1 Chemical reactions in the NO-NO$_2$-O$_3$ triad

The main gas phase reactions for the NO-O$_3$-NO$_2$ triad in the troposphere are (Seinfeld and Pandis, 2016):

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad [k_r] \tag{SR1}$$

$$NO_2 + O_2 + h\nu \rightarrow NO + O_3 \quad [J_{NO2}] \tag{SR2}$$

Where $k_r = 0.0444 \exp(-1370 / (Ta + 273.15))$ in ppb^{-1} s^{-1}, and J_{NO2}, in s^{-1} is the photolysis frequency, which was retrieved as a function of global radiation R_g in W m^{-2}, $J_{NO2} = B1\ R_g + B2\ R_g$, following the approach of Trebs *et al.* (2009). The coefficients B1 and B2 were determined for our site by fitting measured data of global radiation and photolysis frequency that were available for the summer period in year 2002 (June to September, half hourly data). The fit of our data (4 months of half-hourly measurements of R_g and J_{NO2} accounting for about 5600 data points) results in B1 and B2 1.51×10^{-5} and 6.85×10^{-9} W^{-1} m^2 s^{-1}, respectively. However, in the troposphere, and especially in a polluted atmosphere as in this study (advection from the Paris area and the surrounding roads), reactions with peroxy- and hydroperoxy radicals may be as important as R1-R2 for NO and NO$_2$ chemistry, since peroxy radicals are abundant in the urban area of Paris (Michoud et al., 2012).

$$RO_2 + NO \rightarrow RO + NO_2 \tag{SR3}$$

$$HO_2 + NO \rightarrow OH + NO_2 \tag{SR4}$$

Considering only the (S1) and (S2) reactions, the production and destruction term for O$_3$ is given by:

$$Q = k_r\ [NO]\ [O_3] - J_{NO2}\ [NO_2] \tag{S5}$$

If Q > 0, O$_3$ and NO are consumed and NO$_2$ is formed. If Q < 0 instead, the reaction (S2) dominates and O$_3$ and NO are produced while NO$_2$ is consumed. If Q = 0, the net production of NO$_x$ or O$_3$ is zero and the reactions S1-S2 equilibrate each other. This equilibrium is defined by the Photo-Stationary State ratio (Trebs et al., 2012)) :

$$PSS = k_r\ [NO][O_3]\ /\ J_{NO2}[NO_2] \tag{S6}$$

PSS is unity when Q is zero. If S3-S4 reactions occur, PSS ratio may deviate from unity during night time ($J_{NO2} = 0$), or when S3 and S4 reactions occur, or if the air mass is not at equilibrium with surface fluxes. The production/destruction term Q and the PSS were estimated for the measurement height.

2 Transport and chemical time scales

Transport and chemical time scales τ_{trans} and τ_{chem} were calculated as in (Stella et al., 2012):

$$\tau_{trans} = R_a(z) \times (z_m - z_0) + R_b \times (z_0 - z_{0'}) \approx R_a(z) \times (z_m - z_0) \tag{S7}$$

$$R_a(z) = \frac{u(z)}{u_*^2} - \frac{\Psi_H\left(\frac{z}{L}\right) - \Psi_M\left(\frac{z}{L}\right)}{ku_*} \tag{S8}$$

$$R_b = (B_{St}u_*)^{-1} \tag{S9}$$

Where R_a and R_b are the aerodynamic and quasi-laminar boundary layer resistances, Ψ_H and Ψ_M the integrated correction stability functions for heat and momentum, B_{St} the Stanton number for the gas considered, and z_0 and

z_0, the roughness height for momentum and scalar, respectively. The chemical time scale of the NO-NO$_2$-O$_3$ triad is given by Lenschow (1982):

$$\tau_{chem} = 2[J_{NO2}^2 + k_r^2 \,([O_3] - [NO])^2 \; + 2 \; J_{NO2} \, k_r([O_3] + [NO] + 2[NO_2])]^{-0.5} \tag{S10}$$

3 Evaluating the flux difference between ground and the reference height

When chemical timescale is shorter than transport timescale, chemical reactions affect concentrations and fluxes, resulting in flux divergence. This causes the flux at the measurement point to be different from the surface flux. The flux difference can be evaluated with a method developed by Duyzer et al. (1995) based on the early developments of Lenschow (1982) and Lenschow and Delany (1987). This method assumes a logarithmic profile of the flux divergence and depends on measured mixing ratios, stability function and friction velocity:

$$(\partial F/\partial z)_z = a \ln z + b \tag{S11}$$

$$a_{NO_2} = -a_{NO} = -a_{O_3} = - \, \Phi_H/ku_* \left[k_r \left(\overline{[NO]} F_{O_3,z_{ref}} + \overline{[O_3]} F_{NO,z_{ref}} \right) - j_{NO_2} F_{NO_2,z_{ref}} \right] \tag{S12}$$

Here $\overline{[NO]}$ and $\overline{[O_3]}$ are mixing ratios which should ideally refer to the geometric mean height of the profile measurements but was taken from the measurement height in our study, z_{ref} is the measurement height and Φ_H is the stability correction function for heat estimated at z$_{ref}$ (Dyer and Hicks, 1970). Coefficient b of Eq. (S11) can be computed as $b = -a \ln(z_2)$ where z_2 is the height above which the flux divergence is zero. Duyzer et al. (1995) showed with numerical simulations that the NO$_x$ flux divergence could be approximated by Eq. (S11) below a height of 4m, while it was negligible above. We refer to 4 m as the reference height z_2 at which we assume the flux divergence to be zero. Equation (S11) can be integrated from measurement height to any height, for each compound giving:

$$F(z_{z0}) = F(z_{ref}) + \, a\big(1 + \ln(z_2)\big)\big(z_{ref} - z_0\big) - a\big[z_{ref}\ln(z_{ref}) - z_0\ln(z_0)\big] \tag{S13}$$

4 Flux and concentration footprint

The flux and concentration footprint was roughly estimated for each of the major roads around the site. Each road was geo-localised and assumed 10 m width. The FIDES model was computed with field roughness (z_0), friction velocity (u_*) and Obukhov length (L).


2
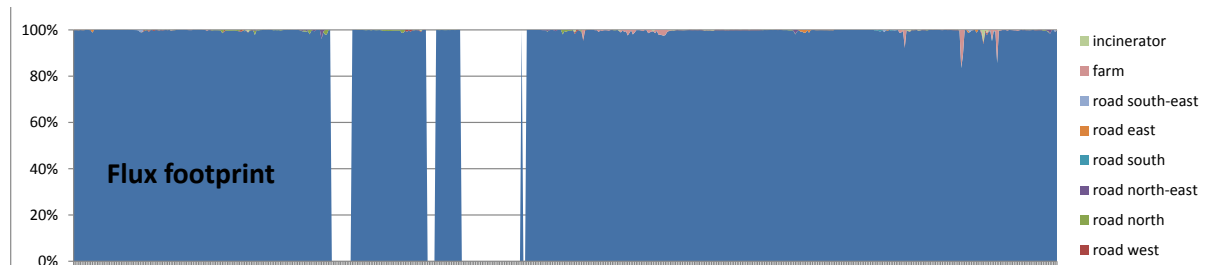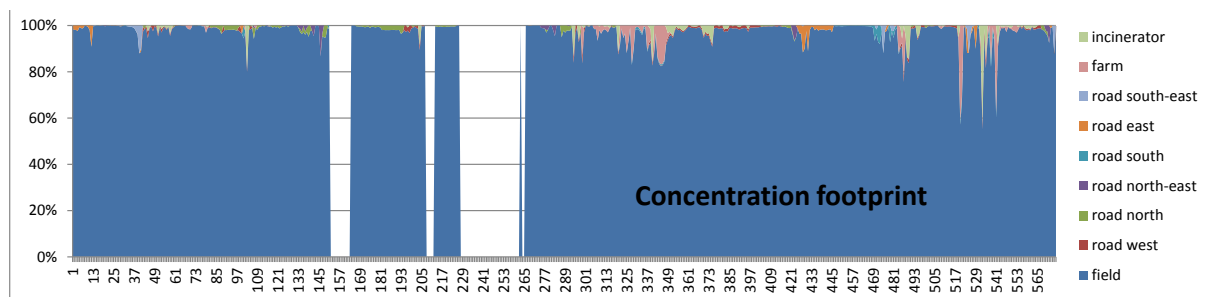
Figure S1. Flux and concentration footprints of the field and surrounding roads calculated with the FIDES model.

60

5 Wind roses and histograms of NO, NO$_2$ and O$_3$ concentration at the site
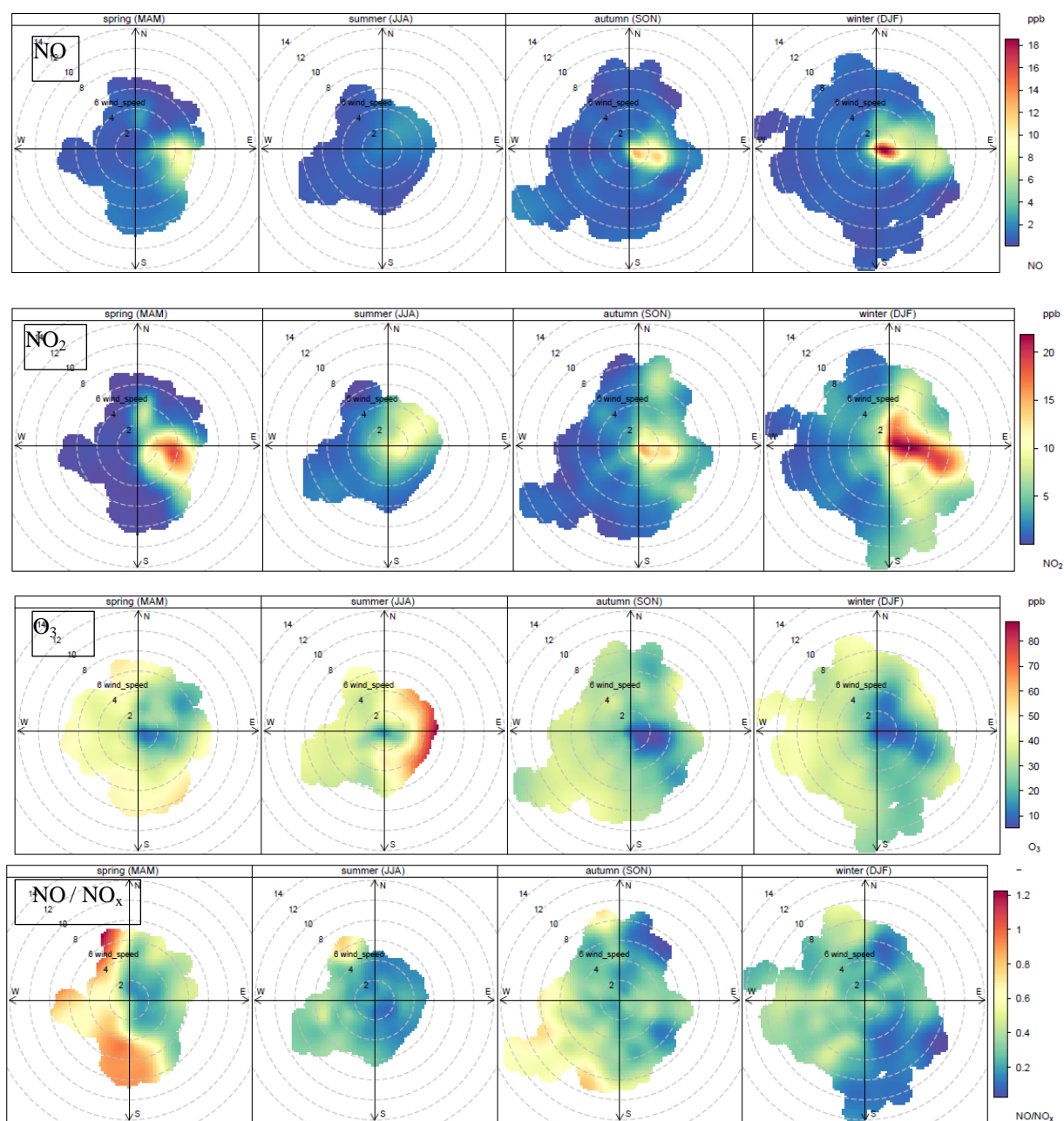

Figure S2. Angular distribution (wind roses) of wind direction, wind speed, NO, O$_3$ and NO$_2$ mixing ratios over the whole experimental period separated by seasons measured at the Grignon field site from 07/08/2012 to 13/03/2013.
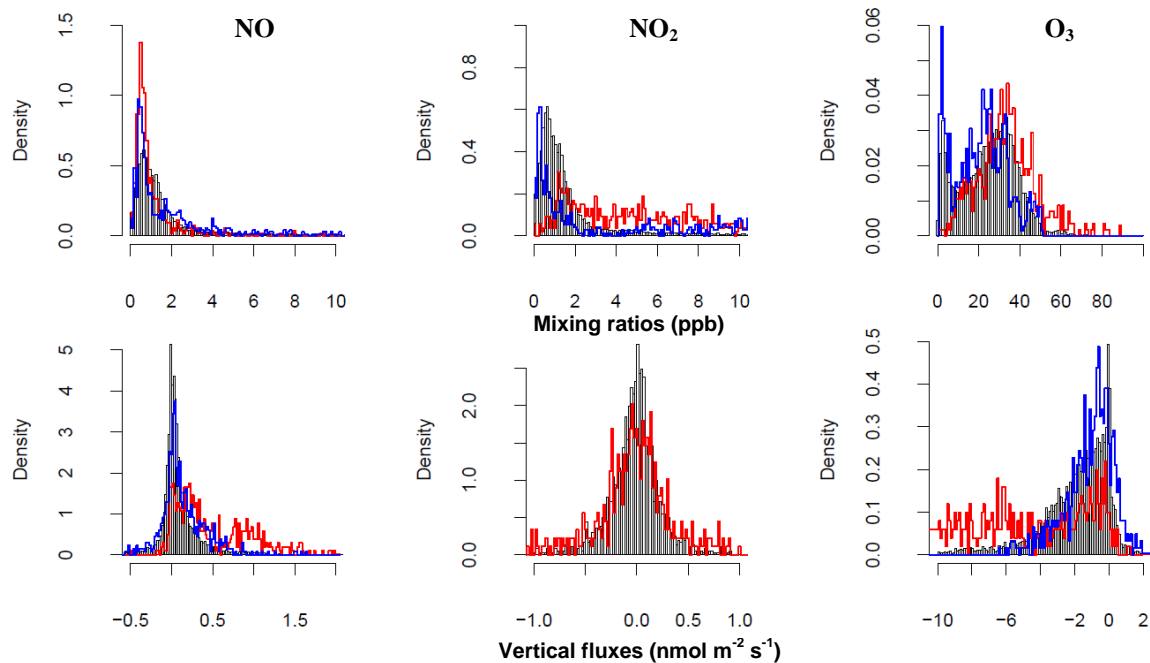
Figure S3. Histograms of (a) O_3, NO and NO_2 mixing ratios and (b) fluxes (black), following organic spreading (red) and mineral fertilisation (blue) measured at the Grignon field site. In y-axes are shown the density which is the frequency divided by the number of elements.

6. Link between residual ozone deposition flux and NO fluxes

In order to evaluate whether the increase of ozone deposition following organic fertilisation may be due to reaction with NO in the ground layer or above we have plotted the difference between the measured and the modelled ozone flux, using Stella et al. (2011), against the measured NO flux and NO concentration from 18 to 20 august 2016, which is the period after slurry injection and before the first rain, and from 24 to 27 august, after the first rain event (Figure S4). Figure S4 shows that part of the additional in O_3 deposition following the first rain event after slurry injection is correlated with the soil NO flux and also that those two fluxes are in a 1:5 proportion. So only a fraction of the additional O_3 deposition could be explained by NO emissions.
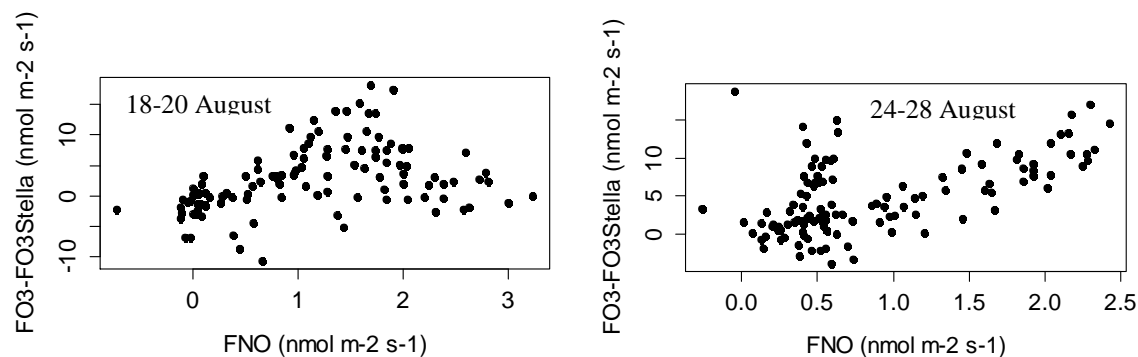
Figure S4. Residual ozone flux as a function of NO flux at the ground during two periods following organic fertilisation: 18-20 August which following slurry injection and 24-28 following the first rain event.

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130