# N<sub>2</sub>O and CO<sub>2</sub> dynamics in a frozen pasture soil

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# ABSTRACT

Since gas dynamics in agricultural soils is mainly studied during plant growth, only few researches have focus on their dynamics in frozen soils covered with snow. Spatio-temporal concentrations of CO<sub>2</sub> and N<sub>2</sub>O have been measured from the pre-freezing to the thawing period in a pasture soil during these seasons. Three periods related to gas dynamics were observed during both cold seasons. Both gases behaved differently during pre-freeze and thawing periods and their spatial dynamics depended on the spatial and temporal variability of soil temperature as long as the soil surface temperature was above 0°C. However, both concentrations increased and their spatial variability was independent from temperature as long as the soil was frozen, under which condition their correlation was up to 90%. 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.

# RÉSUMÉ

Peu de recherches ont porté sur la dynamique du CO<sub>2</sub> and N<sub>2</sub>O en sols gelés et couverts de neige. La variabilité spatiotemporelle de ces gaz a été mesurée du pré-gel au dégel dans un pâturage durant deux saisons froides. Trois périodes ont été identifiées concernant leur dynamique. Leur variability spatio-temporelle était différente et dépendait de celle de la température tant qu'elle se maintenait au-dessus de 0°C. Toutefois, leur dynamique était similaire et leur concentration a augmenté lorsque le sol était gelé, si bien que leur concentration était corrélée à 90% sous cette condition. Deux occurrences de relâchement des gaz ont été observées au dégel dans une courte période de temps. Le premier, similaire pour les deux, est lié au gaz piégé, alors que l'autre, différent, est lié à la réactivation des microorganismes.

# 1 INTRODUCTION

Although we know that winter respiration  $(CO_2)$  is a significant component of the annual carbon budget and that N<sub>2</sub>O winter emissions may account for more than half of the total annual emissions (Maljanen et al., 2007), 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. At the end of each fall, these soils are usually very humid. They are then 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 in water than in air and even slower in ice.

Considering this low gas permeability, the models tend to indicate a potential lack of oxygen for soil respiration and temperature 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  $CO_2$  (Oechel et al., 1997). It may be in part caused by the snow cover via its insulation function, which may significantly decreases frost depth (Mariko et al. 2000). These more favourable soil temperatures, with a critical threshold for active respiration around -7 to -5 °C, correspond to the presence or the absence (threshold temperature) of unfrozen water in soil (Osterkamp and Romanovsky, 1997). It may also be associated to soil microorganisms that are efficient at low temperatures (Panikov and Dedysh, 2000) and to the fact that oxygen may enter the frozen soil through different pathways.

N<sub>2</sub>O forms in agricultural and forest soils during winter despite the presence of ice at the soil surface and liquid or frozen water. The short period of highly variable emissions during thawing indicates formation and heterogeneous distribution during winter (van Bochove et al., 2001), but the processes are ill known.

This study aims at better understanding the spatial variability of soil  $CO_2$  and  $N_2O$  concentrations in a pasture soil during the cold season and their relationship with soil temperature. Other papers from this study will discuss spatio-temporal variability of  $CO_2$  and  $N_2O$  emissions and concentrations, and their correlations with several soil parameters and environmental conditions.

#### 2 METHODOLOGY

2.1 Site and soil description

The site is situated at Saint-Narcisse-De-Beaurivage (Qc, Canada). As typical of the region, the field presents rounded field beds 15 m wide with a slope of 1 to 3%.

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.

Animals are allowed to graze freely until the end of October. No tillage or other soil preparation was done since 1989. Three amendments were added in 2011 and 2012: a liquid veal manure in May and October at a rate of 25 000 L ha<sup>-1</sup> and 12 500 L ha<sup>-1</sup> respectively and a liquid pig manure in July at a rate of 25 000 L ha<sup>-1</sup>.

Beaurivage Series describes this soil. It is classified as an Orthic Humo-ferric Podzol (Lamontagne et al., 2010) (Table 1). The soil contains 10% of pebbles near the soil surface to 60% in deeper horizons. It is moderately well drain.

## 2.2 Field instrumentation and soil analysis

The plot was 15 m x 15 m. A regular square grid of 49 sampling points (7\*7) spaced at 2.5 m interval was installed and instrumented. An additional sampling point (the reference point) was located at 2.5 m for intensive vertical measurement in the soil profile and in the air above ground. Measurement started on Dec.  $21^{st}$  2011 during the first year and on  $25^{th}$  Nov. 2012 during the second year.

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. Soil temperature and water content were obtained at 0.125 m depth with a type T thermocouple and a three-branch time domain reflectometry (TDR) probes 0.15 m long horizontallv inserted. The reference was point instrumented with 6 TDR, thermocouples and soil gas sampling probes at 0.125; 0.25; 0.4; 0.55; 0.70 m depths with additional thermocouples every 0.1 m from 0 to 1 m above the soil surface to determine air and snow cover temperature. Two dataloggers recorded hourly temperature and soil dielectric constant (Ka) Topp's equation was used to calculate the soil volumetric water content ( $\theta_v$ , m<sup>3</sup> m<sup>-3</sup>) (Topp et al., 1980) when soil water was not frozen. Soil water saturation (SWS, %) was then calculated with SWS=  $\theta_{v}/\Phi$  \*100 where  $\Phi$  is the total soil porosity  $(m^3 m^{-3})$ .

Additional physico-chemical soil properties were measured by horizon at the reference point (Table 2). Bulk density  $\rho_b$  (Mg m<sup>-3</sup>) was measured with the core method at each depth. Total soil porosity ( $\Phi$ , m<sup>3</sup> m<sup>-3</sup>) was calculated with  $\Phi$ =1–( $\rho_b$  / $\rho_s$ ) (Flint and Flint, 2002) where  $\rho_s$  is the particle density assumed constant at 2.65 Mg m<sup>-3</sup>. The air filled pore space ( $\theta_a$ , m<sup>3</sup> m<sup>-3</sup>) was then calculated with  $\theta_a$ =  $\Phi$ - $\theta_v$ . A power function as described by the Millington and Quirk's equation (1961)  $D_s/D_o$ = $\theta_a^{10/3}/\Phi^2$  was used to determine the relative soil gas diffusion coefficient.

Chemical parameters were also measured on soil samples three times during each year. Total organic carbon content ( $C_{total}$ , g g<sup>-1</sup>\*100) was determined with the dry combustion method. Soluble organic carbon ( $C_{soluble}$ , mg Kg<sub>soli</sub><sup>-1</sup>) was measured with the colorimetric

determination of oxidizable carbon in acid soil solutions (Bartlett and Ross, 1988). Total nitrogen ( $N_{tot}$ , mg Kg<sub>soil</sub><sup>-1</sup>) was quantified with Kjeldahl method (McGill et Figueiredo, 1993) while nitrate content ( $NO_3^-$ , mg Kg<sub>soil</sub><sup>-1</sup>) was determined with Keeney's method (Keeney and Nelson, 1982). Soil pH was completed with a pH-meter in water.

 $CO_2$  and  $N_2O$  concentrations in soil ( $CO_{2-soil}$  and  $N_2O_{-soil}$ ,  $\mu g m L^{-1}_{soil air}$ ) were measured 15 times during winter 2011-2012 and 24 times during winter 2012-2013 as in Allaire et al. (2015).

## 2.3 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 ordinary kriging methods with Surfer 8.01 (Golden Software, CO, USA) using the variogram parameters defined with a spherical model. Spatial analysis in addition to spatial and temporal correlations with physico-chemical soil properties will be completed soon.

## 3 RESULTS

#### 3.1 Soil properties and gases

The  $\rho_b$  was slightly higher than usually found in agricultural soil probably because the soil was not tilled for a long period of time (Table 1) because it was formed on a till. It resulted in a relatively low  $\Phi$  with less than 0.45% of pores. The soil is semi-permeable. Its acid pH is standard while the  $C_{Total}$  is relatively high for this region.

Although soil properties greatly varied from one winter to the next and from the pre-freeze to the thawing periods, general tendencies were identified. During both cold seasons, SWS was lower on the top of the field bed where drainage was better. 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. Due to snow melt, the SWS variability increased during thawing. Before the freezing period of the second winter, the SWS was about twice higher varying from 57 to 100% although precipitations during the fall season was half that of the first winter. Therefore, the soil was wetter and the water was more homogeneously distributed during the second (Figure 1) than the first year (spatial distribution not shown). SWS spatial distribution shows the same trends between the pre-freeze and the thawing periods.

 $C_{soluble}$  showed a 60% (from 193 to 307 mg Kg<sub>sol</sub><sup>-1</sup>) and 20% (from 210 to 255 mg Kg<sub>sol</sub><sup>-1</sup>) increase between the beginning and the end of the season, during the first and the second season respectively. It was 30% lower at the end of the second year than at the end of the first one. The CV of C<sub>soluble</sub> was lower during the second winter (34-46%) compare to the first one (56-63%). It was probably because cows were more present for grazing during the fall of the first year than during the second year. Cow

dungs also explain the relatively high CV of C<sub>soluble</sub> as the cows did not homogeneously graze the field.

|                                | Units                          | Horizon      |                 |                  |                |  |
|--------------------------------|--------------------------------|--------------|-----------------|------------------|----------------|--|
| Variable                       |                                | Ap           | B <sub>f</sub>  | B <sub>fj</sub>  | BC             |  |
| Depth                          | m                              | 0-0.2 ± 0.05 | 0.2-0.35 ± 0.05 | 0.35-0.55 ± 0.05 | 0.55-0.9± 0.05 |  |
| Bulk density, <mark>δ</mark> a | Mg m⁻³                         | 1.49         | 1.47            | 1.73             | 1.78           |  |
| Total porosity, <mark>Φ</mark> | m <sup>3</sup> m <sup>-3</sup> | 0.44         | 0.45            | 0.35             | 0.33           |  |
| Sand content                   | g g <sup>-1</sup>              | 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 <sub>water</sub>            |                                | 4.63         | 4.54            | 5.08             | 5.0            |  |
| C <sub>Total</sub>             | g g⁻¹ *100                     | 4.6          | 2.0             | 0.8              | 0.4            |  |

| Table 1. Soil | physico-chem | cal properties | s considered ( | constant durin | a the ex | periment |
|---------------|--------------|----------------|----------------|----------------|----------|----------|
|               |              |                |                |                |          |          |

NA: Not available

N<sub>tot</sub> was twice (58 mg Kg-soil<sup>-1</sup>) higher at the end of the first winter than at the beginning (23 mg Kg<sub>soil<sup>-1</sup></sub>) while it decreased by 40% (from 49 to 29 mg Kg<sub>soil<sup>-1</sup></sub>) during the second winter. Comparatively, a reduction of 40% (from 3.0 to 1.8 mg Kg<sub>soil<sup>-1</sup></sub>) and 90% (from 8.3 to 0.8 mg Kg<sub>soil<sup>-1</sup></sub>) in nitrate content occurred during the first and the second winters. Nitrate may come from the transformation of N content in the cow dungs released by the animals during grazing and from manure residuals. Thus, a production of C<sub>soluble</sub> occurred during winter while nitrate was consumed and no trends could be identified for N<sub>tot</sub>.

The reason for the differences in physico-chemical properties between years may partly be due to the presence of cows that was different between both years in addition to differences in rain, snow cover and winter duration. The presence and the distribution of cow dungs, different between years, may in part influence  $CO_2$  and  $N_2O$  distribution since  $C_{soluble}$ , nitrate and  $N_{tot}$  have quite a large variability that changed between years (Figure 1), and with cow dungs. The spatial distribution of  $C_{soluble}$  showed that the higher concentrations were often localized at the same places as  $N_{tot}$ . This trend was maintained throughout the year although their spatial distribution changed over time (Figure 1). Correlations

and spatial statistical analyses will be completed at later time.

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 season and from -10.8 °C to 12.5°C during the second year (Figure 2). During the second winter, the soil temperature at 0.125 m depth was below the freezing point from approximately 15<sup>th</sup> Jan. 2012 until the 15<sup>th</sup> April 2012. During winter 2012-2013, the coldest period was about 3 weeks later and about 2 weeks longer than during the first winter. The soil was partially frozen starting at the beginning of December (Figure 2). The soil thawed later during the second year due to lower air temperature at the end of March and to the thicker snow cover. During winter, when the soil was totally frozen and when the snow cover was installed, soil temperature was almost homogeneous throughout the field (Figures 4). However, at the beginning and at the end of both winters, soil temperature presented much higher spatial variations, in part due to variability in snow cover depth, in variation in thawing and in the distribution of water content in the liquid state (Figures 1 and 4).



Figure 1. Spatial distribution of soil water saturation (SWS), nitrates, total N ( $N_{tot}$ ) and soluble carbon ( $C_{soluble}$ ) contents at 0.125 m depth during the winter 2012-2013

# 3.2 Temporal variability of soil CO<sub>2</sub> and N<sub>2</sub>O concentrations

 $CO_{2-soil}$  and  $N_2O_{soil}$  presented similar tendencies although  $CO_{2-soil}$  was about 200 to 500 times higher than  $N_2O_{soil}$ . The final concentrations in spring were within the range observed in other studies for summer seasons (Allaire et al., 2012 and 2015). The concentrations were lower near the soil surface as usually observed because of soil emissions to the atmosphere.

Nevertheless, three periods were identified over the course of each winter relatives to soil gas concentration dynamics. The period duration depended on soil temperature.

# 3.2.1. First period.

During the first period of each cold season, e.g. during the pre-freeze period, gas concentrations were relatively constant at approximately 30  $\mu g \ m L_{soil \ air}^{-1}$  for  $CO_{2\_soil}$  and often below detection limit for N<sub>2</sub>O<sub>soil</sub> (0.005 µg mL<sub>soil air</sub><sup>-1</sup>) (Figure 2). The values correspond to values measured in other field studies during fall seasons under very moist soil conditions (Allaire et al., 2012 and 2015). During this period, the soil was up to 75% saturated. Nevertheless a sufficient number of pores were air-filled ( $\theta_a \ge 25\%$ ) allowing gas diffusion and exchanges with the atmosphere and supporting microbial activity. It is usually considered that soil gas can diffuse when  $\theta_a$  is at least 10%. The CV during this first period varied from 52 to 60% for CO<sub>2-soil</sub> and from 248 to 256% for N<sub>2</sub>O<sub>soil</sub>. The CV values were quite similar for each depth. The range of values of CV for both gases was within the ranges observed in other field studies between spring and fall seasons (Allaire et al., 2012).

This period occurred as long as soil temperature was higher than 0°C. Below this temperature, ice formed on soil surface and within the soil profile. In this case, a different behaviour of soil gas concentration was identified. This leads to the second period.

## 3.2.2. Second period.

The second period started at the end of December during the first winter and in mid-January during the second one. It started when the soil temperature was below 0°C. CO2soil reached 110 to 160 µg mLsoil air<sup>1</sup> varying with depth (Figure 2). It was 3 to 5 times higher than during the first period e.g. before soil freezing. N<sub>2</sub>O<sub>soil</sub> increased by about 400 times during the entire frozen period to reach 0.4 to 1.8  $\mu$ g mL<sub>soil air</sub> varying with depth and year. At the reference point, maxima of CO<sub>2-soil</sub> and N<sub>2</sub>O<sub>soil</sub> at 0.125 m depth were obtained at the end of each frozen period (8<sup>th</sup> March 2012 and 8<sup>th</sup> April 2013) where CO<sub>2-soil</sub> concentrations reached 142 and 132  $\mu g \ m L_{soil \ air}{}^1$  and N<sub>2</sub>O<sub>soil</sub> reached 0.53 and 1.74 µg mL<sub>soil air</sub><sup>-1</sup> during winter 2011-2012 and 2012-2013 respectively (Figure 2). At 0.25 m depth, maxima of CO<sub>2-soil</sub> was 148 and 160  $\mu$ g mL<sub>soil air</sub> and was 0.55 and 1.40  $\mu g~m L_{soil~air}{}^1$  for  $N_2 O_{soil}$  in 2011-2012 and in 2012-2013 respectively. These maxima were observed at the same date as for 0.125 m depth.

During this frozen period, both gas concentrations drastically increased over time as long as the soil surface did not start to thaw. Gas exchange at the soil surface was limited due to 1) restricted soil gas diffusivity due to ice that filled the pore space when soil temperature reached -5°C (Teepe et al., 2001); 2) ice and snow cover at the soil surface, limiting gas diffusion; 3) high SWS resulting in low gas diffusion coefficient.

Effectively, SWS occupied more than half of the pore space to almost 100% resulting in a  $D_s/D_o$  from almost 0 to 0.03. This low diffusivity considerably decreased gas movement in soil. 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 get trapped in the ice when the water freezes and in  $\theta_a$  surrounded by non-permeable frozen soil (Goldberg et al., 2010). Gases were thus produced at higher rate that they could escape from the low diffusive soil to accumulate and redistribute at different depths. The production of both gases during this entire period indicates, though, a certain level of oxygenation. This oxygen may come from water, ice, and snow and to air already present  $\theta_a$ . These hypotheses will be tested later on with other data from this study.

The CV of CO<sub>2-soil</sub> ranged from 32 to 38% while that of  $N_2O_{soil}$  ranged from 60 to 87% at both depths during the frozen period. The CVs of both gases were 2 to 3 times lower for CO<sub>2</sub> and 3 to 5 times for N<sub>2</sub>O, dependently upon depth and year, during this frozen period than during the two other periods. This is probably because sufficient time was allowed for their diffusion within the profile although they could not rapidly diffuse within it.

During winter 2011-2012, a 10-day warming period occurred in mid-March. It allowed the snow to melt and soil to warm. The 21<sup>th</sup> March 2012, a temperature of 24.5°C was recorded. During this short period, a burst of gas exchange happened at the soil surface with a significant decrease in soil gas concentration.  $CO_{2-soil}$  changed from 140 µg mL<sub>soil air</sub><sup>-1</sup> on 15<sup>th</sup> March to 20 µg mL<sub>soil air</sub><sup>-1</sup> on 26<sup>th</sup> March (Figure 2). N<sub>2</sub>O<sub>soil</sub> dropped from 0.5 to 0.05 µg mL<sub>soil air</sub><sup>-1</sup> during the same period. Seven days later, another cold period of 2 weeks with a new snow cover immediately induced an Increase in both gas concentrations from 20 to 40 µg mL<sub>soil air</sub><sup>-1</sup> for CO<sub>2-soil</sub> and from 0.05 to 0.45 µg mL<sub>soil air</sub><sup>-1</sup> for N<sub>2</sub>O<sub>soil</sub> (Figure 2).

During the second winter, another short warm period occurred. It was however less intense than during the first winter. During 3 days (from 11<sup>th</sup> to 14<sup>th</sup> March 2013), air temperature raised and varied between 0 and 5°C both day and night. This short period induced a net decreased in  $CO_{2-soil}$  from 110 to 60 µg mL<sub>soil air</sub><sup>-1</sup> and in N<sub>2</sub>O<sub>soil</sub> from 1 to 0.5 µg mL<sub>soil air</sub><sup>-1</sup> at both depths (Figure 2). Although this short warm period resulted in a 40 to 50% decrease in gas concentrations in the soil profile, it was not sufficient to complete snowmelt or soil thawing. Immediately after, soil temperatures returned to below the freezing point and gases accumulated again.

These data clearly indicate that, 1) even when the soil is deeply frozen, microorganisms still produce both gases but at a lower rate; 2) even when gas diffusion is very limited, microorganisms find sufficient oxygen for their activities although the lower oxygenation may decrease their activities; 3) gases get trapped in the soil profile until the thawing; 4) the gases diffusion to the atmosphere occurs very rapidly as soon as only a part of the soil thaws.

Thus, gas accumulation in soil began immediately when temperature allows surface ice and snow cover accumulation (at 0°C) and ice lenses formation in soil rather than when water freezes in the soil profile at -5°C.



Figure 2. Average daily temperature (°C) at 1 m above soil surface (grey line) and at 0.125 m depth (black line) recorded in the field for both winters and evolution of  $CO_{2-soil}$  and  $N_2O_{-soil}$  concentrations (µg mL<sub>soil air</sub><sup>-1</sup>) at the reference point during both winters.

# 3.2.3. Third period.

The last period corresponded to the end of winter and the beginning of spring thaw, when gas concentrations rapidly decreased. Both gases were released from the soil to the atmosphere during a very short lapse of time (a couple of days). This occurred whenever 1) snow and ice partly melted at the soil surface; 2) a small part of the soil profile warmed up to  $-5^{\circ}$ C allowing melting of ice from the soil pore space; 3) soil water drainage occurs; and 4) gas diffusion and other gas movement processes take place.

The concentration of  $CO_2$  decreased from 100 and 160 µg mL<sub>soil air</sub><sup>-1</sup> to 10 to 20 µg mL<sub>soil air</sub><sup>-1</sup> at the end of the measured period within a couple of days, dependently upon depth at the beginning of the period (Figure 2). It then returned to the soil concentration measured at the beginning of the pre-freeze period. Its CV ranged from 81 to 98%, similar to values for summer conditions in other studies (Allaire et al., 2015). Comparatively, N<sub>2</sub>O decreased from 0.4 and 1.8  $\mu$ g mL<sub>soil air</sub><sup>-1</sup> to undetectable level (0.005  $\mu$ g mL<sub>soil air</sub><sup>-1</sup>) within about the same time period, but the process was slightly faster (about 1-3 days). Its CV ranged from 195 to 309% as observed in other studies (Wagner-Riddle et al., 2008).

Sudden decrease in N<sub>2</sub>O soil concentration also occurred when soil temperature rose to  $-5^{\circ}$ C and above as observed by van Bochove et al. (2001). It would be due to winter that kills some microbes and fine roots, ice expansions and contractions during freeze-thaw cycles causing soil aggregate breakdown. The N and C from these dead materials and broken aggregates become available to microbes, favourable for N<sub>2</sub>O formation during a short period of time at spring thaw. Indeed, C<sub>coluble</sub> strongly increased during spring (Figure 1).

During this period, gas diffusion considerably increased at the soil surface because the soil dried quit fast mostly at the top of the field bed due to soil drainage, 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), particularly for  $N_2O$  formed by the cold-adapted microflora (Wagner-Riddle et al., 2008).

# 3.3 Correlation between CO<sub>2</sub> and N<sub>2</sub>O

 $N_2O$  is usually more variable during the unfrozen conditions because of the requirement for specific local conditions to produce it (Wagner-Riddle et al., 2008). This is why it is usually difficult to correlate  $CO_{2\text{-soil}}$  with  $N_2O_{\text{soil}}$ . Indeed, the correlation was weak between both gases during the pre-freeze and the thawing periods. Comparatively, average  $CO_{2\text{-soil}}$  and  $N_2O_{\text{soil}}$  were highly correlated together during the frozen period of both years (Figures 3, 4).

Soil temperature  $> 0^{\circ}C$ 

#### 3.4 Spatial variability of CO<sub>2</sub> and N<sub>2</sub>O

#### 3.4.1 Vertical variability

The vertical variability of  $CO_{2-soil}$  was higher during prefreeze and thawing periods than during the frozen one. During the pre-freeze period (only 2012-2013),  $CO_{2-soil}$ increased with depth. Max  $CO_{2-soil}$  were obtained at 0.85 m depth most of the time while Min in  $CO_{2-soil}$  were obtained at 0.125 m depth. Ratios of Max/Min  $CO_{2-soil}$ reached 3.8. Contrarily, Max  $CO_{2-soil}$  were obtained in upper soil layers until 0.4 m depth while Min were obtained in deeper soil layers during the frozen period of both years. Max/Min ratios were always under 2, which indicates more homogenous gas distribution in the soil profile. During the last period, Max  $CO_{2-soil}$  were obtained in middle layers (at 0.25 m or 0.4 m) and Min were always observed near the soil surface at 0.125 m depth. Nevertheless, Max/Min ratios were higher than during the two first periods ranging from 4 to 12.

Soil temperature  $< 0^{\circ}C$ 

![](_page_5_Figure_6.jpeg)

Figure 3: Relationships between average  $CO_{2-soil}$  and  $N_2O_{-soil}$  for both winters at 0.125m depth. At left when soil temperature was above 0°C (pre-freeze and thawing periods) and at right when soil temperature was under 0°C (Frozen period).

The inversion of the Max concentrations in the soil profile during the frozen period suggests either or both, 1) gas were formed near the soil surface and got trapped, and then, based on gas diffusion, move toward depth where gas concentration was lower because of a lower activity; 2) gases were formed in the whole profile and diffuse vertically from higher concentration to lower depth, but its reabsorption by different processes were higher at lower depth than their rate of formation; 3) the depth of the dominant processes for formation and transformation of the gases changed over time.

For N<sub>2</sub>O<sub>soil</sub>, the vertical variability was similar during the two first periods. The ratios were similar to that of CO<sub>2</sub> during the freezing period indicating a similar gas distribution in the soil profile. During thawing, two subperiods were identified. During the first sub-period, when the soil profile was not totally defrosted, Max and Min were obtained in the same layers as for CO<sub>2-soil</sub>, but their ratios were higher (38) showing that the N<sub>2</sub>O<sub>soil</sub> vertical distribution was very heterogeneous. During the second sub-period when soil was totally defrosted, Max were obtained in deeper soil layers while Min were obtained at the soil surface. Max/Min ratios decreased but remained higher than 4.

Thus vertical variability during the frozen periods was low for both gases during both winters. Homogenisation of their soil concentrations occurred probably due to gas diffusion that had several months to produce this impact although limited. During the two other periods, the vertical variability was higher, particularly during the thawing period when soil warming, snow and ice melting and SWS distribution were very heterogeneous.

#### 3.4.2. Spatial variability

The analysis of the spatial correlations between gases and soil parameters are not completed yet, nevertheless, few results are presented below. During pre-freeze and frozen periods, average  $CO_2$ and  $N_2O$  concentrations and variability at both depths were very similar although the variability was twice higher during the pre-freeze period (CV from 52 to 60%) than during the frozen one (32 to 37%). During thawing, gas concentrations varied with depth but variability at different depth was similar. Thus, only the results relative to 0.125 m depth and only for the second winter are presented (Figure 4).

General observations show that the hotspots of soil gas concentrations were not situated at the same place from one year to the other. The distributions patterns of few parameters at the beginning of each winter as SWS, cow dungs,  $C_{soluble}$ ,  $N_{tot}$  and nitrate may explain these differences (Figure 1).

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 4). Microbial activity decreased with temperature as gas concentrations decreased while emissions still occurred (data not shown). For N<sub>2</sub>O<sub>soil</sub>, the correlation was less obvious since the N<sub>2</sub>O concentrations were close to detection limit and more variable.

During the second period,  $CO_{2-soil}$  distribution was no longer correlated to the spatial distribution of soil temperature (Figure 4).  $CO_{2-soil}$  and  $N_2O_{soil}$  increased with a distribution pattern maintained over time as long as the soil remained completely frozen. Their spatial distributions showed the same trends with hot spots situated in the same part of the field. This indicates that although the soil reached very low temperature, soil microbial activity remained. However, correlation with  $N_{tot}$  or to nitrate contents was not obvious (Figures 1 and 4).

During the third period,  $CO_{2-soil}$  and  $N_2O_{soil}$  rapidly decreased except at local spots where the soil remained frozen (Figure 4). Once completely thawed all around the field,  $CO_{2-soil}$  concentrations were higher where the soil was warmer indicating the recovery of soil microbial activity. At this time,  $CO_{2-soil}$  spatial distribution tended to present a positive correlation with the spatial distribution of  $C_{soluble}$  (Figures 1 and 4). For  $N_2O_{soil}$ , no obvious correlations were identified due to its high variability and low concentration in soil.

![](_page_6_Figure_5.jpeg)

Figure 4: Spatial distribution of soil temperatures (°C),  $CO_{2-soil}$ , and  $N_2O_{soil}$  (µg mL<sub>soil air</sub><sup>-1</sup>) at 0.125 m depth at different times during winter 2012-2013.

# 4. CONCLUSION

Although both seasons were different in term of weather conditions, gas concentrations and distribution, the results clearly suggest three distinct periods.

The first occurred when soil temperature at the soil surface was higher than 0°C, allowing gas diffusion between soil and atmosphere and with higher gas concentrations in deeper soil layers. The second period started when the entire soil was below the freezing point. Gas accumulation in soil suggests a continuous production of both gases at low temperature, with limited

exchange with the atmosphere and limited movement of oxygen. The long duration of this period allowed a homogenisation of soil gas concentration in the soil profile even though the soil gas diffusivity was very low. This homogenisation resulted in a strong correlation between both gases, which was not the case during the other periods. During thawing, the third period, gases were emitted to the atmosphere as soon as ice and snow partially thawed. These emissions occurred in few days only. As thawing was heterogeneous across the field, the spatial variability was also very high. Temporal and spatial variability of  $CO_2$  and  $N_2O$  were very similar during the frozen period, while different during the unfrozen periods. Their hot spots were localised at the same place. Their spatial distribution was clearly dependant on soil temperature distribution as long as the soil was not totally frozen while they were not related to it once frozen. Additional statistical and spatio-temporal analyses will be performed on these data.

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# REFERENCES

- Allaire, S.E., Baril, B., Vanasse, A., Lange, S.F., MacKay, J. and Smith, D.L. 2015. Carbon dynamics in a biochar-amended loamy soil under switchgrass. *Canadian Journal of Soil Science*, 95: 1-13.
- Allaire, S.E., Lange, S.F., Lafond, J.A., Pelletier, B., Cambouris, A.N. and Dutilleul, P. 2012. Multiscale spatial variability of CO<sub>2</sub> emissions and correlations with physicochemical soil properties. *Geoderma*, 170: 251–260.
- Bartlett, R.J. and Ross, D.S. 1988. Colorimetric Determination of Oxidizable Carbon in Acid Soil Solutions. *Soil Science. Society of America Journal*, 52: 1191-1192.
- Flint, L.E. and Flint, A.L. 2002. Porosity. Pages 241-254 in Dane J.H. and Topp G.C. 2002, eds. *Methods of soil* analysis. Part 4. Physical methods. Soil Science Society of America, Inc, Madison, WI. USA
- Goldberg, S.D., Borken, W. and Gebauer, G. 2010. N<sub>2</sub>O emissions in a Norway spruce forest due to soil frost: concentration and isotope profiles shed a new light on an old story. *Biogeochemistry*, 97: 21-30.
- Keeney, D.R., and Nelson, D.W. 1982. Chap 33: Nitrogen—Inorganic Forms Page, pp. 643-698 in A.L., Miller, R.H. and Keeney, D.R. 1982. *Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties*, 2<sup>nd</sup> ed. American Society of Agronomy, Inc, Soil Science Society of America, Inc, Madison, WI. USA
- Lamontagne, L., Martin, A. and Nolin, M.C. 2010. Étude pédologique du bassin versant du Bras d'Henri (Québec). Agriculture et Agroalimentaire Canada. Québec (Qc, CANADA). 78 pp.
- Maljanen, M., Kohonen, A.R., Virkajarvi, P. and Martikainen, P.J. 2007. Fluxes and production of N<sub>2</sub>O, CO<sub>2</sub> and CH<sub>4</sub> in boreal agricultural soil during winter as affected by snow cover. *Tellus*, 59B(5): 853–859.
- Mariko, S., Nishimura, N., Mo, W., Matsui, Y., Kibe, T. and Koizumi, H. 2000. Winter CO<sub>2</sub> flux from soil and snow surfaces in a cool-temperate deciduous forest, Japan. *Ecological Research*, 15(4): 363-372.

- McGill, W. and Figueiredo, C. 1993. Chap. 22: Total nitrogen, pp. 201-211. In Carter, M.R. 1993 Soil Sampling and Methods of Analysis, Ed., Carter, M.R. for Canadian Soil Science Society, CRC Press, London, ON, CANADA.
- Millington, R.J. and Quirk, J.P. 1961. Permeability of porous solids. *Transactions of the Faraday Society*, 57: 1200–1207.
- Oechel, W.C., Vourlitis, G. and Hastings, S.J. 1997. Cold season CO2 emission from arctic soils. *Global Biogeochemical Cycles*, 11(2): 163-172.
- Osterkamp, T.E. and Ramanosvsky, V.E. 1997. Freezing of the active layer on the coastal plain of the Alaskan Arctic . *Permafrost and Periglacial Processes*, 8(1): 23-44.
- Panikov N.S. and Dedysh, S.N. 2000. Cold season  $CH_4$ and  $CO_2$  emission from boreal peat bogs (West Siberia): winter fluxes and thaw activation dynamics. . *Global Biogeochemical Cycles*, 14(4): 1071–1080
- SAS Institute Inc. 2008. SAS user guide: Statistics.Version. 9.2. SAS Institute Inc., Cary. NC, USA.
- Teepe, R., Brumme, R. and Beese, F. 2001. Nitrous oxide emissions from soil during freezing and thawing periods. *Soil Biology and Biochemistry*, 33: 1269-1275.
- Topp, G.C., Davis, J.L., Annan, A.P., 1980. Electromagnetic determination of soil water content: measurements in coaxial transmission lines. *Water Resources Research*, 16, 574–582.
- Van Bochove, E. Thériault, G., Rochette, P., Jones H.G. and Pomeroy, J.W. 2001. Thick ice layers in snow and frozen soil affecting gas emissions from agricultural soils during winter. *Journal of. Geophysical Research*. 106: 23 061-23 071.
- Wagner-Riddle, C., Hu, Q.C., van Bochove, E. and Jayasundara, S. 2008. Linking nitrous oxide flux during spring thaw to nitrate denitrification in the soil profile. Soil Science. Society of America Journal, 72: 908-916.