\text{O}$  can enter the atmosphere by diffusing through the overlying soil to the soil surface or by quick outgassing at wells or springs (Rice & Rogers, 1993; Smith & Duff, 1988; Ueda et al., 1993). It has been estimated that 10–20% of biogenic  $\text{N}_2\text{O}$  sources may originate from polluted aquifers (Ronen et al., 1988).

Additionally, in eutrophicated streams, lakes, etc., much  $\text{N}_2\text{O}$  may be produced, solubilized and emitted (Chan & Knowles, 1979; Dowdell et al., 1979; Duyzer, 1995). As pollution of aquatic ecosystems increases worldwide their importance in the global  $\text{N}_2\text{O}$  budget will even increase in the future.

Wastewater treatment plants are further sources of  $\text{N}_2\text{O}$  (Benckiser et al., 1996; Bruins et al., 1995; Dowdell et al., 1979), but their global contribution is probably of little account (IPCC, 1997). This seems also to be true for sewer systems (Clemens & Haas, 1997). However, temporarily high amounts of dissolved  $\text{N}_2\text{O}$  may be transported from wastewater treatment plants into streams, where  $\text{N}_2\text{O}$  may escape to the air due to turbulent water flow (Sümer et al., 1995).

Up to now there have been only few investigations on soil solution and its effects on  $\text{N}_2\text{O}$  dynamics in soils. Therefore the available literature on this subject has been compiled in this review in order to evaluate the processes governing, and the factors controlling, these interactions, and to summarize the results in a simple qualitative scheme.

### **Concentrations of $\text{N}_2\text{O}$ within soil profiles and their correlations to $\text{N}_2\text{O}$ emissions**

During the last decade numerous studies have been conducted to quantify the emissions of  $\text{N}_2\text{O}$  from soils. Closed and open chamber systems, as well as micrometeorological methods, have been used for this purpose. Most of the researchers have tried to correlate the  $\text{N}_2\text{O}$  fluxes from the soil surfaces to the atmosphere with biological, chemical and physical soil parameters.

In contrast only few investigations are available on the quantities, distributions and dynamics of  $\text{N}_2\text{O}$  within soil profiles. There is evidence, however, that under conditions of intense  $\text{N}_2\text{O}$  production and restricted gas transport, a significant accumulation of  $\text{N}_2\text{O}$  in the soil solution and in the soil air can take place.

Insight into the dynamics of  $\text{N}_2\text{O}$  within the soils themselves may be relevant in the context of different problems, e.g. the localization of soil horizons with high  $\text{N}_2\text{O}$  productivity or with diffusional restrictions. The proportion of  $\text{N}_2\text{O}$  produced to  $\text{N}_2\text{O}$  actually emitted may be estimated. Thus an observation of  $\text{N}_2\text{O}$  accumulations in soils could be a tool for improving the prediction of further  $\text{N}_2\text{O}$  fluxes (Clemens & Vandr , 1997). In addition,  $\text{N}_2\text{O}$  leaching or lateral transport can be taken into account in  $\text{N}_2\text{O}$  modeling.

Since the temporal and spatial dynamics of  $\text{N}_2\text{O}$  in soil profiles are the result of its production, consumption and upward, downward or horizontal movement, very different patterns of  $\text{N}_2\text{O}$  concentrations in soil profiles are reported.

The concentrations of  $\text{N}_2\text{O}$  in soil solutions are of very high temporal and spatial variability (Bowden & Bormann, 1986; Dowdell et al., 1979; Minami & Fukushi, 1984; Minami & Ohasawa, 1990; Ronen et al., 1988; Schnabel & Stout, 1994; Terry et al., 1981). Transitorily significant quantities of  $\text{N}_2\text{O}$  can be dissolved in the soil solution. The maximal concentrations of dissolved  $\text{N}_2\text{O}$  reported are up to three orders of magnitude above ambient (Table 1). On the other hand, temporary  $\text{N}_2\text{O}$  undersaturation is also possible (Bowden & Bormann, 1986; Davidson & Firestone, 1988; Terry et al., 1981).

Concentrations of  $\text{N}_2\text{O}$  in soil air are also extremely variable over space and time (Albrecht et al., 1970; Ball et al., 1997; Benckiser et al., 1986; Burford, 1976; Burford & Stefanson, 1973; Burton & Beauchamp, 1994; Burton et al., 1997; Cates &

Table 1. Maximal concentrations of dissolved N<sub>2</sub>O in different sampling fractions

Ecosystem	Location	Sample period	Sampling fraction	Max. conc. of dissolved N <sub>2</sub> O	Reference
<i>Forest</i>					
Podzol, undisturbed forest	New Hampshire, USA	1984–1985	Seep water	0.5 µg N <sub>2</sub> O-N l <sup>-1</sup>	Bowden & Bormann, 1986
Podzol, clear-cut forest	New Hampshire, USA	1984–1985	Seep water	496 µg N <sub>2</sub> O-N l <sup>-1</sup>	Bowden & Bormann, 1986
Hillside, wood	Appalachian Mountains, USA	1987–1988	Soil solution	1.5 µg N <sub>2</sub> O-N l <sup>-1</sup>	Davidson & Swank, 1990
Riparian zone, wood	Appalachian Mountains, USA	1987–1988	Soil solution	8 µg N <sub>2</sub> O-N l <sup>-1</sup>	Davidson & Swank, 1990
Saturated zone, wood	Appalachian Mountains, USA	1987–1988	Soil solution	6 µg N <sub>2</sub> O-N l <sup>-1</sup>	Davidson & Swank, 1990
Wood, acid rain	The Netherlands	1986	Water table region	20 µg N <sub>2</sub> O l <sup>-1</sup>	Ronen et al., 1988
<i>Grass</i>					
Silt loam, riparian zone, grass	California, USA	1987	Soil solution	2 µg N <sub>2</sub> O-N l <sup>-1</sup>	Davidson & Firestone, 1988
Silt loam, midslope, grass	California, USA	1987	Soil solution	4 µg N <sub>2</sub> O-N l <sup>-1</sup>	Davidson & Firestone, 1988
<i>Rice</i>					
Rice field	Japan	-	Floodwater	4 µg N <sub>2</sub> O-N l <sup>-1</sup>	Minami & Fukushi, 1984
Volcanic ash soil, rice field	Japan	1982	Floodwater	10 µg N <sub>2</sub> O l <sup>-1</sup>	Minami & Fukushi, 1984
<i>Vegetables</i>					
Volcanic ash soil, vegetables field	Japan	1982–1983	Drainage water	109 µg N <sub>2</sub> O-N l <sup>-1</sup>	Minami & Fukushi, 1984
Volcanic ash soil, vegetables	Japan	-	Drainage water	120 µg N <sub>2</sub> O l <sup>-1</sup>	Minami & Ohsawa, 1990
<i>Other agricultural systems</i>					
Clay soil, winter oilseed rape	U.K.	1979	Drainage water	625 ppmv	Burford et al., 1981
Heavy clay, agricultural field	Uffington, U.K.	1977–1978	Drainage water	132 µg N <sub>2</sub> O-N l <sup>-1</sup>	Dowdell et al., 1979
Heavy clay, agricultural field	Drayton, U.K.	1977–1978	Drainage water	27 µg N <sub>2</sub> O-N l <sup>-1</sup>	Dowdell et al., 1979
Heavy clay, agricultural field	Northfield, U.K.	1977–1978	Drainage water	25 µg N <sub>2</sub> O-N l <sup>-1</sup>	Dowdell et al., 1979
Drained, cultivated organic soil	Florida, USA	1979	Drainage water	27 ppmv	Terry et al., 1981
Histosol	New York, USA	–	Drainage water	900 ppmv	Guthrie & Duxbury, 1978
Field soil	Japan	–	Drainage water	7060 nM	Ueda et al., 1993

Table 1. Continued

Heavy clay, agricultural field	U.K.	1977–1978	Lysimeter drainage	415 $\mu\text{g N}_2\text{O-N l}^{-1}$	Dowdell et al., 1979
Heavy clay, agricultural field	Uffington, U.K.	1975–1978	Soil solution	9984 $\mu\text{g N}_2\text{O-N l}^{-1}$	Dowdell et al., 1979
Heavy clay, agricultural field	Northfield, U.K.	1977–1978	Soil solution	544 $\mu\text{g N}_2\text{O-N l}^{-1}$	Dowdell et al., 1979
Clay soil, subsoil	U.K.	1976–1977	Soil solution	1600 ppmv	Burford et al., 1978
Sewage irrigation	Israel	1986	Unsaturated zone	15 $\mu\text{g N}_2\text{O l}^{-1}$	Ronen et al., 1988
Sewage irrigation	Israel	1986	Water table region	400 $\mu\text{g N}_2\text{O l}^{-1}$	Ronen et al., 1988
Flooded organic soil	Florida, USA	1979	Floodwater	0.37 ppmv	Terry et al., 1981
–	Japan	–	Spring water in channel	280 nM	Ueda et al., 1993

Keeney, 1987; Clayton et al., 1994; Delwiche & Rolston, 1976; Dowdell & Smith, 1974; Eggington & Smith, 1986; Flühler et al., 1976b; Goodroad & Keeney, 1985; Lessard et al., 1996; Lind, 1985; Velthof et al., 1996). Maximum concentrations of  $\text{N}_2\text{O}$  in soil air can reach up to 23000 times the  $\text{N}_2\text{O}$  concentration in the atmosphere (Table 2). During intense denitrification, however, a consumption of atmospheric  $\text{N}_2\text{O}$  may occur. In these cases the concentrations of  $\text{N}_2\text{O}$  in the soil air are below the atmospheric background and the soils become temporal sinks for  $\text{N}_2\text{O}$ .

Goodroad & Keeney (1985) demonstrated that the spatial variability of  $\text{N}_2\text{O}$  concentrations in the soil atmosphere culminated when the  $\text{N}_2\text{O}$  concentration levels were very high in general. For example, coefficients of variation up to 100% were observed at the peak  $\text{N}_2\text{O}$  soil air concentrations in an agricultural field, suggesting the existence of hot spots or localized areas of limited gas diffusion. In contrast, at low  $\text{N}_2\text{O}$  concentrations the spatial variability was less than 10% (Cates & Keeney, 1987).

Similar to the horizontal, the vertical distribution of  $\text{N}_2\text{O}$  in soils is very different. In some studies the concentrations of  $\text{N}_2\text{O}$  in the soil atmosphere were equal at all soil depths (Albrecht et al., 1970; Parkin & Meisinger, 1989). In other cases the spatial variability was in general so high that a distinction between the layers was impossible (Cates & Keeney, 1987). Most often,  $\text{N}_2\text{O}$  peaks occurred in the upper soil horizons containing the highest mineral nitrogen concentrations

(Burford, 1976; Burford & Stefanson, 1973; Clayton et al., 1994; Delwiche & Rolston, 1976; Dowdell & Smith, 1974; Goodroad & Keeney, 1985; Rolston, 1978; Rolston et al., 1976). Elsewhere, the highest  $\text{N}_2\text{O}$  concentrations in soil air were measured in layers at the middle of the soil bodies (Arah et al. 1991; Benckiser et al., 1986; Goodroad & Keeney, 1985). Exceptionally, the highest accumulation of  $\text{N}_2\text{O}$  appeared below 40 cm in the subsoil. (Albrecht et al., 1970; Burton & Beauchamp, 1994; Dowdell & Smith, 1974; Dowdell et al., 1972; Velthof et al., 1996).

The high temporal variability of  $\text{N}_2\text{O}$  concentrations in the soil profiles is in part the result of seasonal fluctuations of the predominant biological, physical and chemical factors regulating  $\text{N}_2\text{O}$  dynamics.

Some investigations revealed seasonal dynamics of  $\text{N}_2\text{O}$  concentrations in the soil solution (Bowden & Bormann, 1986; Minami & Fukushima, 1984). Other reports, however, could not confirm such systematic relations (e.g. Minami & Ohasawa, 1990).

Long-term studies often described extensive oscillations in  $\text{N}_2\text{O}$  concentrations in soil air which followed seasonal patterns (Burford & Stefanson, 1973; Burton et al., 1997; Dowdell & Smith, 1974; Eggington & Smith, 1986; Lind, 1985) even in subsoils (Burton & Beauchamp, 1994). A comparison of different ecosystems during the same period exhibited partly parallel seasonal patterns of  $\text{N}_2\text{O}$  concentrations in the soil atmospheres (Goodroad & Keeney, 1985). At a field cropped with spring barley in 1980 and 1982, similar seasonal fluctuations of  $\text{N}_2\text{O}$  concentra-

Table 2. Maximal N<sub>2</sub>O concentrations in soil air

Ecosystem	Location	Sample period	Max. N <sub>2</sub> O conc.	Reference
<i>Natural ecosystems</i>				
Sand, forest and grass	Germany	1968–1969	1.5 ppmv	Albrecht et al., 1970
White pine plantation	Wisconsin, USA	1981	2066 µg N <sub>2</sub> O l <sup>-1</sup>	Goodroad & Keeney, 1984
White pine plantation	USA	1980	10 µg N <sub>2</sub> O l <sup>-1</sup>	Goodroad & Keeney, 1985
Tallgrass prairie	USA	1980	0.4 µg N <sub>2</sub> O L <sup>-1</sup>	Goodroad & Keeney, 1985
Alpine (3286 m NN), alpine vegetation, snow-covered	Wyoming, USA	1991–1992	∅ 0.37 ppmv	Sommerfeld et al., 1993
Sub-alpine (3182 m NN), meadow, snow-covered	Wyoming, USA	1991–1992	∅ 0.36 ppmv	Sommerfeld et al., 1993
<i>Pasture</i>				
Loam, 2nd year grass ley field, mineral N-fertilization	UK	1993	250 ppmv	Ball et al., 1997
Sand soil, mown grassland, mineral N-fertilization	The Netherlands	1992–1993	4 ppmv	Velthof et al., 1996
Peat soil, mown grassland, mineral N-fertilization	The Netherlands	1992–1993	200 ppmv	Velthof et al., 1996
Silt loam, poorly drained, pasture, without N fertilization	New Zealand	1992	7 ppmv	Carran et al., 1995
Gley soil, pasture, cow slurry application	UK	1972–1973	680 ppmv	Burford, 1976
Loam, pasture, mineral N-fertilization	Australia	1968	161 ppmv	Burford & Stefanson, 1973
Drained loam, pasture, mineral N-fertilization	The Netherlands	1995	231 ppmv	Rappold & Corré, 1997
Clay soil, pasture, mineral N-fertilization	UK	1992	158 ppmv	Clayton et al. (1994)
<i>Ryegrass</i>				
Ryegrass, mineral N-fertilization, near water saturation	–	–	8000 ppmv	Delwiche & Rolston, 1976
Stagnogleyic brown earth, ryegrass, unfertilized control	UK	1978–1980	30 ppmv	Eggington & Smith, 1986
Stagnogleyic brown earth, ryegrass, Ca(NO <sub>3</sub> ) <sub>2</sub> fertilization (500 kg N ha <sup>-1</sup> )	UK	1978–1980	700 ppmv	Eggington & Smith, 1986
Stagnogleyic brown earth, ryegrass, cattle slurry (1528 kg N ha <sup>-1</sup> )	UK	1978–1980	150 ppmv	Eggington & Smith, 1986
Loam, perennial ryegrass, mineral N-fertilization	California, USA	1974	8300 ppmv	Rolston et al., 1976

Table 2. Continued

<i>Sudan grass</i>				
Sandy loam, Sudan grass, without N fertilization	California, USA	–	1.6 ppmv	Flühler et al., 1976a
Sandy loam, Sudan grass, with mineral N-fertilization	California, USA	–	1.6 ppmv	Flühler et al., 1976a
Sudan grass, 20 T manure acre <sup>-1</sup>	California, USA	1973–1974	> 60 ppmv	Focht, 1978
Sudan grass, 80 T manure acre <sup>-1</sup>	California, USA	1973–1974	>80 ppmv	Focht, 1978
<i>Fallow</i>				
Loam, fallow field	Germany	1968–1969	8 ppmv	Albrecht et al., 1970
Silt loam, fallow, without nitrogen fertilization	Canada	1992	220 ppmv	Burton et al., 1997
Silt loam, fallow, 50 kg N ha <sup>-1</sup> of liquid cattle manure applied	Canada	1992	45 ppmv	Burton et al., 1997
Sandy loam, fallow, with mineral N-fertilization	California, USA	–	9 ppmv	Flühler et al., 1976b
Loam, uncropped, almost water saturated, NO <sub>3</sub> <sup>-</sup> -fertilization	–	–	40 ppmv	Rolston, 1978
Uncropped field, manure amendment + NO <sub>3</sub> <sup>-</sup> -fertilization	–	–	> 500 ppmv	Rolston, 1978
<i>Wheat</i>				
Loam, wheat field on former pasture, mineral N-fertilization	Australia	1968	highest ∅ 61 ppmv	Burford, & Stefanson, 1973
Loam, wheat field on arable land, mineral N-fertilization	Australia	1968	100 ppmv	Burford & Stefanson, 1973
Clay soil, grass, winter wheat	UK	1971	2500 ppmv	Dowdell et al., 1972
Clay soil, Denchworth series, winter wheat/oilseed rape, directly drilled, mineral N-fertilization	UK	1977–1978	highest ∅ 410ppmv	Burford et al., 1981
Clay soil Denchworth series, winter wheat/oilseed rape, plowed mineral N-fertilization	UK	1977–1978	highest ∅ 25ppmv	Burford et al., 1981
Clay soil Lawford series, winter wheat/oilseed rape, directly drilled, mineral N-fertilization	UK	1977–1978	highest ∅ 16ppmv	Burford et al., 1981
Clay soil Lawford series, winter wheat/oilseed rape, plowed, mineral N-fertilization	UK	1977–1978	highest ∅ 2ppmv	Burford et al., 1981
Loam, winter wheat, mineral N-fertilization	UK	1994	1 ppmv	Ball et al., 1997
Clay soil, winter wheat, direct drilled, mineral N-fertilization	UK	1981	highest ∅ 1200	Colbourn et al., 1984

Table 2. Continued

<i>Barley</i>				
Loam, plowed, winter barley, mineral N-fertilization	UK	1986	> 100 ppmv	Arah et al., 1991
Loam, directly drilled, winter barley, mineral N-fertilization	UK	1986	> 200 ppmv	Arah et al., 1991
Clay loam, plowed, winter barley, mineral N-fertilization	UK	1986	> 20 ppmv	Arah et al., 1991
Clay loam, directly drilled, winter barley, mineral N-fertilization	UK	1986	50 ppmv	Arah et al., 1991
Sandy loam, spring barley, mineral N-fertilization	Denmark	1983–1984	highest $\phi$ > 55 ppmv	Christensen, 1985
Loam sand, spring barley, slurry amended	Denmark	1980–1982	> 60 ppmv	Lind, 1985
Loam sand, spring barley, 40 kg $\text{NH}_4\text{NO}_3 \text{ ha}^{-1}$ amended	Denmark	1980–1982	> 35 ppmv	Lind, 1985
Loam sand, spring barley, 160 kg $\text{NH}_4\text{NO}_3 \text{ ha}^{-1}$ amended	Denmark	1980–1982	> 50 ppmv	Lind, 1985
Loam sand, spring barley, manure amended	Denmark	1980–1982	190 ppmv	Lind, 1985
<i>Corn</i>				
Loamy sand, corn, mineral N-fertilization	Canada	1988–1990	100 ppmv	Burton & Beauchamp, 1994
Loam soil, corn, manure + mineral N-fertilization (total 181 kg N $\text{ha}^{-1}$ ), between-row	Wisconsin, USA	1981–1982	213 ppmv	Cates & Keeney 1987
Loam soil, corn, manure + mineral N-fertilization (total 181 kg N $\text{ha}^{-1}$ ), in-row	Wisconsin, USA	1981–1982	310 ppmv	Cates & Keeney 1987
Loam soil, corn, manure + mineral N-fertilization (total 237 kg N $\text{ha}^{-1}$ ), between-row	Wisconsin, USA	1981–1982	1700 ppmv	Cates & Keeney 1987
Loam soil, corn, manure + mineral N-fertilization (total 237 kg N $\text{ha}^{-1}$ ), in-row	Wisconsin, USA	1981–1982	1900 pmv	Cates & Keeney 1987
Corn, mineral N-fertilization, furrow irrigation	–	–	73 ppmv	Delwiche & Rolston, 1976
Loam, corn, without manure amendment	Canada	1993	4 ppmv	Lessard et al., 1996
Loam, corn, manure amendment (56000 kg N $\text{ha}^{-1}$ )	Canada	1993	14 ppmv	Lessard et al., 1996
Loam, corn, manure amendment (112 kg N $\text{ha}^{-1}$ )	Canada	1993	16 ppmv	Lessard et al., 1996
Silt loam, corn, no tillage, mineral N-fertilization	Illinois, USA	1981	$\phi$ 35 $\mu\text{g N}_2\text{O l}^{-1}$	Linn & Doran 1984
Silt loam, corn, plowed, mineral N-fertilization	Illinois, USA	1981	$\phi$ 12 $\mu\text{g N}_2\text{O l}^{-1}$	Linn & Doran 1984
Silt loam, corn, no tillage, mineral N-fertilization	Kentucky, USA	1981	$\phi$ 41 $\mu\text{g N}_2\text{O l}^{-1}$	Linn & Doran, 1984
Silt loam, corn, plowed, mineral N-fertilization	Kentucky, USA	1981	234 $\mu\text{g N}_2\text{O l}^{-1}$	Linn & Doran 1984

Table 2. Continued

Silty clay loam, corn, no tillage, mineral N-fertilization	Nebraska, USA	1981	$\varnothing 80 \mu\text{g N}_2\text{O l}^{-1}$	Linn & Doran 1984
Silty clay loam, corn, plowed, mineral N-fertilization	Nebraska, USA	1981	$\varnothing 39 \mu\text{g N}_2\text{O l}^{-1}$	Linn & Doran 1984
Clay loam, corn, no tillage, mineral N-fertilization	Minnesota, USA	1981	$\varnothing 73 \mu\text{g N}_2\text{O l}^{-1}$	Linn & Doran 1984
Clay loam, corn, plowed, mineral N-fertilization	Minnesota, USA	1981	$\varnothing 50 \mu\text{g N}_2\text{O l}^{-1}$	Linn & Doran 1984
Silt loam, corn, no-tillage, without N-fertilization	Illinois, USA	1981	$\varnothing 6 \mu\text{g N}_2\text{O l}^{-1}$	Linn & Doran 1984
Silt loam, corn, plowed, without N-fertilization	Illinois, USA	1981	$\varnothing 2 \mu\text{g N}_2\text{O l}^{-1}$	Linn & Doran 1984
Silt loam, corn, no-tillage, without N-fertilization	Kentucky, USA	1981	$\varnothing 5 \mu\text{g N}_2\text{O l}^{-1}$	Linn & Doran 1984
Silt loam, corn, plowed, without N-fertilization	Kentucky, USA	1981	$\varnothing 2 \mu\text{g N}_2\text{O l}^{-1}$	Linn & Doran 1984
Silty clay loam, corn, no-tillage, without N-fertilization	Nebraska, USA	1981	$\varnothing 6 \mu\text{g N}_2\text{O l}^{-1}$	Linn & Doran 1984
Silty clay loam, corn, plowed, without N-fertilization	Nebraska, USA	1981	$\varnothing 34 \mu\text{g N}_2\text{O l}^{-1}$	Linn & Doran 1984
Clay loam, irrigated corn field, mineral N-fertilization	Colorado, USA	1978	> 80 ppmv	Mosier & Hutchinson, 1981
<i>Diverse systems</i>				
Loam sand, beets, slurry amendment	Denmark	1981	120 ppmv	Lind, 1985
Loam sand, beets, manure amendment	Denmark	1981	> 15 ppmv	Lind, 1985
Loam sand, beets, 40 kg $\text{NH}_4\text{NO}_3 \text{ ha}^{-1}$ amended	Denmark	1981	> 50 ppmv	Lind, 1985
Loam sand, beets, 160 kg $\text{NH}_4\text{NO}_3 \text{ ha}^{-1}$ amended	Denmark	1981	> 70 ppmv	Lind, 1985
Silt loam, alfalfa	Canada	1992	490 ppmv	Burton et al., 1997
Compacted sandy loam, green fodder, mineral N-fertilization	Norway	1991	1900 ppmv	Hansen et al., 1993
Loam, garden	Germany	1968–1969	3.5 ppmv	Albrecht et al., 1970
Sandy loam, mineral N-fertilization	UK	1952	2000 ppmv	Arnold, 1954
Clay soil	Denchworth, UK	1970–1971	highest $\varnothing$ 800 ppmv	Burford et al. (1978a)
Clay soil	Denchworth, UK	1975–1976	highest $\varnothing$ 9 ppmv	Burford et al. (1978a)
Clay soil	Evesham, UK	1972–1973	highest $\varnothing$ 370 ppmv	Burford et al. (1978a)
Clay soil	Evesham, UK	1973–1974	highest $\varnothing$ 460 ppmv	Burford et al. (1978a)
Clay soil	Evesham, UK	1974–1975	highest $\varnothing$ 325 ppmv	Burford et al. (1978a)
Clay loam, Drayton	UK	1971–1972	1000 ppmv	Dowdell & Smith, 1974
Clay loam, Buckland	UK	1971–1972	6500 ppmv	Dowdell & Smith, 1974



Table 2. Continued

Silt loam, manure-amended soil	Wisconsin, USA	1980– 1981	1663 $\mu\text{g}$ $\text{N}_2\text{O l}^{-1}$	Goodroad & Keeney, 1984
Silt loam, straw-amended soil	Wisconsin, USA	1981	1082 $\mu\text{g}$ $\text{N}_2\text{O l}^{-1}$	Goodroad & Keeney, 1984
Silt loam, manure + $\text{NH}_4\text{NO}_3$ amendment	USA	1980	243 $\mu\text{g}$ $\text{N}_2\text{O L}^{-1}$	Goodroad & Keeney, 1985
Silt loam, $\text{NH}_4\text{NO}_3$ amendment	USA		7 $\mu\text{g}$ $\text{N}_2\text{O L}^{-1}$	Goodroad & Keeney, 1985

○ = average; – all  $\text{N}_2\text{O}$  concentrations in soil air were measured in field experiments without the application of acetylene ( $\text{C}_2\text{H}_2$ ).

tions in soil air were measured in spite of different patterns of rainfall. In part, these parallel seasonal dynamics were attributed to the seasonal nutrient uptake of the crop, thus regulating the nitrate content of the soil (Lind, 1985). At other locations the  $\text{N}_2\text{O}$  concentrations could be close to ambient levels almost throughout the year (Albrecht et al., 1970).

Denitrification being a major  $\text{N}_2\text{O}$  production process, clear relationships between increasing concentrations of  $\text{N}_2\text{O}$  and decreasing availability of oxygen in the soil air have often been shown (Burford et al., 1981; Dowdell & Smith, 1974; Eggington & Smith, 1986; Hansen et al., 1993; Parkin & Meisinger, 1989; Rolston et al., 1976). Furthermore, parallel dynamics of the  $\text{N}_2\text{O}$  and carbon dioxide concentrations in the soil atmosphere were observed as both rose during oxygen depletion (Ball et al., 1997; Linn and Doran, 1984; Parkin and Meisinger, 1989). A close positive correlation between  $\text{N}_2\text{O}$  and ethylene – which is also a parameter for anaerobiosis in soils was found in clay soils during the winter period (Dowdell et al., 1972).

Attempts at correlating changes in  $\text{N}_2\text{O}$  concentrations in soil air with the  $\text{N}_2\text{O}$  emission dynamics have led to inconsistent findings. Some studies showed close positive relationships, the greatest concentrations of  $\text{N}_2\text{O}$  in the soil air coinciding with the strongest  $\text{N}_2\text{O}$  fluxes (Arah et al., 1991; Cates & Keeney, 1987; Christensen, 1985; Hansen et al., 1993; Lind, 1985; Mosier & Hutchinson, 1981). In another investigation good correlation was observed in parts merely in summer. During a period of extremely high  $\text{N}_2\text{O}$  release the  $\text{N}_2\text{O}$  concentrations in soil air and soil solution increased simultaneously. In contrast, during winter the highest  $\text{N}_2\text{O}$  accumulation in the soil air occurred just as the  $\text{N}_2\text{O}$  emissions were the lowest ones for the entire season (Burford et al., 1981). Benckiser et al. (1986) noted that the relationship between  $\text{N}_2\text{O}$  entrapped in soil air and its release to the at-

mosphere became closer when the soil water content rose. Christensen (1985) also confirmed an influence of the soil moisture on this correlation. In wet soils the  $\text{N}_2\text{O}$  flux increased four times more slowly with rising  $\text{N}_2\text{O}$  concentrations in soil air than in dry soils due to a much smaller diffusion coefficient.

Other studies found no or only weak positive correlations of the  $\text{N}_2\text{O}$  concentrations in the soil air and the  $\text{N}_2\text{O}$  emissions (Ball et al., 1997; Clayton et al., 1994; Goodroad & Keeney, 1985; Lessard et al., 1996; Velthof et al., 1996).

There may be many different explanations for these discrepancies. The main  $\text{N}_2\text{O}$  production may take place either in the upper few centimetres of the soil with rapid diffusion out of it, or too deep in the soil profile causing a time lag between production and emission of  $\text{N}_2\text{O}$  (Goodroad & Keeney, 1985). Other factors may be the large spatial variability of  $\text{N}_2\text{O}$  concentrations and  $\text{N}_2\text{O}$  fluxes or the dissolution of  $\text{N}_2\text{O}$  in the soil solution (Velthof et al., 1996). Furthermore, high water contents may restrict  $\text{N}_2\text{O}$  diffusion and enforce the microbial reduction of  $\text{N}_2\text{O}$  to  $\text{N}_2$  (Lessard et al., 1996).

In addition, there are difficulties with regard to the measurement technique. The estimation of the gas transfer factor between soil air and atmosphere is problematic under field conditions. In general, the soil volume represented by the measurement of  $\text{N}_2\text{O}$  in soil air is not clearly defined. Therefore, Clemens & Vandr  (1997) developed a simple technique to determine the total  $\text{N}_2\text{O}$  content ( $\text{N}_2\text{O}$  in soil air and in soil solution) of a defined soil volume. Thereby, significant positive correlations of the total  $\text{N}_2\text{O}$  content in the upper 5 cm of the soils and  $\text{N}_2\text{O}$  emissions were shown in both laboratory and field experiments.

## Factors and processes controlling the dynamics of N<sub>2</sub>O within the soils

### Properties of N<sub>2</sub>O

Nitrous oxide is linear, mesomer and, due to its non-symmetric structure, it is slightly polar and has a weak dipolemoment (quadrupolemoment) of  $0.55 \times 10^{-30}$  C m (Christen, 1988). Under temperature regimes common in soils it is chemically inert. However, Moraghan and Buresh (1977a) suggested that N<sub>2</sub>O can be chemically reduced by Fe<sup>2+</sup> in the presence of Cu<sup>2+</sup>.

Nitrous oxide is quite similar to carbon dioxide in mass, size, shape, electronic configuration, molecular interaction parameters, and Lennard–Jones potential (Browning & Weiland, 1994; Henni & Mather, 1995; Laddha et al., 1981; Weiss & Price, 1980). Since in general N<sub>2</sub>O does not react chemically with a solvent — in contrast to CO<sub>2</sub> — their physical analogy is used in chemical technologies. Many recent studies have been conducted with N<sub>2</sub>O to indirectly obtain information on CO<sub>2</sub> solubility and diffusion in various solvents (Table 3, 5).

In water, N<sub>2</sub>O is highly soluble and forms two alternative structures of complexes, a planar N···O bonding and a OH···N hydrogen bonding (Cox et al., 1994). In nonpolar solutions, however, the solubility of N<sub>2</sub>O is even much greater than in water due to its small dipolemoment.

### Solubility of N<sub>2</sub>O

The solubility of a gas can be described by Henry's law (Eq. (1)), which asserts that the partial pressure of a gas  $P$  (kPa) in equilibrium with a liquid is proportional (Henry's constant for pure water  $H^0$ ; kPa l mol<sup>-1</sup>) to the concentration of the dissolved gas  $C_{liquid}$  (mol l<sup>-1</sup>). Henry's law only holds for real gases at low pressures of about  $P \leq 500$  kPa (Browning & Weiland, 1994).

$$P = H^0 C_{liquid} \quad (1)$$

In closed vessels the volume of a gas dissolved in a given liquid volume at a fixed temperature is independent of the partial pressure (Davidson & Firestone, 1988; Moraghan & Buresh, 1977b). Therefore the following simple formula (Eq. (2)) can be used to determine the amount of dissolved N<sub>2</sub>O in closed systems, where  $y$  is the mass of dissolved N<sub>2</sub>O (mg),  $x$  is the mass of N<sub>2</sub>O (mg) in the headspace and  $\alpha$  is

Table 3. Solubility of N<sub>2</sub>O in water at 25 °C (from Davis and Pogainis, 1995)

Author	Solubility (Pa m <sup>3</sup> mol <sup>-1</sup> )
Joosten & Danckwerts, 1972	4151
Haimour & Sandall, 1984	4173
Versteeg & van Swaaij, 1988	4132
Al-Ghawas et al., 1989	3910
Xu et al., 1991	4176
Saha et al., 1993	4120
Browning & Weiland, 1994	4234
Rinker et al., 1995	4101
Davis & Pogainis, 1995	4179

the Bunsen absorption coefficient (cm<sup>3</sup> N<sub>2</sub>O dissolved per cm<sup>3</sup> water):

$$y = \alpha x (\text{solution volume/headspace volume}) \quad (2)$$

The solubility of N<sub>2</sub>O (Table 3) depends on temperature, salt concentration and pH of the solvent. Dissolved organic matter may also alter N<sub>2</sub>O solubility, but this has not yet been explored. The effects of temperature and salt concentration on the solubility of N<sub>2</sub>O shall first be discussed separately.

### Temperature

An increase in temperature decreases the solubility of N<sub>2</sub>O in a non-linear way. This temperature-induced solubility change is relatively strongest at the low temperatures prevalent in soils. For example, at 0 °C the N<sub>2</sub>O solubility is about twice the solubility at 19 °C, while between 19 °C and 38 °C the solubility decreases only by about 18%.

The temperature dependence of gas solubility can be expressed with the following empirical expression (Eq. (3)) where  $\beta$  is the Ostwald solubility coefficient (cm<sup>3</sup> gas adsorbed per cm<sup>3</sup> liquid at given pressure and temperature) and  $T$  is the absolute temperature (K).  $A_1, A_2, A_3$  are gas specific coefficients (Macintyre et al., 1995; Wilhelm et al., 1977):

$$\ln \beta = A_1 + A_2 T^{-1} + A_3 \ln T \quad (3)$$

### Salinity

The increase of the ionic strength of a solvent causes a reduction of the solubility of non-polar gases because of the polarizing effect of salts on the solvent (salting-out effect, Setchenow effect). This can be expressed

by (Eq. (4)), where  $B$  is a constant and  $S$  is the salinity (g salt  $l^{-1}$ , Macintyre et al., 1995):

$$\ln \beta = BS \quad (4)$$

Next to the total concentration of ions, the type of cations and anions is important for the salting-out effect. With the modified empirical equation from Van Krevelen & Hoftijzer (1948) based on the original method from Setchenow (1889) the Henry's law constant  $H$  for differently composed electrolyte solutions can be estimated using (Eq. (5)), where  $h$  is a proportionality factor and  $I$  is the ionic strength (mol  $l^{-1}$ ):

$$\log(H/H^0) = hI \quad (5)$$

The ionic strength of the solution is given by (Eq. (6)), where  $C_i$  is the concentration of the ion  $i$  (mol  $l^{-1}$ ) and  $z_i$  is the valency of the ion  $i$ :

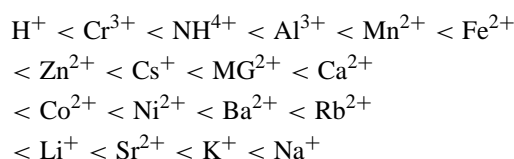
$$I = \frac{1}{2} \sum C_i z_i^2 \quad (6)$$

The proportionality factor  $h$  (Eq. (7)) is the sum of three constants that depend on the system, where  $h_+$  is the van Krevelen coefficient for the cation,  $h_-$  is the van Krevelen coefficient for the anion, and  $h_g$  is the van Krevelen coefficient for the dissolving gas type:

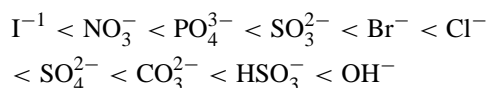
$$h = h_+ + h_- + h_g \quad (7)$$

In general, cations have a stronger salting-out potential than anions. Empirical observations lead to the following hierarchy of increasing salting-out potentials on non-polar gases:

*Hierarchy of salting-out potentials of cations*  
(Ueyama & Hatanaka, 1982):



*Hierarchy of salting-out potentials of anions*  
(Ueyama & Hatanaka, 1982):



The  $H^+$  ion has a very weak salting-out potential, whereas the  $OH^-$  ion has got a strong one. Therefore  $N_2O$  is more soluble in acidic solutions than in alkaline ones. There seems to be a linear relation between pH and  $N_2O$  solubility (Lapègue et al., 1997). In the drainage water of a vegetable field the pH changed between 5.0 and 7.5. The highest concentrations of dissolved  $N_2O$  were measured at the lower pH (Minami & Ohsawa, 1990).

The empirical method of Van Krevelen & Hoftijzer (1948) has several restrictions concerning the influence of pressure, temperature, ionic strength and types of electrolytes on the coefficients  $h_+$ ,  $h_-$ ,  $h_g$  (Browning & Weiland, 1994; Onda et al., 1970; Ueyama & Hatanaka, 1982; Yasunishi & Yoshida, 1979). Furthermore, a standard reference system for  $h_+$ ,  $h_-$ ,  $h_g$  is required (Ueyama & Hatanaka, 1982).

For mixed electrolytes the gas solubility change could be determinable by the following equation (Eq. (8)); (Danckwerts, 1970; Joosten & Danckwerts, 1972). This has not yet been experimentally proven, however:

$$\log(H/H^0) = \sum h_i I_i \quad (8)$$

The combined temperature and salt concentration dependency of the solubility  $K^o$  (mol  $l^{-1}$  atm $^{-1}$ ) of  $N_2O$  can be sufficiently determined by an empirical equation (Eq. (9)), which is based on the integrated van't Hoff equation and the logarithmic Setchenow salinity dependence of gas solubility:

$$\begin{aligned} \ln K^o &= A1 + A2(100T^{-1}) + A3 \ln(T100^{-1}) \\ &+ S[B1 + B2(T100^{-1}) + B3(T100^{-1})^2] \end{aligned} \quad (9)$$

The  $A$  and  $B$  are constants. They were determined for seawater (0–40 °C; 0–40 g salt  $l^{-1}$ ) by Weiss & Price (1980;  $A1 = -62.7062$ ,  $A2 = +97.3066$ ,  $A3 = +24.1406$ ,  $B1 = -0.058420$ ,  $B2 = +0.033193$ ,  $B3 = -0.0051313$ ).

Due to its complexity, Browning & Weiland (1994) stated that it seems impossible to create a system predicting Henry's law constants of gases for mixed electrolyte solutions from pure component or single electrolyte data. It may be possible to solve this problem by means of the progress of the physical theory of gas solubility.

Formerly, different theories on the salting-out effect of aqueous salt solutions on non-polar gases like the hydration theory, the electrostatic theory, the van der Waals theory and the internal pressure concept were developed. Yet none of them could accurately ex-

plain the phenomena of gas solubility in salt solutions in total (Long & McDevit, 1952).

Nowadays an applicable model of molecular thermodynamics of gas solubility exists, which is based on the extended scaled-particle theory. It successfully predicts the solubility of gases in non-polar and polar solvents as well as in aqueous electrolyte solutions (Hu et al., 1984; 1985). For N<sub>2</sub>O this model was even used with success to predict the solubility in ternary and quaternary mixed solvents over a wide range of temperatures and concentrations (Li & Mather, 1994).

A very comprehensive listing of the experimental solubility data on N<sub>2</sub>O in different liquids (water, seawater, electrolyte solutions, organic compounds, etc.) has been documented by Young (1981) for data up to 1979.

There are difficulties in transferring the solubility data for N<sub>2</sub>O measured in laboratories in controlled two-phase systems to the conditions in soils.

For instance it has been suggested that there is an influence of the interfacial areas of soil–water, soil–air and water–air on the solubility of N<sub>2</sub>O. In soil laboratory experiments the N<sub>2</sub>O solubility was several times higher (up to a factor of 16) for water contents ranging from 0 to 8% than would be expected from Henry's Law for unbound, pure water (Stegemann, 1989). Since the N<sub>2</sub>O 'solubility' increased with clay content, adsorption effects may have been the cause.

In general, salt concentrations of soil solutions are very low compared to sea water, for example; thus the salting-out effect on N<sub>2</sub>O should be small. But in exceptional situations high electrolyte concentrations may appear (e.g. after fertilizer application, during freezing when salts are excluded from ice and concentrate in liquid water films, during dry periods with nitrate accumulation or due to other human activities increasing the salt content of soils, like the use of de-icing salts).

## N<sub>2</sub>O transport

The movement of gases in soils is based on molecular diffusion and convection. The air permeability of a soil is determined by air-filled porosity, pore geometry and pore continuity, and therefore depends indirectly on soil texture, soil structure, bulk density and soil water status. The air permeability is an indirect parameter for the soil aeration status. The proportion of inter-aggregate pores to intra-aggregate pores is of importance as the highest quantities of gases are transported

Table 4. Diffusion coefficients of N<sub>2</sub>O in air at 25 °C

Author	Diffusion coefficient (cm <sup>2</sup> s <sup>-1</sup> )
Barr & Watts, 1972	0.141
Pritchard & Currie, 1982	0.168

within the macropores, whereas the microbiological production of N<sub>2</sub>O occurs to a great extent in the water-filled micropores.

### Molecular diffusion

Diffusion is a molecular motion caused by a gradient in concentration created in soils by microbial production and consumption of gases. Molecular diffusion is the main transport mechanism for gases in soils, whereas Knudsen diffusion is of no relevance. For air and water, the diffusion of a gas can be described by the empirical First Fick's Law (Eq. (10)) where  $F$  is the gas flux (mol cm<sup>2</sup> s<sup>-1</sup>),  $D_0$  is the diffusion coefficient (cm<sup>2</sup> s<sup>-1</sup>),  $C$  is the gas concentration (mol l<sup>-1</sup>) and  $s$  is the diffusion distance (cm):

$$F = -D_0(\delta C \delta s^{-1}) \quad (10)$$

In air the diffusion coefficient  $D_{0air}$  is a function of the properties of the diffusing gas, temperature and atmospheric pressure.  $D_{0air}$  increases at a rate of about 0.7% per K increase in temperature, and decreases at a rate of about 1% per kPa increase in atmospheric pressure. These influences are represented by (Eq. (11)).  $D_{0air1}$ ,  $D_{0air2}$  are the diffusion coefficients for a certain gas in a particular combination at total pressure  $P1$  and  $P2$ , respectively, and at the absolute temperature  $T1$  and  $T2$ , respectively (Kennard, 1938).

$$D_{0air1} = D_{0air2} P2/P1 (T1/T2)^{1.75} \quad (11)$$

The literature data for the diffusion coefficient of N<sub>2</sub>O in the gaseous phase at 25 °C vary from 0.141 to 0.166 cm<sup>2</sup> s<sup>-1</sup> depending on the determination procedure (Table 4).

The diffusion coefficient of N<sub>2</sub>O in water is around four orders of magnitude smaller than in air (Table 5). Additionally, the diffusion coefficient of N<sub>2</sub>O in electrolyte solutions  $D_{liquid}$  is smaller than that in pure water  $D_{0liquid}$ . The presence of ions in the liquid alters the free energy of activation and therefore the movement of gas molecules by diffusion. The change of the activation energy is proportional to the constant  $y$ , which is described by (Eq. (12)), where  $x_i$  is the mole

Table 5. Diffusion coefficients of N<sub>2</sub>O in water

Author	Temperature (°C)	Diffusion coefficient (cm <sup>2</sup> s <sup>-1</sup> 10 <sup>-5</sup> )
Joosten & Danckwerts, 1972	25	1.92
Versteeg & van Swaaij, 1988	25	1.84
Al-Ghawas et al., 1989	30	1.607
Tamimi et al., 1994	25	1.88

fraction of electrolyte  $i$  which dissociates in solution into  $ni$  particles:

$$y = \sum xi / (1 - \sum xi + \sum ni xi) \quad (12)$$

Under simplifying assumptions the variation in diffusivity with  $y$  is given by (Eq. (13)), where  $A$  is a constant:

$$D_{\text{liquid}}/D_{\text{oliquid}} = \exp(-Ay) \quad (13)$$

The variation in viscosity of the solution with  $y$  can be expressed with a similar (Eq. (14)), where  $\eta_o$  is the viscosity of pure water (g cm<sup>2</sup> s<sup>-1</sup>),  $\eta$  the viscosity of the electrolyte solution and  $B$  is a constant:

$$\eta_o/\eta = \exp(-By) \quad (14)$$

Each special electrolyte causes differences in ion-solute, water-solute, ion-water and water-water interactions to a different extent. In an experiment for determining the diffusivity of N<sub>2</sub>O in an equimolar mixed solution of K<sub>2</sub>CO<sub>3</sub> and KHCO<sub>3</sub> a linear relationship between  $\log D_{\text{liquid}}/D_{\text{oliquid}}$  and  $y$  as well as between  $\log D_{\text{liquid}}/D_{\text{oliquid}}$  and  $\log \eta_o/\eta$  was measured (Joosten & Danckwerts, 1972).

In order to adapt Fick's Law to the porous media of the soils, the relative diffusion coefficient  $D_{\text{air}}/D_{0\text{air}}$  was established.  $D_{\text{air}}/D_{0\text{air}}$  in soils is mainly controlled by air-filled porosity, pore tortuosity, pore constrictivity and pore continuity. This can be expressed for dry soils by the semi-empirical (Eq. (15)), where  $D_{\text{air}}$  is the diffusion coefficient in dry porous media,  $E_g$  is the air-filled porosity (cm<sup>3</sup> cm<sup>-3</sup>),  $a$ ,  $b$  are empirical specific material constants for pore tortuosity and pore continuity (e.g. Currie, 1960):

$$D_{\text{air}}/D_{0\text{air}} = aE_g^b \quad (15)$$

In a loose dry packing of spherical particles, where the pores are continuous but the path length is increased by pore tortuosity, the maximal gas diffusivity (Eq. (16)) will be (Penman, 1940):

$$D_{\text{air}}/D_{0\text{air}} = 0.66E_g \quad (16)$$

Generally, the diffusion coefficient  $D_{\text{air}}$  of a real dry soil is about one order of magnitude smaller than the diffusion coefficient in pure air  $D_{0\text{air}}$  (Lalisse-Grundmann & Chalamet, 1987; Stegemann, 1989). The exact relative diffusion coefficients, however, vary largely between different soils.

The cited formulas for the relative diffusion coefficient are only applicable for a two-phase system, as in a three-phase system of an unsaturated soil different interface effects can occur. The diffusivity of soils with volumetric water contents under 10% seems to be uninfluenced by water and can therefore be calculated as for dry soils (Reible & Shair, 1982).

The relative diffusion coefficient of an unsaturated soil depending on water content and total porosity can be described by (Eq. (17)) of Millington & Quirk (in: Jin & Jury, 1996) where  $E$  is the total porosity (cm<sup>3</sup>/cm<sup>3</sup>):

$$D_{\text{air}}/D_{0\text{air}}(E_g) = E_g^2/E^{2/3} \quad (17)$$

A detailed comparison and discussion of different theoretical methods for the estimation of the gas diffusivity of an unsaturated soil was made for example by Collin & Rasmuson (1988). When the soil moisture increases from air dry to field capacity, the diffusion coefficient decreases by four orders of magnitude as the cross-sectional area for flow is drastically reduced and the tortuosity of the flow path rises. Not till the soil is almost water saturated does the gas diffusion through the water-filled pore space itself start to contribute significantly to the total diffusional transport (Collin & Rasmuson, 1988).

### Convection

Convection is the mass transport of molecules caused by a total gradient in pressure due to wind, barometric pressure changes, temperature fluctuations or infiltrating water. It can be described by Darcy's equation (Eq. (18)):

$$dV/dt = -A(k_a/\eta_{\text{gas}}dP/ds) \quad (18)$$

where  $dV/dt$  is the mass of gas flow per unit time ( $\text{g cm}^{-2} \text{s}^{-1}$ ),  $A$  is the cross-sectional area of the porous medium ( $\text{cm}^2$ ),  $k_a$  is the intrinsic air permeability coefficient of the porous medium ( $\text{cm}^2$ ),  $\eta_{\text{gas}}$  is the dynamic viscosity of the gas, and  $dP/ds$  is the pressure gradient.

Generally, mass flow in soils may be relevant only over very short distances. Therefore it is ignored in most gas transport models (Jury et al., 1982). Exceptionally diffusive and convective gas transport processes are combined in gas transport models, for example by Pritchard & Currie (1982) or by Grant et al. (1993a,b) for  $\text{N}_2\text{O}$ . Very seldom is convection taken into account to explain  $\text{N}_2\text{O}$  field experiment data. One example is the study of Christensen (1985) for an arable field, where part of the increase of the  $\text{N}_2\text{O}$  flux over 9 h was explained by the decrease in air pressure. Other cases where convection may become important are soils with strong groundwater table fluctuations. For instance in a peat soil the rise of the water table lead to an increase in the  $\text{N}_2\text{O}$  concentration in the remaining soil air, in part probably due to the displacement of soil air from the deeper layers (Velthof et al., 1996).

#### *Adsorption*

In general, the adsorption of gases at the solid matrix is of no relevance under field conditions. In laboratory experiments  $\text{N}_2\text{O}$  was strongly adsorbed only by oven-dried soils. This adsorption was a linear function of the clay content. Air-dried soils (water content 1–3%), however, did not adsorb  $\text{N}_2\text{O}$  (Stegemann, 1989; Stegemann & Cammenga, 1990).

#### *Cultivation practices and $\text{N}_2\text{O}$ accumulation*

Cultivation practices may alter soil physical structure, water regime, distribution of nutrients and microbiological processes. Therefore they have an influence on the composition of the soil atmosphere (Burford & Stefanson, 1973). For example, in soils compacted by tractors,  $\text{N}_2\text{O}$  concentrations in the soil air were significantly higher than in the control plots (Hansen et al., 1993).

There are indications that in non-tilled soils more  $\text{N}_2\text{O}$  may accumulate in the soil air than in plowed soils. For instance, in an investigation by Linn & Doran (1984), at four locations in the USA, the bulk density of the non-tillage soils was higher and the pore space was less than in the plowed soils. Thus the water-filled pore space at a depth of 0 – 75 mm av-

eraged 62 and 44%, respectively. In average the  $\text{N}_2\text{O}$  concentration in the soil atmosphere (0 – 75 mm) of the non-tilled soils was 9.4 times higher than in the plowed soils during a 24 h period.

During a long-term study, significantly larger concentrations of  $\text{N}_2\text{O}$  were reported for the soil air of direct-drilled clay soils (maximal monthly average 410 ppm) compared to plowed clay soils (maximal monthly average 25 ppm) especially during the winter period (Burford et al., 1981).

The interpretation of the effects of cultivation practices must take into account the depth of the  $\text{N}_2\text{O}$  measurement. A study conducted during a single vegetation period with many soils and treatments showed that  $\text{N}_2\text{O}$  concentrations in the soil atmosphere of the deeper layers were generally about one order of magnitude higher than those at the soil surface. No significant differences between the variants could be shown for the depth of 5 cm. But the  $\text{N}_2\text{O}$  concentrations in the direct-drilled plots at 20 and 40 cm depth generally exceeded those in the plowed fields. Additionally, an effect of the soil type on  $\text{N}_2\text{O}$  concentrations in soil air was reported (Arah et al., 1991).

Although differences between cultivation practices have been observed, in general, there are also studies which do not support this finding. Burton & Beauchamp (1994), for example, found no significant differences between  $\text{N}_2\text{O}$  concentrations in the soil atmospheres of non-tilled soils compared to plowed soils. This points to the complex interactions of processes governing  $\text{N}_2\text{O}$  concentrations in soils, which may be affected in different directions through soil cultivation. On the one hand, plowing may increase soil air permeability thus decreasing  $\text{N}_2\text{O}$  concentrations. On the other hand, organic material may be buried by plowing, which may in turn enforce  $\text{N}_2\text{O}$  production.

#### *Factors regulating $\text{N}_2\text{O}$ production*

A common procedure in natural science is to try to interpret observations from field experiments by correlating the parameters measured. Thereby, hypotheses about the dominant processes and the factors controlling them can be made.

In biotic systems denitrification is generally assumed to be the most important process from which  $\text{N}_2\text{O}$  evolves as a byproduct. Therefore many attempts were undertaken to correlate the temporal dynamics of  $\text{N}_2\text{O}$  accumulation in soil solution or soil air with the temporal dynamics of the main factors assumed to

regulate denitrification (nitrogen, water, temperature). The summary of these correlations — reported in a large number of studies — shows concurrent patterns but also contradictions.

It has also to be taken into account that during nitrification  $\text{N}_2\text{O}$  may be generated too. As nitrification and denitrification may be coupled and may occur simultaneously in soils, a clear distinction between these  $\text{N}_2\text{O}$  sources is often impossible.

### *Nitrogen*

According to many reports there were strongly positive correlations between nitrate ( $\text{NO}_3^-$ ) concentrations in soil solution and concentrations of  $\text{N}_2\text{O}$  in soil air (e.g. Arah et al., 1991; Benckiser et al., 1986; Dowdell & Smith, 1974) or soil solution (e.g. Bowden & Bormann, 1986; Davidson & Firestone, 1988; Davidson & Swank, 1990) in several ecosystems.

Therefore the  $\text{N}_2\text{O}$  accumulation in soil air and soil solution was often also closely correlated with factors altering the  $\text{NO}_3^-$  concentrations of the soil solution, mainly mineralization dynamics and external nitrogen inputs.

Among other things ecosystems differ with regard to their inherent characteristics of mineralization potentials. For this reason, extremely high concentrations of  $\text{N}_2\text{O}$  dissolved within the soil solutions of organic soils (Guthrie & Duxbury, 1978; Terry et al., 1981) could be an indirect indicator of a large potential of these soils for the release of nitrogen through the process of mineralization. This hypothesis was supported by a comparative analysis, which showed that the  $\text{N}_2\text{O}$  concentrations in the soil air of a peat soil were one order of magnitude higher than in a sandy soil (Velthof et al., 1996). Significant differences between the  $\text{N}_2\text{O}$  soil air concentrations of a coniferous forest soil and of a prairie soil — though both sites gained nitrogen solely from biological fixation and wet deposition — may also be an indicator for different nitrogen turnover rates in these ecosystems (Goodroad & Keeney, 1985).

The mineralization rates of soils may temporarily be intensified, leading to  $\text{N}_2\text{O}$  accumulations. For example, at different locations during springtime an increase in dissolved  $\text{N}_2\text{O}$  concentrations simultaneously with increasing nitrate concentrations in the soil solutions were observed (Davidson & Firestone, 1988; Davidson & Swank, 1990). At a forest site the dissolved  $\text{N}_2\text{O}$  concentrations rose up to two orders of magnitude above ambient due to recent clear cutting and the subsequently highly enhanced mineralization rates (Bowden & Bormann, 1986).

There are several studies revealing a strongly positive correlation between external nitrogen (N) inputs into soils and increasing  $\text{N}_2\text{O}$  concentrations in soil solution or soil air.

In many investigations, directly after N fertilization of the soils, the concentrations of solubilized  $\text{N}_2\text{O}$  in soil solution/drainage water (Minami & Fukushima, 1984; Minami & Ohasawa, 1990; Samson et al., 1990; Schnabel & Stout, 1994) or soil air rose drastically (Arnold, 1954; Burford, 1976; Burford & Stefanson, 1973; Cates & Keeney, 1987; Delwiche & Rolston, 1976; Eggington & Smith, 1986; Flühler et al., 1976a; Goodroad & Keeney, 1985; Hansen et al., 1993; Lessard et al., 1996; Lind, 1985; Linn & Doran, 1984; Mosier & Hutchinson, 1981; Rolston, 1978; Rolston et al., 1976; Velthof et al., 1996).

High  $\text{N}_2\text{O}$  accumulations in soil air as a result of N application were usually short lived and started to decrease after some days (Mosier & Hutchinson, 1981; Rolston et al., 1976). In other studies, however, N amendment led to significantly increased  $\text{N}_2\text{O}$  concentrations in soil air compared with unfertilized variants, which could last for several months (Eggington & Smith, 1986) or even for longer than 1 year (Burford, 1976; Cates & Keeney, 1987; Eggington & Smith, 1986).

The extent of the  $\text{N}_2\text{O}$  accumulation in soils is partly a function of the quantity of mineral N fertilizer supplied. For instance, in a long-term study conducted at a floodplain with well and poorly drained soils under ryegrass the concentrations of dissolved  $\text{N}_2\text{O}$  in the soil solution varied by orders of magnitude dependent on the N-amendment rates (0–252 kg  $\text{KNO}_3$  ha<sup>-1</sup>; Schnabel & Stout, 1994). Following N-fertilizer band application in a maize field  $\text{N}_2\text{O}$  concentrations in soil air were larger within the rows than between them and higher in the variants that had obtained 237 kg N ha<sup>-1</sup> than in those that had received 181 kg N ha<sup>-1</sup> (Cates & Keeney, 1987).

Apart from the quantity of N fertilizer applied, its type and availability may be of relevance for the extent of the  $\text{N}_2\text{O}$  accumulation in soils. A comparison of three different field treatments showed that the  $\text{N}_2\text{O}$  concentrations in soil air were highest after the application of  $\text{Ca}(\text{NO}_3)_2$ , followed by the cattle slurry variant and the unfertilized control, although most total N was added by the cattle slurry (Eggington & Smith, 1986). In contrast, in a study which lasted for 3 years, the  $\text{N}_2\text{O}$  concentrations in soil air were not significantly different between variants treated with slurry, manure or mineral fertilizer (Lind, 1985).

Nitrogen fertilization of soils caused no increase of the  $\text{N}_2\text{O}$  concentrations in soil air when factors other than N were limiting denitrification. For example, the addition of nitrate to a field in autumn led to  $\text{N}_2\text{O}$  peaks in the soil air but not during spring and summer, although the oxygen levels were low (Eggington & Smith, 1986). Another study registered differences between the just fertilized and the unfertilized plots only under wet conditions, whereas under dry conditions there was no  $\text{N}_2\text{O}$  evolution at all within the soils (Flühler et al., 1976a).

A further type of external N-input is the application of sewage sludge to soils. On land excessively irrigated with municipal sewage effluents  $\text{NO}_3^-$  leached into the subsoil and there it was denitrified. As a consequence, highly increased  $\text{N}_2\text{O}$  concentrations in the soil solution in the unsaturated zone were observed (Ronen et al., 1988).

No information is available on the influence of atmospheric N depositions on  $\text{N}_2\text{O}$  concentrations in soil air or soil solution. But atmospheric N depositions may be locally significant external N-inputs, which may alter the nutrient cycling in ecosystems.

#### *Water*

The water regime of a soil plays a key role in the dynamics of  $\text{N}_2\text{O}$  production, reduction and transport. High water contents stimulate denitrification and thus enforce the production of  $\text{N}_2\text{O}$ . On the other hand, high soil moisture means a restriction of the diffusion of  $\text{N}_2\text{O}$ . Therefore the residence time of  $\text{N}_2\text{O}$  in the soil increases and microorganisms gain time to reduce it to  $\text{N}_2$ .

In many studies a highly positive correlation between increasing water content in the soil and rising concentrations of  $\text{N}_2\text{O}$  in the soil solution (Davidson & Firestone, 1988; Davidson & Swank, 1990; Dowdell et al., 1979; Schnabel & Stout, 1994) and soil air was demonstrated (Benckiser et al., 1986; Burford, 1976; Burford & Stefanson, 1973; Cates & Keeney, 1987; Christensen, 1985; Flühler et al., 1976a,b; Goodroad & Keeney, 1985; Hansen et al., 1993; Lind, 1985; Linn & Doran, 1984; Mosier & Hutchinson, 1981; Rappold & Corré, 1997; Velthof et al., 1996).

On the long run there is an interdependence between the position in the landscape and the water regime. Therefore concentrations of dissolved  $\text{N}_2\text{O}$  in the soil solution may be indirectly connected with the landscape position (Davidson & Firestone, 1986). For example, in a catena from a hillslope to a stream the solubilized  $\text{N}_2\text{O}$  concentrations were in general

highest in the riparian zone and in the saturated area close to the stream (Davidson & Firestone, 1988). In a floodplain the concentrations of dissolved  $\text{N}_2\text{O}$  were much larger in poorly drained soils than in well drained soils (Schnabel & Stout, 1994).

Short-lived additions of high amounts of water to soil by precipitation, irrigation or flooding can also cause an accumulation of  $\text{N}_2\text{O}$  in the soil profile. For instance, extremely high concentrations of dissolved  $\text{N}_2\text{O}$  were observed in the drainage water of agricultural fields during the winter months when the rainfall exceeded the evapo-transpiration by about 250 mm (Dowdell et al., 1979). In different soils, concentrations of dissolved  $\text{N}_2\text{O}$  in the soil solution rose drastically following major precipitation events (Davidson & Firestone, 1988; Davidson & Swank, 1990). The irrigation of a N-fertilized field immediately caused a strong increase in  $\text{N}_2\text{O}$  concentrations in soil air (Mosier & Hutchinson, 1981). Nonetheless, the input of rainwater, for example, does not automatically enhance denitrification since oxygen may be dissolved in it (Rice & Rogers, 1993).

Flooding of soils may enforce denitrification. Even in the floodwater itself  $\text{N}_2\text{O}$  may accumulate. For example, concentrations of  $\text{N}_2\text{O}$  dissolved in the floodwater of a N-rich rice field ranged from undersaturation up to approximately 30 times above ambient with regard to the atmosphere (Minami & Fukushi, 1984). In a flooded corn field, transitory high undersaturation (23%) and a weak supersaturation (146%) of  $\text{N}_2\text{O}$  were also registered (Terry et al., 1981). Undersaturation probably resulted from a temporary use of atmospheric  $\text{N}_2\text{O}$  as an electron acceptor by microorganisms under anoxic conditions.

The amount of the  $\text{N}_2\text{O}$  dissolved in floodwater actually released to the atmosphere depends partly on the level of the water table. In a field study the influence of different water table levels on  $\text{N}_2\text{O}$  emission was studied. At a water table of 15 cm above the soil much more  $\text{N}_2\text{O}$  outgassed than at a water table of 45 cm above the soil. At the higher water table level almost no  $\text{N}_2\text{O}$  emitted, since most of it had been converted microbiologically into  $\text{N}_2$  during the transport (Kliewer & Gilliam, 1995).

Changes in the water table level may also alter the composition of the soil air. For example rising water tables of a peat soil and of a sandy soil were accompanied by increasing  $\text{N}_2\text{O}$  concentrations in the soil atmosphere. In part these increases were caused by enhanced denitrification activity with the rising anaerobic front, and in part they were caused by the



displacement of soil air from deeper layers and by a reduction in soil gas diffusivity (Velthof et al., 1996).

In some field experiments, however, no correlations were observed at all between increasing water contents of the soils and concentrations of  $N_2O$  in the soil atmospheres (Albrecht et al., 1970; Dowdell & Smith, 1974; Goodroad & Keeney, 1985).

### *Temperature*

An increase in soil temperature positively influences microbiological activity and gas diffusion, while it negatively affects the solubility of  $N_2O$ . Thus it is difficult to predict the impact of a change in soil temperature on concentrations of  $N_2O$  in soil air and soil solution. The correlations observed can be interpreted differently: either the temperature-induced solubility change of  $N_2O$  is the dominant factor, or the effect of temperature on microbial processes is more important. Often both processes are not distinguishable.

In many field experiments concentrations of  $N_2O$  in soil solution (Davidson & Swank, 1990), drainage water (Harris et al., 1984) and soil air (Benckiser et al., 1986; Cates & Keeney, 1987; Dowdell & Smith, 1974; Lind, 1985; Lind & Doran, 1984) increased with rising temperatures. Only exceptionally was there no apparent interaction between temperature and  $N_2O$  concentrations in soil air (Albrecht et al., 1970; Burford & Stefanson, 1973).

Probably an enhanced  $N_2O$  production rate was the major process, in those cases where the  $N_2O$  concentrations in soil solution increased with rising temperature. For instance,  $N_2O$  concentrations in the soil solution of a clear cut forest, where intense mineralization took place, varied extremely and peaked during summer. In contrast, at an undisturbed forest location the concentrations of  $N_2O$  in soil solution peaked during the coldest season. There the  $N_2O$  concentrations were close to ambient throughout the year and their small alterations could sufficiently be explained by temperature induced solubility changes (Bowden & Bormann, 1986).

In cases of increasing  $N_2O$  concentrations in soil air with rising temperature, simultaneous impacts of temperature on physical and on biological processes are possible. In many studies it was therefore merely hypothesized that observed increases of  $N_2O$  in the soil air were partially caused by physical outgassing of  $N_2O$  from the soil solutions due to diminished solubility (Benckiser et al., 1986; Burton & Beauchamp, 1994; Lessard et al., 1996; Linn & Doran, 1984).

In contrast, under the controlled conditions of a laboratory experiment this process could be proven exactly on sterilized frozen soil cores when the temperature rose from 1 to 10 °C. During this time a subsequent  $N_2O$  accumulation in the soil atmosphere was measured as a result of  $N_2O$  solubility decrease (Goodroad & Keeney, 1984).

Temperature changes also influence  $N_2O$  emissions. In a field experiment an attempt was made to explain the diurnal variability of  $N_2O$  fluxes in part by a temperature-induced solubility change of  $N_2O$  dissolved in the soil solution of the soil surface. It was suggested that, due to altering  $N_2O$  solubility, the rates of  $N_2O$  emissions were higher than the actual microbial  $N_2O$  generation when the soil was warming up and were lower when the soil was cooling down (Blackmer et al., 1982).

In contrast, in a flooded rice field the diurnal cycle of  $N_2O$  fluxes — which was close in phase with the water temperature — was interpreted exclusively by variations in microbiological activity: the temperature dependence of  $N_2O$  solubility was ignored, although diffusion and dissolution of  $N_2O$  were considered (Denmead et al., 1979).

For several sites drastic increases in  $N_2O$  concentrations in the soil air were reported during the winter period with its low temperatures (Albrecht et al., 1970; Burford, 1976; Burford & Stefanson, 1973; Burton & Beauchamp, 1994; Eggington & Smith, 1986; Lind, 1985; Velthof et al., 1996). These  $N_2O$  peaks were often the highest ones for the entire season: there are different reasons for this phenomenon.

Even at temperatures around 0 °C microbial activity does not cease totally (Sommerfeld et al., 1993). Nitrous oxide may be produced in the unfrozen subsoils. Even in frozen soils microorganisms are still active in the remaining liquid water films (Goodroad & Keeney, 1984).

Once  $N_2O$  is slowly generated its diffusion may be inhibited, resulting in a substantial accumulation in the long run. For example, during winter the water contents of several soils were the highest ones of the whole measuring period (Burford & Stefanson, 1973). In other cases there was a water layer above the soil surface caused either by thawing snow, water movement to the freezing front or impeded drainage (Burton & Beauchamp, 1994; Goodroad & Keeney, 1984). Beneath a large ice lens the  $N_2O$  production rate was higher than its diffusion rate. For that reason the concentration of  $N_2O$  in the soil air rose drastically (Burton & Beauchamp, 1994).

At other sites, an intense accumulation of  $N_2O$  in the soil air corresponding with extremely high  $N_2O$  emissions took place merely during thawing (Cates & Keeney, 1987; Dowdell & Smith, 1974; Eggington & Smith, 1986; Goodroad & Keeney, 1984). This  $N_2O$  was generated partially at the soil surface during thawing-freezing cycles by denitrification or nitrification (Burton & Beauchamp, 1994; Cates & Keeney, 1987; Dowdell & Smith, 1974). In addition, a physical release of  $N_2O$  due to physical disruption of the soil structure, quick diffusion of entrapped  $N_2O$  from the unfrozen subsoils or outgassing from the soil solution was possible (Burton & Beauchamp, 1994; Cates & Keeney, 1987; Goodroad & Keeney, 1984).

### Modeling interactions of $N_2O$ and the soil solution

#### *Examples of existing models*

Up to now modeling of  $N_2O$  dynamics put an emphasis on  $N_2O$  production processes, whereas  $N_2O$  transport processes in soils were more or less neglected. Therefore, only few gas transport models exist which consider the interactions of  $N_2O$  with the soil solution. These models are of different levels of complexity. There are models of one-, two-, or three-dimensional gas transport, as well as macroscopic or microscopic approaches.

In many macroscopic  $N_2O$  models the sole gas transport process taken into account is gas diffusion in the soil air, as this is the dominant mechanism. For example, the common gas gradient method calculates the  $N_2O$  flux at the soil surface from the distribution and the diffusion coefficient of  $N_2O$  in soil air (Albrecht et al., 1970; Benckiser, 1994; Benckiser et al., 1986; Burford, 1976; Burford & Stefanson, 1973; Eggington & Smith, 1986; Goodroad & Keeney, 1985; Kimball, 1978; Rolston, 1978; Rolston et al., 1976; Smith, 1978).

Apart from many other essential drawbacks of this method, several authors hypothesized that the estimation of  $N_2O$  diffusion in soils may be incorrect due to the incomplete consideration of  $N_2O$  solvation in soil solution (Benckiser, 1994; Benckiser et al., 1986; Burton & Beauchamp, 1994; Goodroad & Keeney, 1984; Lalisse-Grundmann & Chalamet, 1987; Mosier et al., 1990; Rolston and Marino, 1976; Rolston et al., 1976).

Therefore Stegemann (1989) included the interphase transfer of  $N_2O$  between soil air and soil solution by adding a sink term for dissolved  $N_2O$  in

his model of  $N_2O$  diffusion in soils. Using a numerical computer simulation model and laboratory tests he demonstrated that large systematic errors may occur for cases like the highly soluble  $N_2O$  when the diffusion coefficients in soils are estimated without paying attention to the solubility.

More complex models involve both the  $N_2O$  diffusion in soil air as well as in soil solution and the exchange between these phases. Only under very wet conditions does the gas diffusion within the soil solution contribute significantly to the total gas transport. Therefore Letey et al. (1980), for example, created two different  $N_2O$  transport equations for an unsaturated and a saturated soil. For the case of saturated soils, a storage term for dissolved  $N_2O$  was integrated as well as a term for  $N_2O$  diffusion within the soil solution. In incubation tests of water-saturated soils, an entrapment of large amounts of  $N_2O$  was measured. This entrapment could in part be described by the  $N_2O$  storage term. For a hypothetical Canadian clay soil, Cho et al. (1997) simulated a substantial retention of dissolved  $N_2O$  in the soil solution during the winter period. It was assumed that  $N_2O$  may accumulate in the subsoil due to diminished denitrification intensity at low temperatures.

In real three-dimensional soils the temporal and spatial dynamics of the water content have to be considered with respect to their influence on  $N_2O$  transport. For the first time the combined effects of the development of a water content profile,  $N_2O$  solubility and  $N_2O$  diffusional transport were studied by Tindall et al. (1995) in a lysimeter experiment. The associated gas transport model consisted of  $N_2O$  diffusion coefficients in soil air and soil solution,  $N_2O$  solubility, dispersive flow of the infiltrating water and  $N_2O$  fluxes upwards and downwards. As a restriction of the model the convective transport of  $N_2O$  by moving water was ignored. A lack of correspondence between  $N_2O$  emissions and  $N_2O$  concentrations within differently wet soil layers of the lysimeter was observed. This may have been caused by the solubility of  $N_2O$ , its very slow diffusion or its being retained in the soil solution for long periods.

Apart from diffusion and solubility, more complex models of  $N_2O$  transport also include the convection of  $N_2O$ . One example is the model of Grant et al. (1993a,b) which was tested in laboratory and field experiments. The influence of convection on  $N_2O$  transport was taken into account during thawing and drainage of water-saturated soils. The measured  $N_2O$  evolution was explained in part by volatilization of

dissolved  $\text{N}_2\text{O}$  into recently drained soil pores. In the model of van Faasen and Bril (1994) even the removal of dissolved  $\text{N}_2\text{O}$  with drainwater at the lower soil boundary was included in the calculation.

There also are microscopic approaches for describing  $\text{N}_2\text{O}$  transport in soils. Understanding  $\text{N}_2\text{O}$  transport processes at the aggregate scale should permit a prediction of the  $\text{N}_2\text{O}$  transport dynamics for the whole soil profile. Microscopic models also vary in complexity.

In the simple model of Smith (1980), for example, merely  $\text{N}_2\text{O}$  diffusion was considered a relevant transport process. Nitrous oxide diffusion within and between aggregates was described as a function of aggregate size, water content and extent of anaerobic zones. Thereby the much better aeration status and quicker drainage of inter-aggregate pores compared to intra-aggregate pores was taken into account.

In contrast, the much more detailed model of Lefelaar (1988) included  $\text{N}_2\text{O}$  diffusion and convection in soil air and  $\text{N}_2\text{O}$  diffusive, dispersive and mass transport in water as well as  $\text{N}_2\text{O}$  solubility. Experimental data of an unsaturated soil showed that the reactions of  $\text{N}_2\text{O}$  with the soil solution complicated the prediction of  $\text{N}_2\text{O}$  emissions by the model.

These examples of  $\text{N}_2\text{O}$  transport modeling demonstrate that the interactions of  $\text{N}_2\text{O}$  and soil solution may be involved to varying degrees. On the one hand, these differences are the result of the different complexities of the models. On the other hand, they reflect the just recently growing insight into the relevance of  $\text{N}_2\text{O}$  leaching. The simple qualitative scheme described in the next section, shows that the interactions between  $\text{N}_2\text{O}$  and soil solution may be of importance for the  $\text{N}_2\text{O}$  dynamics in soils.

#### *New approach*

The new aspect of our approach is that the multitude of existing literature on  $\text{N}_2\text{O}$ –soil solution interactions is systematically summarized to a simplified concept. In our scheme, soil solution affects the dynamics of  $\text{N}_2\text{O}$  in the soil in three principle manners: it can act as a barrier, a store or as a transport medium for  $\text{N}_2\text{O}$ . This can cause a temporal retardation and spatial separation (vertical, lateral) of  $\text{N}_2\text{O}$  production and  $\text{N}_2\text{O}$  emission (Bowden & Bormann, 1986; Rice & Rogers, 1993; Rolston & Marino, 1976; Tindall et al., 1995).

#### *Barrier function of soil solution*

In unsaturated soils there is a more or less quick diffusive gas exchange between the soil air and the atmosphere. The concentration of dissolved  $\text{N}_2\text{O}$  is assumed to equilibrate with the soil air. At drastically increased water contents, however, gas diffusion between soil air and atmosphere is strongly inhibited, which may result in a  $\text{N}_2\text{O}$  accumulation in the soil air. Additionally the  $\text{N}_2\text{O}$  production rate may exceed the diffusive equilibration rate between soil solution and soil air, therefore,  $\text{N}_2\text{O}$  supersaturation may occur.

Furthermore, a spatial lack of correspondence of the locations of  $\text{N}_2\text{O}$  production and those of  $\text{N}_2\text{O}$  accumulation due to diffusion limitations was described by several authors: in a corn field with irrigation of alternate furrows the greater resistance to diffusive gas transport of the water-filled furrows caused  $\text{N}_2\text{O}$  produced there to move laterally to the drier soil. Thus the  $\text{N}_2\text{O}$  emissions from the dry soil were larger than those from the wet soil (Guenzi et al., 1994). In a lysimeter study with an unsaturated sandy soil at 20 and 30 cm depth, the water content was high. The  $\text{N}_2\text{O}$  generation was higher than the possible  $\text{N}_2\text{O}$  solvation in the soil solution. Therefore  $\text{N}_2\text{O}$  diffused vertically through the liquid-filled pores to the upper, drier layer (10 cm) with less diffusion limits. The  $\text{N}_2\text{O}$  concentration in the soil air here later rose dramatically, although  $\text{N}_2\text{O}$  production was low (Tindall et al., 1995).

A drastic temporal lack of correspondence between  $\text{N}_2\text{O}$  production and  $\text{N}_2\text{O}$  emission was observed when the extent of denitrification at different water table levels above soils was investigated using the acetylene inhibition technique. As long as steady-state diffusion was not reached the amount of N gases produced was highly underestimated (Kliewer & Gilliam, 1995).

#### *Storage function of soil solution*

In wet soils significant amounts of  $\text{N}_2\text{O}$  may remain for quite a while after production due to high solubility and slow diffusion. During spring time in a clay soil at 60 cm depth the concentration of dissolved  $\text{N}_2\text{O}$  was equivalent to  $2 \text{ kg } \text{N}_2\text{O-N ha}^{-1}$ . It was unclear how much of this  $\text{N}_2\text{O}$  stored was released to the atmosphere, reduced to  $\text{N}_2$  or leached (Burford et al., 1978b).

High soil water contents combined with a soil structure unfavorable for gas transport can cause  $\text{N}_2\text{O}$  to be entrapped for several weeks. Especially in watered puddled soils with a hardpan, destroyed soil

aggregates and interrupted pore systems, the gas transport is strongly reduced. Substantial deficits in the balances after  $^{15}\text{N}$  application to flooded puddled rice fields may to some extent — apart from  $\text{NH}_3$  volatilization, for example — have been caused by the entrapment of  $\text{N}_2\text{O}$  and  $\text{N}_2$ . In several studies the measured loss of nitrogen gases was only 0.1–2.2% of the  $^{15}\text{N}$ -fertilizer added, whereas due to the indirect difference method 10–56% of the added  $^{15}\text{N}$  urea should have been denitrified (Buresh & De Datta, 1990). Another reason for the low recovery may have been a supersaturation of  $\text{N}_2\text{O}$  in the floodwater of the rice fields or a transmission of N-gases through the rice plants, which were usually not included in the closed measuring chambers (Buresh & Austin, 1988).

Evidence for entrapment was given in an experiment with fertilization of  $^{15}\text{N-NO}_3^-$  to a flooded puddled soil without plants. There was a good correlation between the fraction of  $^{15}\text{N}$  of the N-gases dissolved in water and the fraction of  $^{15}\text{N}$  of the gaseous emissions. After the evolution of  $^{15}\text{N}$   $\text{N}_2\text{O}$  and  $\text{N}_2$  at the water surface had stopped, the soil at a depth of 0.04 m was still enriched with  $^{15}\text{N}$   $\text{N}_2\text{O}$  and  $\text{N}_2$ . Therefore, the recovery of  $^{15}\text{N}$  ( $\text{N}_2\text{O}$ ,  $\text{N}_2$ ) represented only 34–42% of the estimated denitrification loss (Samson et al., 1990). At another flooded rice field 25 g  $\text{N}_2\text{O m}^{-2}$  were entrapped in the soil for 20 days after  $\text{KNO}_3$  had been added, and 36 g  $\text{N}_2\text{O m}^{-2}$  remained there for 15 days after the application of urea (DeLaune et al., 1990).

In a watered rice field without plants, as much as 33% of the total nitrogen gases produced were entrapped for the duration of 1 week. In contrast, in a flooded planted plot evolved  $\text{N}_2$  and  $\text{N}_2\text{O}$  diffused through the rice plants and no entrapment took place (Mosier et al., 1990). When rice plants are planted in fields the transport of  $\text{N}_2\text{O}$  through their aerenchyma is probably much more important than diffusion through the soil/water/atmosphere interface. For instance, in experiments with closed chambers, more than 80% of the  $\text{N}_2\text{O}$  emitted was conducted to the atmosphere via the aerenchyma of the rice plants (Yu et al., 1997).

Recently there have been hints that, under special conditions, significant amounts of  $\text{N}_2\text{O}$  may be released to the atmosphere by upland plants without aerenchyma via plant transpiration. In laboratory experiments with canola and barley Chang et al. (1998) demonstrated that  $\text{N}_2\text{O}$  which was dissolved in the soil solution was emitted by the foliage after transportation with the transpiration stream. This type of  $\text{N}_2\text{O}$  emis-

sion took place either after watering of the soils with a solution containing much  $\text{N}_2\text{O}$ , or at water saturation levels of the soils but not at field capacity.

In laboratory studies on the denitrification potential of soil cores, entrapment of  $\text{N}_2\text{O}$  is a serious problem. Usually the  $\text{N}_2\text{O}$  concentration in the headspace of the incubation cubes was measured and the fraction of  $\text{N}_2\text{O}$  dissolved was calculated (Moraghan & Buresh, 1977b). This method requires a diffusion equilibrium between the two phases, which is often inhibited because relevant proportions of produced  $\text{N}_2\text{O}$  and/or  $\text{N}_2$  are trapped in the soils. For example entrapments of up to 38% (Rice & Smith, 1982), 40% (Lindau et al., 1988), 65% (Aulakh & Doran, 1990), 70% (Letey et al., 1980), 83% (Ambus & Christensen, 1993), 97% (Holt et al., 1988) of the generated N-gases were estimated. Therefore an intense shaking of the soil cores was necessary, which destroyed their structures. Thus, trapped gas bubbles could be released, and the diffusion between water and air was enforced.

#### *Soil solution as transport medium for $\text{N}_2\text{O}$*

So far, only few investigations take the transport of dissolved  $\text{N}_2\text{O}$  with the soil solution and further outgassing into the atmosphere at wells, drainage outlets, etc., into consideration. However, this may be a relevant pathway of  $\text{N}_2\text{O}$  release, eventually even of the same order of magnitude as the gaseous  $\text{N}_2\text{O}$  emissions from the soil surfaces of agricultural fields (Bowden & Bormann, 1986; Davidson & Firestone, 1988; Davidson & Swank, 1990; Dowdell et al., 1979; Minami & Fukushima, 1984; Minami & Ohsawa, 1990; Rice and Rogers, 1993; Ronen et al., 1988; Ueda et al., 1993).

Leaching of dissolved  $\text{N}_2\text{O}$  requires high  $\text{N}_2\text{O}$  production rates and great amounts of infiltrating water causing fast preferential flow (Dowdell et al., 1979; Schnabel & Stout, 1994). In a laboratory experiment of denitrification in columns of organic soils at the drained variants 11–52% and at the flooded variants, 78–98% of the total recovered  $\text{N}_2\text{O-N}$  was leached (Guthrie & Duxbury, 1978).

Once dissolved  $\text{N}_2\text{O}$  has reached the subsoil there are different possibilities for further transport or microbial reduction to  $\text{N}_2$ .

Nitrous oxide dissolved in groundwater may diffuse during its transit time through the overlying soil to the atmosphere (Rice & Rogers, 1993; Ueda et al., 1993). In Israel, for example, it was estimated that from an organically polluted aquifer with a maximal concentration of 270 g  $\text{N}_2\text{O l}^{-1}$   $\text{H}_2\text{O}$ , probably

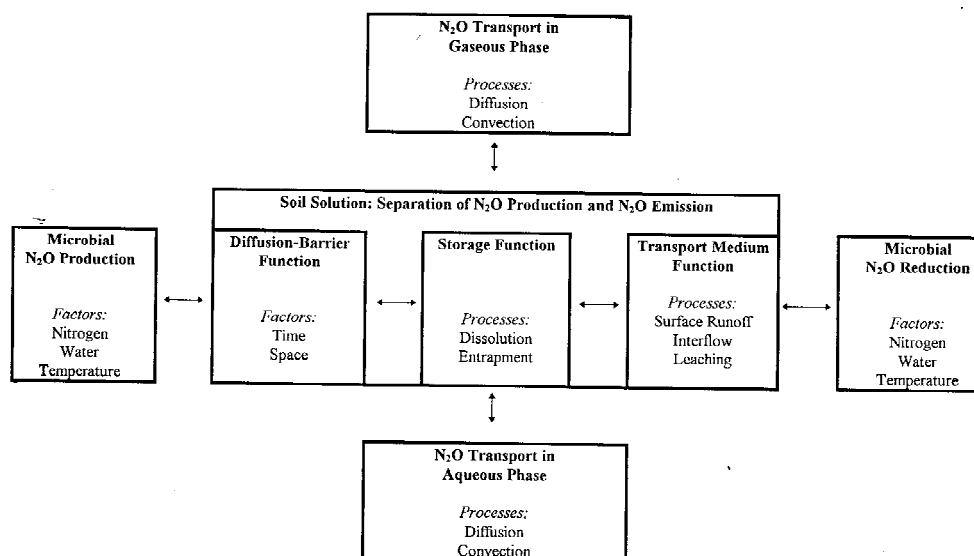


Figure 1. The soil solution: an important link between  $\text{N}_2\text{O}$  production, reduction and transport.

$3.4\text{--}7.8 \text{ kg N}_2\text{O-N ha}^{-1} \text{ a}^{-1}$  may diffuse into the unsaturated zone above the aquifer. Nitrous oxide concentrations in the soil air of this unsaturated zone were calculated to be up to 12 ppm (Ronen et al., 1988). It is speculative, which portion of the  $\text{N}_2\text{O}$  in subsoils may be microbiologically converted into  $\text{N}_2$  during its diffusion to the soil surface.

Another potential transport mechanism for  $\text{N}_2\text{O}$  dissolved in groundwater is the flow along a hydraulic gradient to a spring or surface stream (Ueda et al., 1993). For instance in the seeps of a watershed where the forest had just been clear cut, the concentrations of dissolved  $\text{N}_2\text{O}$  increased drastically up to  $495 \text{ g N}_2\text{O-N l}^{-1} \text{ H}_2\text{O}$ . In the corresponding stream the maximal concentration of leached  $\text{N}_2\text{O}$  was  $57 \text{ g N}_2\text{O-N l}^{-1} \text{ H}_2\text{O}$  (Bowden & Bormann, 1986). In other streams, which received leached  $\text{N}_2\text{O}$ , the  $\text{N}_2\text{O}$  concentrations were much smaller (Davidson & Firestone, 1988; Davidson & Swank, 1990).

Furthermore, in the water in drainage channels much  $\text{N}_2\text{O}$  may be dissolved and leave agricultural fields via these systems (Harris et al., 1984). Particularly in the drainage ditch water of soils with high nitrogen turnover rates,  $\text{N}_2\text{O}$  supersaturations of more than 100 times with respect to the atmospheric  $\text{N}_2\text{O}$  concentration were registered (Guthrie & Duxbury, 1978; Minami & Fukushima, 1984; Minami & Ohsawa, 1990; Terry et al., 1981; Ueda et al., 1993). In England during winter, large concentrations of dissolved  $\text{N}_2\text{O}$  (maximal  $132 \text{ g N}_2\text{O-N l}^{-1} \text{ H}_2\text{O}$ ) were measured

in the drainage system of an agricultural field. Since these drain pipes were not totally filled with water, part of the solubilized  $\text{N}_2\text{O}$  diffused into the atmosphere of the drains where  $\text{N}_2\text{O}$  concentrations 100-fold that in the soil atmosphere were observed (Dowdell et al., 1979).

Other possible transport mechanisms of dissolved  $\text{N}_2\text{O}$  are interflow (Davidson & Swank, 1990; Harris et al., 1984) or surface runoff (Harris et al., 1984). For instance, it was suggested that significant quantities of solubilized  $\text{N}_2\text{O}$  were transported by the floodwater (maximal concentration, 27 ppm  $\text{N}_2\text{O}$ ) of an agricultural field since the concentrations of dissolved  $\text{N}_2\text{O}$  in the floodwater of a field receiving this water increased abruptly (Terry et al., 1981).

The rate of subsequent degassing of dissolved  $\text{N}_2\text{O}$  exposed to the atmosphere depends on the turbulence and flow-rate of water and on the shape of the waterbed. In a well-aerated stream, dissolved  $\text{N}_2\text{O}$  outgassed within a transit time of a few minutes and after a transport distance of only some meters (Bowden & Bormann, 1986). In contrast, in another study, even after a distance of more than 800 m within 2 h, there was no equilibration of dissolved  $\text{N}_2\text{O}$  with the atmosphere. It was suggested that the decrease of dissolved  $\text{N}_2\text{O}$  was solely caused by physical outgassing (Ueda et al., 1993). On the contrary, in large drainage channels dissolved  $\text{N}_2\text{O}$  probably originated, apart from leaching, also from denitrification in the ditch sediments and from nitrification in the drainage water. The

transit time was even long enough for a microbial conversion of  $\text{N}_2\text{O}$  into  $\text{N}_2$  (Minami & Ohsawa, 1990). In these large drainage channels the  $\text{N}_2\text{O}$  emissions had not ceased after a flow distance of several hundreds of meters (Minami & Fukushima, 1984; Minami & Ohsawa, 1990).

Calculations of the extent of  $\text{N}_2\text{O}$  exported by leaching differ widely. From an almost undisturbed hardwood forest only  $0.056 \text{ kg dissolved N}_2\text{O ha}^{-1} \text{ a}^{-1}$  seemed to be released (Davidson & Swank, 1990). In contrast, after whole-tree harvesting during 19 months approximately  $0.33 \text{ kg N}_2\text{O-N ha}^{-1}$  were degassed from soil water entering a stream. (Bowden & Bormann, 1986). In the drains of a N-rich field during five winter months about  $0.25 \text{ kg}$  of dissolved  $\text{N}_2\text{O-N ha}^{-1}$  were transported. However, even larger  $\text{N}_2\text{O}$  escape was expected periodically (Dowdell et al., 1979). For the mole drains of a fertilized wheat field during winter, the substantial loss of  $4.35 \text{ kg}$  of dissolved  $\text{N}_2\text{O-N ha}^{-1}$  during 3 months was estimated (Harris et al., 1984).

Despite these high variations, the amounts of  $\text{N}_2\text{O}$  leached are of no quantitative significance from the perspective of the nitrogen budgets of the ecosystems. Usually the losses of nitrate-N were several times larger than losses as dissolved  $\text{N}_2\text{O-N}$  (Bowden & Bormann, 1986; Davidson & Firestone, 1988; Davidson & Swank, 1990; Dowdell et al., 1979; Harris et al., 1984). Leaching of  $\text{N}_2$  is probably even less important to the nitrogen budgets of ecosystems as its solubility is around 50 times less than that of  $\text{N}_2\text{O}$  (Dowdell et al., 1979).

### Concluding remarks

The literature review has shown that large amounts of  $\text{N}_2\text{O}$  can be stored in soil solution as well as in soil air. In both cases, water is the dominant factor for these accumulations as it controls the  $\text{N}_2\text{O}$  production and consumption as well as diffusive and convective transport (Figure 1). Therefore the soil solution is at a central position and an important link between gas transport models, water transport models and microbiological models of  $\text{N}_2\text{O}$ .

### Acknowledgement

We thank the Deutsche Forschungsgemeinschaft (DFG) for founding this study.

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