Nitrogen oxides and ozone fluxes for an oilseed-rape management cycle: influence of organic fertilisation

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Abstract. This study reports NO, NO_2 and O_3 mixing ratios and flux measurements using the eddy-covariance method during a 7 month period over an oilseed rape field, spanning an organic and a mineral fertilisation event. Mean NO emissions during the whole period were in agreement with previous studies and showed quite small emissions of 0.26 kg N ha^{-1} with an emission factor of 0.27%, estimated as the ratio between total N emitted in form of NO and total N input. The NO emissions were higher following organic fertilisation in August due to conditions favouring nitrification (soil water content around 20% and high temperatures), while mineral fertilisation in February did not result in large emissions. The ozone (O_3) deposition velocity was significantly larger following organic fertilisation. The analysis of the chemical and turbulent transport times showed that reactions between NO, NO_2 and O_3 below the measurement height occurred at all time during the 7 month period. Following organic fertilisation, the NO ground fluxes were 30% larger than the NO fluxes at the measurement height (3.2 m), while the NO_2 fluxes changed sign during some periods, being negative at the surface and positive at the measurement height. This phenomenon of "apparent NO_2 emissions" reveals to be important during strong NO emissions and high O_3 ambient mixing ratios, even on a bare soil during August.

Keywords: eddy covariance, chemical reaction, transport time, oilseed rape, NO, O_3, NO_2

1. Introduction

Agricultural soils represent an important source of atmospheric nitric oxide (NO), especially in highly fertilized regions (Oikawa et al., 2015). Global estimates of total NO_x (NO + NO_2) emissions from soils range between 4 and 21 Tg N yr^{-1}, which represents between 10% and 15% of the global NO_x budget (Davidson and Kingerlee, 1997; Houghton et al., 2001; Yienger and Levy, 1995). NO_x inventories are subject to error in magnitude and especially in spatial distributions (Martin et al., 2003), which can be constrained by satellite observations, and ranges around 30% at the global scale (Toenges-Schuller et al., 2006). They are of considerable interest also for atmospheric photochemistry, and acting as ozone (O_3) precursors, they indirectly have an impact on climate. O_3 is indeed an important greenhouse gas, contributing to 25% of the anthropogenic net radiative forcing (Forster et al., 2007).

NO_x, and especially NO_2, are toxic gases for humans, increasing risks for various respiratory diseases. The World Health Organization gives guidelines for NO_2 exposure limits, both annual means (40 µg m^{-3}) and 1-

hour mean (200 µg m^{-3}) (Prüss-Üstün et al., 2016). For O_3, only a short-term threshold is given (100 µg m^{-3} for the 8-hour mean) because there are fewer studies on long-term exposure. These thresholds are established both on epidemiological and toxicological studies on humans and animals. Similarly, nitrogen deposition leads to serious adverse effects on vegetation (eutrophication, biodiversity erosion and acidification being the most serious ones), while O_3 has a direct adverse effect on plant health through oxidation of photosynthesis pathways and direct tissue destruction above large thresholds. For nitrogen, the concept of critical load has been developed which gives the amount of nitrogen deposition above which an ecosystem is impacted. These critical loads range from 5 kg N ha^{-1} yr^{-1} for sensitive habitats to 20 kg N ha^{-1} yr^{-1} for less sensitive ones (APIS, 2016). For these reasons, national and international authorities regulate atmospheric levels of these pollutants.

NO_x emissions from soils are mostly due to nitrification and denitrification processes and through the chemical decomposition of HNO_2 (Laville et al., 2005; Meixner, 1997; Remde et al., 1989). Many authors emphasized that for most agricultural soils, nitrification is the dominant process of NO emissions (Bollmann et al., 1999; Dunfield and Knowles, 1999; Godde and Conrad, 2000). Organic and mineral fertilizers, rich in ammonium, increase NO emissions both by stimulating NO production by nitrification and by decreasing NO consumption.

There is a significant knowledge gap in understanding NO_x exchange between agricultural ecosystems and the atmosphere, partly due to a lack of direct measurements over long periods. NO emissions by soils can either be measured by dynamic chambers (Breuninger et al., 2012; Laville et al., 2009; Laville et al., 2011; Pape et al., 2009), aerodynamic gradient (Kramm et al., 1991), or eddy covariance methods (Rummel et al., 2002; Stella et al., 2013a). Each method has its drawbacks and challenges: the dynamic chamber method may change the surface exchange parameters (Pape et al., 2009), and modify the fluxes due to fast reactions between the triad O_3-NO-NO_2, but thoroughly designed Teflon chambers can overcome this problem (Skiba et al., 2009). The aerodynamic gradient method (AGM) is nowadays applied for water-soluble compounds such as NH_3 (Milford et al., 2009), but has several biases of which flux divergence due to chemical reaction is the most limiting for NO-NO_2-O_3 (Duyzer et al., 1995; Kramm et al., 1991; Loubet et al., 2013). Non-stationarity and integration time is also limiting (Lenschow et al., 1994; Stella et al., 2012). The eddy covariance method is adapted for measuring NO fluxes. It is however also exposed to flux divergence issues due to NO-NO_2-O_3 chemical reactions. It is therefore essential to measure the fluxes and mixing ratios of the three compounds together.

The eddy covariance (EC) method is the state of the art flux measurement method for energy and CO_2 fluxes (Baldocchi, 2003), and due to the development of new analysers such as fast chemiluminescence, quantum cascade lasers absorption spectroscopy, or proton time of flight mass spectrometers (Ammann et al., 2012; Brodeur et al., 2009; Ferrara et al., 2012; Li et al., 2013; Muller et al., 2010b; Park et al., 2014; Peltola et al., 2014; Sintermann et al., 2011; Stella et al., 2013a; Wolfe et al., 2009) it can nowadays be applied for several other trace gases. The main advantage of the EC method is that it is a "direct" measurement of the flux at a given height, which depends on fewer assumptions than the AGM, namely the Reynolds averaging and ergodicity hypothesis requiring that *the averaging time must be much larger than the time scales of variation of the air velocity* (Kaimal and Finnigan, 1994). This method has been successfully applied for measuring NO fluxes in a limited number of studies (Eugster and Hesterberg, 1996; Lee et al., 2015; Marr et al., 2013; Min et al., 2014; Rummel et al., 2002; Stella et al., 2013a). The main difficulties of EC measurements are the high frequency losses due to adsorption to the tubing system, size of the absorption cell (Eugster and Senn, 1995) and differential advection caused by the radial variation of the mean velocity and simultaneous radial diffusion of the sample gas (Lenschow and Raupach, 1991). Moreover, since NO_2-to-NO photolytic converters typically applied in combination with chemiluminescence analysers have a conversion efficiency below 100%, measuring both NO and NO_2 with such a converter remains a challenge that requires to use two analysers simultaneously (Lee et al., 2015).

Due to these limitations, simultaneous measurements of NO, NO_2 and O_3 fluxes by eddy covariance have hence seldom been made. To our knowledge, only a few studies report such measurements and none over a crop. There is therefore a gap in knowledge as to whether NO, NO_2 and O_3 are interacting above crops and how nitrogen application will modify these fluxes and their interactions. Eugster and Senn (1995) report NO_2 fluxes by eddy covariance and analyse the errors of the method. Andreae et al. (2002) report comprehensive flux measurements in the Amazonian forest showing evidence of within forest cycling of the nitrogen oxides emitted from the soil. Horii et al. (2004) report NO_x and O_3 fluxes over a temperate deciduous forest showing consistent NO_x deposition. Ammann et al. (2012) report total reactive nitrogen fluxes by eddy covariance above grassland which compared well with dynamic chambers NO and NO_2 fluxes during periods with no NH_3 emissions. Geddes and Murphy (2014) report such measurements over two mixed hardwood forests in North America, under very low NO concentrations regime, which shows mainly NO_x deposition with evidence of chemical reactions in the canopy. Min et al. (2014) report such flux measurements over ponderosa pine which shows evidence of within canopy chemical removal of NO_x. Lee et al. (2015) and Marr et al. (2013) report fluxes of NO and NO_2 over urban areas which differ in their comparison with national emissions inventories: while Lee et al. (2015) found fluxes 80% larger than national inventories, the second study found similar fluxes but with large disagreements at the local scale.

In this study we are addressing the following science questions: (1) is the eddy covariance method adapted for quantifying the seasonal dynamics and diurnal cycles of the NO, NO_2 and O_3 fluxes above a crop rotation? (2) How are organic and mineral fertilisations affecting these fluxes and their dynamics? (3) To what extent are the chemical reactions between NO, NO_2 and O_3 modifying the fluxes above the ground? And finally, (4) why is O_3 deposition increasing following organic fertilisation? Is that a consequence of interactions with NO emissions?

For answering these questions we report measurements of NO, NO_2 and O_3 fluxes by eddy covariance using a system similar to Lee *et al.* (2015) for one month following slurry spreading over a bare soil at the FR-GRI fluxnet and ICOS site (Loubet et al., 2011). The NO and O_3 fluxes were measured over an additional further 6 month period to study the seasonality of these fluxes and to measure the fluxes following application of mineral fertiliser.

2. Materials and methods

2.1 Site description and management

The experiment took place in a 19 ha field located at Grignon (48°51' N, 1°58' E), 40 km west of Paris (France) and lasted more than 7 months from 07/08/2012 to 13/03/2013. The field was surrounded by heavy traffic roads on the east, south and south-west. The field belongs to a large farm (buildings at around 450 m to the south west) with around 210 dairy cows, 500 sheep, and a production of approximately 900 lambs. The terrain has a gentle slope of ~1% and the mean annual temperature and precipitation are 10.9°C and 575 mm between 2005 and 2013. The main wind directions are north-west during clear days and southwest during cloudy and rainy days.

The soil type is a *luvisol* or loamy clay (25% clay, 70% silt, 5% sand in the top 15 cm). The soil organic carbon content was ~20 g C kg^{-1}, pH (in water) = 7.6, and bulk soil density was 1.3 g m^{-3}. A detailed description of the site can be found in Laville et al. (2009; 2011), and Loubet et al. (2011).

The field was cultivated with winter wheat (a mix of Atlass and Premio species), which was harvested on 3 August 2012 (16.7 Mg ha^{-1} of dry matter). Cattle slurry was applied on the field with a trailing hose from the 18 to the 19 August 2012, at a rate of 42 kg N ha^{-1} of which 78% was ammonium (NH_4^+). The slurry had a very low dry matter content of 3.2% and a C/N ratio of 15.7. The total C applied was 666 kg C ha^{-1}. A gentle tillage was performed the 29 August 2012 to incorporate the crop and slurry residues and prepare the soil for oilseed rape sowing (variety Adriana) at a density of 35 plants per square meter. The crop developed slowly during the winter with a dry matter above ground (leaf area index) of 37 g m^{-2} (0.65 m^2 m^{-2}) the 25 October 2012 and 104 g m^{-2} (0.7 m^2 m^{-2}) the 18 February 2013. The canopy height stayed below 10 cm during the whole winter. Ammonium nitrate pellets were applied on oilseed rape the 20 February 2013 at a rate of 54 kg N ha^{-1}. Two selective herbicides were applied on the 2 (Springbok: 200 g L^{-1} of Metazachlore and 200 g L^{-1} of DMTA-P at 3 L ha^{-1}) and 31 October 2012 (Devin / Cycloxydime: 100 g L^{-1} at 1 L ha^{-1}) which only destroyed the weeds. In Decembre 2012 antilimaces pellets were applied.

2.2 Micrometeorological and ancillary measurements

Meteorological measurements included wind speed, air and soil temperatures and humidity as well as rainfall, global, net and photosynthetic active radiation. The meteorological measurements were performed on a mast (3.17 m high) near the centre of the field and close to the flux measurement site (Fig. 1). Soil was sampled ~monthly for water content, total nitrogen and mineral nitrogen analysis. Measurements are described in (Loubet et al., 2011) and will not be detailed here.

A simplified sketch of the EC measurement system is shown in Figure 1. Three-dimensional wind and temperature fluctuations were measured near the centre of the field at 3.17 m above ground by a sonic anemometer (Gill R3 3-axis anemometer, Gill Instruments Limited, UK). A fast response open-path CO_2/H_2O infrared gas analyser (IRGA LI-7500A, LI-COR, USA) installed in a lateral distance of around 0.2 m to the sonic path measured CO_2 and H_2O fluctuations. O_3 mixing ratios were measured by a high-frequency, dry chemiluminescence O_3 detector (NOAA, USA) and its Teflon PFA inlet tube (length = 2.8 m, internal diameter = 0.32 mm) was positioned in between the sonic path and the IRGA at a lower height. The high-frequency signals were recorded at 20 Hz by Labview program developed in the laboratory. In accordance with (Lee et al., 2015), high-frequency (10 Hz) time series of NO and NO_2 were determined by two fast-response and closed-path chemiluminescence NO analysers (CLD 780TR, EcoPhysics, Switzerland), one being coupled to a photolytic converter (blue light converter, BLC, Droplet Measurement Technologies Inc, USA) for the detection of NO_2 (see Figure 1). The horizontal separation of the trace gas inlets from the sonic path was 20 cm. Air was sampled through two heated and shaded PFA tubes with a length of 20 m and an inner diameter of 9.55 mm. The first CLD was used for measuring NO and the second one connected to the BLC was used for detecting NO_2. Conversion efficiencies for NO_2 to NO of around 30% were achieved. The high-frequency signals of NO, NO_2 and O_3 were calibrated with mixing ratios measured at 30 min time resolution by slow-response analysers (ThermoScientific, Waltham, USA) (Figure 1). These instruments were calibrated every 3 to 6 weeks using the gas-phase titration (GPT) method and a 17 ppm NO standard (Air Liquide, FR). The fetch of the field site extended at least to 150 m in all directions and a footprint analysis showed that 90% of the time the entire field was in the footprint during neutral and moderately stable or unstable conditions (Loubet et al., 2011). NO and O_3 fast sensors were functioning during the whole campaign (07/08/2013 to 13/03/2013) together with NO, NO_2 and O_3 slow-response analysers and meteorological station. High frequency NO_2 measurement was performed from 14/08/2012 to 30/09/2012. In this study we focus on two periods: (1) from 14/08/12 to 29/08/12 during which all fluxes were measured and NO fluxes were the highest in order to investigate the interactions between the fluxes and mixing ratios of the NO-NO_2-O_3 triad, and (2) over the whole period for NO fluxes analysis. **[INSERT FIGURE 1]**

2.3 Eddy covariance fluxes computations

The turbulent fluxes were computed as the covariance between the fluctuations of the scalar of interest and the vertical component of the wind. As the EC method and its theoretical background are described in the literature - e.g. (Foken, 2008) - details will not be provided here.

For closed-path sensors (NO, NO_2 and O_3), the lag time between w' and the dry mole fraction χ, had to be determined. This was done by searching for the maximum of the covariance function $(\overline{w'(t)\chi'(t-lag)}$. The lag for NO was 3.1 s [2.4-3.65 s] (Q50 [Q25-Q75]), for NO_2 it was 4.0 s [3.65-4.55 s], and for O_3 it was 2.9 s [2.5-3.25 s]. The lag was filtered for outliers (points outside of median lag ± standard deviation were considered as outliers) and the covariance was computed as the value of the covariance function at the filtered lag.

As fast-response sensors for NO, NO_2 and O_3 were not absolute, the fluxes were computed following the ratio method for O_3 described by (Muller et al., 2010a), and in accordance with (Lee et al., 2015) for NO and NO_2:

$$F_{O3} = \frac{\overline{\chi_{O3}}}{V_{dry}} \frac{\overline{w'O_3'}}{\overline{O_3}} \tag{1}$$

$$F_{NO} = \frac{\overline{w'NO'}}{S_{NO}V_{dry}} \tag{2}$$

$$F_{NO} = \frac{1}{\alpha V_{dry}} \left(\frac{\overline{w'NO_x'}}{S_{NO2}} - \frac{\overline{w'NO'}}{S_{NO}} \right) \tag{3}$$

where O_3(in mV), NO and NO_x (in counts s^{-1}) are the uncalibrated fast signals, χ_{O3} is the 30 min average of the slow-sensor reference O_3 mixing ratio (in ppb), while S_{NO} and S_{NO2} are the sensitivity of the analysers (in counts s^{-1} ppb^{-1}). α is the blue light converter conversion efficiency, and V_{dry} is the molar volume of dry air (in m^3 mol^{-1}). All fluxes (momentum, heat, CO_2, H_2O, NO, NO_2, O_3) were computed by the Eddypro software and final flux data were averaged for 30 min intervals. Evaluation methodologies from the CarboEurope project were applied - see (Aubinet et al., 2000 ; Loubet et al., 2011).

2.4 Spectral corrections and flux uncertainties

Spectral attenuation of the flux is due to differential transport time of the compound in the tube and interaction with tube walls and filter surfaces (Massman and Ibrom, 2008). We tend to minimize this effect by insuring a large flow rate in the tubes with Reynolds number well above the critical threshold for turbulence - see (Lenschow and Raupach, 1991) - as well as heating the tubes to around 5°C above ambient temperature. The residence time of the air samples inside the tubing was around 1 s, ensuring low chemical conversions and the

Reynolds number was 11700, hence largely in the turbulent range. However, water vapour interaction is still expected, and sensor separation also generates high frequency losses.

The NO, NO_2 and O_3 random instrument noises were estimated as the 1-σ random uncertainty of the signals as in Lenschow (2000), Langford et al. (2015) and Mauder et al. (2008). This noise is assumed to be "white" and hence uncorrelated to itself apart at lag = 0. It is therefore estimated as the difference between the autocorrelation at lag = 0 s and at lag = ± 0.05 s. The flux random uncertainty was itself evaluated as the covariance detection limit. It was determined as the root mean square error of the covariance function over 60 second periods at lag times well away from the position of the time lag. In practice, these were taken at lags larger than 120 s as absolute value as proposed by Langford et al. (2015).

2.5 Chemical reactions, time scales and flux divergence

Chemical reactions between NO, NO_2 and O_3 are important to consider when interpreting the measured fluxes as they can affect the fluxes above the ground. A common way to determine whether these reactions may indeed affect the flux is through comparison of chemical and transport time scales. Details of the reactions rates, time scales and flux divergence calculations are given in supplementary material sections S1-S3.

3. Results and discussion

3.1 Uncertainty in NO, NO_2 and O_3 flux measurements

The largest uncertainty were the high frequency losses, which was estimated with the in-situ ogive method (Ammann et al., 2006), and amounted to 10% for O_3, 20% for NO and 30% for NO_2 on average over the August-September period (when all fluxes were measured, see Figure 2). As a bias, they can be corrected for, and this was performed in the following of this manuscript. **[INSERT FIGURE 2]**

The second largest uncertainty on flux measurements was the random uncertainty which was lower than 20% in most cases for O_3, NO (and similar to H_2O) and around 30% to 40% for NO_2 (Figure 3). For NO and NO_2 the random uncertainties peaked during the morning traffic hour around 6:00-8:00 UTC, which is explained by the non-stationarity generated by the local traffic on the mixing ratios. Hence overall the eddy covariance method proved to be usable for measuring NO fluxes over part of the season with an overall uncertainty similar to H_2O. A higher random uncertainty was found for NO_x fluxes which were smaller than NO fluxes and with a relatively low conversion ratio from NO_2 to NO (30%). **[INSERT FIGURE 3]**

3.2 Meteorological conditions

Daily averages of the air temperatures decreased during the measurement period, starting from about 20°C in summer and reaching minima around -5°C from December to March. Daily averages of global radiation decreased from 250 W m^{-2} in August to around 0 W m^{-2} in December, back to around 150 W m^{-2} in the end of March (Fig. 4). Daily average of the relative humidity was around 65% in August and September, and it increased to about 85% for the rest of the period. The wettest period was between October and November, and cumulative rain was 319 mm over the 7 month, which is quite high. The prevailing wind direction was south-west while the most intense winds were observed from north and south (Fig. S2). Figure S2 also shows that wind regimes were quite different in summer and winter: prevailing wind directions during August and February were from south-west and north-east, respectively. Soil water content (SWC) ranged between 20% and 40% (volume) (Fig. 4), with a long period between October and January with values around 28% and increased further in January to 35%, with sharp decrease during some periods. **[INSERT FIGURE 4]**

3.3 Seasonal dynamics and diurnal cycles of the NO, NO_2 and O_3 fluxes above a crop rotation

3.3.1 Seasonal dynamics of NO-NO_2-O_3 mixing ratios

Average daily NO, NO_2 and O_3 mixing ratios were 3.6, 6.9 and 24.8 ppb, respectively. The NO and NO_2 mixing ratios were higher when winds blew from the East (Paris), while O_3 showed the opposite behaviour, which can be explained by depletion of O_3 by NO sources from the surrounding traffic (as shown in Fig. S2) and reactions (S1-S2). Daily NO_2 / NO_x ratios were on average 66%, which is typical for traffic and urban pollution (Carslaw, 2005; Minoura and Ito, 2010), and ranged from 4% to 93% during the entire period. The NO_2 mixing ratio was significantly higher (Student t-test) than the NO mixing ratios in August and early September, end of January and mid-February, and end of March. During sporadic episodes, NO peaks were of the same order or even higher than NO_2 peaks (Fig. 4).

3.3.2 Seasonal dynamics of NO NO_2 and O_3 fluxes

The daily averaged NO fluxes were very small, except during a period of strong emission following organic fertilisation on two days in August (18-19/08/2012), with maximum daily average fluxes of around 1.5 nmol m^{-2} s^{-1} (Fig. 4). Other emissions episodes, including mineral fertilisation in February (20/02/2013), were characterized by mean daily fluxes below 0.5 nmol m^{-2} s^{-1}. The NO fluxes were slightly negative part of the time (Q25, Q50 and Q75 equal -0.013, 0.031 and 0.11 nmol m^{-2} s^{-1}, Fig. S3). The O_3 fluxes ranged between -13.8 and 0 nmol m^{-2} s^{-1}, and averaged to -3.12 nmol m^{-2} s^{-1}. The largest O_3 deposition fluxes were observed following organic fertilisation in August, and were correlated with the strongest NO emissions. This period also corresponded to large daily O_3 mixing ratios (Fig. 4). The NO_2 fluxes were only measured during the first one and a half months (16 August to 30 September 2012) and were mostly negative (deposition), except during the first week following organic fertilisation (Q25, Q50 and Q75 equal -0.11, -0.07 and 0.08 nmol m^{-2} s^{-1}) (Fig. S3). O_3 fluxes were in the same range of magnitude, typically between -20 and 0 nmol m^{-2} s^{-1}, than those reported by previous studies at the same site (Stella et al., 2013b; Stella et al., 2011b; Tuzet et al., 2011) and in the literature over various canopy such as grassland (Stella et al., 2013a), barley (Gerosa et al., 2004), potatoes field (Coyle et al., 2009), or forests (Fares et al., 2010; Gerosa et al., 2005), although O_3 flux magnitude is sharply dependant on local O_3 mixing ratio. The deposition velocity (see supplementary material section 6 and Figure S4), which does not account for O_3 mixing ratio variations but which is height-dependant, was similar with those reported by previous studies carried out at the same site (i.e., with the same measurement height): Stella et al. (2011a) reported deposition velocities ranging from 0.1 and 1 cm s^{-1} during bare soil periods, and from O_3 fluxes and mixing ratios reported by Stella et al. (2013b) it can be deduced deposition velocities around 0.1-0.2 cm s^{-1} for comparable short wheat canopy in autumn and winter. It must be noted that deposition velocity exhibited large seasonal variation, with larger deposition velocities in summer and lower ones in winter, due to the large dependence of deposition velocity on u_* (Zhu et al., 2015).

3.3.3 Diurnal cycles of mixing ratios and fluxes over periods of interest

O_3 mixing ratios exhibited a typical diurnal cycle that was governed by photochemistry and convective mixing within the boundary layer and from the free troposphere during daytime. It started to increase with sunlight around 7 a.m., and declined in the evening starting from 6 p.m. due to lack of photochemical formation in the absence of sunlight, deposition and destruction with NO in this high NO_x emission area. In general, NO mixing ratios featured a marked peak in the early morning and remained high until around 13:00 UTC (Fig. 5b). During the early afternoon, the O_3 increase was correlated with the NO decrease. NO_2 mixing ratios showed a bi-modal diurnal cycle with its maxima in correspondence with morning and evening traffic peaks, i.e. around 6 a.m. and 7 p.m..

The NO fluxes also showed a diurnal cycle similar to the one of soil temperature with an emission peak around 12 a.m. (Fig. 5a and b). This suggests that NO emissions are related to nitrification, for which the emission rate is an exponential function of soil temperature (Henault et al., 2005). This was already shown for the Grignon soil by Laville et al. (2011). The fact that NO fluxes decrease earlier than soil temperature is most likely due to titration of NO by O_3 in the late morning and early afternoon, causing the NO emissions at the reference height to be reduced with respect to ground emissions. This is also indicated by the positive NO_2 flux observed during the same time of the day. The O_3 flux was mainly negative (deposition) and follows the diurnal dynamics of measured mixing ratios. **[INSERT FIGURE 5a and 5b]**

3.6 Influence of organic and mineral fertilisations on NO emissions

The NO flux averaged over the whole period was 0.09 nmol m^{-2} s^{-1} (mean), which is smaller than previous findings for the same site. Laville (2011) and Loubet et al. (2011) reported yearly averaged NO fluxes varying between 0.07 and 0.15 nmol m^{-2} s^{-1} for 2007-2009. The NO flux distribution was shifted towards positive values after the organic fertilisation in August (Fig. S3), with the mean NO flux during the two weeks following the fertilisation (0.49 nmol m^{-2} s^{-1}) being six times larger than over the whole period. For the same period, the ozone flux distribution was shifted towards more negative values. Fig. S3 also shows that fluxes distributions after mineral fertilization do not differ much from the ones relative to the whole period. Following the February mineral fertilisation the NO flux increased less and was only 1.7 larger than over the whole period (0.14 nmol m^{-2} s^{-1}). These numbers are also in line with those reported following fertilisation on the same soil in the 2007-2009 period by Laville (2011) and Loubet et al. (2011), which also showed some periods with slightly negative NO fluxes. Stella et al. (2012) measured larger peak of NO emissions following slurry spreading, but only lasting two to three days, which was probably due to a dryer soil in our study compared to Stella et al. (2012).

Following the slurry application, the NO emissions amounted to 0.1 kg N ha^{-1}, which represents 0.25% of the applied nitrogen. Following the mineral fertilisation, the NO emissions amounted to 0.02 kg N ha^{-1}, which represents 0.037% of the applied nitrogen. On average, the NO emissions corresponded to 0.27% and 0.037% of the applied organic and mineral fertilizers (42 and 54 kg N), respectively. Over the whole period from August 2012 to March 2013, we evaluate a loss of 0.26 kg N ha^{-1}. With a total N input of 96 kg N ha^{-1}, this gives an estimate of the NO emission factor of 0.27%, which is similar to values reported earlier (Laville et al., 2011).

The reasons for smaller emissions following winter mineral fertilisation than following summer manure application are manifold. Even if the amount of applied nitrogen was similar for the two cases (42 and

54 kg N ha^{-1}), meteorological and soil conditions were much more favourable for nitrification in summer than in winter (Davidson, 1992; Williams and Fehsenfeld, 1991). Indeed, NO emissions from agricultural soils are mostly due to nitrification, and this hypothesis was tested for the Grignon site by Laville et al., (2011). Nitrification is inhibited by low soil temperature and high water content that causes anoxia. Soil temperature was much lower in February than in August (2.5 compared to 20 °C on average). February was particularly humid, with a total precipitation of 10 mm, while in August no significant rain event occurred after the first week, and the soil was only humidified by the organic manure supply (layer thickness of 4.8 mm) and occurred on a dry soil. The soil water content at 5 cm depth in September 2012 was around 21% in volume, while in February it was 33% in volume. These two factors led to more favourable conditions for nitrification in August than in February.

3.7 Influence of surrounding roads on the measured fluxes and concentrations of the NO-NO_2-O_3 triad

Using the FIDES flux and concentration footprint model (Loubet et al., 2010) we evaluated the footprint of nearby roads. Overall the flux footprint from the nearby roads was smaller than 1% (which means that only 1% of the road emissions contributes to the flux at the mast) most of the time, but the concentration footprint reaches up to 10% during some episodes, with separate roads contributing differently depending on periods (Fig. S1). Assuming a conservative emission of 250 mg km^{-1} $vehicle^{-1}$ and an average vehicle count 10000 vehicles per day (2010 counts, “Statistiques du département des Yvelines pour 2010” shows range between 5000 and 15000), we evaluate a contribution from 4% to 40% of the roads on the measured fluxes. However, since vehicles emissions of NO_x have a sporadic nature,10000 vehicles per day means a maximum of ~1 vehicle every 2 seconds (if we consider, conservatively, that most of the traffic is condensed during 9 hours only). These vehicles are also moving at about 90 km h^{-1} (25 m s^{-1}), hence, leading to a moving point source of NO_x. We therefore expect that the signal of this moving and sporadic source is not captured by the eddy-covariance method, and would be filtered out by despiking and flux calculation procedures (Foken, 2008 ; Mahrt, 2010).

3.8 Chemical interactions: the NO-NO_2-O_3 triad and effect on the fluxes

In order to investigate the interactions between the fluxes and mixing ratios of the NO-NO_2-O_3 triad, we focus on the period from 14/08/12 to 29/08/12, during which all fluxes were measured and NO fluxes were the highest.
The two weeks following the organic manure application (from 18/08 to 19/08) are characterized by hot sunny days, with maximal global radiation above 800 W m^{-2}, except for the 24 August when the only rain event occurred (Fig. 6). The period of 18 to 23 August was warmest, with soil surface temperatures above 40°C at noon during most of the days, while the air temperature decreased from around 35°C to around 20°C during the same period. The soil temperature at 5 cm depth followed the same trend, but with lower daily maximum and higher night-time minimum. Although, due to sensor breakdown the soil water content was not measured during this period. The small latent heat flux (LE) after the 19 August, (17 W m^{-2} on average between 19 and 31 August) the large sensible heat flux (60 W m^{-2} on average) and radiation (212 W m^{-2} on average) indicate that the soil humidity of the top soil layer was low. Hence, we assume that the SWC was probably close to the one measured in September (around 20 % in volume), which is ideal for nitrification to occur (Laville et al., 2011; Oswald et al., 2013). **[INSERT FIGURE 6]**

The 18/08 was the first day when NO emissions from the soil occurred. The emissions lasted around two weeks following the organic fertilisation (Fig. 4), during which the NO flux during daytime exceeded 0.5 nmol m^{-2} s^{-1}, peaking around 12 a.m. The nocturnal NO flux usually decreased to zero, except for the night of 25/08, characterized by strong winds (Fig. 6). The maximum of the NO emissions was 2.7 nmol m^{-2} s^{-1} observed six days after fertilisation on the 21/08.

The NO_2 flux daily pattern was different during the two weeks following organic manure application compared to the period before (Fig.6). It was in general positive during the day and around zero at night during the period 18/08 to 29/08, except for the night of the 25/08 when it was large and negative. Positive NO_2 fluxes might be explained by chemical reactions between NO and O_3 in the surface layer (De Arellano et al., 1993), which will be discussed in the next section.

The O_3 flux was also significantly higher (Student t-test) following organic fertilisation than during the rest of the experimental campaign (Fig. S3). Since the mixing ratio of O_3 was quite variable during the campaign (Fig. 4), it is more interesting to look at the deposition velocity which underpins the surface exchange processes (Fig. 5b and 6). The median V_{dO3} during the organic fertilisation event exceeded the median over the rest of the experimental campaign by a factor of two. However, this increase in O_3 deposition velocity cannot be explained by reaction with soil emitted NO alone as the O_3 flux is an order of magnitude larger than the NO flux.

Different pathways for the near-surface O_3 removal are likely: i) photolysis of O_3 by ultraviolet light in the presence of water vapor forming OH radicals, ii) gas phase reactions with reactive VOCs and iii) heterogeneous reactions on soil or with adsorbed molecules on soil.

The NO mixing ratio was well correlated with the NO flux, with a correlation coefficient of 40% for the two weeks following the organic fertilisation (excluding 24-25 August), while it was only 2% for the 7 month period. This suggests that, following fertilisation, the ambient NO levels were mainly due to local emissions. The NO_2 mixing ratio was less correlated with the NO_2 flux, suggesting that NO_2 levels were more related to advection from surrounding traffic roads than from local emissions. Indeed, both NO and NO_2 are emitted from traffic roads and urban pollution, but the NO_2 component quickly becomes prevalent as the plume is advected, especially in presence of high O_3 levels, as in our case (Carslaw, 2005; Minoura and Ito, 2010). The minimum night-time mixing ratio is mainly controlled by night-time wind velocity: the higher the night-time velocity, the higher the mixing ratio, due to a better mixing in the atmospheric surface layer. During conditions with lower wind speed, deposition and reaction with local NO_x sources lead to a high depletion of O_3 during the night.

3.8.1 To what extent are the chemical reactions between NO, NO_2 and O_3 modifying the fluxes above the ground?

Measured mixing ratios and fluxes of NO, NO_2 and O_3 are affected by chemical reactions (S1 to S4) in addition to emissions and deposition processes. Especially, the diurnal fluxes of NO_2 observed from the 18 to the 23 August, were positive (emissions) and of the same order of magnitude as the NO fluxes, while they were negative afterwards. The simultaneous observation of positive NO and NO_2 fluxes are typical for the NO-to-NO_2 transformation below the flux observation level in the presence of high O_3 mixing ratios. This phenomenon is called “apparent NO_2 emissions” and was observed in other studies mainly above dense or tall canopies (Ammann et al., 2012; Min et al., 2014; Plake et al., 2015). For the reactions (S1-S2) to occur below the measurement height, the turbulent transport time (τ_{trans}) needs to exceed the chemical reaction time (τ_{chem}) (Arellano and Duynkerke, 1992; De Arellano et al., 1993; Lenschow and Delany, 1987; Plake et al., 2015; Stella et al., 2013a; Stella et al., 2011a; Stella et al., 2012). The Damköhler number Da = τ_{trans} / τ_{chem} is often used to determine the conditions favourable for chemical reactions: in cases when Da is higher than unity chemical reactions are faster than the transport (flux divergence), whereas values for Da smaller than 0.1 indicates that the influence of chemical reactions was negligible. The aerodynamic resistance $R_a(z)$ (Eq. S8) was overall quite small and ranging from 45 to 128 s m^{-1} (1st and 3rd quantiles), hence leading to a quite short transport time scale (but larger than 100 s most of the time). The boundary layer resistance was around 22 and 43 s m^{-1} (1st and 3rd quantiles) for O_3 (Fig. 7). The surface resistance for O_3 was estimated as $R_{soil}(O_3) = V_{dO3}^{-1} - R_a - R_b(O_3)$, and dominated the other resistances (100 to 480 s m^{-1}). The O_3 penetration depth in the soil was estimated as the depth necessary to explain the measured $R_{soil}(O_3)$ if molecular diffusion drives transfer in the soil. In practice this corresponded to the dry soil layer used in (Personne et al., 2009). This depth ranged from 2 to 10 mm on average and was smaller at noon than during the night (Fig. 7). Overall, the chemical time τ_{chem} and the transport time τ_{trans} were of the same order of magnitude at any time of the day between applications and during mineral fertilisation, and τ_{chem} was smaller than τ_{trans} during the organic fertilisation. As a consequence, the Damköhler number was around unity most of the time and larger than unity during the organic fertilisation period, showing that reaction between O_3, NO and NO_2 happened during transport from the ground to the mast at all times at this site. During the fertilisation event, the Damköhler number was especially high at night, when the transport time increased more substantially than the chemical timescale. These results are similar to findings by Stella et al. (2012) for the same site over bare soil. During the periods with vegetation, the increase of the transport time scale above the canopy was less than of that of the chemical time scale during nighttime, as the presence of vegetation increases the mixing, and, hence diminishes $R_a(z)$. **[INSERT FIGURE 7]**

The Damköhler number shows that NO reacts with O_3 and that photolysis also plays a role. How does this affect the NO flux measured at the reference height compared to the one at the ground? We quantified this variation by numerically solving Eq. S13, based on the model of Duyzer et al. (1995). Due to the reaction with O_3, the calculated NO flux at the ground surface was on average 32% larger than that at the measurement height during the period 17-29/08 (0.93 instead of 0.63 nmol m^{-2} s^{-1}). This would represent an increase of 37 g N emission following slurry spreading. For NO_2, the calculated flux at the ground surface was mostly negative while it was mainly positive at the reference height during the period 18-22/08. On average the NO_2 flux at the ground was -0.33 nmol m^{-2} s^{-1} over the period 17-29/08 while it was -0.03 nmol m^{-2} s^{-1} at the reference height. For NO fluxes, the major discrepancy between fluxes at the surface and the measurement height occurs during periods with relatively large and stable values of the Damköhler number (Fig. 8), as this is the case when chemical reactions consume NO before it reaches the measurement height.

[INSERT FIGURE 8]

Since the O_3 deposition flux was much larger than the NO flux, the reaction with NO changed the absolute value by only 3% when comparing the flux at the measurement height to the ground surface. Indeed, as only reactions (S1) and (S2) are considered in eqs. (S12) and (S13), which we used to numerically evaluate surface fluxes, we obtain: $\Delta[FNO] = \Delta[FO_3] = -\Delta[FNO_2] = 0.3$ nmol m^{-2} s^{-1} where Δ stands for the difference between surface and measurement height.

3.8.2 Why is O_3 deposition increasing following organic fertilisation?

We observed that following organic fertilisation O_3 (performed by injection and hence soil tillage), deposition increased by a factor of two (as shown by the deposition velocity, Figs. 7 and 8). Several hypotheses may explain this increase: (1) the increased surface exchange due to soil tillage, (2) the reaction with NO emitted by the ground, and (3) the reaction with VOCs emitted by the ground:

(1) A first hypothesis would be that the increase in deposition velocity following the organic fertilization could be due to a change in physical characteristics of soil surface. Indeed, the application of cattle slurry with a trailing hose modifies the soil structure at the surface which has as a consequence to increase the available surface for O_3 deposition, and therefore the deposition velocity. This hypothesis is consistent with the comparison of measured deposition velocities and modelled deposition velocities using Stella et al. (2011a) R_{soil} parameterization (see supplementary material section 7 and Figure S5). Indeed, while there is a good agreement between measured and modelled V_d after 26th August (i.e., after the rainfall event), modelled V_d systematically underestimates measured V_d between slurry application and rainfall event. Since the parameterization of R_{soil} was obtained for Grignon site over different periods, that means R_{soil} accounts for the mean soil structure of the Grignon site. Therefore, it can be hypothesized that (i) R_{soil} is underestimated from slurry application to the rainfall event due to the change of soil surface structure, and (ii) after the rainfall event, soil surface recovers its mean structure corresponding to the R_{soil} parameterization.

(2) Although the reactions with NO during transport are shown to be small compared to the NO flux (Figure 8), reactions in the soil surface layer may be more important due to large NO concentrations in the soil, despite the fact that this layer is very small. A graph of the difference between the measured and the modelled ozone flux following fertilisation (Figure S7) seem to show that the additional O_3 deposition is correlated with the NO flux. This would, mean that the NO_2 produced in the soil by reaction with NO would be adsorbed on the soil surface either on the mineral phase or dissolved the water phase as NO_2. To evaluate this assumption further, we evaluated the Damköhler number in the soil surface layer by assuming that the layer depth is equal to the O_3 penetration depth δ_{O3soil} (Fig. 7), in this layer the transport time is equal to soil resistance for O_3 times the penetration depth $R_{soilO3} \times \delta_{O3soil}$. We can evaluate the NO mixing ratio that would explain the additional O_3 destruction at the surface, by searching for the value of $[\mathrm{NO}]_{\mathrm{soil}}$that satisfies $\tau_{trans}(\mathrm{Soil}, O_3) = \tau_{chem}(\mathrm{Soil}, O_3)$. By doing so, we found that $[\mathrm{NO}]_{\mathrm{soil}}$ would need to reach 5 to 40 ppm to explain the increase in O_3 deposition following organic fertilisation. Gut *et al.* (1998) and Gut *et al.* (1999) measured NO mixing ratios at 2 cm depth in soil under wheat with the membrane tube technique and report mixing ratios around 100 ppb and always below 400 ppb following fertilisation, which is one order to two order of magnitude below the mixing ratio which would be needed to explain the observed O_3 flux. Moreover, the rate of NO production in the soil surface layer would have to be equal to the O_3 flux to the ground (around 20 nmol m^{-2} s^{-1}) which is an order of magnitude larger than what Gut *et al.* (1998) or Laville *et al.* (2009) report as maximum NO flux. However we should stress that both Gut *et al.* and Laville *et al.* report NO fluxes that were measured in the presence of ozone and hence would have been depleted by reaction with in a similar way as in here.

(3) Reactive VOCs such as sesquiterpenes and monoterpenes were previously found to be emitted from soils (Horvath et al., 2012; Penuelas et al., 2014), and some of these sesquiterpenes species react with O_3 in the order of a few seconds. The reactions of O_3 with larger terpenes are important sources of OH, as well as the ozonolysis of simpler unsaturated compounds. (Donahue et al., 2005). Currently, there is little or no data available on the emission of VOCs from slurry application. However, a recent study mainly focusing on quantification of odor emissions from soil application of manure slurry, shows the formation of a certain number of VOCs, included organic sulfur compounds, carboxylic acids, alcohols, carbonyl compounds (ketones and aldehydes), aromatic compounds (phenols and indoles) and nitrogen compounds (Feilberg et al., 2015). Based on their analyses, the compound most responsible for the overall odor impact from the VOC emissions was 4-methylphenol. These authors showed also the emission of trimethylamine, a compound that can react quickly with O_3, leading to formation of secondary organic aerosols (Murphy et al., 2007). Furthermore, these authors suggest that a large part of these VOCs are formed through ozonation reactions (i.e. byproducts of ozonation: methanol, acetone, and acetaldehyde). Indeed, the slurry will be transported downwards through the soil, where efficient heterogeneous reactions can take place at particle interfaces. It has been shown that the heterogeneous reaction probabilities may be much greater than anticipated. For example, measurements on oxide surfaces with chemical structure commonly found in VOCs (i.e. alkenes, terpenes, carbonyls) showed that the O_3 reaction probability of a surface-attached alkene can be up to five orders of magnitude greater than for the same reaction in the gas-phase (Stokes et al., 2008). In the same way, Fick et al. (2005) observed that ozonolysis reaction rates of some terpenes were much higher than predicted, possibly as a result of reactions on the surfaces used in their experiments. These results suggest that terpenes can remain on the surfaces, enhancing the O_3 reactivity. Similarly, some other authors observed that surface reaction probabilities with O_3 were 10 to 120 times greater than their corresponding gas-phase values (Dubowski et al., 2004; Springs et al., 2011). It is also known that soils can act as a sink of VOCs, by their adsorption to soil mineral particle surfaces and humic substances (Penuelas et al., 2014). Hence, it is likely that surface chemistry including photo-enhanced O_3 uptake on organic matter (Jammoul et al., 2008; Reeser et al., 2009) may explain the increase in O_3 deposition, a process yet not described in the literature. It may also be likely that O_3 is destroyed by very reactive VOCs in the gas phase as hypothesized by Wolfe et al. (2011). These gas-phase reactions, however, require that the chemical reaction time to be shorter than the turbulence transport time (Plake et al., 2015; Stella et al., 2012).

Among these three hypotheses, our study does however not allow to conclude definitely.

4. Conclusions

Eddy covariance flux measurements of the NO-NO_2-O_3 triad during a 7 months period allowed evaluating several mechanisms controlling the exchange of these reactive trace gases with an agricultural soil. Eddy covariance technique revealed to be suitable to catch seasonal and diurnal dynamics of the fluxes, and allowed to interpret fluxes behaviour according to meteorological variables, fertilisation practices and chemical reactions. In particular, the magnitude and temporal variability of NO emission fluxes following two fertilisation episodes were analysed, one in summer and the other one in winter. Mean NO emissions during the whole period were in agreement with previous studies on the same site. Emissions were significantly higher (Student t-test, with a factor of seven on the mean) during two weeks following organic fertilisation in August than during the rest of the experimental period. These large emissions are mainly due to favourable conditions for nitrification: soil water content around 20% and high temperatures. In February, following mineral fertilisation, the increase of NO emissions was less pronounced, although the same amount of N was applied. This difference is likely due to less favourable conditions for nitrification in February (low temperature and higher soil water content), rather than to the different form of fertilizer. On average over the whole period, we derived a loss of 0.26 kg N ha^{-1} as NO from the field. With a total N input of 96 kg N ha^{-1}, this results in an NO emission factor of 0.27%, which is on the lower range of earlier reported values on this site (Laville et al., 2011).

Our findings show that NO emissions from agricultural soils are limited (0.27% of the N-NO applied over the 8 month period, which with a conservative estimation can be extended to a yearly amount). When hypothetically extended to France with an average nitrogen fertiliser use of 80 kg N ha^{-1} over a fertilised area of around 26 Mha, this would lead to emission of NO_x of around ~5.6 t N-NO ha^{-1}, which is negligible compared to transport and industry which is several hundreds of thousand larger (CITEPA, 2015). The seasonality and spatial distribution of these emissions may, however, lead to air quality issues during spring and late summer-autumn which are the main fertiliser application periods in rural environments. Indeed, most of the emission we measured occurred within a few weeks following fertilisation. In terms of ozone, our findings are in accordance with previous ones, showing that ozone is efficiently deposited throughout the year. This means that crops are participating through this process in the reduction of the atmospheric oxidising capacity.

The O_3 deposition velocity was significantly larger following organic fertilisation than during the rest of the experiment (Student t-test), despite the fact that vegetation was absent. This increase in O_3 deposition could not be explained by reaction of O_3 with NO in the atmosphere as the NO flux was an order of magnitude smaller than that of O_3. The process behind this ozone deposition increase is still to be discovered. We hypothesised three underlying processes: (1) increase in soil surface due to soil tillage, (2) reaction with NO in the soil layer, and, (3) reactions of O_3 with VOCs emitted by the slurry. None of these hypotheses can be invalidated and it would require further investigation to conclude. Controlled conditions experiments are desirable to better understand these processes.

The evaluation of the chemical and turbulent transport times showed that reactions between NO, NO_2 and O_3 below the measurement height occurred during the whole measurement period, leading to a depletion of NO and a build-up of NO_2 from the ground to the measurement height. Following organic manure application, NO fluxes were reduced by 30% from the surface to measurement height, while the NO_2 fluxes changed sign, being negative at the surface and positive at the measurement height. This phenomenon of “apparent NO_2 emissions” was reported in other studies, especially above forests. Here it also reveals to be important above a bare soil and at moderate measurement heights, in conditions of strong NO emissions and high ambient O_3 mixing ratios.

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Figures

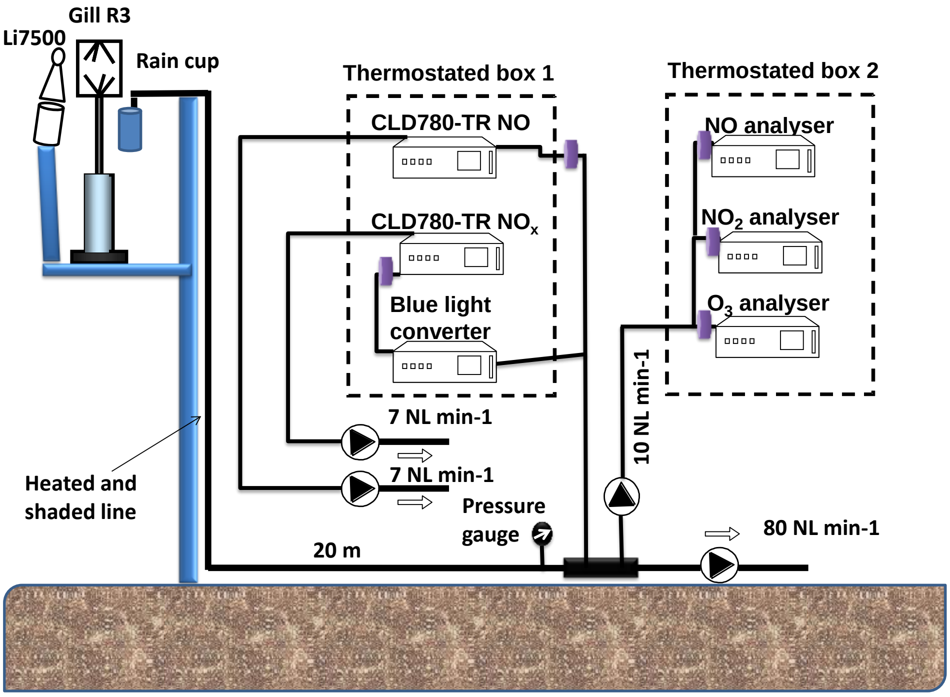

Figure 1. Simplified sketch of the field and instrument setup to measure EC fluxes. Gill R3 is the ultrasonic anemometer, Li7500 is the open path infrared CO_2 and H_2O gas analyser, the rain cup is the air sampler for NO and NO_2 detection. CLD780-TR NO and NOx are the fast-response NO analysers (Ecophysics) operating in parallel, one connected to a BLC measuring NO + αNO_2. The NO, NO_2, and O_3 slow analysers (ThermoScientific, Waltham, USA) are placed behind a Teflon pump ensuring atmospheric pressure at the inlet. A large pallet pump ensured a flow rate of 80 NL min^{-1} in the heated inlet line. Teflon filters (1µm) were installed at the front of the instrument inlets (purple cylinders).

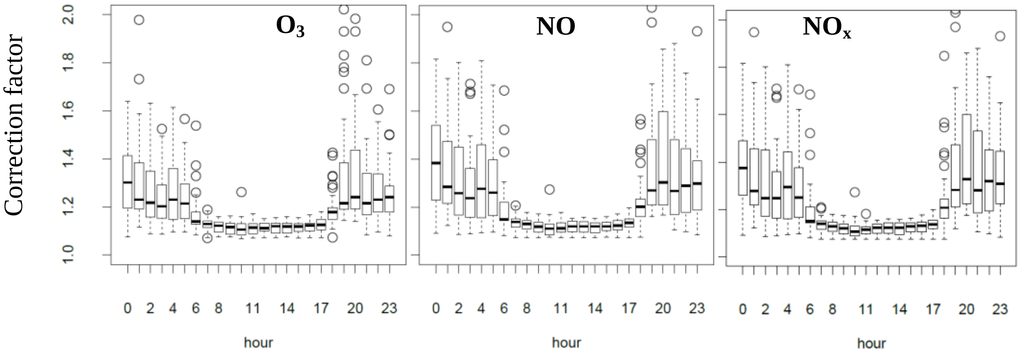

Figure 2. Hourly averaged high frequency loss correction factors for O_3, NO and NO_x over the 15 August-7 September period determined with the in situ ogive method. The corrected flux equals the measured flux multiplied by the correction factor. Black bars are medians, boxes show the interquartile, error-bars show the minimum and maximum of the whisker and empty dots shows the outliers.

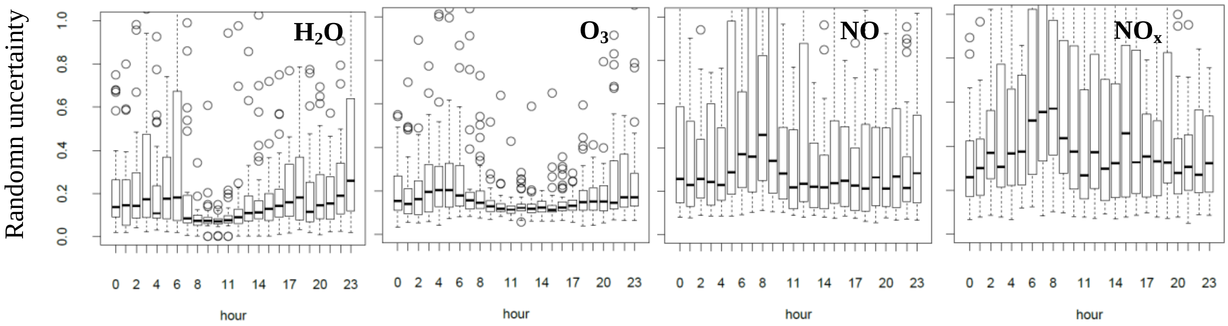

Figure 3. Daily variations of the ratio of the random uncertain to the flux for H_2O, O_3, NO and NO_x during august 2012 (15 August to 9 September). Black bars are medians, boxes show the interquartile, error-bars show the minimum and maximum of the whisker and empty dots shows the outliers.

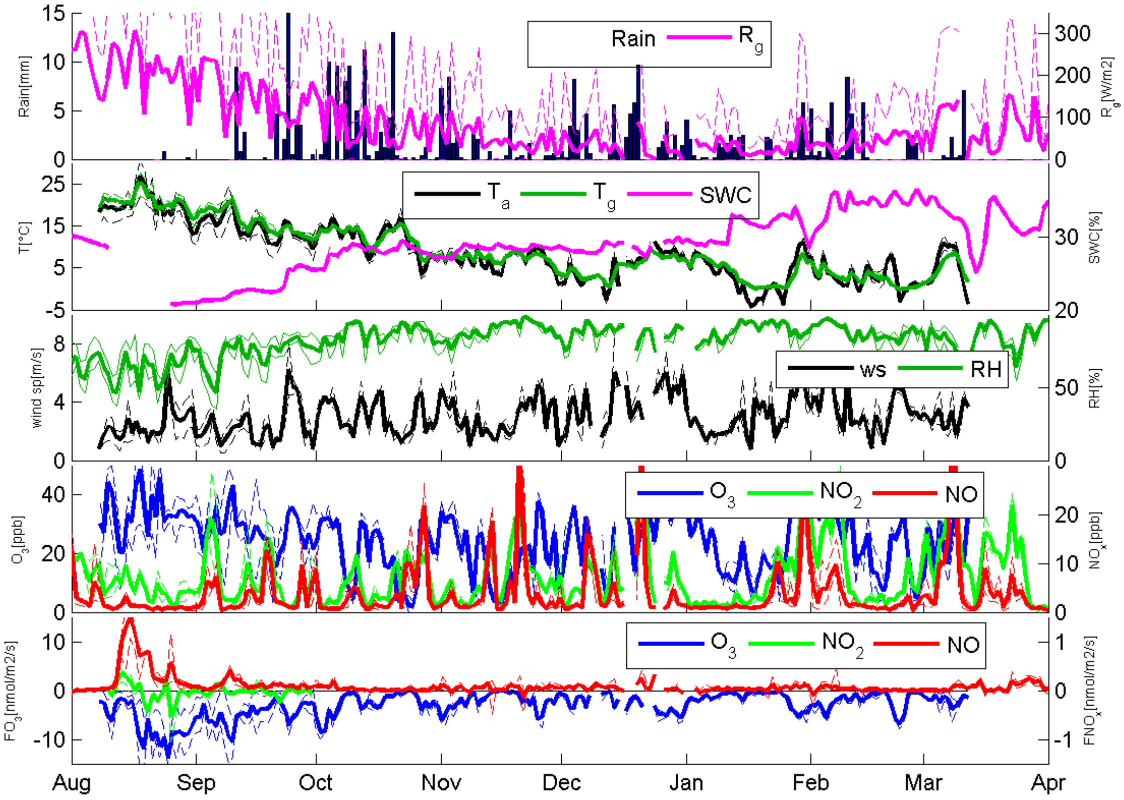

Figure 4. **Meteorological and soil conditions (daily averages, sums for rainfall), NO, NO_2 and O_3 mixing ratios and fluxes during the entire measurement period from 07/08/2012 to 13/03/2013 at the Grignon field site. Averages for night-time and daytime are also given as dotted lines. R_g is the global radiation, T_a and T_g the air and ground temperature, SWC the soil water content, ws the wind speed, RH the air relative humidity.**

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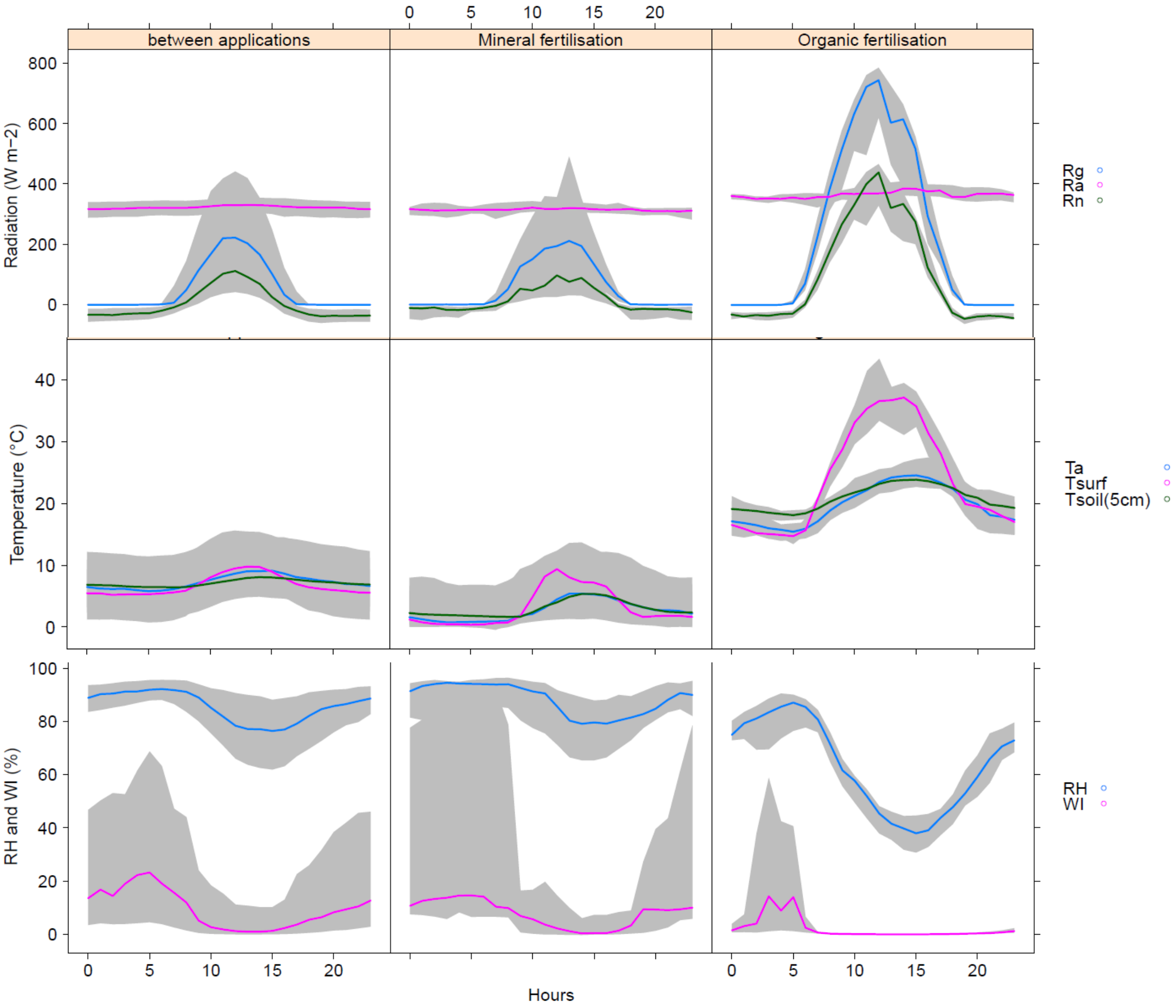

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839 **Figure 5a. Diurnal cycles of global irradiance and net radiation, air and soil temperatures, relative humidity and**
840 **wetness index averaged over the three periods of interest at the Grignon field site. The shaded areas represent the**
841 **interquartile range.**

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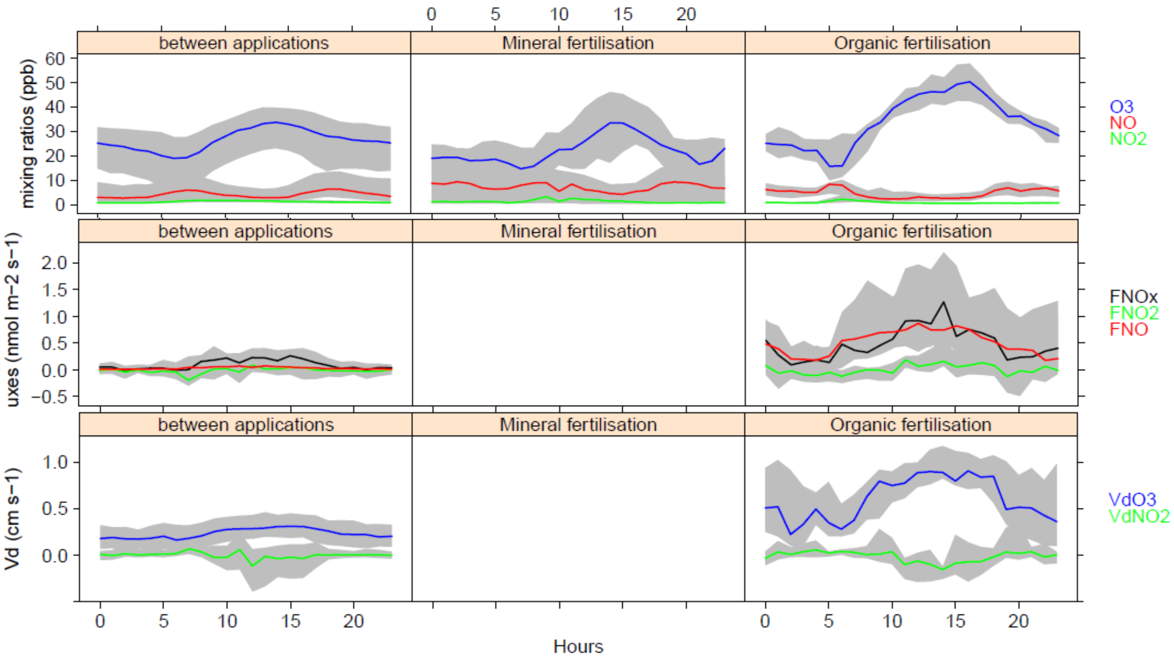

Figure 5b. Diurnal cycles of NO, NO$_2$ and O$_3$ mixing ratios and fluxes as well as the deposition velocities of NO$_2$ and O$_3$, averaged over the three periods of interest at the Grignon field site. The shaded areas represent the interquartile range.

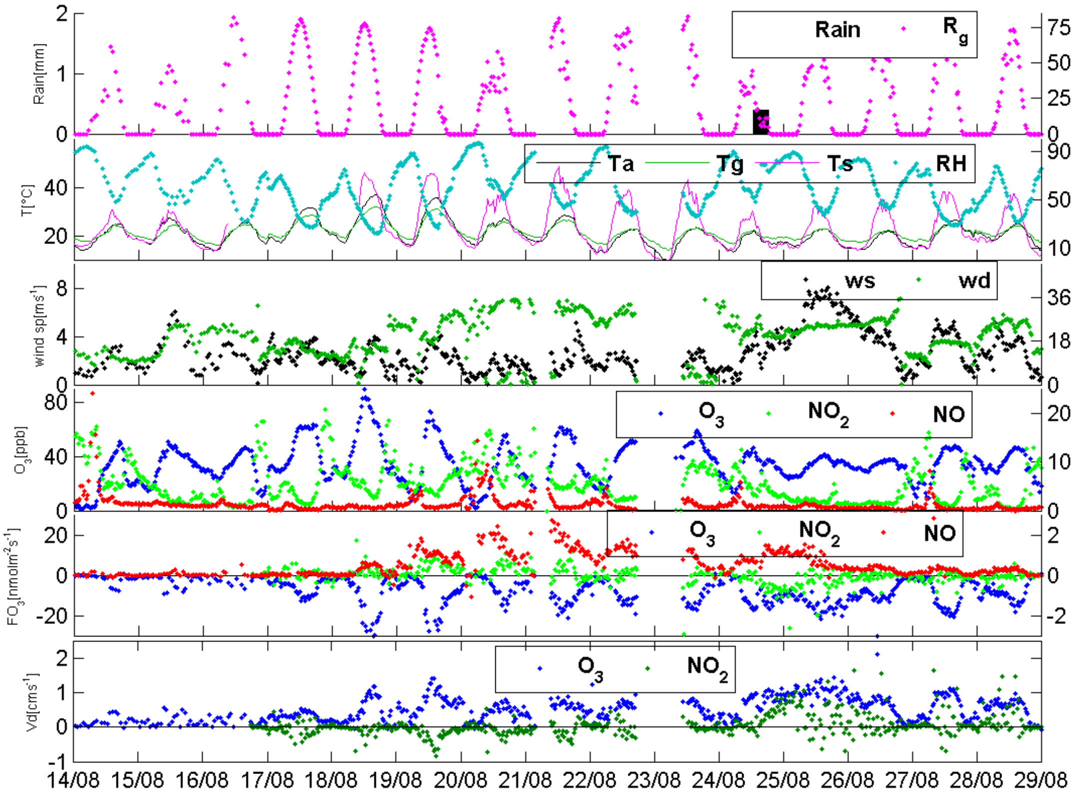

Figure 6. Meteorological variables and NO_x-O_3 mixing ratios and fluxes measured during the period 14/08/12 to 29/08/12 at the Grignon field site. Ticks on the x-axis correspond to midnight.

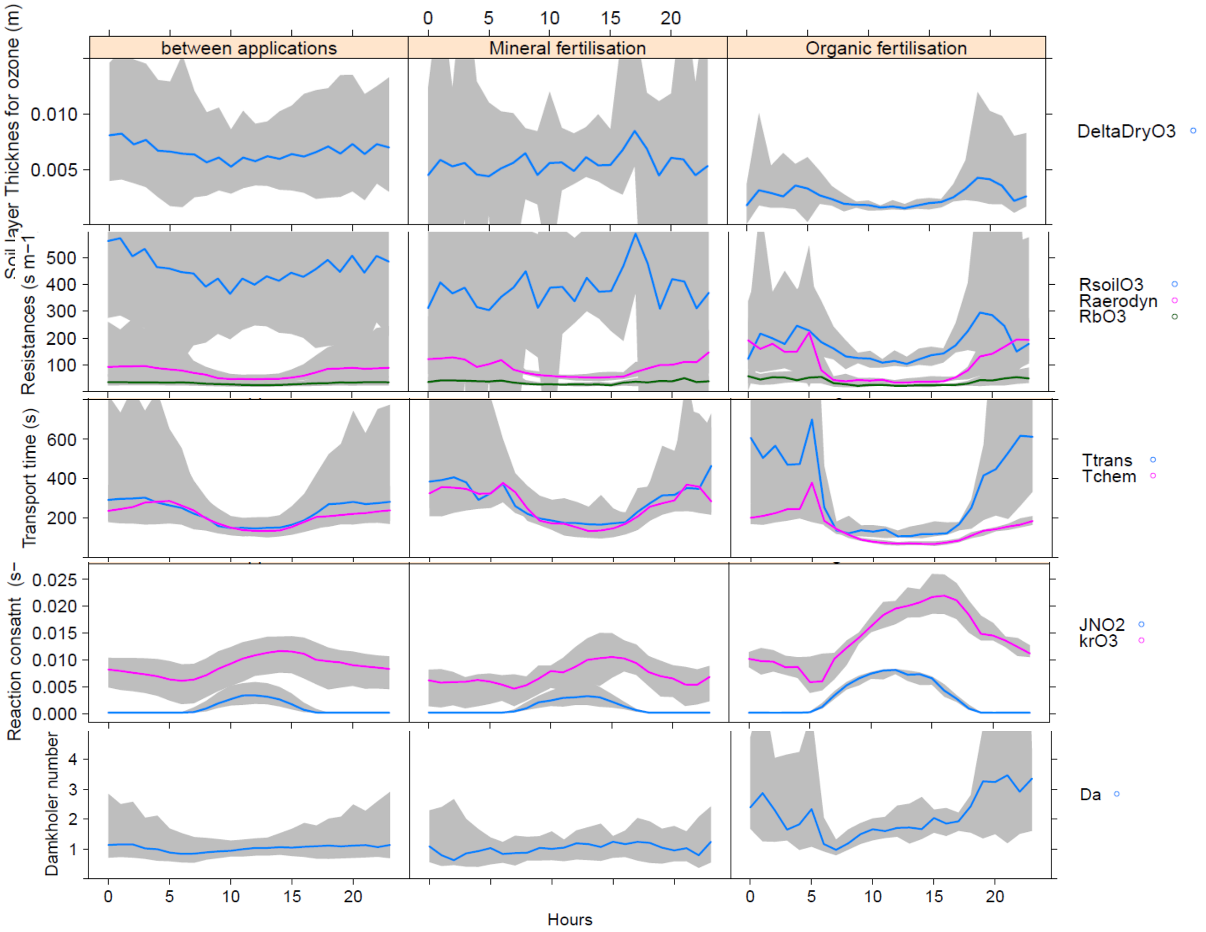

Figure 7. Diurnal cycles of the O_3 penetration depth in the soil (DeltaDryO3), the aerodynamic (Ra), boundary layer (RbO3) and soil resistances (RsoilO3) for O_3, the chemical reaction time τ_{chem} and transport time τ_{trans}, the chemical reaction rates for NO_2 photolysis J_{NO2} and NO depletion by O_3 ($k_r \times [O_3]$), and the Damköhler number (Da), averaged over the periods of interest at the Grignon field site. The shaded areas represent the interquartile range.

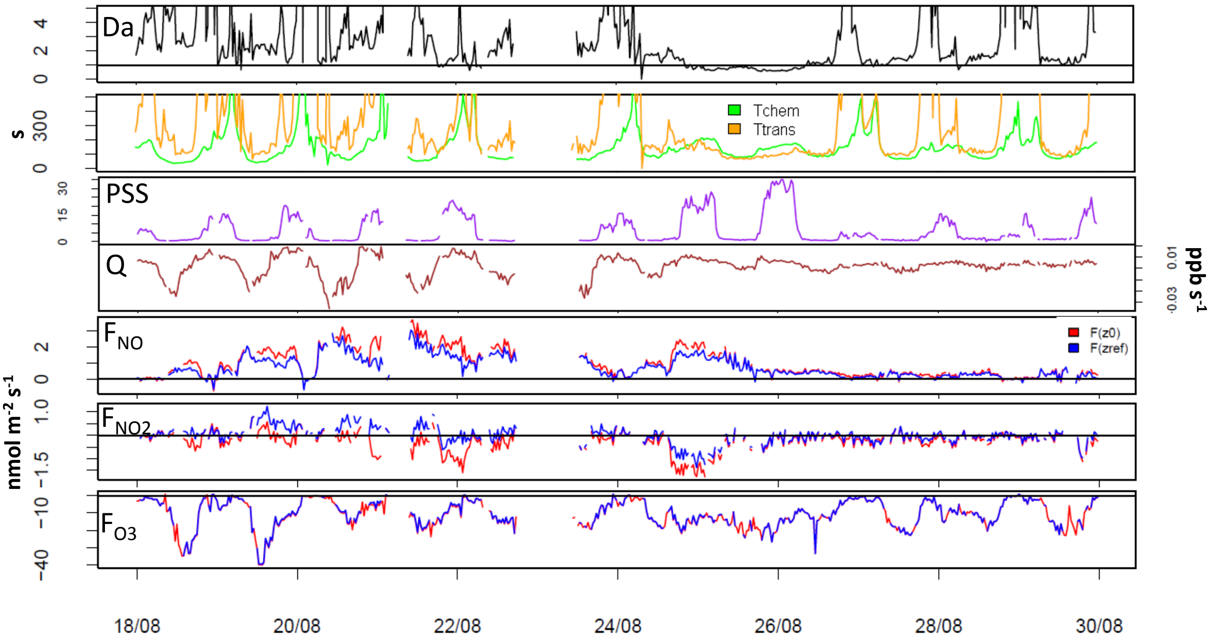

Figure 8. Half-hourly values of photo-stationary state ratio (PSS) and Q = k_r [NO][O$_3$] - J_{NO2}[NO$_2$] (s) ; chemistry and transport timescales (Tchem and Ttrans) and Damköhler number (Da); measured NO, NO$_2$ and O$_3$ fluxes and surface fluxes as computed by assuming a logarithmic flux divergence profile (F$_{NO}$, F$_{NO2}$ and F$_{O3}$) at the Grignon field site.