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Supplement of

A comparison of measured HONO uptake and release with calculated source strengths in a heterogeneous forest environment

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1 Site description

A detailed description of the research area and measurement sites can be found in Gerstberger et al. (2004), Staudt and Foken (2007) and Foken et al. (2012). A detailed description of the clearing site and the intensive campaign EGER IOP-3 can be found in Serafimovich et al. (2011). Figure S1 shows the heterogeneity of the area and the three measurements sites.

Figure S1: Aerial view (data source: Bayerische Vermessungsverwaltung – www.geodaten.bayern.de) of the measurement sites shows the heterogeneous forest landscape of the research area with the marked sites forest floor (FF), clearing (CL) and “Pflanzgarten” (PF). The white area on the left side of the picture is a stone pit. Most roads are forest roads except the curvy road running from the middle of the bottom of the picture to the upper left corner (i.e. from the south to the north-west of the measurement sites). This road is a country road with about 2100 cars per working day (Foken et al., 2012). The clearing has the dimensions of ~ 300 x 400 m.

2 Lift system

Figure S2 shows the lift system used for sampling at different heights. The system consists of a vertical linear guide system (Igus, Cologne, Germany) and a stepper motor with a custom built control unit (electronics workshop, University of Bayreuth). The heights are programmable and ranged between 0.1 m above ground level to 1.6 m above ground level.

Figure S2: External sampling unit of the LOPAP (grey box) and inlet for NO_x installed on the lift system at the forest floor. Three positions (1.6 m, 0.4 m and 0.1 m) used for the profile measurements are indicated in red.

3 Measured trace gas profiles (all heights)

The following figures (Figure S3 to S5) show the trace gas profiles of NO, NO_2 and HONO that were measured consecutively by the above described lift system. The first period (27th of June to 30th of June 2011) of the 2011 campaign is shown in Fig. S3, the second part (11th of July to 13th of July) in Fig. S4. In between the instrument was broken. Measurements were made in a clearing (see Fig. S1). Figure S5 shows the measurements at the forest floor (see Fig. S2) during the 2012 campaign (3rd of September to 9th of September 2012).

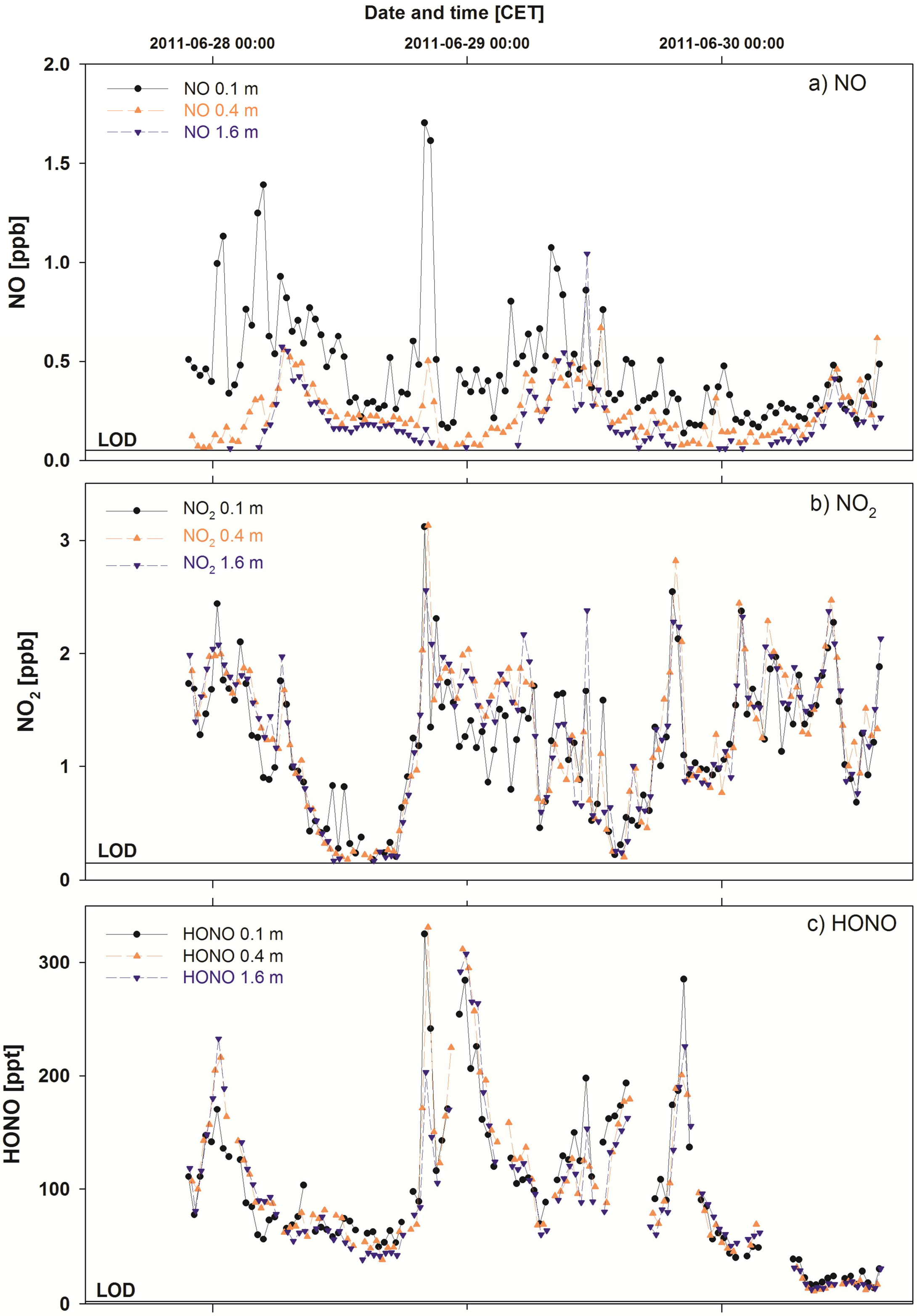

Figure S3: Trace gas profiles measured during the first period of the 2011 campaign in the clearing. The profiles were measured consecutively with a lift system. Heights are 0.1 m, 0.4 m and 1.6 m above ground. Panel a) NO, panel b) NO_2 and panel c) HONO

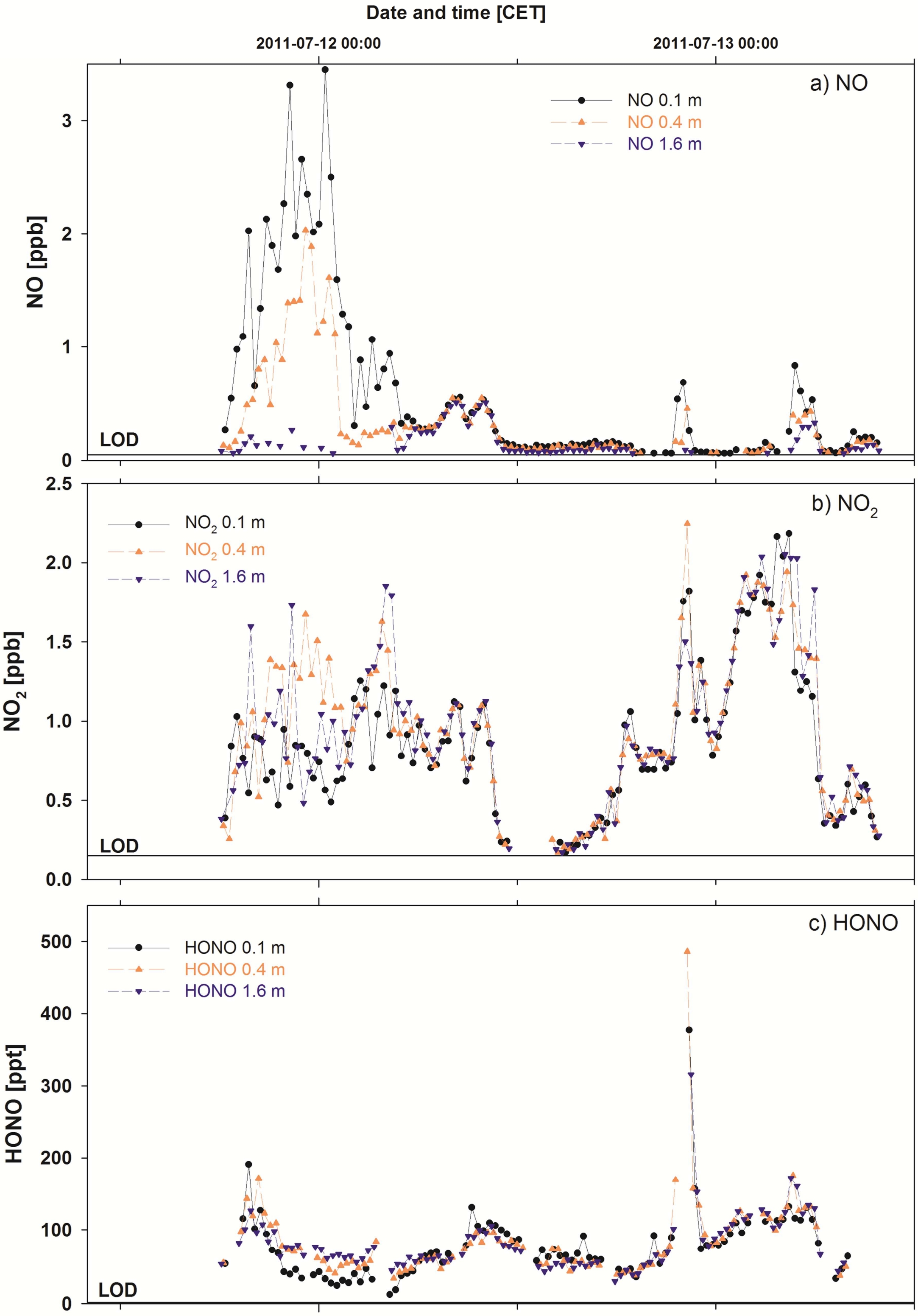

Figure S4: Trace gas profiles measured during the second period of the 2011 campaign in the clearing. The profiles were measured consecutively with a lift system. Heights are 0.1 m, 0.4 m and 1.6 m above ground. Panel a) NO, panel b) NO$_2$ and panel c) HONO.

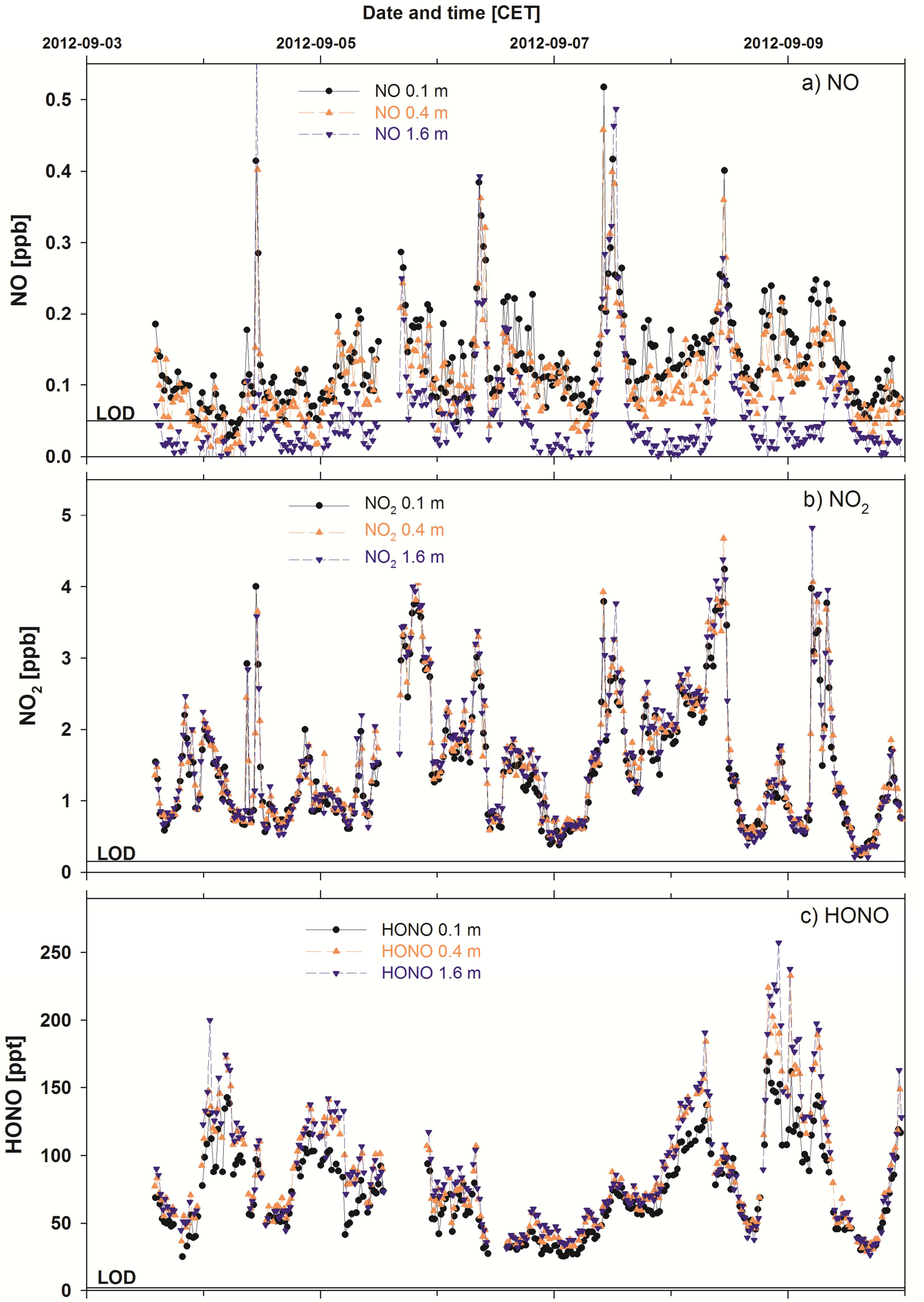

Figure S5: Trace gas profiles measured during the 2012 campaign at the forest floor. The profiles were measured consecutively with a lift system. Heights are 0.1 m, 0.4 m and 1.6 m above ground. Panel a) NO, panel b) NO_2 and panel c) HONO.

4 Laboratory measurements of soil fluxes

In order to evaluate potential soil HONO emissions, several soil samples were taken from the sites where the lift system was located. The soil type is classified as haplic podzol over granite bedrock (Gerstberger et al., 2004) for this area, but only the soil organic layer (O horizon) was sampled. This organic layer is characterized by a high water holding capacity and very low pH values (Gerstberger et al., 2004). On 30 Aug 2012, the first soil sample (Sample 1) was taken from a hemicycle with a radius of about 10 m around the lift system. The green moss on top of the soil (0.8 – 1.5 cm) was removed, and the Oe and Oa horizons were sampled separately in three replicates. These samples were transported on ice in a cooling box to the laboratory. The Oe soil sample was measured immediately after sampling, and the Oa soil sample was stored in a refrigerator for 24 h at 4 °C before measurement. For samples 2-4, which were taken on 11 June 2013, the vegetation cover was removed and the upper 5 cm of the O horizon was sampled by sampling rings. Three sampling rings have been taken for one subsample. These samples were transported in a cooling box for about 10 h and then stored at 4 °C in a refrigerator prior to analysis within the following 3 to 5 days. For each site (forest/clearing) we chose two different types of understory vegetation for sampling. In the forest, the soil was covered by moss (Sample 1). As a prior study found higher NO emissions for blueberry than for moss in that respective forest patch (Bargsten et al. 2010), we also sampled a stand of blueberries nearby (Sample 2). At the clearing, the understory close to the lift system consisted mainly of grass and some small blueberry plants (Sample 4). We also took soil samples from the surrounding, which was dominated by blueberries on moist soil (Sample 3).

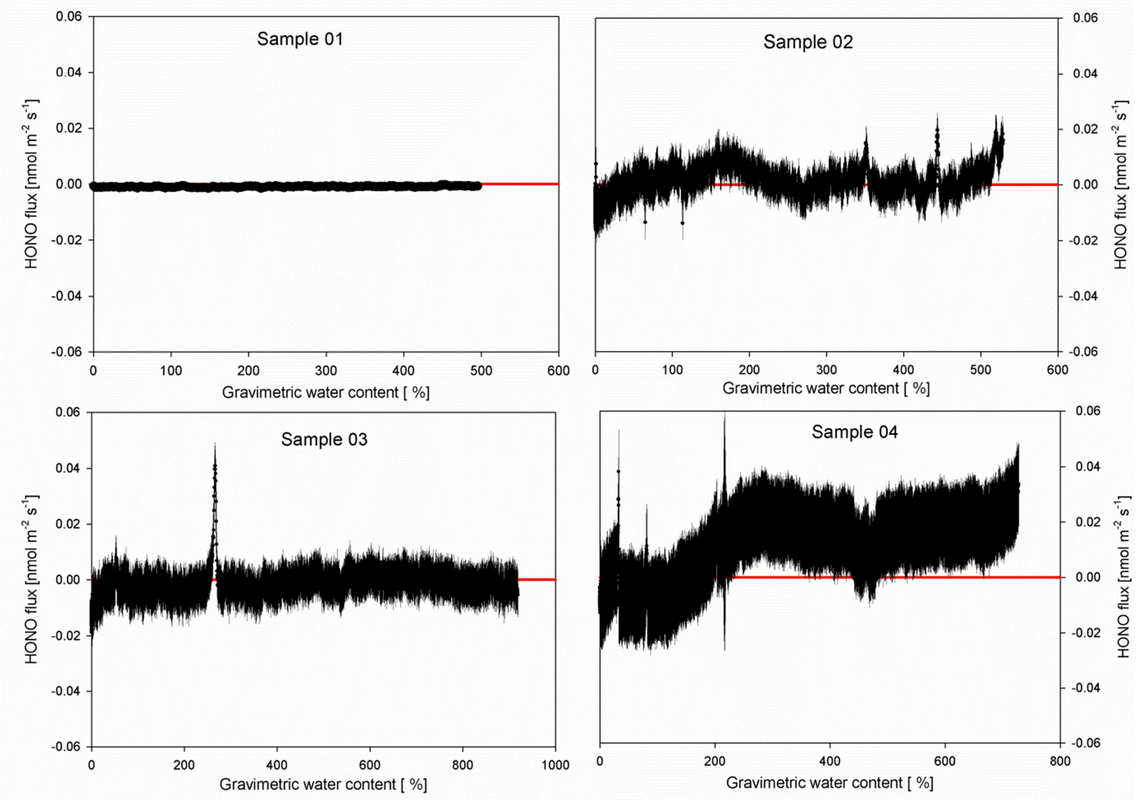

Figure S6: HONO fluxes from four different soil samples measured in a dynamic laboratory chamber according to Oswald et al. (2013). Sample 1 was taken from the forest floor covered with moss, whereas for sample 2 the ground was covered by blueberries. Samples 3 and 4 were taken on the clearing from moist soil covered by blueberries and from ground covered by grass, respectively. The differences in the errors are due to different detection limits (0.5 ppt to 6 ppt) for the LOPAP instrument.

For each understory type, three subsamples were taken. These have been combined into one sample which was measured in the laboratory system. The laboratory setup to measure the emission fluxes was described in detail elsewhere (Oswald et al., 2013, Wu et al., 2014). Briefly, the soil samples were passed through 16 mm sieves (instead of 2 mm), reducing the influence of the destruction of the structure of soil organic matter on trace gas emission (Bargsten et al., 2010). Roots were removed to the extent possible, 50 g of soil were put in a petri dish (OD = 88 mm), and purified water (resistivity 18.2 MΩ cm^{-1}) was added to reach water holding capacity. The dish was placed in a Teflon chamber (47 L) within a climate cabinet at 15 °C for Sample 1 and 25 °C for samples 2-4. The chamber was flushed with 8 L min^{-1} of dry purified air, and the trace gas mixing ratios (NO, NO_2, O_3, CO_2, H_2O and HONO) were monitored in the chamber outflow. NO_x was measured by chemiluminescence (Model 42i-TL Thermo Scientific, Franklin, MA, USA), ozone by UV-absorption (Model 49iThermo Scientific, Franklin, MA, USA), CO_2 and H_2O by infrared absorption (Model 840A, LI-COR, Lincoln, Nebraska, USA), and HONO was measured by long path absorption (LOPAP-03, QUMA Elektronik & Analytik GmbH, Wuppertal, Germany). The least sensitive detection limit of the LOPAP was 6 ppt, and the resulting minimum detectable flux was 0.004 nmol m^{-2} s^{-1}. The detection limit for NO was 50 ppt, and the minimum detectable flux was 0.04 nmol m^{-2} s^{-1}. The uncertainties of the fluxes were calculated using Gaussian error propagation according to Oswald et al. (2013). The gravimetric soil water content during the laboratory soil measurements was calculated from the loss of water using the water vapor measurements in the sample air (see Oswald et al. 2013).

Soil properties were analyzed according to standard procedures: pH was measured according to DIN ISO 10390 in a 0.0125 mol l^{-1} $CaCl_2$ solution. Mineral nitrogen (ammonia, nitrite, nitrate) was measured according to DIN ISO/TS 14256-1 in a 0.0125 mol l^{-1} $CaCl_2$ extract with photometric detection of nitrite after reduction of nitrate to nitrite.

Table S1: Soil pH and nutrient content (NH_4^+; NO_2^- and NO_3^-) for the measured samples in comparison to previously published values (Bargsten et al., 2010 and Gerstberger et al., 2004). * pH values measured by pH electrode in soil solution (water).

Sample **bm = before measurement** **am = after measurement**	**pH** –	**NH_4-N** [mg/kg]	**NO_2-N** [mg/kg]	**NO_3-N** [mg/kg]
This study				
Sample 1 (bm)	3.2	239.6	0.35	36.9
Sample 2 (bm)	3.4	49.7	0.50	5.0
Sample 2 (am)	3.4	6.3	0.33	2.3
Sample 3 (bm)	3.1	29.2	0.89	4.9
Sample 3 (am)	2.9	19.4	0.13	1.7
Sample 4 (bm)	3.0	36.7	0.99	12.9
Sample 4 (am)	2.8	16.8	0.12	3.4
Sample 4 (am) replicate	2.8	17.9	0.13	3.3
Mean (bm)	**3.2**	**38.5**	**0.79**	**7.6**
Bargsten et al. (2010)				
M1 (moss)	4.6*	194	-	2
M2 (moss)	5*	148	-	7
G1 (grass)	4.1*	207	-	1
G2 (grass)	3.6*	204	-	2
S1 (spruce)	3.5*	56	-	11
S2 (spruce)	3.5*	86	-	1
B1 (blueberry)	4.7*	139	-	1
B2 (blueberry)	3.7*	148	-	2
Mean	**4.1***	**148**	**-**	**3.4**
Gerstberger et al. (2004)				
pH in water Oi horizon	4.5*	-	-	-
pH in $CaCl_2$ Oi horizon	3.6	-	-	-
pH in water Oe horizon	3.8*	-	-	-
pH in $CaCl_2$ Oe horizon	2.9	-	-	-
pH in water Oa horizon	3.5*	-	-	-
pH in water Oa horizon	2.6	-	-	-

5 HNO_3 photolysis

We determined the nitrate loading of three spruce trees (Samples 1-19, Table S2) at the clearing site by foliar rinsing, a method previously used to determine HNO_3 deposition fluxes. It was shown that nitrate recovery rates are generally better than 90 % for this method (e.g. Marshall and Cadle, 1989; Cadle et al., 1991).

Nitrate was washed off the needles using purified water (18 MΩ) by exposing a branch length of about 8 cm to 20 ml purified water in a 40 ml polyethylene flask, and swirling the flask for 2 min to assure mixing in the solution and wetting of all parts of the branch. The solution was measured by ion chromatography (Central Analytical Laboratory, University of Bayreuth). The amount of measured nitrate was then normalized to the total needle area, which was determined by harvesting the branch, separating all needles and taking photographs of the needles on a white background containing a scale. These pictures were converted to black and white pictures. By measuring the pixels of the scale, the number of dark pixels (projected needle area) was converted to the needle area (in cm²).

Table S2: Measured leaf nitrate and needle areas of small spruce trees at the clearing site.

Sample number	Time of day (CET)	NO_3^- mg l^{-1}	NO_3^- mol	Projected needle area cm³	Geometric needle area cm³
1 (tree 1)	16:00	0.12	3.87E-08	17.2	45.5
2 (tree 1)	16:00	0.12	3.87E-08	12.7	33.8
3 (tree 2)	16:00	0.09	2.90E-08	11.7	31.0
4 (tree 2)	16:00	0.04	1.29E-08	12.0	31.7
5 (tree 3)	16:00	0.05	1.61E-08	21.1	56.0
6 (tree 1)	18:15	0.06	1.94E-08	14.7	38.8
7 (tree 1)	18:15	0.10	3.23E-08	18.9	50.1
8 (tree 2)	18:15	<		16.3	43.2
9 (tree 2)	18:15	0.09	2.90E-08	16.9	44.8
10 (tree 3)	18:15	0.04	1.29E-08	12.1	32.1
11 (tree 1)	20.15	0.10	3.23E-08	17.8	47.3
12 (tree 1)	20.15	0.08	2.58E-08	23.4	62.1
13 (tree 2)	20.15	0.08	2.58E-08	19.7	52.2
14 (tree 2)	20.15	0.06	1.94E-08	16.0	42.5
15 (tree 3)	20.15	<		12.1	32.2
16 (tree 2)	22:00	0.09	2.90E-08	16.0	42.5
17 (tree 1)	22:00	0.09	2.90E-08	14.5	38.3
18 (tree 3)	22:00	0.11	3.55E-08	19.7	52.2
19 (tree 3)	22:00	0.13	4.19E-08	13.8	36.5
Mean		**0.09**	**2.8E-08**	**16.1**	**42.8**
Standard deviation		**0.03**	**8.9E-09**	**3.4**	**9.0**

Additionally, three field blanks have been taken close to the institute building in Bayreuth, where higher HNO_3 levels are expected in the gas phase. The blank flasks were kept open to the atmosphere for two minutes instead of being exposed to a branch. The field blanks were below the detection limit of the method (i.e. < 0.03 mg L^{-1} NO_3^-). Nitrite (NO_2^-) concentrations remained below the detection limit in all samples (LOD = 0.04 mg L^{-1} NO_2^-). The measured nitrate loadings on the trees close to the institute building in Bayreuth (not shown) were 3 to 20 times higher than the maximum values at the Waldstein site.

The advantage of the nondestructive method (i.e. not cutting the branches before washing off), which can at least be applied to spruce trees, is that the branches can be marked and sampled several times to establish time series using the same branches. Finally, the branches can be harvested to measure the leaf area index (LAI). The error of the sampling area for the repeated sampling should be low (a few needles more or less). It should be noted that neither the method proposed by Zhou et al. (2011) nor our method discriminates between ammonium nitrate and adsorbed nitric acid, which is supposed to be photolysed to finally yield HONO. Thus the amount of adsorbed HNO_3 might be overestimated.

The projected needle area can be converted to the total needle area by multiplying by a factor of 2.65 derived by Oren et al. (1986). Thus, if HNO_3 is distributed homogeneously on the needle, the amount of HNO_3 directly exposed to sunlight is a factor of 2.65 lower. If we then consider only the projected area of the whole branch with needles instead of the single needles, the amount of HNO_3 exposed is further reduced by a factor of 2.2 as derived from our branch photographs.

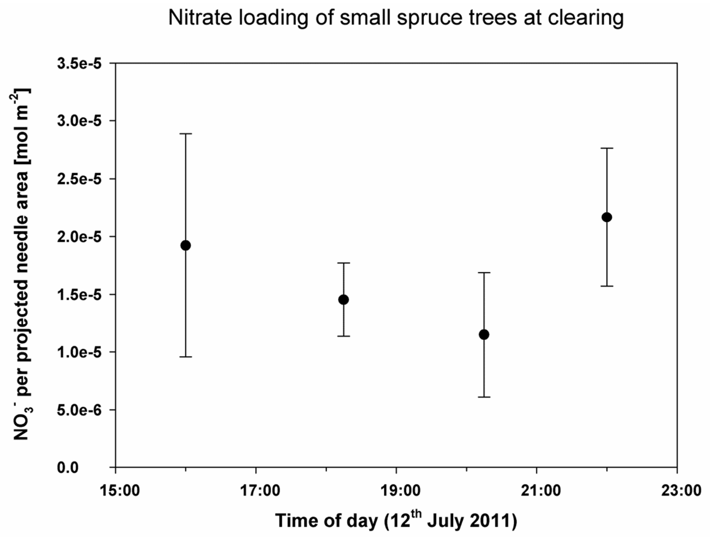

Figure S7: Calculated leaf nitrate loadings for 12 July 2011.

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