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N₂O and CO₂ dynamics in a pasture soil across the frozen period

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ABSTRACT

Since the process of gas dynamics in agricultural soils is mainly studied during plant growth, only few studies have focussed on these dynamics in frozen soils covered with snow. Nevertheless, gas dynamics during the cold season is important to quantify the yearly mass balance of gas emitted to the atmosphere. Spatio-temporal concentrations of CO₂ and N₂O have been measured from the pre-freezing to the thawing period in a pasture soil during two cold seasons along with soil temperature and other soil properties. The spatial dynamics of these gases differed from each other and depended on the spatial and temporal variability of soil temperature as long as the soil surface temperature was above 0°C. Two main occurrences of gas release occurred during thawing, one related to trapped gases, similar for both gases, and the other to reactivation of microorganisms, different between both gases. Once the soil was frozen, both gas concentrations increased throughout the frozen period, even during very cold conditions, indicated a gases production faster

than the loss. Under frozen condition, their spatial variability was independent of soil temperature during which their correlation was up to 90%. Three periods related to gas dynamics were observed during both cold seasons: freezing with spatio-temporal trends different between both gases, completely frozen with similar trends, partial to complete thawing with trends different between both gases.

Key words:

Carbon dioxide, nitrous oxide, greenhouse gases, gas emissions, winter

INTRODUCTION

Greenhouse gas (GHG) emissions occur throughout the year at various intensities. The evaluation of GHG emissions from agricultural soils is complex due to their high level of variability (Allaire et al., 2012). The coefficient of variation may reach up to 173% for CO₂ (Allaire et al., 2012) and 493% for N₂O during summer (Clemens et al., 1999). Although we know that winter respiration (CO₂) is a significant component of the annual carbon budget (Elberling and Brandt, 2003) and N₂O winter emissions may account for more than half of the total annual emissions (Maljanen et al., 2007; Regina et al., 2004), only few data were found relative to their spatial variability during winter.

Nevertheless, half of the Northern hemisphere has a significant frozen season with a thawing period. The thawing period seems critical for gas dynamics. In addition, global warming scenarios predict an increase in the number of thawing periods during winter (Teepe et al., 2001). In southern Quebec, agricultural, forest and mining soils are frozen during 4 to 5 months of the year. At the end of each fall, these soils are usually very humid before being covered by ice and snow. The presence of liquid water, ice lenses and snow at the surface suggest very low permeability to gases as they move about 10,000 times slower through water and more than 50,000 times slower through ice than through air (Yanful, 1993; Loosse et al., 2009).

Considering this low gas permeability in water and ice at the soil surface, models tend to indicate a potential lack of oxygen for soil respiration and temperatures, too low for microbial activities. However, heterotrophic soil respiration appears to be active even under snow cover and very cold conditions, releasing significant amounts of CO₂ (Bubier et al., 2002; Brooks et al., 2004). It may be in part caused by the snow cover via its insulation function, which may significantly decrease frost penetration (Mariko et al. 2000; Swanson et al. 2005). Soil insulation by the snow cover may

keep the soil temperature above critical threshold for active respiration (around -7 to -5°C). This threshold also corresponds with the limit between the presence or the absence of unfrozen water in soil pore space (Brooks et al. 1997; Osterkamp and Romanovsky 1997). A temperature of -5°C represents the threshold between solid and liquid water state in soil pore space as measured in our laboratory in this soil (result not presented). It is different from the freezing point of pure water due to the presence of salts and impurities. In addition, gas dynamics during winter may be associated with the fact that oxygen may enter into the frozen soil through different pathways. Also, the activity during winter may be attributed to different microbes, specific soil microorganisms that are more efficient at low temperatures (Panikov and Dedysh, 2000).

It was suggested that N_2O may be also formed in agricultural and forest soils during winter despite the presence of ice lenses at the soil surface and liquid or frozen water. Indeed, Müller et al. (2002) show that NO_3^- and NH_4^+ soil concentration increased during winter due to the availability of a nitrogen pool that is immobilized on soils colloids or by the microbial biomass. This nitrogen pool may then be used by microorganisms during winter to produced N_2O as long as oxygen is available. The oxygen may come from preferential flow from the surface, contained in infiltrating water, the oxygen from NO_3^- by denitrification or from CO_2 , which may be produced from fermentation and methanogenesis. The short period of highly variable N_2O emissions during thawing indicates formation and heterogeneous distribution of N_2O during winter (van Bochove et al., 2001). However, the processes and the parameters influencing N_2O winter formation and distribution remain poorly understood.

The goal of this research was to assess the spatio-temporal variability of CO_2 and N_2O soil concentrations in a pasture soil across the cold season. We also discuss their relationship with soil temperature.

MATERIALS AND METHODS

Site and soil description

The site was situated within a large field at Saint-Narcisse-De-Beaurivage (QC, Canada). As typical of the region, the field presented ridges between two drains 25 m apart with a slope of 1 to 3% to favor soil drainage. The experimental setup was installed in the middle of this bed between two agricultural ditches (Figure 1).

The study was conducted during two cold seasons from November to April of 2011-2012 and 2012-2013 in a pasture field implanted in 1989 (75% Timothy-grass (*phleum pratense*) and 25% clover (*trifolium pratense*)). Climatic conditions were obtained with the closest Environment Canada weather station (Table 1).

Cattle butchers (35 cows and 30 calves principally from charolais and simmental breed) were typically allowed to graze freely in this area of the pasture until the end of October. No tillage or other soil preparation has been done since 1989. Three amendments (not analysed) were added in 2011 and 2012: a liquid veal manure in May and October at a rate of 25 000 L ha⁻¹ and 12 500 L ha⁻¹ respectively and a liquid pig manure in July at a rate of 25 000 L ha⁻¹.

Under the Canadian soil classification, this soil is classified as an Orthic Humo-ferric Podzol of the Beaurivage Series (Lamontagne et al., 2010) (Table 2). The soil contains 10% pebbles near the soil surface to 60% in deeper horizons. It is moderately drained. Since the soil has not been worked for more than 12 years, earthworms, insect burrows, and dense rooting systems are present in the uppermost horizons.

Field instrumentation and soil analysis

The studied plot occupied a small surface of 15 m x 15 m on a much larger field of several hectares. The size of the experimental setup was chosen to perform field sampling as quickly as possible. The setup was installed relatively near the farm of the producers to ensure security during field measurement and to have an easy field access during winter but far enough so that the barns do not influence measurements and gas dynamics. A regular square grid of 49 sampling sites (7*7) spaced at an interval of 2.5 m was instrumented (Figure 1).

The plot was permanently instrumented during each cold season. Two gas sampling probes were installed at each sampling point at 0.125 and 0.25 m depths. These probes were installed in PVC piping having a length of 0.5 m and an internal diameter of 0.005 m. They were capped with a rubber stopper (EW-62995-80; Cole-Parmer Canada Company, Montreal, QC, CANADA). A large metal washer was added at the end of the tubes to maintain the probe at the desired depth to counter effect the soil movement during freezing/thawing cycles. Soil temperature and volumetric water content (WC) were obtained at 0.125 m depth with a type T thermocouple (copper-constantan) and a 0.15 m three-branch time domain reflectometry (TDR) probes horizontally inserted. An additional sampling site (called 'the reference site' in this paper) was located at 2.5 m of the regular grid for intensive vertical measurement in the soil profile and in the air above ground (Figure 1). This site was instrumented with 6 TDR probes, thermocouples and soil gas sampling probes at depths of 0.125, 0.25, 0.4, 0.55 and 0.70 m. Additional thermocouples were also installed every 0.1 m from 0 to 1 m above the soil surface to measure air and snow cover temperature. Two dataloggers (CR23X Micrologger and CR3000 Micrologger, Campbell Scientific, Edmonton, AB, CANADA) hourly recorded temperature from thermocouples and soil dielectric constant (K_a) from TDR probes

through a connection to a TDR100 (Campbell Scientific). Topp's equation was used to calculate the soil volumetric water content (WC, $\text{m}^3 \text{m}^{-3}$) (Topp et al., 1980) when water in soil was not frozen.

Measurement started on Dec. 21st 2011 during the first year and one month earlier during the second year (25th Nov. 2012) in order to better understand the pre-freeze period and compare gas dynamics between the pre-freeze and the frozen period.

Additional physico-chemical soil properties were measured by horizon at the reference site (Table 2). Bulk density (BD, Mg m^{-3}) of each soil horizon was measured with the core method (Blake and Hartge, 1986). BD was assumed constant for the whole field during the entire experiment. The BD was slightly higher than usually found in agricultural soil probably because the soil was not tilled for a long period of time (Table 2). It was very dense at depth because it was formed on a till. Total soil porosity (TP, $\text{m}^3 \text{m}^{-3}$) was calculated from $\text{TP} = 1 - (\text{BD} / \text{SD})$ (Flint and Flint, 2002a) where SD is the particle solid density assumed constant at 2.65 Mg m^{-3} (Flint and Flint, 2002b). The high BD resulted in a relatively low TP with less than 45% of pore space. The saturated hydraulic conductivity (K_s , m d^{-1}) was determined with a constant head permeameter (Reynolds, 1993). Based on K_s , the soil is considered as being semi-permeable although it is a loamy sand in part because of its high density (Table 2). Although the soil heaves, TP and K_s were considered constant during the experiment because the data for corrections were not available. Although the estimated values were slightly bias by this assumption, it did not influence the overall trends neither the conclusion.

Soil water saturation (SWS) was calculated from $\text{SWS} = \text{WC} / \text{TP} * 100$. The air filled pore space (AP, $\text{m}^3 \text{m}^{-3}$) was then calculated with $\text{AP} = \text{TP} - \text{WC}$. A power function, as described by the Millington–Quirk's equation $D_s/D_o = \text{AP}^{10/3} / \text{TP}^2$ (Millington and Quirk, 1961), was used to determine the relative soil gas diffusion coefficient.

Chemical parameters were also measured on soil samples at different times during each year (beginning, middle, and end of both cold seasons). Soil pH_{water} was measured with a pH-meter (CPVQ, 1997). Total organic carbon content (C_{Total} , $\text{g g}^{-1} \times 100$) was determined with the dry combustion method. Its acidic pH is comparable to other similar soils of this region while the C_{Total} is relatively high for this region (Table 2) and is likely related to the permanent pasture management. The pH and C_{Total} were considered constant for the experiment. Soluble organic carbon ($\text{C}_{\text{soluble}}$, $\text{mg kg}_{\text{soil}}^{-1}$) was measured with the colorimetric determination of oxidizable carbon in acid soil solutions (Bartlett and Ross, 1988). Total nitrogen (N_{tot} , $\text{mg kg}_{\text{soil}}^{-1}$) was quantified with Kjeldahl method (McGill and Figueiredo, 1993) while nitrate content (NO_3^- , $\text{mg kg}_{\text{soil}}^{-1}$) was determined with Keeney's method (Keeney and Nelson, 1982).

Soil gas concentration

CO_2 and N_2O concentrations in soil ($\text{CO}_{2\text{-soil}}$ and $\text{N}_{2\text{O-soil}}$, $\mu\text{g mL}^{-1}_{\text{soil air}}$) were measured 15 times during winter 2011-2012 (from 21st Dec., 2011 to 2nd May, 2012) and 24 times during winter 2012-2013 (from 25th Nov., 2012 to 30th April, 2013). Gas samples (10 mL) were withdrawn through septa with hypodermic gastight syringes (10 mL, Becton-Dickinson 309643, Franklin Lakes, NJ) and were immediately inserted into gastight vials (10 mL model 5182-0838, Agilent, Wilmington, DE) that were previously vacuumed and capped with aluminum seal (20 mm, 224178-01, Wheaton, Millville, NJ) and rubber butyl septa (Wheaton cat. 224 100202, Millville, NJ) specifically chosen for CO_2 and N_2O (Lange et al., 2008).

The concentration of gases in the vials were measured within 4 days using a gas chromatograph (6890 N Agilent, Wilmington, DE) with 30-m HP-PLOT-Q column (19095P-QO4PT) and a TCD

(for CO₂) or an ECD (for N₂O) detector. The gas sampling and concentrations analysis were done as described in Allaire et al. (2015).

During the study, ice accumulated in several gas probes, blocking the access for gas sampling. These sampling points were considered as missing values. During snowmelt and very wet soil conditions, water rather than gas was withdrawn from gas probes. The values of these samples were considered as zero concentration rather than missing values.

Statistical analyses and mapping

Descriptive statistics for gas concentrations and soil physico-chemical properties were obtained with PROC UNIVARIATE of SAS 9.2 (SAS Institute Inc., 2008). Spatial variability of the dataset was mapped using universal kriging or ordinary kriging depending on whether a constant, unknown mean was a tenable assumption (ordinary kriging), or not (universal kriging), for the variable in question. Both types of kriging were performed with Surfer 8.01 (Golden Software, CO, USA), using the variogram parameters estimated with a spherical model because it allows autocorrelation to decrease with distance at a rate slower than with the exponential model, and faster than with the Gaussian model. Maps were produced, and are presented, only to give some insight on the spatial distribution of gases in the field. Due to the small amount of data (49 maximum), no further geostatistical analysis was performed, thus following Webster and Oliver (1992).

RESULTS

Climate conditions

The average air temperature, rain and snow precipitation during winters 2011-2012 and 2012-2013 are presented in Table 1. The average temperature during the winter of 2012-2013 was 1.1°C lower than that of the cold season of 2011-2012 (Table 1). The air temperature ranged from -30°C to 29°C during the first cold season and from -33.5°C to 24.6°C during the second one. During the first cold season, total liquid precipitations was approximately twice and the total precipitation as snow was 30% less than during the second winter. Nevertheless, January and February received approximately the same precipitation totals with substantial snow depths and negligible rains. The most important differences were observed at the beginning of each winter season. The field received three times more rain in November and three times less snow in December during the first winter than during the second one. Thus, at the beginning of the first winter, the soil had a thinner snow cover and higher water content.

During March 2012, warm weather conditions ($> 15^{\circ}\text{C}$ for 10 consecutive days) allowed soil warming and snow melting. On 21st March 2012, a temperature of 24.5°C was recorded. This warm period was followed by another cold period (air temperature $< 0^{\circ}\text{C}$) for 2 weeks with a new snow cover that reached a thickness of approximately 0.1 m before its final melting in mid-April. During the second winter, no comparable climatic variation occurred. Nevertheless, during 3 days (from 11th to 14th March 2013), air temperature rose and varied between 0 and 5°C both day and night. Thawing began around mid-April and was completed by the end of April 2013.

Soil properties

Although, soil properties greatly varied from one winter to the next and varied from the pre-freeze to the thawing periods (Table 3), general tendencies were identified. During both cold seasons, the SWS was lower in the middle of the field which corresponded to the top of the bed

where drainage was better and where the snow melted earlier than at the field edge. Before the freezing period of 2011-2012, SWS varied between 25 to 75% while it varied from 11 to 100% at the end of the winter. This is important since gas diffusion is 10 000 times lower in water than in air. Thus a saturated soil, such as measured in certain areas of the field, would have tendency to slow down considerably CO₂ and NO₂ diffusion toward the atmosphere and O₂ toward the soil profile. Due to snow melt distribution, the SWS variability increased during thawing. Before the freezing period of the second winter, the SWS was about twice higher than the previous winter, varying from 57 to 100% although precipitations during this fall season were half that of the first winter. Therefore, the soil was wetter and the water was more homogeneously distributed during the second (Figure 2) than during the first year (spatial distribution not shown). SWS spatial distribution showed the same distribution pattern between the pre-freeze and the thawing periods for both winters.

C_{soluble} showed a 60% (from 193 to 307 mg kg_{soil}⁻¹) and 20% (from 210 to 255 mg kg_{soil}⁻¹) increase between the beginning and the end of both seasons, respectively. It was 30% lower at the end of the second year than at the end of the first one. The CV of C_{soluble} was lower during the second winter (34-46%) compare to the first one (56-63%). N_{tot} content increased by more than 100% from the beginning (23 mg kg_{soil}⁻¹) to the end of the first cold season (58 mg kg_{soil}⁻¹) but decreased from 49 to 29 mg kg_{soil}⁻¹ during the second winter. Comparatively, a reduction of 40% (from 3.0 to 1.8 mg kg_{soil}⁻¹) and 90% (from 8.3 to 0.8 mg kg_{soil}⁻¹) in nitrate content occurred during the first and the second winters. The spatial distribution of C_{soluble} showed that the higher concentrations were often localized at the sites of higher concentration of N_{tot} and nitrate. This trend was maintained throughout the year although their spatial distribution changed over time (Figure 2). Nevertheless, during both winters, a production of C_{soluble} occurred while nitrate was consumed and no trends could be identified for N_{tot}.

During the first winter, soil temperatures at 0.125 m depth at the reference point varied from -5.5°C at the beginning of Jan. 2012 to 13.1°C at the end of the experiment (mid-April 2012) and from -10.8°C (beginning of Feb. 2013) to 12.5°C during the second year (mid-April 2013) (Figure 3). During the first winter, the soil temperature at 0.125 m depth was below the freezing point from approximately mid-December 2011 until mid-March 2012. During winter 2012-2013, the coldest period was shifted later (~ 3 weeks) and lasted longer (~ 2 weeks) than during the first winter. The soil was partially frozen starting at the beginning of December and it was completely frozen only from mid-January 2012 to mid-April (Figure 3). At the end of the second winter, the soil remained frozen for a longer time due to lower air temperature at the end of March and thicker snow cover. Overall, the early winter season of 2012 was colder than 2013 but the mid-winter was warmer. During winter, when the soil was totally frozen and when the snow cover was present, soil temperature was almost homogeneous throughout the field (Figures 4 and 5). However, at the beginning and at the end of both winters, soil temperature presented much higher spatial variations (Figures 4 and 5) with CVs reaching up to 195% (Table 2).

Temporal variability of soil CO₂ and N₂O concentrations

CO_{2-soil} and N₂O_{soil} presented similar pattern although their ranges of concentration were at least two orders of magnitude different (Table 4). Effectively, during both winters, CO_{2-soil} was 200 to 500 times higher than N₂O_{soil}. The final concentrations in spring were within the range observed in other studies for summer seasons (Allaire et al., 2012 and 2015). During freezing and thawing, the concentrations were lower near the soil surface as usually observed because of soil emissions to the atmosphere (Allaire et al., 2012).

At the end of autumn, gas concentrations were relatively constant at approximately $30 \mu\text{g mL}_{\text{soil air}}^{-1}$ for $\text{CO}_{2\text{-soil}}$ and often below detection level for $\text{N}_2\text{O}_{\text{soil}}$ ($0.005 \mu\text{g mL}_{\text{soil air}}^{-1}$) (Table 4, Figure 3). The values correspond to those measured in other field studies during fall seasons under moist soil conditions (Allaire et al., 2012 and 2015).

At the end of December during the first winter and in mid-January during the second winter, gas concentrations started to increase (Figure 3). $\text{CO}_{2\text{-soil}}$ increased continuously during the frozen period to reach a concentration range of 110 to $160 \mu\text{g mL}_{\text{soil air}}^{-1}$ depending of the depth. It was 3 to 5 times higher than at the end of autumn e.g. during or before soil freezing. Similarly, $\text{N}_2\text{O}_{\text{soil}}$ increased by about 400 times during the entire frozen period to reach 0.4 to $1.8 \mu\text{g mL}_{\text{soil air}}^{-1}$ varying with depth and year (Table 4; Figure 3).

During mid-March 2012, $\text{CO}_{2\text{-soil}}$ changed from $140 \mu\text{g mL}_{\text{soil air}}^{-1}$ on 15th March to $20 \mu\text{g mL}_{\text{soil air}}^{-1}$ on 26th March (Figure 3) near the soil surface. $\text{N}_2\text{O}_{\text{soil}}$ dropped from 0.5 to $0.05 \mu\text{g mL}_{\text{soil air}}^{-1}$ during the same period at 0.125 m depth because of a warm event of several days occurred, as stated earlier. The cold period following this warm event immediately induced an increase in both gas concentrations. These increases took place at different rates for CO_2 and N_2O . The $\text{CO}_{2\text{-soil}}$ was moderate and reached only 30% of the concentrations measured just before the warming period while $\text{N}_2\text{O}_{\text{soil}}$ returned to the same level (Figure 3). Gas concentrations increased from 20 to $40 \mu\text{g mL}_{\text{soil air}}^{-1}$ for $\text{CO}_{2\text{-soil}}$ and from 0.05 to $0.45 \mu\text{g mL}_{\text{soil air}}^{-1}$ for $\text{N}_2\text{O}_{\text{soil}}$ (Figure 3). These dynamics were similar at 0.25 m depth for both gases. During the second winter, from 11th to 14th March 2012, $\text{CO}_{2\text{-soil}}$ decreased from 110 to $60 \mu\text{g mL}_{\text{soil air}}^{-1}$ and from 1 to $0.5 \mu\text{g mL}_{\text{soil air}}^{-1}$ for $\text{N}_2\text{O}_{\text{soil}}$ (Figure 3). These drops resulted in a 40 to 50% decrease in gas concentrations in the soil profile. Immediately after, gases accumulated again for a period of approximately one month.

At the end of each winter, during thawing, the concentration of CO_2 decreased from a range of 100 to $160 \mu\text{g mL}_{\text{soil air}}^{-1}$, to a range of 10 to $20 \mu\text{g mL}_{\text{soil air}}^{-1}$ within a couple of days dependent

upon depth (Figures 3 and 4, Table 4). It thus returned to the basic soil concentration measured at the beginning of the pre-freeze period. Comparatively, N_2O decreased from 1 to $1.8 \mu\text{g mL}_{\text{soil air}}^{-1}$ to undetectable level ($0.005 \mu\text{g mL}_{\text{soil air}}^{-1}$) within about the same time period, but the process was slightly faster than for CO_2 (Figure 3).

Spatial variability of soil CO_2 and N_2O concentrations

General observations shows that the hot spots of CO_2 and N_2O were situated near the same place during each cold season, but the distribution of gas concentrations in soil differed between both years (Figures 4 and 5). CO_2 and N_2O distributions over the field remained the same from the pre-freeze to the end of the frozen period, their concentration increased and the difference between the hot spots and the low spots became less important. The homogeneity increased with the time of freezing.

Indeed, the CV during this pre-freeze period varied from 52 to 60% for $\text{CO}_{2\text{-soil}}$ and from 248 to 256% for $\text{N}_2\text{O}_{\text{soil}}$ (Table 4). The CV values were quite similar for each depth. The range of CV values for both gases was within the ranges observed in other field studies for cool but not frozen conditions (Allaire et al., 2012, Clemens et al., 1999). During this accumulation period (frozen), the CV of $\text{CO}_{2\text{-soil}}$ ranged from 32 to 38% while that of $\text{N}_2\text{O}_{\text{soil}}$ ranged from 60 to 87% for both depths (Table 4). The CVs of both gases were 2 to 3 times lower for CO_2 and 3 to 5 times lower for N_2O (dependent upon depth and year) during this period than during the thawing and pre-freeze period. N_2O CV ranged from 195 to 309% (Table 4), indicating the complex nature of N_2O formation and movement. These CV values of the thawing period were similar to values for unfrozen conditions in other studies (Allaire et al., 2015; Lange et al., 2009) and to thawing conditions (Wagner-Riddle et al., 2008).

In addition, although CO₂ and N₂O distribution differed, their respective distribution at both depths was very similar, except that the concentration of both gases was higher in depth as long as the soil was not completely frozen. Thus, for simplifying purposes, only the maps relative to the gas distribution at 0.125 m depth are presented and this, for only few dates during each cold season.

DISCUSSION

Three distinct periods were identified over the course of the two winters relative to soil gas concentration dynamics mainly depending upon on soil temperature.

The pre-freeze and freezing period

During the freezing period, the concentration of both gases was similar to other studies (Allaire et al., 2012), indicating that the microorganisms were still active, but at lower rate than during the warm period. The higher soil wetness could decrease oxygen and CO₂ diffusion in depth based on the Millington-Quirk equation, but it was not sufficient to block it. Indeed, based on TP and SWS (Tables 2 and 3), the average AP was greater than 25%. Considering that gas can diffuse when AP is at least 10%, it is presumed that gas could diffuse within the soil profile. This allowed gas exchanges between the soil and the atmosphere allowing microbial activity as long as soil temperature was higher than 0°C.

However, water distribution was not homogeneous throughout the field (Figure 2), which influenced gas diffusion, and thus the microbial activity and gas exchange with the atmosphere. Higher SWS corresponded to higher CO_{2-soil} and N₂O_{soil} concentrations (Figure 4). In addition, the heterogeneous distribution of cattle dungs, may have indirectly influenced the distribution of gases

by affecting the distribution on nitrate, N_{Tot} , and $C_{soluble}$ (Lowell and Jarvis, 1996; Williams and Haynes, 1995).

In comparing both years, the thin snow cover rather than rain accumulated in December 2011 allowed faster soil cooling compared to December 2012. The frozen period had probably started earlier during the first winter than the second one, but soil temperature data were not available during this period in 2011-2012. In addition, the presence of cattle changed between both years. Cattle were grazing more during the fall of the first year than during the second year and did not homogeneously graze the field. Cattle dungs distribution partly explains the relatively high CV of $C_{soluble}$ which in turn may have affected gas variability (not measured during fall of the first year).

Nevertheless, data of 2012-2013 showed that CO_{2-soil} distribution was correlated to soil temperature distribution during the first period. The concentration was higher at spots where the soil was not frozen indicating higher microbial activity (Figure 5) although gas emissions still occurred (data not shown). For N_2O_{soil} , the correlation between temperature and gas distribution is less obvious as the N_2O concentrations were very low and highly variable and more sensitive to micro-variability due to SWS variability.

Frozen period

During winter, when the soil was totally and continuously frozen and when the snow cover was present, soil temperature was almost homogeneous throughout the field (Figures 4 and 5) and presents little temporal variations (Figure 3). These little variations were principally due to very cold periods with delay due to insulation from the snow cover (Figure 3). At the end of the second winter, the soil remained frozen for a longer time compare to the first winter. This is due to lower air temperature at the end of March and to the thicker snow cover that melted later and insulated the

soil surface for a longer period (Table 1; Figure 3). The high variability of soil temperature at the beginning and at the end of both winters was in part due to variability in snow cover thickness that varied across each winter and between both winters, in variation in thawing associated to snow cover and in the distribution of water content in the liquid state (Figures 2, 4 and 5).

When the soil surface froze near 0°C , ice lenses formed on the soil surface (by different processes including exclusion of pure water) and ice replaced liquid water in the pores of the upper soil layer modifying soil gas dynamics. During this frozen period, both the ice and snow at the soil surface and the frozen water in the soil profile created a barrier to gas release (Teepe et al., 2001). Comparatively to the soil surface where the water freezes at 0°C , the water froze at about -5°C in the soil profile because of water impurities. Effectively, SWS ranged from 50% to almost 100% (Table 3) resulting in an AP from 0 to 50%. Considering TP and AP, then D_s/D_o greatly varied from almost 0 to 0.03 decreasing considerably gas movement in soil mostly because the AP become not connected to each other when the AP is lower than 10%. In addition to ice, snow, and low D_s/D_o , CO_2 and N_2O are more soluble in cold than in warm water (van Bochove et al., 2001). These gases become trapped in the ice when the water freezes (not measured) and in AP surrounded by non-permeable frozen soil (Goldberg et al., 2010). Thus, during the frozen period, gas exchange at the soil surface was limited due to 1) restricted soil gas diffusivity due to ice that filled the soil pore space when soil temperature reach 0°C at the soil surface or -5°C in deeper soil layer or; 2) ice and snow cover at the soil surface, limiting gas diffusion to the atmosphere ; 3) high SWS that imply low gas diffusion coefficient in the soil profile.

Although gases were produced at a lower rate than during autumn due to a low microbial activity during this period, they were produced at higher rate that they could escape. These restrictions resulted in soil gas concentrations that drastically increased over time as long as the soil surface remained frozen even if the profile was partly defrosted (Figures 3 to 5). Despite these restrictions,

gas concentrations presented lower horizontal (Table 4, Figures 4 and 5) and vertical (Figure 3) variations compared to the two other periods because sufficient time was allowed for their diffusion. The long winter facilitated homogenisation of gases distribution within the soil profile although the gas diffusion coefficients were low in these conditions.

The production of both gases during this entire period indicated, though, a certain level of oxygenation. This oxygen may come from water, ice, snow and air already present in AP in addition to some that may enter the profile by slow diffusion from the surface and by convection with the infiltrating water.

During winter 2011-2012, the warming period occurred in mid-March (Figure 3) allowed snow melt and soil warming and consequently a burst of gas exchange occurred at the soil surface with a concomitant decrease in soil gas concentration (Figures 4 and 5). During this period, ice in the soil pores, ice lenses and snow at the soil surface melted rapidly facilitating gas diffusion through the soil profile to the atmosphere. In addition, liquid water from melting ice and snow drained into the soil and increased the effectiveness of convection processes boosting the escape of gases to the atmosphere.

The cold period following this warming event rapidly induced an increase in both gas concentrations. These increases took place at different rates for CO₂ and N₂O because the intense thawing during few days had favoured liquid water infiltration; soil warming and had made a new pool of N sources available to microbes. These processes promoted denitrification and N₂O production. This is in agreement with soil nitrates content that decreased during this period.

Once the cold conditions returned, new ice and snow at the soil surface blocked gas release again but only for a short period of time (Figure 3).

During the second winter, from 11th to 14th March 2013, another short warm period occurred. Although it was less intense than during the first winter, a net decrease of gases concentrations was

observed at every depth of the reference site (Figure 3). These resulted in a 40 to 50% decrease in gas concentrations in the soil profile. The warm period was not sufficiently long to complete snowmelt and soil thaw. As soon as temperatures returned to below the freezing point, gases accumulated again because the new ice formed at the soil surface and in superficial pore space were sufficient to block exchange with the atmosphere.

When soil temperature decreased below the freezing point throughout the field, $\text{CO}_{2\text{-soil}}$ distribution was no longer correlated to the spatial distribution of soil temperature (Figures 4 and 5). $\text{CO}_{2\text{-soil}}$ and $\text{N}_2\text{O}_{\text{soil}}$ increased with a distribution pattern that tended to be maintained with time as long as the soil remained completely frozen without correlation with soil temperature distribution. Their spatial distributions showed the same trends with hot spots in the same part of the field. This indicates that although the soil reached very low temperature, soil microbial activity remained active at the same spots. However, $\text{N}_2\text{O}_{\text{soil}}$ distribution did not seem correlated to N_{tot} or to nitrate contents during this period (Figures 2 and 5).

However, average $\text{CO}_{2\text{-soil}}$ and $\text{N}_2\text{O}_{\text{soil}}$ were highly correlated during the frozen period of both years (Figure 6). During the period of 2011-2012, $\text{N}_2\text{O}_{\text{soil}}$ was lower than during 2012-2013 while $\text{CO}_{2\text{-soil}}$ remained constant between both winters. This lower N_2O production (or lower trapping) may be due to lower SWS or to the N_{tot} that was almost three times smaller in fall 2011 than in 2012 (Table 3) and was consistent with a lower loss in nitrates during 2011-2012 (40%) compared to 2012-2013 (90%). In addition, the correlation was higher in 2012-2013 because $\text{CO}_{2\text{-soil}}$ was less variable (Figures 3, 5).

These data clearly indicate that, 1) even when gas diffusion is limited due to soil freezing, microorganisms find sufficient oxygen for their activities but at lower rate; 2) their hot spot remained the same over time during the same year; 3) gas accumulated in the soil profile whenever the soil surface is completely frozen and there was ice and snow cover to block the AP that

normally connects with the atmosphere (0°C) when the soil profile is frozen (-5°C); 4) gases get trapped in the soil profile until partial thawing; 5) concentration of both gases are highly correlated as long as the soil is frozen; 6) gas diffusion to the atmosphere occurs very rapidly as soon as only a part of the soil surface thaws.

The frozen period ended in mid-March during the first winter and in mid-April for the second winter (Figure 3).

Thawing period

The frozen period was followed by the third period (called Thawing in this paper) that began as soon as thawing was initiated and AP became present at the soil surface.

At the end of each winter (partial thawing to complete thawing), gas concentrations rapidly decreased. The thawing period started approximately mid-March 2012 for the first winter and one month later (mid-April 2013) for the second winter (Figure 3). During this period, both gases were released from the soil to the atmosphere during a very short period of time (a couple of days) (Figure 3). Concentrations returned to the basic soil concentration measured at the beginning of the pre-freeze period. This occurred whenever 1) snow and ice partly melted at the soil surface freeing some AP; 2) a small part of the soil profile warmed up to -5°C allowing melting of ice from some pores; 3) soil water drainage occurs; and 4) gas diffusion and other gas movement processes can occur.

Sudden decreases in N_2O concentration was also observed by van Bochove et al. (2001) when soil temperature rose to $\geq -5^{\circ}\text{C}$. During this period, gas diffusion increased considerably at the soil surface because the soil dried quite fast, mostly at the top of the micro topography due to soil drainage resulting in higher AP, allowing the release of trapped gases. New gas was also probably

formed during spring thaw because of an increase in microbial activities (Risk et al., 2013). Indeed, it seems that soil conditions are favourable to specific microbial activities during spring thaw particularly for N_2O (Wagner-Riddle et al., 2008), especially in the case of the cold-adapted microflora (Kurganova et al., 2007). In addition, due to low soil temperature and low availability of O_2 in the soil profile, winter kills some microbes and fine roots. Ice expansions and contractions during freeze-thaw cycles cause soil aggregate breakdown (Müller et al., 2002; Oztas and Fayetorbay, 2003). The N and C from these dead materials and broken aggregates become available to microbes as the soil thaws, favourable for N_2O formation during a short period of time during spring thaw (Wagner-Riddle et al., 2008). Indeed, $\text{C}_{\text{soluble}}$ strongly increased during spring (Table 3, Figure 2).

During thawing, $\text{CO}_{2\text{-soil}}$ and $\text{N}_2\text{O}_{\text{soil}}$ rapidly decreased except at localized spots where the soil remained frozen (Figure 4). Once completely thawed all around the field, $\text{CO}_{2\text{-soil}}$ concentrations were higher where the soil was warmer as during the freezing process. This is due to the recovery of soil microbial activity induced by soil warming (usually following the Arrhenius equation). At this time, the $\text{CO}_{2\text{-soil}}$ spatial distribution seems to present a positive correlation with the spatial distribution of $\text{C}_{\text{soluble}}$ (Figures 2 and 4). For $\text{N}_2\text{O}_{\text{soil}}$ during the completely thawed period, no obvious correlations were identified due to its high variability and low concentration (often below detection limits) in soil.

The correlation between both gases was much weaker during the pre-freeze and the thawing periods of both years than during the frozen period. N_2O is usually highly variable during the unfrozen conditions because it is produced and sorbed where specific conditions are reached for soil microorganisms to produce it (Wagner-Riddle et al., 2008). Any small variability in soil properties influenced its production and consumption. This is why it is usually difficult to correlate $\text{CO}_{2\text{-soil}}$ and $\text{N}_2\text{O}_{\text{soil}}$.

General observations shows that the hotspots of gas concentrations in soil were not situated at the same place between years although they remained constant within a year. It was principally associated to variable distribution of soil parameters (SWS, cattle dungs, C_{soluble} , N_{tot} and nitrate) both at the beginning of each winter and during winter (e.g. distribution of snow depth). Nevertheless the level of variability was consistent between years and periods.

CONCLUSION

This study allows a better understanding of soil gas dynamics in an old pasture field across the cold season. Although both seasons were different in term of weather conditions, gas concentrations and distribution, the results clearly suggest three distinct periods in terms of gas dynamics across the cold season.

The first period occurs when temperature at the soil surface was higher than 0°C , allowing gas diffusion within the soil profile and exchange with the atmosphere. Gas concentrations were higher at depth. $\text{CO}_{2\text{-soil}}$ and $\text{N}_2\text{O}_{\text{soil}}$ soil concentrations were poorly correlated.

The second period started when the entire soil was below the freezing point. Gas accumulated in the soil profile; suggesting a production rate of both gases higher than the loss to the atmosphere or by consumption. The long duration of this period allows homogenisation of soil gas concentration in the soil profile, even with the limited soil gas diffusivity. This homogenisation resulted in a strong correlation in time and space between both gases at both depths, which was not the case during the other periods.

During the third period, gases were emitted to the atmosphere as soon as ice and snow partially melted at the soil surface. These emissions occurred within a short period of time of a couple of

days. As thawing was highly heterogeneous across the field, the spatial variability in gas concentration was very high as well. Soil gas concentrations remained high in areas where thawing had not yet started. During this period, soil gas concentration varied in two steps: first, a reduction corresponding to the release of trapped gas that occurred at the same time for both gases followed by an augmentation at different times between both gases probably related to microbial activity being different for both gases. Global warming scenarios predict an increase of the number of thawing periods during winter that may imply more gas release events and involves an increase in N_2O production due to changes in soil conditions induced by the winter thaws as it was observed during the first winter.

Temporal and spatial variability of CO_2 and N_2O were very similar during the frozen period. Their hot spots were localised at about the same place within a year while changed between years, and differing during the unfrozen periods. Their spatial distribution was clearly dependent upon soil temperature distribution as long as the soil was not totally frozen while they were not related to it once frozen.

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Table 1. Climatic data of both winters

Month	Average Temperature		Rain		Snow	
	(°C)		(mm)		(cm)	
	2011/2012	2012/2013	2011/2012	2012/2013	2011/2012	2012/2013
November	4.2	-0.7	41.2	14.6	7	3
December	-4.6	-4.4	58.8	45.3	31	92
January	-10.4	-9.5	11.8	14.8	66	44
February	-7.1	-9.3	2.2	1.2	49	59
March	-0.4	-0.3	41.8	15.6	38	34
April	4.6	4.1	58.6	37.4	3	22
Nov. to April	-2.3	-3.4	214.4	128.9	194	254

Source (Data: Scott station, Environment Canada, 2013)

Table 2. Soil physico-chemical properties considered constant during the experiment

Variable	Horizon			
	A _p	B _f	B _{fj}	BC
Depth (m)	0-0.2	0.2-0.35	0.35-0.55	0.55-0.9
Bulk density, BD (Mg m ⁻³)	1.49	1.47	1.73	1.78
Total porosity, TP (m ³ m ⁻³)	0.44	0.45	0.35	0.33
Saturated hydraulic conductivity, K _s (m d ⁻¹)	2.1	3.3	1.2	NA
Sand content (g g ⁻¹)	0.78	0.92	0.31	NA
Clay content (g g ⁻¹)	0.05	0.02	0.01	NA
Texture (--)	Loamy sand	Sand	Silt loam	Sand
pH _{water} (--)	4.63	4.54	5.08	5.0
C _{Total} (g g ⁻¹ x 100)	4.6	2.0	0.8	0.4

NA: Not available

Table 3. Descriptive statistics of soil water saturation (SWS), soluble carbon (C_{soluble}), Total nitrogen (N_{tot}) and nitrate content at 0.125 m depth ($\pm 0.05\text{m}$) during the pre-freeze and thawing periods of both winters

Soil properties	Date	Winter 2011-2012		Winter 2012-2013	
		21 st Dec.	4 th	25 th	4 th
		2011	April 2012	Nov. 2012	April 2013
SWS (%)	n	24	34	20	37
	Min	25	11	57	38
	Max	75	100	100	74
	Av. ^a	45	68	71	65
	CV ^b	30	27	15	12
C_{soluble} (mg kg ⁻¹ soil ⁻¹)	n	46	48	40	49
	Min	22	83	77	98
	Max	478	828	472	569
	Av.	193	307	210	255
	CV	63	56	46	34
N_{tot} (mg kg ⁻¹ soil ⁻¹)	n	46	48	40	49
	Min	2	18	25	14
	Max	75	139	256	54
	Av.	23	58	49	29
	CV	76	51	78	26
Nitrates content	n	47	49	41	49

(mg kg _{soil} ⁻¹)	Min	0	0	2,4	0
	Max	13.4	10,7	48.7	8.5
	Av.	3	1.8	8.3	0.8
	CV	110	188	88	187

^a: Average

^b: Coefficient of variation (%)

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Table 4. Descriptive statistics of soil temperature and soil gas concentrations of the 49 sampling points for each period during both winters

Year (n)	Period (estimated dates)	Parameter	Soil	CO ₂	CO ₂	N ₂ O	N ₂ O
			Temp. ^a	0.125 m	0.25m	0.125m	0.25m
			(°C)	depth	depth	depth	depth
				μg mL ⁻¹ _{soil air}			
2011-2012 (15)	Frozen	n (8)	392	236	277	236	277
	21 st December 2011 ^b	Min	-2.32	22	1	0.00	0.00
	To	Max	0.30	193	195	0.89	0.85
	15 th March 2012	Mean	-0.51	110	109	0.26	0.26
		CV (%)	82	32	33	60	60
	Thawing	n (7)	294	248	212	255	218
	15 th March 2012	Min	-0.13	0 ^d	0 ^d	0.00 ^d	0.00 ^d
	To	Max	10.06	99	149	0.39	0.44
	2 nd May 2012 ^c	Mean	2.76	14	26	0.01	0.03
		CV (%)	119	86	81	309	210
2012-2013 (24)	Pre-Freeze	n (7)	343	340	338	340	338
	25 th November 2012 ^a	Min	-1.09	3	0	0.00	0.00
	To	Max	2.06	56	57	0.53	0.42
	15 th January 2013	Mean	0.28	19	21	0.02	0.02
		CV (%)	195	60	52	256	248
	Frozen	n (13)	628	518	507	518	507

15 th January 2013	Min	-4.85	2	0 ^d	0.00	0.00 ^d
To	Max	0.24	150	147	1.71	1.70
12 th April 2013	Mean	-0.86	79	78	0.39	0.39
	CV (%)	110	37	38	87	87
<hr/>						
Thawing	n (4)	144	153	167	153	167
12 th April 2013	Min	-0.15	0 ^d	0 ^d	0.00 ^d	0.00 ^d
To	Max	9.22	118	188	1.48	2.24
30 th April 2013 ^b	Mean	3.20	25	39	0.08	0.16
	CV (%)	80	98	91	230	195

Values in parenthesis are the number of gas sampling event

^a: Soil temperature at 0.125 m depth at 17h

^b: First sampling event of each winter

^c: Last sampling event of each winter

^d: Assumed at 0 due to absence of soil air induced by soil saturation

Figure 1: A) localisation of the field (red point; map data © Google 2015); B) landscape and topography of the experimental plot and C) experimental setup.

Figure 2. Spatial distribution of soil water saturation (SWS), nitrates, total N content (N_{tot}) and soluble carbon (C_{soluble}) at 0.125 m depth during the winter 2012-2013.

Figure 3. Average daily temperature (°C) at 1 m above soil surface (grey line) and at 0.125 m depth (black line) recorded in the field (above graphics), and evolution of CO₂-soil (middle graphics) and N₂O-soil (lower graphics) concentrations (μg mL_{soil air}⁻¹) at the reference point during both winters.

Figure 4. Spatial distribution of soil temperatures ($^{\circ}\text{C}$), $\text{CO}_2\text{-soil}$ ($\mu\text{g mL}_{\text{soil air}}^{-1}$), and $\text{N}_2\text{O}_{\text{soil}}$ ($\mu\text{g mL}_{\text{soil air}}^{-1}$) at 0.125 m depth at different times during winter 2011-2012.

Figure 5. Spatial distribution of soil temperatures (°C), CO₂-soil (µg mL_{soil air}⁻¹), and N₂O-soil (µg mL_{soil air}⁻¹) at 0.125 m depth at different times during winter 2012-2013.

Figure 5. Relationships between winter average $\text{CO}_2\text{-soil}$ and $\text{N}_2\text{O-soil}$ at 0.125m depth when soil temperature was above 0°C (pre-freeze and thawing periods, left graphic) and when soil temperature was below 0°C (Frozen period, right graphic).