Chapter 14

BIOGENIC EMISSIONS OF NITRIC OXIDE AND NITROUS OXIDE FROM ARID AND SEMI-ARID LAND

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1. Introduction

Carbonaceous trace gases in the atmosphere, like carbon monoxide, methane, volatile organic compounds, are oxidized by hydroxyl and other radicals through various catalytic cycles (Crutzen, 1987). Nitrogen oxide (NO) and nitrogen dioxide (NO_2) are the key catalysts in these cycles and their ambient concentrations determine whether ozone is generated or destroyed in the troposphere (Chameides et al., 1992). A mixing ratio of NO_x (= $NO+NO_2$) of only ≈30 pptv establishes a critical threshold between ozone destruction (<30 pptv) and generation (>30 pptv). Ozone is usually generated in polluted, industrialized regions, where ambient levels of nitrogen oxides are high, and it is destroyed in remote parts of the globe. The present evolution of sources of nitrogen oxides in non-industrialized regions triggers a potential increase of global tropospheric ozone concentrations and thus attracts scientific attention. Nitrous oxide (N_2O) is important because it absorbs the outgoing infrared radiation (like other radiatively effective trace gases, e.g., CO_2, H_2O, methane). It contributes by approximately 5% to the anthropogenic greenhouse effect. N_2O is chemically inert in the troposphere. However, once transported into the stratosphere, it contributes to the destruction of the ozone layer, which protects terrestrial life from incoming solar ultra-violet radiation. Fossil-fuel combustion in power stations and in car engines is still the most important (and best documented) global source of nitrogen oxides. The corresponding global source strength was estimated to be 21 Tg a^{-1} (in terms of mass of nitrogen) by Kasibhatla et al. (1993); the corresponding, most recent estimate by IPCC (2001) is 33 Tg a^{-1}. The strongest global sources for N_2O are natural soils (6 Tg a^{-1}), followed by N_2O emissions from agricultural (fertilized) soils (4.2 Tg a^{-1}), and other anthropogenic sources (IPCC, 2001). Nitrification and denitrification processes in soils give rise to strong NO and N_2O emissions. There is continuous interest to quantify worldwide biogenic sources of these trace gases (e.g. Hutchinson et al., 1993; IPCC, 2001). A global inventory of NO emissions from soils, based on field measurements worldwide, has been provided by Davidson and Kingerlee (1997). Their estimate of the global NO soil source strength is 21Tg a^{-1} (with an error margin of 4 to 10 Tg a^{-1}), while the most recent IPCC (2001) estimate is 5.6 Tg a^{-1}. Stratifying soil sources according to major biomes, it turned out, that the combined biomes "tropical savanna/woodlands" and "chaparral/thorn forests" contribute more than half to the global source (Davidson and Kingerlee, 1997). However, the uncertainties in the NO emission data for these strata are very large. Emissions from semi-arid and arid lands, which are part of these biomes, particularly contribute to the high error margins, simply because a very small number of corresponding measurements is available (both in the laboratory and in the field). Before we try to re-compile and to up-date the data base of NO and N_2O emissions from semi-arid and arid lands, we like to describe processes and controlling

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factors of these emissions, (a) in general, and (b) under the specific conditions of semi-arid, arid, and hyper-arid landscapes.

2. Biogenic emission of NO and N_2O from soils and plants – general aspects

Nitric oxide (NO) and nitrous oxide (N_2O) are produced and consumed within soils. Generally, soils contribute to the global budgets of NO and N_2O as sources (Table 1) and their contribution as sinks is likely but considered to be small (c.f. Meixner and Eugster, 1999). As plants are concerned, there are no mechanisms known for biogenic emission or uptake of N_2O. Wildt et al. (1996) observed biogenic emission of NO from several higher plant species. However, the plants' contribution to the global atmospheric budget of nitrogen oxides is presumably less than 4% (see Table 1). Generally, there is (stomatal) uptake of nitrogen dioxide (NO_2). Stomatal uptake of NO is thought to occur in polluted environments (cf. Meixner, 1994), but - due to the low solubility of NO - this uptake is expected to be low. The values in Table 1 are are estimated with uncertainty due to a number reasons (Conrad, 1996). The fluxes of NO and N_2O are reliably measured by a variety of techniques, ranging from small-scale soil- and/or leaf enclosures to tower-based and airborne micrometeorological techniques (c.f. Matson and Harriss, 1995). It is by far not trivial, however, to estimate atmospheric budgets from local NO and N_2O flux measurements (Andreae and Schimel, 1989). NO and N_2O fluxes are controlled by a diversity of abiological and microbiological processes which themselves depend on environmental conditions. Thus, fluxes are highly variable with respect to time and space. Most of observed uncertainties and problems with NO and N_2O flux data can be traced to this fact. However, the mentioned problems are not necessarily solved by integration of fluxes over larger areas and longer time periods, since—according to Conrad (1996)—"each individual flux event is caused by deterministic processes that change in a non-linear way, even when conditions change slightly".

Table 1. Contribution of soils (NO and N_2O) and plants (NO) to the global cycles of nitric and nitrous oxides (after Meixner and Eugster, 1999).

trace gas	ambient conc. [ppb]	lifetime [days]	total budget [Tg a^{-1}]	annual increase [%]	contribution of soils or plants as source [%]	contribution of soils or plants as sink [%]
N_2O (soils)	310	60000	15	0.2–0.3	70	?
NO (soils)	< 0.1–20	1	60	?	20	?
NO (plants)					< 4	?

2.1. SOIL-AIR EXCHANGE OF NO AND N_2O: PROCESSES

Soil processes can be classified into chemical (abiotic) and microbial (biotic) processes. Abiotic formation of NO (and N_2O) in soils is imporant in acid soils (e.g. Davidson, 1992). However, microorganisms are considered to be responsible for most NO and N_2O production and consumption processes in soils. In their oxidative and reductive metabolisms, these trace gases act as growth substrates and/or co-metabolites; or they are considered to be stoichiometric and other products (see comprehensive review by Conrad, 1996). In principle, all microbial processes, which involve oxidative or reductive transformation of nitrogen involving its +2 valence state, were identified as both, biogenic sources or sinks for NO and N_2O (Conrad, 1996). Nevertheless, it is widely accepted that microbial nitrification and denitrification constitute the principal processes. In this context, it is important to keep in mind, that the production and consumption

and hence exchange of NO and N_2O between soils and atmosphere is predominantly controlled at the microscopic scale, i.e., at the level of the metabolism of microorganisms. However, for the study of biogenic emissions from whole landscape patterns (topographically and/or climatologically stratified), higher scales of organization and control must be considered (Meixner and Eugster, 1999). Therefore, (a) processes and (b) controls of biogenic NO and N_2O emission from soils (of at least plot to ecosystem scales) are considered next.

2.1.1. Chemodenitrification

Chemical oxidation of NO by O_2 is limited by the requirement of unrealistically high NO mixing ratios in soil air (Conrad, 1996). Abiotic formation of NO in soils can be of importance in acid soils (pH<5) with high nitrite (NO_2^-) concentrations: under these conditions HNO_2 undergoes self-decomposition and reacts with soil organic matter. Addition of NO_2^- to both, sterile and nonsterile soils has been observed to stimulate NO and N_2O emissions (Davidson, 1992). Recently, it has been argued, that burning of tropical ecosystems may decouple different nitrogen cycling processes in soils due to microbial sterilization (e.g. Weitz, et al., 1998). Therefore, soil NO emissions, observed immediately after typical "slash and burn" activities, require abiotic (chemodenitrification) NO production processes (Kirkman, 2001). Laboratory work on gamma irradiated Brazilian pasture soils (50 kGy day^{-1}) indicated abiotic NO production to be responsible for up to 50% of the total NO production (Trebs, 2001).

2.1.2. Denitrification

Denitrification is the bacterial respiratory reduction of nitrate (NO_3^-) and nitrite (NO_2^-) to N_2O, NO, and N_2. Because of the gaseous products, this process is commonly associated with the loss of soil nitrogen to the atmosphere. Denitrifying bacteria can grow in anaerobic environments due to their capability to use and reduce oxidised forms of soil nitrogen when oxygen is limited. The latter conditions occur at high soil water content or large respiration and oxygen consumption rates. The presence of readily oxidizable organic carbon is a requirement for most denitrifying bacteria (heterotrophs). A broad diversity of bacterial groups is capable of this metabolic pathway (Conrad, 1996). Therefore, denitrifiers are present in almost all natural and cultivated soil. It is generally accepted that NO and N_2O are obligatory intermediates in the denitrification sequence. This fact suggests that denitrifiers not only can produce but also consume NO and N_2O. The rates of NO and N_2O production (or consumption) and the overall denitrification rate are strongly affected by numerous parameters entering the complex reaction scheme. One parameter for instance, oxygen availability, is in turn regulated by various factors, e.g., soil water content, soil texture, activity of plant roots, and microbial respiration (see Chapters 3 and 11).

2.1.3. Nitrification

Nitrification involves the biological oxidation of nitrogen compounds, typically the oxidation of soil ammonium (NH_4^+) to NO_3^- (with NO_2^- as an intermediate), but there are also bacteria which oxidize NH_4^+ to NO_2^- and NO_2^- to NO_3^-. The capacity for nitrification is restricted to a few genera of strictly aerobic, mainly chemoautotrophic bacteria, which require only CO_2, H_2O, O_2, and either NH_4^+ or NO_2^- for growth. Nitrifying bacteria produce NO and N_2O as a by-product of NH_4^+ oxidation. It is unknown which biochemical pathway is the most important one for NO production; the N_2O production, however, occurs most likely via reduction of NO_2^- by NH_4^+ oxidizers. Using NO_2^- as an electron acceptor, nitrifiers can sustain oxidation of NH_4^+ even at low O_2 partial pressures. Overall nitrification rates will increase in well-aerated soils and at soil pH > 4–5.Under these conditions the nitrification rate is predominantly controlled by the availability of NH_4^+. The yield of NO typically ranges between 0.1% to 10% of the NH_4^+ oxidized (Veldkamp and Keller, 1997).

2.1.4. Nitrification vs. denitrification

It has been shown that NO production may be dominated by nitrification in a particular soil and by denitrification in another one (Conrad, 1996). It is still a difficult task to assess the importance of nitrification versus denitrification for the exchange of NO and N_2O. Results of most recent studies are still contradictory: in many field situations it is difficult to ascribe NO (and N_2O) production to one of both processes, because nitrifying and denitrifying bacteria might act simultaneously due microsite heterogenities within the same soil profile (cf. Ludwig et al., 2001).

2.1.5. Transport processes in soil, canopy and surface boundary layers

Commonly, molecular diffusion accomplishes the transport of NO and N_2O in soil pores (see Chapter 2); some laboratory studies, however, demonstrated the importance of convective transfer (Rudolph et al., 1996; Rudolph and Conrad, 1996). NO and N_2O diffusion coefficients in water are several orders of magnitude lower than in air; therefore, water-filled pores form strong barriers to the emission of NO and N_2O into the atmosphere. The soil water content also impacts strongly the diffusion of O_2 into the soil and consequently the microbial activity (Skopp et al., 1990). Thus, denitrifier activity will benefit from high soil water contents, but NO and N_2O diffusional removal will be the limiting factor. This situation enhances the probability of NO and N_2O being reconsumed by denitrifiers; consequently, emission of NO and N_2O to the atmosphere deviates significantly from the production of NO and/or N_2O in the soil (cf. Skiba et al., 1997). Chemistry, plant physiology and turbulent transport determine the further fate of NO once emitted from soil. In (dense) canopies, NO is rapidly oxidized by ozone (O_3) to nitrogen dioxide (NO_2). NO_2 uptake by plants (and soil) is much more effective than NO uptake (Meixner, 1994). As a result, only a fraction of NO emitted from soils reaches the atmospheric boundary layer and the free troposphere. This effect is usually termed the "canopy reduction factor" (CRF). Due to the fast and reversible conversion of NO to NO_2 in the presence of ozone and sunlight, NO_x, i.e. the sum of NO and NO_2, is the more suitable quantity for the description of the fate of soil derived NO. CRF-values are frequently given as that fraction of soil derived NO, which escapes a vegetation canopy in the form of NO_x (i.e. 100×(1-CRF) is the percental "loss" of NO_x in the canopy). For (dense tropical) forests, current estimates of the CRF are around 0.55 (Meixner et al., 2002).

2.2. SOIL-AIR EXCHANGE OF NO AND N_2O: INFLUENCING FACTORS

Any environmental factor that regulates the processes of NO and N_2O production and consumption in soils potentially affects the exchange of NO and N_2O between soil and the atmosphere. We will confine the following sub-sections to those factors, which have been identified as major controllers within a wide range of field situations. Under more specific environmental conditions (e.g. Meixner, 1994), other variables like soil pH, concentration and composition of organic C, soil texture, plant cover, as well as some cultivation practices (tillage, burning) might be of importance. Though correlation of soil parameters with observed NO and N_2O fluxes will depend on the vertical distribution of the relevant processes within the soil column, there is broad evidence that primary production and consumption zones for NO are located within a very shallow layer at the soil surface (0.01 to 0.1 m, e.g. Rudolph et al., 1996, Yang and Meixner, 1997). For N_2O, however, the situation is more complex; commonly it is assumed, that the major contribution to N_2O fluxes arises from (well) below 0.5 m, since major production zones of N_2O might be at the ground water level. However, Neftel et al. (2000) reported experimental evidence for a N_2O scale length of 0.007–0.03 m soil depth only.

2.2.1. Nitrogen availability and fertilization

It is evident, that all biological processes controlling nitrogen and carbon availability are of fundamental importance for NO and N_2O emission fluxes. Here, special emphasis is given to the pool size of soil NH_4^+ and NO_3^- serving as substrates for nitrifying and denitrifying bacteria.

Recently, some sophisticated ecosystem models became available, which describe local, regional, and global NO and N_2O emission patterns (monthly and diel) on the basis of carbon availability, gross nitrogen mineralization, denitrification, nitrification, decomposition, and soil carbon–nitrogen fluxes (e.g. Potter et al., 1993, 1996; Parton et al. 1998; Li et al., 2000; Parton et al., 2001). Field and laboratory studies have demonstrated numerous correlations between fluxes of N_2O and NO and NO_3^- or NH_4^+ concentrations in soil. Studies, however, were very site specific, and there is hardly a consistent trend to be recognized (e.g. Ludwig et al., 2001). The importance of nitrogen availability direcly links to fertilizers which strongly affect the exchange of NO and N_2O. A strong stimulation of NO emission by addition of N fertilizers has been noticed at uncultivated as well as agricultural sites. Input of nitrogen by (a) excreta of grazing animals or (b) wet (dry) deposition of NO_3^- (HNO_3, HNO_2, NO_2) and NH_4^+ (NH_3) resulted in enhanced levels of the NO and N_2O release over grasslands (Thornton et al., 1998) and forests (Butterbach-Bahl et al., 1997). Independently of fertilizer type and land use, a rapid increase of NO emissions is observed within one or two days after fertilization (nitrogen input, wet/dry deposition). Maximum emission rates are typically approached within 1–2 days, and pre-fertilization levels might be reached again within a few days or several weeks. Presently, the global mean of released NO is approximately 0.5% of the applied fertilzer nitrogen. For the most recent review and a very comprehensive global compilation of fertilizer induced emissions of NO and N_2O, the reader is referred to Bowman et al. (2000a, 2000b).

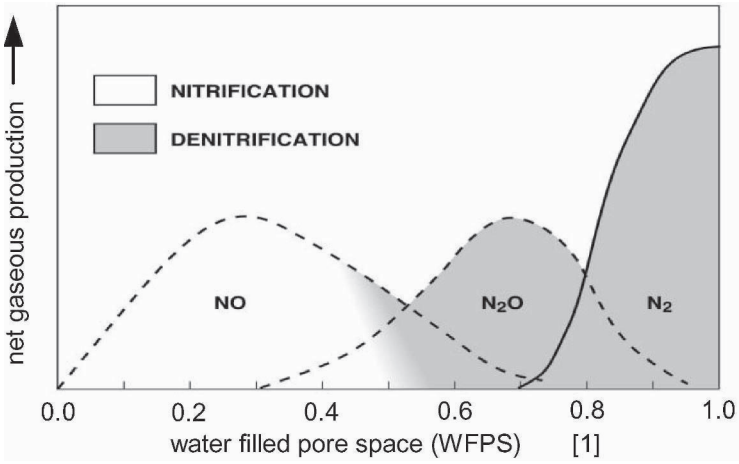

Fig. 1: The relationship between percent water-filled pore space (WFPS) of soil and the relative fluxes of nitrogen trace gases (Kirkman (2001), adapted from Davidson, 1991).

2.2.2. Soil moisture content

Nitrification and denitrification are intimately related to the soil water content for two important reasons: (a) the substrate supply for soil microorganisms (e.g., NH_4^+ for nitrifying bacteria) is accomplished by diffusion of the substrates in soil water films, and (b) water in soil pores is the dominant controller of gaseous diffusion in soils. The ratio of volumetric soil water content to total porosity of the soil, which is termed the water-filled pore space (WFPS), is commonly considered to be a suitable expression of the soil water content, since WFPS is largely comparable among soils of different texture (see Chapters 2 and 3 for the definitions of soil water content). In the context of NO and N_2O sources and source partition, Davidson and Schimel (1995) have suggested, that (a) if WFPS < 60%, nitrification is more important than denitrification and the N_2O:NO emission ratio is < 1, while (b) if WFPS > 60%, denitrification overrides nitrification

and N_2O:NO > 1. N_2 may be the dominant end product of denitrification under completely anaerobic conditions. The relationship between WFPS of soil and the relative fluxes of nitrogen trace gases is shown in Figure 1, which is adapted from Davidson (1991). Most of the current ecosystem models make use of this conceptual relationship: the shape of relative NO, N_2O, and N_2 emissions curves, as a result of two opposing processes, namely the substrate diffusion limit (towards low WFPS) and the O_2 diffusion limit (towards high WFPS), is a more general issue of soil water content vs. soil microbial activity (Skopp et al., 1990).

2.2.3. Soil temperature

The dominance of soil microbial processes in the production of NO and N_2O anticipates a marked influence of soil temperature on NO and N_2O emission rates. Most studies have only demonstrated the increase of NO emissions with increasing soil temperatures. This is in line with the fact that rates of chemical and/or enzymatic processes generally increase exponentially with temperature, as long as other factors (substrate or moisture availability) are not limiting. A convincing example obtained from laboratory studies on actual field samples is presented in Fig. 2. Doubling of NO emission rates was often observed when soil temperatures increased by 10°C (commonly dubbed as $Q_{10} = 2$). Valente and Thornton (1993) reported an average $Q_{10} = 5$ with a considerable variation between different ecosystems. Further restrictions to the validity of a uniform temperature response concern the emission of NO at more elevated temperatures and soil water contents (see *3.1*). It should be noted that soil temperature often cannot explain seasonal variations of NO fluxes (cf. Ludwig et al., 2001). It seems to be more appropriate that soil temperature modulates short-term variations of the NO and N_2O exchange, whereas the magnitude of the biogenic emissions is predominantly controlled by other factors, especially soil moisture (see Otter et al., 1999; Gut et al., 2002; Kirkman et al., 2002).

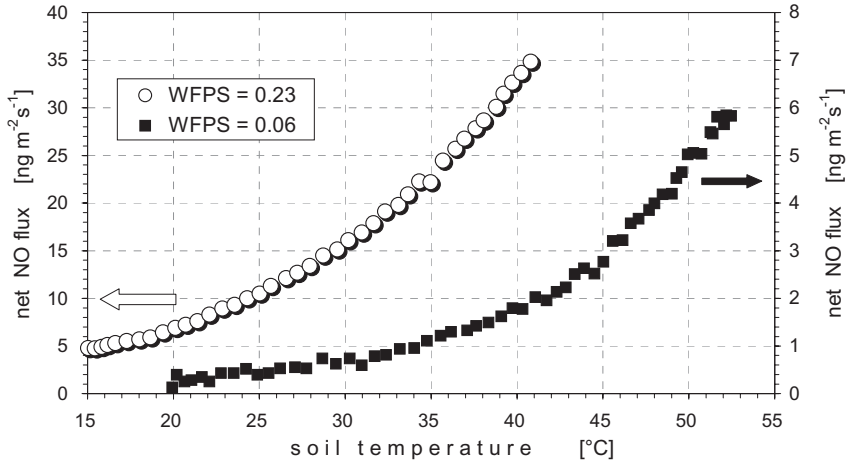

Figure 2: The relationship between (near surface) soil temperature and the net flux of nitric oxide (NO) from a bare soil taken from a semi-arid grassland site (results of laboratory experiments on a soil sample taken on 14 December 1994 at the Marondera Grassland Research Station, Mashona-land-East, Zimbabwe).

2.2.4. Atmospheric concentrations of NO and N_2O

Trace gas production and consumption processes occur simultaneously in the soil. Consequently, bi-directional fluxes of NO and N_2O have been observed under laboratory and field conditions. Within aggregated soils, soil crumbs may be considered as units of trace gas metabolism, in nonaggregated soils, sand grains covered with a microbial biofilm may play that role. Particularly,

surfaces near soil crumbs are usually heterogeneous with regard to their aerobic–anaerobic metabolism. Even (generally well) aerated upland soils contain anoxic microniches. Then, the ambient NO (and N_2O) concentration determines whether a given soil acts as source or as sink for NO (and N_2O). The equilibrium concentration at which the rate of NO (N_2O) production equals the rate of NO (N_2O) consumption (i.e., at which the apparent net flux equals zero) is commonly termed NO (N_2O) compensation concentration (or "compensation point"). Whether compensation points are of major importance for the exchange of NO and N_2O on a larger (regional, global) scale, is currently not clear. There are only a few reports of NO (N_2O) compensation concentrations, and their range is extremely wide (< 1 ppbv to several hundreds of ppb). In most studies, the average ambient air concentration of NO (or N_2O) was found to be well below the compensation concentration. Consequently, the mean net flux was directed from the surface to the atmosphere (mean net emission).

3. Biogenic emissions of NO and N_2O from semi-arid and arid soils

More than one third of the global land area are deserts and drylands (see Chapter 1): semi-arid, arid and hyper-arid land constitute respectively 17.7 %, 12.1 %, and 7.5 % of planet Earth's total land area of 13049 million hectares (Harrison and Pearce, 2000). In this review of recent literature on NO and N_2O emissions from natural and semi-natural soils of semi-arid and arid regions studies on agricultural fields (fertilizer effects) have not been included. The reader is referred to the extensive work of Bowman et al. (2000a, 2000b), who made a global compilation of 846 N_2O emission and 99 NO emission measurements in agricultural fields; however, a subset of only 8 measurements remains for regions with an annual rainfall less than 450 mm. With respect to natural and semi-natural soils, we have used the global inventory by Davidson and Kingerlee (1997) as a starting point. When stratifying all data (field and laboratory measurements) according to the Koppen-Geiger climate classification scheme (cf. Strahler and Strahler, 1999), only 17 NO and N_2O flux measurements have been identified for BW (desert) and BS (steppe) climates (for NO: 3 (BW), 8 (BS); for N_2O: 2 (BW); 4 (BS)). We enlarged this rather small database by (a) addition of some results from our laboratory studies on semi-arid and desert soils (see below), and (b) consideration of all data obtained in transition regions (e.g. Cwa/BSh, Csa/Bsk). Our compilation is presented in Table 2. To facilitate comparison between NO and N_2O fluxes, all data are given in terms of mass of nitrogen (N). NO and N_2O fluxes are listed for "dry soil" and "wet soil" conditions. Whenever possible, the column "wet soil" contains those NO and N_2O fluxes, which have been found at respective optimum soil moisture conditions (Section.2.2.2, Fig.1). Low and very low NO and N_2O fluxes are generally observed from dry arid and dry/hot semi-arid soils (< 1.5 ng $m^{-2}s^{-1}$). This low number might be compared to the 10 to 100-fold NO and N_2O fluxes emitted from temperate grasslands and forests (NO), as well as from rainforests soils (N_2O) (cf. Davidson and Kingerlee, 1997; Verchot et al., 1999; Ludwig et al., 2001). However, semi-arid and arid soils, which are generally believed to be (a) nutrient poor, (b) nitrogen limited, and (c) of low microbiological activity due to water and starvation stress, release considerable amounts of NO and N_2O, as soon as they are wetted (e.g. even by low and/or sporadic rainfall). The ratio of fluxes from wet to those from dry soils ranges between 1.5–325 and 2.3–23 for NO and N_2O, respectively. It should be mentioned, that emissions (at least of NO) from semi-arid soils at the onset of the rainy season could have an "explosive" character (Meixner et al. 1997, Otter et al. 1999). For Chihuanan desert soils, Hartley and Schlesinger (2000) reported a 10-fold increase of biogenic NO emission within only 10 min after a 20 mm artificial rainfall.

Table 2 : Compilation of recent literature concerning field and laboratory measurements of NO and N_2O fluxes from semi-arid, arid, and hyper-arid soils (Harris et al (1996) have not reported NO fluxes under dry soil conditions; data of Aranibar et al. (2004) have been used to calculate the corresponding wet/dry ratio).

location	description	mean flux dry / wet [ng m^{-2}s^{-1}]		flux meas. method	wet/dry ratio [1]	geographic position lat. / long.	elevation [m a.s.l.]	annual precip. [mm]	annual air temp. [°C]	climate (Koppen-Geiger)	reference
fluxes of nitric oxide (NO) :											
New Mexico,USA	Chihuahua desert, grassland	0,06	3,6	chamber (field)	65	32.6166° N 106.6666° W	1250	230	27,5	BWk	Hartley & Schlesinger 2000
New Mexico,USA	Chihuahua desert, Creosotebush	0,06	18	chamber (field)	325	32.6166° N 106.6666° W	1250	230	27,5	BWk	Hartley & Schlesinger 2000
Israel	Negev desert	3,2	29	chamber (laboratory)	9,3	30.8500° N 34.7800° E	470	100	18,5	BWh	this work
Namibia	Savanna, Kalahari sands (Oshivelo)	1,5	30	aircraft gradient	20	18.7000° S 17.2000° E	1102	358	22,4	BWh	Harris et al. 1996
Namibia	Namib desert, gravel desert	0,3	3,6	chamber (laboratory)	12	23.1117° S 15.0219° E	670	23	21,1	BWh	this work
Namibia	Namib desert, dune	0,3	7,0	chamber (laboratory)	23	23.3407° S 15.0230° E	464	23	21,1	BWh	this work
Namibia	Namib desert, interdunal plane	0,3	3,1	chamber (laboratory)	10	23.3410° S 15.0210° E	434	23	21,1	BWh	this work
Botswana	Kalahari sands (Tshane)	1,5	5,0	chamber (laboratory)	3,3	24.1600° S 21.8900° E	1118	296	20,6	BWh	Aranibar et al. 2004
China	Gobi desert Inner Mongolia	0,5	20	chamber (laboratory)	40	49.2333° N 119.7166° E	614	352	-1,6	BWk / BSk	this work
Colorado, USA	Shortgrass steppe	2,0	23	chamber (field)	12	40.8166° N 104.7666° W	1650	322	8,6	Bsk	Epstein et al. 1998
Colorado, USA	Shortgrass steppe, sandy loam	4,7	28	chamber (field)	5,8	40.8166° N 104.7666° W	1650	322	8,6	Bsk	Martin et al. 1998
Colorado, USA	Shortgrass steppe, sandy clay loam	2,3	9,3	chamber (field)	4,0	40.8166° N 104.7666° W	1650	322	8,6	Bsk	Martin et al. 1998
Colorado, USA	Shortgrass steppe, clay loam	2,5	17	chamber (field)	7,0	40.8166° N 104.7666° W	1650	322	8,6	Bsk	Martin et al. 1998
Colorado, USA	Grassland	0,2	1,2	chamber (field)	6,0	40.0166° N 105.2833° W	1885	478	10,7	Bsk / H	Parrish et al. 1987

Table 2 :Compilation of NO and N_2O fluxes from semi-arid, arid, and hyper-arid soils (cont'd).(For the Niger site, Le Roux et al. (1995) have not given any NO fluxes under dry soil conditions; half of their NO flux detection limit has been used here, since no detectable NO fluxes have been observed there under dry soil conditions).

location	description	mean flux dry / wet [ng $m^{-2}s^{-1}$]		flux meas. method	wet/dry ratio [1]	geographic position lat. / long.	elevation [m a.s.l.]	annual precip. [mm]	annual air temp. [°C]	climate (Koppen-Geiger)	reference
fluxes of nitric oxide (NO) :											
Niger	Savanna, topical, dry	0,1	5,7	chamber (field)	57	13.5000° N 3.0000° E	305	540	29,0	BSh	Le Roux et al. 1995
Zimbabwe	Kalahari sands (Victoria Falls)	0,5	22	chamber (laboratory)	44	18.1000° S 25.8500° E	1061	659	20,9	BSh	this work
Botswana	Kalahari sands (Pandamatenga)	1,5	10	chamber (laboratory)	6,7	18.6600° S 25.5000° E	950	659	20,9	BSh	Aranibar et al. 2004
Botswana	Kalahari sands (Maun)	1,5	36	chamber (laboratory)	24	19.9200° S 23.5900° E	945	452	22,4	BSh	Aranibar et al. 2004
Botswana	Kalahari sands (Okwa)	1,5	61	chamber (laboratory)	41	22.4100° S 21.7100° E	1131	439	21,2	BSh	Aranibar et al. 2004
South Africa	Savanna, nutrient poor	1,3	8,0	chamber (laboratory)	6,2	24.6500° S 28.7000° E	1250	625	19,0	BSh	Otter et al. 1999
South Africa	Savanna, nutrient rich	0,9	5,5	chamber (laboratory)	6,1	24.6500° S 28.7000° E	1250	625	19,0	BSh	Otter et al. 1999
South Africa	Savanna (Nylsvley)	1,9	20	chamber (field)	10	24.6500° S 28.7000° E	1250	625	19,0	BSh	Scholes et al. 1997
Spain (Andalusia)	arable land, non-fertilized	2,0	109	chamber (field)	55	37.0000° N 5.6000° W	20	585	18,5	BSh / Csa	Slemr & Seiler 1984
Venezula	managed natural savanna	1,9	12	chamber (field)	6,1	8.8833° N 67.3166° W	500	1300	27,6	Aw / BSh	Cardenas et al. 1993
California, USA	Grassland, unburned	4,0	11	chamber (field)	2,8	34.2000° N 117.7667° W	366	420	16,8	Csa / Bsk	Levine et al. 1988
California, USA	Grassland, burned	2,4	16	chamber (field)	6,5	34.2000° N 117.7667° W	366	420	16,8	Csa / Bsk	Levine et al. 1988
California, USA	Chaparral, unburned	10	15	chamber (field)	1,5	34.2000° N 117.7667° W	366	420	16,8	Csa / Bsk	Levine et al. 1988
California, USA	Chaparral, burned	8,8	45	chamber (field)	5,1	34.2000° N 117.7667° W	366	420	16,8	Csa / Bsk	Levine et al. 1988
California, USA	Chaparral, burned	15	23	chamber (field)	1,5	34.2000° N 117.7667° W	366	420	16,8	Csa / Bsk	Anderson & Poth 1989

Table 2 :Compilation of recent literature concerning field and laboratory measurements of NO and N_2O fluxes from semi-arid, arid, and hyper-arid soils (cont'd).

location	description	mean flux dry / wet [ng m^{-2}s^{-1}]		flux meas. method	wet/dry ratio [1]	geographic position lat. / long.	elevation [m a.s.l.]	annual precip. [mm]	annual air temp. [°C]	climate (Koppen-Geiger)	reference
fluxes of nitric oxide (NO) :											
Zambia	Kalahari sands (Mongu)	1,5	13	chamber (laboratory)	8,7	23.2500° E 117.7667° W	1053	979	22,6	Cwa / BSh	Aranibar et al. 2004
Zimbabwe	Savanna, period. flooded	2,2	142	chamber (laboratory)	65	31.4666° E 117.7667° W	1630	800	15,4	Cwa / BSh	this work
Zimbabwe	Savanna, sheep grazing	0,5	33	chamber (laboratory)	66	31.4666° E 117.7667° W	1630	800	15,4	Cwa / BSh	this work
Zimbabwe	Savanna, cattle grazing	0,5	51	chamber (laboratory)	102	31.4666° E 117.7667° W	1630	800	15,4	Cwa / BSh	this work
Zimbabwe	Miombo, burned	2,0	90	chamber (laboratory)	45	31.4666° E 117.7667° W	1630	800	15,4	Cwa / BSh	this work
Zimbabwe	Miombo (Marondera)	0,5	1,5	chamber (field)	3,0	31.4666° E	1630	800	15,4	Cwa / BSh	Meixner et al. 1997
Zimbabwe	grassland (Marondera)	1,8	5,6	chamber (laboratory)	3,1	18.1833° S 31.4666° E	1630	800	15,4	Cwa / BSh	this work
Zimbabwe	grassland (Marondera)	0,5	4,4	chamber (field)	8,8	18.1833° S 31.4666° E	1630	800	15,4	Cwa / BSh	Meixner et al. 1997
Zimbabwe	agricultural soil, fallow	0,2	5,3	chamber (field)	27	18.1833° S 31.4666° E	1630	800	15,4	Cwa / BSh	Meixner et al. 1997
Zimbabwe	Savanna, maize unfertilized	0,6	3,5	chamber (laboratory)	5,8	18.1833° S 31.4666° E	1630	800	15,4	Cwa / BSh	this work
Zimbabwe	Savanna, ground-nut unfertilized	1,8	9,0	chamber (laboratory)	5,0	18.1833° S 31.4666° E	1630	800	15,4	Cwa / BSh	this work
Zimbabwe	Savanna, ground-nut unfertilized	0,5	27	chamber (field)	54	18.1833° S 31.4666° E	1630	800	15,4	Cwa / BSh	Meixner et al. 1997
Zimbabwe	Savanna, ground-nut fertilized	2,7	16	chamber (laboratory)	5,8	18.1833° S 31.4666° E	1630	800	15,4	Cwa / BSh	this work
Zimbabwe	Savanna, ground-nut fertilized	0,5	8,5	chamber (field)	17	18.1833° S 31.4666° E	1630	800	15,4	Cwa / BSh	Meixner et al. 1997
South Africa	Savanna (Krueger National)	1,4	28	chamber (field)	20	31.2333° S 25.2500° E	600	740	21,0	Cwa / BSh	Levine et al. 1996, Parsons et al. 1996

Table 2 :Compilation of recent literature concerning field and laboratory measurements of NO and N_2O fluxes from semi-arid, arid, and hyper-arid soils (cont'd).

location	description	mean flux dry / wet [ng $m^{-2}s^{-1}$]		flux meas. method	wet/dry ratio [1]	geographic position lat. / long.	elevation [m a.s.l.]	annual precip. [mm]	annual air temp. [°C]	climate (Koppen-Geiger)[C]	reference
fluxes of nitrous oxide (N_2O) :											
Nevada, USA	Mojave desert	0,3	N/A	chamber (field)	N/A	36.8166° N 115.9166° W	968	140	20,2	BWk	Billings et al. 2002
Arizona, USA	Sonoran desert	0,5	4,3	chamber (field)	8,6	32.2500° N 110.9666° W	648	305	17,3	BWk	Guilbault & Matthias 1998
Colorado, USA	Shortgrass steppe	0,2	2,9	chamber (field)	13	40.8166° N 104.7666° W	1650	322	8,6	Bsk	Epstein et al. 1998
Colorado, USA	Shortgrass steppe, non-fertilized	0,2	1,1	chamber (field)	5,0	40.8166° N 104.7666° W	1650	350	8,6	Bsk	Mosier et al 1996
South Africa	Savanna (Krueger National)	1,0	N/A	chamber (field)	N/A	31.2333° S 25.2500° E	600	740	21,0	BSh / Aw	Levine et al. 1996
Spain (Andalusia)	arable land, non-fertilized	4,2	9,7	chamber (field)	2,3	37.0000° N 5.6000° W	20	585	18,5	BSh / Csa	Slemr et al. 1984
Washington, USA	shrub-steppe	0,4	8,5	chamber (field)	23	46.4550° N 119.4231° W	200	220	10,5	Csb / H	Mummey et al. 1997
Canada	fallow, black soil zone	0,4	4,6	chamber (field)	11	53.0166° N 105.7500° W	350	395	2,2	Dfc / Bsk	Corre et al. 1996

[C] The used shorthand code of letters are those of the Koppel-Geiger climate classification system (see Strahler and Strahler, 1999). *First letter*: A=tropical climates; B=dry climates, C=warm temperature climates, D=snow climates; H=highland climates. *Second Letter*: S=steppe climates (semi-arid); W=desert climates (arid); f=sufficient precipitation in all months; s=dry season in summer of the respective hemisphere; w=dry season in winter of the respective hemisphere. *Third Letter*: a=warmest month over 22 °C; b=warmest month under 22 °C; c=fewer than 4 months with means over 10 °C; h=dry and hot (mean annual temperature over 18 °C); k=dry and cold (mean annual temperature under 18 °C).

3.1 THE ROLE OF SOIL MOISTURE AND SOIL TEMPERATURE

As already mentioned above, field data do not allow to easily seperate the effects of soil moisture and soil temperature on biogenic NO and N_2O fluxes. Only few authors have performed a comprehensive analyses of their field data (Slemr and Seiler, 1984; Cardenas et al., 1993; Parsons

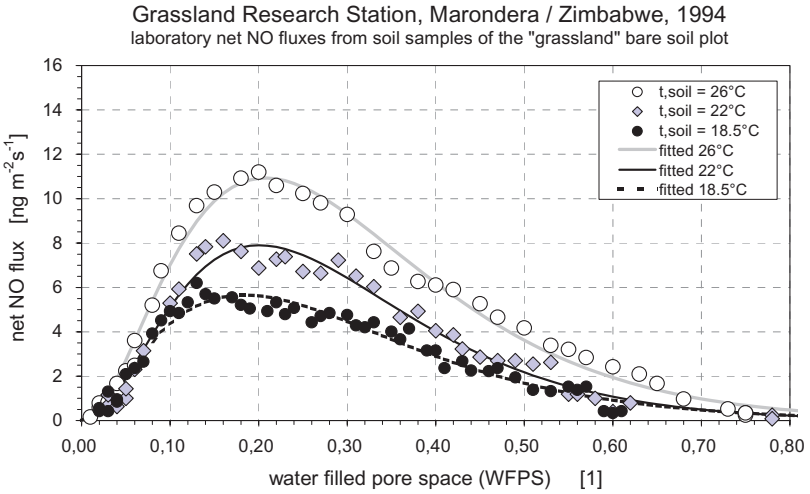

Figure 3a: The dependence of net NO flux from soil moisture (WFPS) and soil temperature for a semi-arid, unfertilzed savanna grassland soil (results of laboratory experiments on a soil sample taken on 14 December, 1994 at the Mariner Grassland Research Station, Mashonaland-East, Zimbabwe).

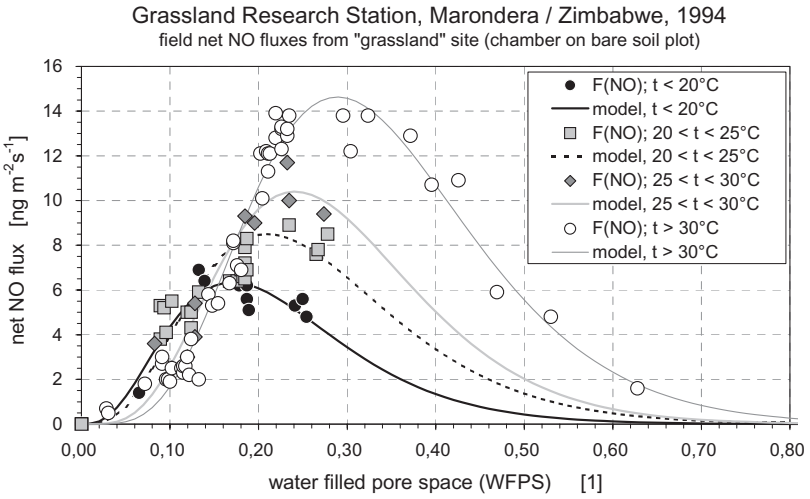

Figure 3b:Net NO flux as dependent on soil moisture (WFPS) and soil temperature at bare soil plot of a semi-arid, unfertilized savanna grassland site (results of field experiments using dynamic soil chambers; September–December 1994, Marondera Grassland Research Station, Mashonaland-East, Zimbabwe; see Meixner et al., 1997).

et al., 1996; Scholes et al., 1997; Epstein et al., 1998; Martin et al., 1998; Pilegaard et al., 1999; Hartley and Schlesinger, 2000). However, laboratory investigations on soil samples offer the unique chance to study responses of one factor, while the other is held constant (Yang and Meixner, 1997; Otter et al., 1999; van Dijk and Meixner, 2001; Aranibar et al., 2004). Corresponding laboratory results on soil samples from a semi-arid, unfertilized grassland site in Zimbabwe are presented in Figure 3a. A characteristic optimum curve for the response of the net NO flux to soil moisture and an exponential increase with soil temperature ($Q_{10} \approx 2$; see 2.2.3.) is observed. Optimum soil moistures ($WPPS_{opt}$) are around 0.20 with a tendency to slightly decrease with decreasing soil temperature. Kirkman et al. (2001) used these laboratory results for the first countrywide estimate of spatio-temporal soil emissions in southern African (Zimbabwe).

Soil samples (0–5 cm) at Marondera were taken exactly from those soil plots, which have been enclosed by the steel frames of the dynamic chambers used during field measurements. Results of the field experiments (see Meixner et al., 1997) have been classified according to measured WFPS and ranges of measured soil temperatures at –5 cm ($t_{soil} < 20°C$, $20 < t_{soil} < 25°C$, $25 < t_{soil} < 30°C$, and $t_{soil} > 30°C$). While there is larger scatter of the field data and low data coverage for WFPS > 0.3 and $t_{soil} < 30°C$, differences between laboratory and field data are small, as already reported earlier (Yang and Meixner, 1997; Ludwig et al., 2001). There is a significant increase of $WFPS_{opt}$ with increasing soil temperature.

An algorithm has to be developed to fit the laboratory as well as the field data. The net NO flux, F_{NO} (in ng $m^{-2}s^{-1}$) is described by

$$F_{NO}(WFPS) = a\ WFPS^b \exp(-c\ WFPS)$$

where WFPS is the water filled pore space. The parameters a, b, and c are related to observed values by

$$a = F_{NO}(WFPS_{opt}) / [WFPS_{opt}{}^b \exp(-b)]$$

$$b = \ln[F_{NO}(WFPS_{opt}) / F_{NO}(WFPS_{upp})] / [\ln(WFPS_{opt}/WFPS_{upp}) + WFPS_{upp}/WFPS_{opt} - 1]$$

$$c = -b / WFPS_{opt}$$

where $WFPS_{opt}$ is the soil moisture at which the maximum net NO flux is observed; $F_{NO}(WFPS_{opt})$ equals $\max[F_{NO}(WFPS)]$; and $WFPS_{upp}$ is the soil moisture at which $F_{NO}(WFPS) = F_{NO}(WFPS_{upp}) \approx 0$ for $WFPS > WFPS_{opt}$. Numerical values of the parameters a, b, and c can be determined by minimizing the sum product of the difference between measured and fitted data points.

We applied this algorithm also to the results of laboratory studies on soil samples that have been taken in the Namib desert (Gobabeb Research Station, 23.34°S, 15.02°E). Results are shown in Figure 4. To our knowledge, these are the first results of net NO fluxes from a hyper-arid region. Compared to the results obtained with semi-arid soils (Fig. 3a), net NO emissions are lower, and –at comparable soil temperatures– $WFPS_{opt}$ of Gobabeb desert soils are approximately two third of the semi-arid Marondera soils. Since the work of Linn and Doran (1984), $WFPS_{opt}$ of approximately 0.6 is often be quoted for a number of microbial processes. However, this value is definitely not applicable with respect to the emission of NO from semi-arid and arid soils (see also Cárdenas et al. (1993), Parsons et al. (1996), Yang and Meixner (1997), Scholes et al. (1997), Epstein et al. (1998), Martin et al. (1998), Otter et al. (1999), Hartley and Schlesinger (2000), and Aranibar et al. (2004)). Very low values for $WFPS_{opt}$ (< 0.15) might be typical for hot arid regions: similar and even lower values have been found for the Chihahuan desert (Hartley and Schlesinger, 2000) and for the southern part of the Kalahari transect (Aranibar et al., 2004). As already pointed out by Aranibar et al. (2004), these low $WFPS_{opt}$ values indicate that even relatively dry soils can emit considerable amounts of NO. Nevertheless, NO emissions from desert soils are at the very low end of those observed globally, since emission rates decrease strongly with aridity.

It is well known that addition of water to dry soils typically produces strong increases not only of NO, but also of N_2O emission (e.g. Davidson, 1992; Meixner and Eugster, 1999). It seems, that this increase is caused by a “dormant” water-stressed microbial community. As soon as the first

water drops are supplied to the desiccated soil, this microbial community "wakes up". It is fed by

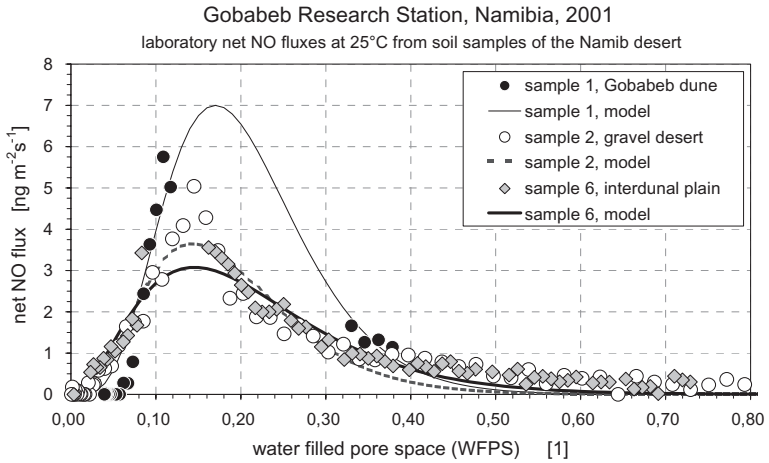

Figure 4: The dependence of net NO flux from soil moisture (WFPS) and soil temperature for hyper-arid desert soils (results of laboratory experiments on soil samples taken on 14 December, 1994 at the Gobabeb Research Station, Namib, Namibia).

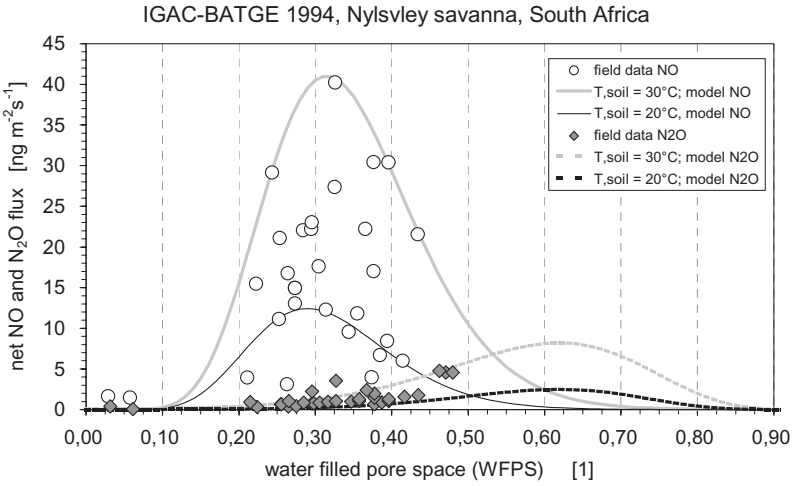

Figure 5: The dependence of net NO and net N_2O fluxes from soil moisture (WFPS) and soil temperature for semi-arid svanna soils (results of field experiments 12-30 November, 1994 at Nylsvley Nature Reserve, South Africa).

nutrients (nitrate and or ammonium), which have accumulated during the dry season (semi-arid regions) or longer dry periods between infrequent/sporadic rainfalls (deserts). Indeed, nitrifying bacteria (e.g. autotrophic nitrifiers) and persistent denitrifying enzymes have been found (a) to be well adapted to survive extreme drought and starvation stresses and (b) to become very active

within minutes after wetting (Davidson, 1992). In turn, since soil microbes in semi-arid ecosystems have a strong sensitivity to water deficit, they experience water stress earlier than starvation due to the depletion of soil mineral nitrogen (D'Odorico et al., 2003). For a mechanistic description of wetting and drying effects on nutrient cycles see Chapter 11.

The relationship between WFPS and relative fluxes of NO, N_2O, and N_2 shown in Fig. 1 suggests that low N_2O fluxes are to be expected for semi-arid and arid soils. Indeed, whenever detected at all, N_2O fluxes are low in these enviroments. Data in Table 2 show that there is a strong tendency for much higher NO than N_2O fluxes under "wet soil" conditions. Out of the few studies with NO and N_2O fluxes having been measured simultaneously in semi-arid regions, the results of Scholes et al. (1997) have been selected for presentation in Figure 5. This data set was obtained during subsequent wetting experiments on nutrient-poor and nutrient-rich soils of the Nylsvley Nature Reserve (South Africa). Since soil temperatures between 21and 32°C have been reported for this experiment, t_{soil} = 20 and 30°C have been used to calculate enveloping curves in Figure 5 by the new algorithm. The highest WFPS observed was 0.48, where N_2O fluxes still have not started to decrease. A value of $WFPS_{opt}$ = 0.62 has arbitrarily been chosen for the calculation of the N_2O flux, this value being in accordance with the results of Parsons et al. (1996) and Davidson (1992). Under actual conditions at Nylsvley, the ratio of N_2O and NO fluxes was on the average 0.09. This result led Scholes et al. (1997) to the conclusion, that undisturbed and unfertilized semi-arid savanna soils are unlikely to make a major contribution to global N_2O emissions.

3.1. PRODUCTION AND CONSUMPTION OF NO UNDER SEMI-ARID CONDITIONS

During the laboratory studies on savanna grassland soil samples from Marondera (c.f. Fig. 3a), a selection of soil samples (grassland and Miombo woodland plots (both unfertilized); unfertilized

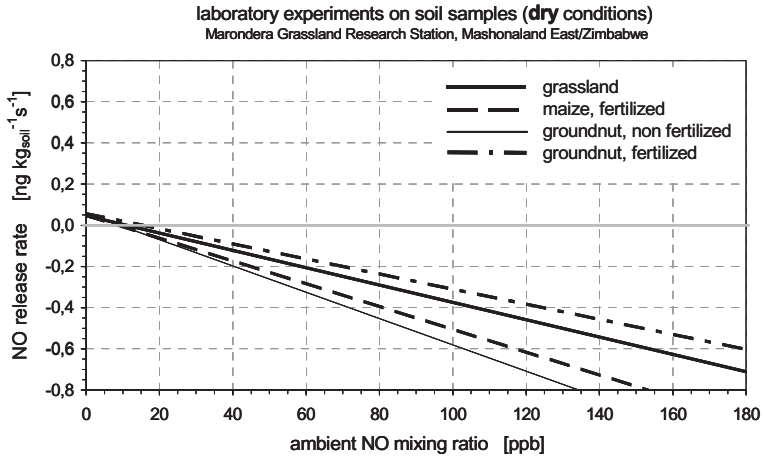

Figure 6a: Results of NO fumigation experiments on different soil samples under "dry soil conditions" (i.e. volumetric soil water content < 3 %). NO release rates are measured in ng of nitrogen per kg of soil and per sec. Soil samples have been taken on 14 December 1994 at the Marondera Grassland Research Station, Mashonaland-East, Zimbabwe.

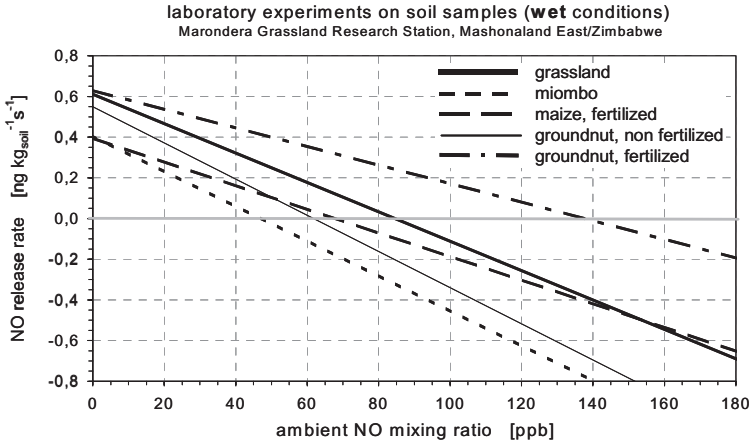

Figure 6b: Same as Figure 6a, but for "wet soil conditions" (i.e. volumetric soil water content = 13 %).

and fertilized maize and groundnut plots) have been fumigated with known NO concentrations. Corresponding NO release rates versus NO concentration in the headspace of the dynamic soil chamber are plotted in Figures 6a ("dry soil conditions") and 6b ("wet soil conditions"). The intercepts of the individual lines with the y-axis are equivalent to the NO production rates of the different soils at natural conditions. The intercepts with the x-axis are equivalent to the corresponding NO compensation concentrations (see Section 2.2.4), and NO consumption rates are calculated from the slope of the lines (see Remde et al., 1993; Yang et al., 1996). NO production and consumption rates, as well as NO compensation concentrations are much lower under dry soil than under wet soil conditions, elucidating again a "dormant" water-stressed microbial community, which "wakes up" after the first water is supplied to the desiccated soils. The observed ambient NO concentrations at the Marondera site are typically well below 1 ppb (Meixner et al. 1997). Nevertheless, these semi-arid soils are -at least in the wet season- definitely a source for atmospheric NO. However, during the dry season, when wide spread savanna fires cause massive pyrogenic NO emissions and consequently higher ambient NO concentrations, soils may also act as temporary sinks of NO.

3.2. SOIL TEXTURE: A CONTROLLING FACTOR FOR NO AND N_2O EMISSION FROM SEMI-ARID, ARID, AND HYPER-ARID LANDS?

There is evidence from a recent modelling study (Ridolfi et al., 2003) that N_2O emissions from fine-textured soils typically exceed those from coarser soils, while the opposite is the case for NO emissions (see Chapters 3 and 11). Moreover, NO emissions from clayey soils might be very low, while N_2O emissions become significant. From a soil physical/chemical point of view these results are very plausible with respect to NO fluxes, since coarser (sandy) soils (below field capacity) reveal higher rates of diffusion than fine-textured (clayey) soils. Furthermore, in sandier soils the importance of advective transport increases, which has the potential to increase the soil-atmosphere exchange severalfold over that by molecular diffusion (Martin et al., 1998). Consequently, NO has a higher chance to escape from sandier soils before it is biologically consumed and/or takes part in any reactions (Scholes et al., 1997). The escape efficiency by physical pathways is more important for NO than for N_2O because the chemical reactivity of NO is much higher. However, during a 2-year, large-scale study in the Colorado shortgrass steppe, Martin et al. (1998) observed highest average NO fluxes from sandy loam soils and lowest fluxes

from clay loam soils. Admittedly, the trend of increasing NO fluxes with increasing sand content was statistically not significant. There is, however, increasing evidence that there is a textural influences on the optimum water filled pore space ($WFPS_{opt}$) for NO emission.

Table 3. Optimum water filled pore space ($WPFS_i$) for NO emission from semi-arid, arid, and hyper-arid soils.

location	biome	sand [%]	silt [%]	clay [%]	bulk density [kg m^{-3}]	$WFPS_{opt}$ [1]	Reference
New Mexico, U.S.A.	Chihuahuan desert, shrubland	71	NA	8	1580	< 0.15	Hartley & Schlesinger 2000
New Mexico, U.S.A.	Chihuahuan desert, grassland	69	NA	10	1580	< 0.10	Hartley & Schlesinger 2000
New Mexico, USA.	Chihuahuan desert, playa	18	NA	51	1580	0.38	Hartley & Schlesinger 2000
China	Gobi desert / Inner Mongolia	NA	NA	NA	1290	0.25	this work
Namibia	Namib desert, gravel	NA	NA	NA	1390	0.12	this work
Namibia	Namib desert, dune	NA	NA	NA	1330	0.14	this work
Namibia	Namib desert, interdunal	NA	NA	NA	1390	0.12	this work
Zambia	Kalahari sands (Mongu)	98	2	1	1260	0.14	Aranibar et al. 2004
Botswana	Kalahari sands (Pandamatenga)	97	2	1	1580	0.23	Aranibar et al. 2004
Botswana	Kalahari sands (Okwa)	96	2	2	1530	0.10	Aranibar et al. 2004
Botswana	Kalahari sands (Maun)	96	1	3	1600	0.17	Aranibar et al. 2004
Zimbabwe	savanna, grassland	87	3	10	1430	0.16	Meixner et al. 1997
S. Africa	savanna (Nylsvley)	88	NA	4	1560	0.26	Scholes et al. 1997
S. Africa	savanna, biennial burned	85	5	10	1600	0.20	Parsons et al. 1996
S. Africa	savanna, fire exclusion	83	7	11	1600	0.22	Parsons et al. 1996
S. Africa	savanna, thornveld	36	8	56	1700	0.35	Parsons et al. 1996
S. Africa	savanna, nutrient poor	74	6	20	1560	0.28	Otter et al. 1999
S. Africa	savanna, nutrient rich	71	7	22	1560	0.40	Otter et al. 1999
S. Africa	savanna, floodplain	34	12	54	1100	0.51	Otter et al. 1999
Spain	agricultural, non-fertilized	89	4	7	1630	0.15	Slemr & Seiler 1984
Venezuela	Savanna	70	13	17	1500	0.41	Cardenas et al. 1993
Colorado, U.S.A.	shortgrass steppe	72	15	13	1400	0.35	Martin et al. 1998
Colorado, U.S.A.	shortgrass steppe	42	18	30	1300	0.66	Martin et al. 1998

For a total of 35 soil samples from the Brazilian tropics, van Dijk (2001) found a clear relationship between increasing $WFPS_{opt}$ and increasing clay content . Studying NO fluxes under semi-arid field conditions, Otter et al. (1999) detected $WFPS_{opt}$ values between 0.3 and 0.4 for sandy soils, while for a clayey floodplain soil $WFPS_{opt}$ was 0.6. Table 3 contains those results for NO fluxes from semi-arid, arid, and hyperarid soils where soil texture data and/or $WFPS_{opt}$ values have been reported too. For clay contents > 30 %, corresponding $WFPS_{opt}$ values for NO emission are higher than 0.35. Lowest $WFPS_{opt}$ (< 0.15) have been observed for arid and hyper-arid soils with clay contents less than 10%. This leads us to the hypothesis, that arid and hyper-arid lands will emit NO after very low-intensity rainfalls. But also dew fall and/or deposition of fog droplets (as occurring in the Namib desert) might add enough moisture to the first millimetres of the surface to trigger temporarily limited NO emission.

3.3. NITRIFICATION VS. DENITRIFICATION: OBSERVATIONS FROM SEMIARID AND ARID LANDS

Generally, if nitrification is dominating NO and N_2O fluxes from soils, than the major controllers are soil moisture, O_2 and NH_4^+ availability (see Chapter 11). If denitrification is dominating, soil moisture and the availability of reduced C and terminal electron acceptors (O_2, NO_3^-, NO_2^-) are most important (Smart et al., 1999). The limiting factors for any biological activity in semi-arid and arid systems are known: soil moisture and nitrogen availability (in that order; D'Odorico et al., 2003). Nitrogen availability in semi-arid and arid ecosystems depends considerably on the area and time (Fisher et al., 1987). This is especially true for the surface soil layers where NO production and NO consumption processes are located (Conrad, 1996). It is no surprise, that early reports about the dominance of nitrification vs. denitrification for NO and N_2O emissions from semi-arid and arid soils have been somewhat contradicting and rely on the choice of the site, such as wet tropical savannas or semi-arid / arid regions (Smart et al., 1999). Addition of NO_3^- (NH_4^+) led to higher (lower) NO fluxes in wet tropical systems. Consequently denitrification has been accounted for the dominant process. In warm (hot) semi-arid and arid regions, addition of NH_4^+ (NO_3^-) led to higher (lower) NO fluxes, respectively. Therefore, nitrification has been claimed to be the more important process. Considering, that nitrification is a highly aerobic process, there is growing evidence that arid soils are characterized by high nitrification activities due to their warm, dry and aerobic nature (Smart et al. 1999). Indeed, Martin et al. (1998) clearly state that nitrification is the dominant process for both NO and N_2O emissions from shortgrass steppe. According to Parsons et al. (1996), Scholes et al. (1997), Otter et al. (1999), and Aranibar et al. (2004) this holds (at least) for NO emissions from semi-arid and arid southern African savannas and deserts. Hartley and Schlesinger (2000) state, that in (semi-) deserts, with a short wet season, corresponding NO fluxes from nitrifying bacteria could be extremely high (see Table 2) because soil NH_4^+ accumulates by mineralization of organic nitrogen (e.g. from litterfall of shrubs) (Fisher et al., 1987). Finally, it should be mentioned, that in semi-arid, particularly in arid soils, where generally low nutrient pools are prevailing, high microbial metabolism and high turnover rates of (few) nutrients might be major factors of observed NO fluxes (Le Roux et al., 1995). Davidson (1992) has specifically addressed the (small) NO_2^- pool of these soils, but also the potentially high (and at least temporarily) nitrogen flux through this pool.

3.4. NITROGEN INPUTS TO SEMI-ARID AND ARID ECOSYSTEMS

Input of plant available nitrogen to semi-arid and arid systems is caused by two major processes: (a) biogenic fixation of atmospheric molecular nitrogen (N_2) and (b) to deposition of nitrogen compounds from the atmosphere (see also Chapter 11). For arid areas, N_2 fixation is a desirable process only when nitrogen is the major limiting nutrient; overall costs are high (Aranibar et al., 2004). Nitrogen fixating legumes (Fabaceae) are also dominant in the driest regions of the Kalahari sands. Cyanobacteria, also capable of fixing atmospheric N_2, are widely distributed in semi-arid and arid soils. An estimate of nitrogen inputs by N_2 fixation of soil crusts is difficult, corresponding values range from a few grams to 100 kg $ha^{-1}a^{-1}$. Scholes et al. (2003) have estimated biological N_2 fixation at southern African fine leafed and broad-leafed semi-arid sites to 18 and 5 kg $ha^{-1}a^{-1}$, respectively. Deposition of nitrogen compounds from the atmosphere to semi-arid and arid lands can occur in the form of (a) wet deposition (i.e. in-cloud and below-cloud scavenging) of soluble gases (HNO_3, HNO_2, NH_3) and aerosol particles (NO_3^-, NO_2^-, NH_4^+), (b) dry deposition of gases NO, NO_2, HNO_3, HNO_2, NH_3 and PAN (peroxyacetylnitrate), (c) dry deposition of aerosol particles (NO_3^-, NO_2^-, NH_4^+), and (d) deposition during the dew forming process (see Meixner, 1994). Since most semi-arid and arid areas are (very) remote, atmospheric input from the industrialized, polluted regions is thought to be generally small; nitrogen inputs

through dry and wet deposition of 3 and < 2 kg $ha^{-1}a^{-1}$ were reported for Sonoran desert and Utah semi-arid sites, respectively (Guilbault and Matthias, 1998; Smart at al. 1999). Galy-Lacaux et al. (2003) estimated 2 kg $ha^{-1}a^{-1}$ as total nitrogen deposition to West African semi-arid and arid ecosystems (65% by dry, 35% by wet deposition). However, there is a very particular situation for large-scale nitrogen deposition in southern Africa. Pyrogenic and anthropogenic emissions of NH_3, NO and NO_2 are dispersed into a well-mixed, persistent, atmospheric boundary layer, which is typically capped by a strong temperature inversion (see Chapters 11 and 16 for a discussion of fire effects on nitrogen cycling and fire regimes). This leads to considerable accumulation of nitrogen containing gaseous and particulate pollutants in the atmospheric boundary layer; here NO and NO_2 will be transformed to HNO_3 and/or aerosol NO_3^- within a few days. Within very persistent anti-cyclons (see Garstang et al., 1996), air of the atmospheric boundary layer is frequently cycling over southern Africa, transporting pollution (and products) from industrialized (burning) regions to the remote semi-desert and desert areas. This specific situation enhances dry deposition of nitrogen compounds also at remote semi-arid and arid ecosystems. In particular, HNO_3 and NH_3 are deposited, since their dry deposition rates are at least one order of magnitude higher than that of NO_2 (see Meixner, 1994). Scholes et al. (2003) have estimated corresponding average inputs of 8 and 7–21 kg $ha^{-1}a^{-1}$ by wet and dry deposition processes, respectively.

3.5. GLOBAL IMPORTANCE OF NO AND N_2O EMISSIONS FROM NATURAL SEMI-ARID AND ARID SOILS

According to Davidson and Kingerlee (1997), who stratified worldwide NO emissions according to major biomes, the categories “chaparral/thorn forest” and “tropical savanna/woodland” comprise more than half of the total global NO soil source (21 Tg a^{-1}). It is most likely, that humid tropical savannas contribute most to this figure. According to Otter et al. (1999), large NO emissions from tropical savannas are determined by the length of long, hot and wet summers, providing optimal conditions for biogenic production of NO (and N_2O) in the soil. However, towards sub-tropical semi-arid, and particularly for arid regions, this determinant may become less important. Scholes et al. (1997) state that NO fluxes from sub-tropical savannas generally exceed those from sub-tropical forest soils. Concerning N_2O fluxes, they consider (a) N_2O fluxes from tropical forest soils (warm and wet) to be the globally most important, and (b) N_2O fluxes from sub-tropical savannas to be always lower than those from corresponding forest soils. The argument is based on the fact that denitrification benefits from the carbon-rich and somewhat wetter soils in the forests. The undoubtedly large effect of the first rains to the “wetting” pulse of the NO emission from semi-arid and arid African soils is thought to contribute little to the global NOx budget. However, Scholes et al. (1997) consider this pulse to be an important contributor to episodes of high ambient ozone in southern Africa.

Despite the few additional results from desert and semi-desert soils presented in this paper, the statement of Davidson and Kingerlee (1997) is still valid.These biomes still constitute a major gap in our knowledge, but are probably very significant for the global NOx budget. They emphasize that, despite the fact that deserts have low plant productivity in general, inorganic nitrogen can accumulate in desert and semi-desert soils during (long) dry periods. During regular or short wet periods, microbial activity will peak and lead to substantial NO emissions, which are additionally favoured by mostly sandy soils with high porosity (see 3.3.).

Due to the fact, that biogenic N_2O emission is favoured by denitrification processes at high soil moisture contents ($WFPS_{opt} \approx 0.6$), N_2O fluxes from semi-arid soils are expected to be low. Those from desert soils are very low, if detectable at all. Indeed, based on field measurements, there is broad consensus that the contribution of biogenic N_2O emissions from these (unfertilized) ecosystems does not contribute much to the global N_2O budget (e.g. Scholes et al., 1997; Billings et al., 2002).

Effects of land-use changes on N_2O fluxes have been reported for semi-arid shortgrass steppe of the Great Plains of central North America (Mosier et al., 1996), which comprise approximately 19% of the global temperate grasslands. Conversion of grasslands to croplands led to 8-fold higher N_2O emissions for about 18 months following tillage. Still 25-50% higher N_2O emissions from tilled soils are observed even after 3 years. Reversion of cultivated soils back to grasslands will bring N_2O emissions from tilled soils down to those of native state in a period longer than 8 but shorter than 50 years. Guilbault and Matthias (1998) focussed the practice to change low-latitude desert ecosystems by fertilization and irrigation for agricultural, recreational, and landscaping purposes. The conversion of a natural Sonoran desert soil into a golf course (by regular irrigation with secondary sewage effluents) resulted in a considerable increase of N_2O fluxes. Information about the effects of (long-term) land use change on soil biogenic NO emissions are hardly available. There is only the suggestion of Hartley and Schlesinger (2000) that NO fluxes from Chihuahuan desert soils may have declined with the conversion of grassland to shrubland. However, it can be assumed that future land use changes of natural semi-arid and arid lands will (a) either include irrigation and fertilization (which will presumably cause higher NO emissions), or (b) will lead to degradation (e.g. through overgrazing and salinization, which will cause generally lower NO emission. Chapter 18 discusses in detail the main factors contributing to land degradation and desertification. According to Harrison and Pearce (2000), approximately 20 % of the world's susceptible dryland soils (1.035×10^9 ha) were degraded at the end of the 1990s (either by water and wind erosion or by chemical and physical deterioration); partitions to region constitute 7.7, 7.6, 9.6, 30.9, 35.8, and 8.4 % for North America, South America, Europe, Africa, Asia, and Australasia, respectively. Prominent and very important targets in this respect are the arid and semi-arid lands of Africa, East and Central Asia (Chuluun and Oijma, 2002). Particularly the latter deserve future attention, since virtually no measurements of soil NO and N_2O emissions are known for these regions.

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