Consumption and Production of NO from European Forest Soils: Effects of Forests and Textures

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Abstract

Relationship between the optimum soil water content and clay content on soil samples from mid-latitude European forest was tested. Soil samples from 4 different experimental sites (two forest sites in the Netherlands and a Danish forest) were collected, and analyzed for the soil physical and chemical characteristics. Water retention curves for the soil samples were determined according to the standard procedure ISO 11274, and pF decreased with increase in soil water contents. NO is simultaneously produced and consumed by microbiological processes, which comprise of nitrification and denitrification. NO consumption and production rates were determined from the soil samples and compared to their corresponding water retention curves in order to find the optimum soil water content and matric potential for maximum NO release from mid-latitude soils. NO consumption rate coefficient (k) in Hollandse Hout was significantly lower than those in other soil sites. Maximum NO production was observed at an intermediate soil moisture (0.2~0.3 kg/kg) in all the soil samples. Resulting from the NO consumption and production rates for the soils, the empirical NO fluxes of the different soils were calculated in the laboratory.

Key words : NO consumption rate, NO production rate, Water retention curve, Soil NO emission, Forest soil

1. INTRODUCTION

Soils have been shown to emit largely differing quantities of nitric oxide. Nitric oxide (NO) plays an important role in the photochemical production of ozone, which can cause damage to vegetation and human health problems at high concentrations (>40 ppb). The biological production of NO in soil can occur both through nitrification and denitrification by the consumption of NH_4^+ (and organic nitrogen) and NO_3^-, respectively. The NO production in soil increases exponentially with soil temperature. The degree of exponential increase was found to depend on the soil water content (Conrad, 1996a). Furthermore, many field- and laboratory studies have presented optimum soil water content where maximum NO is emitted from the soil. This optimum soil water content enables gas diffusion in soil (Peirce and Aneja, 2000; Pilegaard *et al.*, 1999; Martin *et al.*, 1998; Sullivan *et al.*, 1996; Cardenas *et al.*, 1993), while at the same time enough water is present for

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the microbial production of NO.

Van Dijk and Meixner (2001) found a relationship between the optimum soil water content and clay content on soil samples from the Brazilian Amazon. These tropical soils released most NO under wetter soil conditions when having higher clay content. A soil with higher clay content generally has a smaller bulk density and therefore contains a larger pore volume in soil. The pore volume in soil (ε) can be calculated from the soil bulk density (BD) and the particle density (PD): $\varepsilon = 1 - (BD/PD)$. Several expressions exist to describe the water content in soil. In most (laboratory) studies, the soil water content is determined by the gravimetric method (e.g. from the weight loss of the sample before and after drying), which results in the gravimetric water content θ_g in unit mass of water per unit mass of soil (kg kg^{-1}). However, at the same gravimetric water content, a fine-textured soil (clay) with a larger pore volume will have a smaller part of its pore space filled with water than a course-textured soil (sand). In order to compare the soil water content amongst different soils, soil water content is often expressed as *water-filled pore space* (WFPS). Gravimetric water content (θ_g) can be converted into water-filled pore space (θ_{wfps}) according to $\theta_{wfps} = (\theta_g \times BD)/(\varepsilon)$. Since soils with a finer soil texture contain a larger pore volume, the optimum water content for NO release was found to increase with clay content (van Dijk and Meixner, 2001).

The distribution of the individual pore sizes also seemed to have an important influence on the optimum conditions for NO release from soils. An expression to describe the influence of soil pores on the soil water is matric potential ψ_m (e.g. the energy potential that results from the attractive and adsorptive forces between the soil matrix and the water (Monteith and Unsworth, 1990). Values of ψ_m are ≤ 0. At $\leq \psi_m = 0$, the soil water level equals the soil surface and no (capillary) forces are induced by the soil pores. At $\psi_m < 0$, water is released from the soil pores. Large pores have weaker capillary forces and therefore will drain at less negative values of ψ_m than smaller pores. Van Dijk and Meixner (2001) found that maximum NO release from soil samples

in the Brazilian Amazon ($n=13$) occurred at $\psi \approx -10$ kPa, independent of their corresponding soil textures. At this matric potential, soil micropores (<30 μm) were water-saturated, whereas soil mesopores and macropores (>30 and >100 μm, respectively) were drained. This situation enabled the production of NO in biologically active pores as well as the bulk diffusion of NO through the larger open pores. In the present study, the relation of optimum soil water content for NO production with clay content was tested for soils from mid-latitude soils. For this reason, in total 4 different sites soil samples were collected from two forest sites in the Netherlands and a Danish forest. NO production and consumption rates were determined from the soil samples and compared to their corresponding water retention curves in order to find the optimum soil water content and matric potential for maximum NO release from mid-latitude soils.

2. SITE DESCRIPTION AND METHODS

2.1 Site descriptions

One composite sample (*Sorø*) was collected from the 85-year old beech forest "*Lille Bøgeskor*" near Sorø in Denmark, which is one of EuroFlux site. Another sample (*Hollandse Hout*) was collected from the beech forest "Hollandse Hout" near Lelystad in the Netherlands (52°26′N, 5°28′E). Two additional composite samples were collected from a beech plantation (*Speuld beech*) and a douglas fir plantation (*Speuld douglas fir*) in the mixed forest "Speulderbos" near Apeldoorn in the Netherlands (52°13′N, 5°39′E). The study area at Speuld is a 35 year old forest stand which has several different plantations all on identical coarse textured acidic soil (Tables 1 and 2).

Samples were collected from the first 0.05 m topsoil after removing the litter layer in a 10 × 10 m^2 area during the period from July 28 to August 15, 2001. Each sample was composed of 10 subsamples that were thoroughly mixed and sieved at a 2 mm. The clay sample from *Hollandse Hout* was not sieved, partly because the sample did not con-

Table 1. Soil physical data for the 4 soil samples.

Sample	Texture class (USDA)	Clay %	Total silt %	Total sand %	Gravel %	BD Mg m^{-3}	PD Mg m^{-3}	ε[†] m^3 m^{-3}
Sorø	Sandy loam	11.33	23.77	64.9	3.64	0.91±0.13 (n=7)	2.36	0.61
Hollandse Hout	Silty clay loam	36.55	48.58	14.87	0	1.11±0.07 (n=8)	2.53	0.56
Speuld Beech	Loamy sand	4.41	12.15	83.45	2.01	1.03±0.03 (n=8)	2.47	0.58
Speuld Douglas fir	Sandy loam	5.76	21.59	72.66	0.5	1.05±0.18 (n=8)	2.39	0.56

[†] Soil porosity was calculated using BD and PD according to equation 1.

Table 2. Soil chemical data for the 4 soil samples.

Sample	pH CaCl$_2$	pH KCl	CaCO$_3$ %	C-org %	NO$_3$-N mg/kg	NH$_4$-N mg/kg	Total N %	Total P mg/kg	P[†] mg/kg	K[†] mg/kg
Sorø	3.21	3.09	0.00	4.774	2.51	1.80	0.3351	185.91	25.60	31.61
Holl. Hout Beech	7.02	7.00	6.01	4.236	7.33	0.83	0.335	191.37	20.78	56.36
Speuld Beech	2.83	2.69	0.00	6.301	4.24	0.76	0.3098	903.59	107.17	64.97
Speuld Douglas fir	2.75	2.62	0.00	6.087	10.39	18.14	0.3247	307.58	9.88	18.65

[†] Plant available

tain any roots or rocks. In addition, soil cores were collected at sampling location to estimate soil bulk density by cylindrical shaped stainless steel soil core samplers (5 cm-height, 5 cm-diameter).

2. 2 Experimental setup

Net NO release was determined in the laboratory from soil samples for a broad range of soil temperatures T (10~35°C) and soil moistures θ (0~100% water-filled pore space (WFPS)) and for various ambient NO mixing ratios (0~130 ppb). The experimental setup (see Fig. 1), first described by Yang and Meixner (1997), was slightly modified.

In short, approximately 0.060 kg of dry soil was placed in a Plexiglas cuvette of approximately 1-litre volume, and either zero air (NO-free) or air with a certain NO mixing ratio was flushed through the headspace of the cuvette at a flow rate of 4.17 × 10^{-5} m^3 s^{-1}. NO was measured by a chemiluminescence analyser (TECAN AL 770 PPT, Ecophysics, Switzerland). The instrument was calibrated using NO gas standards (200 ppm; Messer Griesheim, Germany) and a home-built gas dilution system, consisting of a mass-flow controller (0~10 mL min^{-1}; Bronckhorst, Netherlands) and a glass-mixing chamber. Calibration was conducted every 4 weeks in the range from 0 to 200 ppb NO mixing

ratio. The standards could be reproduced with a precision better than 3%. With an integration time of 10 seconds, the detection limit of the NO analyser was 100 ppt (2σ).

Net NO release (J) (i.e., the released mass of NO-N per soil mass-time) was calculated from the difference in the NO mixing ratios at the inlet ([NO]$_{in}$ in ppb) and outlet ([NO]$_{out}$ in ppb) of the soil cuvette, the soil mass (M_{soil} in kg) and the flow rate of the carrier gas (Q in m^{3}s^{-1}):

$$J=(Q/M_{soil})\ ([NO]_{out}-[NO]_{in})\ (M_N/V_m)$$

where the ratio (M_N/V_m) is used to convert NO mixing ratios (ppb) into gas density units (ng m^{-3}). M_N is the molecular weight of nitrogen (14.0 g mole^{-1}) and V_m is the molar volume (2.45 × 10^{-2} m^3 mole^{-1}) at 298 K. NO release could be determined above 0.04 ng kg^{-1} s^{-1}. It should be emphasized that net NO release is negative (J<0) when NO consumption exceeds the NO production in soil ([NO]$_{out}$ < [NO]$_{in}$). This will also be referred to as net NO release. In total, soil samples in four measurement cuvettes and one blank cuvette were analysed in turn, by switching a valve manifold system every 1.5 minutes. The cuvettes were enclosed in a climate chamber, which enabled the control of soil temperature either at constant temperature or by
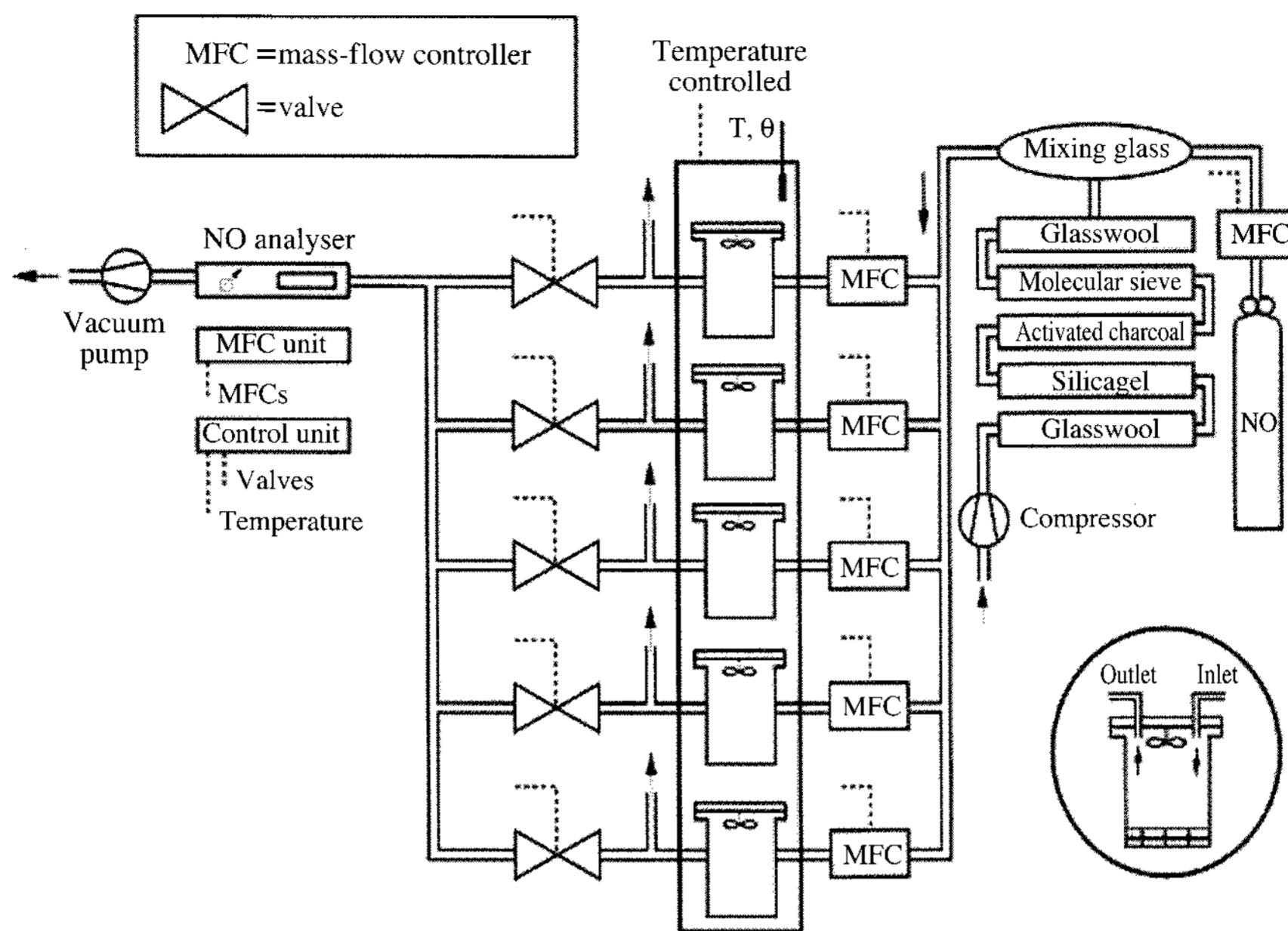
Fig. 1. Experimental setup for laboratory investigation of NO production and consumption in soil samples.

continuous heating at 0.25°C/min. Soil temperature was measured in the centre of two soil samples, since no significant thermal gradient within the sample was detected. Soil moisture was calculated every hour from the gravimetrically measured water loss of the soil sample in the measurement cuvettes. Variation in the initial gravimetric water content of replicate soil samples ($n=5$) was 5%. Water loss during the experiment was measured using a balance (PG5002-S, Mettler Toledo) with an accuracy of 0.01 g. Considering a typical sample amount of 0.06 kg dry soil, gravimetric moisture content could be determined within 2% in all cases. The hourly gravimetric water contents were fitted with Gaussian functions in order to derive soil moisture data for the full measurement period. For saturated soils to soils with approximately 0.06 g H_2O/g soil, negligible uncertainty was introduced by interpolating the hourly moisture measurements. However, for relatively dry soils (<0.06 g/g) the Gaussian curve was extrapolated to calculate the moisture content. In these cases, the maximum deviation from zero that was calculated for completely dry soil was

-0.025 g/g. For this reason, the maximum absolute error in the soil moisture content due to the fitting method was estimated to be ±0.025 g/g. The use of an inverted Nafion dryer system, which extracts water vapour from the outlet air of every cuvette and directs it back into the atmosphere of the soil cuvettes, enabled measurements at approximately constant soil moisture. The typically observed water loss rate with the inverted Nafion dryer was 0.37 g H_2O h^{-1} (without Nafion dryer 1.79 g H_2O h^{-1}), which corresponded to a reduction in the soil moisture content of only 1% per hour. Soil samples were composed of 6 subsamples from a 10×10 m^2 sampling plot. Samples were cooled during transport and stored in the laboratory at 4°C. Large pieces of roots and rock were removed by sieving the soil samples at 2 mm. All experiments were conducted within 1 month after sampling. Each experiment was initiated with pristine soil. Soil samples were packed in the cuvette to their equivalent field bulk density. The soil was allowed to adjust to the soil temperature set point for approximately 30 minutes, after which NO release measurements were initiat-

ed. Gravimetric soil moisture (g/g) was converted into water filled pore space (WFPS) using the field bulk density. The individual subsamples proved excellent duplicates in the former experiment (Saskia, 2001). NO release was measured from four replicate samples of a pasture soil (P87) from Fazenda Nova Vida (for details on the pasture site see Neill *et al.* (1999)). The variation in the NO release amongst the replicate soil samples was in all cases within 10%. After the first experiment the samples were stored for 17 days at 4°C. Repetition of the experiment using two of the replicate samples, indicated that the results could be reproduced within 0.02 ng NO-N kg s^{-1}, which corresponds to a precision of 15%. Nevertheless it was decided to take fresh soil from the sample bag for each new experiment.

2.3 Experiments

Net NO release (J) by soil samples has been observed to be linearly related to the NO mixing ratio in the head space of the measurement cuvette (cf. Remde *et al.*, 1993). Consequently, the NO consumption process is assumed a first-order reaction with respect to the NO mixing ratio [NO]. Therefore by conducting a series of experiments at varying NO mixing ratios (0, 80 and 130 ppb), the rate constant of NO consumption k can be determined from the slope of the corresponding plot of J versus [NO] (i.e., $k=\Delta J/\Delta[NO]$). Selection of 0, 80 and 130 ppb was made since the NO compensation points (Conrad, 1996) (and ambient NO mixing ratio) were typically 76.0 ppb (2.6 ppb) and 10.2 ppb (0.37 ppb) for the forest and pasture, respectively. Furthermore, the NO production P equals the release of NO at [NO]=0 (i.e., P is the y-axis intercept of the linear regression line of J versus [NO]). The rate constant k was determined for soil samples at 3 different soil temperatures (16, 26 and 32°C) and at the whole range of soil moistures (0~100% WFPS). NO production P was derived directly from measurements of NO release J at NO-free air. Since the NO mixing ratio is determined in the headspace of the cuvette ([NO] slightly above zero), P equals J only by approximation.

For both the forest and the pasture soils, the differ-

ence between the observed J and P (i.e., J at [NO] =0) was estimated to be less than 5%. The dependence of NO production P on soil temperature and soil moisture was determined from several experiments. These included measurements at constant soil temperatures with varying soil moistures (0~100% WFPS) and measurements at constant soil moistures with varying soil temperatures (10~35°C). In addition, experiments were conducted to determine the response of NO release to additions of NH_4^+ and NO_3^-. Soil samples, with the original field moisture content (ranging from 0.20 to 0.35 g/g), received 0, 80, 400 or 800 mg N/kg dry soil in 3-mL demineralized water from either a NH_4Cl or a KNO_3 solution, and the net NO release from soil was determined.

2.4 Soils physical and chemical characteristics

In addition, 8 other undisturbed soil cores (0.05 m diameter, 0.05 m height) were collected per sampling location in order to accurately determine the soil bulk density (e.g. unit of dry soil mass per unit of volume). The weight difference before and after drying the soil sample provided the gravimetric water content and together with the sample volume resulted in the soil bulk density (Mg m^{-3}). The particle density was measured using the pycnometer method by the Landwirtschaftliche Untersuchungs- und Forschungsanstalt (LUFA). The method is based on the isothermal change of ideal gases. The soil sample is placed in a closed chamber of known volume ($V_{chamber\ 1}$), which is filled with Helium to a certain pressure. Once the gas has filled the pore volume of the soil sample, the equilibrium pressure (P_1) is determined. Next, a valve is opened and the gas expands into an expansion chamber of known volume ($V_{chamber\ 2}$). The particle volume of the sample (V_{sample}) is calculated from the new equilibrium pressure (P_2) according to the following equation:

$$P_1 \times (V_{chamber\ 1} - V_{sample}) = P_2 \times (V_{chamber\ 1} + V_{chamber\ 2} - V_{sample}).$$ Finally, the particle density is M_{sample}/V_{sample}, where M_{sample} is the mass of the soil sample.

Soil acidities, $CaCO_3$, NH_4^+, NO_3^-, organic C, total N, total P and plant-available P and K were measured using the disturbed soil samples by the Geography Department of the Johannes-Gutenberg

Universität in Mainz (Germany). Soil acidities were measured in suspensions of 0.010 kg soil and 0.01 M CaCl$_2$ and 1 M KCl solutions (2.5 : 1), according to ISO 10390 (ISO=International Organization for Standardizing, Switzerland). Total destruction of the soil with concentrated H$_2$SO$_4$ and distillation with Kjeldahl (Merck reagent 15348) provided information about the total N, P and K contents of the soil samples. Plant available N, P and K content was determined by NH$_4^+$ and NO$_3^-$ is extracted from the soil samples by 2M KCl (5 : 1), organic C, total N, total P, total K, plant-available P, plant-available K. The CaCO$_3$ content was determined according to the Scheibler method standard DIN 19684 (German Institute for Standardization), adding 10% HCl and using the CO$_2$ gas volume that is formed to calculate the CaCO$_3$ content.

Summary of these soil physical and chemical parameters for the four soil samples were shown in Table 1 and 2, respectively.

Particle size classes were analyzed with the pipette method following the USDA (U.S. Department of Agriculture) classification: clay (<2 μm), fine silt (0.002~0.005 mm), medium silt (0.005~0.02 mm), course silt (0.02~0.05 mm), very fine sand (0.05~0.1 mm), fine sand (0.1~0.25 mm), medium sand (0.25~0.5 mm), course sand (0.5~2 mm), and gravel (>2 mm). Soil size distributions for four different site locations during the sampling period were shown in Fig. 2.

2.5 Matric potential of the sampled soils: water retention curves

In order to determine the water release characteristics of the individual soils, 10 undisturbed soil cores (0.05 m diameter, 0.05 m height) were collected per sampling location. Water retention curves were determined according to the standard procedure ISO 11274. Water retention curves were measured using the undisturbed soil cores by the Geography Department of the Johannes-Gutenberg Universität in Mainz (Germany).

The soil samples were first saturated in a water bath, after which samples were placed on a pressure plate and a certain pressure was applied. The weight
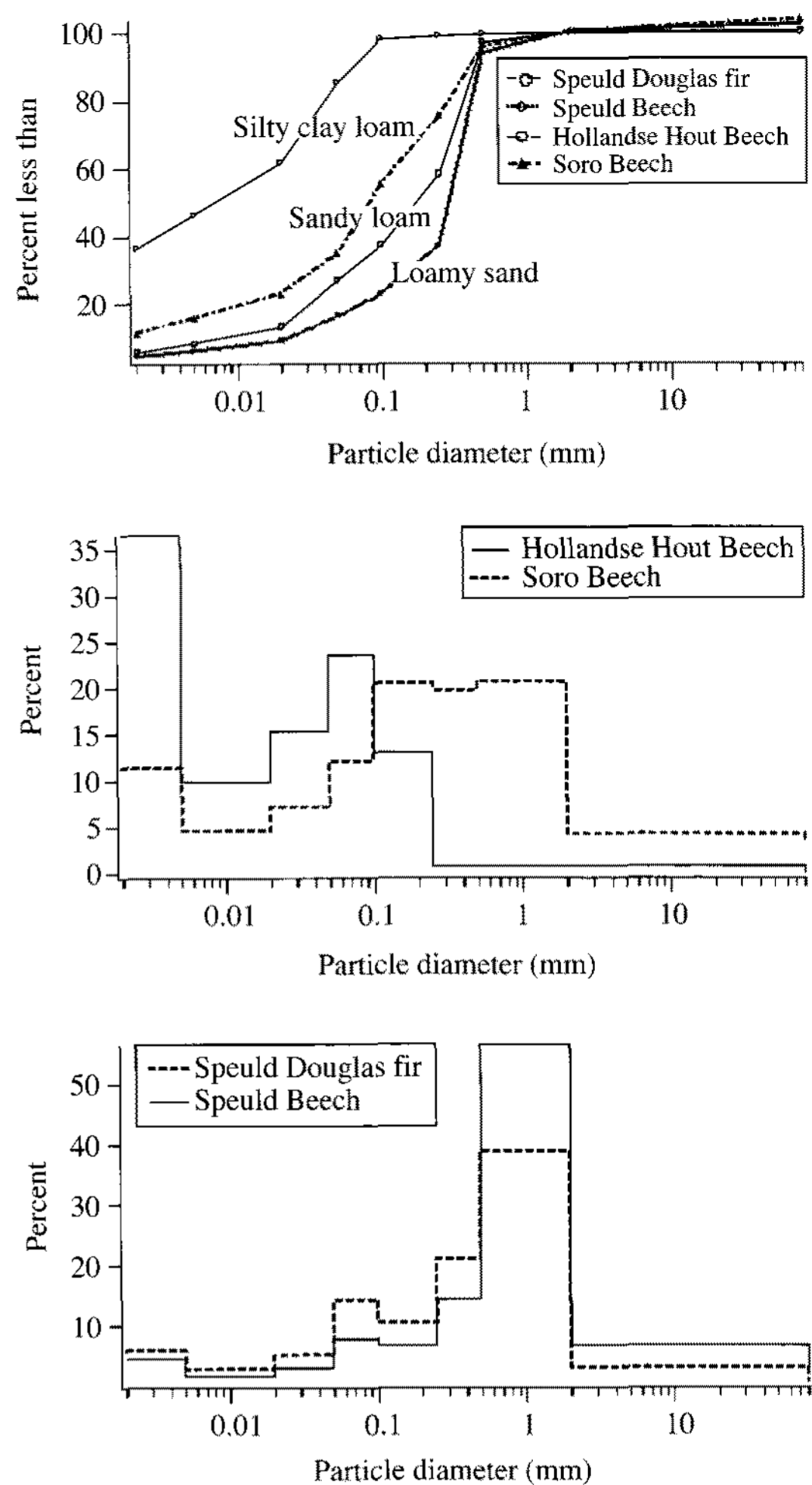
Fig. 2. Soil particle size distributions for the four different sampling sites.

difference between the saturated soil sample and the pressurized sample is the mass of water that was released from the pores. Matric potential is an expression which characterizes the tenacity with which soil water is held by the soil matrix (Hillel, 1982). The relation between matric potential and the soil water content (also, water retention curve or water release characteristics) thus depends on the soil matrix. Matric potential is presented on a log scale, and pF is the logarithmic of the applied pressure (HPa), e.g. pF 1.0=10 HPa. The following pressures were applied pF 1.0, 1.7, 2.0, 2.2, 2.3, 2.5, 3.0, 4.0, and
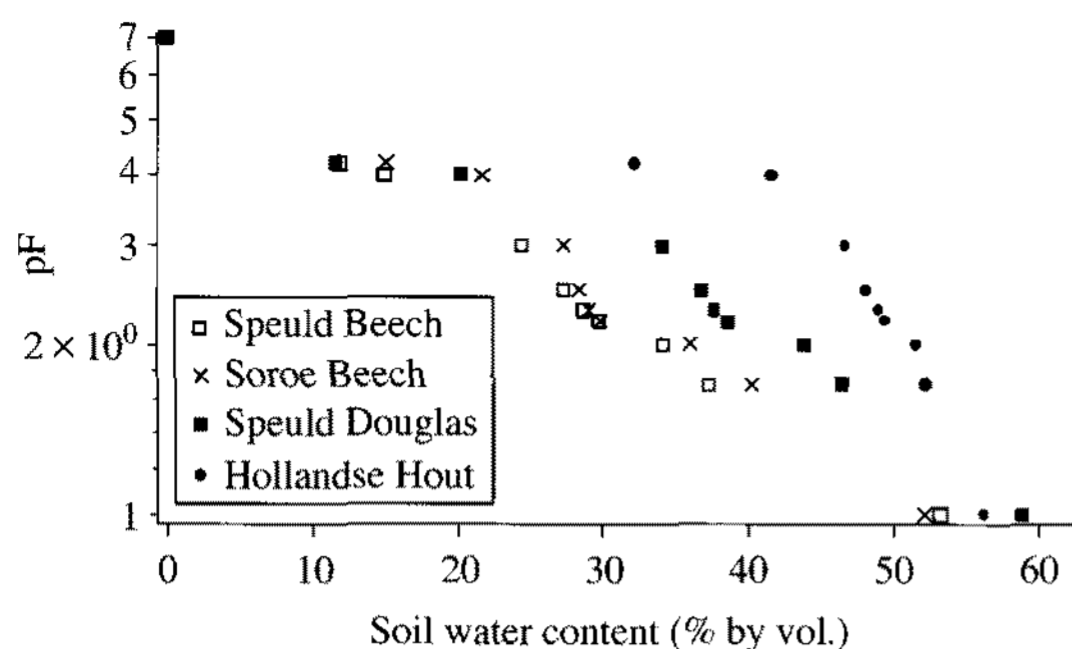
Fig. 3. Water retention curves for the four soil samples (n=10).

4.2. After completing the measurement at the selected pressures, the soil samples were dried and their corresponding bulk densities were determined from the dry soil mass and the soil core volume. Using these soil bulk densities, the volumetric water content (e.g. unit volume of water per unit volume of dry soil) can be calculated ($\theta_v = \theta_g \times$ bulk density). The relationship between the applied pressure and the retained volumetric water content gives the water retention curve, and Fig. 3 shows their relationship for the four different soils sampled at the experimental sites.

3. RESULTS AND DISCUSSION

3.1 Soil physical and chemical data

Table 1 and 2 show the summary of the soil physical and chemical parameters sampled from the four different experimental sites. Summary data revealed that each soil has a different characteristic from others, physically and chemically. More clay contents have been found in Hollandse Hout and Soro, and relatively less contents in Speuld Beech and Speuld Douglas fir. Significantly high contents of total silt in Holland Hout soils were measured; however, the lowest contents of total sand were measured from Holland Hout. Particle densities of the soil samples were relatively consistent, and ranged from 2.36 to 2.53 Mg m^{-3}. Soil porosity were also calculated with the bulk densities, and ranged

from 0.91 to 1.11 Mg m^{-3}. All of the soil samples likely have more sand except in Hollandese Hout soil. Soil pH has been known to affect soil NO production since soil acidity is an informative soil parameter that influences several soil processes including microbial activity (Conrad, 1996b). Only Hollandes Hout soil acidity was found to be neutral (pH 7.00 and 7.02), and others were acidic ranging from pH 2.75 to 3.21. About 6% of CaCO$_3$ was measured in Hollandse Hout soil, but no CaCO$_3$ measured in other experimental site soils. Average of total nitrogen contents in the four sampled soils was 0.3262±0.0119%. The ratios of NH$_4^+$-N to NO$_3^-$-N in Soro, Hollandese Hout, Speuld Beech and Speuld Douglas fir soils were 0.72, 0.11, 0.18 and 1.75, respectively. Contents of P and K in Speuld Beech soil was one order of magnitude higher than other soils, and remains of plant roots were found in the soil sample.

Particle size distributions in soil could affect soil NO production since gas diffusion through the soil is more effective in a coarse particle dominant soil with relatively larger pores compared to fine particle dominant soil with relatively fine pores (Currie, 1983). Fig. 2 presents cumulative particle size distributions in the four different soil samples. More than 85% of total particle in Hollandse Hout Beech soil, which classified in silty clay loam, consist of fine particles (less than 0.1 mm in diameter). On the other hand, less than 35% of total particle consist of only fine particle (less than 0.1 mm in diameter) in other three soils, i.e. Soro, Speuld, and Speuld Douglas fir. The data revealed that soil texture in Speuld Beech site (loamy sand) more likely compose of coarse particles.

3.2 Water retention curves

Many studies have shown presence of optimum soil moisture for maximum soil NO emission. When examining soils from different regions, one can encounters different soil textures and moisture regimes that could influence the optimum moisture for NO emission from soil. For instance, a course-textured soil generally has a relatively smaller total pore volume, compared to a fine-textured soil (Hillel,

Table 3. Statistical differences between the 4 soil samples in the soil water contents. Presented is the least significant level at which the samples were significantly different over the range from pF 1.7 to 4.2.

	Sorø	Hollandse Hout	Speuld Beech	Speuld Douglas fir
Sorø	–	$p<0.001$	not different	$p<0.03$
Hollandse Hout	$p<0.001$	–	$p<0.001$	$p<0.001$
Speuld Beech	not different	$p<0.001$	–	$p<0.01$
Speuld Douglas fir	$p<0.03$	$p<0.001$	$p<0.01$	–

1982). Thus, at the same amount of soil moisture, a coarse-textured soil would be relatively wet compared to a fine-textured soil.

Water retention curves were determined for 10 soil cores per sampling location. Fig. 3 showed matric potential pF (water retention curves) of the four different soil samples. At a given pF, a fine textured soil (clay) with relatively fine pores will retain more water than a coarse textured soil (loam and sand) with relatively large pores. Thus, in Fig. 3, Hollandse Hout soil (more like clay) seems like retain more water than other soil samples (more like loam and sand) at a given matric potential other than pF=1. At pF=1 in Fig. 3, at saturation, the 4 samples had similar soil water contents and no significant differences were observed. At the other pF-values (1.7~4.2), there were significant differences in the water contents between the 4 samples. Only the samples Sorø and Speuld beech showed no significant differences at any of the pF-values (see Table 3).

3.3 NO consumption

Experiments to determine one NO consumption rate coefficient took about 3~4 hours, since NO release (J) was measured 5 times at 4 different ambient NO concentrations. Despite the use of inverted Nafion dryers, some soil water was lost from the soil sample, changing the soil water content about 0.03 kg kg^{-1} during the course of the experiment. Since the first and last NO release rates were measured at zero air ($[NO]_{amb}=0$), it could be seen that NO release was relatively constant during the course of the experiment. Fig. 4 (NO release J versus ambient NO concentration) gives a typical example of the determination of k for Sorø at a constant soil temperature (T=16°C) and soil water content of 0.46
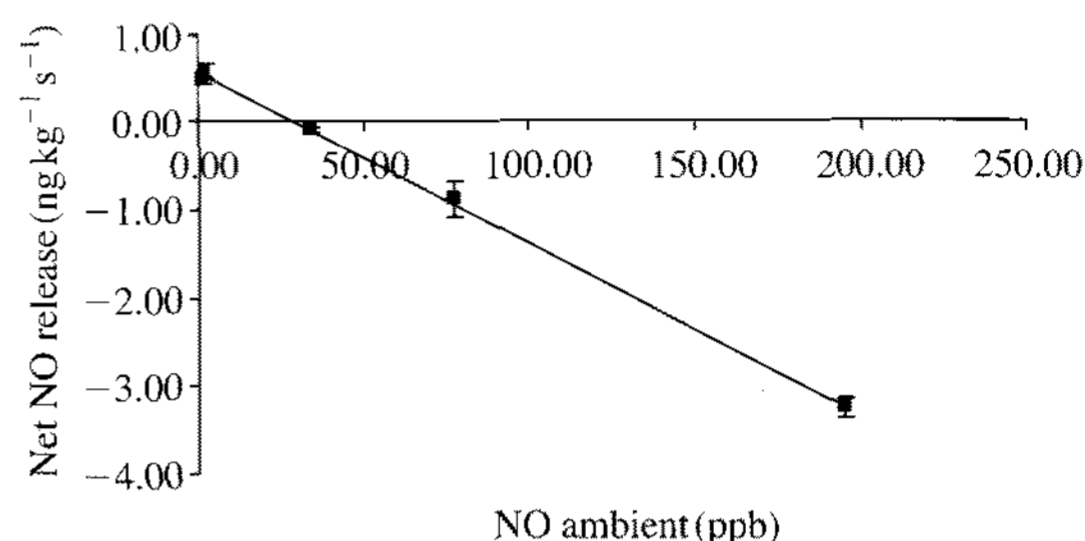
**Fig. 4. Net NO release (ng kg^{-1} s^{-1}) versus the ambient NO concentration (ppb) for Sorø at a constant soil temperature (T=16°C) and soil water content of 0.46 kg kg^{-1}. NO consumption rate k is determined as a slope of the line.**

kg kg^{-1}. Individual data points are averages of 3~4 successive NO release rates (over a time span of about 20 minutes) and the error bars indicate the corresponding standard deviations.). The NO consumption coefficient k ($-\Delta J/\Delta[NO]_{amb}$) is 123.5 cm^3 g^{-1} h^{-1} (or 0.0196 ng kg^{-1} s^{-1} ppb^{-1} or 0.0486 s^{-1}) according to least square linear regression. It can be seen that the variation within the individual NO release measurements is much smaller than the differences amongst the NO release at different ambient NO concentrations. Furthermore, the two NO release measurements at zero air, measured at the beginning and end of the experiment, were almost identical, indicating that the water loss from the soil sample did not change the NO release significantly.

NO consumption coefficients k for Sorø, Speuld douglas fir, Speuld beech and Hollandse Hout were illustrated in Fig. 5. Small squares indicate the median k-values of 3 replicate samples of each soil, and the boxes indicate the 25% percentiles. Rate constant of NO consumption rate k in Hollandse Hout is significantly different from the rate in other
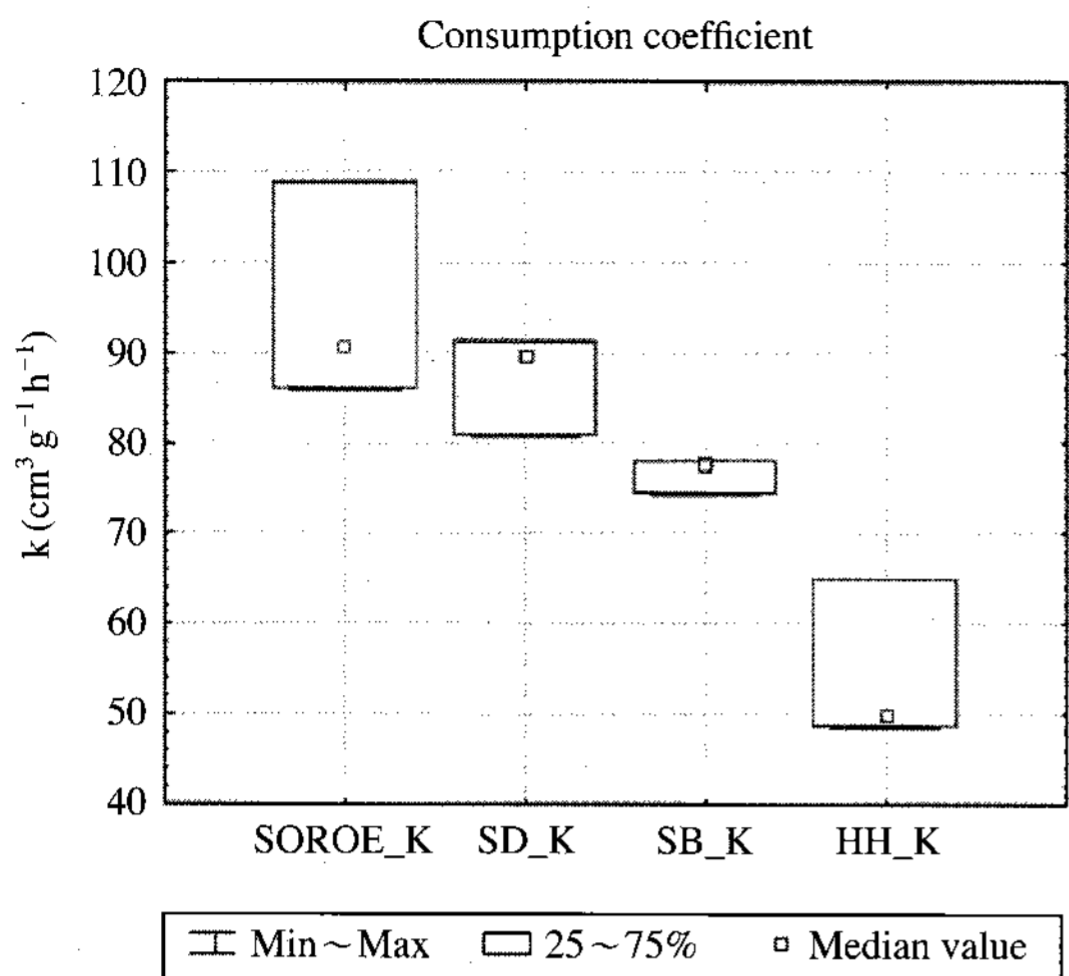
Fig. 5. NO consumption coefficients for Sorø, Speuld douglas fir, Speuld beech and Hollandse Hout. Indicated are the median *k*-values of 3 replicate samples (small squares), and the 25% percentiles (boxes).

soil sites.

Median of the consumption rates k in Hollandse Hout is approximately $50 \, \text{cm}^3 \, \text{g}^{-1} \, \text{h}^{-1}$ which is significantly lower than $78 \, \text{cm}^3 \, \text{g}^{-1} \, \text{h}^{-1}$ in Speuld beech, $90 \, \text{cm}^3 \, \text{g}^{-1} \, \text{h}^{-1}$ in Speuld Douglas fir and $92 \, \text{cm}^3 \, \text{g}^{-1} \, \text{h}^{-1}$ in Soro.

3.4 NO production, *P*

NO production P of Soro, Hollandse Hout, Speuld beech and Speuld Doglas fir verse soil moisture at constant soil temperature (T=15°C) were presented in Fig. 6(a), (b), (c) and (d), respectively. NO production P was determined by extrapolation of the regression $(\Delta J/\Delta[\text{NO}]_{\text{amb}})$ to the y-intercept ($[\text{NO}]_{\text{amb}}$ =0) in Fig. 4. As can be seen from the figures (NO production vs soil moisture), the NO production was maximum at an intermediate soil moisture. The trends of the NO production with respect to the soil moisture are similar (e.g. concave line) for the four different soil samples. Results are shown for 3 individual sub-samples. The individual sub-samples have maximum NO release at different times, but all at similar soil moisture. The optimum gravimetric water content θ_g (opt), volumetric water content θ_v
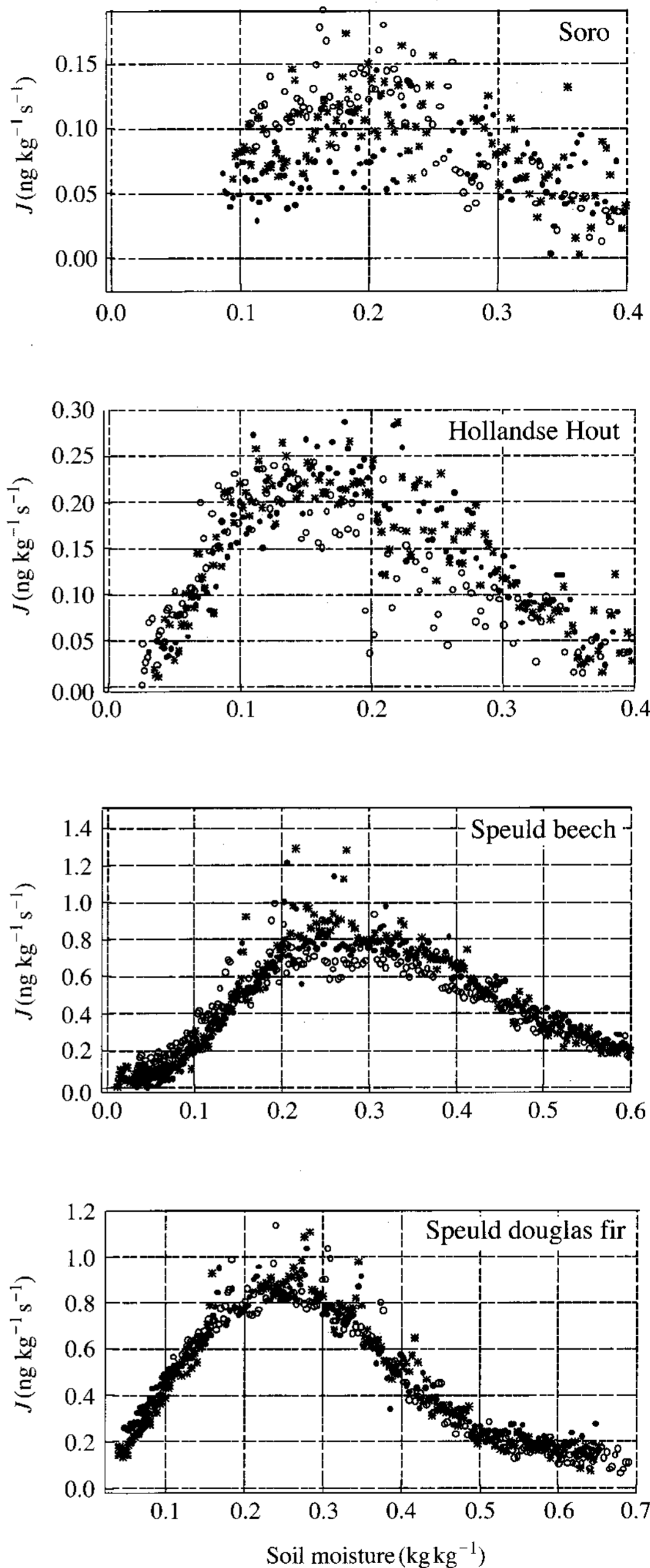
Fig. 6. (a) NO production from Soro and (b) Hollandse Hout versus soil moisture at constant soil temperature (T=15°C). Results are shown for 3 replications. (c) NO production from Speuld Beech and (d) Speuld Douglas fir versus soil moisture at constant soil temperature (T=15°C). Results are shown for 3 replications.

(opt) and optimum waterfilled pore space θ_{wfps} (opt) for Sorø, Hollandse Hout, Speuld Beech and Speuld Douglas fir are shown in Table 4.

By combining these results with the water retention curves in Fig. 3, it can be seen that all samples have maximum NO release at a different matric potential. Matric potential of approximately -10 kPa did not result in maximum NO release from all samples, as it did for the tropical soil samples from the Brazilian Amazon (van Dijk and Meixner, 2001).

In Fig. 6, ranges of maximum NO production at the optimum moisture for Sorø, Hollandse Hout, Speuld Beech and Speuld Douglas fir were $0.05 \sim 0.16$, $0.16 \sim 0.27$, $0.7 \sim 1.1$, and $0.75 \sim 1.1$ ng kg^{-1} s^{-1}, respectively. Thus, NO productions in Speuld Beech and Speuld Douglas fir soil was approximately one order of magnitude higher than in Soroe and Hollandse Hout soil. It could be attributed to the different soil texture for the sampling soils. Content of clay in the former soils (Soroe and Hollandse Hout) is less than in the letter soils (Speuld beech and Speuld Doglas fir) (see Table 1). NO production could be influenced by the gas diffusivity in the soils. As discussing it before, gas diffusion through the soil is more effective in a coarse-textured soil (i.e. sandy) with relatively larger pores compared to a fine-textured soil (i.e. clay) with relatively fine pores. Soil chemical parameters, like pH and NO_3^--N and NH_4^+-N, also could be the factors to make the differences in NO production between the soils. Saskia (2001) has discussed the differences in NO production between forest soil and pasture soils by comparing soil NO_3^--N and NH_4^+-N contents of the soils.

The net NO flux derived from laboratory measurements is denoted as F_{lab}, and is calculated according to the following equation (Galbally and Johansson, 1989);

$$F_{lab} = \sqrt{BD \cdot k \cdot D} \times \left([NO]_{amb} - \left(\frac{P}{k}\right)\right),$$

where BD is soil bulk density, and D is diffusion coefficient of NO through the soil and ambient NO concentration. The bulk diffusion of NO through soil was not measured in situ, and therefore was calculated according to Millington (1960). The results

Table 4. Optimum gravimetric water content θ_g (opt), volumetric water content θ_v (opt) and optimum water-filled pore space θ_{wfps} (opt) for Sorø, Hollandse Hout, Speuld Beech and Speuld Douglas fir.

Sample	θ_g (opt)	θ_v (opt)	θ_{wfps} (opt)
Sorø	0.20	0.18	0.30
Hollandse Hout	0.15	0.17	0.30
Speuld Beech	0.25	0.26	0.44
Speuld Douglas fir	0.20	0.21	0.38

Table 5. NO fluxes calculated from the NO production and consumption.

Sample	Calculated NO flux (F_{lab}) (ng m^{-2} s^{-1})
Speuld Douglas fir	2.30
Sorø	1.37
Speuld Beech	0.19
Hollandse Hout	0.07

The bulk Diffusion of NO through soil was not measured in situ, and therefore was calculated according to Millington 1960.

of the calculated NO fluxes (F_{lab}) were presented in Table 5. According to the results, calculated NO flux F_{lab} with known soil parameters, in highest order, is Speuld Doglas fir (sandy loam) > Soroe (sandy loam) > Speuld beech (loamy sand) > Hollandse Hout (silty clay loamy). It shows that calculated NO flux from sandy loam soils are relatively higher than from silty clay loam and loamy sandy soil.

4. CONCLUSIONS

In order to elucidate the relation of optimum soil water content for NO production from mid-latitude soils, soil samples were collected from the first 0.05 m topsoil after removing the litter layer in a 10×10 m^2 area during the period from July 28 to August 15, 2001 from 4 different forest sites. Each sample was composed of 10 subsamples that were thoroughly mixed and sieved at a 2 mm. The clay sample from *Hollandse Hout* was not sieved, partly because the sample did not contain any roots or rocks. In addition, soil cores were collected at sampling location to estimate soil bulk density by cylindrical shap-

ed stainless steel soil core samplers (5 cm-height, 5 cm-diameter). The soil samples from 4 different experimental sites were analyzed for the soil physical and chemical characteristics. Water retention curves for the soil samples were determined according to the standard procedure ISO 11274, and pF decreased with increase in soil water contents. NO consumption and production rates were determined from the soil samples and compared to their corresponding water retention curves in order to find the optimum soil water content and matric potential for maximum NO release from mid-latitude soils. Rate constant of NO consumption rate in Hollandse Hout was approximately 50 cm^3 g^{-1} h^{-1} which is significantly lower than the rates in other soil sites (78 cm^3 g^{-1} h^{-1} in Speuld beech, 90 cm^3 g^{-1} h^{-1} in Speuld Douglas fir and 92 cm^3 g^{-1} h^{-1} in Soro). Maximum NO production at constant temperature (T=15°C) was observed at an intermediate soil moisture (0.2 ~ 0.3 kg/kg) in all the soil samples. Maximum NO productions in Speuld beech and Speuld doglas fir soils were approximately one order of magnitude higher than those in Soro and Hollandse Hout soils. The net NO flux was derived from laboratory measurement. Resulting from the NO consumption and production rates for the soils, the empirical NO fluxes of the different soils were calculated in the laboratory. The highest calculated NO flux was in the Speuld Douglas fir soil.

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