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Title page

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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.

Key words: nitric oxide, nitrogen dioxide, black soil, NO budget, fertigation, rewetting

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

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 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 et al., 2013 and references therein) and indirectly by influencing carbon monoxide, methane and non-methane hydrocarbon transformations (Liu are 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 et al., 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" (46º27'22.12"N; 30º20'9.94"E), 27 km southeast of Odessa and was established in 2006 within the framework of the EU FP6 NitroEurope IP (Medinets et al., 2014b). 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., 2014b). 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 north-western part of the Black Sea (Medinets and Medinets, 2012; Medinets et al., 2014a).

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 hours. 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 gas mixture (4 ppm NO in N_2, Air Liquid Gmbh, Germany), which was blended with synthetic air to reach a calibration NO concentration of 40 ppb. More details on the dynamic chamber system and the $NO/NO_2/O_3$ concentration measurements can be found in Butterbach-Bahl et al. (1997). To allow for irrigation and fertigation water to enter into the flux chambers six pieces of small tubing (Ø 7 cm) were inserted through the stainless steel frames (10 cm height), onto which the autochambers were fitted and connected to the irrigation network. Chamber positioning in the field followed two experimental schemes. From the beginning of the measurements (September 21, 2012) to May 21, 2013 chambers were located in the inter-row space. However, to address expected micro-site variability due to drip irrigation we moved three of the five measuring chambers from an inter-row to a row position on the May 22, 2013, as shown in Fig. 1.

2.4. Soil sampling and analyses

Monthly soil sampling (0-5 cm as well as 0-30 cm), all in triplicate, was done from October 2012 to December 2013 in the vicinity (1-3 m) of the chambers. Soil samples were collected using soil corers with a diameter of 7 cm and 5 cm or 30 cm long (ISO 10381-2 2002). The bulk density and soil moisture content were determined on intact soil samples (collected with bulk density rings) according to standards of ISO:11272 (1998) and ISO:11465 (1993) respectively. For further chemical analyses the triplicate soil samples from 0-5 cm (as well as from 0-30 cm) were integrated to one composite sample. These samples were analyzed for chemical characteristics, by the Soil Laboratory of the ONU. Methods (chromic acid oxidation), described in detail by Kaurichev (1980) and Vadyunina and Korchagina (1986), were used for determination of total organic carbon (TOC). KCl extractable (2% KCl) NH_4^+-N, and water extractable NO_2^--N and NO_3^--N, were determined by colorimetric analysis. The pH of a soil suspension in water (ratio soil:water = 1:5) was determined using a pH-meter Hydrus 400 (Fisherbrand, UK) according to ISO 10390 (1994). All chemical analyses were undertaken on three replicates; if differences between results and the mean values exceeded by 10% the analyses were repeated.

2.5. Auxiliary data

Measurements of chamber air temperature and soil temperature (5 cm soil depth with the sensor installed in soil below a chamber was done using PT100 probes (UMS, Germany). The soil moisture content (integrated 0-6 cm profile) was determined using Theta ML2X probes (Delta-T Devices, UK). Basic meteorological parameters at the field site were measured in 10 sec intervals by a MiniMet (Skye Inst., UK) climate station recording rainfall, air temperature and relative humidity (1.5 m height), atmospheric pressure (1.2 m height), soil temperature (5 and 10 cm depth) and moisture (5 cm depth), soil heat flux (10 cm depth), wind speed and direction, photosynthetic active radiation, global and net radiation measurements (all at 2 m height).

2.6. Statistical analysis

Correlation as well as multiple regression analyses were performed to investigate relationships between the fluxes of NO, NO_2, concentrations of NO, NO_2, O_3, soil parameters, fertilizer composition, irrigation and above-mentioned environmental parameters. We also calculated

significance tests for comparison of the average values using Student t-test following testing for normal distribution. All the analyses were carried out with STATISTICA 7.0 (StatSoft Inc., USA) and SPSS 20.0 (SPSS Inc., USA). Graphs and diagrams were built using MS Excel 2010 (Microsoft Corp., USA) and STATISTICA 7.0 (StatSoft Inc., USA).

3. Results

3.1. Climatic parameters

Precipitation in the study years 2012-2014 (Table 3) was 15-27% lower than the long term average of 432 mm (2000 - 2014). During the soil NO_x flux measurements period (September 2012 - March 2014) the average soil moisture content was 53.9%. Several severe rainfall events (November 2, 2012; June 6 and 15, 2013), and prolonged periods of rain (e.g., in June, September and October 2013) or snow melting (February and March 2013; February 2014) resulted in significant increases in soil moisture from values around 20-40% up to 74-87% (Fig.2). Lowest soil moisture of 15.9% was observed at the end of a 35 days drought period starting July 21, 2013. Differences in soil temperature between 'in-row' and 'inter-row' positions were less than 1%, whilst soil moisture between the two chamber positions differed at most by 7%.

3.2. Soil parameters

Soil bulk density at 0-5 cm depth varied from 0.99 g cm^{-3} to 1.28 g cm^{-3} with a mean value of 1.13±0.07 g cm^{-3}. Neither pH nor total organic carbon (TOC) measured in the 0-5 cm soil layer varied significantly over the observation period, with mean values of 7.17±0.18 and 1.82±0.06%, respectively. Mean soil NH_4^+ content at 0-5 cm was 7.6±3.7 μg N g^{-1} soil dry matter (sdm) and ranged from 3.3 to 15.2 μg N g^{-1} sdm. Mean soil NO_3^- concentrations were 6.8±4.2 μg N g^{-1} sdm, varying from 0.6 to 13.8 μg N g^{-1} sdm. Soil NO_3^- concentrations were higher than soil NH_4^+ concentrations in September, October and May of all years. Soil inorganic N concentrations at 0-5 cm and 0-30 cm soil depths were mostly comparable, although field management, such as disking (July and August, 2013) or ploughing (October, 2012 and 2013), resulted in higher topsoil NH_4^+ concentrations due to the incorporation and mineralization of residues (Fig. 3). Fertigation resulted in elevated soil mineral N concentrations (Fig. 3; Table 2).

3.3. Temporal dynamic of soil NO and NO_2 fluxes

Soil NO fluxes showed a pronounced temporal variability with peak emissions close to 90 μg NO-N m^{-2} h^{-1} and background NO fluxes being close to zero. The coefficient of variation across the entire observation period was 177%. Peak emissions of soil NO were closely related to field management events, such as fertilization and fertigation, or rewetting of soils following extended drought periods. The average NO flux for the study period of September 21, 2012 to March 11, 2014 was 4.9±8.6 μg N m^{-2} h^{-1} (range: -2.1 – 88.4 μg N m^{-2} h^{-1}) (Fig. 2; Table 4). Winter time NO fluxes were generally low (values <5 μg NO-N m^{-2} h^{-1}) and infrequent. When there was snow cover a weak net NO uptake was observed. Over the entire observation period average NO_2 fluxes varied from -29.7 to 17.2 μg N m^{-2} h^{-1} with a mean value of -2.7±4.0 μg N m^{-2} h^{-1} (Fig. 2; Table 4). NO_2 deposition was found to be largest during periods of largest NO emissions.

Fig. 4 shows 2-hourly measurements of soil NO and NO_2 fluxes for the period May to mid of July 2013, during which largest soil NO fluxes were recorded. The graph shows that peak emissions of NO were observed following fertigation events but only when the volumetric soil moisture content increased to approx. 70%. Later fertigation and rainfall events hardly resulted in any change of soil NO fluxes. Highest NO_2 deposition values were monitored during peak NO emissions, i.e. NO_2 fluxes mirrored NO fluxes.

Also chamber position, i.e. "in-row" and "inter row", was found to affect soil NO/NO_2 fluxes (Fig. 5). In general 'in-row' NO emissions were larger in response to fertigation events, while 'inter-row' NO emissions responded more intensively to rain events, though those events only resulted in moistening the very top cm of the soil, with little or no change of soil moisture at 5 cm soil depth.

The largest NO fluxes during the entire observation period were observed from the 12th to the 14th of September 2013. These peaks were triggered by rewetting the soils with a series of slight rainfall events after a prolonged dry period of 35 days (Fig. 6). During this soil rewetting period the high NO emissions were accompanied by large NO_2 deposition rates (i.e. -24.7 μg N m^{-2} h^{-1}) as well as large NO_2 emissions (up to 17.2 μg N m^{-2} h^{-1}) (Fig. 6). For the entire measurement period the mean NO_2 deposition rate accounted for 54.5% of the mean NO emission rate.

The total annual NO and NO_2 budget for 2013 was calculated to be 0.44±0.78 kg N ha^{-1} yr^{-1} and -0.20±0.35 kg N ha^{-1} yr^{-1}, respectively.

3.4. Contribution of different climatic and agronomic events to the annual NO budget

In order to understand the contribution of the different activities in the agricultural calendar to the annual NO flux, the 2013 data were split into logical periods, based on agricultural activity and climate conditions (Table 5). We found that the 'post-harvest warm period' contributed most to the annual NO budget, being 12.2% higher than NO emissions during the 'vegetation growth period'. The duration of both periods was the same. The often neglected cool periods (< 5 °C), which in our case are the 'pre-sowing' and 'post-harvest 'cool' periods', still contributed with more than 10% to the annual NO flux budget. This contribution may have even been larger, as we could not make flux measurements in March 2013 due to technical problems. This further emphasizes the need of at least one year of measurements, preferable multi-year, to allow for calculations of reliable annual NO emission budgets.

3.5. Correlation of NO fluxes to environmental parameters

NO fluxes were significantly ($p < 0.001$) correlated to changes in soil ($r = 0.31$) and air ($r = 0.30$) temperature as well as atmospheric air pressure ($r = -0.30$). The strength of these correlations did not differ for 'in-row' and 'inter-row' chamber positions.

By applying a multiple regression analysis to the whole dataset we have found, that ca. 45% of NO fluxes were affected by soil temperature, atmospheric NO concentration and ambient pressure fluctuations ($r = 0.45$; $F(3,3764) = 315.48$; $p < 0.00001$); whilst approximately 63% of NO_2 deposition rates were associated with NO emissions and ambient NO_2 concentration ($r = 0.63$; $F(2,3628) = 1206.7$; $p < 0.00001$). For the periods of drought, transition or moderate rainfall multiple factors such as soil moisture and air temperature together with atmospheric NO concentration and ambient pressure emerged as the main drivers, explaining ca. 68% of NO emission ($r = 0.68$; $F(4,705) = 157.44$; $p < 0.00001$).

The relationship of NO fluxes with the main environmental drivers (soil moisture and temperature) is shown in Fig. 7. The graph shows that peak NO emissions were observed over a wide range of soil moisture rates from approximately 25% to up to 80%, while temperature during those peak emission periods was mostly in the range of 10-22°C.

Besides soil moisture, also soil DIN concentrations (NO_3^- plus NH_4^+) affected the magnitude of NO fluxes over a range of soil temperatures (Fig. 8a) and moisture contents (Fig. 8b). The graphs show that peak NO emissions were predominantly observed at a DIN concentration of ca. 15-18 mg N kg^{-1} sdm within a narrow soil temperature range of 10-20 °C, but with a wider soil moisture range of ca. 25-80%. Noteworthy, an increase of DIN concentrations at the constant moisture level of around 30% was associated with a rise in NO emissions (Fig. 8b).

3.6. Diurnal variations in soil NO fluxes

Using the entire dataset and stratifying observed fluxes by time of the day it was investigated if diurnal variations in NO and NO_2 fluxes could be demonstrated (Fig. 9). Diurnal NO flux variations correlated best with changes in air temperature ($r = 0.97$; $p < 0.01$) closely followed by the correlation with soil temperature at 5 cm soil depth ($r = 0.94$; $p < 0.01$). Smallest NO fluxes (4.07-4.09 μg N m^{-2} h^{-1}) were found in the early morning hours (4:00-7:59), whilst peak emissions were found at noon (12:00-13:59) (Fig. 9).

In contrast to NO fluxes, a diurnal pattern for NO_2 fluxes could not be demonstrated (Fig. 9).

4. Discussion

4.1. Soil and environmental variables effects on NO emission

Here we presented the first dataset on soil NO/NO_2 fluxes from an arable cropping system under a continental temperate climate in Ukraine. Average NO emissions over the entire observation period from September 2012 to March 2014 were 4.9±8.6 μg N m^{-2} h^{-1}, with peak emissions reaching up to 88.4 μg N m^{-2} h^{-1} and maximum NO uptake rates of -2.1 μg N m^{-2} h^{-1}. The calculated annual NO emission for the year 2013 was 0.44±0.78 kg N ha^{-1} yr^{-1}. The observed magnitude of NO fluxes is relatively small compared to published emission rates. For example, Laville et al. (2009, 2011), Liu et al. (2011) and Cui et al. (2012) reported NO fluxes from arable cropping systems in temperate continental climate region of 6.12 - 8.28 μg N m^{-2} h^{-1} (barley-maize; France), 5.0 - 27.7 μg N m^{-2} h^{-1} (wheat-maize; North-central China) and 4.6-34.6 μg N m^{-2} h^{-1} (wheat-maize; North China), respectively. However, the magnitude of NO-N loss triggered by N-fertilizer application (69.4 kg N ha^{-1}) under beetroot vegetation in 2013 was estimated to be 0.63%, which is in good agreement with other estimated fertilizer NO-N loss for various crops: of 0.50% for barley (Laville et al., 2011), 0.50% for cotton (Cruvinel et al., 2011), 0.14-1.46% for wheat and maize (Cruvinel et al., 2011; Liu et al., 2011; Cui et al., 2012; Mu et al., 2012), 0.33-1.07% for onion (Mu et al., 2006, 2012), and 0.60% for sugarcane (Paton-Walsh et al., 2011 and references therein). This fertilizer-induced emission (FIE) was also in reasonable agreements with previously reported global estimates 0.70% proposed by Bouwman (2002) and IPCC (2007), 0.50% estimated by Veldkamp and Keller (1997) and 0.30% postulated by Skiba et al. (1997), but significantly lower than earlier (2.5%) assessment of Yienger and Levy II (1995).

The diurnal NO flux distribution demonstrated a clear dependence on daily temperature variations (Fig. 9), which corresponded very well with previous studies (Ludwig et al., 2001; Butterbach-Bahl et al., 2004). Even though a clear correlation between NO fluxes and soil inorganic N concentrations could not be demonstrated, high NO fluxes coincided with high DIN concentrations of soil moisture content was in the range of 26-34% (Fig. 8b), which corresponded well with studies of Vallejo et al. (2006), McCalley and Sparks (2008) and Laville et al. (2009). Overall, an *in-situ* optimum for NO emission was found at a soil temperature range of 10-20 °C and DIN concentrations of 15-18 mg N kg^{-1} sdm, for a wide range of soil moisture levels (ca. 25-80%), emphasizing the significance of both aerobic and anaerobic soil conditions most likely contributing to the production and release of NO from soils (Medinets et al., 2015).

Our data imply that ambient pressure, which is usually neglected in the data analysis, appears to be a physical facilitating factor of releasing NO (as well as other gases obviously) from the soil into the atmosphere, although more field data and targeted experiment are needed to confirm this assumption.

4.2. Peak NO emission periods

Fertigation

To improve the representativeness and account for the spatial variability of 'in-row' and 'inter-row' parts of the field the chamber positioning was slightly altered (Fig. 1), as recommended by Parkin and Venterea (2010). We have shown that NO emissions were larger from the 'in-row' positions during the fertigation period compared to the 'inter-row' chambers. However, slight rainfall triggered 1.7 times larger NO emissions from 'inter-row' spaces than that from 'in-row' positions. Both observations can be explained by the distance from the irrigation tubes, with 'inter-row' chambers being ~4.5 times further away from irrigation tubes, than 'in-row' chambers (Fig. 1). Thus, "in-row" chambers received more fertigation, resulting in general higher NO emissions. "Inter-row" chambers were exposed to more frequent and more intensive changes in soil moisture, which could explain while rainfall could be identified to be a stronger trigger for NO emissions as compared to "in-row" chambers.

This interpretation is in line with earlier observations about the importance of the top few cm of soil for NO fluxes. Ludwig et al. (2001) as well as Laville et al. (2009, 2011) emphasized the importance of the top few cm of soil for NO fluxes and that rapid soil drying can lead to a fast decrease in NO flux. At very low soil moisture conditions microbial N turnover rates are low and available DIN is only processed until a precipitation and/or irrigation event revives topsoil microbial activity (e.g., Kemmitt et al., 2008; Butterbach-Bahl et al., 2004; Yao et al., 2010; Kim et al., 2012). Our field data also shows that NO emissions temporarily declined during irrigation, presumably by partial blocking aerobic micropores and thereby limiting NO diffusivity (Skiba et al., 1997; Russow et al., 2009). Since during such fertigation events soil moisture was often >70%, this might even indicate that the remaining NO emission was due to anaerobic NO forming processes as recently argued by Mori et al. (2012). These authors found that NO_3^- and even stronger NO_3^- together with phosphorus (P) can stimulate NO emission *in vitro* under strict anaerobic condition.

Dry-wet transition periods

Disking of beetroot plant residues (Fig. 3a) followed by long dry period (35 days; Fig. 6) led to a large organic matter accumulation. Partial mineralization started already during the dry period as evidenced by a significant increase in soil NH_4^+ concentrations (from 3.45 mg N kg^{-1} sdm on June, 11 to 15.16 mg N kg^{-1} sdm on August, 28) (Fig. 3b). First slight rainfalls, and moistening

of the topsoil was accompanied by a large NO pulse lasting for approx. 3 days, followed by a series of smaller pulses under rather light, but regular rainfall events (Fig. 6). Such NO flux pulses with the rewetting of the topsoil is well documented in previous studies (e.g., Davidson et al., 1991, 1993; Ludwig et al., 2001; Butterbach-Bahl et al., 2004; Laville et al., 2009, 2011). The decline of NO emissions to < 10 μg N m^{-2} h^{-1} from the end of September 2013 onwards (Fig. 2d, 6) could be explained by substrate limitation, i.e. depletion of soil NH_4^+ (from 15.2 mg N kg^{-1} on August 28th via 4.7 mg N kg^{-1} on September 24th to 3.3 mg N kg^{-1} on October 15th; Fig. 3b). Since simultaneously soil NO_3^- content increased (from 5.7 via 9.9 to 13.0 mg N kg^{-1}; Fig. 3c), one can assume that during this period NO was formed mainly by nitrification (Medinets et al., 2015). This emphasizes a direct effect of NH_4^+ availability in soil on NO production/release, supporting observations by a number of previous studies (e.g., Levine et al., 1988; Anderson et al., 1988; Hutchinson et al., 1993; Ludwig et al., 2001; Vallejo et al., 2006; McCalley and Sparks, 2008; Laville et al., 2009).

It is noteworthy, that under cool condition (< 5 °C) temperature fluctuations, influencing soil moisture availability (including freeze-thaw events), stimulated NO pulses (e.g., 13.01.2013, 15.01.2013, 11.02.2013, 20.02.2013, 18.02.2014; Fig. 2d). These NO fluxes were rather small compared to the summer/autumn fluxes, but still 4-9 times higher than 'background' emission at that time. Pulses of NO under cool conditions, triggered by changes in soil moisture, have also been observed by Yao et al. (2010) and Laville et al. (2011).

4.3. Uncertainties in NO_2 fluxes

NO_2 in the atmosphere air can be produced in a rapid reaction of emitted NO with atmospheric O_3 (as well as with $NO_3^{\bullet}$, $HO_2^{\bullet}$, CHOH, R-$OO^{\bullet}$) or during the combustion of plant biomass (e.g., Hertel et al., 2011; Medinets et al., 2015 and references therein), whilst NO_2 production pathways in soils remain unknown. While re-deposition of emitted soil NO has been frequently observed (e.g., Geßler et al., 2000; Butterbach-Bahl et al., 2004; Sparks, 2009), regular emission of NO_2 from soils, as in our study, is rather unusual (Fig. 2). Due to regular calibration a malfunctioning of our instrument can be excluded. However, the instrument used (CLD 88p and PLC 860, EcoPhysics AG, Switzerland) measures NO_2 only indirectly, i.e. following the photolytic (hv = 320-400 nm) conversion of NO_2 to NO. Following this conversion, NO_2 is calculated as the difference of a previous measuring cycle without photolytic conversion and the measuring cycle with photolytic conversion. However, the step of photolytic conversion is not compound specific to NO_2 (Helmig et al., 2009) and might also result in the conversion of HONO (nitrous acid) into NO and $OH^{\bullet}$ (Oswald et al., 2013; Sörgel et al., 2015). Recently it was shown that emissions of HONO from arid and arable soils can be in the same magnitude as NO emissions (Oswald et al., 2013; Sörgel et al., 2015), so that the periodically observed NO_2 emissions, specifically during the dry-wet transition periods (Fig. 6d), might in reality show substantial soil HONO emissions which are overcompensating NO_2 deposition fluxes. The supplier of the measuring instrument, the EcoPhysics AG (pers. comm.) confirmed that HONO conversion is feasible, but argued that the cross sensitivity of NO_2 against HONO is assumed to be negligible, since HONO concentrations in the sampling air are assumed to be low as compared to NO_2. Currently, our hypothesis of high soil HONO emissions cannot be validated, but our observations calls for targeted, compound specific HONO, NO, and NO_2 flux measurements.

5. Conclusions

For the first time, the results of long-term NO flux measurements from an intensively managed cropland in Southern Ukraine are presented. Average mean annual NO fluxes (5.07±8.87 μg N m^{-2} h^{-1}) as well as the annual NO budget (0.44±0.78 kg N ha^{-1} yr^{-1}) were calculated. The fertilizer induced emission factor was 0.63%, thus, being in the range of published values.

Our results show that post-harvest pulse emissions following re-wetting of dried soils are of outstanding importance for the annual budget of the investigated arable cropping systems. If such pulse emissions are a major contributor to elevated rural tropospheric O_3 concentrations in the region remains unclear but deserves further investigations.

The distinct periods of net NO_2 emissions from soils is calling for further measurements, as those might be associated with significant soil HONO emissions.

Overall our study shows that long-term measurements, covering at least an entire observation year, are needed to reliably estimate annual budgets and seasonal dynamics of soil NO fluxes. However, such measurements remain extremely scarce, thereby constraining the development and testing of biogeochemical models which are increasingly used for inventory purposes and development strategies to mitigate the environmental footprint of cropping systems.

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652 **Table 1.** Soil physical and chemical characteristics for the four soil layers. Data are averages of
653 4 measurements per year for the period Dec 2006 – Oct 2009 (Medinets et al., 2014).

Parameter	1st layer (0-27 cm)		2nd layer (27-44 cm)		3rd layer (44-60 cm)		4th layer (60-74 cm)		Number of observations
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	N
pH	6.96	0.49	7.09	0.41	7.79	0.57	8.48	0.24	33
Bulk density ($g\ cm^{-3}$)	1.29	0.15	1.43	0.05	1.48	0.09	1.53	0.10	33
Clay (%)	59.43	0.04	60.64	0.73	60.90	0.15	55.15	0.24	4
Sand (%)	11.59	0.21	9.10	0.98	11.93	0.23	9.76	0.43	4
Silt (%)	28.98	0.17	30.26	0.39	27.17	0.21	35.09	0.23	4
Soil moisture (% by volume)	31.1	3.1	33.4	2.6	31.6	3.4	31.2	2.3	33
SOM (%)	3.12	0.23	2.65	0.46	2.04	0.59	1.20	0.46	33
TOC (%)	1.81	0.13	1.53	0.27	1.19	0.34	0.65	0.23	33
Inorganic C (%)	0.01	0.04	0.01	0.04	0.13	0.25	0.90	0.66	27
TN (%)	0.18	0.05	0.17	0.06	0.18	0.10	0.13	0.04	33

654 SD: standard deviation of the mean; N: number of valid observations

655

Table 2. Details of the agricultural management for the three year crop rotations practiced on the the study field.

Year	Crop	Date of Sowing/Planting	Date of Harvest	Type of Residue	Tillage [date]	Fertilizers [kg ha^{-1}]			Drip Irrigation [mm]
						N	P	K	
2012	Tomato	09/05[1] [seedlings]	01/08 – 05/09	Whole plants with ungathered tomato-fruits	Irrigation [09/05 - 19/09] Cutting [14/09] Ploughing [12/10] Cultivation [19 - 22 Oct]	67.8	8.8	59.5	2806
2013	Beetroot	03/04 [seeds]	19/06 – 09/07	Whole plants with ungathered beetroot in soil	Dragging [06/03] Irrigation [04/05 - 09/07] Inter-row cultivation [17/05] Cutting [09/07] Disking [22/07, 01/10] Ploughing [11/10 Cultivation [13/10]	69.4	14.0	44.0	476
2014	Onion	13/03 [seeds]	21-22/09	Ungathered onion heads lying in/on soil	Harrowing [28/02] Irrigation [28/04 - 20/09] Disking [14/10 Cultivation [15/10]	47.5	17.1	43.3	3285
	Winter wheat	05/11 [seeds]							

[1] dd/mm

660 **Table 3.** Annual meteorological parameters for the study years.

Data	Precipitation[1], mm	Air temperature, °C			Wind speed, m s^{-1}	Relative humidity, %
		Average	January	July		
2012	340.0	10.3	1.1	23.7	2.4	79.4
2013	394.5	9.5	-2.5	20.4	2.6	81.0
2014	336.6	8.4	-1.9	21.7	2.1	79.3
2012-2014	357.0	9.4	-1.1	21.9	2.4	79.9

661 [1]rain only, estimates for snow fall precipitation are not available

662

663 **Table 4.** Minimum, maximum and mean NO and NO_2 fluxes for individual chambers over the
664 entire measurement period.

	Chamber 1	Chamber 2	Chamber 3	Chamber 4	Chamber 5	Average of chambers 1-5
			NO flux, μg N m^{-2} h^{-1}			
Minimum	-2.1	-1.6	-1.8	-2.8	-1.5	-2.1
Maximum	90.5	77.0	89.3	99.0	95.3	88.4
Mean±SD	4.6±7.1	4.8±8.3	4.2±7.9	4.5±8.8	5.1±8.5	4.9±8.6
N	2938	3022	3048	2988	2969	3822
			NO_2 flux, μg N m^{-2} h^{-1}			
Minimum	-33.4	-30.9	-34.7	-35.0	-37.2	-29.7
Maximum	19.6	12.1	9.9	17.4	14.5	17.2
Mean±SD	-3.0±5.0	-2.8±4.6	-2.2±4.1	-2.7±4.8	-2.5±4.7	-2.7±4.0
N	2891	2939	2961	2898	2857	3774

665 SD: standard deviation of the mean; N: number of valid 2-hourly flux observations

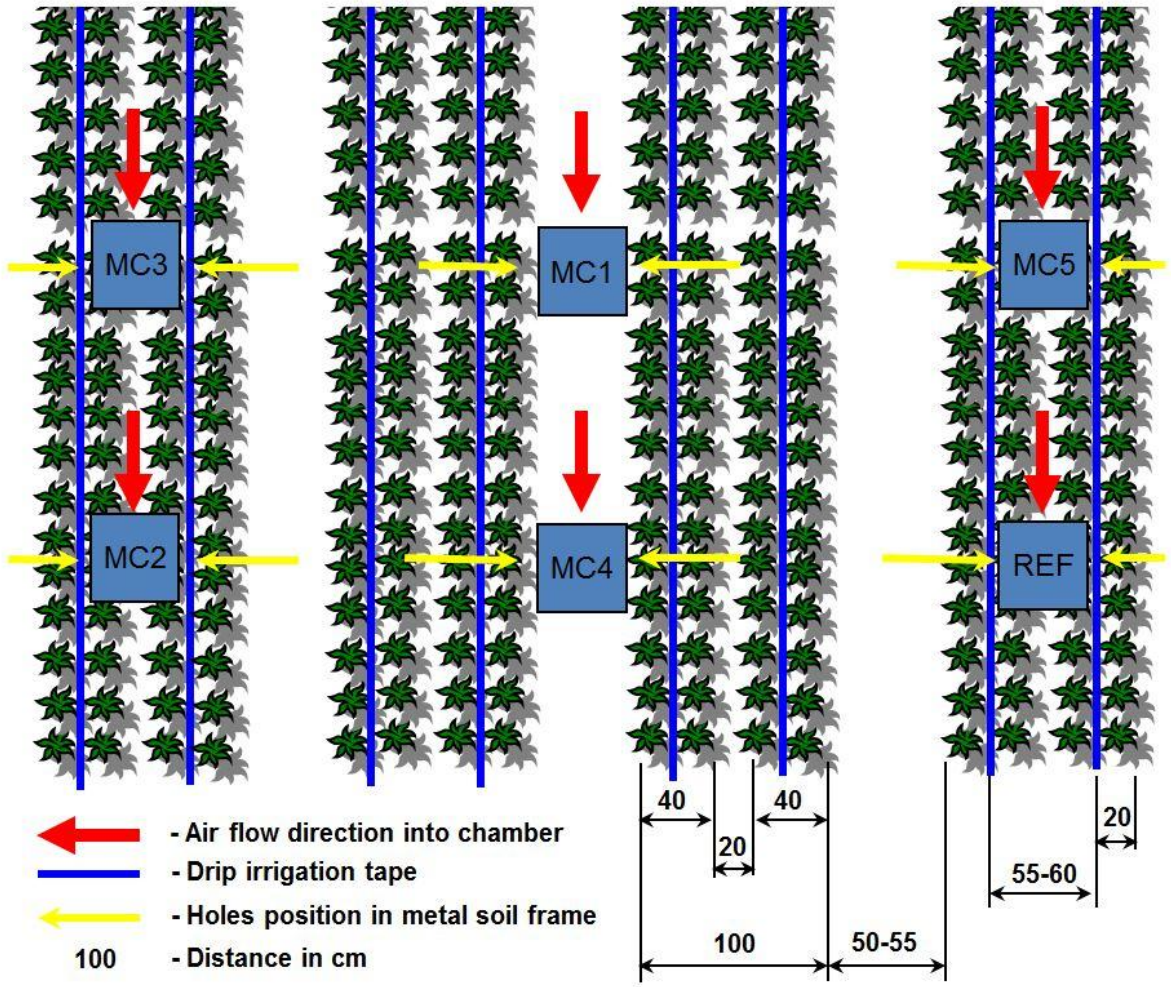
666

667 **Table 5.** Mean fluxes of various time intervals throughout the 2013 year and its contribution to
668 annual NO budget assessment.

Time Period in 2013	Mean NO flux μg N m^{-2} h^{-1}	Time interval days	Days of missing observation % of time	Cumulative NO flux kg N ha^{-1}	Contribution to the annual flux %
Pre-sowing (01 Jan - 02 Apr)	0.40±0.46	92	32 (34.8%)	0.01±0.01	2.3
Vegetation growth (03 Arp - 09 Jul)	6.09±7.13	98	18 (18.4%)	0.14±0.17	34.2
Post-harvest 'warm' period (10 Jul - 15 Oct)	9.78±13.04	98	14 (14.3%)	0.23±0.55	55.4
Post-harvest 'cool' period (16 Oct - 31 Dec)	1.81±2.02	77	17 (22.1%)	0.03±0.04	8.1
Entire year	**5.07±8.87**	**365**	**81 (22.2%)**	**0.44±0.78**	**100**

669

670



671

672 **Fig. 1.** Chamber location layout (after May 22, 2013). MC1 and MC4 are in "inter-row", while
673 MC2, MC3 and MC5 are in "row" position [MC: measuring chamber, REF: reference chamber].

674

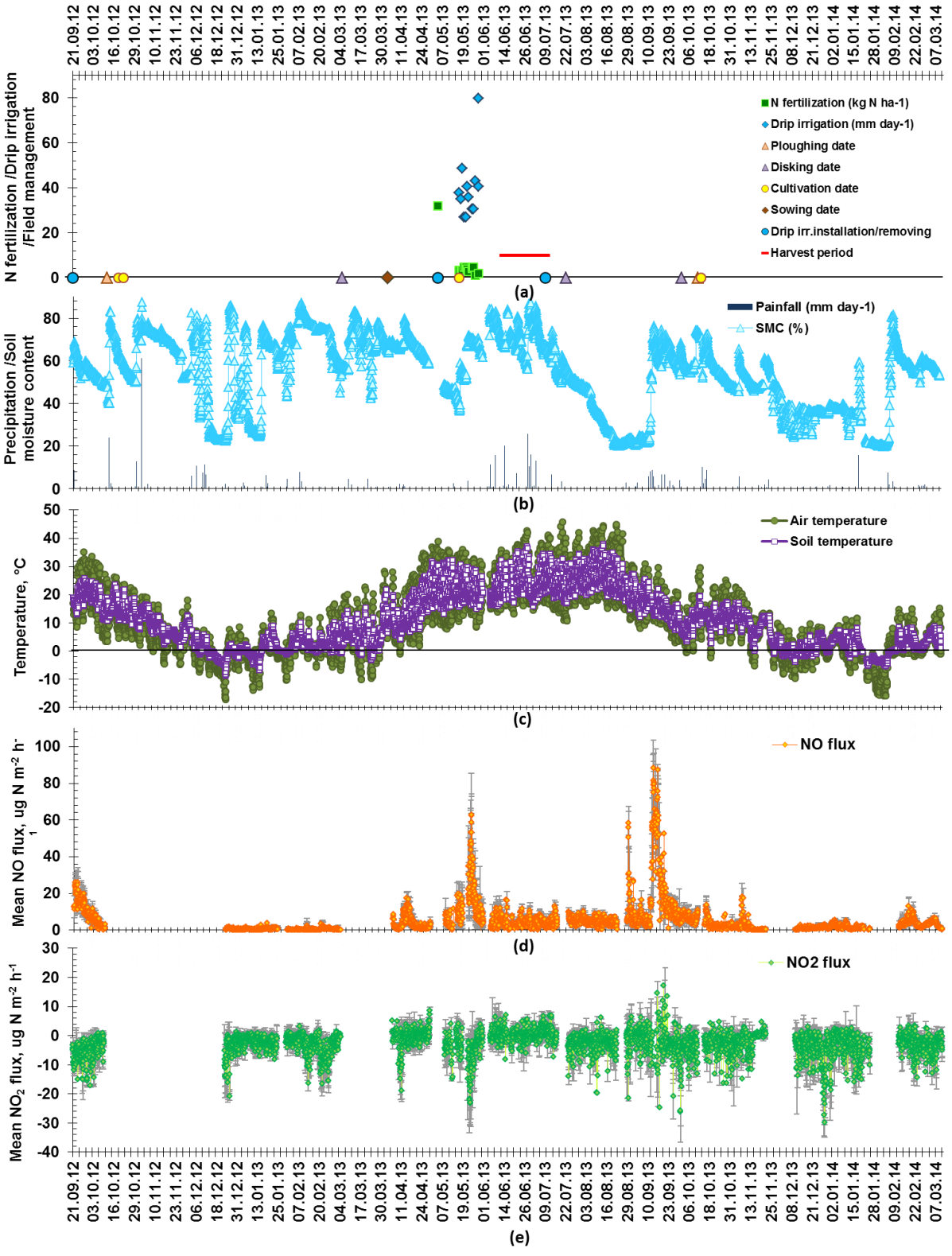
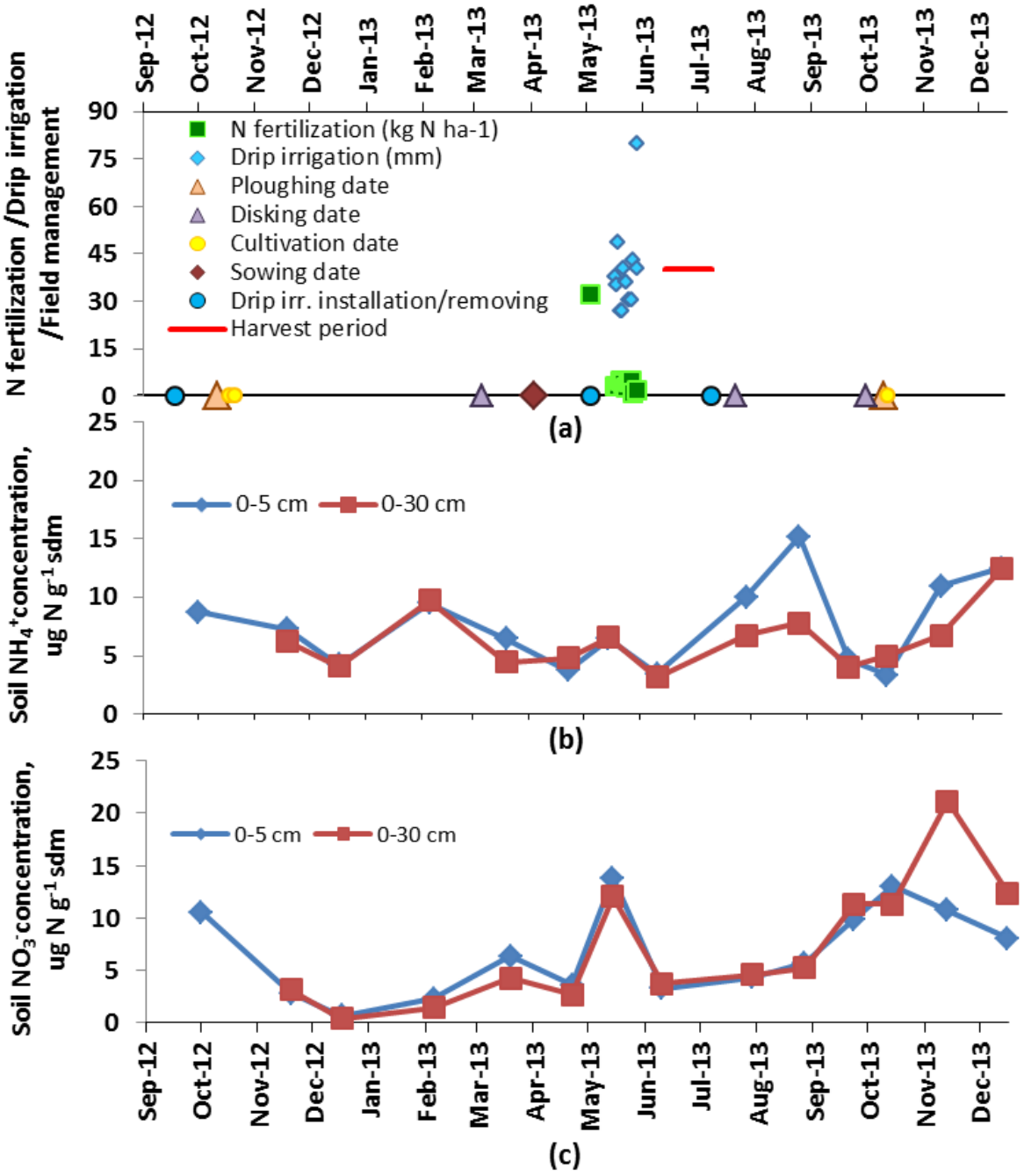


Fig. 2. The impact of timing of field operations and fertigation events (a), temporal variability of soil moisture content (SMC) and rainfall (b), soil (5 cm soil depth) and air temperature (c) on soil NO (d) and NO_2 fluxes (e) over the entire study period.

680



681

682 **Fig. 3.** Field management dates (a) and temporal changes in soil NH_4^+ (b) and NO_3^- (c)
683 concentration changes in two soil layers (0-5 cm and 0-30 cm) [sdm: soil dry matter].

684

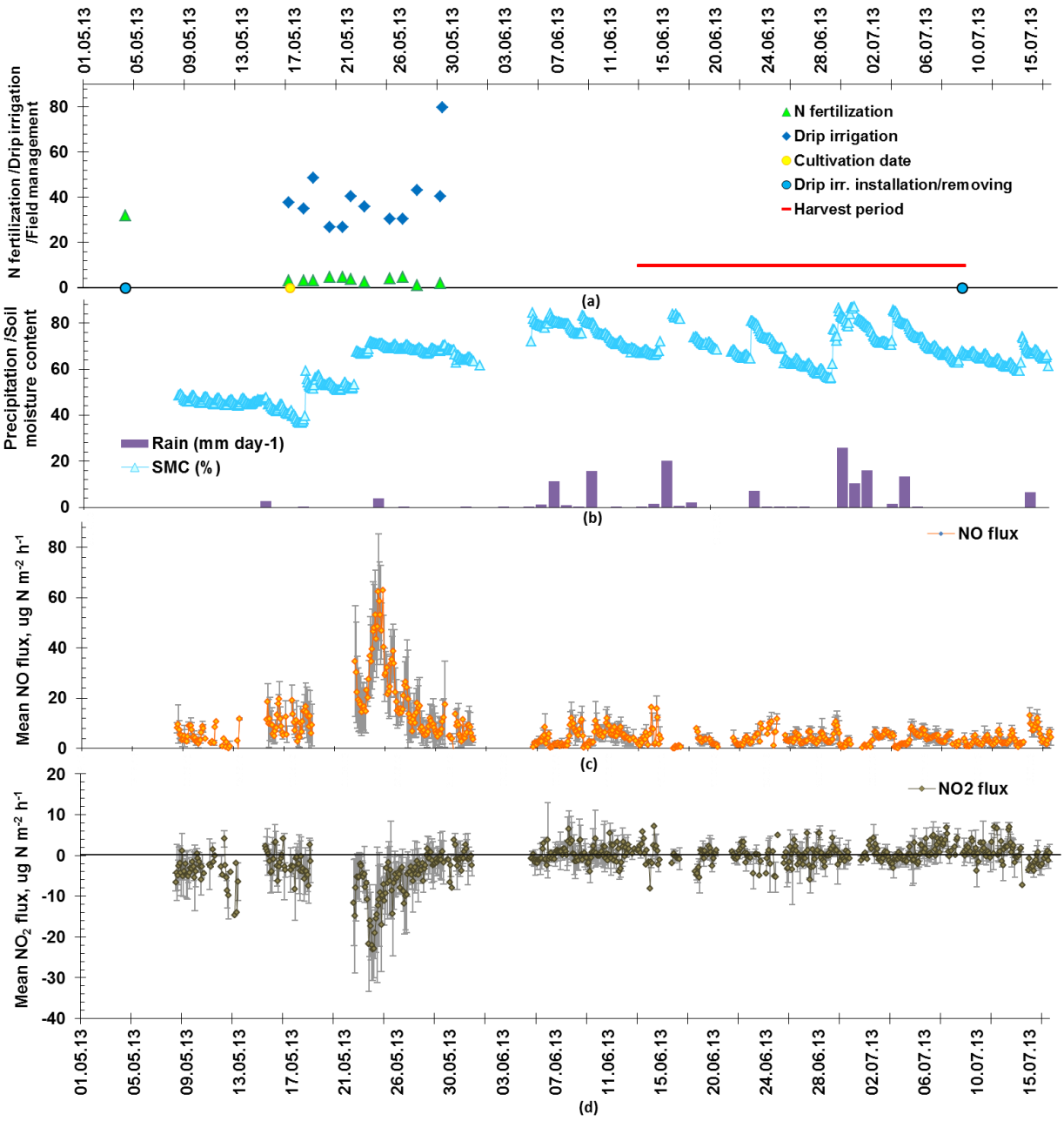


Fig. 4. The effect of fertigation on soil NO and NO_2 fluxes. Field management (a), volume weighted soil moisture content (0-6 cm) and precipitation amount (b), mean 2-hourly NO (c) and NO_2 (d) fluxes before, during and after fertigation events.

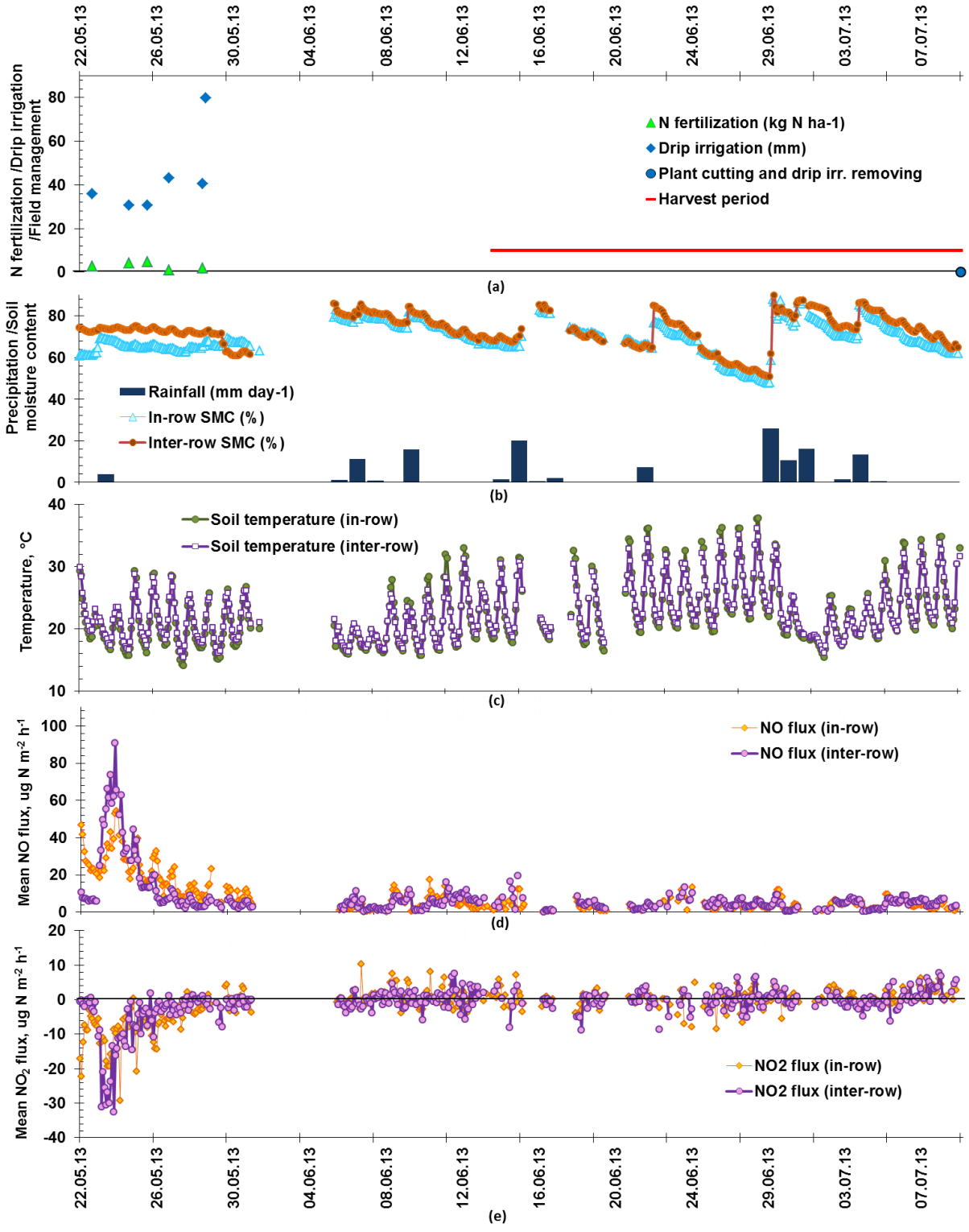


Fig. 5. The impact of chamber placement on NO and NO_2 fluxes. Field management (a), soil moisture content (SMC) and precipitation (b), soil temperature (c), 2-hourly NO (d) and NO_2 (e) flux averages for chambers either placed at 'in-row' or 'inter-row' positions for the period May 22 – July 9, 2013.

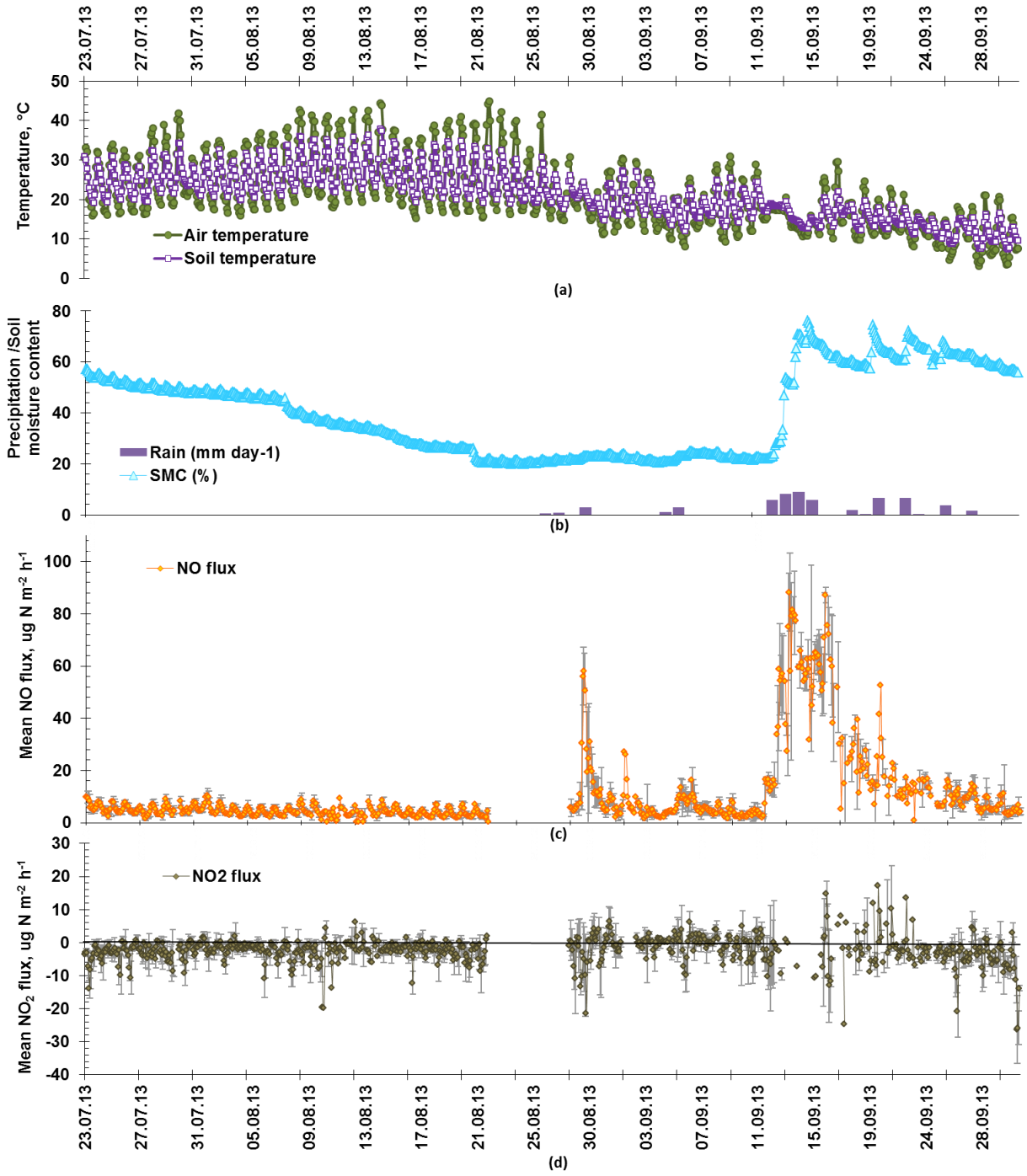


Fig. 6. The rain-induced mean 2-hourly average NO (c) and NO_2 (d) fluxes, air and soil temperatures (a), soil moisture and daily precipitation (b) for the period July to September 2013.

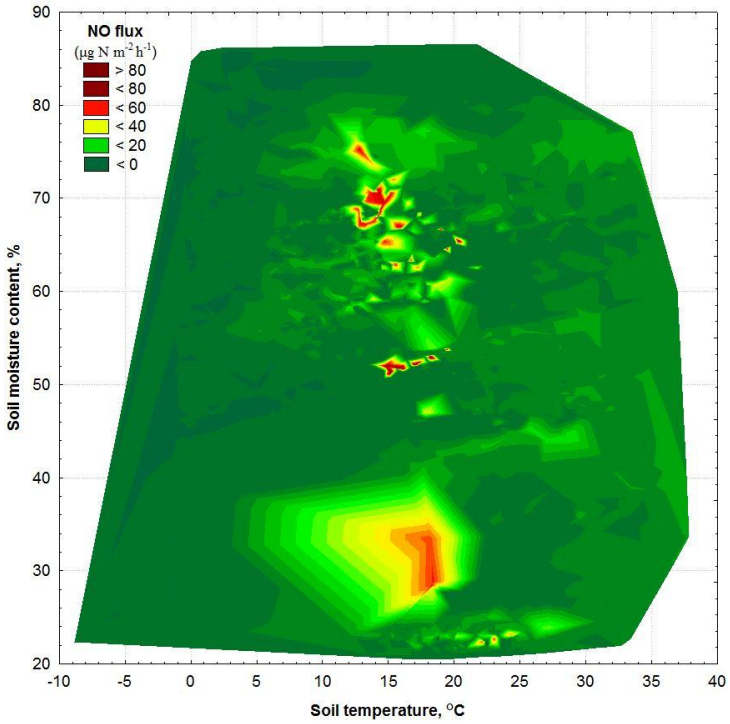


Fig. 7. The relationship of NO flux with soil moisture content and soil temperature based on the entire dataset (September 21, 2012 – March 11, 2014) and displayed by a 2D projection of a 3D wafer plot.

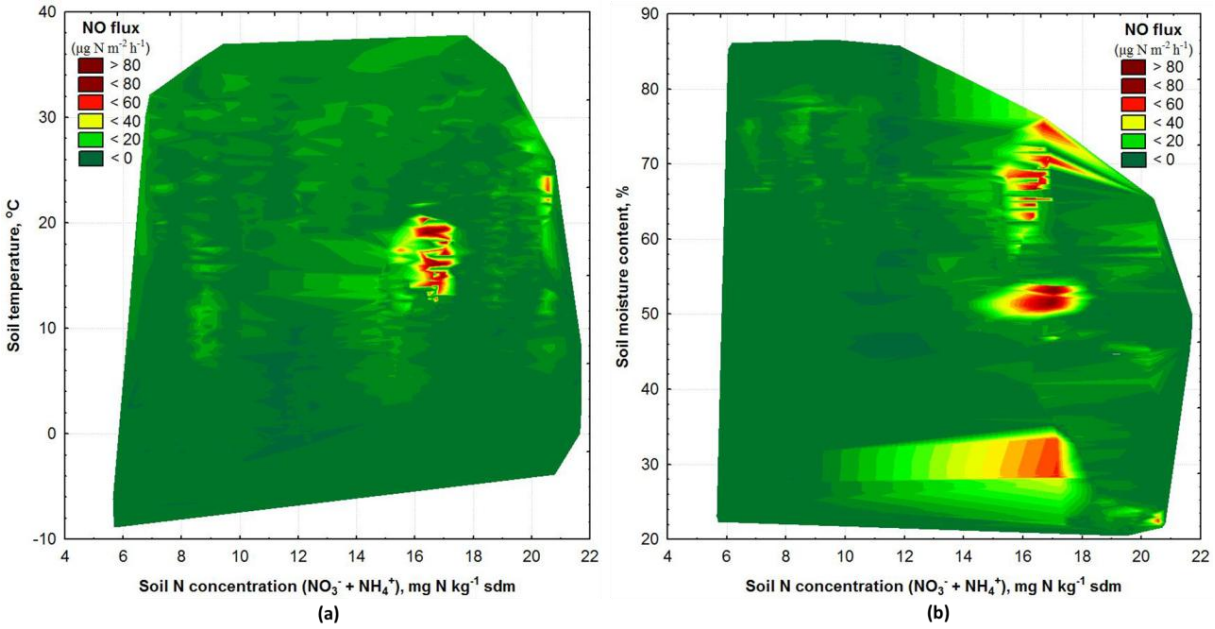


Fig. 8. The relationship of soil NO flux with soil DIN concentrations (NH_4^+, NO_3^-) and soil temperature (a) and soil moisture content (b) displayed by a 2D projection of a 3D wafer plot.

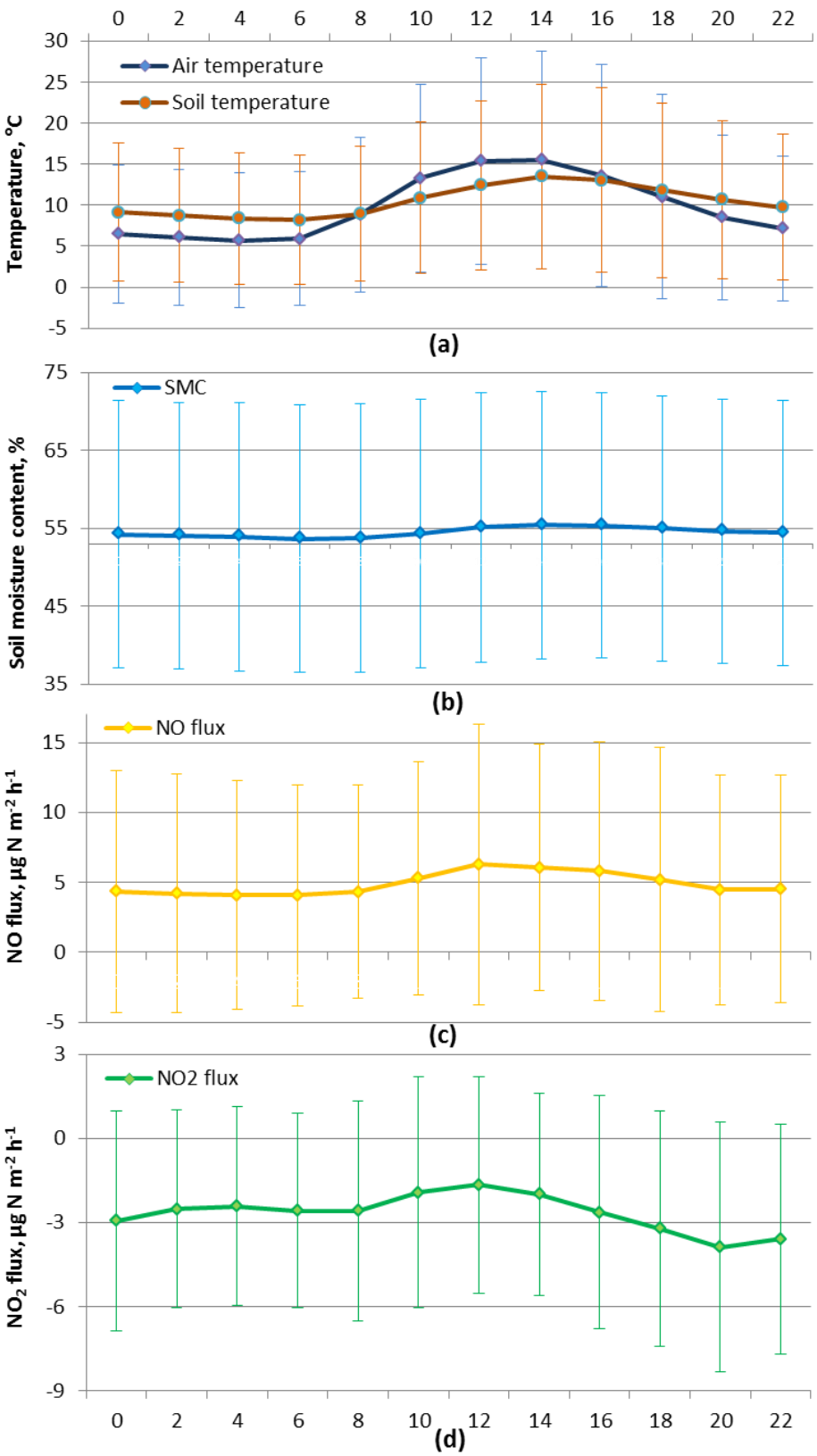


Fig. 9. Diurnal variation of NO (c) and NO_2 (d) fluxes, soil moisture content (b), air and soil temperature (a) [presented are average values aggregated for different times of the day in 2-hourly steps; error bars reflect standard error of mean].