Reports

Nitrous Oxide Emissions from an Irrigated Cornfield

Abstract. *During the 1978 growing season, nitrous oxide (N_2O) emissions from a typical well-managed northern Colorado field of corn (*Zea mays *L.) totaled approximately 2.6 kilograms of nitrogen per hectare, or about 1.3 percent of the applied fertilizer nitrogen. Thirty percent of the loss occurred during the 3 weeks following fertilization while ammonia was being rapidly nitrified, and 59 percent was emitted during the week after the field's first irrigation, when restricted oxygen diffusion favored denitrification. Considering the large spatial and temporal variability of N_2O emissions from soil, micrometeorological estimates of vertical N_2O flux density compared favorably with estimates based on a simple soil cover method.*

During the last decade, public anxiety regarding air pollution has expanded from concern about obvious effects at ground level to consideration of effects on the upper atmosphere, and particularly to possible depletion of the stratospheric ozone that controls the intensity of ultraviolet radiation reaching the earth's surface. According to Thrush (*1*), ozone concentration in the atmosphere is determined by the relative rates of its net photochemical formation from molecular oxygen and its catalytic destruction by other species, principally nitric oxide formed in the stratosphere from nitrous oxide (N_2O) transported upward from the surface. Recognizing that biological denitrification (*2*) is the largest known source of N_2O in our environment, several authors have recently attempted to estimate the effect that agriculture's increasing use of industrially fixed nitrogen (N) fertilizers might have on increasing atmospheric N_2O concentration and, therefore, ozone destruction (*3–5*). Such an estimate requires knowledge of the fraction of fertilizer N returned to the atmosphere as N_2O. Unfortunately, very little information concerning N_2O evolution from agricultural soils under field conditions is available for use in assessing the probable value of that fraction (*6*). We report here field measurements of N_2O emissions from an irrigated agricultural area of northern Colorado throughout the 1978 growing season, and we compare two methods of making these measurements.

Vertical N_2O flux density measured above a 120-ha field of corn (*Zea mays* L.) about 4 km northeast of Berthoud, Colorado (*7*), is plotted as a function of time in Fig. 1. Temporal variability was extremely high, with emissions ranging from a low of 0.08 kg of N per hectare per year on 28 August to a high of 150 kg per hectare per year on 22 July. Such high variability emphasizes the uncertainty in predicting stratospheric ozone concentration changes from limited surface N_2O flux data. During the period from corn seedling emergence (17 May) until crop maturation (18 September), N_2O emissions totaled approximately 2.6 kg of N per hectare or about 1.3 percent of the 200 kg of N per hectare applied as ammonia on 23 June. The field under study was more heavily fertilized and watered than most of the world's cropland. Thus our data are not much different from those of the Council for Agricultural Science and Technology (*5*), which estimated that an average of 1 kg of N as N_2O is liberated annually per hectare of harvested cropland on earth (*5*). However, the data appear inconsistent with the large N_2O fluxes computed by others from the estimated normal atmospheric lifetime and abundance of the gas (*3, 4*).

Figure 1 contains data points acquired by two independent methods. The data points shown as closed circles joined by straight lines were obtained by monitoring the accumulation of N_2O beneath thermally insulated, radiation-shielded glass bell jars placed over the soil for a 1-hour period. Air samples (30 ml) taken by syringe from the bell jars at 15-minute intervals were analyzed by a gas chromatograph with an electron capture detector (GC-EC) (*8*). Nitrous oxide flux was computed by multiplying the concentration increase per unit time by the average height of the soil cover, assuming that the buildup of N_2O beneath the cover had negligible effect on the concentration gradient in underlying soil (*9*). Large spatial variability in the data was apparently real and does not reflect negatively upon the method. Biggar's discussion of the spatial variability of N in soils (*10*) indicates that high variability should not be unexpected.

Data obtained by the soil cover method were compared periodically with vertical N_2O flux densities measured by the aerodynamic profile method described in detail by Thom (*11*). Data from the latter method, shown as triangular points in Fig. 1, were computed as the product of an eddy diffusivity and the vertical concentration gradient of N_2O in the lower atmospheric boundary layer. Standard micrometeorological sensors were used to measure the wind speed and temperature profiles from which eddy diffusivity was estimated. Nitrous oxide concentration profiles were determined, a constant-rate syringe pump being used to fill simultaneously eight 60-ml polypropylene syringes, each with air from a different sampling height. Air samples accumulated over a 1-hour period were then analyzed by GC-EC. Unlike the soil cover approach, the aerodynamic profile method imposed no artificial conditions or constraints upon the area under study, and it provided a vertical flux estimate integrated over a large soil area. However, use of the method was limited to periods of high N_2O flux, because only then were the differences in N_2O concentration between sampling heights larger than the minimum detectable difference of GC-EC (1 to 2 parts per billion, by volume).

Whenever both methods could be used simultaneously, agreement between the two was acceptable, considering the large spatial and temporal variability of N_2O emissions from soil. The aerodynamic profile flux, always the larger of the two estimates, never exceeded twice the mean of four individual simultaneous determinations by the soil cover method, although the range of those four determinations often included values differing more than twofold. Despite this high variability, we concluded that the soil covers employed in this study furnished meaningful estimates of N_2O flux, provided adequate precautions were taken to minimize disturbance of the energy and mass transfer processes normally operating at and above the soil surface. Necessary precautions are discussed in detail by Hutchinson and Mosier (*12*).

Except for a 3-week period following fertilization of the field on 23 June, the data in Fig. 1 are similar to measurements of N_2O loss in the many laboratory studies of denitrification in soil. Both are well summarized by the statement of

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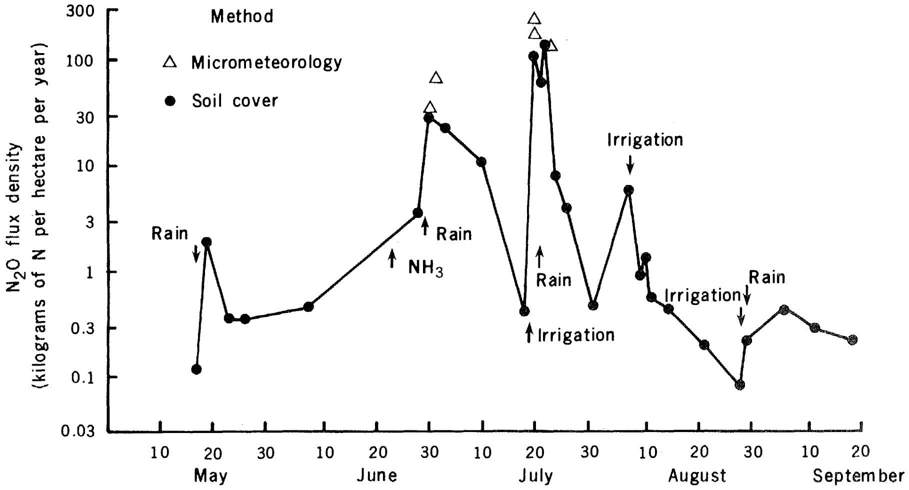

Fig. 1. Vertical N_2O flux density, as measured by two independent methods, above an irrigated cornfield during the 1978 growing season. Rainfalls exceeding 1 cm, irrigations, and time of fertilization are marked with labeled arrows.

Smith *et al.* (*13*) that "denitrification occurs in periodic bursts, in response to changes in oxygen status, against a background of very slow yet continuous denitrification." Broadbent and Clark (*14*) also concluded that denitrification in soil is slow except during periods when oxygen diffusion is limited, usually by water. The largest N_2O flux at our field site was measured after a heavy irrigation (23 cm of water) on 19 July, followed by rainfall (2 cm) on 21 July, at a time when soil nitrate levels were high as a result of fertilization about 4 weeks earlier. During the week of 19 to 25 July, N_2O emissions amounted to 59 percent of the total lost during the growing season before diminishing to low, preirrigation levels. Although other bursts of N_2O arising from denitrification were much smaller, each incidence of irrigation or of precipitation exceeding 1 cm (marked by labeled arrows in Fig. 1) was followed by an immediate increase in the vertical N_2O flux (see data for 19 May, 30 June, 20 July, 7 August, and 5 September). Our measurements indicated that the cornfield was always a source, never a sink, for tropospheric N_2O, even though some laboratory studies have shown that N_2O can be absorbed and reduced to dinitrogen gas (N_2) in anaerobic soils (*15*).

During the period 23 June to 13 July, high N_2O emissions, accounting for 30 percent of the growing season's total, coincided with the time when applied ammonia fertilizer was being oxidized to nitrate by soil bacteria. Unlike other peaks in Fig. 1, the N_2O flux continued high for a comparatively long time, even though the soil remained aerobic, and apparently represented N_2O produced by autotrophic nitrification. Recent studies with soils in the laboratory (*16*) have corroborated studies with bacterial cultures (*17*) showing that significant quantities of N_2O can be evolved during the nitrification of ammonia. The data in Fig. 1 are discussed in more detail in (*8*), where we also present the additional measurements needed to support the conclusions outlined here.

Remembering that N_2O emissions totaled approximately 2.6 kg of N per hectare during the 1978 growing season, and that most of this loss occurred in two special situations unlikely to be repeated except on an annual basis, we project that annual emissions at our field site probably did not exceed 4 kg/ha. This projection conflicts with the model outlined in figure 1 of McElroy (*3*) which proposes that nearly one-half of the fertilizer N applied to soil is lost within 10 years by denitrification in situ, with 74 percent of the denitrified N appearing as N_2O (and only 26 percent as N_2) in the atmosphere. Our measurements represented only the first annual installment of denitrification from the 200 kg of N applied per hectare during the 1978 growing season, but they should also have included contributions from chemical fertilizers, crop residues, and animal manures mixed with the soil in earlier years. Although previous fertilizer application rates at the site were smaller than that used in 1978, N additions during the past 10 years have been high enough that McElroy's model forecasts N_2O emissions at least an order of magnitude higher than we measured.

Our data are also inconsistent with the theses (i) that global production of N_2O is of the order 120 × 10^9 kg of N per year (*3*, *18*), based on its abundance and a 10-year atmospheric lifetime estimated by Junge's (*19*) empirical formula from measurements of the spatial and temporal variability in N_2O concentration, and (ii) that N_2O production in the oceans is small compared to emissions from land surfaces (*3*). If our projected annual N_2O emission rate could be considered typical of the world's cropland (probably an overestimate for reasons already given), annual production of N_2O by the 1.5 × 10^9 hectares of harvested cropland on the earth would amount to only 6 × 10^9 kg of N per year. And if emissions from the 13.4 × 10^9 hectares of noncropped land were as much as one-fourth as great (*5*), then total N_2O production from land surfaces would be about 20 × 10^9 kg of N per year. Combining this total with the two arguments above yields the unlikely conclusion that denitrification associated with freshwater media, or else some unknown source, accounts for most of the N_2O load imposed on the atmosphere. Not accepting this conclusion requires that one or both of these two theses must be in error. The first has recently been questioned by Cicerone *et al.* (*20*) and by Pierotti *et al.* (*21*) who, after incorporating refinements in their analytical techniques, found that the standard deviation of their atmospheric N_2O concentration measurements declined substantially. The lower standard deviation implies a longer atmospheric lifetime and, therefore, smaller global emissions. Regarding the second thesis, Crutzen (*18*), citing data of Hahn (*22*), contends that the oceans represent a substantial source of N_2O.

The ozone depletion question is a complex issue crossing several disciplinary boundaries. The projections we have made are based on data for one crop growing at one location during one season, and their interpretation must be limited accordingly. We concur with many of the authors cited here that much additional research is prerequisite to understanding the global nitrogen cycle and its interactions with stratospheric ozone.

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Carbon-13 in Tree Rings Indicates No Record of Sea-Surface Temperature

Abstract. *When the correct values for the temperature coefficient of carbon dioxide solubility in seawater are used, theoretical calculations show that no measurable carbon-isotope redistribution occurs between sea and air for any plausible change in the sea-surface temperature. Although this fact invalidates one possible paleothermometer, it somewhat simplifies the interpretation of carbon-13 data in terrestrial biological samples.*

The possible consequences of the "CO_2 greenhouse" are of increasing concern. Unfortunately, the historical data on atmospheric CO_2 concentrations are of such uncertain accuracy that they put few constraints upon mathematical models of the CO_2 system. The range of future projections is accordingly large, and it is rash to make predictions more precise than that the CO_2 concentration will double by about A.D. 2030. This uncertainty makes alternative data sources imperative, and $^{13}C/^{12}C$ ratios provide an important addition. One of the stated goals of the *Comprehensive Plan for CO_2-Effects Research and Assessment* is increased "use of the isotopes of carbon as clues to the contribution of the biosphere to recent changes in atmospheric CO_2" (*1*, p. v).

Because the surface ocean contains so much more total CO_2 than the atmosphere, air-sea exchange is an important determinant of the $^{13}C/^{12}C$ isotope ratio in the atmosphere and thus in nonmarine biological materials. Because this exchange is temperature-dependent, there has been speculation about a measurable influence on tree-ring isotopes arising from changes in the ocean temperature. (*2*).

The object of this report is to demonstrate that the sea-surface temperature does not appreciably affect isotope ratios that depend upon the atmospheric ratio. Conversely, sea-surface temperature changes cannot be inferred from terrestrial records.

Earlier speculations appear to have been influenced by an erroneous estimate of the temperature coefficient of the solubility of CO_2 in seawater. Although Hamberg (*3*) found correct values last century, I have shown (*4*) that the value of 4 percent per degree Celsius in common use today (*5-7*) is $(\partial P/\partial T)_{A,C}$, that is, it is the change in the partial pressure of CO_2 (P) with respect to temperature (T) at constant alkalinity (A) and constant total CO_2 ($C = CO_{2aq} + H_2CO_3 + HCO_3^- + CO_3^{2-}$) in solution. This coefficient is appropriate only to the theory (*6*) and experiment (*7*) for which it was derived and not to air-sea exchange. The condition of constant total CO_2 in solution is clearly violated if CO_2 moves between sea and air. The correct coefficient is $(\partial P/\partial T)_{A,\Sigma}$, where Σ indicates that the sum of CO_2 in sea and air must remain constant. Obviously, the magnitude of the temperature coefficient is a function of the depth (z) of the surface ocean assumed to be in active exchange with the atmosphere. For an ocean 100 m deep, this coefficient is almost exactly ten times smaller than the commonly quoted constant-C value, and reduces tenfold the apparent T sensitivity of P and of isotopic redistribution accompanying a change in T.

The calculation that I present below does not allow the usual approximations that make working with isotopic δ values convenient, and we must resort to the full equations. These are as follows:

$$R_x = {}^{13}C_x/{}^{12}C_x \qquad (1)$$

where x designates a particular sample,

$$R_0 = {}^{13}C_{PDB}/{}^{12}C_{PDB} \qquad (2)$$

where PDB designates the Pee Dee belemnite reference standard and $R_0 = 0.00112372$ (*8*),

$$\delta_x = (R_x/R_0 - 1)1000 \qquad (3)$$

$$K_s = R_{HCO_3^-}/R_{CO_2} = R_{sea}/R_{air} = (\delta_s + 1000)/(\delta_a + 1000) \qquad (4)$$

and

$$\delta_s = (\delta_a + 1000)K_s - 1000 = \delta_a + (K_s - 1)(1000 + \delta_a) \qquad (5)$$

If we ignore interaction with the marine biota, the computation follows the symbolic outline of Table 1. There are 18 equations relating 24 quantities, so that, if six independent parameters are known, the system is determinate.

Of the several evaluations (*9-11*) of K_s, I adopt that of Mook *et al.* (*10*), because it lies in the middle of the range of the other values and is the most internally consistent. Defining ϵ, they write

$$\epsilon = (K_s - 1)1000 = (9483/T) - 23.89 \qquad (6)$$

where T is in degrees Kelvin.

For simplicity, I ignore the oceanic maximum in C at a depth of 1 km, which is supported by the respiration of vertically migrating predators and by detrital oxidation, and assume that C is constant with depth. It is then possible to compute C (*4*) from A and P, for the wind-stirred layer is never far from equilibrium.

The only remaining troublesome quantity is P', the partial pressure after a change in T. This must be calculated (*4*) from the temperature-sensitive reaction functions for H_2CO_3. The exact value will depend upon which set of functions

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