Measurements of nitric oxide emissions from forest soils in the Netherlands

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Abstract. Nitric oxide (NO) fluxes to the atmosphere were determined from different soil types in coniferous forest and deciduous forest in the Netherlands. Dynamic chambers were used to determine the emission every week throughout a whole year. Forest type and soil texture seem important parameters leading to large differences in fluxes between sites. High fluxes of up to 178 ng m^{-2} s^{-1} were observed in summer in a Douglas Fir forest. In a nearby Beech forest, on the same soil, fluxes up to 83 ng m^{-2} s^{-1} were observed. Emissions from clayey soils in a Beech forest were much lower and ranging from 0 to 14 ng m^{-2} s^{-1}. Besides the important effect of the forest community type and the soil texture on the NO flux, a strong correlation with soil temperature was observed (accounting for up to 70% of the variance). Soil moisture could explain up to 60% of the variance of the NO flux. It seems that an optimum range of intermediate moisture contents exists where high temperatures lead to high emissions.

KEY WORDS: NO emission, microbial activity, soil moisture, forest type, soil texture, N-

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addition.

1. Introduction

Nitrogen oxides play together with hydrocarbons an important role in the tropospheric ozone formation. Policies to reduce levels of troposheric ozone are often based on computer simulation models that rely on estimates of emissions from all relevant sources of both species. Especially on a global scale the contribution of emissions of nitric oxide (NO) from natural sources to the NOy (NO plus other nitrogen oxides) budget is very significant. Only few data are available on the emission rates of these trace gases from soils in temperate forests.

Earlier studies indicated that NO emitted from the soil is mainly produced by biological nitrification, the oxidation of organic nitrogen and/or ammonium (NH_4^+) to nitrate (NO_3^-), and denitrification, the reduction of nitrate $^-$ to NO, nitrous oxide (N_2O) and nitrogen. This biological production of nitrogen oxides may vary considerably between soils. The flux is strongly linked to temperature, soil wetness and other variables such as availability of NO_3^- and NH_4^+, soil acidity and organic substrate [Meixner, 1994].

The Netherlands Organization for Applied Scientific Research (TNO) co-ordinated a European project (FOREXNOX) in which measurements of exchange rates of nitrogen oxides are carried out in various forests across Europe. One of the aims of this study was to establish NO fluxes at the soil-atmosphere interface in different forests as well as from different soils and to determine key factors regulating this flux. For this purpose experiments were designed to cover a wide variety of conditions. These included

measurements in areas with high (Netherlands) and low (Scotland) nitrogen inputs from the atmosphere, in deciduous en coniferous forests and measurements from different soil textures (sandy and clayey soils). In this paper only the measurements carried out in the Netherlands are presented. Measurements were carried out throughout the year which made it possible to determine emissions under varying conditions with respect to soil temperature and wetness.

2. Method

2.1 Experimental

Dynamic open chamber techniques as described by Mosier [1989] were used to measure the nitric oxide flux from soil. The stainless steel chambers (150 x 30 x 25 cm) were sunk in the soil for about 10 cm giving a total volume of 0.0675 m^3. Two fans were attached to the Plexiglas lid on top of the chamber to achieve proper mixing of the air inside the chamber. A ventilator enabled ambient air to enter the chamber through a funnel and flow over the enclosed soil. NO concentrations at the inlet and outlet of the chamber were determined with a using a Thermo Environmental Instruments 42 W monitor based on the chemiluminescent reaction between NO and ozone. The sampling procedure and data logging were controlled using a Campbell 21 X. Each measurement sequence took about 1 hour after which the Plexiglas lid was opened and measurements were made from the next chamber. In addition several physical and chemical aspects of the soil were monitored. Soil temperature was recorded simultaneously with the chamber experiments. The gravimetric water content of the soil was determined for each experimental site to represent the soil humidity.

The study area at Speuld is a 35 year old forest stand which has several different plantations all on identical coarse textured acidic soil. Flux measurements were made from three experimental sites. NO emissions were determined from sandy soil in a Douglas fir (*Pseudotsuga menziesii*) plantation and Beech (*Fagus*) plantation at Speuld. Since these two forest types were stocked on identical soil, results could be used to study the impact from tree species on the NO fluxes. Additionally, an experimental site within the Douglas Fir plantation was weekly supplied with a ammonium sulfate (NH_4^+/SO_4^-) solution. By this procedure this site would receive an amount of nitrogen and sulfate equivalent to twice the normal annual deposition.

The study area at Hollandse Hout is a Beech (*Fagus*) plantation in a 25 year forest which has several different forest communities. The soil has a very fine soil texture, consisting mainly of heavy clay. Atmospheric deposition levels are relatively high for both Speuld and Hollandse Hout, averaging to 40 kg N ha^{-1} y^{-1} and 30 kg S ha^{-1} y^{-1}.

From July 1996 to August 1997 flux measurements were made at the experimental site Speulderbos in the central part of the Netherlands. In total three chambers were operational, providing NO fluxes from three different experimental plots. Additionally, flux measurements were made during two campaigns at a different location (Hollandse Hout, Flevoland). During short campaigns in these forests only two chambers were operated and measurements were made at the same plot with every visit.

2.2 Calculation

The NO flux was calculated from the difference in NO mixing ratios [ppb] between inlet and outlet of the dynamic chamber and was corrected for bias due to chemical reactions between NO, NO_2 and O_3 (see below). The fluxes were calculated from the following equation:

$$F_{NO} = \{\frac{Q}{A}(c_{out} - c_{in}) + F_{cor}\} \cdot \frac{M_N}{V_m} \quad (1)$$

Where F_{NO} [ng N m^{-2} s^{-1}] is the NO flux, Q [m^3 s^{-1}] is the flow rate through the chamber, A [m^2] is the area enclosed by the frame and V_m and M_N are the molar volume and molar weight of nitrogen respectively. F_{cor} is a factor used to correct for the amount of NO consumed in the reaction with O_3 (to form NO_2) in the enclosure and can be found by estimating the average reaction rate in the enclosure during monitoring.

The NO flux data were numerically filtered to prevent bias from strong variations of the NO concentrations in the ambient air. Air was alternatively sampled and analyzed at the chamber inlet and chamber outlet, switching every 3 minutes. In cases where the ambient air concentration is strongly variable the calculated flux will show an increased variation too. Averaging two subsequent NO mixing ratios of the ambient air smoothened sudden leaps, and proved to be a good method to reduce the variance in the calculated NO flux. Only few flux measurements with large fluctuations of the NO mixing ratios at the inlet

were rejected.

3. Results and discussion

FIGURE 1

From July 1996 to August 1997 NO fluxes were determined every week at Speuld. In addition NO fluxes were measured during two field campaigns in summer 1997 at Hollandse Hout. Figure 1 presents the hourly averaged NO emissions observed at the different experimental sites at Speuld and Hollandse Hout.

The NO fluxes were found to differ significantly throughout the measuring period. The NO fluxes at Speuld were very high, varying from hardly detectable in winter to 180 ng m^{-2} s^{-1} in summer in a Douglas Fir and up to 85 ng m^{-2} s^{-1} in the Beech plantation. The average observed NO flux from the Beech plantation at Hollandse Hout ranged 0-15 ng m^{-2} s^{-1}.

3.1 Soil Temperature

FIGURE 2

In general maximum NO emission rates were observed in summer whereas in winter the NO flux from soil was very small. Besides this clear seasonal variation, the NO fluxes indicate a diurnal variation with peak emissions occurring during daytime. As a microbiological process nitric oxide production is strongly linked by temperature causing higher fluxes from soil in summer. At most 70% of the variance in the determined NO flux was explained by soil temperature. Figure 2 shows the NO emission as a function of

temperature for all sites. The activation energy was 85 kJ mol^{-1}, as was calculated according to the Arrhenius equation for data from the Douglas Fir stand on sandy soil. This indicates a 2 to 3 fold increase in the NO emission for each 10 degrees rise in temperature, as is commonly observed for microbiological processes [Galbally, 1989, Focht and Verstraete, 1977].

3.2 Soil Moisture

FIGURE 3

As is shown in figure 3 a high NO emission rate was found particularly at a high soil temperature. Furthermore it can be seen that maximum fluxes were observed at a specific range of soil moistures. If soil conditions are extremely dry, the microbial community suffers from water stress limiting the biological production of NO gases. Several studies have shown an explosion of NO emissions after wetting extremely dry soil. On the other hand, blockage of soil pores by water can drastically affect the escape of NO to the atmosphere [Johansson, 1989 and references therein]. An optimum range in the soil water content results in a situation offering sufficiently moist conditions enabling microbial activity without disabling molecular diffusion through the soil. Laboratory studies indicated that production of trace gases in soil (CO_2, N_2O) through aerobic microbial processes is maximum at a water filled pore space of 60%. (Water filled pore space is the ratio of volumetric soil water content to total soil porosity. Volumetric water content is the gravitational water content multplied by bulk density) A water filled pore space of 60% appeared to be the threshold between water limiting and aeration limiting processes and

was also suggested to be the optimum for NO emission from soil [Linn and Doran, 1984, Davidson, 1993].

During our experiments maximum NO fluxes were found at a soil water content varying between 30% and 45% (approximately at a WFPS between 55% and 85%). NO production is possible not only through aerobic nitrification, but also through microbial processes under anaerobic conditions and therefore the optimum soil water content for NO emission may be higher than 60% WFPS.

Compared to our findings, results from a study in Venezuela showed maximum NO emissions from a sandy at a much lower soil water content, ranging 10-20% (dry weight) [Cardenas, 1993]. These different outcomes may suggest that the microbial community adapts to the prevailing soil water conditions and that therefore the optimum soil water content for maximum NO emission depend on the water regime of the study area.

3.3 Atmospheric nitrogen input

Figure 1 shows NO fluxes from two experimental sites in a Douglas Fir forest at Speuld differing in annual atmospheric N deposition levels. There is widespread evidence that the availability of organic and inorganic nitrogen in soils has a strong impact on NO emission rates. The average NO flux from soils in a Sitka Spruce forest in Scotland changed from 0.53 ng m^{-2} s^{-1} to 4.6 ng m^{-2} s^{-1} upon addition of acid mist [Skiba, 1994]. However, the experimental site at Speuld that received an additional amount of nitrogen in addition to the annual atmospheric deposition level is not found to have significantly higher NO emissions. It is thought that the high annual deposition levels of N and S from the atmosphere at Speuld (40 kg $ha^{-1}y^{-1}$ and 30 kg $ha^{-1}y^{-1}$ respectively) have saturated the soil

with nutrients. Addition of extra N would therefore not result in an increase in the NO flux from soil. This finding is in line with experiments carried out by [Koopmans, 1996] who showed on the basis of nitrogen leaching experiments that soils at Speuld are indeed nitrogen saturated.

NO fluxes from soils at Speuld were extremely large compared to results from a coniferous forest in Scotland and results from studies in other temperate forests. For instance, NO emissions from a Spruce forest in Norway were found to be <0.3 and 21 ng m^{-2} s^{-1} in April and September respectively [Pilegaard et al, 1998]. Butterbach-Bahl et al [1997] found relatively high NO emissions up to 40 ng m^{-2} s^{-1} from sandy soils in coniferous forest. These large NO fluxes were explained by very high annual atmospheric deposition levels of 35 kg N ha^{-1} y^{-1}, comparable to the deposition at Speuld.

3.4 Soil texture and forest type

Figure 1 and figure 2 show that differences in forest type, or differences in soil parameters due to differences in forest type, influenced the NO flux from soil. Table 2 compares the average NO flux and standard deviations found for the different experimental sites. NO emission rates from soil in Douglas fir forest were approximately 30 ng m^{-2} s^{-1} higher than NO fluxes from soil in Beech forest. It remains uncertain which soil properties could have caused the higher flux from soil in coniferous forest, since the physical and chemical soil characteristics that were monitored at the two different experimental sites were found to be similar. It has been suggested by Johansson [1989] that the forest environment affects the microbial processes that take place in the soil. Similar experiments in Germany also

demonstrated a smaller NO flux from soil in deciduous forest than from soil in coniferous forest [Butterbach-Bahl et al, 1997]. The very large difference observed during our experiments in the emission rates from these two forest types indicates that the forest community is of major importance to the NO flux from soil. A possible cause for this difference could be the influence the leafs on the penetration of direct sunlight or the difference in throughfall amount and composition on soil processes.

Figure 2 also illustrates how soil texture influences the magnitude of the NO flux from soil. The NO emission rates from sandy soil were higher than the NO emission rates from clayey soil. As is shown in table 2, on average differences of approximately 20 ng m^{-2} s^{-1} were observed. The total pore volume of the fine textured soil (clay) is somewhat larger, but the pores itself are smaller than those of the coarse textured sandy soils. It is suggested that –under similar field conditions- molecular diffusion was slower through the smaller pores in the clayey soil, and that the microbial produced NO gases were consumed in various reactions [van Cleemput and Samater, 1996]. Butterbach-Bahl et al [1997] reported a reduction in the NO flux from a Spruce forest floor when liming the soil (de-acidification). This is in line with our findings of smaller NO fluxes from the less acidic clayey soils at Hollandse Hout, when compared to the high fluxes observed at the acidic sandy soils at Speuld. Whether differences in soil texture alone or additional soil characteristics, such as soil pH, are responsible for the larger NO flux from sandy soil remains unresolved.

4. Concluding remarks

From our study it can be concluded that the environmental factors controlling emissions from NO to soil are soil temperature and water content. Our studies showed how the NO flux from soil is positively correlated to soil temperature, a rise of 10 degrees in the temperature doubling the microbial production rate of the trace gases. Maximum emission rates from soil are observed at an intermediate range of soil moisture contents, where conditions stimulating both microbial production and molecular diffusion are optimal. Our results show maximum NO emissions from soil at a soil water content ranging 30-45% (dry weight).

Across the landscape differences in soil texture and forest community type are probably the most important parameters. Differences between sandy and clayey soils can be very large. The forest type most likely introduces differences in the microbial community in the forest floor, hence strongly influences the NO flux from soil. The emissions observed in our studies in the Netherlands were very large. It has been suggested that these large fluxes are linked to the large input of nitrogen from the atmosphere in these regions. An artificially increased nitrogen input from the atmosphere however did not increased the NO emission. This phenomenon is probably linked to the soil already being saturated with nitrogen. When estimating the NO flux from natural environments on regional scale it is important to take into account differences in forest type, soil texture and perhaps even nitrogen input from the atmosphere. These quantities are likely to differ on a regional scale and are found to have a major influence on the magnitude of the NO flux from soil.

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TABLE 1

	SPEULD			HOLLANDSE HOUT
Forest community	Douglas Fir	Douglas Fir	Beech	Beech
Soil texture	Loamy sand	Loamy sand	Loamy sand	Heavy clay
Soil classification	Podsol	Podsol	Podsol	Luvisol, no distinct horizons
Soil acidity (pH H_2O)	3.7	3.7	3.7	6.8
Org.matter % (top soil)	15	15	15	5
Org.matter % (50cm depth)	1.5	1.5	1.5	5
$CaCO_3$%	0	0	0	1
Special		N added		

Table 1. Summary of the different experimental sites at Speuld (52°13′N, 5°39′E) and Hollandse Hout (52°26′N, 5°28′E).

TABLE 2

Location	Measuring period	Mean flux ng m^{-2} s^{-1}	St. dev
Douglas	Nov 96 - Aug 97	32	21
Douglas N added	Nov 96 - Aug 97	39	16
Douglas sandy soil	May 97 – July 97	49.7	29.7
Beech sandy soil	May 97 – July 97	20.6	6.1
Beech sandy soil	May 97 - July 97	21.7	6.4
Beech clayey soil	June 97 - July 97	3.2	4.8

Table 2. Comparison of the hour average NO emissions (average and standard error) for the different experimental sites at Speuld and Hollandse Houten.

FIGURE LEGENDS

Figure 1. Hourly averaged NO fluxes observed at the different experimental sites at Speuld and Hollandse Hout. Maximum NO fluxes are found during summer and minimum NO fluxes are found during winter.

Open squares = Douglas fir, sandy soil; closed circles = Douglas fir extra N sandy soil; open triangles = Beech, sandy soil; crosses = Beech, clayey soil.

Figure 2. NO flux related to the temperature. The activation energy calculated according to the Arrhenius equation for data from Douglas Fir on sandy soil is 85 kJ mol^{-1}.

Open squares = Douglas fir sandy soil; closed circles = Douglas fir extra N sandy soil ; open triangles = Beech, sandy soil ; crosses = Beech, clayey soil.

Figure 3. NO flux related to both the temperature and the soil water content. High NO fluxes are restricted to a relatively high soil temperature, and maximum fluxes are observed at a certain intermediate range of soil water content (30%-45%).

Figure 1

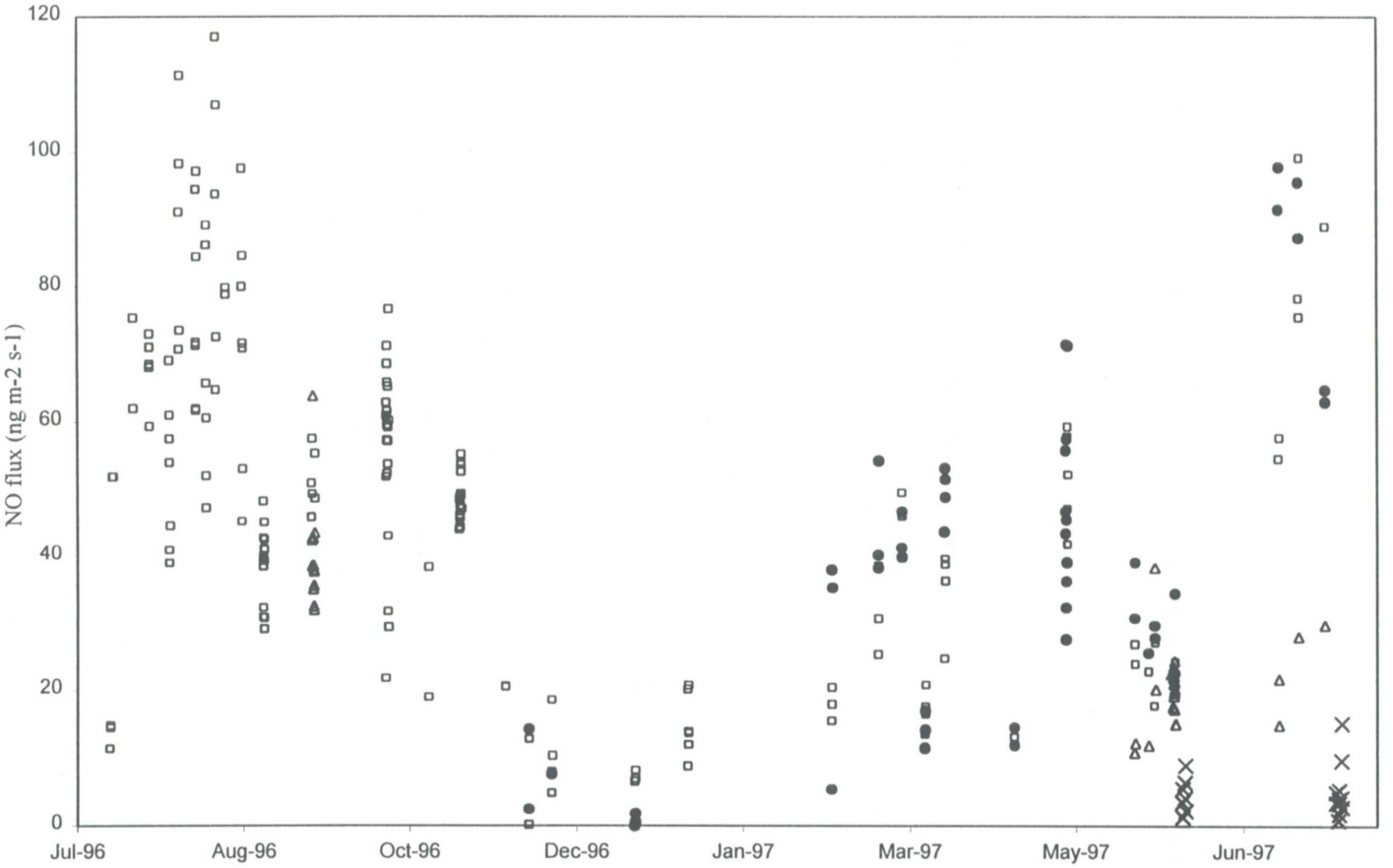

120
100
80
60
40
20
0
NO flux (ng m-2 s-1)
Jul-96
Aug-96
Oct-96
Dec-96
Jan-97
Mar-97
May-97
Jun-97

Figure 2

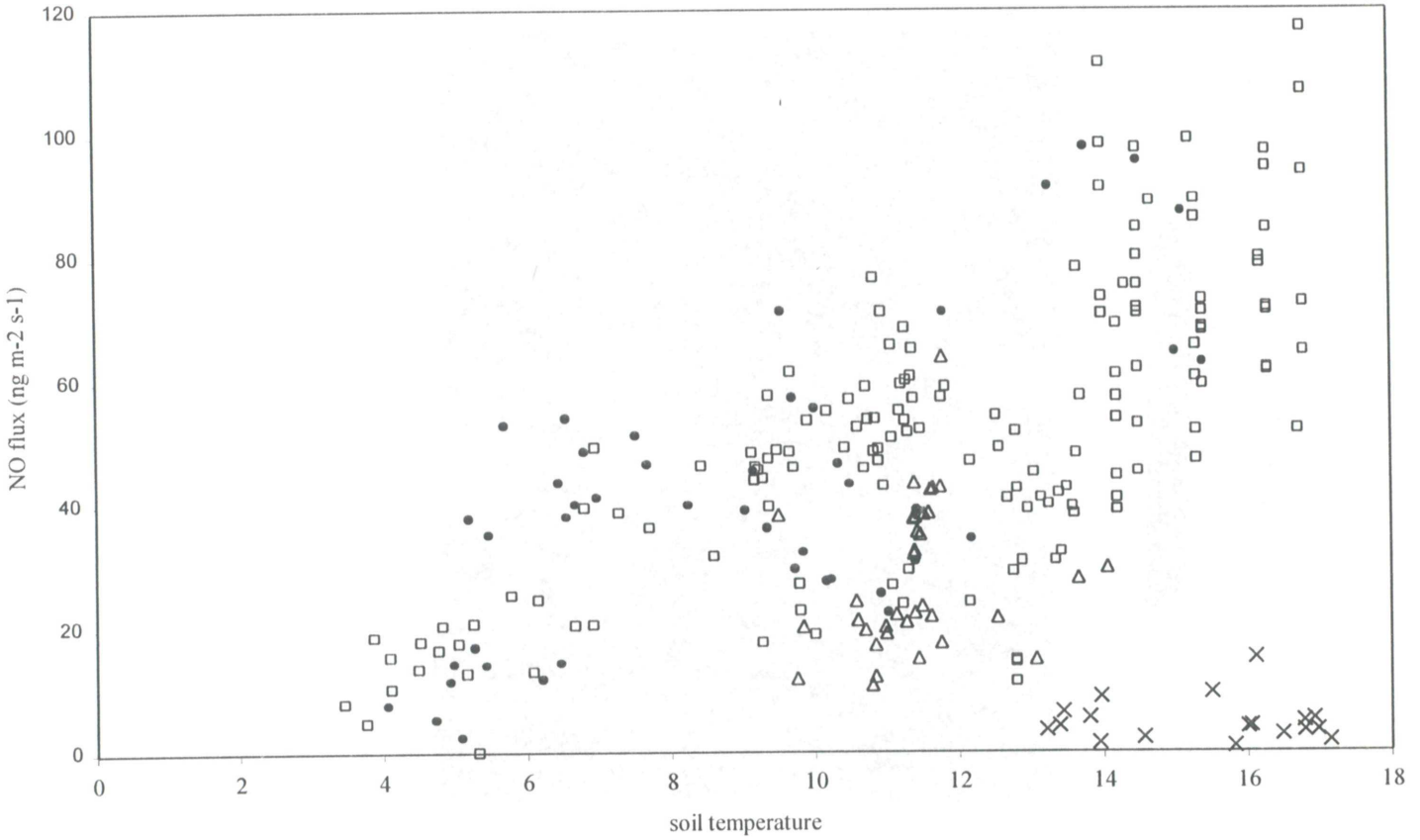
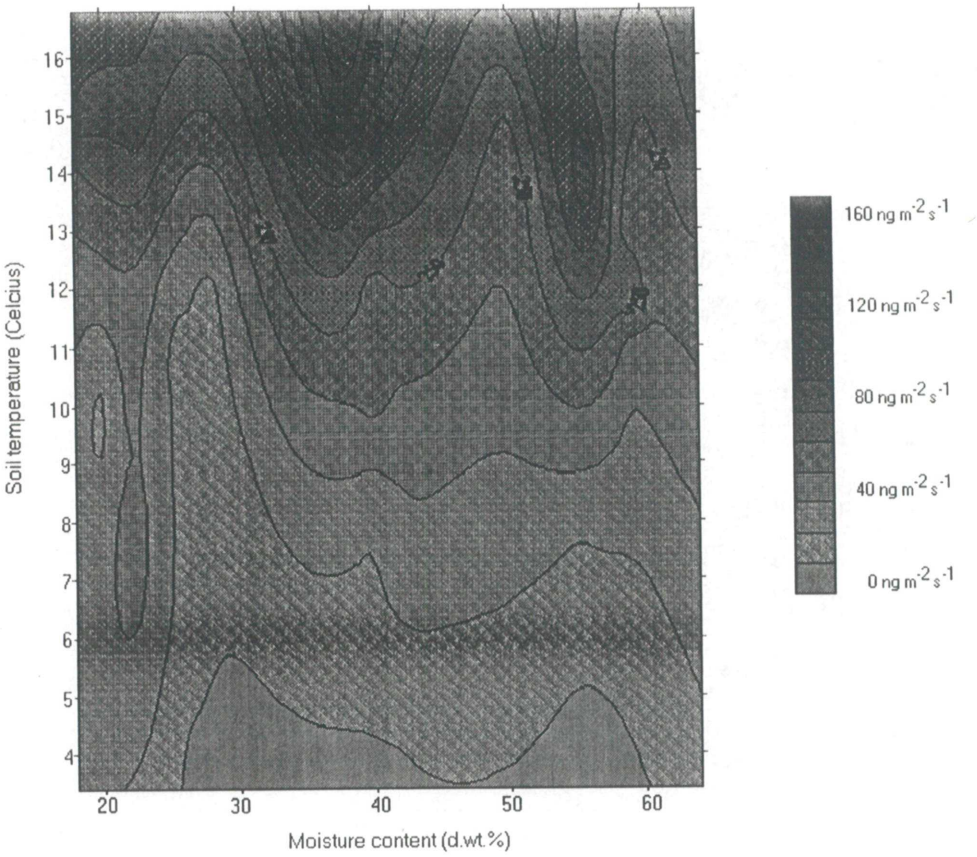

120
100
80
60
40
20
0
NO flux (ng m-2 s-1)
0
2
4
6
8
10
12
14
16
18
soil temperature

Figure 3


Soil temperature (Celcius)
16
15
14
13
12
11
10
9
8
7
6
5
4
20
30
40
50
60
Moisture content (d.wt.%)
160 ng m-2 s-1
120 ng m-2 s-1
80 ng m-2 s-1
40 ng m-2 s-1
0 ng m-2 s-1