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The impact of management and climate on soil nitric oxide fluxes from arable land in the Southern Ukraine

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HIGHLIGHTS

- First long-term soil NO flux measurements from cropland in Eastern Europe.
- Identification of drivers of soil NO fluxes.
- Characterization of hot moments of NO emission periods.
- Indication for HONO emissions contributing to soil NO_x fluxes.

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ABSTRACT

NO fluxes from soils are a significant source for tropospheric NO_x, though global and regional estimates of the soil source strength are constrained by the paucity of measurements. In a continuous 18 month effort (2012–2014) soil NO fluxes from an intensively managed arable site in the black soil region of the Southern Ukraine (Odessa region) were measured using an automated dynamic chamber system. Measurements revealed three periods of peak NO emissions (fertigation, re-wetting of soils, and to a lower extend during winter), with a pulse emission peak during soil re-wetting in summer of 88.4 μg N m^{-2} h^{-1}. The mean annual NO flux was 5.1 ± 8.9 μg N m^{-2} h^{-1} and total annual NO emissions were 0.44 ± 0.78 kg N ha^{-1} yr^{-1}. The fertilizer induced emission factor for NO was 0.63% under beetroot. The combined effect of soil temperature, soil moisture and soil DIN (NH_4^+ and NO_3^-) concentrations were identified as drivers of the temporal and spatial variability of soil NO fluxes. This work shows that long-term measurements are needed for estimating annual fluxes and the importance of soils as a source for tropospheric NO_x as the contribution of different seasons and crop growing periods to the annual budget differed markedly.

1. Introduction

Atmospheric NO is often considered together with NO_2 and expressed as NO_x, since conversion of NO to NO_2 as well as NO_2 photolysis to NO is a rapid process. Even though combustion processes are the dominant source for atmospheric NO_x (here the sum of NO and NO_2), soil NO emissions are a significant source for tropospheric NO, being specifically important in rural areas (Butterbach-Bahl et al., 2009; Medinets et al., 2015). NO_x is

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considered the main precursor of ground-level tropospheric O_3, thereby having impact on both mammal health and ecosystem functioning (Ludwig et al., 2001; Wittig et al., 2009; Medinets et al., 2015). Soil NO emissions may react with volatile organic compounds (VOC) emitted from plants (Bai et al., 2006) and contribute to high tropospheric O_3 episodes in rural regions during summer time. Moreover, atmospheric NO is affecting the oxidizing capacity of the troposphere (Delon et al., 2008; Steinkamp et al., 2009), by directly being involved in OH production (Pilegaard, 2013 and references therein) and indirectly by influencing carbon monoxide, methane and non-methane hydrocarbon transformations (Liu et al., 1987). Soil NO emissions are mainly due to the microbial processes of nitrification (autotrophic and heterotrophic) and denitrification (Braker and Conrad, 2011), via chemodenitrification in acid soils (Kesik et al., 2006; Luo et al., 2012), and recently highlighted other enzymatic pathways and mechanisms (Medinets et al., 2015).

NO released from soil can be immediately re-deposited as NO_2 and taken up by plant leaves as an additional N source (Butterbach-Bahl et al., 2004; Sparks, 2009). Global NO_x emissions are around 40–50 Tg N-NO_x yr^{-1} (Denman et al., 2007), with a soil contribution of 18%–22% or on average *ca.* 8.9 Tg N–NO yr^{-1} (Bouwman et al., 2002; IPCC, 2007). The share of soil NO emission from agricultural soils was estimated as 40% of the total soil NO emission (Yienger and Levy, 1995; Aneja and Robarge, 1996) of which N fertilized soils contribute around 18% only (1.6 Tg N–NO yr^{-1}; IPCC, 2007), most of this is released shortly after fertilization. Recently reported average fertilizer induced emission (FIE) factors vary in a range of 0.50–0.60% (e.g., Yan et al., 2003; Laville et al., 2009; Liu et al., 2011) to 0.70% (IPCC, 2007). The intensification of N fertilizer use, up to 201 Tg N yr^{-1} in 2018, according to FAO projections (FAO, 2015) is likely to lead to a dramatic increase of soil NO emission. Rewetting of dry soil in post-harvest periods has been identified to coincide with short pulses of soil NO emissions (Yao et al., 2010; Laville et al., 2011; Kim et al., 2012).

In view of the importance of NO/NO_2 for atmospheric chemistry a thorough understanding of NO emission sources are urgently needed. With regard to soil NO emissions this requires measurements of fluxes over a time period of at least a year for the most representative terrestrial ecosystems (many studies still cover summer or growing seasons only) in order: i) to calculate accurate annual budgets and FIE factors, ii) to better understand controlling factors (environmental and management) triggering NO emission from soil to the atmosphere as a basis for developing mitigation options, and iii) to develop and validate models for projections and scenario analyses.

This study focuses on an integrated analysis of NO fluxes from arable soil in the Southern Ukraine. Fluxes were measured over a period of 18 months using an automated measuring system allowing to obtain fluxes at high time resolution (6 min individual chamber data; 2 hourly mean data for 5 chambers) and spatial distribution (5 dynamic chambers). In addition we monitored a set of environmental parameters (soil moisture content, precipitation, air and soil temperature), soil chemical and physical properties (bulk density, pH, NH_4^+, NO_3^-, NO_2^-) and soil management practice details (tillage, irrigation, N fertilization, plant growth) allowing to carry out an analysis of drivers and temporal changes in NO and NO_2 fluxes.

2. Materials and methods

2.1. Study site

The study was carried out at the Petrodolinskoye Atmospheric Research Monitoring Station (PTR-UA) of the Regional Centre for Integrated Environmental Monitoring and Ecological Studies (RCIEM) of Odessa National I. I. Mechnikov University (ONU). The study site is situated 8 km from the Dniester River, which enters the Black Sea (29 km from the study site). The station is located near the village "Mirnoe" (46°27′22.12″N; 30°20′9.94″E), 27 km southeast of Odessa and was established in 2006 within the framework of the EU FP6 NitroEurope IP (Medinets et al., 2014). The arable field at which NO fluxes were measured is 10 ha in size with a flat topography at an elevation of 66 m above sea level. The soil is a black soil (FAO definition: Chernozems Vermi-Calcic, CH vec) (Table 1), and representative for the south of Ukraine (Medinets et al., 2014). The climate is temperate continental, with an annual average air temperature of 10.5°C (period of 2000–2014), an annual minimum mean of 8.4°C and an annual maximum mean of 12.5°C. Total average annual precipitation is 432 mm. The atmospheric total N (TN) deposition rate is moderate at ca. 11.4 kg N ha^{-1} y^{-1}. Organic N contributes with circa 67% significantly to the TN deposition; such large contribution is also observed for open waters in the northwestern part of the Black Sea (Medinets and Medinets, 2012; Medinets, 2014).

2.2. Crop rotation and management

The study site has been under active agricultural management for more than 200 years, although a detailed history of the agricultural management is unknown. Before autumn 2006 the area was managed by a collective farm ('kolkhoz'). The study field, 10 ha in size, was leased in autumn 2006 from the Association of Agricultural Enterprises "Granit". The crop rotation started with wheat in 2006, in the period 2007–2014 was onions (2007), tomatoes (2008), barley (2009) and winter wheat (2009/2010) followed by winter onion (2010/2011), carrot (2011), tomato (2012), red beetroot (2013) and onion (2014) followed by winter wheat. This rotation is typical for this region. Crops (except cereals) were grown with drip irrigation (installed in 5–10 cm depth), with fertilizer applied together with the irrigation (fertigation). During the NO flux study period (2012–2014) the field was fertilized with mineral NPK fertilizers (Table 2). To prevent plant diseases and to suppress weeds, pesticides and herbicides were applied to all crops following farmers practice. The following tillage methods were used: deep ploughing (40 cm depths), disking (10 cm depth), harrowing (10 cm depth), cultivation (10 cm depth), inter-row cultivation (5 cm depth); the soil was also disturbed under installation/removing of irrigation tubes (Table 2).

2.3. NO and NO_2 flux measurements

Soil-atmosphere exchange measurements of NO and NO_2 started at the end of September 2012 and continued until the beginning of March 2014. Flux measurements were carried out using the dynamic chamber system as described by Butterbach-Bahl et al. (1997). The system consists of 5 measurements chambers, 1 reference chamber and 1 additional inlet for measuring NO/NO_2 concentrations in ambient air, with the inlet being installed at 2.5 m height on a mast. The procedure of gas sampling from the individual chambers is described in detail by Butterbach-Bahl et al. (1997). Briefly, 50 L of air was pulled through the chambers, whereby a measuring chamber and the reference chamber were alternated every 6 min. The total length of a measurement cycle across all chambers was 2 h. Concentrations of NO/NO_2 in sample air was analyzed with a CLD 88p analyzer and a photolytic NO_2 converter PLC 860 (Eco Physics AG, Switzerland). Concentrations of O_3 in the sample air were measured with 49C analyzer (TEI Inc., USA). Calibration of NO/NO_2 analyzer was conducted weekly with a multi-gas calibrator 6100 (Environics Inc., USA) using a standard