Agriculture, Ecosystems and Environment 133 (2009) 196–207

Contents lists available at ScienceDirect

Agriculture, Ecosystems and Environment

journal homepage: www.elsevier.com/locate/agee

Model evaluation of different mechanisms driving freeze–thaw N_2O emissions

A.M.G. de Bruijn [a], K. Butterbach-Bahl [a,*], S. Blagodatsky [a,b], R. Grote [a]

[a] Karlsruhe Research Centre, Institute for Meteorology and Climate Research, Atmospheric Environmental Research (IMK-IFU), Kreuzeckbahnstr. 19, 82467 Garmisch-Partenkirchen, Germany

[b] Institute of Physicochemical and Biological Problems in Soil Science, Russian Academy of Sciences, 142290 Pushchino, Moscow region, Russian Federation

ARTICLE INFO

Article history:
Received 12 August 2008
Received in revised form 10 February 2009
Accepted 27 April 2009
Available online 4 June 2009

Keywords:
N_2O flux
N_2O modelling
Freezing–thawing
DNDC
Nitrogen modelling
PnET-N-DNDC
Forest-DNDC

ABSTRACT

N_2O emissions from soil contribute significantly to global warming. Pulse emissions of N_2O from soils during freeze-thawing were recently recognized as important atmospheric sources. In this modelling study we explore three different hypotheses for explaining freeze–thaw related N_2O emissions: (1) soil frost or snow cover may reduce gas diffusion and create anaerobic conditions that stimulate N_2O production via denitrification, (2) microbes that die of frost deliver easy decomposable organic carbon and nitrogen to the soil, which stimulates microbial growth and vigorous N_2O production during freeze–thaw, and (3) the enzyme nitrous oxide reductase, which is responsible for the reduction of N_2O to N_2 during denitrification, is more sensitive to low temperatures than other enzymes, so that N_2O becomes the dominating end-product of denitrification at low temperatures. These hypotheses were tested with a biogeochemical model that combines hydrology and physics calculations with a newly developed, parameter-poor biochemistry module. The model was first calibrated with field datasets on soil–atmosphere fluxes of N_2O, NO and CO_2 and soil NO_3 and NH_4 concentrations that were measured in a spruce forest in Southeast Germany in the years 1994–1997. Subsequently, additional model mechanisms were implemented that allow the model to describe the outlined mechanisms potentially driving freeze–thaw N_2O fluxes. After each implementation the model was recalibrated. We were able to mimic dimension and timing of high N_2O emissions when either one of the first two hypotheses were assumed, but found no confirmation for the third. The best model fit was achieved by combining hypothesis one and two, indicating that freeze–thaw N_2O emissions are not mono-causal.

1. Introduction

Nitrous oxide emissions from soils are estimated to contribute 6.1% to anthropogenic global warming (IPCC, 2007). Recent research has shown that winter emissions may significantly effect or even dominate the annual budgets of N_2O emission from temperate and boreal soils (Röver et al., 1998; Papen and Butterbach-Bahl, 1999; Van Bochove et al., 2000; Butterbach-Bahl et al., 2002b; Müller et al., 2002; Groffman et al., 2006; Sharma et al., 2006; Holst et al., 2008). A multitude of physical, chemical and biological hypotheses have been proposed to explain the occurrence of low temperature related N_2O emissions (Table 1). Physical explanations propose that gas diffusion rates become lower when liquids in soil pores are partially frozen (Bremner et al., 1980; Li et al., 2000). A slower diffusion of gases in frozen soils may result in an N_2O peak while thawing, when N_2O would accumulate in the soil and be emitted pulse wise when the soil thaws and soil pores widen again. It could also be an indirect cause as oxygen diffusion into the soil will be reduced if water starts to freeze, thereby expanding and narrowing soil pores. This will create anaerobiosis, with microbes using nitrogen oxides as alternative electron acceptors, i.e. favouring denitrification and, thus, N_2O production via the denitrification pathway (Koponen et al., 2006; Mørkved et al., 2006). Another physical explanation lies with the assertion that freezing disrupts soil aggregates. This may mobilise dissolved organic carbon during thawing. Such enhanced substrate input has been hypothesized to stimulate microbial nitrogen conversions and associated N_2O production (Groffman and Tiedje, 1989; Van Bochove et al., 2000; Sharma et al., 2006). A chemical mechanism has also been proposed to explain N_2O pulse emissions during freeze–thaw. Christianson and Cho (1983) proposed that during freeze–thaw chemodenitrification increases, i.e. that microbial produced nitrite decomposes partially to N_2O. Biological explanations are focusing on higher nitrogen availability for microbial metabolism during freeze–thaw. One mechanism would be that in winter plant uptake of nitrogen is low (Zak et al., 1990; Groffman et al., 1993), thus, leaving more N substrate for microbial N turnover. Microbial activity may still persist even when air temperature is below zero, since snow and upper soil layers buffer the temperature decrease and microbes can remain active in

* Corresponding author. Tel.: +49 8821 183136; fax: +49 8821 183294.
E-mail address: Klaus.Butterbach-Bahl@imk.fzk.de (K. Butterbach-Bahl).

0167-8809/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.agee.2009.04.023

Table 1
Published hypotheses for freeze–thaw related N_2O emissions from soils.

Hypothesis	References
N_2O diffusion rates are lower when water in soil pores is partially frozen	Bremner et al. (1980), Li et al. (2000)
Lower oxygen diffusion stimulates anaerobiosis and denitrification	Li et al. (2000)
Freezing induces soil aggregate disruption and mobilises dissolved organic carbon	Groffman and Tiedje (1989), Van Bochove et al. (2000), Sharma et al. (2006)
Chemodenitrification increases with high nitrate concentration	Christianson and Cho (1983)
More nitrogen is available to microbial populations in winter because plant uptake is low	Zak et al. (1990), Groffman et al. (1993)
Microbial activity continues because snow and upper soil layers buffer the temperature decrease and microbes remain active in deeper ground	Röver et al. (1998)
Microbes, dying of frost, deliver substrate to the soil which is decomposed progressively as temperature increases after the frost	Skogland et al. (1988), Müller et al. (2002), Röver et al. (1998), Groffman et al. (2006)
Fine root mortality increases due to frost and delivers substrate to the soil which is decomposed progressively as temperature increases after the frost	Fitzhugh et al. (2001)
Temperature sensitivity of N_2O reductase will lead to lower N_2 but increased N_2O production during denitrification.	Holtan-Hartwig et al. (2002)

deeper ground (Röver et al., 1998). Another argument for increased substrate availability during freeze–thaw is that microbes, dying of frost, deliver substrate to the soil which is decomposed progressively as temperature increases after the frost (Skogland et al., 1988; Röver et al., 1998; Müller et al., 2002; Sulkava and Huhta, 2003; Groffman et al., 2006; Koponen et al., 2006). This ambivalence, i.e. on the one hand active microbes and on the other hand dying microbes, is commonly explained by employing a concept of microsites and population diversity: High levels of microbial activity may also locally increase temperatures (Parkin, 1987) or low temperature resistant microbial populations remain active at some microsites. The decomposition of microbial tissues, produced by microbes that died of frost, could continue at these hotspots and produce N_2O as a respiratory by-product (Parkin, 1987). Similarly, Fitzhugh et al. (2001) propose an increase in fine roots mortality as the main source of nitrogen loss during winter. Finally, it has also been hypothesized that changes in the activity of selected enzymes of the denitrification chain at low temperatures may be involved in freeze–thaw N_2O pulse emissions. Holtan-Hartwig et al. (2002) indicate that the enzyme N_2O reductase may be more sensitive to low temperatures than other enzymatic steps in the denitrification chain from NO_3 to N_2. This would minimize the reduction of N_2O to N_2 and may cause an increased production of N_2O in the soil at low temperatures.

There are objections to some of these hypotheses: (i) it is unlikely that chemodenitrifcation plays an important role during freeze–thaw because chemodenitrification is only of importance for soil N_2O production at pH values lower than 3.5 (Mørkved et al., 2007), but freeze–thaw N_2O pulses have a more general character, i.e. such pulses were also observed for soils with neutral pH values such as steppe soils (e.g. Holst et al., 2008). Moreover, significant chemodenitrification conversions presuppose high nitrite levels, but Röver et al. (1998) found that N_2O is also released from soils when nitrite concentrations in the soils were low. Also the hypothesis that diffusion restrictions are leading to N_2O accumulation in the soil matrix during winter, which is subsequently released during thawing has been challenged. Several authors have reported that N_2O emission from soils are not seriously hampered by diffusion restrictions either by frost or snow pack (Duxbury et al., 1982; Sommerfeld et al., 1993; Kammann et al., 1998; Röver et al., 1998; Teepe et al., 2001). Moreover, also the view of increased substrate availability as driver for N_2O pulses during winter can be seen critical at least as far as the role of fine roots is discussed. Fine root biomass generally has a low nitrogen content (1.0–2.0%), so that the increased availability of nitrogen due to the dying of fine roots in winter is assailable. Since high winter N_2O emission have also been observed (and for the first time) from unvegetated agricultural fields (Christensen and Tiedje, 1990), there should be additional factors in addition to fine root dying be involved to explain N_2O pulses during freeze-thawing.

Whereas many field, and laboratory studies have been published on the phenomenon of N_2O winter emissions, comprehensive model studies to explain freeze–thaw N_2O emissions are scarce, even though biogeochemical models are commonly understood as a useful tool to describe plant and microbial C and N turnover in ecosystems and soils. DNDC for example, relates nitrogen dynamics to agricultural practices (Li et al., 1992a,b). The agricultural version had been further developed towards a forest version by implementing a forest vegetation model (PnET, Aber and Federer, 1992) which was modified to consider also nitrogen uptake and release (Li et al., 2000). Forest-DNDC (previously PnET-N-DNDC) has been evaluated for N trace gas emissions from various forest ecosystems (Li et al., 2000; Stange et al., 2000; Butterbach-Bahl et al., 2001; Kiese et al., 2005; Kesik et al., 2005), even though it was not explicitly used for explaining freeze–thaw related N_2O emissions. Norman et al. (2008) were able to mimic measured N_2O winter emissions with a physics (diffusion and heat transfer) oriented biogeochemical model (CoupModel) that was adjusted to include microbiological process implementations from Forest-DNDC. However, the authors did not provide details what may have caused the peaks that were measured or simulated with their model.

Forest-DNDC has recently been integrated into a new framework called MoBiLE (modular biosphere simulation environment) (Grote et al., submitted for publication). MoBiLE allows modellers to combine elements from different ecosystem models in order to apply the most appropriate selection for a specific task or to facilitate comparison of particular modules. In the framework of this study, an alternative soil biochemistry module for simulating microbial C and N turnover (DNDC2) was developed that interacts with the MoBiLE modelling environment.

We used DNDC2 within the new mobile framework to evaluate different hypotheses. The aim was to single out those that may cause freeze–thaw related N_2O emissions and excluded others. For this purpose, the new module was calibrated using measurements that were taken in the Höglwald forest during a longer period (January 1994–December 1997). Consequently, model mechanisms were introduced that would be needed to enable the model to respond according to the mechanisms that are considered to explain N_2O emission bursts during freeze-thawing. We excluded a priori: (a) N_2O accumulates under snow or frozen soil and N_2O is released during freeze–thaw (not in-line with observations); (b) the microsites hypothesis was not tested since a significant