

Greenhouse Gas Accumulation in the Soil Profile is not Always Related to Surface Emissions in a Prairie Pothole Agricultural Landscape

Xiaopeng Gao

Dep. of Soil Science
Univ. of Manitoba
Winnipeg, MB
R3T 2N2
Canada

and

State Key Lab. of Desert and Oasis Ecology
Xinjiang Institute of Ecology and Geography
Chinese Academy of Sciences
Urumqi
China
830011

Nandakumar Rajendran

Dep. of Soil Science
Univ. of Manitoba
Winnipeg, MB
R3T 2N2
Canada

currently at:

Nexen Inc.
Long Lake
P.O. Box 6010,
Fort McMurray, AB
T9H 4V9
Canada

Mario Tenuta*

Dep. of Soil Science
Univ. of Manitoba
Winnipeg, MB
R3T 2N2
Canada

Adedeji Dunmola

Dep. of Soil Science
Univ. of Manitoba
Winnipeg, MB
R3T 2N2
Canada

currently at:

Shell Canada Limited
3655 36 Street NW
Calgary, AB
T2L 1Y8
Canada

David L. Burton

Dep. of Environmental Sciences
Dalhousie Univ.
P.O. Box 550
Truro, NS
B2N 5E3
Canada

A field study was conducted to examine the influence of landscape position on greenhouse gases (GHG) accumulation in the soil profile and surface emissions from an undulating cropped field in the Prairie Pothole Region (PPR) of Manitoba. The field was segmented into four landscape elements: cropped Upper, Middle, and Lower, and uncropped Riparian. In fall 2005 and from spring-thaw through a growing season of flax (*Linum usitatissimum* L.) in 2006, soil concentrations of N₂O, CH₄, CO₂, and O₂ at 5-, 15-, 35-, and 65-cm depths and surface emissions were measured. Gas contents in gaseous and aqueous form were estimated at soil depths of 0 to 65 cm. Spring-thaw increased concentrations and contents of N₂O at 15 to 35 cm in the Lower and Riparian elements, though surface emissions occurred only in the former. This suggested N₂O accumulated during spring-thaw in both elements but was consumed under prolonged anaerobic conditions of the Riparian element before reaching the soil surface. For the Lower element, addition of N fertilizer to the soil surface resulted in shallow (5 cm) accumulation of N₂O but higher surface emissions than at spring-thaw. The Riparian element consistently had the highest CH₄ emissions. These occurred after the spring-thaw N₂O emissions and with the accumulation of CH₄ in the soil profile and declining O₂ concentration. Soil concentrations and profile contents of CO₂, as well as surface emissions, were consistently higher in the Riparian than the cropped elements and showed a similar increase with progression of the growing season. Thus, unlike N₂O and CH₄, CO₂ was not subject to consumption processes in soil. The results suggest limiting N₂O emissions in depression areas may be possible by shifting N₂O production from the near soil surface to lower depths. Promotion of aeration to encourage CH₄ consumption in the soil surface may lower CH₄ emissions in wet years. Generally, the accumulation depth of GHG varied across the landscape elements reflecting differences in the biophysical factors controlling production and consumption and, thus, determining the surface emissions.

Abbreviations: DOC, dissolved organic C; EC, electrical conductivity; GHG, greenhouse gases; MAP, monoammonium phosphate; PD, particle density; PPR, Prairie Pothole Region; TOC, total organic C; UAN, urea ammonium nitrate; VWC, volumetric water content; WFPS, water filled pore space.

The PPR of North America covers 715,000 km² and extends from the north-central United States to south-central Canada. It is characterized by a complex undulating topography of uplands and wetlands. Cropped landscapes in the PPR typically contain relatively well-drained Upper and Middle landscape elements and poorly drained Lower elements. Lower elements can grade into uncropped Riparian elements around water-filled depressions. Riparian elements are

Soil Sci. Soc. Am. J. 78:805–817

doi:10.2136/sssaj2013.05.0157

Received 1 May 2013.

*Corresponding author (mario.tenuta@umanitoba.ca).

© Soil Science Society of America, 5585 Guilford Rd., Madison WI 53711 USA

All rights reserved. No part of this periodical may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher. Permission for printing and for reprinting the material contained herein has been obtained by the publisher.

dominated by short-grass, tall grass, and mixed perennial grass vegetation (Sharratt et al., 1999). These topographically complex agricultural landscapes pose a significant challenge to understanding the production and emissions of GHG in the PPR.

Few studies have examined the landscape controls on N_2O and CH_4 emissions from the PPR. In a hummocky wetland area in Saskatchewan, Pennock et al. (2010) reported greater N_2O emissions from depressions than Riparian elements. For wetland basins located in central North Dakota, Phillips and Beerli (2008) found greater CH_4 emissions from Riparian than pasture or cropland. For the undulating agricultural field in Manitoba used in this current study, earlier work reported N_2O emissions to be greatest from poorly drained Lower elements while CH_4 emissions were consistently greater in Riparian than cropped elements, with hotspots for both gases being associated with high soil water and organic C contents (Dunmola et al., 2010). Results of these studies consistently demonstrate the influence of soil moisture on surface emissions, yet the landscape effect on the production or consumption of GHG in the soil profile and its relationship to the surface emissions remains unresolved.

Surface emission of GHG depends on the balance between production and consumption in a soil profile, concurrent with the transport of gases to the surface. Nitrous oxide is predominantly produced in soils by bacteria through nitrification and denitrification in aerobic and anaerobic conditions, respectively (Beauchamp, 1997; Kool et al., 2011). Denitrifiers may reduce N_2O using it as an electron acceptor to produce N_2 (Conrad, 1996). Methane is produced under anaerobic conditions by methanogens, and it is oxidized to CO_2 by methanotrophic chemoautotrophic bacteria under aerobic conditions (Le Mer and Roger, 2001). The total content of these gases in the soil profile includes gaseous and aqueous phases described by Henry's law. Soil O_2 content is a good indicator of soil aeration. Measures of the total content of GHG and O_2 in the soil profile can, therefore, provide a real estimation of gas storage and increase the understanding on the biophysical processes regulating production, consumption, transport, and ultimately emission of GHG.

While many studies have reported surface emissions, few studies have linked surface emissions to GHG production in the soil profile. The accumulation of N_2O in the soil profile does not always lead to surface emissions. Investigating concentration profiles of GHG can highlight regions of production and consumption of gases related to surface emissions. Understanding the biophysical factors controlling production and consumption of N_2O in the soil profile may suggest practices to either decrease production and/or increase consumption.

Tenuta and Beauchamp (2003) reported elevated soil concentrations near the surface of soil following surface application of urea to a grassed soil resulted in emissions of N_2O . However, surface emissions may not match accumulation of N_2O at lower depths. Using the stable isotope ^{15}N , Wagner-Riddle et al. (2008) reported that the burst in N_2O emission during spring-thaw was dominated by newly produced N_2O from the near soil surface. The N_2O contained in the soil profile was further

reduced to N_2 before reaching the soil surface. By comparing changes in soil content of N_2O to surface emissions during spring-thaw on an agricultural field in Ontario, Risk et al. (2014) determined physical release of N_2O stored in the soil profile contributed to only 24% of the emissions of the first spring-thaw event. Further, Wagner-Riddle et al. (2008) showed the buildup of N_2O over winter did not correspond with surface N_2O emissions at the onset of spring-thaw due to N_2O consumption by denitrification. The importance of microbial activity compared to physical release of stored N_2O during thaw events is likely dependent on soil conditions affecting production and consumption of N_2O . These studies explored the biological processes regulating the N_2O production or consumption by linking subsurface N_2O profile concentration with surface emission. Such approaches may particularly be helpful to manage spring-thaw or post-fertilizer period emissions when significant N_2O losses have been reported from cultivated soils in cold temperate climates (Beauchamp, 1997; Wagner-Riddle et al., 2008). Dunmola et al. (2010) reported that significant N_2O emissions occurred during spring-thaw and post-fertilizer periods from poorly drained Lower cropped elements but did not occur or were substantially less from other cropped landscape elements. It, however, remains unclear whether such variability in the emission of N_2O within landscapes was a result of differences in the magnitude of production of N_2O or location of N_2O production in the soil profile and potential for consumption before surface emission. For CH_4 , studies comparing soil concentrations to independently measured emissions are rare for agricultural soils. Maljanen et al. (2007) found on a boreal agriculture soil that CH_4 concentrations in the soil increased after thaw whereas surface emissions remained unchanged. In an arctic soil, there was no association between soil CH_4 concentration and surface emissions, likely due to the limitation of gas transport across soil layers (Brummell et al., 2012).

Thus, the objectives of the current study were to (i) determine when and where soil GHG accumulates in the soil profile as a function of landscape position, with particular focus on spring-thaw and post-fertilizer periods, (ii) examine the relationship between soil profile conditions and soil GHG accumulations, and (iii) determine whether the dependency of surface emissions to depth of GHG accumulation in soil profiles varied with landscape position in the PPR.

MATERIALS AND METHODS

Site Description and Sampling Positions

This study was conducted at the Manitoba Zero Tillage Research Association farm (49°55' N lat; 99°57' W long), located 18-km north of the city of Brandon, MB, Canada from August 2005 through August 2006. Soils at the site are of the Newdale Association (Orthic Black Chernozem in the Canadian Soil Classification System, clay-loam, mixed frigid, udorthentic Haploboroll in the USDA-NRCS system) formed on calcareous glacial tills (Podolsky and Schindler, 1993).

The experimental site was located along a 445 m long transect. Details of the sample positions were described by Dunmola et al. (2010). Briefly, 128 positions were classified into four landscape elements (Upper, Middle, Lower, and Riparian) using digital elevation data. Of the positions, four toposequences on the transect, each with a profile gas sample position for Upper, Middle, Lower, and Riparian landscape elements was selected. The number of sample positions for surface emissions was one per landscape element of each toposequence in 2005 and increased to two in 2006. The Riparian element of one toposequence was not in the transect line with that of the cropped positions (Fig. 1).

In 2005, the Upper, Middle, and Lower landscape elements were planted to Canadian Prairie Spring Red wheat (*Triticum aestivum* L. '5701PR') on May 6th (126 d from 1 Jan. 2005), and fertilized with 67 kg N ha⁻¹ of urea ammonium nitrate (UAN) solution and 7 kg N ha⁻¹ of monoammonium phosphate (MAP) 1 d before planting. In 2006, the field was planted to flax (*Linum usitatissimum* L. 'Bethune') on May 12th (Day 497), with an application of 67 kg ha⁻¹ total N as UAN. In both years, MAP was applied with seed, and UAN solution was side-dribbled on the soil surface beside the seed row. Riparian areas were in landscape depressions with perennial plants such as corn sow thistle (*Sonchus arvensis* L.), bobtail barley (*Hordeum jubatum* L.), Canadian goldenrod (*Solidago canadensis* L.), wheat sedge (*Carex atherodes* Spreng.), eastern line aster [*Symphotrichum lanceolatum* (Willd.) G. L. Nesom], and wheatgrass (*Agropyron* spp.).

Before installation of gas samplers, soil samples were collected from all sampling positions at 0- to 10-, 10- to 20-, 30- to 40-, and 60- to 70-cm depths. Samples were analyzed for bulk density, pH, electrical conductivity (EC), soil texture, extractable concentrations of NH₄⁺-N, NO₃⁻-N, dissolved organic C (DOC), and total organic C (TOC). Bulk density was determined using the soil core method. Soil pH and EC were determined on a 1:2 soil/water suspension. Soil texture was determined by the pipette method (Loveland and Whalley, 1991). Further descriptions of soil analyses are available in Dunmola et al. (2010).

Soil Gas Sampling and Analysis

Monitoring was undertaken in three periods: post-crop (8 Aug. to 12 Nov. 2005 after harvest of spring wheat, Day 220–316), pre-crop (29 Mar. to 12 May 2006 before planting of flax, Day 453–497), and crop (13 May to 3 Aug. 2006 during the flax growing season, Day 498–580). Soil gas samples were collected on four, six, and five occasions in the post-crop, pre-crop and crop periods, respectively. Based on the pattern of surface gas emissions in 2005 at this site (Dunmola et al., 2010), the soil

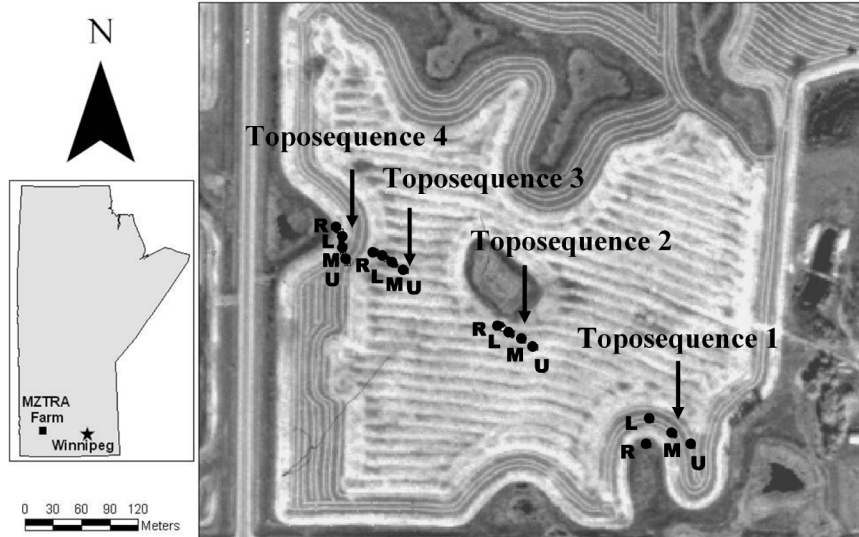


Fig. 1. Aerial photograph of the experimental site at the Manitoba Zero Tillage Research Association (MZTRA) farm showing the location of toposequence sections and landscape element positions of the profile gas samplers and sample positions for determining surface gas emissions. The map to the left shows the location of the site respective to the City of Winnipeg in Manitoba. The gas sample positions were located at the Upper (U), Middle (M), Lower (L), and Riparian (R) landscape elements of the replicate toposequence 1 to 4.

gas samplings were more frequent during spring-thaw and post-fertilizer periods to match N₂O emission episodes.

Soil gas samples were collected using modified silicone diffusive equilibrium samplers of Kammann et al. (2001). The samplers were a 13 cm long peroxide cured silicone tube (13-mm i.d and 17.8-mm o.d.; Cole-Parmer Canada, Anjou, QC) allowing gases, but not water, to pass. To avoid being crushed in soil, the silicone tube was covered with an 18 cm long perforated polyvinyl chloride pipe (19-mm i.d. with 5-mm i.d. holes at 15-mm intervals). One end of the silicone tube was sealed with a silicone rubber septum (Sub-Seal no. 13, Sigma-Aldrich Canada Ltd., Oakville, ON), and the other had a septum connected to a stainless steel tube (1.6-mm i.d. and 2.6-mm o.d.) with a Swagelok sample port fitted with a rubber septum (M-9, Alltech Canada, Mandel Scientific, Guelph, ON).

At each sample position, a soil pit (1 m wide, 0.75 m long, 0.9 m deep) was dug, and horizontal holes were bored to insert the gas samplers at depths of 5, 15, 35, and 65 cm. The pit was backfilled with soil from the same depth. The stainless steel tubes protruded from the soil surface and were covered with protective wooden boards during major field operations (seeding, fertilizer application, herbicide application, and harvesting). Thus, four samplers were installed at each position, for a total of 64 samplers.

Soil gas, as well as atmosphere at the surface (0 cm depth), was collected using a 10-mL syringe and then injected into 6-mL Exetainer vials (Valco Ltd., Buckinghamshire, UK). All vials were previously evacuated and flushed three times with helium to a final pressure ≤0.05 kPa. A low and high reference gas mixture (N₂O, CH₄, and CO₂) spanning the range of expected concentrations of the gases were also added to vials and handled as the gas samples to confirm integrity of samples during storage.

Concentrations (mass fraction in the soil profile) of N₂O (mL L⁻¹), CH₄ (mL L⁻¹), and CO₂ (mL L⁻¹) in sample vials were determined using a Varian CP-3800 (Varian Inc., Mississauga, ON) gas chromatograph equipped with thermal conductivity, flame ionization, and electron capture detectors and a Combi-Pal auto sampler system (CTC Analytics AG., Zwingen, Switzerland). Concentrations of O₂ were determined using a portable gas chromatograph (Varian CP4900, Varian Inc., Mississauga, ON) equipped with a thermal conductivity detector by manually injecting 1 mL of sample gas. Calibration gases were prepared from pure N₂O, CH₄, CO₂, and O₂ by dilution of atmosphere with N₂. Analysis runs were either repeated or the gas chromatograph columns reconditioned and calibration redone if check vials of freshly prepared reference gases placed every 25 samples were off by more than 5% of expected concentration.

Surface Emissions

Surface emissions were determined by a static-vented chamber technique, as previously reported in Dunmola et al. (2010). Briefly, collars made from white polyvinyl chloride (14.7-cm i.d.; 7.5 cm high) with beveled lower edges were inserted 5 cm into the soil at each sample position. Collars were held firmly by three 7/16 in diameter eye bolts fastened to the outer wall and a 15-cm metal spike driven through the eye bolts into the soil. Gas samples (20 mL) were collected using disposable 20-mL plastic syringes at 0, 9, 18, and 27 min and injected into 12-mL Exetainer vials as previously explained. Gas samples were analyzed for N₂O, CH₄ and CO₂ concentrations by gas chromatography and gas emissions calculated with the ideal gas law ($PV = nRT$) from gas concentration, molecular mass of N or C in the gas, chamber area and volume, air temperature, and atmospheric pressure at sampling. Emissions for a chamber were estimated by fitting a linear regression model through at least three of the four sampling points, removing any outlier to achieve a minimum R^2 of 0.85 and $P < 0.001$ (Petersen et al., 2006). Emissions of CO₂ in the current study were from soil heterotrophic and autotrophic respiration as the chambers allowed no penetration of sunlight.

Other Determinations

Soil temperatures were recorded hourly at 5-, 15-, 35-, and 65-cm depths using Type T thermocouples (Cole-Parmer Canada Inc., Montreal, QC) in 2.5-cm o.d. polyvinyl chloride dowels placed in the pit positions. Soil volumetric water content (VWC) at 15- and 35-cm depths was recorded hourly using CS616-L water content reflectometers (Campbell Scientific Canada, Edmonton, AB). In 2006, soil VWC at the 5-cm depth was also measured manually using a Delta-T WET Sensor (Delta-T Devices Ltd., Cambridge, UK) at the time of profile gas sampling. Water-filled pore space (WFPS, %) was calculated using

$$\text{WFPS} = \frac{\text{VWC}}{1 - (\rho_b / \text{PD})} \times 100$$

where ρ_b is the bulk density (Mg m⁻³) of soil determined from core samples, which were taken by driving a metal corer into the soil at 0- to 5-, 10- to 15-, 30- to 35-, and 60- to 65-cm depths, and PD is particle density (assumed 2.65 Mg m⁻³). Daily precipitation and air temperature were obtained from an Environment Canada weather station 3.5 km southeast of the field site.

Soil Gas Content

Contents of N₂O, CH₄, CO₂, and O₂, including both gaseous and aqueous phases, were calculated on a per m² area and per cm depth basis. The gas concentrations at an interval of 1 cm were estimated by linear interpolation of concentration values at the 0-, 5-, 15-, 35-, and 65-cm depths. Gas contents over 0- to 5-, 5- to 15-, 15- to 35-, and 35- to 60-cm layers, as well as total profile (0–65 cm), were calculated. The gaseous contents were calculated from gas concentrations and volume of soil atmosphere, with the latter estimated from VWC and total soil pore space. The aqueous or dissolved contents were calculated knowing the volume of soil water and solubility (Henry's law) constants of 0.882 for N₂O (Tiedje, 1982), 0.042 for CH₄ (Yamamoto et al., 1976), 1.195 for CO₂, and 0.038 for O₂ (Hodgman et al., 1954). The solubility constants of gases are dependent on temperature. In the current study, constants at 10°C were used, as mean soil temperature over the monitoring periods were similar between landscape elements with an average of 10.3°C.

Cumulative profile contents and emissions of N₂O, CH₄, and CO₂ for pre-crop and cropped periods in 2006 were estimated as the summation of their respective daily values. Since soil gas requires transport to the surface, measurement of emissions and concentrations on 1 d may not be related. Thus, cumulative emissions and soil profile contents of GHG were used to remove any time lag between measures. Gap-filling of gas contents and emissions for days with no determinations was done by linear interpolation of values from the day before and after the gap. The cumulative gas content estimates were, thus, used as an assessment of the magnitude and duration of GHG contents that could affect emissions. The post-crop period was not included for cumulative calculations because soil gas contents and emissions after soil freeze-up had not been monitored.

Statistical Analysis

All statistical analyses were performed using SAS 9.0 (SAS Institute, Inc., Cary, NC). Data of soil variables, gas concentrations and contents, cumulative emissions, and cumulative gas contents were tested using PROC MIXED, with landscape element and depth considered fixed effects and block (topo-sequence) as a random effect. Means were compared using the Fisher's protected least significant differences test. The relationship of soil gas contents to surface emissions and soil variables, as well as the relationship of cumulative gas contents to cumulative emissions, were determined by Pearson product moment correlation analysis. Differences were declared significant at $P < 0.05$. Gas content, cumulative gas content, and cumulative surface emission data were log(10) transformed and gas concentration

Table 1. Initial soil characteristics at different landscape elements. Means ± standard error (SE) are presented.

Landscape element	Depth	Bulk density	pH (H ₂ O)	Electrical conductivity	Texture			NH ₄ ⁺ -N	NO ₃ ⁻ -N	Dissolved organic carbon	Total organic carbon
					Sand	Silt	Clay				
	cm	Mg m ⁻³		mS cm ⁻¹	g kg ⁻¹			mg N kg ⁻¹		mg C kg ⁻¹	g C kg ⁻¹
Upper	0–10	1.29 ± 0.03	7.4 ± 0.1	0.26 ± 0.06	360 ± 30	320 ± 40	320 ± 30	4.1 ± 0.3	2.7 ± 0.6	258 ± 13	33 ± 4
	10–20	1.29 ± 0.06	7.5 ± 0.2	0.23 ± 0.05	350 ± 20	300 ± 20	350 ± 10	3.7 ± 0.5	2.3 ± 0.8	226 ± 20	23 ± 3
	30–40	1.27 ± 0.03	7.7 ± 0.2	0.22 ± 0.04	360 ± 10	330 ± 10	310 ± 20	3.1 ± 0.2	1.7 ± 0.5	143 ± 14	11 ± 2
	60–70	1.29 ± 0.08	7.8 ± 0.4	0.29 ± 0.08	380 ± 80	360 ± 50	260 ± 50	3.2 ± 0.3	0.6 ± 0.1	106 ± 17	8 ± 3
Middle	0–10	1.25 ± 0.03	7.6 ± 0.2	0.19 ± 0.02	370 ± 40	310 ± 40	320 ± 20	4.3 ± 0.3	5.1 ± 2.7	244 ± 14	38 ± 3
	10–20	1.33 ± 0.04	7.7 ± 0.2	0.18 ± 0.02	330 ± 30	340 ± 20	330 ± 40	3.7 ± 0.3	3.4 ± 2.1	180 ± 19	23 ± 3
	30–40	1.36 ± 0.06	7.5 ± 0.1	0.32 ± 0.12	270 ± 40	370 ± 20	360 ± 30	2.8 ± 0.2	10.2 ± 9.6	139 ± 13	13 ± 3
	60–70	1.21 ± 0.05	7.7 ± 0.2	0.45 ± 0.13	330 ± 50	300 ± 30	370 ± 10	2.7 ± 0.4	5.1 ± 2.7	120 ± 7	8 ± 1
Lower	0–10	1.20 ± 0.03	7.4 ± 0.1	1.65 ± 0.54	350 ± 40	340 ± 50	310 ± 20	4.6 ± 0.2	7.0 ± 1.2	297 ± 18	37 ± 2
	10–20	1.29 ± 0.05	7.4 ± 0.1	1.36 ± 0.45	360 ± 40	320 ± 30	320 ± 20	3.8 ± 0.2	7.3 ± 5.6	224 ± 30	27 ± 4
	30–40	1.35 ± 0.08	7.5 ± 0.1	1.18 ± 0.42	280 ± 40	390 ± 50	330 ± 20	3.0 ± 0.5	4.6 ± 3.7	150 ± 36	15 ± 4
	60–70	1.27 ± 0.05	7.5 ± 0.1	0.98 ± 0.31	300 ± 20	400 ± 30	300 ± 20	2.7 ± 0.5	4.0 ± 1.8	83 ± 10	7 ± 1
Riparian	0–10	0.87 ± 0.12	7.3 ± 0.1	4.45 ± 1.42	330 ± 10	340 ± 10	330 ± 10	5.5 ± 1.3	8.1 ± 6.2	434 ± 122	55 ± 12
	10–20	1.03 ± 0.13	7.4 ± 0.1	3.71 ± 1.19	290 ± 20	380 ± 50	330 ± 40	4.3 ± 0.7	8.8 ± 7.5	348 ± 77	50 ± 8
	30–40	1.15 ± 0.16	7.4 ± 0.1	2.87 ± 0.93	280 ± 30	420 ± 40	300 ± 20	4.0 ± 0.5	11.1 ± 7.8	294 ± 51	45 ± 7
	60–70	1.23 ± 0.08	7.4 ± 0.1	1.94 ± 0.65	320 ± 40	360 ± 50	320 ± 20	2.9 ± 0.4	2.9 ± 1.4	109 ± 7	9 ± 1

data power transformed to satisfy the requirements of normality (Kolmogorov–Smirnov test) before the above analyses.

RESULTS

Soil Initial Characteristics

Soil initial characteristics varied between landscape elements (Table 1). Across the 0- to 70-cm depth, bulk density tended to be lower at the Riparian than cropped elements. In contrast, the 0- to 70-cm soil EC and concentrations of NO₃⁻, DOC, and TOC were higher at the Riparian element. Across the 0- to 70-cm depth, the pH was similar for all elements with an average of 7.5, and the texture was generally clay loam for all elements with an average of sand 330 g kg⁻¹, silt 350 g kg⁻¹, and clay 320 g kg⁻¹. Bulk density tended to increase with depth at the Riparian element. Soil EC tended to increase with depth at the Middle element but the contrary was observed for Lower and Riparian elements. Extractable NH₄⁺ and NO₃⁻, DOC, and TOC generally decreased with the increasing depth of the soil profile, irrespective of the landscape element.

Weather Conditions

Total rainfall was 63, 67, and 128 mm for the post-crop, pre-crop, and crop periods, compared to 123, 78, and 183 mm for the long-term (1991–2010) normal for the respective periods. Thus, the post-crop period in 2005 and crop period in 2006 were drier while the pre-crop period in 2006 was close to normal. The rainfall events for the pre-crop and crop periods in 2006 were more evenly distributed than the post-crop period in 2005 (Fig. 2). Mean air temperature for the post-crop and pre-crop periods were 9.5 and 9.1°C, being similar to

and approximately 3°C higher than the long-term average for the respective periods. The crop period had a mean air temperature of 18.3°C, being warmer than the long-term normal of 16.8°C.

Soil Temperature and Water Content

Over the study periods, soil temperature was similar between elements. Across elements, soil temperature was higher ($P < 0.001$) at 5 cm than at other depths. For all depths and elements, soil temperature followed the trend of air temperature, with temperature decreasing in the post-crop period, and then increasing following spring-thaw towards the end of the crop period (Fig. 3). The highest soil temperature was consistently observed closest to the surface on Day 552 (6 July 2006). In all elements, soil temperature at 65 cm was close to 0°C through winter while temperature at 5-, 15-, and 35-cm depths were below 0°C.

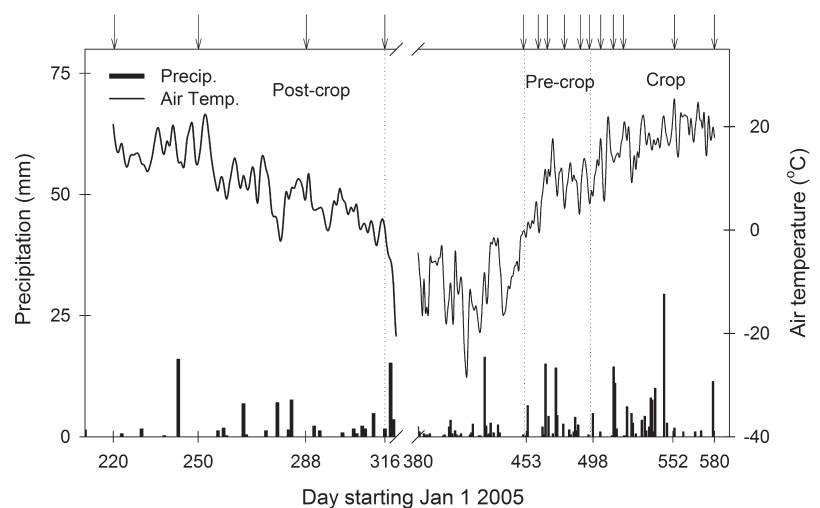
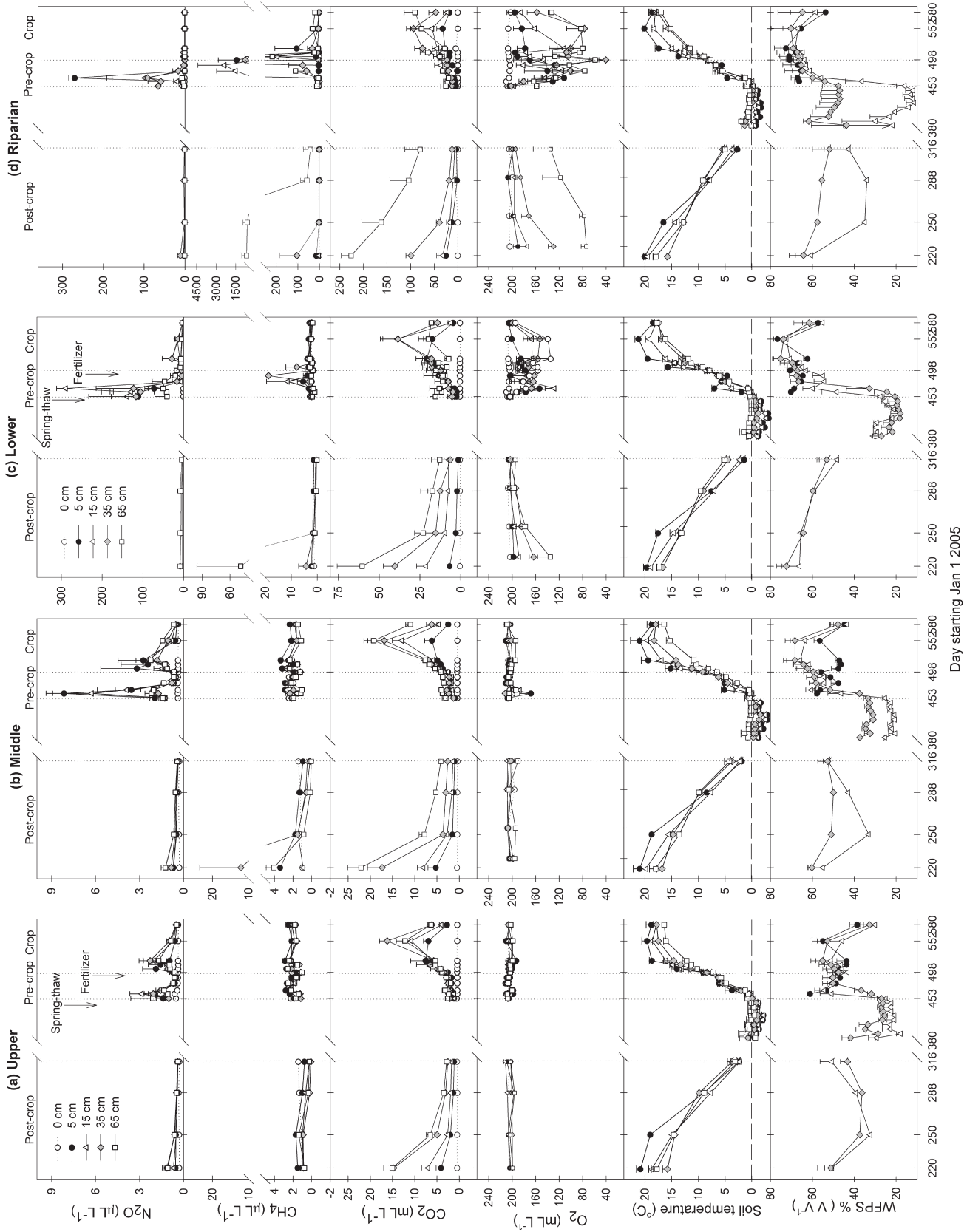


Fig. 2. Daily rainfall and mean daily air temperature for post-crop (Day 220–316), pre-crop (Day 453–497), and crop (Day 498–580) periods. Arrows indicate dates of soil gas sampling.



Day starting Jan 1 2005

Fig. 3. Soil concentrations of N_2O , CH_4 , CO_2 , and O_2 , soil temperature, and water-filled pore space (WFPS) at different soil depths of four landscape elements [(a) Upper, (b) Middle, (c) Lower, and (d) Riparian] in 2005 and 2006. Values shown are the mean plus 1 standard error ($n = 4$). Arrows indicate occurrence of spring-thaw and fertilizer application. Note the different scales of gas concentrations among plots.

For the current study, the onset of spring-thaw refers to soils of all measured depths at temperature rose above 0°C and occurred around Day 450 (26 Mar. 2006) at all elements.

Soil WFPS averaged 45, 52, 61, and 58% v/v in the Upper, Middle, Lower, and Riparian elements, respectively, with values higher ($P < 0.001$) in Lower and Riparian than other elements (Fig. 3). In the post-crop period, WFPS tended to decrease with time in all elements and was generally lower at 15 than 35 cm in the Middle and Riparian elements but not in the other elements. In the pre-crop and crop periods, WFPS tended to be highest near the surface in the Lower and Riparian elements, and the general temporal patterns were similar in all elements. WFPS was lowest through winter, increased following the spring-thaw until Day 552 (6 July 2006), and dropped thereafter.

Concentrations and Contents of Gases in the Soil Profile

O₂

Profile O₂ concentrations averaged 204, 203, 185, and 157 mL L⁻¹ in the Upper, Middle, Lower, and Riparian elements, respectively. The concentrations were lower ($P < 0.001$) in the Riparian than cropped elements, while within cropped elements, they were lower in the Lower than Upper and Middle elements. Generally, soil O₂ decreased with increasing depth, especially in Lower and Riparian elements (Fig. 3).

Soil O₂ concentrations were stable at all depths of the Upper and Middle elements, with values ranging between 180 and 200 mL L⁻¹, except at 5 cm of the Middle element where the concentrations dropped to 160 mL L⁻¹ on Day 461 (6 Apr. 2006). For the Lower and Riparian elements, however, profile O₂ concentrations were initially low in the post-crop period and tended to increase gradually to the atmospheric level. In the pre-crop and crop periods, profile O₂ at the Lower and Riparian elements started to decrease 2 to 3 d following the onset of spring-thaw and thereafter were stable at relatively low levels until Day 552 (6 July 2006). The decrease in concentrations following spring-thaw could likely be due to changes in soil water content by snow melt.

N₂O

Soil N₂O concentrations varied with landscape element, depth, and time. Profile N₂O averaged 1.0, 1.2, 19.7, and 6.2 mL L⁻¹ in the Upper, Middle, Lower, and Riparian elements, respectively, with the concentration being higher ($P < 0.001$) in the Lower than other elements while there was no difference between the other elements. Generally, soil N₂O increased from the surface to the 15- or 35-cm depth and then decreased towards 65 cm (Fig. 3).

Soil N₂O concentrations were relatively low in the post-crop compared to the other two periods, with background values below 1.2 mL L⁻¹ in the Upper and Middle elements, and below 11.1 mL L⁻¹ in the Lower and Riparian elements. In all elements, the N₂O concentrations throughout the soil profile were elevated at onset of spring-thaw and peaked during Days 461 to 467 (6–12 Apr. 2006), with a maximum concentration of

289 mL L⁻¹ at 15 cm in the Lower element on Day 467 (12 Apr. 2006). Thereafter, N₂O concentrations in all elements decreased rapidly to near atmospheric level by Day 489 (4 May 2006). In all cropped elements, concentration peaked 1 to 3 wk following fertilizer application while the magnitude especially in the Lower element was small compared to the peak following spring-thaw.

Similar to N₂O concentrations, the temporal changes in soil profile (0–65 cm) N₂O contents varied with landscape element (Fig. 4). Spring-thaw resulted in accumulation of N₂O in both the Lower and Riparian elements with maximum profile content occurring on Day 467 (12 Apr. 2006), reaching 44.0 and 28.7 mg N m² for Lower and Riparian, respectively. Profile N₂O contents in the Lower element also increased approximately 3 wk following fertilizer application, reaching 5.7 mg N m² on Day 518 (2 June 2006). High accumulations of N₂O in the soil profiles of the Lower and Riparian elements were associated with soil conditions. In the Lower element, profile N₂O content was associated positively ($r = 0.88$) with profile O₂ content and negatively ($r = -0.49$ to -0.94) with the WFPS and temperature at all measured depths (Table 2). Also in the Riparian element, profile N₂O content was negatively ($r = -0.53$ to -0.71) associated with soil temperature.

CH₄

Soil CH₄ concentrations also varied with landscape element, depth, and time. Profile CH₄ averaged 1.7, 2.0, 3.3, and 131 mL L⁻¹ in the Upper, Middle, Lower, and Riparian elements, respectively, with the concentrations being higher ($P = 0.014$) in the Riparian than cropped elements. Generally, soil CH₄ tended to increase from the surface to 15 cm and then decreased towards the 65-cm depth, and this trend was more evident in the Lower and Riparian than other elements (Fig. 3).

In the post-crop period, initial soil CH₄ concentrations were high at 35 or 65 cm in all except the Upper element. Concentrations then decreased to atmospheric background level by Day 250 (7 Sept. 2005) in the Middle and Lower elements and by Days 288 to 316 (15 Oct. to 12 Nov. 2005) in the Riparian element. In the pre-crop period, concentrations in the Lower and Riparian but not the other elements started to increase on Day 466 (11 Apr. 2006), approximately 15 d after onset of the spring-thaw, and then peaked on Days 480 to 489 (25 Apr. to 4 May 2006), approximately 10 to 20 d after occurrence of peak soil N₂O. The highest CH₄ concentration of 2366 mL L⁻¹ occurred at 15 cm in the Riparian element. Thereafter, CH₄ concentrations in the Lower and Riparian elements then decreased to atmospheric background level by Days 518 to 552 (2 June to 6 July 2006) in the crop period.

The profile CH₄ content increased only in the Riparian element following spring-thaw, reaching 43.6 mg C m⁻² on Day 489 (4 May 2006) (Fig. 4). In contrast, profile CH₄ contents were negligible for all cropped elements. Accordingly, the profile O₂ content was negatively ($r = -0.64$) associated with profile CH₄ content for only the Riparian element (Table 2). The WFPS at the 15-cm depth was associated with profile CH₄ content either positively for the Upper element or negatively for the

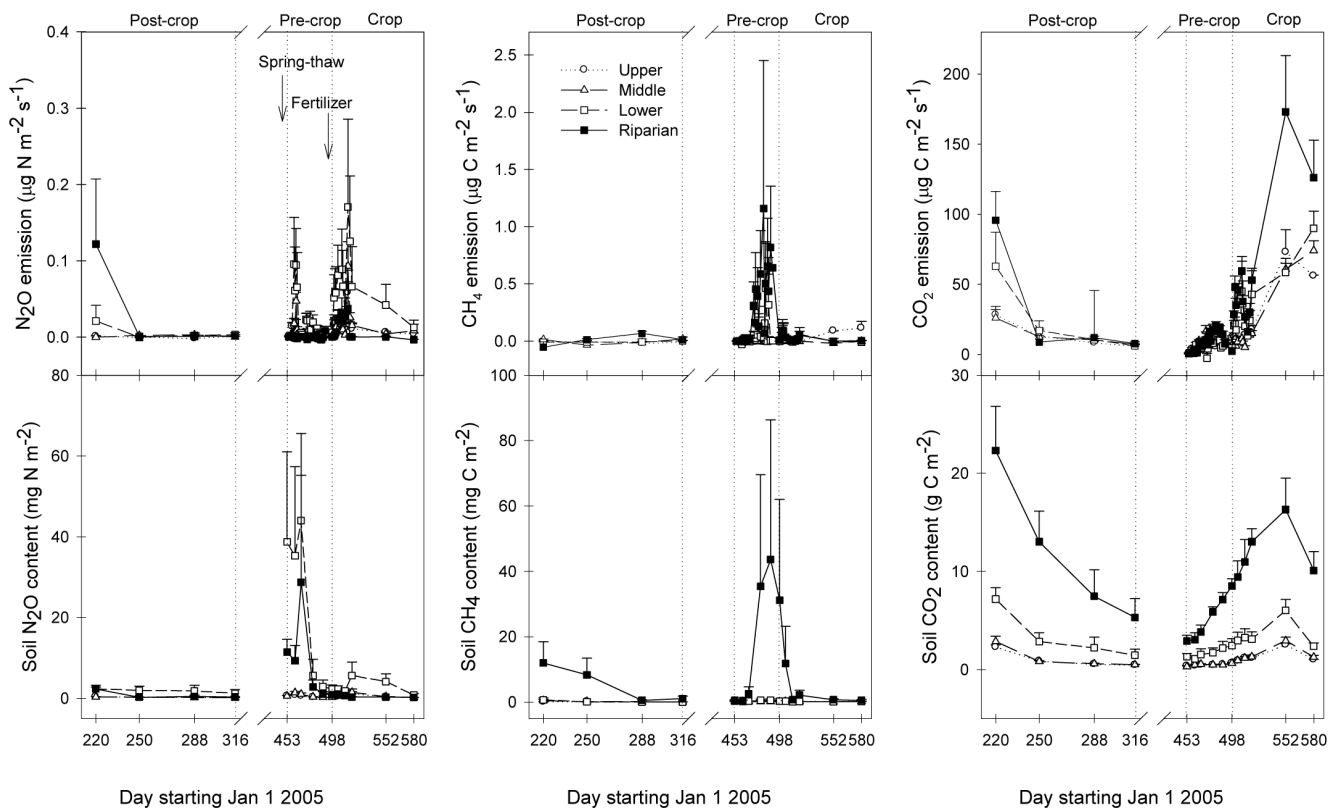


Fig. 4. Soil (0–65 cm) content and surface emission rate of N_2O , CH_4 , and CO_2 for four landscape elements (Upper, Middle, Lower, and Riparian) in 2005 and 2006. Values shown are the mean plus 1 standard error ($n = 8$ for surface emission and $n = 4$ for soil gas content). Arrows indicate occurrence of spring-thaw and fertilizer application.

Lower element. When all the landscape elements were considered, profile CH_4 content was negatively ($r = -0.55$) associated with profile O_2 content and weakly positively ($r = 0.25$ – 0.29) with the WFPS.

CO_2

Soil CO_2 concentrations also varied with landscape element, depth, and time. Profile CO_2 averaged 3.6, 4.0, 11.3, and 36.1 mL L^{-1} in the Upper, Middle, Lower, and Riparian elements, respectively. The concentrations were higher ($P < 0.001$) in the Riparian than cropped elements. Generally, CO_2 concentrations increased with depth irrespective of element (Fig. 3).

In contrast to N_2O and CH_4 , the temporal changes for profile CO_2 content were similar for all elements, following a trend of gradually declining through the post-crop period, then increasing after the spring-thaw towards Day 552 (6 July 2006), and thereafter declining (Fig. 4). In all elements, peak concentrations occurred at 65 cm on Day 220 (8 Aug. 2005), being 15, 22, 61, and 226 mL L^{-1} for the Upper, Middle, Lower, and Riparian elements, respectively. Soil temperature at all depths, as well as soil NH_4^+ concentration, was strongly and positively ($r = 0.74$ – 0.95) associated with profile CO_2 content for all landscape elements (Table 2). Only for the Lower element was profile CO_2 content negatively ($r = -0.56$) associated with profile O_2 content, and positively ($r = 0.45$) with the WFPS at 15 cm. When all the landscape elements were considered, profile CO_2 content

was positively associated with soil temperature, the WFPS at 35 cm, and NH_4^+ concentration.

Relation of Soil Profile GHG Contents to Surface Emissions

Accumulation of profile N_2O in the Lower element following spring-thaw coincided with increasing emissions (Fig. 4). In contrast, N_2O accumulation in the Riparian element following spring-thaw did not result in an increase in emissions. Profile N_2O accumulations in the Lower element following fertilizer application coincided with an even higher emission peak than that following spring-thaw. For the Upper and Middle elements, profile N_2O contents and emissions were negligible.

Accumulation of CH_4 in the soil profile of the Riparian element following spring-thaw coincided with increasing emissions. In contrast, profile CH_4 contents and emissions were negligible for all cropped elements. There was a noticeable time lag for accumulations between N_2O and CH_4 in the Riparian element. Increased profile N_2O content occurred with the first measurement on Day 453 (29 Mar. 2006), approximately 2 to 3 d following the onset of spring-thaw whereas CH_4 increased later on Day 467 (12 Apr. 2006). Accordingly, peak accumulation for CH_4 was approximately 13 to 14 d later than that for N_2O .

The temporal trend of CO_2 emissions was similar to that of its contents in the soil profile, except a small emission event occurred in the Lower and Riparian elements on Day 507 (22 May 2006) when CO_2 content did not change.

Across the elements, emissions of the gases increased steadily with cumulative gas contents (Fig. 5). For N₂O in the Lower element and CH₄ in the Riparian element, however, the relationships were highly dependent on one replicate measurement, which had extremely high accumulations of gases and cumulative emissions. Such high dependency was also confirmed by correlation analysis between soil gas contents and emissions (Table 3). Across all elements, contents of CH₄ and CO₂, but not N₂O, across the depth intervals and over the 0- to 60-cm profile were positively associated with emissions. Such association for CH₄ was predominantly for the Riparian element whereas association for CO₂ was observed for all elements. Beyond our expectation, soil profile O₂ contents was not associated with CH₄ emissions in any element though negatively ($r = -0.29$ to -0.52) with N₂O emissions for the Upper and Middle elements.

DISCUSSION

The current study demonstrated that soil conditions at landscape elements influenced where and when GHG accumulated in the soil profile and if GHG emissions occurred. Higher GHG emissions from Lower landscape elements have been reported for other study locations (Sehy et al., 2003; Pennock et al., 2010; Gacengo et al., 2009) as well previously from this current study site (Dunmola et al., 2010). In the current study, high emissions of N₂O and CH₄ from Lower and Riparian elements were relegated to spring-thaw and post-fertilizer periods during accumulation of these gases in the soil profile. However, the amount of accumulation of N₂O and CH₄ did not always relate to the occurrence or magnitude of the emissions. Emissions were, thus, affected by accumulation and apparent consumption of N₂O and CH₄ associated with soil conditions (i.e., elevated moisture, reduced temperature, and decreased aeration) in the profile.

Accumulation of N₂O and CH₄ During Spring-thaw

Nitrous oxide has been shown to accumulate in soil profiles during the thawing of soil (Burton and Beauchamp, 1994; van Bochove et al., 2000; Risk et al., 2014). In the current study, the amount of N₂O accumulation during thawing of soil varied with landscape element. A two order of magnitude greater concentration and soil profile content of N₂O in the Lower and Riparian elements relative to the Upper and Middle elements highlighted the importance of soil moisture in determining N₂O accumulation. Soil thawing in the Lower and Riparian elements had increased the WFPS to approximately 70% and decreased soil O₂ concentration. Bateman and Baggs (2005) found denitrification to be the sole source of N₂O emissions in a silt loam soil at 70% WFPS. For the current study, increasing soil moisture and decreasing O₂ could have resulted in anaerobic conditions at the Lower and Riparian elements and, thus, stimulated denitrification. This is consistent with findings from a laboratory incubation study (Tenuta and Sparling, 2011) and a field study using ¹⁵N tracers (Wagner-Riddle et al., 2008) that identified denitrification of soil NO₃⁻ as the main contributor to N₂O production and consumption during soil thawing.

Besides the newly produced N₂O by denitrification, the accumulation of N₂O during spring-thaw could also be attributed to the N₂O produced during freezing, trapped below an ice layer, and released at thaw (van Bochove et al., 2000). The current experiment does not distinguish between the two

Table 2. Pearson correlation coefficients for soil profile (0–65 cm) content of N₂O, CH₄, CO₂, with soil variables over post-crop, pre-crop, and crop periods.

Soil variables	Profile gas content at landscape elements														
	Upper			Middle			Lower			Riparian			All elements		
	N ₂ O	CH ₄	CO ₂	N ₂ O	CH ₄	CO ₂	N ₂ O	CH ₄	CO ₂	N ₂ O	CH ₄	CO ₂	N ₂ O	CH ₄	CO ₂
Profile O ₂ content	-†	-	-	-	-	-	0.88***	-	-0.56*	-	-0.64**	-	-	-0.55*	-0.64**
WFPS ₁₅	-	0.65**	-	-	-	-	-0.47*	-0.49*	0.45*	-	-	-	-	0.25*	-
WFPS ₃₅	-	-	-	-	-	-	-0.94*	-	-	-	-	-	-0.30*	0.29*	0.38**
Temp ₅	-	-	0.81***	-	0.74***	-	-0.49*	-	0.77***	-	-0.53*	-	0.92***	-	0.31**
Temp ₁₅	-	-	0.83***	-	0.77***	-	-0.64**	-	0.83***	-	-0.62**	-	0.94***	-	0.35**
Temp ₃₅	-	-	0.75***	-	0.68**	-	-0.77***	-	0.80***	-	-0.71**	-	0.92***	-	0.28*
Temp ₆₅	-	-0.58**	0.81***	-	0.75***	-	-0.74***	-	0.83***	-	-0.68**	-	0.95***	-	0.39*
NO ₃ ⁻	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-0.26*
NH ₄ ⁺	-	-	0.89***	-	0.87***	-	-	-	0.89***	-	-	-	0.83***	-	0.65***

* Indicates significance at $P = 0.05$.

** Indicates significance at $P = 0.01$.

*** Indicates significance at $P = 0.001$.

† The symbol - indicates nonsignificance at $P > 0.05$.

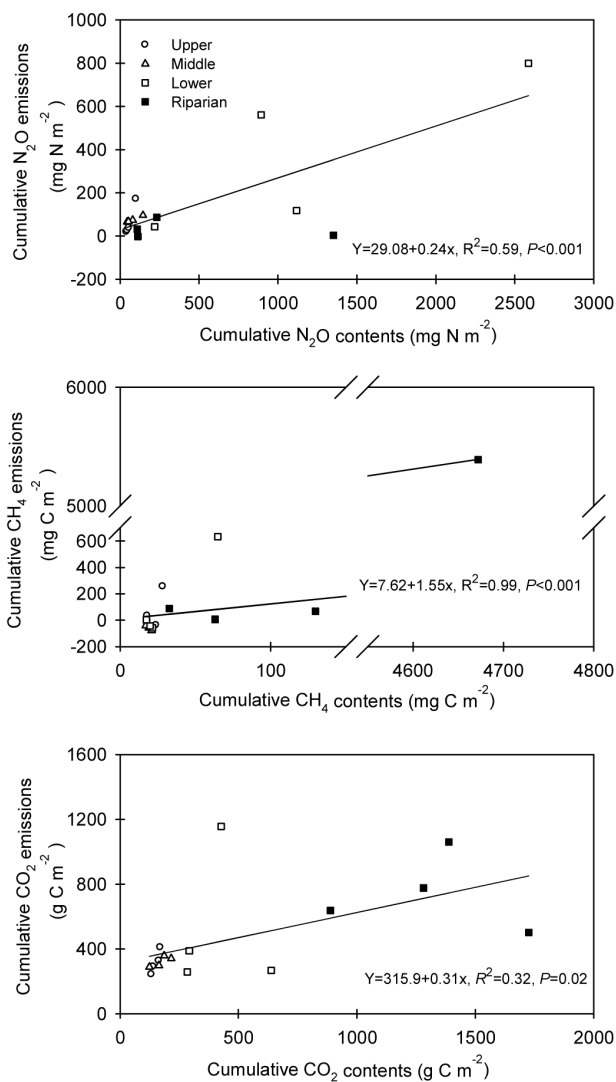


Fig. 5. Relationship between cumulative emissions and soil (0–65 cm) cumulative gas contents of N₂O, CH₄, and CO₂ over pre-crop and crop periods in 2006.

sources due to the absence of measures over winter. Risk et al. (2014) compared soil profile N₂O concentration with surface emissions during spring-thaw on an agricultural field in Ontario and found that soil N₂O accumulation over winter contributed up to a quarter of emissions for the first spring-thaw event.

The Riparian element was the only landscape position showing high accumulations of CH₄ following spring-thaw, which occurred after that for N₂O. Further, N₂O accumulation did not coincide with a surface emission event. These results suggest that prolonged anaerobic conditions following thawing in the Riparian element had promoted complete denitrification of N₂O to N₂ and methanogenic CH₄ production. This assertion is supported by observation of decreasing soil O₂ concentrations and increasing WFPS following soil thawing as well as the negative relationship between O₂ content and CH₄ content in the soil profile. Similarly, Maljanen et al. (2007) found in a boreal agriculture soil that CH₄ concentrations remained low during winter and only increased after soil thawed. Without measuring changes in soil CH₄, Hargreaves et al. (2001) attributed CH₄

emissions following spring-thaw in a mire in Finnish Lapland to the release of CH₄ trapped in frozen soil over winter. For the current study, however, the accumulation of CH₄ mainly occurred in the 0- to 15-cm depth following thaw for the Riparian element. Thus, the emission of CH₄ following thaw in that element was concurrent with de novo methanogenesis rather than over-winter accumulation of the gas.

Accumulation of N₂O Following Fertilizer Application

Numerous studies have reported increased N₂O emissions from soils receiving application of synthetic N fertilizers, but few have linked emissions to the production of gaseous or aqueous N₂O contents in the soil profile. Results of the current study showed that the post-fertilizer emissions were largely associated with the accumulation of N₂O in soils. The greater N₂O concentration and soil profile contents at the Lower than other cropped elements suggested soil moisture stimulated N₂O production. Similarly, for fertilized grassland on the Swiss plateau, high N₂O concentrations in the soil profile were observed following precipitation after fertilizer addition (Schmid et al., 2001). Granli and Bockman (1994) proposed that increasing soil moisture up to 60% WFPS can enhance both nitrification and denitrification. Increasing soil moisture post-fertilizer application may also stimulate the hydrolysis of the fertilizer and, thus, provides more available inorganic N sources for nitrification and denitrification. Following application of ¹⁵N-labelled fertilizer, Bateman and Baggs (2005) demonstrated denitrification was the sole source of N₂O emissions from a silt loam soil at 70% WFPS while nitrification predominated between 35 and 60% WFPS. Tenuta and Beauchamp (2003) also found nitrification proceeded denitrification as WFPS decreased from 65% to less than 50% following granular N fertilizer additions in laboratory experiments. For the current study, soil WFPS post fertilizer application was approximately 70% for the Lower element and between 40 and 60% for the Upper and Middle elements. Also, soil profile O₂ concentrations were approximately 130 to 180 mL L⁻¹ at the Lower element but at atmospheric concentration for the Upper and Middle elements. Nitrifier-denitrification, the reduction of NO₂⁻ by nitrifiers, is promoted under intermediate O₂ concentrations (Kool et al., 2011). Thus, greater N₂O accumulation and emissions post-fertilizer application for the Lower than other elements was likely due to enhanced denitrification.

The concentrations and soil profile contents of N₂O at the Lower element post-fertilizer were rather small relative to that during spring-thaw, yet emissions were greater for the former. This is consistent with N₂O accumulation near the surface (0–5 cm) following fertilizer application whereas accumulation occurred at greater depth (15–35 cm) in the profile during spring-thaw. Van Groenigen et al. (2005) also reported but for a sandy soil with shallow water tables that high subsoil N₂O concentrations during frost-thaw cycles did not lead to high surface emissions. A combination of high N₂O concentrations at depth in the soil profile with low surface emissions during spring-thaw could

Table 3. Pearson correlation coefficients for surface emissions of N₂O, CH₄ and CO₂ with soil content of N₂O, CH₄, CO₂, and O₂ at different soil depths over post-crop, pre-crop and crop periods.

Soil content	Gas emissions at landscape elements														
	Upper			Middle			Lower			Riparian			All elements		
	N ₂ O	CH ₄	CO ₂	N ₂ O	CH ₄	CO ₂	N ₂ O	CH ₄	CO ₂	N ₂ O	CH ₄	CO ₂	N ₂ O	CH ₄	CO ₂
N ₂ O															
0–5 cm	0.59***	–†	–	–	–	–0.27*	–	–	–	–	–	–	–	–	–
5–15 cm	0.57***	–	–	–	–	–0.26*	–	–	–	–	–	–	–	–	–
15–35 cm	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
35–65 cm	–	–	–	0.28*	–	–	–	–	–	–	–	–0.30*	–	–	–
0–65 cm	0.41***	–	–	–	–	–	–	–	–	–	–	–	–	–	–
CH ₄															
0–5 cm	–	–	–	–	–	–	0.33**	–	–	0.76***	–	–	0.75***	–	–
5–15 cm	–	–	–	–	–	–	0.42***	–	–	0.89***	–	–	0.89***	–	–
15–35 cm	–	0.28*	–	–	–	–	0.33**	–	–	0.90***	–	–	0.90***	–	–
35–65 cm	–	–	–	–	–	–	–	–	–	–	–	–	0.16**	–	–
0–65 cm	–	–	–	–	–	–	–	–	–	0.84***	–	–	0.84***	–	–
CO ₂															
0–5 cm	0.67***	–	0.38*	–	–	0.30*	–	0.46***	–	0.75***	–	0.56***	0.35***	0.28***	0.51***
5–15 cm	0.28*	–	0.52***	–	–	0.44***	–	–	0.32*	0.62***	–	0.53***	0.28***	0.29***	0.53***
15–35 cm	–	–	0.49***	–	–	0.39**	–	–	0.26*	0.53***	–	0.41***	0.24***	–	0.54***
35–65 cm	–	–	0.37**	–	–	0.36***	–	–	–	0.29*	–	–	0.18**	–	0.39***
0–65 cm	–	–	0.43***	–	–	0.38***	–	–	–	0.37**	–	0.24*	0.22***	–	0.47***
O ₂															
0–5 cm	–0.29*	–	–	–	–	–	–	–	–	–	–	–	–	–	–0.15*
5–15 cm	–0.46***	–	–	–0.31*	–0.28*	–	–	–	–	–	–	–	–0.14*	–	–0.17**
15–35 cm	–0.48***	–	–	–0.42***	–	–	–	–	–	–	–	–	–0.16**	–	–0.29***
35–65 cm	–0.52***	–	–0.27*	–0.41***	–	–	–	–	–0.34**	–	–	–	–0.17**	–	–0.34***
0–65 cm	–0.51***	–	–	–0.42***	–	–	–	–	–0.28*	–	–	–	–0.17**	–	–0.31***

* Indicates significance at $P = 0.05$.

** Indicates significance at $P = 0.01$.

*** Indicates significance at $P = 0.001$.

† The symbol – indicates nonsignificance at $P > 0.05$.

be due to anaerobic conditions near the soil surface resulting in N₂O reduction to N₂. This is also confirmed by the fact that a time lag between accumulation of N₂O and emissions occurred during spring-thaw but not following fertilizer application in the current study. Under both field (Wagner-Riddle et al., 2008) and lab (Tenuta and Sparling, 2011) conditions, emissions following N fertilization were attributed to presence of NO₃[–] in surface (0–10 cm) soils, rather than to deeper soils. In the current study, fertilizer N was surface dribble-applied and N₂O produced near the soil surface (0–10 cm) could be transported rapidly to the soil surface. Therefore, N₂O emissions from agricultural fields may be reduced by limiting N availability in the surface layer, such as applying fertilizer at deeper depths or minimizing fall residual N in surface soils.

Relationship Between Soil Profile Accumulation and Emission

Though there were positive relationships between cumulative surface emissions and cumulative gas contents of N₂O and CH₄ in the soil profile, they were largely dependent on a few replicates that had relatively high values. This suggests that soil gas storage is not the primary factor driving surface emissions.

Brummell et al. (2012) also found no association between soil N₂O and CH₄ concentrations and surface emissions at a high arctic polar oasis. They also reported poor prediction of emissions based on soil gas concentration profiles and estimated soil diffusivity, a finding we also concluded using the dataset of this current study (Rajendran, 2009). The weak relationship could be an inaccuracy of estimating diffusivity by empirical models relative to that measured by experimental methods (van Bochove et al., 1998). However, it is more likely that the consumption of N₂O during transport to the soil surface results in the lack of relation of N₂O in soil and surface emission, during periods of high water content.

Compared to N₂O and CH₄, the relationship for CO₂ emissions and soil profile contents was more robust, as demonstrated by the positive relationships between surface emissions and contents across individual depth intervals or in the profile (0–65 cm). Both surface emissions and contents showed a highly significant dependence on temperature. A number of field and laboratory studies with soils under natural vegetation also reported coherence of soil accumulations and emissions of CO₂ closely followed temperature (Grogan et al., 2004; Groffman et al., 2006). Risk et al. (2008) also reported consistent and close

correlation between emissions and CO₂ production estimated by site-specific diffusivity measurements across eight experimental sites with varying soil water contents. The more robust relationship for CO₂ than the other two gases may reflect the role of the biological sinks for N₂O and CH₄ in the soil profile, which is not present in soil for CO₂. Additionally, soil respiration occurs over a broader range of redox conditions whereas N₂O and CH₄ production and consumption occur only over a specific range in redox (Smith et al., 2003).

CONCLUSIONS

This study examined the temporal and spatial variation of soil profile GHG contents in relation to emissions in four landscape elements in the PPR. The major emission events for N₂O and CH₄ occurred following spring-thaw and fertilizer application under anaerobic conditions of the Lower and Riparian elements while emissions and contents of CO₂ in the soil profile of all elements corresponded to soil temperature. Thawing of soil in spring increased N₂O accumulations at both the Lower and Riparian elements, but emissions occurred for only the former. This suggests N₂O was likely reduced to N₂ in the soil profile under prolonged anaerobic conditions in the Riparian element. Addition of synthetic N fertilizer resulted in N₂O accumulations and emissions from the cropped elements, with those in the Lower being an order of magnitude greater than those in the Upper and Middle elements. Local soil conditions, that is, high WFPS (approximately 70%) and low O₂ concentration (130–180 mL L⁻¹) in the Lower element indicated that denitrification was likely the source of accumulation and emissions of N₂O. Compared to spring-thaw, the addition of N fertilizer to the soil surface resulted in less N₂O accumulation in the soil profile but higher emissions from the Lower element. Greater distance for vertical transport as indicated by a deeper profile accumulation for spring-thaw than fertilizer addition, as well as increased WFPS during thawing of soil, likely further reduced N₂O to N₂. This likely accounted for the lower emissions of N₂O at spring-thaw than following surface addition of fertilizer N. Emissions of CH₄ occurred only in the Riparian element following spring-thaw and during CH₄ accumulation and decreasing O₂ concentration in soil. This suggested development of anaerobic conditions and resulting *de novo* methanogenesis being the source of emissions.

Generally, the accumulation of GHG in soil profiles varied with the landscape element reflecting differences in the biophysical factors controlling production and consumption and determining surface emissions. The results of the current study indicate that N₂O emissions from cropped depression areas could be achieved by shifting N₂O production from the near soil surface to lower in the profile. Whether or not subsurface rather than surface placement of synthetic fertilizer N can promote N₂O reduction to decrease emissions requires investigation. Also, promotion of aeration to encourage CH₄ consumption in the soil surface, by practices such as drainage and tillage in cropped depressions, warrants examination of lower CH₄ emissions in wet years.

ACKNOWLEDGMENTS

Funding for this project was provided by the Natural Science and Engineering Research Council Strategic and Discovery Grant Programs, BIOCAP, Ducks Unlimited Canada, the Canada Research Chair Program in Applied Soil Ecology, and the Agricultural Greenhouse Gas Program of Agriculture and Agri-Food Canada. The assistance of Dr. David Lobb in establishing the study site and staff of the Manitoba Zero Tillage Research Association farm in field operations is greatly appreciated. Technical support by Mervin Bilous, Robert Ellis, Bo Pan, Brad Sparling, and Tim Stem is appreciated.

REFERENCES

- Bateman, E.J., and E.M. Baggs. 2005. Contributions of nitrification and denitrification to N₂O emissions from soils at different water-filled pore space. *Biol. Fertil. Soils* 41:379–388. doi:10.1007/s00374-005-0858-3
- Beauchamp, E.G. 1997. Nitrous oxide emission from agricultural soils. *Can. J. Soil Sci.* 77:113–123. doi:10.4141/S96-101
- Sharratt, B., G. Benoit, J. Daniel, and J. Staricka. 1999. Snow cover, frost depth and soil water across a Prairie Pothole landscape. *Soil Sci.* 164:483–492. doi:10.1097/00010694-199907000-00004
- Brummell, M.E., R.E. Farrell, and S.D. Siciliano. 2012. Greenhouse gas soil production and surface fluxes at a high arctic polar oasis. *Soil Biol. Biochem.* 52:1–12. doi:10.1016/j.soilbio.2012.03.019
- Burton, D.L., and E.G. Beauchamp. 1994. Profile nitrous oxide and carbon dioxide concentrations in a soil subject to freezing. *Soil Sci. Soc. Am. J.* 58:115–122. doi:10.2136/sssaj1994.03615995005800010016x
- Conrad, R. 1996. Soil microorganisms as controllers of atmospheric trace gases (H₂, CO, CH₄, OCS, N₂O and NO). *Microbiol. Rev.* 60:609–640.
- Dunmola, A.S., M. Tenuta, A.P. Moulin, P. Yapa, and D.A. Lobb. 2010. Pattern of greenhouse gas emission from a Prairie Pothole agricultural landscape in Manitoba, Canada. *Can. J. Soil Sci.* 90:243–256. doi:10.4141/CJSS08053
- Gacengo, C.N., C.W. Wood, J.N. Shaw, R.L. Raper, and K.S. Balkcom. 2009. Agroecosystem management effects on greenhouse gas emissions across a coastal plain Catena. *Soil Sci.* 174:229–237. doi:10.1097/SS.0b013e31819f5fce
- Granli, T., and O.C. Bockman. 1994. Nitrous oxide from agriculture. *Nor. J. Agric. Sci.* 12:1–128.
- Groffman, P.M., J.P. Hardy, C.T. Driscoll, and T.J. Faheys. 2006. Snow depth, soil freezing, and fluxes of carbon dioxide, nitrous oxide and methane in a northern hardwood forest. *Glob. Change Biol.* 12:1748–1760. doi:10.1111/j.1365-2486.2006.01194.x
- Grogan, P., A. Michelsen, P. Ambus, and S. Jonasson. 2004. Freeze-thaw regime effects on carbon and nitrogen dynamics in sub-arctic heath tundra mesocosms. *Soil Biol. Biochem.* 36:641–654. doi:10.1016/j.soilbio.2003.12.007
- Hargreaves, K.J., D. Fowler, C.E.R. Pitcairn, and M. Aurela. 2001. Annual methane emission from Finnish mires estimated from eddy covariance campaign measurements. *Theor. Appl. Climatol.* 70:203–213. doi:10.1007/s007040170015
- Hodgman, C.D., R.C. Weast, and C.W. Wallace. 1954. *Handbook of Chemistry and Physics*. 35th ed. Chemical Rubber Publishing Co., Cleveland, Ohio.
- Kammann, C., L. Grünhage, and H.J. Jäger. 2001. A new sampling technique to monitor concentrations of CH₄, N₂O and CO₂ in air at well-defined depths in soils with varied water potential. *Eur. J. Soil Sci.* 52:297–303. doi:10.1046/j.1365-2389.2001.00380.x
- Kool, D.M., J. Dolfing, N. Wrage, and J.W. van Groenigen. 2011. Nitrifier denitrification as a distinct and significant source of nitrous oxide from soil. *Soil Biol. Biochem.* 43:174–178. doi:10.1016/j.soilbio.2010.09.030
- Le Mer, J., and P. Roger. 2001. Production, oxidation, emission and consumption of methane by soils: A review. *Eur. J. Soil Biol.* 37:25–50. doi:10.1016/S1164-5563(01)01067-6
- Loveland, P.J., and W.R. Whalley. 1991. Particle size analysis. In: K.A. Smith and C.E. Mullins, editors, *Soil analysis: Physical methods*. Marcel Dekker, Inc., New York, p. 271–328.
- Maljanen, M., A.R. Kohonen, P. Virkajärvi, and P.J. Martikainen. 2007. Fluxes and production of N₂O, CO₂ and CH₄ in boreal agricultural soil during winter as affected by snow cover. *Tellus* 59:853–859. doi:10.1111/j.1600-0889.2007.00304.x
- Pennock, D., T. Yates, A. Bedard-Haughn, K. Phipps, R. Farrell, and R.

- McDougal. 2010. Landscape controls on N₂O and CH₄ emissions from fresh water mineral soil wetlands of the Canadian Prairie Pothole region. *Geoderma* 155:308–319. doi:10.1016/j.geoderma.2009.12.015
- Petersen, S.O., K. Regina, A. Pöllinger, E. Rigler, L. Valli, S. Yamulki, M. Esala, C. Fabbri, E. Syväsalö, and F.P. Vinther. 2006. Nitrous oxide emissions from organic and conventional crop rotations in five European countries. *Agric. Ecosyst. Environ.* 112:200–206. doi:10.1016/j.agee.2005.08.021
- Phillips, R., and O. Beerli. 2008. The role of hydrogeologic vegetation zones in greenhouse gas emissions for agricultural wetland landscapes. *Catena* 72:386–394. doi:10.1016/j.catena.2007.07.007
- Podolsky, G.P., and D. Schindler. 1993. Soils of the Manitoba Zero Tillage Research Association Farm. Manitoba Land Resource Unit, Agriculture and Agri-Food Canada, Univ. of Manitoba, Winnipeg, Canada.
- Rajendran, N. 2009. Dynamics of profiles of soil greenhouse gases in a topographically variable landscape in Western Canada. M.Sc. thesis, Univ. of Manitoba, Winnipeg, Canada.
- Risk, D., L. Kellman, and H. Beltrami. 2008. A new method for in situ soil gas diffusivity measurement and applications in the monitoring of subsurface CO₂ production. *J. Geophys. Res.* 113:G02018.
- Risk, N., C. Wagner-Riddle, A. Furon, J. Warland, and C. Blodau. 2014. Comparison of simultaneous soil profile N₂O concentration and surface N₂O flux measurements overwinter and at spring thaw in an agricultural soil. *Soil Sci. Soc. Am. J.* 78:180–193.
- Schmid, M., J. Fuhrer, and A. Neftel. 2001. Nitrous oxide concentrations in the soil of a mown grassland: Comparison of model results with soil profile measurements. *Water Air Soil Pollut.* 1:436–447.
- Sehy, U., R. Ruser, and J.C. Munch. 2003. Nitrous oxide fluxes from maize fields: Relationship to yield, site-specific fertilization, and soil conditions. *Agric. Ecosyst. Environ.* 99:97–111. doi:10.1016/S0167-8809(03)00139-7
- Smith, K.A., T. Ball, F. Conen, K.E. Dobbie, J. Massheder, and A. Rey. 2003. Exchange of greenhouse gases between the soil and atmosphere: Interactions of soil physical factors and biological processes. *Eur. J. Soil Sci.* 54:779–791. doi:10.1046/j.1351-0754.2003.0567.x
- Tenuta, M., and E.G. Beauchamp. 2003. Nitrous oxide production from granular nitrogen fertilizers applied to a silt loam soil. *Can. J. Soil Sci.* 83:521–532. doi:10.4141/S02-062
- Tenuta, M., and B. Sparling. 2011. A laboratory study of soil conditions affecting emissions of nitrous oxide from packed cores subjected to freezing and thawing. *Can. J. Soil Sci.* 91:223–233. doi:10.4141/cjss09051
- Tiedje, J. 1982. Denitrification. In: A.L. Page., editor, *Methods of soil analysis*. Part 2. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI. p. 1011–1026.
- van Bochove, E., N. Bertrand, and J. Caron. 1998. In situ estimation of the gaseous nitrous oxide diffusion coefficient in a sandy loam soil. *Soil Sci. Soc. Am. J.* 62:1178–1185. doi:10.2136/sssaj1998.03615995006200050004x
- van Bochove, E., D. Prevost, and F. Pelletier. 2000. Effects of freeze-thaw and soil structure on nitrous oxide produced in a clay soil. *Soil Sci. Soc. Am. J.* 64:1638–1643. doi:10.2136/sssaj2000.6451638x
- van Groenigen, J.W., P.J. Georgius, C. van Kessel, E.W.J. Hummelink, G.L. Velthof, and K.B. Zwart. 2005. Subsoil ¹⁵N-N₂O concentrations in a sandy soil profile after application of ¹⁵N-fertilizer. *Nutr. Cycling Agroecosyst.* 72:13–25. doi:10.1007/s10705-004-7350-6
- Wagner-Riddle, C., Q.C. Hu, E. van Bochove, and S. Jayasundara. 2008. Linking nitrous oxide flux during spring thaw to nitrate denitrification in the soil profile. *Soil Sci. Soc. Am. J.* 72:908–916. doi:10.2136/sssaj2007.0353
- Yamamoto, S., J.B. Alcauskas, and T.E. Crozier. 1976. Solubility of methane in distilled water and seawater. *J. Chem. Eng. Data* 21:78–80. doi:10.1021/jc60068a029