AP42 Section:	9.2.1
Background Ch	3
Reference:	6
Title:	J. C. Ryden et al., "Direct In-Field Measurement of Nitrous Oxide Flux from Soils," *Soil Science Society of America Journal*, 42:731-737, 1978.

Section 3
Ref-6

Direct In-field Measurement of Nitrous Oxide Flux from Soils[1]

J. C. RYDEN, L. J. LUND, AND D. D. FOCHT[2]

ABSTRACT

A method was developed whereby nitrous oxide (N_2O) effusing from a soil surface could be contained and selectively trapped for subsequent analysis. Containment of N_2O was achieved by inserting a steel cover box with inlet and outlet ports into the soil. The enclosed air space above the soil surface was continuously swept by drawing external air through the cover at a flow rate of 20 liters/hour. N_2O in the air swept from the enclosed airspace was adsorbed on 5Å molecular sieve. Adsorbed N_2O was displaced for gas chromatographic analysis by addition of water to the molecular sieve in a closed system. N_2O evolved from the soil surface was distinguished from that drawn into the cover during operation by concurrent measurement of the amount of N_2O adsorbed from an equivalent flow of the external atmosphere. The adsorption and recovery of N_2O by molecular sieve was affected by the N_2O concentration in the air flow and the amount of N_2O passed through the molecular sieve. Preliminary experiments in which N_2O-air mixtures were passed through 20g molecular sieve demonstrated that for N_2O concentrations up to 34 μg N/liter, a flow rate of 20 liters/hour and sampling periods of 4 hours or less, complete recovery of N_2O passed into the molecular sieve was achieved upon displacement with water. N_2O released into the enclosed air space from an unsealed syringe was also quantitatively recovered providing a flow rate of at least 20 liters/hour was used to sweep the cover box. Flow rates of 10 to 40 liters/hour through covers inserted into moist soil had no effect on the measured rate of N_2O evolution from the soil surface. Preliminary measurements at an irrigated, fertilized (120 kg N/ha) celery-production block on a Haploxeroll indicated an overall mean N_2O flux of 9.42 g N/ha per hour over a period of 76 hours. There was a diurnal variation in the N_2O flux with mean peak fluxes of up to 15.8 g N/ha per hour occuring during the early afternoon. The method provides a basis for monitoring N_2O flux from field soils under on-going agricultural practice.

Additional Index Words: **denitrification, 5Å molecular sieve, gas chromatography.**

Ryden, J. C., L. J. Lund, and D. D. Focht. 1978. Direct in-field measurement of nitrous oxide flux from soils. Soil Sci. Soc. Am. J. 42:731–737.

THE MAJOR GASEOUS products of the microbial reduction of nitrate during denitrification are dinitrogen (N_2) and nitrous oxide (N_2O). Nitrous oxide produced during denitrification is considered to be the principle source of atmospheric N_2O. Consequently, any increase in the pool of nitrate available for denitrification provides for a potential increase in the amount of N_2O produced in soils which may be subsequently released to the atmosphere. An increase in the nitrate pool may arise from increased reliance of agriculture on biologically and, in particular, industrially fixed N, 68% of which is used as N fertilizer (Council Agri. Sci. Tech., 1976). This potential for increased atmospheric N_2O concentration has given rise to concern over its ensuing effect on the amount of stratospheric ozone (Crutzen, 1974, 1976; Johnston, 1972; McElroy et al., 1976; Hahn and Junge, 1977).

The amount of stratospheric ozone is dependent upon the balance between its formation from oxygen and its destruction largely by reaction with nitric oxide and nitrogen dioxide, which are formed in the stratosphere from N_2O. Consequently, an increase in the amount of N_2O reaching the stratosphere has serious implications in that a depletion of stratospheric ozone will increase the incidence of biologically harmful ultraviolet radiation at the earth's surface.

A small number of measurements have demonstrated that field soils are indeed a source of N_2O under conditions expected to induce denitrification (Arnold, 1954; Burford and Millington, 1968, Schutz et al., 1970; Rolston et al., 1976; Burford and Hall, 1977). Although some of these measurements have permitted estimates of N_2O flux from soils, a direct and simple method of flux measurement has yet to be developed. Nitrous oxide flux from soils has been calculated from measurements of N_2O concentration in the soil atmosphere (Burford and Millington, 1968; Burford and Stefanson, 1973; Rolston et al., 1976). The reliability of such estimates of N_2O flux, however, is limited by the reliability of the diffusion model used in their calculation. Burford and Hall (1977) and Rolston and Broadbent (1977) have estimated the N_2O flux by enclosing the atmosphere directly above an area of the soil surface and measuring the increase in N_2O concentration with time. Flux measurements using this approach, however, have to be corrected for the effects of increasing N_2O concentration in the enclosed air space on the rate of N_2O diffusion from the soil surface (Focht, 1978; Rolston and Broadbent, 1977). Furtbermore, a closed soil cover isolates the soil surface from atmospheric influences, particularly pressure fluctuations, experienced by the external soil surface.

As a basis for a routine method for the direct measurement of N_2O flux from soils, it would seem preferable to slowly sweep a soil cover which is coupled to the external atmosphere through an air inlet vent. Such an approach is expected to minimize differences between conditions at the enclosed and open soil surface, as the enclosed air will be continuously replaced with external air. Furthermore, the inlet vent will allow external pressure variation to be reflected within the enclosure. Nitrous oxide swept from the air space may be conveniently adsorbed on a quantity of 5Å molecular sieve (Bock and Schutz, 1968; LaHue et al., 1971; Hahn, 1972) placed in an air-flow line connected to one end of the enclosure. Until recently, the displacement of adsorbed N_2O has presented technical difficulties, but a method reported by Dowdell and Crees (1974) has greatly simplified this procedure.

Although direct measurements of N_2O evolution from soils have intrinsic value for the reasons outlined above, a simple method for the direct measurement of N_2O evolution may also be valuable in the development of a method for direct measurement of denitrification N loss. Due to the high ambient concentration of N_2, amounts of N_2 produced

[1]Contribution from the Dep. of Soil and Environmental Sci., Univ. of Calif., Riverside, CA 92521. Research supported by R.A.N.N. Div. of the Nat. Sci. Found., Project AEN74-11136A01. Received 17 Oct. 1977. Approved 15 June 1978.

[2]Research Soil Scientist, and Associate Professors, respectively.

during denitrification cannot be reliably measured. Only recently have direct field estimates of denitrification N loss been achieved (Rolston et al., 1976). These estimates were based on a diffusion model and measurements of the concentrations of N_2O and ^{15}N-labeled N_2 in the soil atmosphere of field plots treated with ^{15}N-labeled nitrate. It has recently been shown, however, that small concentrations of acetylene inhibit the reduction of N_2O to N_2 during denitrification. (Balderston et al., 1976; Yoshinari and Knowles, 1976; Yoshinari et al., 1977). Consequently, measurement of N_2O evolution from field sites treated with acetylene may provide a convenient approach to field measurement of net denitrification N loss.

The purpose of the present paper is to report the development of a method for direct measurement of N_2O flux from soils. The efficiency of the method was evaluated in laboratory studies and preliminary data from its field use are reported.

DEVELOPMENT OF METHODS

Equipment Used

The apparatus used for in-field measurement of N_2O flux is illustrated in Fig. 1a. The soil cover boxes (50 by 10 by 17 cm) were made from 20-gauge galvanized sheet metal with 0.953-cm female pipe fittings at each end to provide 0.64 cm diameter ports. The covers were checked for airtightness by submersion in water. When inserted into the soil to a depth of 10 cm, 0.05 m^2 of the soil surface was covered. Columns for water- and CO_2-removal materials (Drierite and Ascarite, respectively) were made from 20-cm lengths of clear rigid plastic tubing (I.D., 3.5 cm; O.D., 4.45 cm), sealed at one end with screw caps fitted with rubber O-rings. The 5A molecular sieve (Davison Chemical, grade 626, 8-12 mesh), on which N_2O is adsorbed, was contained in screw-cap glass vials which could be plugged into the air-flow line at appropriate times using a neoprene stopper fitting (Fig. 1a). Needle valves were used to regulate flow which was measured using bead-type gas flow meters. Flow calibration was checked as described below. During operation, the enclosed air space was swept using a small pump (Gast, model no. 033-127-149) powered by a 12-V lead-acid battery, both built into a portable unit. At least eight cover boxes could be operated in parallel from each of these units. Each part of the apparatus was joined with 0.318-cm (ID) nylon pressure tubing and coupled with Swagelok fittings.

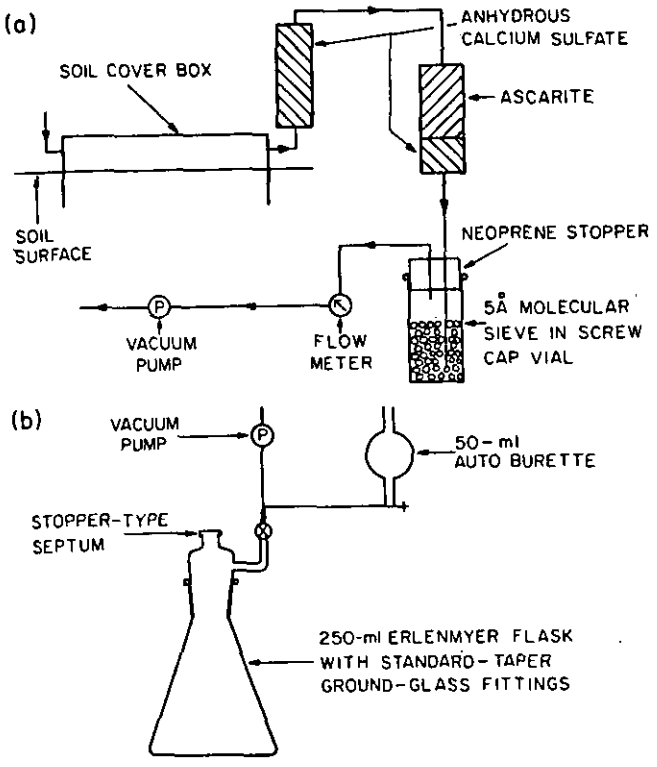

Fig. 1—Schematic representation of the apparatus required for (a) the collection and adsorption and (b) subsequent recovery of N_2O effusing from a field soil using 5A molecular sieve.

Adsorption and Recovery of Nitrous Oxide

The efficiency of 5Å molecular sieve as an absorbent of N_2O was determined under various conditions relevant to its use in field experiments. Various amounts of standard N_2O-air mixtures, calibrated against pure N_2O, were passed at different measured flow rates through 20-g samples of molecular sieve contained in screw-cap vials. In these experiments, a controlled flow of the N_2O standard was passed through a column containing Ascarite and calcium sulfate and subsequently through the vial of molecular sieve. Before each use, the molecular sieve was activated by heating to 350°C for 5 hours and then allowed to cool in an air-tight can.

After passage of a known amount of N_2O, calculated from the concentration in the standard N_2O supply and the measured flow rate, N_2O was displaced from the molecular sieve using the method described below. In some cases, samples of molecular sieve were stored in capped vials for up to 4 weeks before displacement of the adsorbed N_2O.

The method used for displacement of N_2O from the 5Å molecular sieve was based on that described by Dowdell and Cress (1974). The molecular sieve on which N_2O had been adsorbed was placed into a 250-ml Erlenmyer flask which had a standard-taper ground-glass neck (Fig. 1b). The top of the displacement flask (Fig. 1b) was connected after the ground-glass joint had been coated with Apiezon-L grease. The assembled flask was evacuated and 50 ml water was run into the flask from an automatic burette. After a suitable equilibration time, the pressure inside the flask was returned to atmospheric by back filling with helium through a supply line connected to a monometer. Samples of the entrapped gas were removed through the septum seal, using a 1-ml gas-tight syringe, for gas chromatographic analysis.

Nitrous oxide was separated from other gases in the sample removed from the displacement flask by injection through a 0.46-ml sampling loop onto a column of Porapak Q material (550 by 0.16 cm, ID) heated to 50°C in a Varian Aerograph 3700 gas chromatograph. For samples with N_2O concentrations > 100 ppm vol./vol., a thermal conductivity detector was used at a filament current of 220 mA and helium carrier gas at 30 cm^3/min. The detection limit in this mode was 4 ppm in the 0.46-ml sample volume. For samples with N_2O concentrations < 100 ppm a ^{63}Ni-source, electron-capture detector, heated to 340°C, was used in conjunction with N_2 carrier gas at 30 cm^3/min. The detection limit in this mode was 0.03 ppm in the 0.46-ml sample volume.

The total N_2O released from the molecular sieve was calculated from the measured N_2O concentration, the volume of the flask, and the solubility of N_2O in water. Blank samples of 5A molecular sieve were also run with each group of samples to correct for the N_2O held by the molecular sieve before use. This amount was found to be significant only in the measurement of atmospheric N_2O concentrations.

The recovery of N_2O adsorbed by the molecular sieve increased with increased equilibration time after addition of water to the displacement flask (Table 1). Complete recovery of N_2O added to the molecular sieve was only achieved after a 5-hour equilibration period. Slow equilibration probably reflects the time necessary for N_2O to diffuse through water in the pore space of the molecular

Table 1—Recovery of N_2O adsorbed by a 5 Å molecular sieve from a 1.25 mg N_2O-*N*/liter gas flow at 20 liter/hour as affected by equilibration time and storage time before displacement of nitrous oxide.

Experimental variable		N_2O passed	N_2O recovered
		mg N	%
Equilibration time (hours)	0.25	2.32	34.9
	0.50	2.32	42.7
	1.0	2.32	69.4
	3.0	2.32	97.4
	5.0	2.32	100.0
	24.0	2.32	99.1
Sample storage time (days)	5	4.17	100.8
	14	4.17	99.7
	28	4.17	99.5

sieve, and the bulk of the water itself, into the gas space above. Essentially, complete recovery was also achieved after 24 hours, demonstrating that negligible leakage of N_2O from the displacement flasks occurred during this time. The absence of N_2O loss was facilitated by the negative pressure which was maintained in the displacement flask during equilibration. For convenience, a 15-hour (overnight) equilibration time was adopted for all subsequent analyses, which could be performed at least 28 days after sample collection without affecting the recovery of the adsorbed N_2O (Table 1).

The adsorption and recovery of N_2O using 20g molecular sieve and the sampling equipment described, was dependent upon sampling time, flow rate, and the concentration of N_2O in the air flow (Table 2). For N_2O concentrations of 34 μg N/liter or less, essentially complete recovery of N_2O was achieved using a flow rate of 20 liters/hr for sampling times up to 4 hours. When the sampling time or the flow rate exceeded these limits, the amount of N_2O adsorbed approached a maximum value for the N_2O concentration used, leading to incomplete recovery of the N_2O passed. The data in Table 2 demonstrate that during adsorption by molecular sieve, N_2O is partitioned between the adsorbed and gas phases. This results in the observed maximum adsorption of N_2O for a given N_2O concentration in the gas phase.

Data in Table 2 indicate that, for the quantity and geometric configuration of the molecular sieve adsorption trap used, a maximum sampling period of 4-hours is imposed for a flow rate of 20 liters/hr and for N_2O concentrations in the air flow of 34 μg N/liter or less. The maximum N_2O flux reported in the literature to date is approximately 30 g N/ha per hour (Rolston et al., 1976). This is equivalent to 150 μg N_2O-N/hour entering the enclosed air space of the soil cover to be used (Fig. 1a). For a flow rate of 20 liters/hour, an N_2O flux of this magnitude will produce an instantaneous N_2O concentration of 7.5 μg N/liter. This value is well within the 4-hour operating limit indicated by the data in Table 2.

If required, the operating period can be increased by increasing the quantity of molecular sieve used. An increase in the quantity of molecular sieve will also be required if operation is desired for periods up to 4 hours at flow rates in excess of 20 liters/hour.

The 5Å molecular sieve may be repeatedly used if, after displacement and measurement of N_2O, the material is dried and heated to 350°C. The adsorption and recovery of N_2O, however, should be occasionally checked as repeated wetting, drying, and heating tends to decrease the adsorption efficiency and increase the equilibration time required for complete recovery of N_2O. This can be conveniently achieved by passing a standardized N_2O-air mixture through the quantity of molecular sieve for the time period and flow rate adopted for field studies. The adsorbed N_2O is then displaced and measured, using the method described, and the recovery determined.

The errors involved in the adsorption and recovery of N_2O using a 5Å molecular sieve were relatively small. The standard deviation for the recovery of N_2O in 30 equilibrated analyses was ± 1.07% for a mean recovery of 99.8%. The essentially complete recoveries of N_2O observed for the various operating conditions used to obtain the data in Tables 1 and 2, reflect the reliability of the flow regulators used. The amounts of N_2O passed were calculated from the measured flow rate and the concentration of N_2O in the supply gas.

Evaluation of Field Equipment

Procedure

The reliability of the field equipment (Fig. 1a), assembled exactly as it would be in the field, was evaluated in two laboratory experiments in which the effects of air flow rate through the cover were investigated. In the first experiment, the soil covers were inserted, to a depth of 10 cm, into trays of moist washed sand. Each cover was positioned so as to enclose a 5-ml unsealed gas syringe, containing pure N_2O, placed on the surface of the sand. Air-flow lines were connected to each cover as shown in Fig. 1a. In separate experiments, the enclosed air space was swept at 10, 20, or 40 liters/hour for 2-hour periods. Immediately after this time the N_2O concentration in the syringe was determined. The amount of N_2O adsorbed by the molecular sieve during each run was determined as described above.

In a second experiment, trays were filled with < 2 mm of air-dry soil collected from the field site, specified below, at which N_2O flux measurements were required. The trays were vibrated so that the soil packed to approximately the same bulk density as that observed in the field (1.32 g/cm^3). Distilled water, containing the

Table 2—Recovery of N_2O passed in various standard mixtures with air through 20 g of a 5A molecular sieve for different sampling periods and at different flow rates.

N_2O concentration in air flow	Flow rate	Sampling time (hours) 2 N_2O passed	2 N_2O recovered	4 N_2O passed	4 N_2O recovered	6 N_2O passed	6 N_2O recovered	Maximum sampling time†
μg N/liter	liters/hr	μg N						hours
0.384‡	10	7.7	7.4	15.4	15.2	23.1	23.6	8.6
	20	15.4	15.6	30.7	30.8	46.2	30.7	4.0
	40	30.7	29.9	61.4	30.9	92.1	31.1	1.9
6.60	20	264	262	528	513	792	507	4.0
34.0	20	1,360	1,350	2,720	2,700	4,080	2,720	4.0
59.9	20	2,400	2,420	4,790	3,400	7,190	3,380	2.9
131	10	2,630	2,650	5,250	5,230	7,880	7,940	6.2
	20	5,250	5,180	10,500	7,630	15,750	8,040	2.8
	40	10,500	7,830	21,000	8,500	31,500	8,370	1.5

† Maximum sampling time for ≥ 98% recovery of the N_2O passed.
‡ Air.

equivalent of 100 kg N/ha as potassium nitrate, was added to the soil to develop an initial moisture content of approximately 25% of oven-dry weight. This is equivalent to an air-filled porosity of 5.2%. The water was allowed to equilibrate with the soil over night. Six soil covers were then inserted into the soil, the air-flow lines were connected (Fig. 1a), and the enclosed air space was swept at different flow rates for periods of 2 hours. Four covers were operated at 20 liters/hour, while the other two were operated at flow rates of 10 or 40 liters/hour. The amounts of N_2O adsorbed by the samples of molecular sieve during each run were subsequently determined. Several runs were made over a period of 7 days as the soil dried. The moisture content was measured at appropriate intervals. The experiment described above was conducted in the laboratory in order to reduce the effect on the data obtained of differences in N_2O evolution rate known to occur from one location to another at the field site to be studied.

Whenever the equipment was operated, the N_2O concentration in the air external to, but being drawn into the cover during operation, was determined. This was achieved using the same equipment as in Fig. 1a, but the first on-line column of calcium sulfate was not connected to a soil cover. The column was positioned so that its inlet was at the same height (7.5 cm) above the soil surface as the inlet to the soil cover. Using this arrangement, external air was drawn at a measured flow rate, through samples of molecular sieve concurrent with and for the same period of time that air was drawn through the soil covers. The amounts of N_2O adsorbed from such equivalent flows of external air were used to correct the amount of N_2O adsorbed from air drawn through a soil cover.

RESULTS

The containment of N_2O released from an unsealed gas syringe into the air space enclosed by the soil cover, was slightly improved as the flow rate through the cover was increased (Table 3). At 10 liters/hour, recovery of N_2O leaked from the syringe averaged 95.0%, whereas at 20 and 40 liters/hour recovery averaged 98.4 and 99.1%, respectively. These recoveries of N_2O (Table 3) are corrected for the amount of atmospheric N_2O drawn into the soil cover during operation of the equipment. This quantity, however, was small (< 0.5%) in relation to the amount of N_2O released from the syringe and adsorbed by the molecular sieve. The mean recovery of N_2O at flow rates of at least 20 liters/hour was 98.6 ± 2.3% based on the six values in Table 3.

The data in Table 3 clearly demonstrate that N_2O released into the enclosed air space is essentially completely recovered from the molecular sieve adsorption trap in the air-flow line, providing an adequate flow rate is maintained during operation of the field equipment. The somewhat lower recoveries of N_2O released at the lowest flow rate possibly resulted from the diffusion of a small portion of the N_2O into the pore space of the moist sand before it was completely swept from the soil cover. At a flow rate of 10 liters/hour the enclosed air space (3.5 liters) was swept only once every 21 min, whereas at flow rates of 20 and 40 liters/hour the air space was swept every 10.5 and 5.3 min, respectively.

Flow rates between 10 and 40 liters/hour did not affect the measured rate of N_2O evolution from the surface of a moist soil (Table 4). The rate of N_2O evolution was calculated from the difference between the amount of N_2O adsorbed from air drawn through the soil cover and that adsorbed from an equivalent flow of external air. The rates of N_2O evolution measured at 10 and 40 liters/hour fell within the standard deviation of the mean evolution rates measured at 20 liters/hour. Even as the soil dried to a moisture content of 15% (21% air-filled porosity), no effect of flow rate on the rate of N_2O evolution was observed. The adsorption capacity of the molecular sieve was not exceeded during the experiments which provided the data in Table 4.

Based on the data in Tables 2, 3, and 4, a flow rate of 20 liters/hour was adopted for field measurement of N_2O flux. This flow rate permitted sampling periods up to 4 hours (Table 2), gave satisfactory recovery of N_2O released into the enclosed air space (Table 3), and had no effect on the rate of N_2O evolution (Table 4).

Table 3—Recovery of N_2O released from an unsealed gas syringe into the enclosed air space of the soil cover box and subsequently adsorbed by a 5 Å molecular sieve using different flow rates.

Flow rate	N_2O released from syringe	N_2O recovered	Recovery
liters/hour	mg N		%
10	1.81	1.75	96.7
10	4.98	4.68	94.0
10	4.26	4.25	99.8
10	4.50	4.03	89.6
20	4.63	4.46	96.5
20	5.13	5.00	97.6
20	4.94	5.06	102.5
20	1.95	1.89	96.9
40	2.67	2.67	100.0
40	3.14	3.09	98.7

Field Measurements

PROCEDURE

The operation of the equipment was tested in the field to establish the nature and extent of the N_2O fluxes likely to be encountered in field studies. Such data were desired in order to develop a rational basis for field sampling. Four covers were installed at one study site (Simas 396) located in the Santa Maria Valley, Santa Barbara County, Calif. This site was within a production unit cropped to celery. The soil at the site sampled is a Haploxeroll. The site had received 120 kg N/ha as ammonium sulfate and was irrigated immediately prior to sampling. The covers were positioned across half of the ridge and half of the furrow. The enclosed air space was swept at 20 liters/hour for 3- to 4-hour periods at different times of the day during a 76-hour

Table 4—Nitrous oxide evolution rate from a 0.05 m² area of Simas soil measured at three different flow rates at various times after water and nitrate addition to the soil.

Time after water addition	Moisture content	N_2O evolution rate† at		
		20 liter/hour	10 liters/hour	40 liters/hour
hours	%	μg N/hour		
24	26.4	423 ± 19	n.d.‡	399
48	24.1	164 ± 25	145	181
72	20.4	26.0 ± 5.6	21.3	23.1
144	18.0	11.1 ± 1.2	11.0	10.2
192	15.2	8.97 ± 1.05	8.43	8.13

† N_2O evolution rates at 20 liters/hour are the means of four concurrent determinations, except that for 24 hours which is the mean of two determinations. N_2O evolution rates at 10 and 40 liters/hour are single values.

‡ Not determined.

period. The covers were left in place during contiguous sampling periods, but were repositioned within the study site after an overnight break in sampling. The vials containing the molecular sieve were replaced after each sampling period. Samples of molecular sieve carrying adsorbed N_2O were returned to the laboratory for displacement and analysis of N_2O. During each sampling period, the amount of N_2O in the external air drawn into the soil cover was concurrently determined as described above, using the same flow rate (20 liters/hour) as that used to sweep the soil covers.

Results

The difference between the amount of N_2O adsorbed from air drawn through a soil cover and that amount adsorbed from an equivalent flow of the air external to the cover, can be used to determine the N_2O flux during each sampling period (Fig. 2). Irrigation was terminated at 0800 hours on 19 June 1977. Within 6 hours, evolution of N_2O had commenced and continued for a period of at least 76 hours (Fig. 2). During this period, the N_2O flux ranged from 0.15 to 20 g N/ha per hour with a range in mean N_2O flux from 0.2 to 15.8 g N/ha per hour. The overall average N_2O flux was 9.42 g N/ha per hour (Table 5). These fluxes indicate that up to 100 μg N_2O-N/hour entered the enclosed air space, resulting in a maximum instantaneous N_2O concentration of 5 μg N/liter. This is well within the adsorption limits of the molecular sieve for the operating conditions used (Table 4).

The relationship in Fig. 2 demonstrates a pronounced diurnal variation in N_2O flux. The peak N_2O flux on each day occurred in the early afternoon. Diurnal variation in the N_2O flux was also observed at other sites in the celery-production block. Diurnal variation in the N_2O flux did not reflect a temperature increase below the soil cover relative to that outside. The air temperature and the soil temperature at the 1.5-cm depth inside even an unshaded soil cover in direct sunlight were the same as those measured outside the cover. This temperature equilibrium probably resulted from the continual replacement of the enclosed airspace with outside air during operation of the equipment.

The average loss of N as N_2O over the 76-hour period, estimated from the area under the relationship in Fig. 2, was 0.716 kg N/ha, or 0.60% of the total N applied, and ranged from 0.585 to 0.986 kg N/ha (Table 5) for the four different locations sampled at the same site. The average standard deviation associated with field variability was ± 30% of the mean flux.

The diurnal variation in N_2O flux poses the problem of establishing a representative sampling time. Ideally, continuous sampling should be adopted, and vials of molecular sieve could be replaced every 3 to 4 hours. Limitations on the amount of equipment may make it feasible to take only one or two samples (three or more replicates) at a particular site each day. With the exception of the value based on the mean peak flux measure about 1300 hours on each day (Table 5), the mean N_2O loss estimated from measurements taken at different times of the day, fell within the range obtained using all mean data in Fig. 2 (Table 5). The most reliable estimate of the N loss as N_2O is obtained using samples collected during the mid-morning or mid to late afternoon, thus avoiding the peak flux occurring in the early afternoon (Table 5).

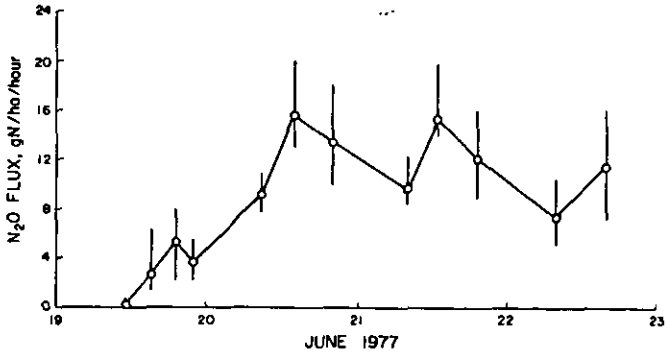

Fig. 2—Flux of N_2O from a Haploxeroll after fertilization (120 kg N/ha) and irrigation of a celery-production block. Data points are the mean of four samples taken at the same site and plotted at the mid-point, with respect to time, of the sampling period. The range of values is indicated by the bars about each mean value. The date on the abcissa represents 0000 hours for that specified.

DISCUSSION

Several aspects of the proposed methodology for the measurement of N_2O flux from soil surfaces make it suitable for field studies. Of particular importance is the similarity of conditions at the enclosed soil surface to those external to the soil cover. This is facilitated by the facts that the cover is coupled to the external atmosphere through the inlet port and that the enclosed air space is continuously replaced by external air. Consequently, changes in external conditions, such as atmospheric pressure and atmospheric N_2O concentration, are quickly translated to the enclosed air space. Furthermore, the continuous flow of air through the soil cover maintains air and soil temperatures close to those external to the cover.

The features outlined above make the continuous-flow open soil cover preferable to a closed soil cover (Rolston and Broadbent, 1977; Burford and Hall, 1977) or a closed continuous-flow system such as that used by Pearson et al. (1965). These approaches isolate the enclosed soil surface from external influences, and in the case of the closed, zero-flow soil cover lead to a build up in N_2O concentration which slows the diffusion of the gas from the soil surface (Focht, 1978). Measured flux, however, can be corrected for the influence of this effect (Rolston and Broadbent, 1977). Furthermore, appreciable temperature increase is frequently induced below closed soil covers (McGarity and Rajaratnam, 1973).

Table 5—Loss of N as N_2O and the overall flux of N_2O at one site in a celery-production block during a 76-hour monitoring period using various combinations of the data in Fig. 2.

Mid-time of sampling period each day	N_2O loss		Overall mean flux†
	Mean	Range	
hours	kg N/ha		g N/ha per hour
0800	0.603	0.467–0.736	7.93
1300	0.994	0.781–1.23	13.1
1900	0.725	0.556–1.03	9.54
1000	0.734‡		9.66
1600	0.870‡		11.5
All mean data	0.716	0.585–0.986	9.42

† Over the 76-hour period sampled.
‡ Values estimated from the relationship in Fig. 2.

In the present methodology, build up in N_2O concentration is kept at a minimum by continuous replacement of the enclosed air space with external air. For the operating conditions adopted, the instantaneous N_2O concentration in the enclosed air space never exceeded 5 μg N/liter and in most cases was approximately 2.2 μg N/liter. The instantaneous concentration of N_2O could be reduced further by using a higher flow rate in conjunction with adjustment of the size of the molecular sieve adsorption trap. A higher flow rate, however, would increase the relative contribution of atmospheric N_2O to the total amount of N_2O adsorbed and would decrease the detection sensitivity for N_2O evolution from the soil surface.

Although the determination of the N_2O flux from a soil surface involves correction for the amount of N_2O drawn into the cover from an equivalent flow of the external atmosphere, this amount of N_2O can be reliably determined by the method described. Data for the atmospheric concentration of N_2O at Riverside for eight samples taken simultaneously using the same method as that used in the field, resulted in a mean concentration of 0.379 ± 0.009 μg N/liter. This compared favorably with a mean of 0.384 ± 0.013 μg N/liter for 10 samples of the same atmosphere concurrently determined by direct gas chromatographic analysis.

During field measurements of N_2O flux, atmospheric N_2O concentrations ranged from 0.370 to 0.600 μg N/liter with a mean of 0.396 μg N/liter for twelve determinations. Values in excess of 0.370 μg N/liter were only observed during periods of high N_2O flux and before 1100 hours each day when calm atmospheric conditions prevailed. A 20-liter/hour flow of air having an N_2O concentration of 0.396 μg N/liter results in an adsorption of 7.9 μg N/hour. For the overall mean flux of 9.42 g N/ha per hour (Table 5), the amount of N_2O adsorbed is 47.1 μg N/hour plus a mean of 7.9 μg N/hour adsorbed from the air which enters the box giving a total of 55 μg N/hour. These values demonstrate that the amount of N_2O adsorbed as a result of external air being drawn through the cover is a fairly small proportion of the total amount adsorbed. In the present study, atmospheric N_2O made a contribution of 7 to 50% to the total N_2O adsorbed with a mean contribution of approximately 14% based on all data.

The field operating conditions and analytical techniques adopted gave a detection limit of 0.16 to 0.24 g N/ha per hour. This was based on the ability to detect a 10% flux contribution to the N_2O adsorbed from air drawn through a cover. This detection limit is comparable to that of the method reported by Burford and Hall (1977), and indicates that the method described in the present study is approximately 40 times more sensitive than the aerometric analysis described by Lemon (1978).

Some workers (Schutz et al., 1970; Kanemasu et al., 1974) have criticized the use of continuous-flow soil covers for field measurement of gas evolution. Such criticism has been based on the assumption that flow through the soil cover decreases the pressure below the soil cover relative to the external atmospheric pressure, and may induce mass flow through the soil atmosphere and into the enclosed air space. Such an effect would result in the sampling of an unknown volume of soil. This is not a problem in the application of the present methodology. Based on the geometry of the soil cover inlet port and the flow rate used, the pressure deficit inside the soil cover can be approximated from Poiseuille's equation for fluid flow through a cylindrical pipe. The pressure deficit for the operating conditions used is not greater than 0.0048 mm water. This, coupled with the fact that the cover is inserted 10 cm into the soil and N_2O production in soils is associated with relatively high moisture contents (Table 4), suggests that mass flow will make an insignificant contribution to the measured flux.

This assumption, based on theoretical considerations, is supported by the observation that rates of N_2O evolution from a soil surface were essentially independent of flow rate in the range 10 to 40 liters/hour (Table 4). A fourfold increase in flow rate results in a fourfold decrease in the internal pressue induced by the air flow. Such a pressure change would have been expected to induce a difference in the measured N_2O evolution rate if mass flow was making a significant contribution to the amount of N_2O evolved. The data in Table 4 also demonstrate that the small accumulations of N_2O which develop below the cover during operation at 20 liters/hour have no observable effect on the rate of N_2O evolution. The instantaneous N_2O concentrations are reduced by a factor of four between 10 and 40 liters/hour, but the measured N_2O evolution rates were essentially the same.

The proposed methodology for N_2O flux measurement is also suited to field studies from a practical standpoint. Of importance in this respect is the relative simplicity of the field equipment adopted. Such equipment was used because measurements were desired at sites of ongoing vegetable crop production involving frequent management practice. A more sophisticated soil cover, such as that described by Kissel et al. (1977), may be preferred when more permanent installations are possible. It is important, however, that the walls of the soil cover be made from relatively fine gauge metal, such as the 20-gauge used in the present study, in order to minimize soil disturbance during installation.

Other advantages of the present method are that in-field volumetric gas sampling is not required and that a molecular sieve carrying N_2O can be stored without N_2O loss for at least 28 days before analysis (Table 1). Total analysis time for each sample was approximately 6 min, excluding the time required for equilibration during N_2O displacement. Consequently, a large number of field samples may be taken and subsequently analysed with convenience and accuracy.

The fluxes of N_2O observed in the present study by direct measurement (Fig. 2), are comparable with those reported by previous workers based on diffusion models coupled with measurements of N_2O concentration in the soil atmosphere. After application of 112 kgN/ha as $NaNO_3$, Burford and Stefanson (1973) reported N_2O fluxes of between 10.7 and 11.5 gN/ha per hour from cropped areas after rain had fallen. These fluxes, which lasted for a period of a few days, are very close to those measured in the present study (Table 5). The N_2O fluxes reported by Rolston and coworkers (1976, 1977) ranged from close to zero up to approximately 30 g/ha per hour at cropped and

uncropped study plots. In contrast, the N_2O fluxes from a ryegrass sward which had received 50 kgN/ha were one to two orders of magnitude lower than the average flux measured in the present study (Burford and Hall, 1977). The extent to which the low N_2O fluxes measured by Burford and Hall (1977) depend upon environmental factors, such as soil pH, which may influence the distribution of gaseous denitrification products (Nommik, 1956) is difficult to assess.

The diurnal nature of N_2O flux (Fig. 2) showed a similar pattern to that observed for NH_3 evolution from soils (McGarity and Rajaratnam, 1973). Although diurnal variation in air temperature is appreciably attenuated with depth in the soil profile (Russell, 1973), it is possible that peak N_2O fluxes observed during the early part of the afternoon arise from the effect of an increase in soil temperature on the activity of denitrifying bacteria (Nommik, 1956; Bailey and Beauchamp, 1973) or on the rate of diffusion of N_2O from the profile. It is also possible that the peak flux is related to the daily wind pattern at the sampling site. This was characterized by gusty conditions between approximately 1100 and 1500 hours. Such conditions will induce fluctuation in atmospheric pressure and may enhance the rate of N_2O evolution from the upper few centimeters of the soil profile.

The methodology proposed in the present study provides a direct measurement of N_2O flux which is integrated over the sampling period used. The methodology is sufficiently simple that it embodies a monitoring capability which can be used to measure N_2O evolution in on-going agricultural practice. The method may also provide a basis for the direct measurement of total N loss as a result of denitrification, if the further reduction of N_2O to N_2 can be inhibited. Recent studies (Balderston et al., 1976, Yoshinari et al., 1977) have shown small concentrations of acetylene block denitrification at the N_2O stage. More detailed studies of N_2O flux from agricultural soils are currently underway, and N_2O evolution at acetylene-treated sites is also being measured to evaluate this method for the determination of total N loss. The results of these studies will be reported at a later date.

ACKNOWLEDGEMENT

The authors wish to thank Drs. J. Letey and W. Gilliam for valuable contributions to the development of this study.

LITERATURE CITED

1. Arnold, P. W. 1954. Losses of nitrous oxide from soil. J. Soil Sci. 5:116–128.
2. Bailey, L. D., and E. G. Beauchamp. 1973. Effects of temperature on NO_3 and NO_2 reduction, nitrogenous gas production, and redox potential in a saturated soil. Can J. Soil Sci. 53:213–218.
3. Balderston, W. L., B. Sherr, and W. J. Payne. 1976. Blockage by acetylene of nitrous oxide reduction in *Pseudomonas perfectomarinus*. Appl. Environ. Microbiol. 31:504–508.
4. Bock, R., and K. Schutz. 1968. Gas-chromatographische Bestimmung von Distickstoffoxid-Spuren in Luft. Fresenius' Z. Anal. Chem. 237:321–330.
5. Burford, J. R., and K. C. Hall. 1977. Fluxes of nitrous oxide from a ryegrass sward. Agric. Res. Council, Letcombe Lab. Annual Rep., 1976:85–88.
6. Burford, J. R., and R. J. Millington. 1968. Nitrous oxide in the atmosphere of a red-brown earth. Int. Congr. Soil Sci., Trans. 9th, (Adelaide) 2:505–511.
7. Burford, J. R., and R. C. Stefanson. 1973. Measurement of gaseous losses of nitrogen from soils. Soil Biol. Biochem. 5:133–141.
8. Council for Agri. Sci. and Tech. 1976. Effect of increased nitrogen fixation on stratospheric ozone, Report no. 53, Iowa State Univ., Ames, Iowa.
9. Crutzen, P. J. 1974. Estimates of possible variation in total ozone due to natural causes and human activities. Ambio 3:201–210.
10. Crutzen, P. J. 1976. Upper limits on atmospheric ozone reductions following increased application of fixed nitrogen to soil. Geophys. Res. Lett. 3:169–172.
11. Dowdell, R. J., and R. Cress. 1974. Measurement of the nitrous oxide content of the atmosphere. Lab. Practice 23:488–489.
12. Focht, D. D. 1978. Methods for analysis of denitrification in soils. p. 429–490. *In* D. R. Nielson and J. G. MacDonald (eds). Nitrogen in the environment. Vol. 2 Academic Press, New York.
13. Hahn, J. 1972. Improved gas chromatographic method for field measurement of nitrous oxide in air and water using a 5A molecular sieve trap. Anal. Chem. 44:1889–1892.
14. Hahn, J., and C. Junge. 1977. Atmospheric nitrous oxide: A critical review. Z. Naturforsch 32a:190–214.
15. Johnston, H. 1972. Newly recognized vital nitrogen cycle. Proc. Natl. Acad. Sci. U.S.A. 69:2369–2372.
16. Kanemasu, E. T., W. L. Powers, and J. W. Sij. 1974. Field chamber measurements of carbon dioxide flux from soil surface. Soil Sci. 118:233–237.
17. Kissel, D. E., H. L. Brewer, and G. F. Arkin. 1977. Design and test of a field sampler for ammonia volatilization. Soil Sci. Soc. Am. J. 41:1133–1138.
18. LaHue, M. D., M. D. Axelrod, and J. P. Lodge, Jr. 1971. Measurement of atmospheric nitrous oxide using a molecular sieve 5A trap and gas chromatography. Anal. Chem. 43:1113–1115.
19. Lemon, E. 1978. Critique of "Soil and other sources of nitrous oxide." p. 493–521. *In* D. R. Nielson and J. G. MacDonald (eds.) Nitrogen in the environment. Vol. 1 Academic Press, New York.
20. McElroy, M. B., J. W. Elkins, S. C. Wofsy, and Y. L. Yung. 1976. Sources and sinks for atmospheric nitrous oxide. Rev. Geophys. Space Phys. 14:143–150.
21. McGarity, J. W., and J. A. Rajaratnam. 1973. Apparatus for the measurement of losses of nitrogen as gas from the field and simulated field environments. Soil Biol. Biochem. 5:121–131.
22. Nommik, H. 1956. Investigations on denitrification in soil. Acta. Agric. Scand. 6:195–228.
23. Pearson, J. E., D. H. Rimbey, and G. E. Jones. 1965. A soil-gas emanation measurement system used for radon-222. J. Appl. Meteorology 4:349–356.
24. Rolston, D. E., and F. E. Broadbent. 1977. Field measurement of denitrification. Environ. Protection Tech. Series, EPA—600/2–77–23, EPA, Washington, D.C.
25. Rolston, D. E., M. Fried, and D. A. Goldhamer. 1976. Denitrification measured directly from nitrogen and nitrous oxide gas fluxes. Soil Sci. Soc. Am. J. 40:259–266.
26. Russell, E. W. 1973. Soil conditions and plant growth. 10th ed. Longman, London.
27. Schutz, K., C. Junge, R. Beck, and B. Albreht. 1970. Studies of atmospheric N_2O. J. Geophys. Res. 75:2230–2246.
28. Yoshinari, T., and R. Knowles. 1976. Acetylene inhibition of nitrous oxide reduction by denitrifying bacteria. Biochem. Biophys. Res. Commun. 69:705–710.
29. Yoshinari, T., R. Hynes, and R. Knowles. 1977. Acetylene inhibition of nitrous oxide reduction and measurement of denitrification and nitrogen fixation in soil. Soil Biol. Biochem. 9:177–183.