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DIRECT MEASUREMENT OF NITROUS OXIDE FLUX FROM SOIL

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A simple technique for direct measurement of nitrous oxide flux from soils is described. These fluxes were measured at several locations in Essex County in southwestern Ontario and were found to be low from bluegrass and clover sod ($3.17 - 4.01 \times 10^9$ molecules cm^{-2} s^{-1}), intermediate from continuous corn and non-agricultural marsh land ($16.8 - 32.2 \times 10^9$ molecules cm^{-2} s^{-1}), and high from corn in rotation following alfalfa sod (133×10^9 molecules cm^{-2} s^{-1}). Considerable variability in rate was observed from day to day and from site to site irrespective of soil type or crop management system. Comparisons are made with measurements obtained in various geographical areas by others.

L'auteur décrit une technique simple de mesure directe de flux d'oxyde nitreux de divers sols. Les mesures ont été effectuées à plusieurs endroits du compté d'Essex dans le sud-ouest de l'Ontario et se sont révélées faibles chez les sols recouverts d'un gazon de pâturin et de trèfle ($3.17 - 4.01 \times 10^9$ molécules $cm^{-2}s^{-1}$), intermédiaires pour les sols en monoculture de maïs et marécageux non agricoles ($16.8 - 32.3 \times 10^9$ molécules $cm^{-2}s^{-1}$) et élevées chez ceux caractérisés par un assolement de maïs après gazon de luzerne (133×10^9 molécules $cm^{-2}s^{-1}$). Il a observé une variabilité considérable du taux de flux jour après jour et d'un emplacement à l'autre, peu importe le type de sol ou le régime de conduite des cultures. L'auteur établit des comparaisons avec des mesures effectuées par d'autres chercheurs dans diverses régions géographiques.

The need for more world-wide studies of nitrous oxide (N_2O) levels in the troposphere and careful assessment of sources and sinks has been expressed in several recent publications (Hahn and Junge 1977); Council for Agricultural Science and Technology (CAST) 1976; Crutzen and Ehhalt 1977; Liu et al. 1977). The need arises because of concern that increasing use of nitrogen fertilizers might lead to an increase in production of N_2O (Crutzen 1974; McElroy 1976; McElroy et al. 1976). Nitrous oxide is removed in the stratosphere by photolysis and by reaction with $O(^1D)$ atoms leading to nitric oxide, NO, which catalytically removes ozone (Crutzen 1970; Johnston 1971). Thus an increase in N_2O may increase average NO levels and result in a depletion of stratospheric ozone which may have serious biological and climatological effects as presented by Crutzen and Ehhalt (1977) in their review.

Bacteriological activity in the biosphere is thought to account for most of the atmospheric burden of N_2O, but so far relatively few measurements of flux from soils have been reported. In general estimates have been based on measured N_2O levels and calculated diffusion coefficients in soil atmospheres. A few direct measurements have recently appeared whereby N_2O levels as a function of time within a canopy installed over a site were monitored (Rolston and Broadbent 1977; Cicerone et al. 1978; Freney et al. 1978; Focht 1978; McKenney et al. 1978; Ryden et al. 1978).

From an agricultural point of view, more efficient use of nitrogen fertilizer depends on an adequate knowledge of potential losses

from soil. Denitrification and other processes of nitrogen removal have not been fully evaluated, partly because of difficulties in measuring fluxes of N_2O and N_2 under natural field conditions.

In this paper, a simple method for N_2O flux measurements over soils in their natural state is described and some results presented.

MATERIALS AND METHODS

Analyses were carried out using a Perkin-Elmer 3920B gas chromatograph equipped with a ^{63}Ni electron capture detector and a 3 m × 0.3 cm (10 foot × 1/8 inch) porapak Q column. Temperature, flow rates and other instrument parameters were similar to those reported by Rasmussen et al. (1976). Temperatures of the detector, interface between column and detector, and column were set at 350, 150 and 50°C, respectively. The carrier gas (95% Ar − 5% CH_4) flow rate was nominally set at 30 ml min^{-1}. The standing current was 3.5×10^{-9} amps. Under these conditions subambient levels of N_2O can be quantitatively measured in 1 cc, or less, air sample injections. Syringe injection was employed.

In the early stages of this research a double-walled canopy of 6-mil polyethylene film, approximately 0.8 m^2 in area was mounted over two concentric steel rings, about 5 cm apart and driven into the soil to a depth of 10 cm, to form a double-walled chamber, approximately 3.8 cm deep. The entire system could be completely purged with N_2 or air. This system was not freely portable because of its size and was used initially to provide preliminary estimates of N_2O flux from soil into a closed chamber. To prevent excessive heat build-up the entire system was shaded from the sun and the temperature inside and outside the sampling chamber was monitored to ensure that chamber temperature was close to ambient during the sampling period.

Subsequently, simple single-ring canopies made from aluminum cylinders (~ 15 cm diameter by ~ 25 cm length with a wall thickness of 2 mm) were used. These canopies were pressed into the soil by hand to a depth of 5–10 cm to provide firm contact with soil and sealed on top with neoprene rubber sheets, 2 mm thick. This cover was installed using a stainless steel gear-type clamp, immediately prior to collection of the first sample which was taken to represent the ambient state in the field. Closure of the chamber and collection of the first sample was accomplished in less than 60 sec. The rubber sheeting was virtually impervious to passage of N_2O. The aluminum chambers were also shaded from the sun.

Initially, samples were collected using evacuated pyrex flasks (~ 500 cm^3) fitted with a greaseless, 0-ring type stopcock for evacuation and filling. Later, much smaller (~ 20 cm^3) pyrex tubes, each sealed with a "slip-on" type septum, were found to be more convenient. These tubes were first evacuated and then filled through a double-end stainless steel needle (20-gauge × 2.5 cm) inserted between the neoprene cover and the "slip-on" type septum. The needle remained open between sample collections to allow equilibration of pressure inside and outside the chamber and to minimize mass flow from the soil. The selection of sample size was a compromise between convenience in the field, an opportunity for repeated instrument analysis and reasonable control of sampling error. Correction for the volume of sample removed from the chamber was not attempted because this volume could be replaced by both soil atmosphere and air.

Instrument calibrations were routinely made using commercial N_2O standards (Liquid Carbonic, analyzed calibration mixtures, 20–100 ppm) from levels < 3.0 to $> 3.0 \times 10^4$ ppb and higher as required. The calibration was essentially linear throughout a range of concentration up to 8.0×10^3 ppb.

Ambient levels in the vicinity of the instrument were usually measured routinely several times each day to provide a reference base and to check on instrument performance. Data from more than 100 trials yielded a value of 303 ± 10 ppb. More recent measurements using other mixtures from the same source yielded higher ambient levels, more in line with other atmospheric measurements (Rasmussen and Pierotti 1978), pointing out the importance of the selection of the primary standard where absolute values are required.

RESULTS

Double-Ring Canopy

A number of preliminary runs were carried out using the large double-ring canopy. Although the earliest experiments showed considerable scatter, the N_2O concentration within the chamber increased from ambient linearly with time over several hours to

levels often in excess of 10 ppm, vol/vol. Figure 1 shows such a N_2O yield-time plot measured over a period of about 70 h using the double-ring system in which the entire system was first flushed with air. Sampling was started immediately after purging of both the sample compartment and space between the walls had been stopped. The data show that N_2O fluxes can readily be obtained from N_2O yield-time measurements using the initial linear portion of the plot. The decrease in concentration gradient beneath the canopy was not of serious magnitude during the first 5–8 h (Fig. 1). Thereafter the apparent flux decreased with time. After 43 h, when N_2O approached a constant equilibrium level of ~ 65 ppm, a flow of N_2 between the walls was started to determine the extent of leakage and/or possible induction of anaerobic conditions. A pronounced decrease in N_2O level followed after some 5 h. It appears that more perfect exclusion of atmospheric O_2 led to rapid depletion of O_2 at the soil-air interface and a subsequent change in the rate of N_2O evolution from the soil. The measurements in Figs. 1 and 2 were made during the initial 43-h period without disturbing the closed canopy configuration of the system. Polyethylene is quite porous to O_2 and somewhat porous to N_2O. The movement of N_2O across the film used in this study was 3×10^{10} molecules N_2O cm^{-2} s^{-1} where the gradient in concentration was 20 ppm. At ambient levels the flux from the soil was 10^3 to 10^4 times greater than the rate of diffusion through the polyethylene film. In this study two thicknesses of polyethylene film constituted the barrier to the atmosphere. Upon admission of N_2 to the outer or locking ring there was an immediate decrease in O_2 levels within the chamber. This evidently caused the alteration in the N_2O evolution described previously. The purging effect of N_2 gas on the O_2 in the chamber is not attributed to system leakage because of the delay in the depletion of N_2O. This conclusion is supported by the oxygen levels within and outside the chamber during the experimental period described by Fig. 1.

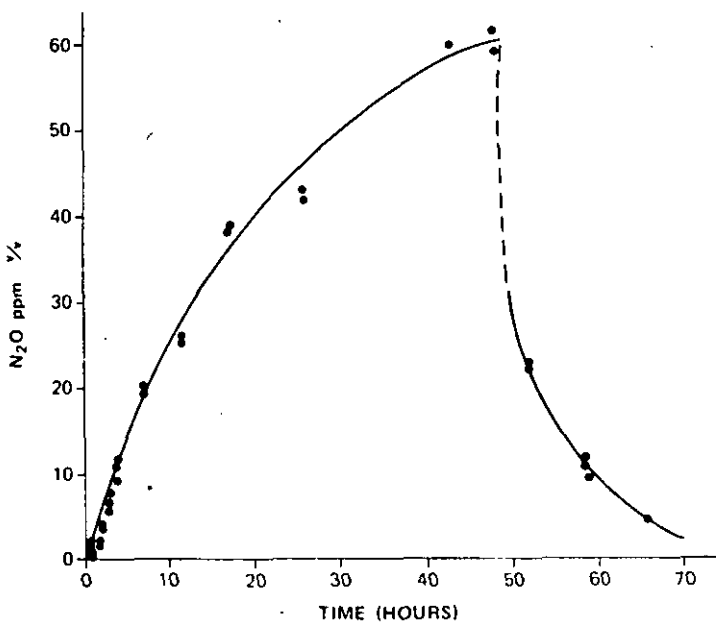


Fig. 1. N_2O yield-time plot. Following initiation of N_2 flow between chamber walls at 43 h, a rapid decrease in N_2O concentration occurred after a 5-h lag period.

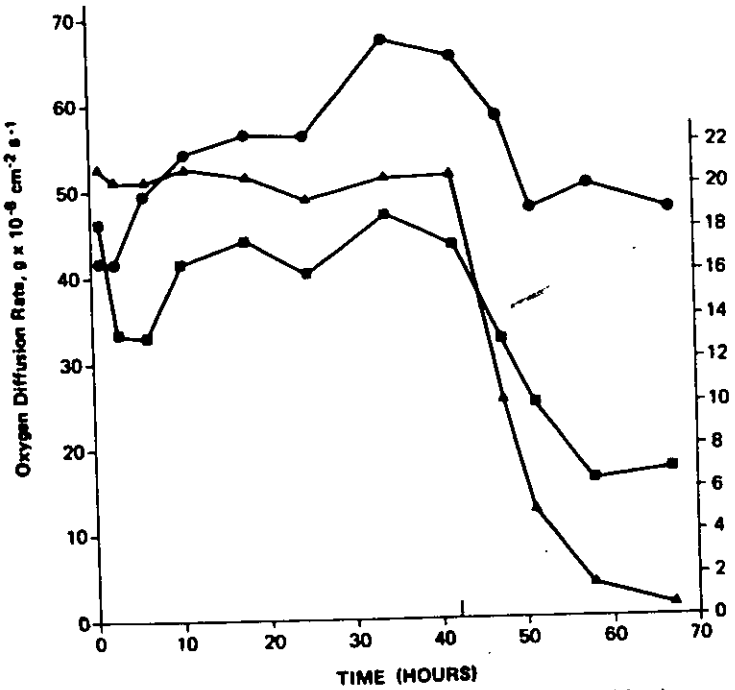


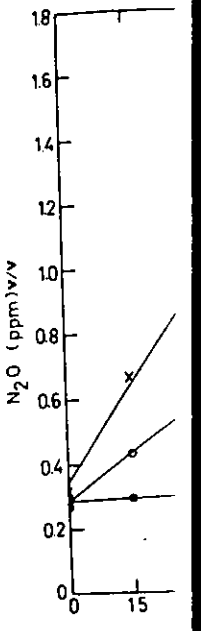
Fig. 2. Oxygen diffusion rates in soil inside (■) and outside (●) the double-ring canopy, and volume percent oxygen in the inner chamber atmosphere (▲) during the sampling period. N_2 purge initiated at 43 h.

Although there is considerable scatter in the oxygen diffusion rate (ODR) measurements made with separate platinum electrodes, as described by Lemon and Erickson (1952), the results show that relatively constant oxygen levels were maintained within the sample chamber (demonstrated by the concentration of oxygen remaining in the headspace and by the ODR measurements in the soil) during the initial 43-h period of N_2O measurement referred to in Fig. 1 (Fig. 2). Oxygen diffusion rates in the soil outside the chamber were higher than within, except during the initial 2- or 3-h period which suggests that some oxygen stress was manifest within the chamber.

Subsequent 75-min runs, each of which involved prior purging of this closed system with air to sweep out residues of soil-N_2O were made under otherwise identical conditions on the same site and the rates were in close agreement with the longer term flux measurements. Results of eight runs taken over an 18-day period showed relatively small fluctuations in rate ($4.3 \pm 1.1 \times 10^{10}$ molecules cm^{-2} s^{-1}) and demonstrated the advantage of shorter, readily repeated sample periods.

Aluminum Single-Ring Canopy

These experiments showed that it was preferable to use the smaller aluminum canopies to which the neoprene cover was applied immediately prior to collecting the first sample. These simpler chambers were easily portable and thus considerably more convenient, permitting greater site replication. A run made with the aluminum chamber, installed on the soil area within the larger ring canopy, yielded results similar to those mentioned above. In contrast to polyethylene the neoprene material was



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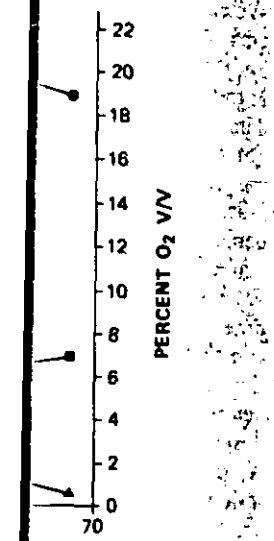

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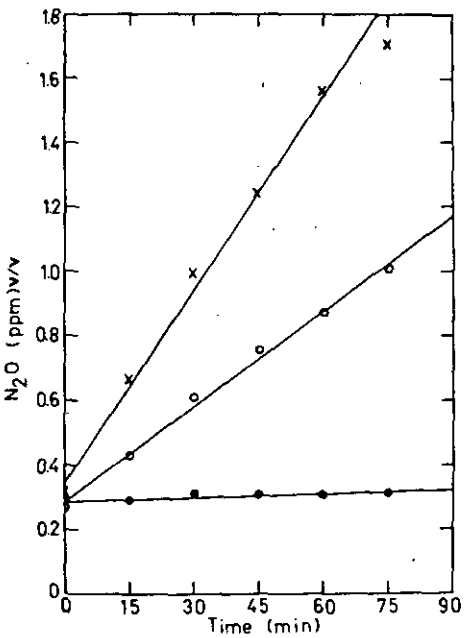

Fig. 3. Typical yield-time plots using small canopies. (x) Corn on alfalfa sod, N_2O flux = 133 $\times 10^9$ *molecules* cm^{-2} s^{-1}; (o) Alfalfa sod, N_2O flux = 73.5 $\times 10^9$ molecules cm^{-2} s^{-1}; (•) Bluegrass sod, N_2O flux = 3.17 $\times 10^9$ molecules cm^{-2} s^{-1}. Rates are calculated from the least squares estimates of slopes converting ppm min^{-1} to molecules cm^{-2} s^{-1} with a multiplication factor which depends on canopy volume.

determined to be impermeable to N_2O.

Figure 3 shows typical yield-time plots using small canopies. Rates of N_2O evolution were calculated from least squares estimates of the slopes. Scatter, which typically leads to a standard error of the regression coefficient of $\pm 1.0 \times 10^{-4}$ ppm min^{-1} ($\pm$ 7.5 $\times 10^8$ *molecules* cm^{-2} s^{-1}), corresponding to $\pm$ 5% uncertainty in calculated rates for rates greater than 2×10^{-3} ppm min^{-1} (15×10^9 molecules $cm^{-2}s^{-1}$), can most readily be explained by leakage around the sample tube septums. Some sacrifice in precision was made in favor of convenience. Several functions to estimate flux may be fitted to yield-time plots such as the one for corn on alfalfa sod (Fig. 3). In this instance a linear, a quadratic and an exponential function of the form $Y = K + AB^X$ accounted for 0.988, 0.998 and 0.95 of the observed variability in N_2O concentration, respectively. Although the accumulation of N_2O in a closed chamber is expected to be curvilinear with respect to time (Matthias et al. 1978), estimates based on relatively short periods of time indicate that the initial portion of the plot is nearly linear. Thus small sampling errors appear to be unduly exaggerated by extrapolation of any curvilinear function to its upper horizontal asymptote within a time period of 700-1500 min (see also Fig. 1). It is for this reason that the simple linear function was chosen as a satisfactory approximation of the rate of diffusion of N_2O from soil under the conditions of this study.

A number of rate measurements were made over a variety of agricultural and other soils in order to observe possible gross differences in N_2O production. The rates all fell within the range 0.1 – 133 $\times 10^9$ molecules cm^{-2} s^{-1} (1×10^9 molecules cm^{-2} $s^{-1} = 4.02 \times 10^{-4}$ kg N ha^{-1} $day^{-1} = 1.68$ μg N m^{-2} h^{-1}) (Table 1) which are comparable in magnitude with measurements by other investigators. Intermediate rates were obtained on the edge of Pelee Marsh where the soil was completely waterlogged and consisted mainly of decaying vegetation. Intermediate levels were also observed on Windsor garden soil and the corn field where corn was grown without rotation. Bluegrass and clover sods showed very low N_2O production as expected. The highest level of N_2O production came from a plot of corn planted following alfalfa.

In order to gauge possible variation in N_2O flux on a given site, simultaneous measurements were made using duplicate canopies located about a meter apart on bluegrass sod, corn and alfalfa fields of Brookston clay soil. The results are shown in Table 2. In all cases duplicate rates agreed within a factor of 10, except for that measured on 8 July over the alfalfa site where an approximate 20-fold variation in rate was observed.

Table 1. N_2O fluxes obtained from yield time plots of N_2O evolution over a variety of sites in Essex County, southwestern Ontario

Site	Date (1977)	Temp (°C)	Rate (10^9 molecules cm^{-2} s^{-1})
Windsor, cultivated garden soil	10 June	27.0	14.8
Windsor, dry clay, grass sod		18.7	<0.1
Windsor, cultivated garden soil	13 June	20.2	18.8
Pelee Marsh, waterlogged, pooled water	23 July	25.0	16.8
Pelee Marsh, waterlogged, pooled water	23 July	25.8	32.2
Woodslee, corn on alfalfa sod	16 June	27.0	133.0
Woodslee, bluegrass sod	16 June	26.5	3.17
Woodslee, red clover sod	16 June	24.4	4.01
Woodslee, continuous corn (168 kg N ha^{-1}) dry soil	16 June	30.3	18.2
Woodslee, continuous corn (168 kg N ha^{-1}) wet soil	16 June	27.5	24.0

Table 2. N_2O flux measurements obtained from duplicate canopies located a meter or more apart on the same sites at Woodslee on three dates

Site	Date (1977)	Temp. (°C)	Rate (10^9 molecules cm^{-2} s^{-1})	
Alfalfa	8July	27.3	3.7	73.5
Corn	8 July	27.3	5.3	2.7
Bluegrass	8July	27.3	4.8	2.1
Alfalfa	26 July	21.0	1.9	1.6
Corn	26 July	21.0	<0.1	<0.1
Bluegrass	26 July	21.0	1.3	0.9
Alfalfa	29 July	23.0	0.8	<0.1
Corn	29 July	23.0	0.5	2.3
Bluegrass	29 July	23.0	<0.1	<0.1

DISCUSSION

Bacterial denitrification which occurs under anaerobic conditions seems to generate most of the N_2O in soils (Hahn and Junge 1977). However, numerous publications, as referred to by Cady and Bartholomew (1961), have reported losses of gaseous nitrogen and nitrous oxide under aerobic or partially aerobic conditions in studies carried out in laboratory soil systems. The rate measurements made in this study probably relate particularly to denitrification and possibly to nitrification processes and provide some further indication of nitrous oxide source strengths of various agricultural and other soils. Most of the initial data were obtained over sites chosen more or less at random from locations where the soils were under different management systems in the local area. The objective in the first instance was to test procedures and equipment and identify any gross differences in fluxes from different soil situations.

It is perhaps noteworthy that the magnitude of the rates obtained in several situations was somewhat surprising. For example, rates measured on the edge of Pelee Marsh, although not exceptionally high, were larger than expected. It has been noted that in a completely waterlogged soil there should be no net N_2O production even though denitrification is maximized (Hahn and Junge 1977). This arises because in the absence of oxygen, after the supply of nitrites and nitrates is exhausted, the rate of conversion of N_2O to N_2 increases faster than the rate of formation of N_2O (Focht 1974).

Burford and Stefanson (1973) point out that the percentage of aerated pore space (which is controlled by water content) is the

most important parameter regulating N_2O flux rates in soils. Many of the rates measured in this study were obtained over Brookston clay, normally a poorly drained soil but which was considered to be well-aerated at the time of sampling. Bremner and Blackmer (1978) in their laboratory study found that well-aerated soils treated with either ammonium sulphate or urea released N_2O at rates ranging from 1.2×10^9 to 84×10^9 molecules N_2O cm^{-2} s^{-1} for applications ranging from 25 to 400 μg N added per gram of soil. For comparison, the continuous corn plots referred to in Tables 1 and 2 had been treated with 168 kg N ha^{-1} NH_4NO_3 which corresponds to 50 μg N per gram of soil.

It is evident from our data that considerable variability in rate is normal, indicative of the complex, dynamic systems involved. Nitrous oxide fluxes obtained from sites over the same soil type, about a meter apart, on the same day, occasionally differed considerably (Table 2). Rates varied from essentially zero over dry hard-packed clay to a very high rate ($\sim 10^{11}$ molecules cm^{-2} s^{-1}) in one instance over arable clay soil planted in alfalfa. Whereas variation in rates from different soil types was expected, it is evident, however, that variability between different sites and at different times preclude characterizing a particular soil type or cropping system at this time.

Table 3 shows a collection of fluxes obtained in several different geographical areas. Most values given are averages obtained over a 1-yr period. Although these rates are not strictly comparable to our own, as they relate to widely differing soils, it can be seen that the rates vary in the range zero ($< 10^9$) to $\sim 10^{11}$ molecules cm^{-2} s^{-1} as was the case in this work with the exception of high evolution on a recently fertilized loam soil (Rolston et al. 1976). It is interesting to

Table 3. N_2O fluxes in various geographical areas

Area	Soil	Rate (10^9 molecules cm^{-2} s^{-1})	Comment	Reference
Mainz, W. Germany	Pararendzina unploughed	47.0		
	Low biological activity sand dunes	5.5	Average 1 yr	(Hahn and Junge 1977)
	Mountainous woodland	6.8		
Cape Verde Islands	Desert soil	<1.4	Average 1 yr	(Lieble, K.H. as cited by Hahn and Junge 1977)
Australia	Urrbrae redbrown earth fertilized with 112 kg N ha^{-1} $NaNO_3$			
	Pasture	25		
	Old cropped area	640	Following rain	(Burford and Stefanson 1973)
	Recently cropped area	680		
Davis, Calif.	Alluvial Yolo loam, fertilized with 300 kg N ha^{-1} KNO_3	2000	(Max. 8 days after fertilization)	(Rolston et al. 1976)
Polar region	Tundra	14	Average 3 mo yr^{-1}	(Soderlund and (Soderlund and Svensson cited by Hahn and Junge 1977)
Australia	Clipped ryegrass sod			
	$NaNO_3$ fertilization	11.9	Max. rate	
	$NaNO_3$ fertilization + irrigation	5.4	Max. rate	(Burford and Hall 1976)
	$NaNO_3$ fertilization + heavy rainfall	3-20	—	
Australia	Unfertilized, clipped grass-clover sod			
	Unirrigated	3.6		(Freney et al. 1978)
	50 mm irrigation	65.5		

note that even desert soil (Cape Verde Islands), cited by Hahn and Junge (1977) was a net producer of N_2O.

Because of wide variability in rates of N_2O evolution and complex dependence on the nature of the soil environment it remains difficult to extrapolate these and other results to a global net production rate of N_2O from soils. Recent estimates are very uncertain. The CAST report (1976) favors a value of 4.2×10^{12} g yr^{-1} with an upper limit of 7×10^{12} g yr^{-1} based on assumed average losses of 1 kg N_2O ha^{-1} yr^{-1} (4.3×10^9 molecules $cm^{-2}s^{-1}$) from cropland and 0.2 kg N_2O ha^{-1} yr^{-1} (8.7×10^8 molecules cm^{-2} s^{-1}), from non-cropped land. Other estimates have been made (Liu et al. 1977; Hahn and Junge 1977). Considerably more systematic data obtained under natural field conditions over longer time periods are required.

Earlier fluxes were usually calculated from N_2O analyses in the soil atmospheres and estimates of diffusion coefficients (Fick's law). These methods are subject to relatively large sources of error as a result of uncertainties in diffusivities, variations in porosity because of air-filled and water-filled pores and difficulties associated with assessment of gaseous concentration gradients (Burford and Stefanson 1973). The technique described in this work provides a direct measurement of N_2O evolution in field situations and appears to be reliable and free from relatively large errors.

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