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Stimulation of nitrous oxide production resulted from soil fumigation with chloropicrin

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Abstract

Agricultural soils are a major source of the atmospheric greenhouse gas nitrous oxide (N_2O). Agronomic practices such as tillage and fertilizer applications can significantly affect the production and consumption of N_2O because of alteration in soil physical, chemical, and biochemical activities. Soil fumigation is an agronomic practice used to control soil-borne disease pathogens, weeds, plant-parasitic nematodes, and fungi. The strong impact of fumigants on soil microorganisms can indirectly affect the production and/or consumption of N_2O and would potentially alter net emissions from agricultural soils. Laboratory incubation and field soil fumigation studies were conducted to determine the potential impact of soil fumigation on the dynamics of N_2O production. Laboratory soil incubations showed an eight-fold increase in the production rate of N_2O as a consequence of chloropicrin (CP) fumigation. This stimulation effect was confirmed by a seven-fold increase in N_2O emission rates in field plots following CP fumigation. The mechanism of N_2O production appeared to be microbial related; however, additional work is needed to fully elucidate the pathways.

Keywords: Greenhouse gas; N_2O emission; Incubation; Flux chamber; Fumigants

1. Introduction

According to a USDA report, over 68,000 hectares of soil in the US is fumigated annually with methyl bromide (MeBr) containing fumigant mixtures before mandatory reductions began in 1999, and over 250,000 hectares of soil are fumigated globally (USDA, 2002). Because of its large volatilization losses (Majewski et al., 1995; Yagi et al., 1995; Wang et al., 1999) and potential for depleting stratospheric ozone (Wofsy et al., 1975; Butler, 1995), MeBr is scheduled to be phased out in 2005 in the USA. A number of replacement fumigants are being actively studied in terms of efficacy and herbicidal functionality (USEPA, 2002). Soil fumigation is a common practice in agriculture using chemicals to control both microbiological organisms (soil-borne disease pathogens, plant-parasitic nematodes, and fungi) and weeds. The major screening criteria that have been used for the MeBr replacements are: (a) lack of ozone depleting properties, and (b) efficacy for soil-borne pathogens and organisms. Chloropicrin (CP) is one of the successful replacements in terms of these properties. CP is also commonly used in mixtures with other fumigants (e.g. MeBr, 1,3-dichloropropene (1,3-D), and methyl isothiocyanate (MITC)) to promote broad-spectrum efficacy and as a warning agent to the presence of fumigant vapors, since CP is a strong lachrymator.

Both biotic and abiotic transformations can result in mineralization of CP to precursors that would possibly be involved in the formation of N_2O. Some *Pseudomonas* species have been shown to successively dechlorinate CP ($CHCl_3NO_2$) (Castro et al., 1983) and other chlorinated fumigants (van der Waarde et al., 1993; Poelarends et al., 1998). This is particularly important due to the prevalence of *Pseudomonas* in soils. However,

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the distribution of microbial populations is extremely heterogeneous, with populations localized around particulate organic matter (Rovira and Sands, 1971) and varying with different microenvironments (e.g. anaerobic/aerobic) coexisting within a few millimeters (Clarholm, 1981; Grundmann and Debouzie, 2000).

There are also abiotic pathways of CP degradation. Photolysis in air or in the shallow surface soil (0–0.3 mm from the surface; Hebert and Miller, 1990; Konstantinou et al., 2001) or hydrolysis with water producing CO_2, Cl^-, NO_3^- and H^+ (Castro and Besler, 1981). However, no reference has been made to increase production of N_2O during the degradation of CP.

Agricultural operations are a significant source of N_2O, accounting for 6.4 Tg N_2O-N per year or approximately one-third of total terrestrial emissions (Kroeze et al., 1999; Chang and Hao, 2001). On a molecule per molecule basis, the global warming potential (GWP) of N_2O is approximately 300 times that of CO_2 over a 100-year time scale. Therefore, even small changes in N_2O emission can have significant impact on global warming.

N_2O can be formed by both nitrification and denitrification reactions. Nitrification is the microbial conversion of ammonium into nitrite and nitrate; denitrification is the anaerobic microbial reduction of nitrate and nitrite to nitrogen gas. These microbial processes are tightly coupled to each other, and also coupled to the microbial mineralization of organic matter (Firestone and Davidson, 1989).

N_2O sources are not limited to nitrification and denitrification reactions. It has been determined that microbial transformations of NO to N_2O can occur in well aerated soils (Schafer and Conrad, 1993; Venterea and Rolston, 2000a). In addition, abiotic pathways have been identified for the production of N_2O from HNO_2 in sterile soils (Venterea and Rolston, 2000b) and ammonium nitrate on atmospheric aerosols (Clemens et al., 1997).

Because microbial carbon and nitrogen liberation could occur following fumigation and CP degrades to nitrogen containing metabolites, it is anticipated that N_2O emission would increase following soil fumigation with CP. The objective of this study was to examine the stimulation of N_2O production through laboratory incubations and field flux measurements as a consequence of CP fumigation.

2. Materials and methods

Laboratory incubations were performed to determine if soil fumigation with CP would increase N_2O production. Soil samples from five depth increments were collected prior to fumigation and stored at 4°C until laboratory incubations could be performed. The soil is a Vilas loamy sand (sandy, mixed, frigid, Entic Haplorthod). Soil bulk density, moisture content, pH, and fractions of sand, silt, clay, and total organic carbon (TOC) were measured for the five depth increments (Table 1). Bulk density was determined by the core method or the excavation method (Blake and Hartge, 1986) at locations where the metal core sampler could not be driven into the soil. Ten sub-samples from each depth were taken for bulk density analysis. Soil water content was determined by oven drying 10 g sub-samples at 105°C for 24 h. Soil pH was measured in a 1:1 (v:v) slurry of soil and deionized water using a Hanna Instrument portable pH/EC/TDS/temperature probe. Soil texture and TOC were determined by the University of Minnesota Soil and Plant Testing Laboratory. The laboratory used the hydrometer method for texture and the loss on ignition method for TOC.

Prior to incubation studies, the soil was initially incubated in the dark for 10 d at room temperature (22 ± 2°C) in a high humidity aerobic environment to reactivate microbial colonies, following procedures similar to Wu et al. (1996). Then 5 g subsamples of the pre-conditioned soil were placed in 125 ml serum vials (Wheaton Glass, Milville, NJ) and sealed with Teflon-lined butyl rubber septa (Agilent Technologies, Palo Alto, CA). CP was injected through the sealed serum vial to prevent volatilization losses of the fumigant and incubated for 10 d. To simulate the effect of an additional carbon source on N_2O production rates, tests were also run with a glucose amendment (0.5 mg glucose $5\,g^{-1}$ soil). Glucose amendments have been used as a simple carbon source to examine stimulation of

Table 1
Summary of soil properties[a]

Depth (cm)	ρ_b (g cm^{-3})	pH	θ (%)	Sand (%)	Clay (%)	Silt (%)	TOC (%)
0–10	1.49 ± 0.07	6.76 ± 0.11	16.8 ± 0.9	83.7	9.0	7.3	1.1
10–20	1.63 ± 0.12	6.25 ± 0.05	16.1 ± 0.6	86.7	6.5	6.8	1.1
20–30	1.72 ± 0.11	5.62 ± 0.03	9.8 ± 0.5	93.5	1.7	4.8	0.1
30–50	1.77 ± 0.21	5.70 ± 0.06	8.4 ± 0.5	96.2	0.3	3.5	<0.1
50–75	1.75 ± 0.25	5.20 ± 0.05	8.2 ± 0.4	97.8	0.0	2.2	<0.1

[a] ρ_b = soil bulk density, θ = soil volumetric water content, TOC = total organic carbon.

N_2O production (Speir et al., 1995; Nobre et al., 2001; Wheatley et al., 2001). Prior research has suggested a complex interaction between heterotrophic bacteria and nitrification rates (Wheatley et al., 2001). No CP injections were made in the soil controls or the glucose only treatments. Incubations of CP were also performed in glass beads due to the difficulty in sterilizing the soil completely as confirmed by CO_2 respiration tests. The glass beads were used to see if N_2O production resulted from the abiotic decomposition of CP, but would not account for the abiotic interactions with the mineral components of the soil. The five different treatments were: (1) control (5 g soil); (2) soil (5 g) and fumigant (0.3 mg CP per vial); (3) glucose (0.5 mg per vial) and soil (5 g); (4) glucose (0.5 mg per vial), CP (0.3 mg per vial), and soil (5 g); and (5) glass beads (5 g) and CP (0.3 mg). Adding 0.3 mg CP in 5 g soil corresponds to 500 kg ha^{-1} at bulk density of 1.65 g cm^{-3} and 0.5 m soil depth. All incubations were run in triplicate and conducted at room temperatures ($22 \pm 2^{\circ}C$).

Headspace gas samples were run on a GC system. The GC system consisted of a HP-5890 GC unit (Agilent Technologies, Palo Alto, CA) with an electron capture detector (ECD) that was used to quantify the amount of N_2O in the gas samples. The injection used a 0.75 ml gas-sampling loop, with helium as the carrier gas. The column used to separate N_2O in the sample was a Porapak N ($2\,m \times 0.32\,cm$; Alltech, Deerfield, IL; 30 ml min^{-1}), with a total analysis time of 8 min per injection. Ar/CH_4 was the make-up gas on the ECD (60 ml min^{-1}). Column temperature was isothermal at $90^{\circ}C$. The amount of N_2O in the headspace samples was quantified through a multiple point external calibration based on height response of the peak for N_2O from certified gas standards (Scott Specialty Gases).

Field N_2O flux measurements were made at the Hayward State Nursery, located at Hayward, WI, which is approximately 450 km northwest of Madison, WI, USA. This location was selected due to ongoing research investigating the distribution, efficacy, and emission of CP and MITC following soil fumigation, and a previous study on fumigant efficacy by Juzwik et al. (1997). Three field flux sites were established for measuring N_2O emissions. Two sites were located on the fumigated plots (one each on MITC and CP/MITC test plot, respectively) and the third site was in an adjacent untreated area (the control plot). Flux measurements were taken with static chambers with a minimum of four samples taken from each chamber (typically at 0, 5, 10, and 20 min). Each air sample was 60 ml in volume. The flux was calculated from the linear portion ($r^2 > 0.90$) of N_2O concentration increase in the chamber air as a result of the surface emissions:

$$\text{flux} = \frac{V}{A}\left(\frac{\Delta C}{\Delta t}\right), \quad (1)$$

where V and A are the volume and area of the chamber, respectively. ΔC is the concentration change over the time increment Δt. The chamber design was identical to the chambers used for monitoring greenhouse gas emissions from the surface of landfills (Bogner et al., 1997).

Daily N_2O flux measurements were taken in the field for approximately 20 d following fumigation. Initially 22 ml headspace vials (Kimble/Kontes, Dusseldorf, Germany) were capped with Teflon-lined butyl rubber septa (Kimble/Kontes, Dusseldorf, Germany). Just before sampling, the vials were evacuated in the field using a Precision® vacuum pump (ultimate vacuum was 1×10^{-3} torr; model D-75, Fisher Scientific). A 60 ml gas sample was then injected through the septum into the sealed headspace vial in the field, which resulted in over-pressurization of the vial ($\sim$2.7 atm pressure). After the vial was over-pressurized with the sample, it was stored in a field cooler (without ice). Headspace vials have been used to collect gas samples in prior studies (e.g. Liou et al., 2003) and the integrity of the sample is ensured if the over-pressurization is still present in the vial when it is analyzed in the laboratory.

In addition to the headspace vials, customized 11 ml stainless steel gas containers (Spokas and Bogner, 1996; Bogner et al., 1997) that were previously developed for trace gas monitoring at landfills were also used. Briefly, each container consists of a 6.35 mm (i.d.) stainless steel tubing capped on one end with a Swagelok® (registered trademark of Swagelok Corp.) plug and the other end with a Swagelok® toggle valve consisting of a Teflon-lined valve stem. These containers were also evacuated directly in the field and 60 ml of the respective gas sample was injected into the containers ($\sim$5.5 atm pressure). These containers were also placed in the field cooler (without ice) after sampling. Unlike the headspace vials, these containers preserved the integrity of the samples without leakage. However, limitations on the number of the available stainless steel containers restricted the total number of flux samples that were taken with these containers. In summary, there were a total of 276 gas samples taken at the field site, 36 samples taken with the stainless steel containers and 240 with the headspace vials. However, only 96 of the headspace vials preserved pressurization upon receipt at the laboratory. The lack of pressure in the vial is an indication that leakage occurred at some point after the sampling in the field. Therefore, to ensure the integrity of the collected data any vial that was not pressurized was eliminated. Furthermore, each flux sample is a set of four vials and only nine flux samples had all four samples preserved (36 vials).

Data were analyzed using an analysis of variance (ANOVA) procedure for independent samples to test for statistically significant differences using MINITAB (Minitab, Inc., State College, PA). If there was a

significant difference among the factors, as indicated by a significant *F*-ratio, the Tukey's honest significant difference (HSD) test was performed to determine which pair-wise interactions were significantly different at the $p<0.01$ and 0.05 levels.

3. Results and discussion

Measured N_2O production rates from the laboratory incubations are summarized in Table 2. Overall, higher N_2O production was found in CP treated soil with or without the glucose addition. Because of the large standard deviation (SD) values in the CP treated soil, the increase in N_2O production was statistically significant ($p<0.01$) only for the 0–10 and 50–75 cm depth intervals (Table 3). The lack of statistically significant differences between all the treatments was caused by the large variability in the production rates of N_2O. High variability in the N_2O production rates has also been reported in other studies (e.g. Robertson, 1994; Frolking et al., 1998; Hénault et al., 1998; Dilly, 2001). Significant differences ($p<0.01$) were found between the glass bead control and all soil-CP treatments with the exception of the 20–30 cm soil-CP treatment without glucose (Table 3).

Overall, there was a stimulation of N_2O production with the glucose addition (Table 2), which is in agreement with results found in other studies (Nobre et al., 2001; Wheatley et al., 2001). Adding glucose alone (without CP) did not affect N_2O production rate. This could indicate insufficient N availability in the soil to support N_2O production. The combination of glucose and CP increased the production rate of N_2O as compared to the soil control and was statistically significant ($p<0.01$) in the 0–10 and 50–75 cm intervals (Table 3). Similar to the findings by Firestone and Davidson (1989) and Nobre et al. (2001), the highest production rate of N_2O occurred in the surface soils (0–20 cm, Table 2) where nutrients and the number of microbes would likely be more abundant.

As an example, increases in N_2O concentration in the headspace for the 50–75 cm soil samples were shown in Fig. 1 for both fumigant only and fumigant with glucose treatments. Gas samples from the incubations were analyzed on day 0, 1, 3, 6, and 10. Without glucose addition, concentrations of N_2O in the headspace following fumigation with CP were slightly higher than the controls, and about 8% increase was found after day 6 (Fig. 1a). Adding glucose did not affect N_2O concentrations in the controls; however, the combination of glucose addition and CP fumigant drastically increased N_2O concentrations starting 1 d after the incubation. About a 70% increase was observed after day 6 (Fig. 1b).

Field flux measurements of N_2O emission are summarized in Fig. 2. In the non-fumigated control plots N_2O fluxes remained about 1 mg m^{-2} d^{-1} for the

Table 3
Statistically significant differences between treatments as a function of depth in laboratory incubations[a]

Depth (cm)	Significant interactions ($p<0.01$)	
	No amendments	Glucose amendment
0–10	Control × CP CP × GB CP × GB	Control × CP CP × GB CP × GB
20–30	*F*-ratio not significant	CP × GB
30–50	N/A	N/A
50–75	Control × CP Control × GB CP × GB	CP × GB Control × CP Control × GB

[a] CP = CP and soil treatment, GB = glass bead treatment, Control = soil only, N/A = not available.

Table 2
Cumulative N_2O production in laboratory incubations (calculated on day 6)[a]

Depth (cm)	No glucose		Glucose amendment	
	Control (μg-N_2O kg-soil^{-1} d^{-1})	CP	Control (μg-N_2O kg-soil^{-1} d^{-1})	CP
0–10	0.10 ± 0.03	0.87 ± 0.32	0.15 ± 0.03	1.87 ± 0.62
10–20	0.12 ± 0.07	0.68 ± 0.37	0.13 ± 0.09	1.36 ± 0.87
20–30	0.08 ± 0.05	0.40 ± 0.28	0.10 ± 0.04	0.86 ± 0.58
30–50	N/A	N/A	N/A	N/A
50–75	0.06 ± 0.04	0.13 ± 0.02	0.05 ± 0.02	0.25 ± 0.06
Glass beads	N/A	0.03 ± 0.03	N/A	0.03 ± 0.02

[a] CP = chloropicrin; values are mean ± SD ($n = 3$), N/A = not available.

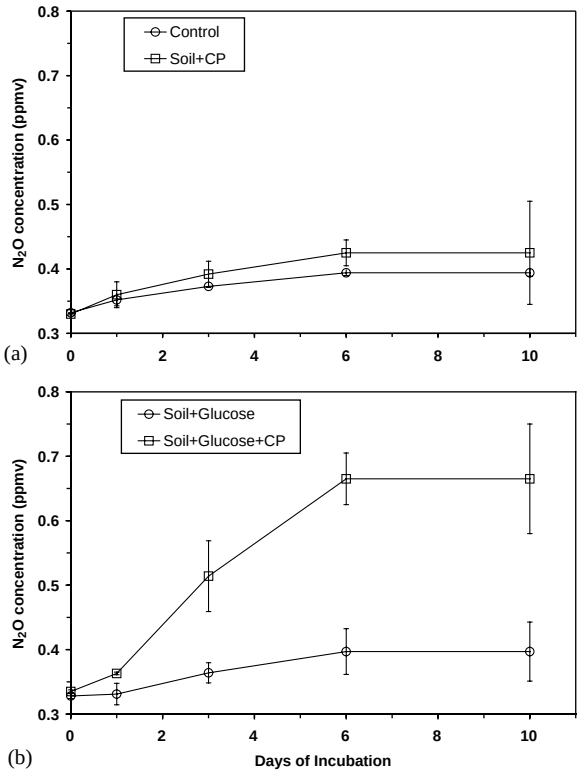

Fig. 1. Headspace concentration of N_2O versus incubation time for 50–75 cm depth increment: (a) CP only, and (b) CP and glucose amendment. Error bars in the figure represent $\pm$one SD of the triplicate samples.

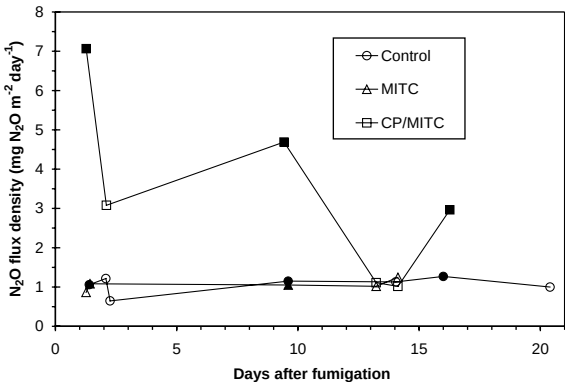

Fig. 2. Emission flux density of N_2O from field plots fumigated with MITC or a mixture of CP and MITC, and an adjacent non-fumigated plot (control). Solid symbol indicate samples collected in the stainless steel containers, and open symbols represent the samples collected in headspace vials.

20-d measurement period (Fig. 2), and the rates were comparable to fluxes measured in agricultural soils (Smith et al., 1998; Kravchenko et al., 2002). N_2O fluxes in the CP/MITC treatment were significantly higher ($p<0.05$), about 3–7 times of that of the control for the first 10 d. The magnitude of the influence could be even higher immediately following fumigation. The flux rates appeared to have decreased over time, returning to near background levels. These high emission rates were in the same order of magnitude as in agricultural fields that received nitrogen fertilizers such as ammonium sulfate or urea (Breitenbeck et al., 1980).

Plots that received only MITC fumigation did not show changes in N_2O emissions compared to the non-fumigated control (Fig. 2). MITC inhibits nitrification in sandy and clay loam soils (Bending and Lincoln, 2000). In aerobic soils the decomposition products of MITC that have been detected are carbon dioxide, sulfate, ammonia, and nitrate (BASF, 2002). So even though MITC decomposes into nitrogen containing compounds, there was no impact detected on the N_2O emissions over the 20-d period. This result indicates that the effect of soil fumigation on N_2O production could be fumigant specific.

It was hypothesized that N_2O production was related to soil microbial processes for two reasons. The first was that the rate of N_2O production declines with depth. The surface soil would be more abundant with nutrients and microbes. Therefore, there should be higher rates in the surface soils if microbes are involved in N_2O production. Secondly, the concentration build-up of N_2O in the laboratory incubations had the same appearance as a microbial growth curve, with a slight lag time followed by an exponential growth phase (Fig. 1). This is further supported by the fact that there was no change in the N_2O production in the glass bead incubations due to the absence of microbes.

A potential concurrent mechanism for the increased N_2O production after soil fumigation with CP could be a consequence of abiotic and biotic breakdown of CP to N-compounds (nitrate, nitrite, and ammonia). Increased inorganic N levels (NO_3^- and NH_4^+) in the soil have already been measured following soil fumigation with CP and MITC (Hansen et al., 1990). In addition, it is postulated that there is also a source of inorganic N and C from the mineralization of killed microorganisms resulting from fumigation (Hansen et al., 1990; Jenkinson and Powlson, 1976). These N-sources would then be available for microbial-aided denitrification, nitrification, coupled nitrification–denitrification, and/or nitrifier denitrification reactions leading to N_2O production (Wrage et al., 2001). Nitrifier denitrification follows the pathway $NH_3 \rightarrow NO_2^- \rightarrow N_2O$ involving solely nitrifier organisms (Wrage et al., 2001), whereas the coupled nitrification–dentrification involves both groups (nitrifiers and denitrifiers) of microorganisms (Arah, 1997).

As a consequence of CP fumigation, the denitrification potential decreased compared to non-fumigated soils in laboratory slurry incubations (Klose, 2002, personal communications). If this reduction in the denitrification occurs in the field, this could support the nitrifier denitrification or nitrification pathways since the denitrifier microbes are not involved. The nitrification pathways would also be substantiated by the lack of N_2O stimulation in the MITC fumigated field plots where nitrification reactions has been shown to be inhibited by MITC (Bending and Lincoln, 2000). In addition, N_2O production in the laboratory incubation ceased when oxygen levels declined below 15% in the incubations (after day 6, data not shown) thus reducing the likelihood that the N_2O production was from anaerobic denitrification. The increase in N_2O production resulting from the glucose amendments would indicate that the production of N_2O is the result of a series of complex hetrotrophic interactions as suggested by Wheatley et al. (2001).

4. Conclusions and implications

The goal of this research was to obtain an assessment of the effects of soil fumigation on N_2O emissions. Based on the laboratory and field measurements, it is evident that soil fumigation with CP can alter the dynamics of N_2O in the soil and emissions to the atmosphere for the soil type analyzed in this study. The results presented here may not be extrapolated to other soil types until further testing. It also appears from the field data that different fumigant compounds have a different effect on N_2O emissions, with CP stimulating N_2O production but no effect with MITC fumigation. The process of soil fumigation could cause long lasting changes in the make-up and biodiversity of soil microorganisms. This will result in changes in the balance of N_2O between soils and the atmosphere during and after fumigation. These effects need to be quantified in order to assess the potential global impact of soil fumigation on N_2O budgets. A better understanding on the interactions between different fumigant formulations and their potential on N_2O emissions can be particularly useful as a screening tool for selecting more sustainable options for soil fumigants.

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