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Emissions of atmospherically important nitrous acid (HONO) gas from northern grassland soil increases in the presence of nitrite (NO_2^-)

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ABSTRACT

Several studies have shown that the use of nitrogen fertilizers increases the emission of nitric oxide (NO) and nitrous oxide (N_2O) from agricultural soils. Nitrous acid (HONO) is another form of gaseous N which increase the reactivity potential in the atmosphere by forming OH radicals in photolysis and further oxidize pollutants e.g. methane. It has recently been discovered that soil is a source of HONO. In our experiment with grassland (*Phleum pratense* L.), we found that HONO emissions increased up to 14 μg N m^{-2} h^{-1} in the plot receiving annually 450 kg N ha^{-1} and were strongly linked with soil nitrite (NO_2^-) concentration and pH. A strong correlation between HONO and NO emissions was also observed. This finding suggests that agricultural soils could be an important source of HONO and its emission is primarily dependent soil NO_2^- concentration. Moreover, in agricultural soils the production pathway of HONO and NO could be similar and more studies on the effect of fertilization on HONO emission are needed.

1. Introduction

The global use of nitrogen (N) fertilizer is expected to increase by 3.5 fold by the year 2050 (Tilman et al., 2001). This will result in increased gaseous N-emissions, such as nitrous oxide (N_2O) and nitric oxide (NO) (IPCC, 2007) and also nitrate (NO_3^-) leaching. N_2O is a greenhouse gas which has 265 times stronger warming potential than carbon dioxide (CO_2) in 100 years reference period (IPCC, 2013), while NO is a readily oxidized by ozone (O_3) gas in the atmosphere and plays a vital role in maintaining the O_3 level (Atkinson, 2000). Recent studies have shown that also nitrous acid (HONO) can be emitted from soils (Su et al., 2011; Maljanen et al., 2013; Oswald et al., 2013; Scharko et al., 2015, Weber et al., 2015; Oswald et al., 2015). Nitrous acid (HONO) is not a greenhouse gas but is an important source of hydroxyl radicals (OH) in the atmosphere contributing ~55% of the total amount during daytime (Elshorbany et al., 2009). The OH radicals are vital for oxidation of pollutants in the atmosphere e.g. the greenhouse gas methane (CH_4) and volatile organic compounds (VOCs) (Riedel and Lassey, 2008; Su et al., 2011).

Fertilized agricultural soils around the globe annually contribute 1.8 and 4.1 Tg of NO-N and N_2O-N, respectively, into the atmosphere (Stehfest and Bouwman, 2006). The effects of N fertilization on NO and N_2O emissions from soils are known and results have been reported for boreal agricultural soils (e.g. Syväsalo et al., 2004, 2006; Maljanen et al., 2007). However, the effect of N fertilization levels on HONO emissions is still unknown. There are various HONO formation pathways in the atmosphere (Spataro and Ianniello, 2014). Su et al. (2011) described the emission of HONO from soils as a function of soil pH and nitrite (NO_2^-). In addition, HONO emissions are connected with ammonia oxidation in soils by either ammonia-oxidizing bacteria (AOB) or ammonia-oxidizing archaea (AOA) (Oswald et al., 2013; Scharko et al., 2015). Other sources are atmospheric acid − nitrite displacement (VandenBoer et al., 2013, 2014, 2015) and chemical reactions as a result of soil surface acidity (Donaldson et al., 2014). Furthermore, during daytime HONO is also formed after photolysis of adsorbed nitrate on forest canopy surface (Zhou et al., 2011) and photosensitized reaction of NO_2 on humid acid surfaces (Stemmler et al., 2006; Ren et al., 2011; Han et al., 2016; Laufs et al., 2017). On the other hand, the formation of HONO via hydrolysis of NO_2 in dark is also proposed (Finlayson-Pitts et al., 2003). HONO emission is also observed from biological soil crusts (Weber et al., 2015) and animal manure (Maljanen et al., 2016). Maljanen et al. (2013) showed the potential for boreal ecosystems, especially drained peatlands, to emit HONO. We hypothesize that HONO emissions are linked to the availability of mineral N in the soil thus the N-fertilization level similarly as NO and N_2O emissions.

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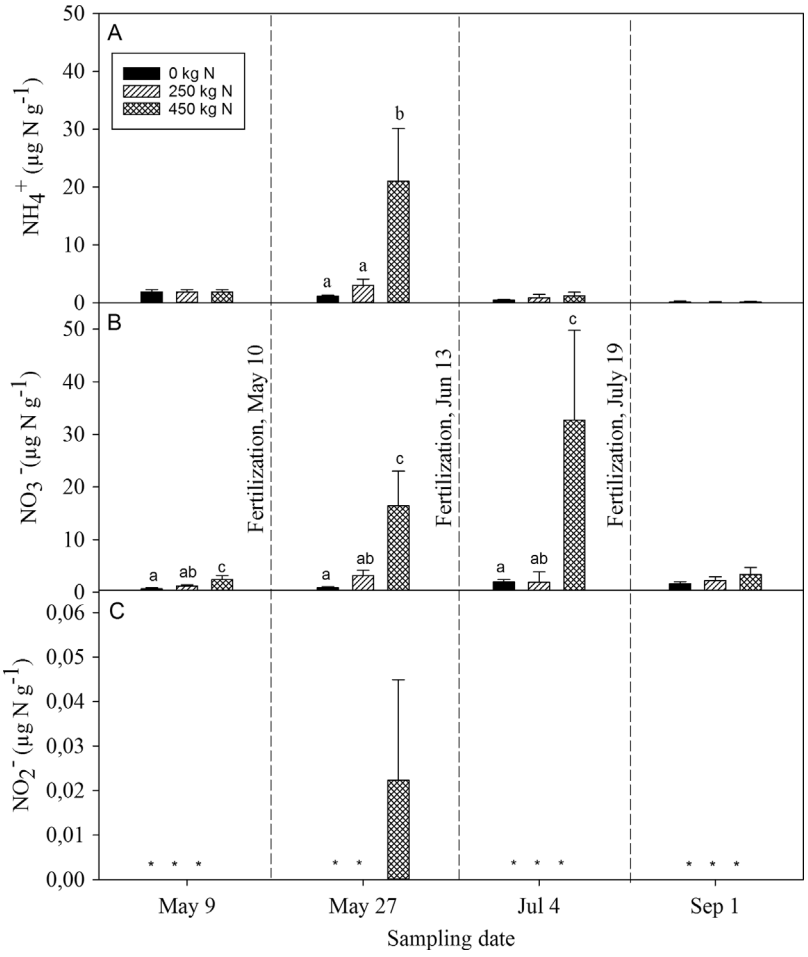

Fig. 1. Soil chemical properties. The concentration of soil NH_4^+ (A), NO_3^- (B) and NO_2^- (C) (µg N g^{-1}) in plots receiving 0, 250 and 450 kg N ha^{-1}y^{-1}. NO_2^- was detectable only on May 27. The error bars (S.D, n = 4) with different letters show the statistical difference between the treatments (Mixed Model ANOVA, $P < 0.05$) and absence of letter indicates the difference is not significant. *Indicates the values under the detection limit of the device (0.01 µg N g_{dw}^{-1}).

2. Methods

The study site, which has been used mainly for growing grass and cereals, was located in Eastern Finland (63°09′N, 27°20′E) at a research station of the Natural Resources Institute Finland (LUKE). The soil type is Dystric Regosol with 2.7% organic matter, and a C:N ratio 10.6. The experiment was established on 6th June 2014 with Timothy (*Phleum pratense L.* cv 'Nuutti') with whole crop barley as a cover crop and was fertilized with 70 kg N ha^{-1} in 2014. The three annual N fertilization levels implemented during the growing seasons 2015 (the first production year) and 2016 were 0, 250 and 450 kg N ha^{-1}. Twelve sampling plots of size 8 × 1.5 m were selected in 2016 on the basis of these three fertilization levels; 0 (0N), 250 (250N) and 450 (450N) kg N ha^{-1} y^{-1} in four replicates. The plots were named on basis of the total annual amount of fertilizer they received during the growing season. Plots were fertilized on three occasions (44, 36 and 20% of the total N amount) (see Table S1). The plots were harvested three times during the growing season 2016 (Table S1). The grass was cut after 34, 36 and 43 days of first, second and third fertilization respectively (See Table S1). The used fertilizer was a combination of NH_4-N (57%) and NO_3-N (43%). During the growing season of 2016 the annual dry matter yield (total mass of dry grass obtained in a year from a designated area) of 1.8, 11.1 and 13.1 Mg ha^{-1} was obtained from the 0N, 250N, and 450N plots respectively.

Intact soil cores were sampled from each experimental plot using PVC rings (ø 18 cm, h 12 cm) four times during the growing season 2016 (Fig. S1, see Supplementary information for details). The PVC rings were hammered into the soil to a depth of 10 cm and then the rings with soil were removed carefully with a spade and transported to the laboratory (Maljanen et al., 2013; Voigt et al., 2017). Prior to sampling, the grass was cut from the rings. Gas flux rates (N_2O, NO, and HONO) from the intact soil cores were measured at room temperature (+21 °C) within 48 h of the soil sampling. HONO, NO, and NO_2 emissions were measured using a dynamic chamber system (Maljanen et al., 2013). The HONO concentrations in the chamber were measured with a commercial LOPAP HONO analyzer (QUMA Elektronik & Analytik GmbH, Germany) while NO and NO_2 concentrations with a Thermo 42i NOx analyzer (Thermo Fisher Scientific, USA). N_2O emissions were measured with a static chamber system and samples were analyzed for N_2O concentration with an Agilent 7890B gas chromatograph (Agilent Technologies, USA) equipped with a Gilson GX – 271 autosampler (Gilson Inc, USA) (See supplement for details). After gas sampling, mineral N was extracted from soil with milliQ-H_2O for nitrate (NO_3^-) and nitrite (NO_2^-) analyses and with 1M KCl for ammonium (NH_4^+) analysis. All the extracts were stored at +4 °C prior to analysis. Analysis methods of all mineral N from the soil extracts were done as in (Maljanen et al., 2013). Gravimetric soil moisture content (amount of water in one gram of dried soil; GWC) was determined by drying the samples for 24 h at 105 °C (See supplement for details). The air temperature and precipitation were measured at the official meteorological station 250 m from the experimental plots. To see the main effect of fertilization and time on all measured parameters we used linear mixed model ANOVA, except for HONO emission. For HONO emission, Kruskal-Wallis test at the significance of $P < 0.05$ was used because residuals of HONO emissions were not normally distributed even after transformation. Results from mixed model ANOVA with $P < 0.05$ were considered significant. Since the data was skewed, it was Log_{10} transformed before mixed model ANOVA was run; except for pH and moisture data, which were normally distributed. We used treatment and time as fixed factors and plot as a random factor. Statistical