

## **Nitrous oxide emissions induced by freeze/thaw: importance and potential mechanisms**

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### **Extended Abstract**

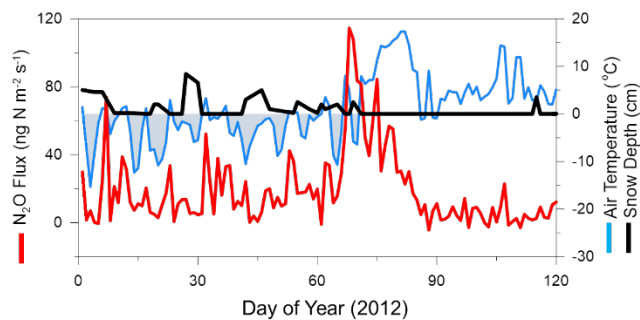
Nitrous oxide (N<sub>2</sub>O) is a long-lived greenhouse gas, an important driver of global climate change [1], and a dominant ozone-depleting substance that continues to have a key role in the delay of stratospheric ozone recovery [2]. Agricultural soils are by far the main anthropogenic source of N<sub>2</sub>O emissions [3]. The main pathways for microbial N<sub>2</sub>O production in soils are heterotrophic denitrification, ammonia oxidation during nitrification, and nitrifier-denitrification [4]. The complex interplay of microbial processes and soil conditions, such as aeration, pH, temperature, C and nitrogen (N) supply regulates N<sub>2</sub>O production in the soil profile, and how and when N<sub>2</sub>O is released from the soil surface [5]. These drivers result in N<sub>2</sub>O fluxes that are highly variable in time with occurrence of emission bursts (‘hot moments’) and highly variable in space with concentrated areas within the soil or landscape (‘hot spots’) [6]. In cold climates, freeze-thaw (F/T) cycles induce large N<sub>2</sub>O emissions representing such hot spots and hot moments [7]. Here, measurement methods that best capture these F/T events at the field scale, the importance of F/T N<sub>2</sub>O emissions for the global agricultural N<sub>2</sub>O budget and the underlying soil processes leading to F/T emissions are discussed. Potential management practices that could be deployed to mitigate the impact of F/T N<sub>2</sub>O emissions are then presented.

The spatial and temporal variability of soil N<sub>2</sub>O fluxes is difficult to capture with typical soil gas chamber methods [8]. During F/T induced emission events there are several logistical issues with chamber deployment as illustrated in Fig. 1. In contrast, measurements of N<sub>2</sub>O fluxes using micromet methods (eddy covariance or flux-gradient) are non-intrusive and integrate small-scale spatial variability over areas >1 ha continuously at half-hourly intervals [9]. Thus, the temporal variations in N<sub>2</sub>O fluxes associated with frequent F/T cycles is captured regardless of the challenging field conditions (Fig. 2). In this example, 64% of annual emissions occurred from January to March, with 31% of annual emissions occurring during the main thaw event of day 65-85 (Fig. 2). A flux-gradient approach that allows for quasi-simultaneous measurement of N<sub>2</sub>O fluxes from four adjacent 4-ha plots with a single trace gas analyzer has been deployed over an extensive time to better characterize



**Figure 1.** View of a soil gas sampling collar after a major thaw snow melting event that left the soil covered with a thick ice layer and prevented chamber placement on the collar for gas sampling. Photo courtesy of Mark Libby.

F/T hot moments in Canada [10, 11]. This extensive dataset allowed us to identify cumulative freezing degree days (i.e. days with soil temperature at 5 cm depth  $< 0^{\circ}\text{C}$ ) as the main predictor of  $\text{N}_2\text{O}$  emissions induced by F/T, a trend confirmed with data from 11 cold-climate sites from around the globe [12]. Model estimates of global soil temperature were then used with this predictor to show that not considering F/T  $\text{N}_2\text{O}$  emissions from seasonally frozen cropland underestimates global agricultural nitrous oxide emissions by 17 to 28% [12].

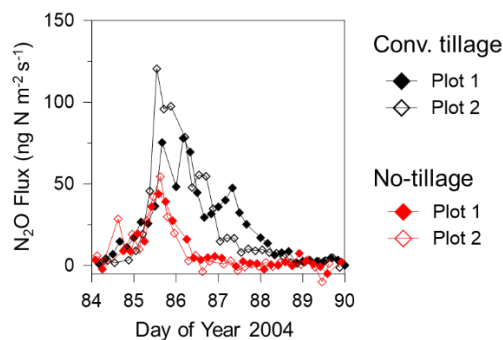


**Figure 2.** Daily nitrous oxide flux (red line) from January to end of April 2012 measured in Elora, ON, Canada, following a fall manure application of liquid dairy manure in November 2011. Air temperature (blue line) and snow depth (black line) are shown for the same period. Shaded grey areas show air temperature below  $0^{\circ}\text{C}$ . Data from [9].

The process of soil freezing is analogous to soil drying because the soil liquid water content decreases, although there are some fundamental differences in the two processes [7]. Upon thawing or rewetting, the soil liquid water content increases, often resulting in anaerobiosis and large  $\text{N}_2\text{O}$  fluxes. In cold climates, up to 90% of annual  $\text{N}_2\text{O}$  emissions from agricultural soils can occur during the non-growing season [10] due to events induced by soil thawing, which can last several days with fluxes several 1000% higher than pre-thawing [7]. Enhanced N losses are related to degree of soil aggregation, freezing temperature and duration, soil water content at freezing, labile C and N content, and N fertilizer input [7].

Studies investigating FT fluxes have suggested a combination of mechanisms related to A) physical trapping and release of N<sub>2</sub>O produced during freezing as ice layer or snow thaw, and B) enhanced microbial processes at thaw due to increased anaerobiosis and substrate availability (via freeze action on soil aggregates, microbial cell lysis and microbial cytoplasmic release) [13]. Denitrification, promoted under mechanism B), appears to be the dominant process as suggested by stable isotope [14] and molecular studies [15], although mechanism A) also plays a role under some conditions [16]. We recently showed that higher thaw N<sub>2</sub>O emissions for corn fields with crop residue removed compared to residue retained were related to less transcription of the *nosZ* gene, which modulates N<sub>2</sub>O reduction to N<sub>2</sub> [15]. In another study comparing tillage and residue treatments we had hypothesized that residue return/no-till would have lower N<sub>2</sub>O emission as the insulating layer of residue plus trapped snow would reduce soil freezing and provide less substrate by mechanism B). Our predictions were correct for lower N<sub>2</sub>O emission, but this was associated with higher dissolved organic C (DOC) potentially reflecting more complete stepwise denitrification to N<sub>2</sub> during winter and possibly related a shift in the preferential C source utilized by the microbial community overwinter [17].

Soil and crop management can play a role in F/T N<sub>2</sub>O emissions due to change in soil biogeochemical and physical conditions. We have shown consistent reductions in the magnitude of N<sub>2</sub>O thaw fluxes due to the reduced freezing intensity during winter associated with surface crop residue and its snow trapping properties as observed with no-tillage [10] (Fig. 3). Likewise, perennial fields showed lower N<sub>2</sub>O thaw emissions than corn grown under



**Figure 3.** Half-hourly nitrous oxide flux the last week of March (day 84 to 90) in 2004 for two plots receiving either conventional tillage (moldboard ploughing of corn residue in previous fall) or no-tillage (corn residue left on the soil surface) measured in Elora, ON, Canada. Data from [10].

conventional tillage corn except for when the perennial hay fields were ploughed down the previous fall [9]. Use of perennials had the lowest thaw N<sub>2</sub>O emissions across two long term datasets, and addition to fall nitrogen either in manure or inorganic fertilizer form resulted in dramatic increases in emissions [12].

In summary, N<sub>2</sub>O emissions induced by freeze-thaw in seasonally frozen croplands recently have been estimated to be a significant underestimated global source. This first estimate is uncertain and year-round N<sub>2</sub>O measurement programs are needed to provide more comprehensive estimates for cold regions, particularly in cropland areas that are intensively managed. Although some soil and crop management practices have been identified which reduced F/T N<sub>2</sub>O emissions, more research is needed in specific soil drivers for emission enhancement and how to manage these to mitigate emissions. This is particularly important as more frequent and severe soil F/T cycles are anticipated in the future with decreased snow cover due to climate change.

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#### **OECD disclaimer**

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