Measurement report: Sources, sinks and lifetime of NO$_X$ in a sub-urban temperate forest at night

Simone T. Andersen[1], Max R. McGillen[2], Chaoyang Xue[2], Tobias Seubert[1], Patrick Dewald[1], Gunther N. T. E. Türk[1], Jan Schuladen[1], Cyrielle Denjean[3], Jean-Claude Etienne[3], Olivier Garrouste[3], Marina Jamar[4], Sergio Harb[5], Manuela Cirtog[5], Vincent Michoud[6], Mathieu Cazaunau[5], Antonin Bergé[5], Christopher Cantrell[5], Sebastien Dusanter[4], Bénédicte Picquet-Varrault[5], Alexandre Kukui[7], Abdelwahid Mellouki[2,8], Lucy J. Carpenter[9], Jos Lelieveld[1], John N. Crowley[1]

[1]Atmospheric Chemistry Department, Max-Planck-Institute for Chemistry, 55128-Mainz, Germany

[2]Institut de Combustion, Aérothermique, Réactivité Environnement (ICARE), CNRS, 1C Avenue de la Recherche Scientifique, CEDEX 2, 45071 Orléans, France

[3]CNRM, Universite de Toulouse, Meteo-France, CNRS, Toulouse, France

[4]IMT Nord Europe, Institut Mines-Télécom, Université de Lille, Center for Energy and Environment, 59000 Lille, France

[5]Univ Paris Est Creteil and Université de Paris Cité, CNRS, LISA, F-94010 Créteil, France

[6]Université Paris Cité and Univ Paris Est Creteil, CNRS, LISA, F-75013 Paris, France

[7]Laboratoire de Physique et Chimie de l'Environnement et de l'Espace (LPC2E), CNRS Orléans, France

[8]University Mohammed VI Polytechnic (UM6P), Lot 660, Hay Moulay Rachid Ben Guerir, 43150, Morocco

[9]Wolfson Atmospheric Chemistry Laboratory, Department of Chemistry, University of York, York, UK

Correspondence to: Simone T. Andersen (simone.andersen@mpic.de) and John N. Crowley (john.crowley@mpic.de)

1 Abstract

Through observations of NO, NO_2, NO_Y and O_3 in the Rambouillet forest near Paris, France, (as part of the ACROSS campaign, 2022) we have gained insight into nighttime processes controlling NO_X in an anthropogenically impacted forest environment. O_3 mixing ratios displayed a strong diel profile at the site, which was driven by a variable but generally rapid deposition to soil and foliar surfaces. The O_3 diel profile was strongly influenced by relative humidity, which impacted the surface resistance to uptake, and temperature inversion, which influenced the rate of entrainment of O_3 from above the canopy. Only when the O_3 mixing ratio was sufficiently low (and thus the NO lifetime sufficiently long), were sustained NO peaks observed above the instrumental detection limit, enabling derivation of average NO emission rates from the soil of ~1.4 ppbv h^{-1}. Observations of the lack of increase in NO_2 at night, despite a significant production rate from the reaction of NO with O_3, enabled an effective lifetime of NO_2 of ~0.5-3 h to be derived. As the loss of NO_2 was not compensated by the formation of gas- or particle-phase reactive nitrogen species it was presumably driven by deposition to soil and foliar surfaces, or any products formed were themselves short-lived with respect to deposition. By comparison, the daytime lifetime of NO_2 with respect to loss by reaction with OH is about 1 day. We conclude that the nighttime deposition of NO_2 is a major sink of boundary layer NO_X in this temperate forest environment.

2 Introduction

Nitrogen oxides (NO_X = NO + NO_2) are pollutant trace gases, which play a key role in the atmosphere by producing or destroying tropospheric ozone (O_3), which can cause respiratory illness (Ciencewicki and Jaspers, 2007) and damage to plants (Emberson et al., 2018). Photolysis of nitrogen dioxide (NO_2) (R1) is the primary source of tropospheric ozone (O_3), and the nitric oxide (NO) product is oxidized back to NO_2 either by O_3 (R2) or by organic peroxy radicals (RO_2, under formation of alkoxy radicals (RO)) or hydroperoxyl radicals (HO_2) (R3, R4) (Lightfoot et al., 1992). The latter results in formation of the hydroxyl radical (OH) radical, and R3 and R4 thus represent routes to recycle the most important atmospheric radical initiator of oxidation (Hens et al., 2014). It is, therefore, essential to understand the sources and sinks of NO_X in the atmosphere.

$$NO_2 + h\nu\ (+O_2) \rightarrow NO + O_3 \tag{R1}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{R2}$$

$$NO + RO_2 \rightarrow NO_2 + RO \tag{R3}$$

$$NO + HO_2 \rightarrow NO_2 + OH \tag{R4}$$

The dominant global sources of NO_X are anthropogenic in the form of combustion of fossil fuels and to a lesser degree biomass burning and agricultural soils. The natural sources, which include lightning (Schumann and Huntrieser, 2007), wildfires (Val Martin et al., 2008), and unperturbed soil emissions from microbial activities (Davidson and Kingerlee, 1997), are important in regions remote from anthropogenic sources. NO_2 and NO both react with peroxy radicals in the atmosphere

66 to produce organic nitrates (R5-R6), including peroxy nitrates (RO_2NO_2) and alkyl nitrates
67 ($RONO_2$), which are important precursors for the formation of secondary organic aerosols (SOA)
68 (Hallquist et al., 2009; Kanakidou et al., 2005; Kiendler-Scharr et al., 2016). NO_2 also reacts with
69 OH radicals, O_3 and nitrate radicals (NO_3) to form nitric acid (HNO_3) (R7), NO_3 radicals (R8), and
70 dinitrogen pentoxide (N_2O_5) (R9), respectively. N_2O_5 is in thermal equilibrium with NO_2 and NO_3
71 and can interact with aqueous aerosol or moist surfaces to form HNO_3 (R10) (Kane et al., 2001)
72 or nitryl chloride ($ClNO_2$) (Phillips et al., 2013; Phillips et al., 2012). Organic nitrates, SOA, and
73 HNO_3 are all removed from the boundary layer through dry and wet deposition which thereby
74 removes NO_X from the atmosphere.

75 $NO_2 + RO_2 + M \rightarrow RO_2NO_2 + M$ (R5)

76 $NO + RO_2 + M \rightarrow RONO_2 + M$ (R6)

77 $NO_2 + OH + M \rightarrow HNO_3 + M$ (R7)

78 $NO_2 + O_3 \rightarrow NO_3 + O_2$ (R8)

79 $NO_2 + NO_3 + M \rightleftharpoons N_2O_5 + M$ (R9)

80 $N_2O_5 + H_2O$ (aq) $\rightarrow 2\ HNO_3$ (aq) (R10)

81 In the planetary boundary layer, NO_2 is also lost through dry deposition to surfaces such as soil
82 and leaves. Deposition takes places both at nighttime and daytime, but is expected to be more
83 efficient during daytime due to increased mixing through turbulence. When NO_2 deposits onto
84 humid surfaces, it can lead to the production of nitrous acid (HONO), which can be released to the
85 atmosphere (Meusel et al., 2016; Elshorbany et al., 2012). NO_2 uptake on leaves takes place
86 through stomatal and non-stomatal processes, which have been reported to depend on multiple
87 factors such as stomata aperture and relative humidity. Stomatal uptake primarily occurs at
88 daytime when the stomata are open, leading to increased NO_2 loss compared to nighttime, when
89 the stomata are not fully open (Delaria et al., 2020; Delaria et al., 2018; Chaparro-Suarez et al.,
90 2011). Non-stomatal uptake occurs through the cuticles, though the importance of cuticular uptake
91 has been reported to be small compared to the stomatal uptake (Delaria and Cohen, 2020; Delaria
92 et al., 2020). NO_2 uptake to leaves is reported to be enhanced in the presence of water films, which
93 may exist when the relative humidity is >70% (Thoene et al., 1996; Weber and Rennenberg, 1996;
94 Burkhardt and Eiden, 1994). There is, however, no consensus on this process, as other studies have
95 not observed this effect (Gessler et al., 2000). Most recent work shows that the interactions with
96 foliar surfaces is uni-directional, i.e. emissions are negligible (Delaria et al., 2020).

97 At nighttime, NO_2 photolysis ceases and as a consequence, in the absence of combustion sources,
98 the main sources of NO are emissions from soils (Jaeglé et al., 2005). Since NO is oxidised
99 efficiently by O_3 at night, its concentration will be highest at the surface and will decrease with
100 altitude. The vertical profile of O_3 is the opposite owing to its physical loss due to deposition near
101 the surface and through chemical reaction with NO and/or alkenes combined with entrainment
102 from the nocturnal residual layer. As NO_2 is produced from the reaction between NO and O_3, its

103 vertical gradient is expected to be weaker than those of NO and O_3 (Geyer and Stutz, 2004; Stutz
104 et al., 2004).

105 In this study we use measurements from the ACROSS (Atmospheric ChemistRy Of the Suburban
106 foreSt) campaign to investigate the nighttime sources and sinks of NO_X in a temperate forest. O_3
107 measurements are used to explain the observed NO features and measurements of NO_2 and total
108 gas-phase nitrogen species (NO_Y) and particulate nitrate are used to investigate the lifetime and
109 fate of NO_X in the forest environment.

110

3   The ACROSS Campaign

112 The ACROSS campaign (13th of June 2022 to 25th of July 2022) was conducted in multiple
113 locations in and around Paris, France (Cantrell and Michoud, 2022). Here we present
114 measurements from the Rambouillet forest supersite located approximately 50 km southwest of
115 Paris (48.687, 1.704). The forest consists of approximately 70% oak, 20% pine, and small
116 contributions from beech and chestnut. The top of the forest canopy around the supersite was
117 around 20-25 m. Several instrumented containers were placed in a clearing (~697 m^2) together
118 with a 41 m measurement tower. Most of the instruments used in this study were located in two
119 different containers (MPIC and Orléans). The sampling inlets of the two containers were
120 approximately 17 m apart and the tower was approximately 9 m from the MPIC container and 16
121 m from the Orléans container. The soil measurements were carried out at the bottom of the tower,
122 approximately 13 m from the MPIC container and approximately 17 m from the Orleans container.
123 All the instruments used in this study are described briefly below.

124

3.1   Measurements
3.1.1   Ground
127 NO_2 was measured using two different cavity ringdown spectroscopy (CRDS) instruments with
128 co-located inlets sampling from a high-volume-flow stainless steel tube ($10\,m^3\,min^{-1}$; 15 cm
129 diameter, 0.2 s residence time) taking air from a height of 5.4 m above ground. One of the
130 instruments (5CH-CRDS) consists of 3 cavities operated at 408 nm to measure NO_2 and, via their
131 thermal dissociation to NO_2, total peroxy nitrates ($\sum$PNs, 448 K) and total alkyl nitrates ($\sum$ANs,
132 648 K). Two additional cavities, operated at 662 nm, measured NO_3 and (via thermal dissociation
133 to NO_3, 373 K) N_2O_5 (Sobanski et al., 2016). During this campaign, the NO_2 cavity had a limit of
134 detection (LOD) of 9.7 pptv for 1 min averaging (3σ). The second instrument (k-NO3) primarily
135 measures the NO_3 reactivity, but also has a cavity operated at 405 nm for the measurement of NO_2
136 (Liebmann et al., 2018).

137 Another CRDS instrument was used to measure NO_X, NO_Y, and particulate nitrate (pNO_3) from
138 co-located inlets near the high-volume-flow stainless steel tube. NO_X was measured by adding O_3
139 to the ambient sample, thereby oxidizing NO to NO_2, which was measured with CRDS at 405 nm
140 (Friedrich et al., 2020). A judicious choice of O_3 and reaction time ensured that minimal (>1%) of
141 NO_2 was oxidized to NO_3. At times with low (or zero) NO, NO_X concentrations were in close

142 agreement with both NO_2 measurements. NO_Y was measured by passing ambient air through a
143 quartz inlet at ~ 900 K which quantitatively converts reactive nitrogen trace-gases to NO or NO_2.
144 Exceptions are N_2O, HCN and NH_3, which are not detected. In this location, NO_Y is expected to
145 consist mainly of NO_X + NO_3 + N_2O_5 + HNO_3 + PNs + ANs + HONO + $ClNO_2$ + particulate
146 nitrates (pNO_3).

147 Particulate nitrates (both organic and inorganic) were separately measured (as NO_Y) after denuding
148 gas-phase reactive nitrogen species (Friedrich et al., 2020). To achieve this, problems involving
149 the ineffective trapping of gas-phase NO_X by the denuder was eliminated, as will be described in
150 a forthcoming technical paper.

151 O_3 was measured from the high-volume-flow stainless-steel tube with a commercial instrument
152 (2B Technologies model 205) using UV absorption at 254 nm. The LOD is 2 ppbv for 10 s
153 averaging time.

154 A spectral radiometer (metcon Gmbh) was installed near the co-located inlets on top of the MPIC
155 container to measure actinic fluxes, which were used to calculate photolysis frequencies as
156 described elsewhere (Meusel et al., 2016).

157 NO was measured from the Orléans container using a commercial chemiluminescence instrument
158 (Ecophysics CLD 780 TR, henceforth CLD) with an LOD of 10 pptv for 1 min averaging time.
159 The sampling height for NO measurements was about 0.6 and 3.2 m above the container top and
160 the ground surface, respectively. The NO measurements required correction due to a change in the
161 CLD sensitivity during the campaign caused by an interruption in the instrument's oxygen supply.
162 The corrections and the corrective procedure are described in the SI.

163 HONO was measured by a commercial long-path absorption photometer (LOPAP-03, QUMA
164 GmbH, Germany) with a sampling height of 2.0 m above the ground level. Details about the
165 LOPAP instrument can be found elsewhere (Heland et al., 2001; Kleffmann et al., 2006). During
166 the campaign, the LOPAP was calibrated by diluted nitrite when changing any supporting
167 solutions. Zero calibration by measuring synthetic air was conducted 2-3 times per day. The
168 detection limit is < 5 pptv.

169 The sum of peroxy radicals, XO_2=HO_2+RO_2, was measured by their conversion to H_2SO_4 in
170 presence of NO and SO_2 and detection of the generated H_2SO_4 using NO_3^- CIMS (Kukui et al.,
171 2008). The calibration coefficient is determined using N_2O actinometry and OH/RO_2 generation
172 in a turbulent flow reactor by photolysis of N_2O or H_2O at 184.9 nm. The calibration of HO_2,
173 CH_3O_2 and other RO_2 is performed by adding into the calibration reactor CO, CH_4 (or other RO_2
174 precursors) converting OH to RO_2. The overall estimated calibration accuracy (2σ) for XO_2 is
175 about 30%, although the uncertainty of the XO_2 measurements is typically higher due to
176 uncertainty in ambient air XO_2 composition. The lower limit of detection for XO_2 radicals at S/N=3
177 and a 4 minute integration time is 2×10^6 molecule cm^{-3}.

178 Time series of the most relevant measurements can be found in Figure S1-2. Due to missing total
179 NO_X and NO_Y measurements prior to June 25th and NO after July 18th, the data analysis is focused
180 on the time period in between these dates.

181

3.1.2 Tower

Measurements at 41 m were conducted with instruments located on the tower as well as through a manifold with an inlet at the top of the tower. The manifold was built from glass tubing (4.9 cm inner diameter, Borodrain) with a residence time in the manifold of 2.1 s. NO_2 was measured using a cavity attenuated phase shift (CAPS) instrument on the tower with an LOD of 40 pptv, which was zeroed every 1-2 hours. NO and O_3 were both measured from the manifold using a chemiluminescence instrument with a LOD of 30 pptv and a HORIBA (APOA370) with an LOD of 2.5 ppbv, respectively. The NO measurements were corrected for losses due to the reaction of NO with O_3 in the manifold and the sampling line (total 5.5 s), with corrections ranging from 1-28%. Time series of all three measurements are plotted in Figure S3.

192

3.1.3 Meteorology and Soil

Ambient temperature was measured at four different heights on the tower; 5 m, 13 m, 21 m, and 41 m using temperature sensors from Atexis (PT1000) and Thermoest (PT100). Relative humidity was measured at 5 m using a Vaisala humidity sensor (HMP45A). Soil temperature and moisture were measured at 5 cm, 10 cm, and 30 cm below the surface using probes from Thermoest (PT100) and Delta T (Thetaprobe ML2X), respectively. Wind speed and direction were measured at 41 m using a wind monitor from Young Company. Time series of all the meteorological and soil measurements are shown in Figure S4-5.

201

3.2 HYSPLIT

To identify different air masses, 48-hour back trajectories were simulated every hour at a terminating height of 40 m using the Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT, version 4, 2019) (Draxler and Rolph, 2011). The back-trajectories were modelled using meteorological data from the Global Data Assimilation System (GDAS) at a resolution of 1 degree. This led to the separation of the data into two periods, 25th of June to 2nd of July and 3rd of July to 18th of July, which are plotted in Figure 1. The first phase is dominated by clean air from over the Atlantic Ocean (henceforth called "Atlantic"). Back trajectories indicated that the vast majority of air masses were transported within the boundary layer prior to reaching the site and thus may have reasonably fresh "marine influence". The second phase is dominated by air that has passed over urban locations including Paris, Brussels and the Ruhr area within the last 48 hours (henceforth called "Continental").

214

4 Results and Discussion

Two 24-hour periods of temperature (at 4 different heights), NO, O_3, relative humidity (RH), NO_2, and NO_2 photolysis rate constant (JNO_2) are plotted in Figure 2. The left panels show 24 hours with Atlantic air and the right panels 24 hours with continental air. Immediately apparent in these datasets (and in Fig S1) is the large diel cycle in O_3 mixing ratios, with net daytime production

220 resulting in mid-afternoon mixing ratios between ~30 and 90 ppbv. In contrast, very low O_3 mixing
221 ratios (often approaching zero) were observed at nighttime.

222 In the lowermost panels (JNO_2 measurements), the nighttime is shown in dark grey and the two
223 light grey areas show the time before sunset (about 5 hours) and after sunrise (about 4.5 hours)
224 when very little direct sunlight reaches the ground of the site due to shading by the trees. This
225 leaves about 6.5 hours centred around midday when direct sunlight reaches the ground. The
226 shading results in radiative cooling of the ground in the late afternoon and associated temperature
227 inversions begin to form prior to sunset as can be observed in the right panels of Figure 2 and in
228 more detail in Figure S6. The temperature inversions begin approximately at the same time as the
229 ground temperature at 5 cm below the surface starts to decrease (see Figure S6). These conditions
230 of insolation were relatively consistent throughout the campaign.

231 Clear temperature inversions were observed for both nights shown in Figure 2, the beginning and
232 end of which are indicated by dashed lines. Vertical mixing can be reduced significantly during a
233 temperature inversion, which is apparent from the O_3 and RH measurements in the right-hand
234 panel. In both examples, O_3 decreases at the ground level (5.4 m) at the beginning of the
235 temperature inversion and increases as the inversion breaks down in the morning. This behaviour
236 is understood in terms of O_3 loss to soil surfaces and through stomatal and non-stomatal uptake on
237 leaves (Zhou et al., 2017; Rannik et al., 2012; Altimir et al., 2006; Ganzeveld and Lelieveld, 1995)
238 as well as through chemical reactions with e.g. NO, NO_2 and unsaturated (biogenic) organics
239 (Kurpius and Goldstein, 2003). Reduced vertical mixing means that during the inversion, O_3 is
240 only slowly replenished by downward mixing of air masses above the canopy where higher O_3
241 levels are observed. In contrast, the RH behaves in the opposite sense as the air above the inversion
242 is drier than close to the ground, where evapotranspiration contributes to enhanced water vapour
243 concentrations.

244 If the only source of NO was the photolysis of NO_2, NO mixing ratios would be expected to follow
245 the NO_2 photolysis rate during the day and tend to zero at night as NO is oxidized on a time scale
246 of minutes (for O_3 > 10 ppb) to NO_2 by O_3. This was not always the case during ACROSS. A
247 pronounced NO peak (up to ~2 ppbv) was observed at ground level between 00:00 and 06:00 UTC
248 (02:00 and 08:00 local time) during the phase dominated by Atlantic air, shown in Figure 2, which
249 is absent in the phase dominated by continental air. The peak occurs prior to sunrise and is only
250 observed by the ground-level measurements suggesting a non-photolytic source of NO close to the
251 ground, which is discussed further below. Very low (0-5 ppbv) O_3 mixing ratios coincide with the
252 sustained nighttime NO peak observed, which is never reached in the example from the continental
253 phase, although in both cases clear temperature inversions were seen. Additional examples of
254 sustained NO peaks (i.e. lasting several hours at level between 1 and 2 ppbv) at night during the
255 first phase are shown in Figure S7. Examples of additional nights with temperature inversions
256 during phase 2, where NO mixing ratios remained close to zero, are shown in Figure S8.

257

4.1 Nighttime Ozone Loss

For each night between June 17th and July 22nd the net O_3 loss rate constant, $k_L(O_3)$ was derived by fitting exponential expressions to the data for periods of 4.5 to 8 hours. $k_L(O_3)$ was highly variable, with values between 1.8×10^{-5} s^{-1} and 3.0×10^{-4} s^{-1}, depending on the strength of the temperature inversion and the relative humidity (see discussion below). These values of $k_L(O_3)$ correspond to lifetimes of 1-15 hours for O_3 at nighttime. Chemical losses of O_3 occur through reactions with NO, NO_2, and unsaturated BVOCs (Zhou et al., 2017). Rate coefficients of reactions of O_3 with NO (1.9×10^{-14} cm^3 molecule^{-1} s^{-1} at 298 K), NO_2 (3.5×10^{-17} cm^3 molecule^{-1} s^{-1} at 298 K), limonene (a reactive terpene, 2.2×10^{-16} cm^3 molecule^{-1} s^{-1} at 298 K), β-caryophyllene (sesquiterpene, 1.2×10^{-14} cm^3 molecule^{-1} s^{-1} at 298 K) are low such that mixing ratios in excess of 1 ppbv for NO and β-caryophyllene would be required to explain the O_3 loss rate constant (IUPAC, 2024). Required mixing ratios of terpenes or NO_2 would be even larger (60-300 ppbv). As such high mixing ratios of NO and NO_2 were not observed continuously and such levels of BVOC are unlikely, we assume that chemical losses of O_3 are insignificant compared to deposition as previously observed (Zhou et al., 2017). Ignoring entrainment from other heights, we can then equate $k_L(O_3)$ to ($2V_d/h$), where V_d is the deposition velocity and h is the boundary layer height; the factor 2 is used to account for a positive vertical gradient (Shepson et al., 1992). Using a boundary layer height of 20 m (arbitrarily set equal to the top of the canopy) gives net deposition velocities varying between 0.018 and 0.3 cm s^{-1}. These values for V_d are in broad agreement with other studies in temperate forests, where deposition velocities for O_3 at nighttime have been reported to be around 0.07-0.3 cm s^{-1} (Padro, 1996, 1993; Finkelstein et al., 2000; Wu et al., 2016).

In Figure 3 the O_3 production rate (JNO_2 × [NO_2]), RH, temperature at 4 different heights and O_3 mixing ratio have been plotted for two nights with high average RH to illustrate the impact of temperature inversions on the net O_3 loss-rate constants. The production rate of O_3 is used to identify periods in which production is negligible. In the left panel a night without a temperature inversion is plotted, where the average RH for the period used to fit the exponential decay is 93 ± 3 %. These conditions resulted in a net O_3 loss-rate constant of 6.0×10^{-5} s^{-1}. In contrast, the night depicted in the right panel has the same average RH (92 ± 3 %) and a very clear temperature inversion, which gives a net O_3 loss-rate constant of 3.0×10^{-4} s^{-1}. This gives a factor of 5 between these two net O_3 loss-rate constants depending on whether a temperature inversion is observed or not. This can be understood in terms of the O_3 being replenished from above when there is no (or a weak) inversion, which is not the case when there is an inversion. Bearing this in mind, the use of $k_L(O_3)$ (a *net* O_3 loss constant) must result in a lower limit to V_d unless strong temperature inversions (preventing O_3 entrainment from above) are present. The O_3 loss rate will also be enhanced under conditions of strong inversion if trace-gases that are reacive towards O_3 are released into a very shallow boundary layer. However, as indicated above, chemical losses are not expected to compete with physical losses.

To investigate the impact of RH on the net O_3 loss-rate constants, two nights with temperature inversions are plotted in Figure S9; one with high RH (92 ± 3 %) and one with a lower RH (63 ± 6 %). Here we see a large decrease in $k_L(O_3)$ from 3.0×10^{-4} s^{-1} to 4.5×10^{-5} s^{-1}, when going from high to lower RH. The individually determined O_3 loss-rate constants are plotted as a function of RH in Figure 4 and coloured depending on whether a temperature inversion is observed or not

300 during the time period which was used for the exponential decay fit. A clear increase in O_3 loss-
301 rate constants can be observed when RH increases above 70-80% when a temperature inversion
302 was observed. A small increase at RH higher than 70-80% was also observed when temperature
303 inversions were absent. The observed dependence of $k_L(O_3)$ on relative humidity is consistent with
304 previous studies in forested regions, which have reported an increase in O_3 loss above 60-70% RH
305 (Altimir et al., 2006; Rannik et al., 2012; Zhou et al., 2017). Altimir et al. (2006) suggested an
306 enhancement factor which is humidity dependent above 70% RH; 1 at 70% RH, 2 at 85% RH and
307 a sharp increase to over 5 when moving towards 100% RH. In a boreal forest these observations
308 have been explained by the formation of a "wet skin" on leaves which enhances surface O_3 losses
309 by modifying (reducing) the surface-resistance to uptake (Zhou et al., 2017). This is in broad
310 agreement with our observations during nights with a temperature inversion (see Figure 4), and
311 the discrepancies between the studies could be explained e.g. by different tree types, the height of
312 the boundary layer, strength of the inversion and temperature.

313 The faster net rate of O_3 loss on nights with high relative humidity and well-defined temperature
314 inversions explain the differences observed in the O_3 mixing ratios at night during the Atlantic and
315 continental phases. The average nighttime (20:00-04:00 UTC) RH for the Atlantic phase was 87.4
316 $\pm$ 7.6 (1σ) % compared to 68.4 $\pm$ 12.7 (1σ) % for the continental phase, indicating that on nights
317 with temperature inversions higher loss-rate constants would be expected for the Atlantic phase.
318 The high RH combined with the significantly lower average peak O_3 mixing ratio in the Atlantic
319 phase (34.5 $\pm$ 6.0 (1σ) ppbv between 14:00-15:00 UTC) compared to the continental phase (52.7
320 $\pm$ 13.6 (1σ) ppbv between 14:00-15:00 UTC) explains why on nights with temperature inversions
321 during the Atlantic phase the O_3 was essentially completely depleted as shown in Figure 2 and S7.

322

323 **4.2 Nitrogen Oxide Soil Emissions**
324 Figure 2 (left panel) and S7 show nighttime periods in which NO was observed when O_3 was
325 depleted during the Atlantic phase. The several hours duration of the period when NO was above
326 the LOD excludes very local combustion as the source, leaving soil emissions resulting from
327 microbial activity (Davidson and Kingerlee, 1997) as the most likely source of NO. At 293 K and
328 2 ppbv of O_3, the lifetime of NO towards reaction with O_3 is around 20 minutes. It is therefore
329 reasonable to assume that NO is close to steady-state when there is 2 ppbv or more of O_3 available.
330 The NO emission rate (E_{NO}) can therefore be equated to the loss rate of NO as described in equation
331 (1) assuming all peroxy radicals (XO_2) react with the same rate coefficient as HO_2:

332 $$E_{NO} = k_{NO+O3}[NO][O_3] + k_{NO+HO2}[XO_2][NO] \tag{1}$$

333 where k_{NO+O3} and k_{NO+HO2} are the temperature-dependent rate constants for the reaction between
334 NO and O_3 and HO_2, respectively, (IUPAC, 2024) and [NO], [O_3] and [XO_2] are the measured
335 concentrations of NO, O_3 and XO_2, respectively. In Figure 5, NO and E_{NO} (when $O_3 > 2$ ppbv) at
336 nighttime ($JNO_2 < 10^{-5}$ s^{-1}) are separated by air masses and plotted against O_3, where the outliers
337 are defined as being outside 1.5 $\times$ interquartile range (IQR). While the nighttime NO mixing ratio
338 increased rapidly when O_3 tended towards 0 ppbv during the Atlantic phase, O_3 was never depleted
339 to less than 5 ppbv during the Continental phase and therefore no sustained periods of enhanced

NO were observed at nighttime. In contrast, no significant trend is found when plotting E_{NO} against O_3 for either of the phases, which shows that the calculated soil emission of NO is not dependent on O_3. This indicates that while the soil is an important but variable source of NO, sustained nighttime NO peaks are only observed above the instrument LOD when O_3 is almost totally depleted so that the lifetime of NO is long enough to allow its concentration to build-up sufficiently.

Water content and temperature have previously been shown to impact the emission rate of NO from soil (Pilegaard, 2013; Rosenkranz et al., 2006). Rosenkranz et al. (2006) found a positive correlation between soil moisture and NO emission up to 40% water-filled pore space (WFPS) and an optimum between 12.5 and 15 °C soil temperature in a sessile oak forest in Hungary. In Figure 6, NO and E_{NO} are plotted against the soil temperature and moisture at 5 cm below the surface. The measured NO mixing ratios peak towards the highest soil moisture and lowest soil temperature measured during this campaign, however, as with O_3, there is no significant trend in the NO emission rates with soil moisture. At the low (11.5-12.5 °C) and high (19.5-20.5 °C) nighttime soil temperatures very few measurements were made (around 2 hours combined) compared to the rest of the temperature intervals. Across the remaining temperature intervals, no significant trend was observed in the estimated NO emission.

The average NO emission rate derived for the two phases is identical with values of 1.45 ± 1.61 ppbv h^{-1} (1σ, median = 1.27 ppbv h^{-1}) and 1.42 ± 5.68 ppbv h^{-1} (1σ, median = 0.71 ppbv h^{-1}) for the Atlantic and Continental phases, respectively, when using data where $O_3 > 2$ ppbv. The Continental phase show much higher variability resulting from more spikes in the data during that period. When O_3 is completely depleted during the Atlantic phase, the increase in NO per hour results in NO emission rates of 0.3-1.8 ppbv h^{-1}, which is in reasonable agreement with the averages across each of the two phases when there is still O_3 present. By assuming a mixed nocturnal boundary layer (NBL) with a height of 20 m (top of the canopy), the average emission rates can be converted to NO emission fluxes of 16.6 ± 18.5 (1σ) and 16.2 ± 65.0 (1σ) µg N m^{-2} h^{-1}, respectively. These values are within the range of previous measurements in different European forests with similar tree types to those found in the Rambouillet forest (see Table 1). The measurements by Pilegaard et al. (2006) and Rosenkranz et al. (2006) were all performed using the chamber technique, whereas Schindlbacher et al. (2004) measured the emission from soil samples collected in the field and exposed to different temperatures and humidity in the laboratory. The chamber-derived emission rates are all either lower or, within combined uncertainties, equal to the values determined in this study, while emission rates from the soil samples were higher than (or, within combined uncertainties, equal to) the values derived in the present study. Davidson and Kingerlee (1997) modelled the global NO emission inventory from soil depending on the biome (e.g. temperate forest, agriculture, and savanna), and split the temperate forest category into regions affected by nitrogen deposition or not. For temperate forests not affected by nitrogen deposition, those authors estimated a flux of 0.0-0.2 kg N ha^{-1} yr^{-1} (0.0-2.3 µg N m^{-2} h^{-1}), which is in good agreement with the lower measurements by Pilegaard et al. (2006). In contrast, the temperate forests impacted by nitrogen deposition had estimated fluxes of 1.1-5.0 kg N ha^{-1} yr^{-1} (12.6-57.1 µg N m^{-2} h^{-1}), which is in good agreement with our measurements at Rambouillet where nitrogen deposition is enhanced by pollution arriving from Paris and other surrounding urbanized

382 / industrialized areas. While noting that our fluxes are broadly consistent with previous
383 measurements, we recognise that the calculations are based on the assumptions of a well-mixed
384 boundary layer of fixed height arbitrarily set at 20 m and should not be over-interpreted.

385

4.3 Nitrogen Dioxide Losses

387 At nighttime, in the absence of its photolysis, NO_2 may be expected to increase in concentration
388 (via R2) when a constant NO source exists (e.g. from soil, as observed here) and when O_3 is
389 present. For both the Atlantic and the Continental phases an average diel profile between 20.00
390 and 04.00 UTC of NO_2 (black) is plotted in Figure 7. No obvious increase in NO_2 can be observed
391 in the Atlantic phase and an average increase of around 1 ppbv can be observed in the Continental
392 phase. The expected NO_2 resulting from the $NO + O_3$ reaction if there were no loss mechanisms
393 of NO_2 is plotted in red. This is determined using the NO_2 measured at 20.00 UTC and
394 incrementing this value by the NO_2 that would have been produced through NO oxidation by O_3
395 and peroxy radicals in each time step. In both phases, the simple assumption of nighttime NO_2
396 production through $NO + O_3$ and $NO + XO_2$ and no NO_2 loss results in significant generation of
397 NO_2 with an overestimation of 10-12 ppbv of NO_2 at the end of the night compared to the measured
398 NO_2. A loss mechanism of around 1.4 ppbv h^{-1} of NO_2 is therefore necessary to explain the
399 observed (lack of increase in) NO_2.

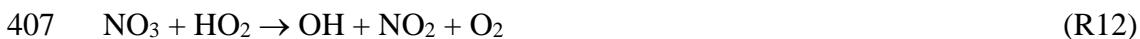
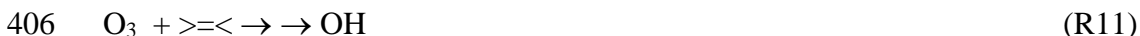
400

4.3.1 Chemical Losses

402 While during the daytime NO_2 is removed in a largely irreversible process through reaction with
403 OH radicals to form HNO_3, this is unlikely to represent a significant sink at nighttime. In the
404 absence of photochemical formation pathways, OH is generated at night in the ozonolysis of
405 olefins and in the reaction of HO_2 with NO_3 and NO.

406 $O_3 + >=< \rightarrow \rightarrow OH$ (R11)

407 $NO_3 + HO_2 \rightarrow OH + NO_2 + O_2$ (R12)

408 $NO + HO_2 \rightarrow OH + NO_2$ (R4)

409 In the forested environment in summer, the emissions of biogenic volatile organic compounds
410 (BVOC) (e.g. olefinic terpenoids) will favour R11 and simultaneously disfavour R12 as NO_3 will
411 be reduced in concentration through its reactions with BVOCs. During the ACROSS campaign
412 ground NO_3 levels were generally below instrument detection limits of 2 pptv and we can
413 reasonably ignore R12. Measurements of OH in forested environments are sparse, though they
414 indicate that nocturnal OH levels are low, with concentrations generally lower than 1×10^5
415 molecule cm^{-3}. Combining the rate coefficient for reaction of OH with NO_2 of $\sim 1 \times 10^{-11}$ cm^3
416 molecule^{-1} s^{-1} (IUPAC, 2024) at ambient pressure and ≈ 300 K with an upper limit (confirmed by
417 measurements) to the OH concentration of 1×10^6 molecule cm^{-3} results in a NO_2 loss constant of
418 1×10^{-5} s^{-1}, or (at the average nighttime $NO_2 = 1650$ pptv) a loss rate of ~ 60 ppt h^{-1}, clearly
419 insufficient to explain the observations.

420   NO_2 is also lost via its reaction with O_3 to form the NO_3 radical (R8). In an upcoming paper, we
421   will show that the majority of NO_3 formed in the forest will react with BVOCs rather than with
422   NO (to re-form NO_2) and, to a good approximation, R8 represents an irreversible loss of NO_2 as
423   the alkyl nitrates will not release nitrogen in the form of NO_2 at nighttime. However, the rate
424   coefficient for this process (3.5×10^{-17} cm^3 molecule^{-1} s^{-1} at 298 K, (IUPAC, 2024)) is very small
425   and with average nighttime O_3 levels reduced by deposition (see above) to 23 ppbv, the lifetime
426   of NO_2 with respect to this reaction is 14 hours and the loss-rate (at the average nighttime NO_2 =
427   1650 pptv) is ~120 pptv h^{-1}, again too slow to contribute significantly to the apparent loss rate of
428   NO_2.

429   The chemical loss of NO_2 via reaction with OH or via formation of NO_3 and its further reactions
430   with BVOC to form alkyl nitrates is expected to result in the conversion of NO_X to NO_Y. As
431   described in section 3.1.1, during the ACROSS campaign we operated a NO_Y instrument to
432   measure NO_Y both in the gas- and particle-phases. Figure 8 displays the average diel profiles of
433   NO_Z (NO_Y-NO_X) and pNO_3 during the Atlantic and Continental phases. For both NO_Z and pNO_3
434   the diel profiles show either a decrease or stable mixing ratio across the period in which losses of
435   10-12 ppbv of NO_2 are required to explain the observations. Clearly, the loss of NO_2 at nighttime
436   is not balanced by the formation of other forms of reactive nitrogen that were long lived enough
437   to be detected. Trace gases such as HNO_3 or alkyl nitrates may be lost via deposition to surfaces,
438   especially at high relative humidity and lifetimes for biogenic alkyl nitrates of a few hours have
439   been reported (Liebmann et al., 2019; Farmer and Cohen, 2008; Browne et al., 2013; Romer
440   Present et al., 2019). However, as shown above, the limiting step in the formation of organic
441   nitrates is the slow reaction of NO_2 with O_3, which will not convert sufficient NO_2 to NO_Z to
442   explain our observations. Formation of organic nitrates that do not require the intermediacy of NO_3
443   (i.e. peroxy nitrates formed from RO_2 + NO_2) would also have been detected by the NO_Y
444   instrument and can thus also be ruled out as major reservoirs of NO_X.

445   NO_2 deposited to humid surfaces can be converted to HONO and released to the atmosphere
446   (Elshorbany et al., 2012; Meusel et al., 2016). A time series of HONO can be found in Figure S2
447   which reveals increases in HONO at nighttime. However, the HONO mixing ratios can account
448   for only a small fraction of the NO_2 loss described above. This may reflect the fact that, if formed
449   at a moist surface, (soluble) HONO is unlikely to desorb quantitatively into the gas-phase. The
450   low HONO mixing ratios measured during the Atlantic phase compared to the Continental phase,
451   could potentially be explained by the difference in soil humidity, however, the factors influencing
452   the formation and release of HONO are complex. The HONO observations will be analysed in
453   detail in a seperate publication from the ACROSS campaign.

454   In the absence of other known gas-phase mechanisms for the removal of NO_2 at night and the fact
455   that very little other reactive nitrogen trace-gases or nitrate particles are formed during the night,
456   we conclude that physical removal of NO_2 (i.e. deposition) is responsible for its lack of build-up
457   at night during ACROSS and that any transformation of NO_2 at the surface does not lead to
458   quantitative release into the gas-phase

459

4.3.2 Physical Losses

NO_2 is known to be lost through dry deposition to surfaces such as soil and leaves, the latter depending on whether the stomata are open (daytime) or not fully open (nighttime) (Delaria et al., 2020; Delaria et al., 2018; Chaparro-Suarez et al., 2011). As for O_3, dry deposition of NO_2 to surfaces can be described by an exponential decay with a first-order decay rate constant, $k_L(NO_2) = (V_d/h)$, where V_d is the deposition velocity and h is the boundary layer height. This expression applies when gradients within the boundary layer are weak, as expected for NO_2 (see above) even though vertical mixing is very slow at night. The net production (or loss) of NO_2 is given by Eq. (2) where the first term on the right-hand side is the NO_2 production rate from the reaction of NO with O_3 or XO_2 (which is identical to the NO soil emission rate) and the second term is the loss rate assuming only depositional losses (see above) and ignoring entrainment of NO_2 from other heights. This will give an upper limit of the NO_2 deposition rate as a small fraction (<10%) of NO_2 is lost through chemical reactions with O_3 and OH (see above).

$$\frac{d[NO_2]}{dt} = E_{NO} - k_L(NO_2)[NO_2]_0 \qquad (2)$$

$[NO_2]_0$ is the NO_2 mixing ratio at 20.00 UTC. The NO_2 concentration at any subsequent time can then be calculated as described in Eq. (3) with variation of $k_L(NO_2)$ in order to match the observed NO_2 mixing ratio.

$$[NO_2]_t = \int_0^t \frac{d[NO_2]}{dt} + [NO_2]_0 \qquad (3)$$

In Figure 7 the grey lines symbolize the calculated NO_2 mixing ratios at nighttime using values of $k_L(NO_2)$ between 1.0×10^{-4} and 4.0×10^{-4} s^{-1}. As expected, no single value of $k_L(NO_2)$ can explain all the measurements as the height of the BL will not be invariant during the whole night. However, for the Continental and Atlantic phases the observed NO_2 can be explained with $k_L(NO_2) = (2.0 \pm 1.0) \times 10^{-4}$ s^{-1} and $k_L(NO_2) = (2.75 \pm 1.25) \times 10^{-4}$ s^{-1}, respectively, which results in lifetimes of ~ 1-3 h and ~ 40-110 min for NO_2 at nighttime. As deposition of NO_2 in this environment represents a permanent loss of NO_X from the gas phase, this lifetime can be compared to e.g. the lifetime of NO_X with respect to its conversion to HNO_3 via reaction of NO_2 with OH which is ~ 1 day (assuming average [OH] = 1×10^6 molecule cm^{-3}). The low aerosol surface area during ACROSS combined with the low uptake coefficient for NO_2 renders losses due to heterogeneous processes insignificant (IUPAC, 2024). Clearly, only ~~nighttime~~ depositional losses of NO_2 in a forested environment contribute substantially to its lifetime at night and to the NO_X budget.

If we continue to assume the nocturnal boundary layer at the forest site is at the top of the canopy (20 m), then the NO_2 loss-rate constants we determined can be converted to a deposition velocity of 0.4 ± 0.2 cm s^{-1} and 0.55 ± 0.25 cm s^{-1} for the Continental and Atlantic phase, respectively. These are comparable to previous measurements of NO_2 deposition velocities of 0.15 cm s^{-1} (Dewald et al., 2022), 0.1-0.57 cm s^{-1} (Rondón et al., 1993), 0.098 cm s^{-1} (Breuninger et al., 2013), 0.2-0.5 cm s^{-1} (Horii et al., 2004), 0.02-0.64 cm s^{-1} (Puxbaum and Gregori, 1998), for a mountain observatory surrounded by coniferous trees, boreal coniferous forests, a temperate coniferous forest, a temperate mixed deciduous forest, and a temperate oak forest, respectively, where a combination of soil and foliage deposition is measured. Horii et al. (2004) saw an increase in

499   deposition velocity with increasing NO_2 mixing ratio; from 0.2 cm s^{-1} at 1 ppbv to 0.5 cm s^{-1} at 30
500   ppbv. Puxbaum and Gregori (1998) reported monthly averages of 0.02-0.64 cm s^{-1}, however, their
501   nighttime deposition velocities averaged below 0.05 cm s^{-1}. The deposition velocities determined
502   here are a factor of 5-40 higher than what has been measured for nighttime foliage deposition
503   velocities to the leaves of different trees native to California (Delaria et al., 2020; Delaria et al.,
504   2018), but in good agreement with measurements for daytime. It is, however, important to note
505   that the deposition velocities estimated here are upper limits as the estimation of the NO emission
506   rate is an upper limit and chemical loss of NO_2 is not taken into account. Using an average
507   nighttime NO_2 mixing ratio of 1650 and 1450 pptv for the Continental and Atlantic phase,
508   respectively, results in NO_2 deposition rates of 13.6 ± 6.8 µg N m^{-2} h^{-1} and 18.7 ± 8.5 µg N m^{-2} h^{-1}
509   ^{1}, which are in reasonable agreement with that measured for soil NO_2 deposition in a sessile oak
510   forest of 9.67 ± 1.92 µg N m^{-2} h^{-1} during the summer (Rosenkranz et al., 2006). The estimated NO
511   soil emission rate and NO_2 deposition rate are, within the uncertainties, identical, which means the
512   Rambouillet forest is not a significant direct source or sink of NO_X.

513

514   **5   Summary:**
515   Measurements of NO, NO_2, NO_Y, and O_3 during the ACROSS campaign (June-July 2022) in the
516   Rambouillet forest southwest of Paris, France, have been used to gain insight into nighttime
517   processes controlling NO_X in an anthropogenically impacted forest environment. Based on
518   HYSPLIT back trajectories, two phases of the campaign were identified; one dominated by air
519   originating over the Atlantic Ocean ("Atlantic"), which on average had high relative humidity and
520   low O_3 mixing ratios, and one dominated by continental air masses from different
521   urban/industrialized regions ("Continental"), which on average had a lower relative humidity than
522   the Atlantic phase and higher O_3 mixing ratios. Strong diel profiles were observed in the O_3
523   measurements across the campaign with daytime peak mixing ratios varying from ~30 to 90 ppbv
524   and nighttime tending towards 0-10 ppbv. The daily variation was driven by a variable but
525   generally rapid O_3 deposition to soil and foliar surfaces, with a strong influence of relative
526   humidity (influencing the surface resistance to uptake) and inversion (influencing the rate of
527   entrainment of O_3 from above the canopy).

528   During the Atlantic phase, periods of sustained NO above the instrumental detection limit was
529   observed at nighttime when O_3 was sufficiently low (i.e. the NO lifetime sufficiently long). This
530   enabled the derivation of an average NO emission rate from the soil (E_{NO}) of ~1.4 ppbv h^{-1}, which
531   was confirmed by the approximately linear increase in NO observed in the absence of O_3 in the
532   Atlantic phase. The estimated E_{NO} is in broad agreement with previous measurements in other
533   European temperate forests with tree types as found in the Rambouillet forest.

534   An increase in NO_2 at night would be expected when having a constant NO emission rate of
535   ~1.4 ppbv h^{-1} in the presence of O_3 as observed in this study, however, this was not the case. The
536   lack of increase in NO_2 was used to estimate first-order decay constants of $(2.0 \pm 1.0) \times 10^{-4}$ s^{-1}
537   and $(2.75 \pm 1.25) \times 10^{-4}$ s^{-1} resulting in an effective lifetime of NO_2 of ~0.5-3 h. The loss of NO_2
538   at nighttime is presumably driven by deposition to soil and foliar surfaces since the lifetime of
539   NO_2 towards its reactions with OH and O_3 at night is >28 and 14 h, respectively. By comparison,

540 the daytime lifetime of NO_2 with respect to loss by reaction with OH is about 1 day. We conclude
541 that the nighttime deposition of NO_2 is a major sink of boundary layer NO_X in this forested
542 environment.

543

6   Data Availability:
545 All data can be found on https://across.aeris-data.fr/catalogue/.

546

7   Author contribution:
548 All authors contributed with measurements. Data analysis was conducted by STA with
549 contributions from JNC and PD. CC and VM organized the field campaign with contributions from
550 the individual group leads. STA and JNC developed the manuscript with contributions from all
551 authors.

552

8   Competing Interests:
554 At least one of the (co-)authors is a member of the editorial board of Atmospheric Chemistry and
555 Physics

556

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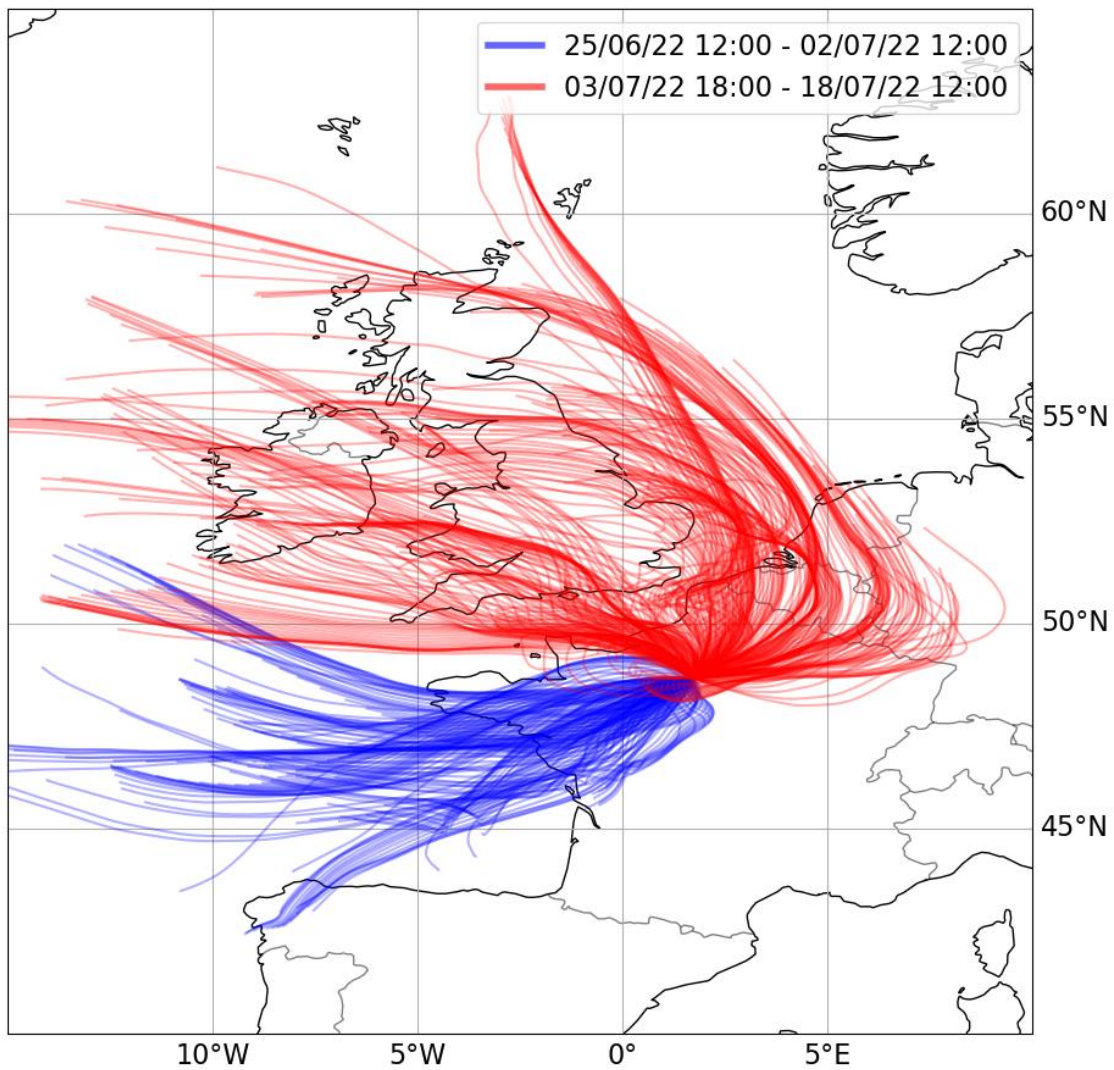
735 **11 Figures:**

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737 Figure 1: 48-hour back trajectories from the Rambouillet forest supersite using the Hybrid Single-
738 Particle Lagrangian Integrated Trajectory model (HYSPLIT, version 4, 2019).
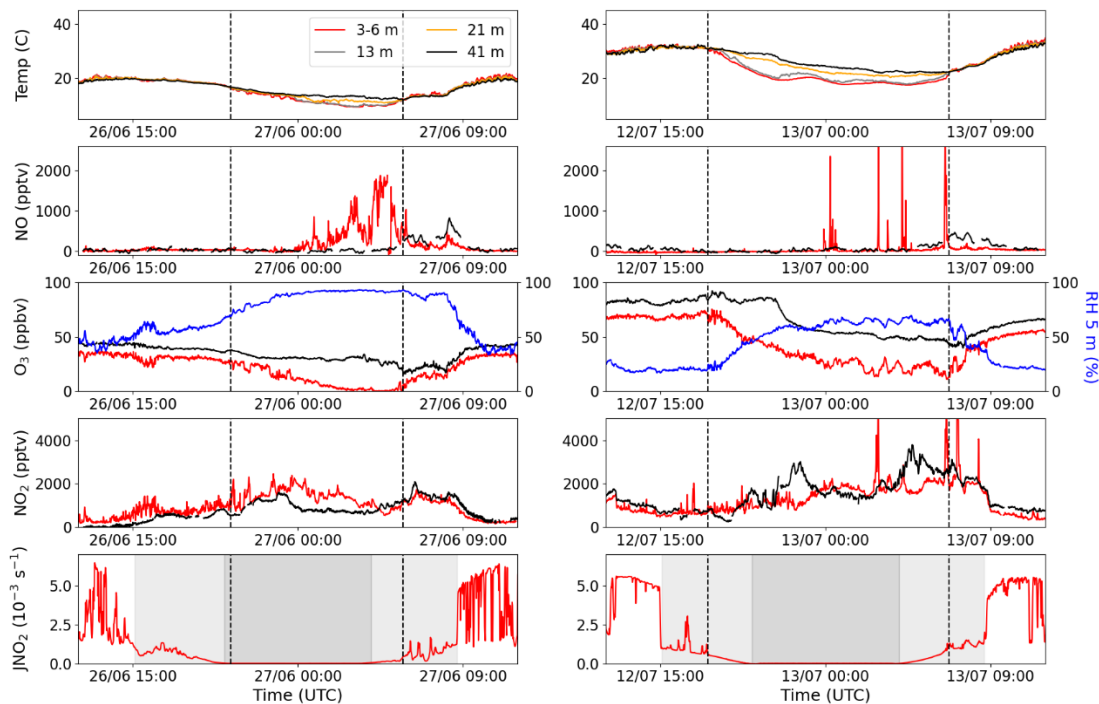
Figure 2: Measurements of temperature, NO, O_3, RH, NO_2, and JNO_2 for two different nights during the campaign; one during the Atlantic phase (left panels) and one during the continental phase (right panels). The different colours symbolize four different heights; red = 3-6 m, grey = 13 m, orange = 21 m, and black = 41 m, and the blue shows the RH at 5 m. The grey shaded areas in the JNO_2 plots shows the time the MPIC container was in shade during the afternoon and morning (light grey) and nighttime (dark grey). The vertical black dashed lines indicate the beginning and end of the observed temperature inversions in the top panels.

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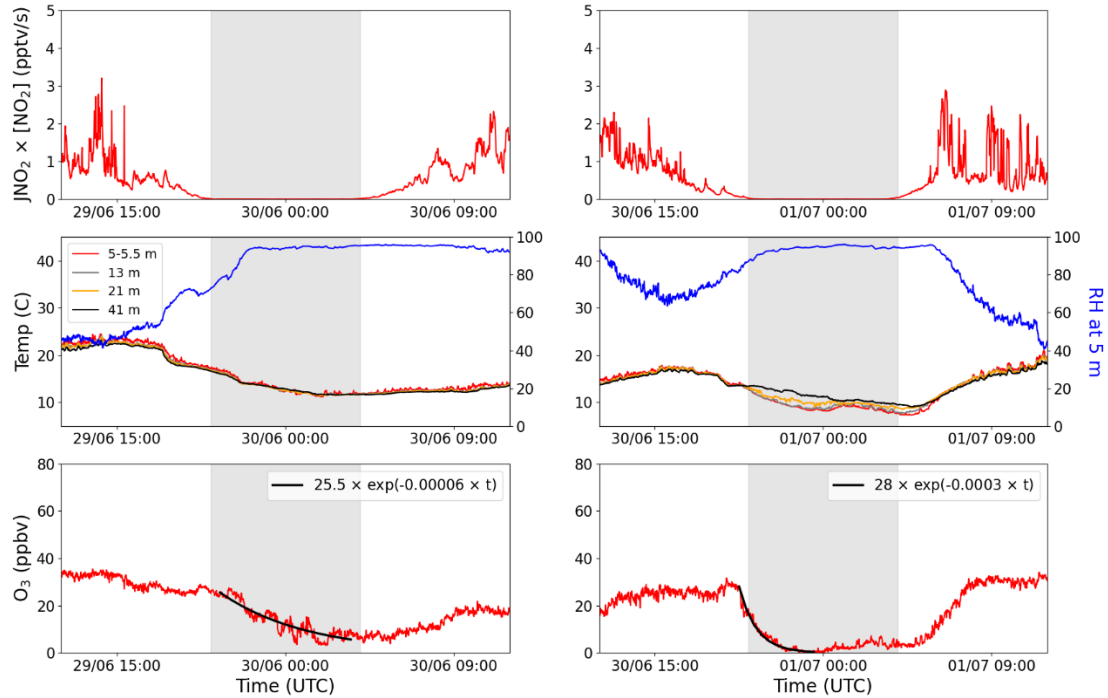
Figure 3: The production of O_3 ($JNO_2 \times [NO_2]$), temperature, RH, and O_3 plotted for two nights
with high average RH; one without a temperature inversion (left panels) and one with a
temperature inversion (right panels). The different colours symbolize four different heights; red =
5-5.4 m, grey = 13 m, orange = 21 m, and black = 41 m, and the blue shows the RH at 5 m. The
net nighttime O_3 loss is fitted with an exponential decay curve (solid black line) in the bottom
plots. The grey shaded areas represent the nighttime.

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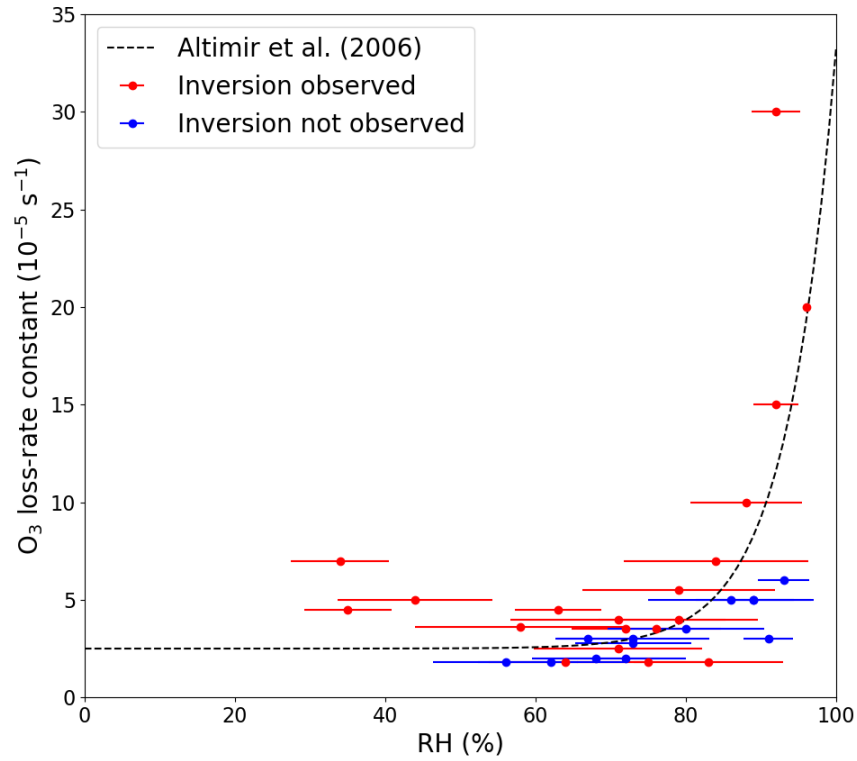
Figure 4: Net O_3 loss-rate constants at 5.4 m plotted against the average relative humidity measured
during the time used to fit the exponential decay of O_3. The error bars represent $\pm 1\sigma$ on the average
RH. The dashed line symbolizes the observations made by Altimir et al. (2006).

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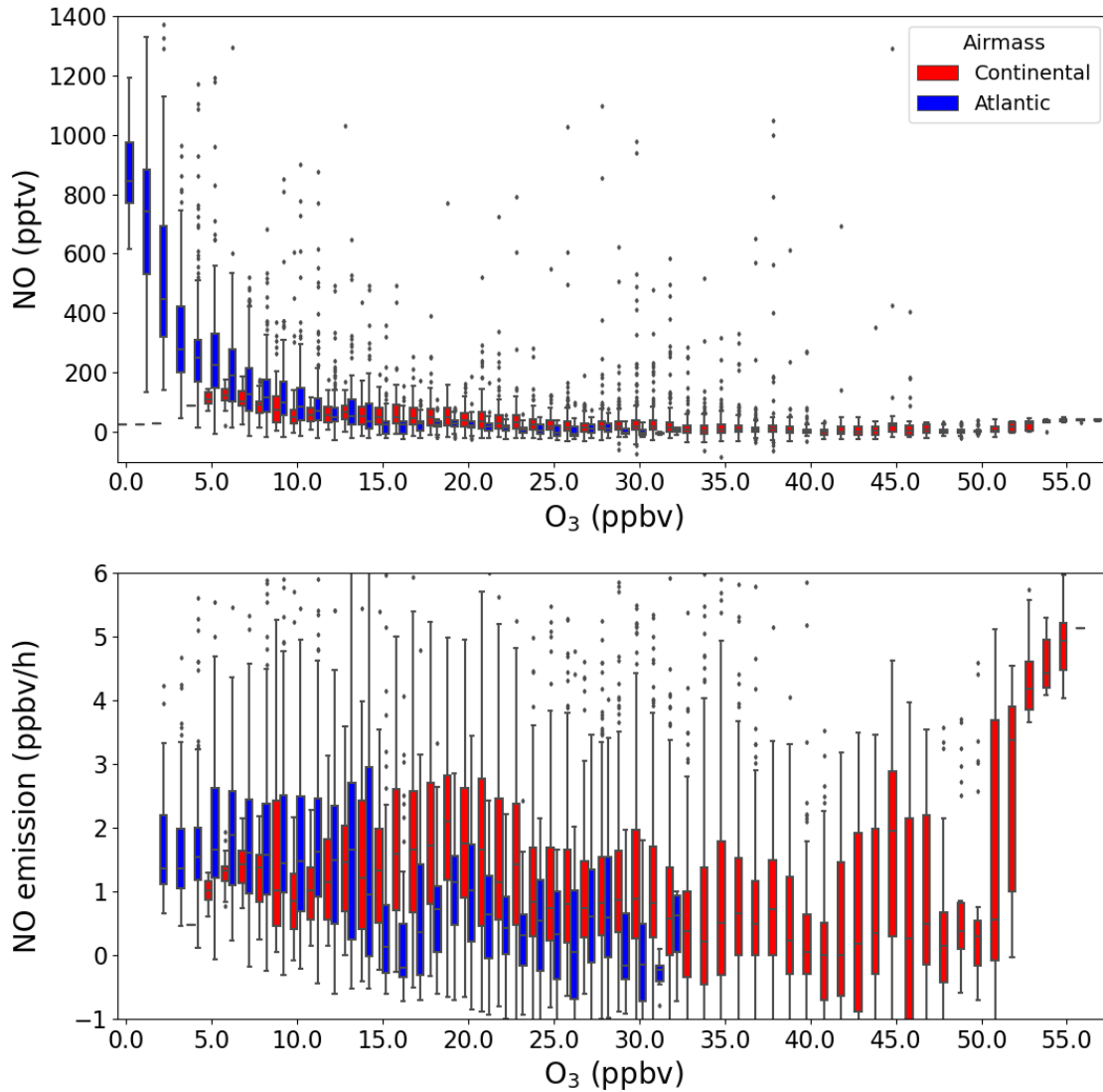
Figure 5: NO (top) and NO emission (bottom) plotted against O_3 in a box-and-whiskers plot, where the outliers are defined as being outside $1.5 \times$ IQR. The colours represent the two different air masses.

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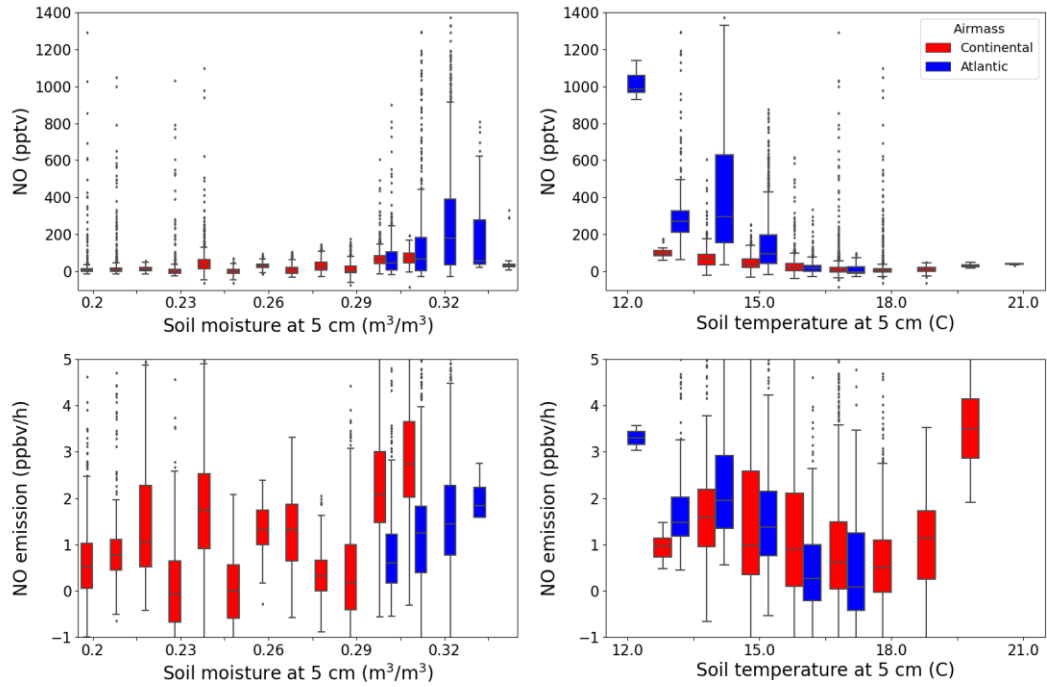
Figure 6: NO (top panels) and NO emission (bottom panels) plotted against soil moisture (left panels) and temperature (right panels) at 5 cm below the surface in a box-and-whiskers plot, where the outliers are defined as being outside $1.5 \times$ IQR. The colours represent the two different air masses.

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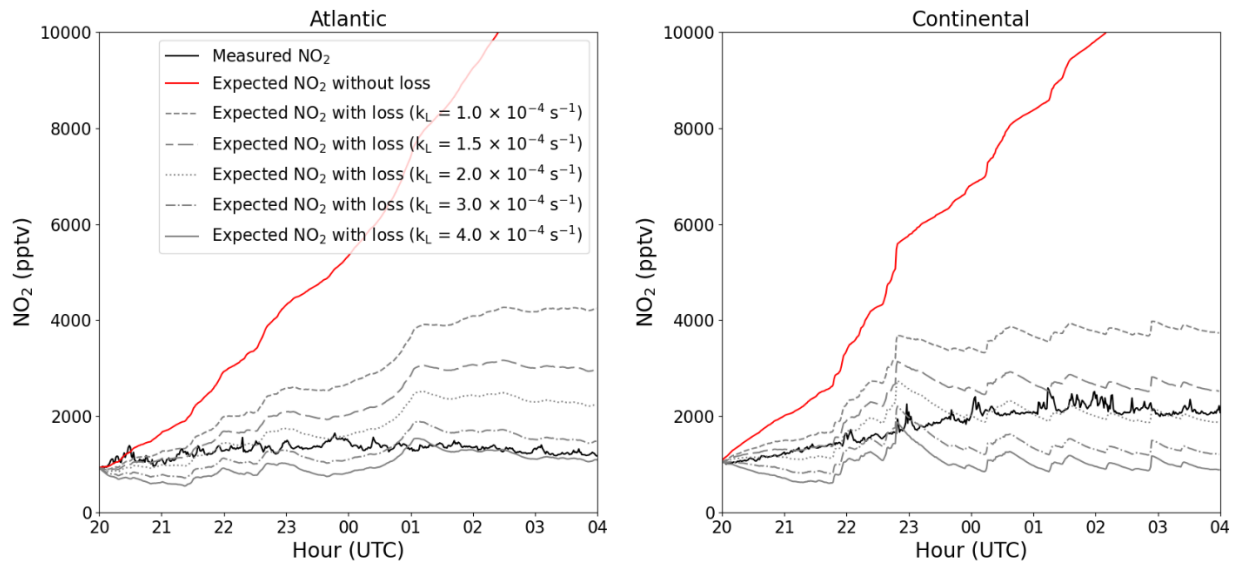
Figure 7: Average nighttime profiles of NO_2 at 5.4 m for each of the two phases (black) plotted
773 together with the expected NO_2 with (grey) and without (red) NO_2 loss.

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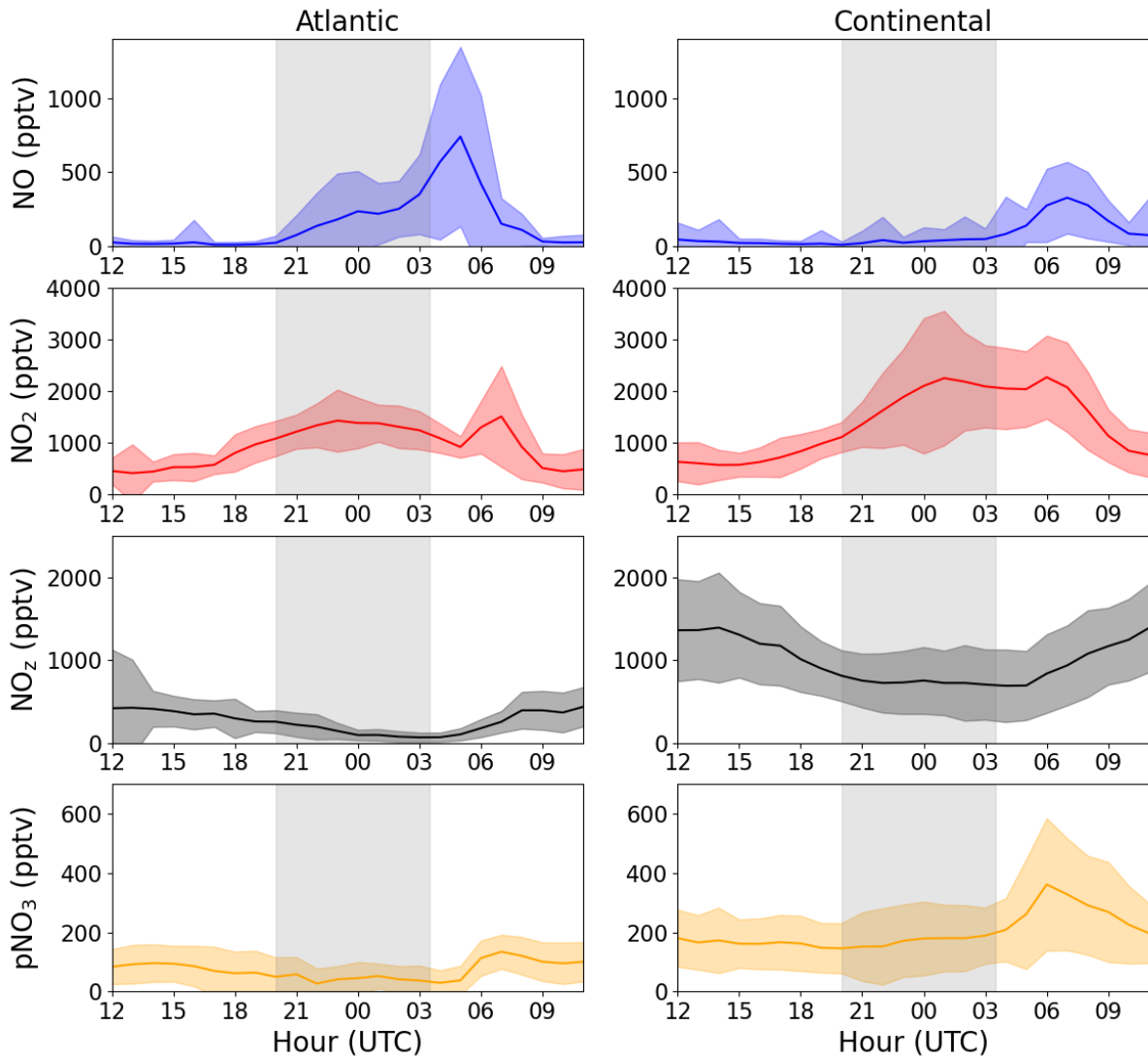
Figure 8: Average diel profiles of NO, NO_2, total gas-phase NO_z, and particulate nitrate (pNO$_3$) at 3-6 m above ground for the Atlantic (left panels) and Continental (right panels) phases. The grey shaded areas symbolize nighttime.

 12 Tables:

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780 Table 1: Measured NO soil emission in European forests with the same tree types as in the
781 Rambouillet forest.

Dominant tree type	Location	NO emission (μg N m^{-2} h^{-1})	Reference
Oak	Matra Mountains, Hungary	2.1	(Pilegaard et al., 2006)
		6.0 ± 3.3 (summer)	(Rosenkranz et al., 2006)
		8.4 ± 2.4 (autumn)	(Rosenkranz et al., 2006)
Pine	San Rossore, Italy	5.4	(Pilegaard et al., 2006)
Beech	Schottenwald, Austria	25.5 ± 7.5	(Schindlbacher et al., 2004)
		4.2	(Pilegaard et al., 2006)
Beech	Klausen-Leopolsdorf, Austria	10.2 ± 3.4	(Schindlbacher et al., 2004)
		0.7	(Pilegaard et al., 2006)
Spruce-Fir-Beech	Achenkirch, Austria	2.8 ± 1.4	(Schindlbacher et al., 2004)
		0.9	(Pilegaard et al., 2006)
Mixed deciduous	Ticino Park, Italy	18.5 ± 5.8	(Schindlbacher et al., 2004)
		Below LOD	(Pilegaard et al., 2006)

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