## GASEOUS NITROGEN LOSSES FROM CROPPED AND SUMMER-FALLOWED SOILS<sup>1</sup>

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A study designed to assess gaseous losses of N as  $N_2O$  and  $N_2$  from soils of conventional till fields seeded to wheat in the Chernozemic soil region of Saskatchewan, together with limited supporting laboratory investigations, has confirmed that for the May-November period losses were in the vicinity of 3 kg N ha<sup>-1</sup> or less. In contrast, total losses from a summer-fallowed field were approximately 300% higher. Comparisons at one site were made of N losses from a conventionally tilled and zero-tilled Dark Brown Chernozemic soil seeded to wheat; the total losses of N were twice as high for the zero till as the conventional till treatments. The N<sub>2</sub>O fluxes were shown to be the result of both reductive (denitrification) and oxidative (nitrification) processes and generally, under the conditions of these field experiments, both occurred simultaneously. This experiment also confirmed that C<sub>2</sub>H<sub>2</sub> inhibited nitrification in a manner very similar to N-serve, a well-known nitrification inhibitor.

Une étude visant à apprécier les pertes de N sous forme gazeuses  $N_2O$  et  $N_2$ dans les terres à blé travaillées selon les méthodes classiques dans la région des Chernozems de la Saskatchewan a montré que de mai à novembre les pertes ne dépassaient pas 3 kg par hectare. L'étude était complétée par quelques travaux en laboratoire. Par comparaison, les pertes totales mesurées dans un champ en jachère étaient approximativement du triple. A un endroit, on a comparé les pertes de N dans une terre sous blé (Chernozem brun foncé) travaillée selon la méthode classique et en régime de culture sans labour. Les pertes totales étaient deux fois plus fortes dans le second mode de conduite. Les flux de N<sub>2</sub>O sont la résultante à la fois de processus réducteurs (dénitrification) et oxydateurs (nitrification), lesquels dans les conditions de culture observées se produisent simultanément. On a pu confirmer aussi que C<sub>2</sub>H<sub>2</sub> inhibe la nitrification au bout de 24 h d'incubation, selon un mécanisme rappelant l'action du N-serve, inhibiteur de nitrification bien connu.

Gaseous N losses occur primarily as  $N_2O$ and  $N_2$  as a result of reductive (denitrification) and oxidative (nitrification) processes according to the following reactions (Knowles 1978; Freney et al. 1979).

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$$NO_{3}^{-} \rightarrow NO_{2}^{-} \rightarrow NO \rightarrow N_{2}O^{\uparrow} \rightarrow N_{2}\uparrow \quad (1)$$

$$NH_{4}^{+} \rightarrow NH_{2}OH \rightarrow (e.g. H_{2}N_{2}O_{2}) \rightarrow NO_{2}^{-} \rightarrow NO_{3}^{-}$$

$$\downarrow \qquad (2)$$

$$N_{1}O$$

Nitrous oxide can easily be measured relative to atmospheric concentrations of this gas, but the amounts of  $N_2$  produced are usually insufficient to be easily distinguished from its ambient concentrations. A new technique proposed by Yoshinari 0008-4271/82/6201-0187 \$2.00

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et al. (1977), based on the blocking of the reduction of  $N_2O$  to  $N_2$  by acetylene ( $C_2H_2$ ) provides a rather simple yet highly quantitative means of assessing gaseous nitrogen losses. However, it has been found that  $C_2H_2$  inhibits nitrification (Knowles 1979; Walter et al. 1979). Therefore, under conditions favoring reaction (2),  $N_2O$ measured in the presence of  $C_2H_2$  may lead to an underestimation of gaseous N losses.

Gaseous losses of nitrogen under greenhouse, lysimeter and field conditions have been estimated primarily by assuming that they are roughly analogous to nitrogen which cannot be accounted for (N deficits) in <sup>15</sup>N-balance studies. Recently Hauck (1979) reviewed the work on <sup>15</sup>N-balance studies and reported that N deficits in 67 experiments ranged from 6% in greenhouse studies to 32% for field studies. Rennie et al. (1976) estimated that approximately 1/3 of the soil organic nitrogen which had been mineralized in prairie soils of western Canada during the past seven decades had been lost by denitrification and soil erosion. They found it impossible to separate these two major loss mechanisms, and both were determined by the difference between total nitrogen mineralized and the sum of that used by the crops and that which had leached below the depth of rooting. The amount of gaseous N loss which would occur on a specific soil in any one cropping season would be expected to be dependent on the cropping and tillage systems being used; two factors which may play a major role in loss of gaseous nitrogen through reductive processes are the moisture content and tilth or structure of the soil.

Not only are quantitative estimates of agriculturally significant gaseous N losses of importance, but also the quantification of global sources of  $N_2O$ .  $N_2O$  results in the catalytic destruction of the stratospheric ozone layer, and its global increase would indirectly increase skin cancer and other harmful environmental effects (Council for Agricultural Science and Technology 1976).

The objectives of the studies reported in this paper were to measure gaseous N losses directly from two Chernozemic Black soils seeded to wheat, and from a Chernozemic Dark Brown soil where comparisons were possible between conventional till-seeded, zero-till-seeded and summer fallow. Measurement of N<sub>2</sub>O was made with and without  $C_2H_2$  in order to assess the extent of reaction (2) under the conditions prevailing in this investigation.

## MATERIALS AND METHODS

Gaseous nitrogen losses were measured at the following three sites. 1. Hamlin cl (Orthic Brown Chernozem) near Cudworth. Wheat was seeded on wheat stubble land with a fall application of 100 kg  $N \cdot ha^{-1}$  (urea). 2. Hoey cl (Orthic Black Chernozem) near Hagen. Wheat

E C<sub>e</sub>

(mmhos/cm)

0.39

0.36

0.40

0.37

0.43

Bulk density<sup>†</sup>

 $(g/cm^3)$ 

 $0.96 \pm 0.11$ 

 $1.10 \pm 0.07$ 

 $1.03 \pm 0.05$ 

 $1.25 \pm 0.06$ 

 $1.17\pm0.07$ 

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Table 1. Important characteristics of the soils (0-15 cm) of the experimental sites

OC

(%)

4.57

4.45

3.00

2.74

2.86

Soil

texture

Clay loam

Clay loam

Clay loam

Clay loam

Clay loam

pН

sat. paste

7.4

6.8

6.8

7.0

6.9

Chernozemic Black soils

Chernozemic Dark Brown soil

 $\dagger$  Four replicate means  $\pm$  SD.

Field

Wheat

Wheat

C-T Wheat‡

Z-T Wheat§

Summer fallow

‡ Conventional till.

§ Zero till.

Soil

Hamlin

Elstow

Hoey

was seeded on rapeseed stubble land with a fall application of a small amount of urea. 3. *Elstow cl* (Orthic Dark Brown Chernozem) near Watrous. The cropped and summer-fallow components of a 3-yr wheat-wheat-fallow rotation were compared to those from a field which had been seeded to wheat in 1978, 1979 and 1980 using a zero-till drill. The major differences between the conventional till (C-T) and zero-till (Z-T) farming system is that in the former crop residues are worked into the soil whereas in the latter, crop residues are left on the surface. A further difference is that the C-T field was left fallow once in 3 yrs (1978).

Within each of the 5-ha C-T wheat, Z-T wheat and summer-fallow treatments at the Watrous site, uniform soil areas were selected to ensure that in all cases measurements were taken on the same slope position and aspect. A few important soil characteristics (0-15 cm) of each soil are listed in Table 1.

Gaseous N losses were measured weekly (from early spring through to the late-fall period) on soil samples taken at sites 1 and 2, and at longer intervals at site 3 following the method used by Colaco (1979) and later modified by L. R. Chatarpaul (pers. commun.). Four replicate areas were selected for each measurement location. Two soil cores were taken from each of the four replicate areas using 6-cm i.d.  $\times$  15-cm-long aluminum cylinders (two cores  $\times$  four replicates = eight cores; four with  $C_2H_2$  and four without  $C_2H_2$ ). Each soil core was then immediately enclosed in a plastic bag to minimize excessive air diffusion into the soil and, as quickly as possible after sampling, each core and a glass vial containing 2 mL of 2 N NaOH were placed in a glass jar; the jar was sealed with an airtight cover having a rubber septum in the center. The NaOH solution completely removed the  $CO_2$ , which had a retention time on the gas chromatography column slightly less than that of the N<sub>2</sub>O and so did not interfere with good N<sub>2</sub>O separation. In one of each replicate jar, 5% (vol/vol)  $C_2H_2$  was injected with an airtight syringe after removing an equal amount of air. Narrow slits in the side of the aluminum cylinder wall encouraged rapid diffusion of C<sub>2</sub>H<sub>2</sub> into the soil core. Thereafter, the rubber septum of all jars was coated with a silicone rubber sealant. The jars containing the soil cores were returned to the laboratory and incubated for a 24-hr period outside the laboratory in the open

environment under shade. Before sampling, the air in the jars was thoroughly mixed by inserting a syringe and pumping the plunger approximately 20 times, and a 1-cm<sup>3</sup> sample was withdrawn. The concentration of N<sub>2</sub>O was determined on this sample using a 5710-A Hewlett-Packard gas chromatograph equipped with a 15-Ci Ni-63 electron-capture detector and 20cm i.d.  $\times$  240-cm-long Poropak Qi column (Freney et al. 1979). The correction for the solubility of N<sub>2</sub>O in soil water was carried out as proposed by Moraghan and Buresh (1978).

The jars were then opened, soil cores were weighed, and the moisture content was determined. The remaining soil was air-dried, crushed to pass through a 2-mm sieve and  $NH_4^+$ -N and  $(NO_3^- + NO_2^-)$ -N in 2 M KCI extractant were measured using an Autoanalyzer (Technicon Autoanalyzer Systems 1973, 1975).

Bulk density  $(g/cm^3)$  was measured on the undisturbed soil cores (four replicates) and from this value, assuming a particle density of 2.65  $g/cm^3$ , air-filled porosity was calculated.

Air temperatures were supplied by the Saskatchewan Research Council weather station on the University campus. Soil temperatures in the field were those measured at the time the soil cores were taken; this was generally between 1000 and 1200 hours. Temperatures were measured at the 6- to 7-cm soil depth and rainfall was recorded for all the three sites.

A laboratory experiment was carried out to elucidate further the production of N<sub>2</sub>O from reaction (2) under aerobic soil conditions. Treatments included control (ambient air), 50% (vol/vol) oxygen (to inhibit reaction (1)). N-serve [2-chloro-6-(trichloromethyl)-pyridine] (to inhibit reaction (2)) and acetylene (5%, vol/ vol). A bulk soil sample (0-15 cm) was collected from the site 1 field and passed through a 2-mm screen in the field-moist condition. Forty-eight soil samples (each 100 g on ovendry basis) were added to 600-mL conical flasks and 40  $\mu$ g NH<sub>4</sub><sup>+</sup>-N · g<sup>-1</sup> soil as (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> was added in solution. Twelve flasks received an application of 10  $\mu$ g N-serve<sup>-1</sup> soil in solution form. N-serve at this rate inhibits reaction (2), but does not affect reaction (1) (Henninger and Bollag 1976). Deionized water was added to bring the soil moisture content to 22% (wt/wt) and the soil was mixed. A glass vial containing 5 mL of 2 N NaOH was placed in each flask and the flasks were stoppered with rubber corks having serum caps in the center. In another set of 12 flasks,  $5\% C_2H_2$  (vol/vol) was injected after removing an equal amount of air from each flask. Another 12 flasks were sufficiently evacuated to enable the addition of 50% oxygen (vol/vol). The flasks were sealed and placed

in an incubator at  $23 \pm 1^{\circ}$ C (a common laboratory temperature). From duplicate flasks, N<sub>2</sub>O was analyzed at 0, 6, 24, 48, 72, and 96 h. To avoid the artificial effects of C<sub>2</sub>H<sub>2</sub> decomposition, incubation for long periods was avoided (Watanabe and De Guzman 1980).



Fig. 1. Results of measurements of gaseous N loss (N<sub>2</sub>O-N), soil moisture, air-filled porosity, rainfall, mineral N and air and soil temperature of Hamlin clay loam (site 1) seeded to wheat for the period May-November 1980.  $\Phi$ , indicates standard deviation within four replicates.

## **RESULTS AND DISCUSSION**

 $(NO_3^- + NO_2^-) - N.$ 

The data obtained from the Hamlin C1 (site 1) differed significantly from that of

the Hoey C1 (site 2) only during the early part of the growing season. Mineral N, initially low, increased rapidly as a result of fertilizer N application (Fig. 1). The inorganic N present in the Hoey C1 soil suggests that very little, if any, fertilizer N had been applied (Fig. 2). At site 1,



Fig. 2. Results of measurements of gaseous N loss (N<sub>2</sub>O-N), soil moisture, air-filled porosity, rainfall, mineral N and air and soil temperature of Hoey clay loam (site 2) seeded to wheat for the period May-November 1980.

the expected relationship between  $NH_4^+$ -N and  $(NO_3^- + NO_2^-)$ -N was obtained; nitrification of the fertilizer  $NH_4^+$ -N resulted in relatively high values of the oxidized nitrogen form during June, but these values dropped rather rapidly, presumably as a result of N uptake by the growing crop. Air-filled porosity, volumetric moisture, soil temperature and mean air temperature all followed practically identical patterns at both locations.

Gaseous losses of N<sub>2</sub>O-N from soil samples taken at site 1 fluctuated between 3 and 6  $g \cdot ha^{-1} \cdot day^{-1}$  for May, June and July; during this period the soil moisture was substantially below the field capacity moisture content and, accordingly, air-filled porosity was relatively high. In response to the heavier precipitation which occurred in late July and August, the volumetric moisture content increased significantly and as a result air-filled porosity dropped sharply. Gaseous losses of nitrogen increased, and approximately 28% of the total gaseous losses of N occurred during the August and early September period.

A series of rainfalls that occurred in late June and early July at site 2 resulted in a very rapid increase in N<sub>2</sub>O-N losses (Fig. 2). It is interesting to note that this was first reflected in losses as a result of denitrification, while the peak in oxidative nitrogen losses occurred at the time losses in denitrification had fallen to their base level.

It is apparent from the data obtained at both sites that losses of N were not influenced by concentrations of either  $NH_4^+$ -N or  $(NO_2^- + NO_3^-)$ -N in the soil, but rather, were closely associated with soil moisture content or air-filled porosity.

Following harvest of the wheat crop in September, the rate of loss of gaseous N remained almost constant and in the general vicinity of 5 g  $N \cdot ha^{-1} \cdot day^{-1}$  at both sites. This low rate probably reflects specifically the relatively dry soil conditions rather than the low level of inorganic nitrogen in the soil. It is of interest to note that this low rate continued even after air temperatures dropped below freezing (however, soil temperature was still above freezing).

The average daily loss for both fields (site 1 and site 2) was 5.3 g  $N \cdot ha^{-1}$  and the total loss of N for this 180-day study was in the vicinity of 1.0 kg  $N \cdot ha^{-1}$ .

Nitrous oxide fluxes measured in the presence of  $C_2H_2$  were equal to, higher or lower than those measured in its absence (Figs. 1 and 2). While it is not possible to differentiate between the N<sub>2</sub>O produced in reactions (1) and (2), respectively (Knowles 1978; Freney et al. 1979), it is reasonable to assume that when air-filled porosity was low (moisture content high), the N<sub>2</sub>O was primarily produced as a result of denitrification. The data support this in that the N<sub>2</sub>O from the C<sub>2</sub>H<sub>2</sub> system was greater than the N<sub>2</sub>O without C<sub>2</sub>H<sub>2</sub>.

In general, when air-filled porosity was average or high, a substantial amount of the N<sub>2</sub>O emission was probably a result of reaction (2) (nitrification); the N<sub>2</sub>O flux in the presence of  $C_2H_2$  was either equal to or less than the flux in its absence.

A laboratory study with treatments designed to evaluate possible inhibition of nitrification by  $C_2H_2$  and hence reduce the production of  $N_2O$  due to reaction (2) clearly confirmed that C<sub>2</sub>H<sub>2</sub> inhibited nitrification in a manner very similar to N-serve, a well-known nitrification inhibitor (Fig. 3). Thus, where either N-serve or  $C_2H_2$  was added,  $N_2O$  emissions after a 24-h period were completely stopped. The data in Table 2 further reveal that in the control and oxygen treatments, reaction (2) resulted in the conversion of  $NH_4^+$ -N into  $(NO_3^- + NO_2^-)$ -N; whereas practically no oxidation of NH<sub>4</sub><sup>+</sup>-N was observed after 24 h in the presence of N-serve and  $C_2H_2$ . The evacuation of air from the flasks, followed by the injection of oxygen (50%) vol/vol), would appear to have substantially reduced the rate of nitrification as compared with the control (Table 2); this explains the lower N<sub>2</sub>O emissions for the



Fig. 3. Effect of oxygen,  $C_2H_2$  and N-serve on N<sub>2</sub>O-N emission from Hamlin clay loam soil incubated at 22% (wt/wt) moisture.

50% vol/vol oxygen vs. the ambient air treatments (fig. 3.). This laboratory study, as well as the data given in Figs. 1 and 2 from the field study, verify the hypothesis of Bremner and Blackmer (1978) and Freney et al. (1979) that  $N_2O$  evolution under aerobic soil conditions can be greater from ammonium oxidation than from nitrate reduction.

In this study, where denitrification rates were low, N<sub>2</sub>O emissions from reaction (2) were, in general, similar to those from reaction (1), indicating that reaction (2)was contributing substantially to the total N losses. In contrast, in a study conducted by L. R. Chatterpaul (pers. commun.) on similar soils but under higher rainfall conditions (during 1979), N<sub>2</sub>O emissions due to reaction (1) were several-fold higher than those reported in this study. Thus, under the conditions prevailing in this investigation, the contribution of reaction (2) was taken into account by estimating the total gaseous N losses from the higher values of N<sub>2</sub>O evolved in the presence or absence of  $C_2H_2$ . The  $N_2O$  values plotted in Fig. 4 were obtained in this manner.

The relatively high losses of N from the summer-fallow treatment at the Watrous site (Fig. 4) are a function of the low airfilled porosity percentage (high moisture content) and also perhaps the high substrate concentration of  $(NO_3^- + NO_2^-) - N$ . The relatively high rate of evolution of gaseous N continued until late October when very cool air and soil temperatures stopped the majority of microbial activity in the soil. The average daily rate of loss during the period was 81.5 g  $\cdot$  ha<sup>-1</sup>. In contrast, the emission of N<sub>2</sub>O-N from the soils from the conventional till wheat (C-T wheat) and zero-till wheat (Z-T wheat) fields were, with certain exceptions, very similar to those for the site 1 and 2 locations discussed earlier. The exceptions are, however, worthy of note. The first occurred during the 15 June to 15 July period; while the evolution of N<sub>2</sub>O-N from the C-T wheat field was very low, that from the Z-T wheat increased to a measured peak of 709 g  $N \cdot ha^{-1} \cdot day^{-1}$ . The reason for the difference between these two treatments at this time has not been established; it is known, however, that biological immobilization of nitrogen in a conventional till treatment would be expected to be considerably greater than that

Table 2. Effect of oxygen,  $C_2H_2$  and N-serve on the nitrification of added  $NH_4^+$ -N in Hamlin clay loam soil incubated at 22% (wt/wt) moisture

reatment		Time (h)				
Treatment	0	6	24	48	72	96
		NH	4 <sup>+</sup> -N	(µg·;	g <sup>-1</sup> )	
Control	30	25	20	14	13	7
Oxygen	28	27	21	20	12	11
N-serve	30	25	24	28	24	24
$C_2H_2$	28	28	28	29	28	29
	(NC	D <sub>3</sub> − +	- NO	2 <sup>-</sup> )-N	(µg∙)	g <sup>-1</sup> )
Control	34	36	39	47	50	55
Oxvgen	33	37	40	44	46	51
N-serve	34	35	37	37	38	39
$C_2H_2$	33	34	34	34	35	35

for the zero till. This explanation is, however, not supported by the inorganic soil N content. A highly plausible reason may lie in the differing structural conditions existing under the tillage systems (Table 1); air diffusion into and out of the more dense zero till surface soil would encourage denitrification and directly result in a



Fig. 4. Results of measurements of gaseous N loss (N<sub>2</sub>O-N), soil moisture, air-filled porosity, rainfall, mineral N and air and soil temperature of Elstow clay loam (site 3) under various tillage systems.  $\Phi$  indicates standard deviation within four replicates.

Table 3. Amount of gaseous nitrogen lost from the experimental sites during the study period

Site	Soil	Field	Gaseous N losses† (kg N $\cdot$ ha <sup>-1</sup> $\cdot$ 180 days <sup>-1</sup> )
1	Hamlin	Wheat	0.95
2	Hoey	Wheat	0.91
	Mean		0.93
3	Elstow	C-T Wheat ‡	3.10
		Z-T Wheat§	6.30
		Summer fallow	9.95

† Includes N<sub>2</sub>O and N<sub>2</sub>.

‡ Conventional till.

§ Zero till.

dramatic increase in the N<sub>2</sub>O-N flux as a result of a short-term increase in soil moisture content. However, the N<sub>2</sub>O-N flux in the Z-T wheat field was less than in the C-T wheat field in the mid-August period, even though the air-filled porosity was less in the former at this time. As most of the NO<sub>3</sub><sup>-</sup>-N was either taken up by the crop or lost, the presence of a very small amount of NO<sub>3</sub><sup>-</sup>-N (2  $\mu g \cdot g^{-1}$ ) in Z-T wheat as compared to 4  $\mu g \cdot g^{-1}$  in C-T wheat reduced the losses. The rate of gaseous N loss in the Z-T wheat and C-T wheat treatments were 36.0 and 14.8 g N · ha<sup>-1</sup> · day<sup>-1</sup>, respectively.

The total gaseous loss of N for this 180day study suggests that in the conventional tillage system, losses to the agricultural industry are insignificant in cropped soil, and are in the vicinity of 1-3 kg  $N \cdot ha^{-1}$ . The reasons for the more than 100% increase in gaseous losses of N under zero till may be due to the higher bulk density of the surface soil. In contrast, substantial and significant losses of N under summerfallow conditions were obtained (Table 3). The relatively high losses for the summerfallow treatments further support the concerns expressed by Rennie et al. (1976) and Campbell et al. (1980) about the use of the summer-fallow practice.

The Council for Agricultural Science and Technology (1976) reported that, on the average, over the harvested cropland

on the earth approximately 1 kg of N as N<sub>2</sub>O is liberated per hectare per year. More recently, Bremner et al. (1980) studied emission of N<sub>2</sub>O from six soils seeded to soybeans and reported that the amounts of N<sub>2</sub>O-N evolved ranged from 0.34 to 1.97 kg  $\cdot$  ha<sup>-1</sup>  $\cdot$  yr<sup>-1</sup> and averaged 1.20 kg  $ha^{-1} yr^{-1}$ . This study, in general, verifies the earlier estimates, namely that loss of gaseous nitrogen as  $(N_2O + N_2)$ -N from cropped soils is generally low. However, while the amount of N<sub>2</sub>O-N lost is not too significant from the standpoint of the agricultural industry, cropped soils, particularly those well fertilized with N and at or near optimum moisture content, clearly serve as a significant source of atmospheric N<sub>2</sub>O.

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