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Nitrous oxide fluxes from grassland in the Netherlands: I. Statistical analysis of flux-chamber measurements

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Summary

Accurate estimates of total nitrous oxide (N_2O) losses from grasslands derived from flux-chamber measurements are hampered by the large spatial and temporal variability of N_2O fluxes from these sites. In this study, four methods for the calculation of mean N_2O fluxes ($n = 6$) on total N_2O losses are compared, namely the arithmetic mean, the geometric mean, the lognormal mean and the mean derived from Finney's method. Mean fluxes were calculated from weekly flux measurements on grassland at four contrasting sites in the Netherlands with three management treatments each. Total losses were calculated by interpolation of the mean fluxes and integration over time. Spatial variation of N_2O fluxes was large. The geometric mean was generally much smaller, up to a factor of 7, than the arithmetic mean. The lognormal mean was much larger, up to a factor of 11, than the arithmetic mean, possibly because this estimator is biased for small sample size. Arithmetic means and Finney's method were generally in reasonable agreement. The order in estimated N_2O loss increased in the order geometric mean < arithmetic mean $\leqslant$ Finney's mean < lognormal mean. Because of the small sample size ($n = 6$), the uncertainty about the precise frequency distribution, the sensitivity of estimators based on logtransformed data, and the problems associated with negative fluxes, the arithmetic mean was preferred as the most appropriate estimator. Evidently, the choice of an estimator of the mean can have great effects on the estimation of total N_2O losses.

Introduction

Soil is suggested to be the major global source of nitrous oxide (N_2O) (Bouwman, 1995). Spatial and temporal variations in N_2O fluxes from soil are large. This is because the variables controlling the production of N_2O in soil during the microbiological denitrification and nitrification also vary in space and time (Firestone & Davidson, 1989). The variables include temperature and the contents of mineral nitrogen (N), mineralizable carbon (C), oxygen and moisture.

Flux-chamber techniques are the most used for measuring N_2O fluxes from soil to atmosphere (Mosier, 1989), and in them, too, variation of N_2O fluxes is often found to be large (Ambus & Christensen, 1994; Folorunso & Rolston, 1984). Increasing the number of replicates may decrease the estimation variance but is not usually feasible for lack of time. Micrometeorological methods have the advantage that they integrate fluxes from a large area (Fowler & Duyzer, 1989). However, they are rather expensive, need large uniform areas, and are less suitable for comparing experimental treatments, e.g. fertilizer applications. For these reasons flux-chamber techniques seem to be a reasonable compromise for field studies.

Flux measurements of N_2O using flux chambers often approximate a lognormal distribution. In reviews of Aitchison and Brown (1966), Koch & Link (1970) and Parkin *et al.* (1988), various estimators of the mean of lognormal distributions are given. Accurate calculations of total N_2O losses from soil are important for accurate estimates of global N_2O budgets, and also for the development of policies to diminish N_2O losses. The global N_2O budget is still unbalanced (Bouwman, 1995), and there is an urgent need for more accurate estimates of the N_2O sources. Therefore, possible differences in mean N_2O fluxes due to the choice of different estimators have to be considered when dealing with total N_2O losses.

In this paper, the effects of the method of calculating mean N_2O fluxes on total N_2O losses from soil is discussed. Mean fluxes were calculated from weekly flux measurements on grassland at four contrasting sites in the Netherlands with three management treatments each. Effects of soil type, grassland management and weather on N_2O fluxes are discussed in a companion paper (Velthof & Oenema, 1995).

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Materials and methods

Experimental set up

A detailed description of the experimental site and set up is given by Velthof and Oenema (1995). Briefly, N_2O fluxes were measured on managed grassland at four contrasting sites in the Netherlands, a clay soil near Lelystad, a sand soil near Heino, and two peat soils near Zegveld, from March to November 1992. There were three grassland management treatments on each site, namely mowing without N-fertilizer application, mowing in combination with N-fertilizer application and predominantly grazing in combination with N-fertilizer application. The experiments were laid out as randomized blocks, in three replicates. Fertilizer N was applied as calcium ammonium nitrate (CAN) in six or seven dressings.

Monitoring of N_2O fluxes

Fluxes were measured using vented closed flux chambers (Mosier, 1989). Flux chambers, PVC cylinders with an internal diameter of 20 cm and height of 15 cm, were inserted 3 cm into the soil using a knife, about 30 min before flux measurements started. All chambers were vented with a tube with an internal diameter of 0.3 cm and length of 20 cm and were insulated with an aluminium foil cover to prevent pressure and temperature fluctuations in the flux chamber. Concentration of N_2O in the headspace was determined in the field at 0, 10, 20 and 30 min after closing the flux chamber, using a photo-acoustic spectroscopic infra-red gas analyzer of Brüel & Kjær. The analyzer was directly attached to six flux chambers via a multipoint sampler in a closed system (Fig. 1), using polytetrafluorethylene tubes with an internal diameter of 0.3 cm and length of 400 cm. Gas samples were taken and analyzed for N_2O automatically every 90 s after the air in the headspace was pumped around for 20 s at a flow rate of 30 ml s^{-1}. Both gas analyzer and multipoint sampler were controlled using a portable computer, which also functioned as a data logger (Fig. 1).

The gas analyzer was fitted with optical filters to measure selectively concentrations of N_2O, carbon dioxide (CO_2) and water vapour (Velthof & Oenema, 1993). Concentration of N_2O was compensated for interferences of CO_2 and water vapour. Traps of soda lime and magnesium perchlorate were placed in the air stream to the gas analyzer to reduce variations in the concentration of CO_2 and water vapour respectively (Fig. 1). The accuracy of the gas analyzer was about 5% in the range of 300–5000 μl N_2O m^{-3} under field conditions. The measured N_2O concentrations in the headspace were corrected for the amount of N_2O which was pumped from one flux chamber into the next flux chamber. This amount was equal to the internal volumes of the multipoint sampler, gas analyzer and connecting tubes times the N_2O concentration. This internal volume was about 2.5% of the headspace volume of the flux chamber. Fluxes of N_2O were calculated from the course of N_2O concentration in the headspace in time, using linear regression analysis.

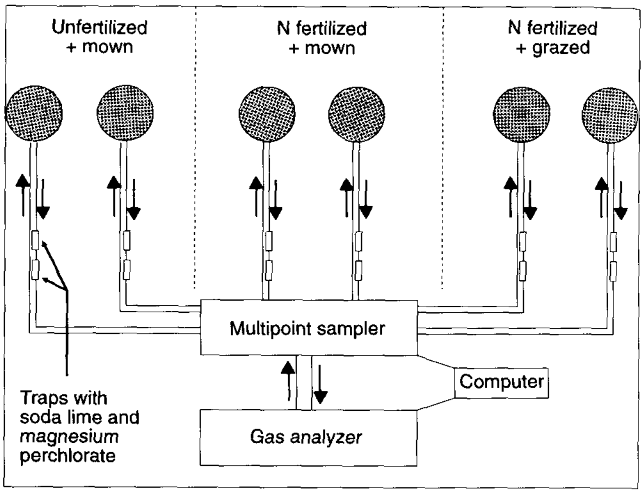

Fig. 1. Schematic set-up of N_2O flux measurements. Six flux chambers were directly attached in a closed system to a multipoint sampler and photo-acoustic spectroscopic infra-red gas analyzer. Two flux chambers were placed in each plot, about 1 m apart.

All three treatments were measured simultaneously in duplicate (Fig. 1). The three replicates (blocks) were measured sequentially, so that six flux measurements were carried out per treatment. The flux chambers were placed on the plots in stratified random design. All flux measurements at one site were carried out within 3 h, usually between 09.00 and 12.00 hours. Generally, fluxes measured once per week. Incidentally, measurements of spatial variation of N_2O fluxes were made using 48 flux chambers within 4 h using two gas analyzers.

Calculation of mean fluxes and total losses

The N_2O-flux measurements were carried out in six replicates, a sample size too small adequately to determine the frequency distribution. In the literature it has been shown that frequency distributions of N_2O fluxes are generally positively skewed and better approximated by lognormal than normal distribution (e.g. Ambus & Christensen, 1994; Folorunso & Rolston, 1984). Four methods were applied to estimate the sample mean of the six replicate fluxes, namely the arithmetic mean, the geometric mean, the lognormal mean and Finney's method.

The arithmetic mean is the common method to estimate the mean of populations which have a symmetric distribution, such as normally distributed populations, and it is the most used estimator of mean N_2O fluxes (e.g. Ryden, 1983). It is an unbiased estimator of the population mean, regardless of the form of the underlying distribution, but it is less efficient for skewed populations than for symmetric ones.

The geometric mean is the antilogarithm of the mean of log transformed data. For lognormally distributed populations, the geometric mean is close to the sample median. The geometric mean of a sample is a biased estimate of the population mean. The geometric mean or median have been used in N_2O studies by e.g. Arah *et al.* (1991) and Skiba *et al.* (1993). The lognormal mean is the geometric mean adjusted for the variance of the distribution (Aitchison & Brown, 1966). It is biased for sample size <100 (Parkin *et al.*, 1988). The lognormal mean has been applied in studies dealing with spatial variability of nitrification, denitrification and mineral N contents in soils by e.g. Folorunso & Rolston (1984), Parkin *et al.* (1985), White *et al.* (1987), and Bramley & White (1991).

A minimum-variance unbiased estimator of the mean of lognormally distributed populations was given by Finney (1941) and is described in detail by Aitchison & Brown (1966). Parkin *et al.* (1988) have recommended Finney's estimator as best estimator for samples of lognormal distributions, and it has been used in recent N_2O studies, e.g. Ambus & Christensen (1994), Clayton *et al.* (1994) and Hansen & Bakken (1993). However, Finney's method is not robust and may result in biased estimates when used for non-lognormal or contaminated lognormal distributions, especially for sample size <40 (Koch & Link, 1970; Myers & Pepin, 1990).

Three of the four estimators are based on log transformation. Some of the calculated fluxes were negative but close to 0. Adding a positive value to all data to obtain positive values only does not solve this problem. Due to the transformations, the added value also changes, and thus cannot be readily subtracted after the transformation. A reasonable alternative is to set all values below a certain value at a certain positive value. This is justified by the fact that negative fluxes were small and imprecise. For a comparison of the four methods, all single fluxes less than 3 μg N m^{-2} h^{-1}, including the negative fluxes, were quite arbitrarily set at 2 μg N m^{-2} h^{-1}. To assess the effect of this procedure, mean N_2O fluxes were also calculated with the four methods, after setting all fluxes less than 3 μg N m^{-2} h^{-1} at 1 μg N m^{-2} h^{-1} and at 3 μg N m^{-2} h^{-1}.

Total N_2O loss was calculated for each treatment from the time course of the mean N_2O flux ($n=6$), by linearly interpolating the mean N_2O fluxes and integrating the area using the trapezoidal method (France & Thornley, 1984). This procedure was carried out for all four estimators of mean.

Results

Single N_2O fluxes

The determination coefficient R^2, derived from linear regression analysis of the N_2O concentration in the headspace in time, increased with increasing flux magnitude (Fig. 2). In Table 1 frequency tabulations are given of all single N_2O fluxes measured per treatment per site during the whole experiment. For all sites and treatments many fluxes were fairly small, i.e. less than 25 μg N m^{-2} h^{-1}, relatively few fluxes were large. Fluxes larger than 100 μg N m^{-2} h^{-1} were found more often on fertilized and grazed than on unfertilized grasslands and more often on the peat soils than on the sand and clay soils. For all treatments negative fluxes were found (Table 1). These negative fluxes were close to 0, ranging from 0 to -19 μg N m^{-2} h^{-1}, and imprecise (Fig. 2).

Mean N_2O flux per measurement time

Measurements of N_2O fluxes using 48 flux chambers indicated that the frequency distributions of N_2O fluxes were positively skewed (e.g. Fig. 3), and better approximated by lognormal

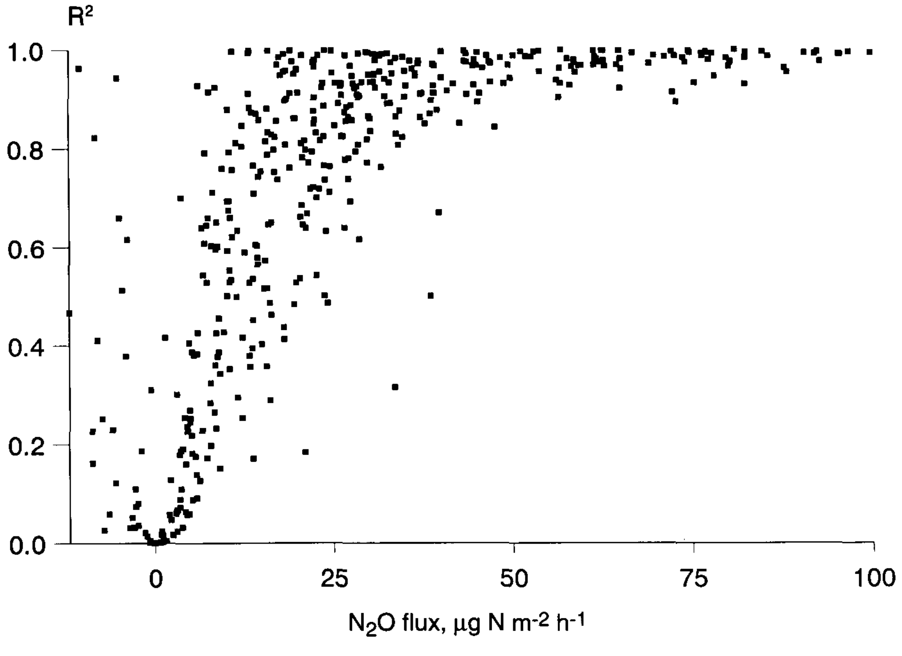

Fig. 2. Relationship between calculated N_2O flux and the determination coefficient R^2, for all fluxes less than 100 μg N m^{-2} h^{-1} of the sandy soil near Heino. Flux of N_2O was calculated using linear regression analysis of N_2O concentration in the headspace and time. Concentration of N_2O was measured four times, with intervals of 10 min. Values of R^2 of fluxes>100 μg N m^{-2} h^{-1} were>0.99, generally.

Table 1. Frequency tabulations of all N_2O fluxes measured at the four sites during the experimental period. Fluxes of N_2O are expressed in $\mu g\ N_2O\text{-}N\ m^{-2}\ h^{-1}$.

	Number of N_2O fluxes						
Treatment	<0	0–25	25–50	50–100	100–500	>500	Total
Sand							
Unfertilized-mown	22	111	45	10	1	0	189
N fertilized-mown	8	86	47	28	19	3	191
N fertilized-grazed	7	41	33	38	62	11	192
Clay							
Unfertilized-mown	42	112	23	13	3	0	193
N fertilized-mown	28	85	22	13	21	8	177
N fertilized-grazed	27	75	26	15	23	15	181
Peat I							
Unfertilized-mown	12	78	38	26	11	0	165
N fertilized-mown	9	40	26	35	41	14	165
N fertilized-grazed	4	43	32	33	34	17	164
Peat II							
Unfertilized-mown	11	47	41	40	64	33	236[a]
N fertilized-mown	5	21	21	14	44	24	129[a]
N fertilized-grazed	6	14	12	19	50	27	128[a]

[a] the mown and grazed treatment were not fertilized for the first cut; all fluxes measured till the second cut are from unfertilized grassland.

than normal distribution. The routine measurements of N_2O fluxes using six flux chambers indicated similar patterns, because the arithmetic mean was generally much larger than the geometric mean, by up to 7-fold (Fig. 4). The arithmetic mean was much smaller than the lognormal mean, by a factor of 11 (Fig. 4). The ratio between the mean derived from Finney's method and the arithmetic mean ranged from 0.6 to 2.5 and was on average 1.0.

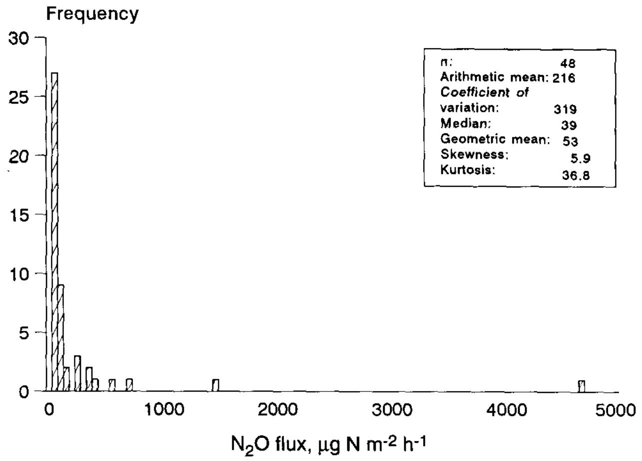

Fig. 3. Frequency distribution of N_2O-fluxes, from 48 flux measurements carried out on grazed grassland on peat soil II, in September 1992.

The effects of setting fluxes less than 3 $\mu g\ N\ m^{-2}\ h^{-1}$ at 1, 2 or 3 $\mu g\ N\ m^{-2}\ h^{-1}$ were larger for the three estimators based on log transformation than for the arithmetic mean (not shown). Effects were most significant for the lognormal mean. In some cases, the calculated lognormal mean of the six fluxes was even larger than the single fluxes. Generally, using the lognormal mean, setting the fluxes at 1 $\mu g\ N\ m^{-2}\ h^{-1}$ resulted in larger mean fluxes than setting fluxes at 3 $\mu g\ N\ m^{-2}\ h^{-1}$.

Total N_2O losses during the experimental period

Peak fluxes were generally found after N-fertilizer application and grazing, except during dry weather (Velthof & Oenema, 1995). The increase of N_2O flux due to N application and the effects of grazing lasted 1–3 weeks, generally. Week-to-week variations were much smaller on unfertilized and mown swards than on fertilized and grazed swards, except for swards on the peat soil II (Velthof & Oenema, 1995).

The estimate of total N_2O loss was smallest when derived from geometric mean and the largest when derived from the lognormal mean (Table 2). The total N_2O losses calculated from arithmetic means and means derived from Finney's method were generally in good agreement. The results indicate that setting all fluxes less than 3 $\mu g\ N\ m^{-2}\ h^{-1}$ at 2 $\mu g\ N\ m^{-2}\ h^{-1}$ did not affect or only slightly affected the estimation of total N_2O losses from arithmetic means (Table 2). This was also the case for the geometric mean and Finney's method, but the effect was much larger for the lognormal mean (not shown).

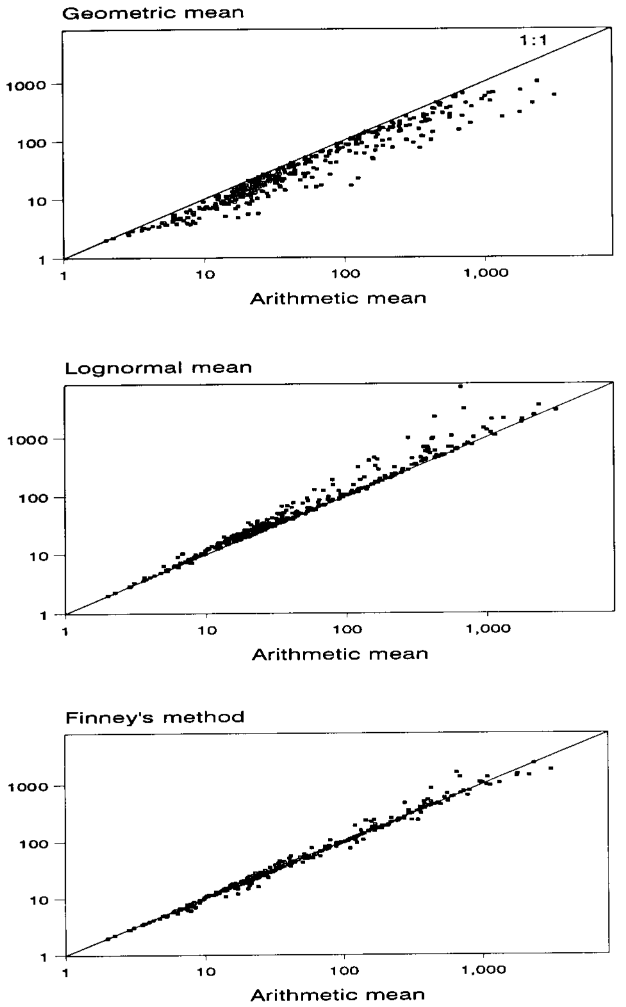

Fig. 4. Relationship between arithmetic means and geometric means, arithmetic means and lognormal means and arithmetic means and means derived from Finney's method. All means were calculated from six replicate N_2O fluxes and are expressed in µg N m^{-2} h^{-1}. Note logarithmic scales.

Discussion

The calculation of total N_2O losses from soils using a flux-chamber technique may be split into three parts, namely the measurement and calculation of single N_2O fluxes, the calculation of the mean flux from replicate flux measurements at one time, and the calculation of the total N_2O loss from the time course of the mean N_2O flux.

Single N_2O fluxes

For N_2O fluxes larger than about 25 µg N m^{-2} h^{-1} the increase of N_2O concentration in the headspace was generally linear (Fig. 2). This agrees with the results of other studies (e.g. Matthias *et al.*, 1980), in which also a linear increase of the N_2O concentration in the headspace was found. Apparently, the diffusion rate of N_2O from the soil to the headspace atmosphere was not significantly influenced by the increasing N_2O concentration in headspace and no correction for a decreasing N_2O diffusion rate had to be applied, as suggested by Hutchinson & Mosier (1981), for example. Therefore, all fluxes were calculated using linear regression analysis.

Table 1 shows than many fluxes were small, i.e. less than 25 µg N m^{-2} h^{-1}. This confirms the findings of other studies on managed grassland, namely a fairly small background flux with relatively few large N_2O fluxes, mostly after rain, N-fertilizer application and grazing (Christensen, 1983; Ryden, 1983). These small N_2O fluxes were measured inaccurately (Fig. 2). Better accuracy for small fluxes could have been obtained by increasing the closure time of the flux chamber and decreasing the ratio headspace volume to soil area. Such measures may, however, contribute to a greater disturbance of the micro climate in the headspace, which is unwanted because it may affect N_2O flux. Accuracy could also have been improved by more accurate measurement of N_2O concentration or by increasing the number of the measurements. Both of these measures require better facilities and more time, and are, therefore, not easily applicable. It may also be questioned whether an increased accuracy of small fluxes would have contributed much to accuracy of the estimated total N_2O loss. Our calculations indicate that the few large fluxes (fluxes > 100 µg N m^{-2} h^{-1}) contributed more strongly to the estimated total N_2O loss than larger number of small fluxes, except to some extent for unfertilized grasslands. For these reasons, we decided not to attempt to increase the accuracy of measurement of the small fluxes.

Negative fluxes suggest adsorption of N_2O from the atmosphere, though they may be caused by experimental error (Fig. 2). Ryden (1983) suggested that the grassland soil may absorb N_2O from the atmosphere during dry periods when grass growth suffers from shortage of N. Absorption of N_2O by the soil is a sink of atmospheric N_2O, but its contribution to the global N_2O budget is still uncertain (Bouwman, 1995).

Mean N_2O flux per measurement time

The estimators of the mean had a large effect on mean N_2O fluxes per measurement time (Fig. 4) and total N_2O losses (Table 2). Mean fluxes and total losses calculated from the arithmetic mean and the mean of Finney's method were in reasonable agreement, but geometric and lognormal means greatly differed from the arithmetic mean and the mean of Finney's method (Fig. 4 and Table 2). The question that arises is, what is the most appropriate estimator of the mean flux in this study? Criteria that are important in choosing the most appropriate estimator are that the estimator should be unbiased, efficient, and robust.

The frequency distribution of the N_2O fluxes provides the first argument, generally. In this study, fluxes were determined from six replicate measurements, a sample size too small to

Table 2. Calculated total N_2O losses during the experimental period, using the four estimators of the mean.

Treatment	Total N_2O losses in kg N ha^{-1}				
	Arithmetic mean		Geometric mean[b]	Lognormal mean[b]	Finney's method[b]
	All values[a]	Positive values[b]			
Sand					
Unfertilized+mown	1.0	1.0	0.8	1.2	1.1
N fertilized+mown	2.7	2.1	2.1	3.0	2.8
N fertilized+grazed	7.1	7.1	4.3	9.0	7.1
Clay					
Unfertilized+mown	0.8	0.9	0.6	1.0	0.9
N fertilized+mown	4.7	4.8	3.1	5.8	4.8
N fertilized+grazed	10.7	10.7	4.4	25.8	11.3
Peat I					
Unfertilized+mown	2.0	2.0	1.4	2.6	2.2
N fertilized+mown	8.2	8.2	5.6	10.2	8.6
N fertilized+grazed	12.1	12.2	6.9	19.3	13.3
Peat II					
Unfertilized+mown	11.0	11.1	5.0	13.1	10.7
N fertilized+mown	17.2	17.2	9.6	21.9	17.7
N fertilized+grazed	32.3	32.3	12.8	38.3	27.7

[a] including negative values.
[b] all values < 3 μg N m^{-2} h^{-1} were set at 2 μg N m^{-2} h^{-1}.

determine the frequency distribution. The large difference between arithmetic mean and geometric mean (Fig. 4), and the measurements using 48 flux chambers suggest that the distributions were positively skewed. It is questionable, however, to state that the distribution of N_2O fluxes were always approximately lognormal during the experiment. Frequency distribution of N_2O fluxes from soil may change during a year because of changes in moisture and mineral N contents of the soil and temperature, as also pointed out by Tiedje *et al.* (1989). Obviously, the exact frequency distributions of the N_2O fluxes at each measurement time, the extent of skewness of the distribution and possible changes of the distribution in time are uncertain. The arithmetic mean is unbiased, regardless of the form of the distribution, whereas the lognormal mean and Finney's method may be biased when applied to non-lognormal distributions. The geometric mean is a biased estimator of the mean of lognormal distributions.

Another important argument in the choice of an estimator arises from the occurrence of negative fluxes. When using the arithmetic mean negative fluxes can be included. When using the geometric mean, lognormal mean and the mean of Finney's method, the negative fluxes cannot be included in the calculations because all three estimators are based on log transformed N_2O fluxes. Setting negative fluxes at a certain positive value strongly affected the lognormal mean and, to a lesser extent, also the mean of Finney's method. Our results indicate that a small change in the value of one of the six replicate measurements may greatly affect the mean of estimators based on log transformed values, suggesting that these estimators are sensitive. The arithmetic mean was not or only slightly affected by small changes in one of the six replicates, indicating that the arithmetic mean was robust. Myers & Pepin (1990) reported that the arithmetic mean is more robust than Finney's method and recommended the arithmetic mean instead of Finney's method where it is uncertain that the data follow a lognormal distribution. This indicates that because of the uncertainty about the exact distributions Finney's method is less suitable than the arithmetic mean as estimator of the mean flux per measurement time in the present study.

In conclusion, because of the small sample size, the uncertainty about the frequency distribution at each measurement time, the sensitivity of the estimators based on log transformed data and the problems associated with negative fluxes, the arithmetic mean seems to be the most straightforward and robust estimator. We therefore prefer this estimator for the calculation of mean N_2O fluxes per measurement time.

Total N_2O losses during the experimental period

Total N_2O losses were calculated by linear interpolation of the mean fluxes per measurement time and integration over time, assuming that the results of flux measurements carried out during morning were representative for day and night. Several papers report distinct diurnal variations in N_2O flux from soil due to diurnal variations in temperature and moisture contents in the soil (e.g. Christensen, 1983; Conrad *et al.,* 1983). Minimum fluxes were observed during early morning, and maximum fluxes during the afternoon in these studies. Assuming diurnal patterns with small fluxes during early morning and large fluxes during the afternoon, it is reasonable to suggest that the mean N_2O flux derived from flux measurements between 09.00 and 12.00 hours, as in the present study, is representative for the mean flux over that day.

Fertilizer-N application and grazing greatly increased N_2O fluxes for 1–3 weeks, when soils were sufficiently wet. This suggests that flux measurements during the first weeks after fertilizer application and grazing are essential for reliable estimation of total N_2O losses. Daily measurements indicate that the increase in N_2O flux following application of N fertilizer and urine may vary greatly, both in terms of flux magnitude and duration (e.g. Velthof & Oenema. 1993). A model pattern of the time course of N_2O flux after fertilizer application and grazing cannot be readily inferred because of the complexity of temporal variability in the major factors controlling N_2O production in soil. Obviously, daily measurements would provide a more accurate total N_2O loss than weekly measurements, but we did not have the resources to make them, as is usual in this type of monitoring. Weekly measurements seem to give reasonably accurate estimates for intensively managed grasslands receiving frequent N-fertilizer applications when viewed over a whole growing season or several years. The weekly measurements will be continued for 2 years on all treatments and sites, and additional daily measurements, simultaneous measurements with micrometeorological methods in combination with modelling might provide a check on the accuracy of the total N_2O loss from grassland as calculated from weekly measurements using six replicates. Because of the unpredictable time course of N_2O fluxes, linear interpolation of the weekly flux seems to be the most straightforward procedure for the calculation of N_2O losses at present.

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