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Ammonia emissions from beech litter as source of reactive nitrogen gas in deciduous forests

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Introduction

Nitrogen is an essential element for all living organisms. As essential part of many biomolecules nitrogen is, together with phosphorous, the major growth limiting factor of autotroph organisms on the planet (Elser et al. 2007). Even though the Earth's atmosphere contains 78% of nitrogen, most of it is not reactive and thus not directly usable for most organisms. The elemental N_2 molecule forms a highly stable covalent triple bond which is biologically and chemically inert. That's why more than 99% of the N contained in soils, water and the atmosphere are not usable for most organisms on the planet (Galloway et al. 2003). Breaking this triple bond requires a lot of energy or specific enzyme machinery, which is why it is only possible by using high temperature processes and by specialized N-fixing microbes to produce reactive nitrogen (N_r) (Galloway et al. 2003).

Historically, so called reactive nitrogen, has been a scarce good and a major limiting nutrient in terrestrial ecosystems, often limiting primary production. It was not until the invention of the Haber-Bosch process at the beginning of the 20th century, when industrial ammonia production turned this historical shortage, into to a surplus, especially in Europe, North America and later China (Sutton et al. 2008). Reactive forms of nitrogen include all forms other than N_2 (Sutton et al. 2011); these include oxidized forms (e.g. NO_x, N_2O, NO_3^-, HNO_3), reduced forms (NH_3 and NH_4^+, collectively NH_x) as well as organic nitrogen compounds such as proteins, urea and nucleic acids. Currently total human N_r production is greater than that of all natural systems combined (Galloway et al. 2003). This is attributed to three main causes: (1) the cultivation of plants which promote biological nitrogen fixation (BNF) (e.g. legumes and rice); (2) the conversion of atmospheric N_2 and fossil nitrogen to NO_x through the burning of fossil fuels; (3) the large amount of ammonia produced by the Haber-Bosch process and the subsequent loss to the environment primarily through fertilizing losses (Galloway et al. 2003). A large number of chemical transformations are possible in the schematic "nitrogen cycle" as the element is found in oxidative states from -3 (NH_3) to +5 (NO_3^-). The transformation of nitrogen atoms to various molecules in different environmental systems has been termed the "Nitrogen Cascade" (Galloway et al. 1998). The origin of an N atom (e.g. combustion, fertilization) loses its relevance once in the cascade (Galloway et al. 2003).

Large quantities of reactive nitrogen added in agriculture are lost from sites of application through different mechanisms back to the atmosphere. Estimates suggest that about 50 % of nitrogen applied on European agricultural fields are either lost as pollution or are converted back to N_2 via denitrification (Sutton et al. 2011), with severe effects on ecosystems, climate and human health

(Galloway et al. 2003). Costs from nitrogen pollution of air, water and soil may exceed benefits to agricultural production by N addition by a factor of 2 (Sutton et al. 2011). Nitrogen pollution can be considered as one of the biggest environmental challenges of the 21st century, thus a solid scientific base is needed to discuss policy options to tackle these problems (Galloway et al. 1998, Erisman et al. 2007, Sutton et al. 2011).

Gaseous N emissions and deposition

Where some oxidized forms of gaseous N, like N_2O and NO_x have been in the focus of ecosystem research for a long time, the interest in NH_3 as a pollutant of highest concern has grown substantially over the last two decades (Singh et al. 2001). Ammonia (NH_3) is estimated to account for approximately half of global N_r emissions, whereas oxidized nitrogen forms are calculated to account for roughly the other half as calculated by the Emissions Database for Global Atmospheric Research (EDGAR) (Flechard et al. 2013). Agricultural emissions are responsible for, by far the largest share of this pie with estimates going up to 39 Tg N y^{-1} (Beusen et al. 2008). Of the estimated annual N_2 fixation (biologically and industrially) of 140 Tg N y^{-1} of N_2, as much as one third may be lost as NH_3 to environments as emissions (Galloway et al. 2003, Flechard et al. 2013). Soil emissions and combustion processes are the main contributors of Nitric oxide (NOx) emission, both adding roughly half the share to the global budget. NO readily reacts with tropospheric ozone to form NO_2, together they are termed NO_x (Pilegaard 2013). Recently Oswald et al. (2013) have shown that emissions of gaseous nitrous acid (HONO) might also be a substantial N_r source and may contribute up to 50% of N_r release of soils in some cases.

Oxidized nitrogen emissions

Nitric oxide (NO) and nitrous oxide (N_2O) emissions from soils have been studied extensively because of strong similarities in their production and emission processes. Both gases, are generally produced by the same processes, however the detailed ratios are not yet very well understood (Pilegaard 2013). Various pathways of microbial nitrification and denitrification, as well as abiotic chemical decomposition can lead to formation of NO and N_2O. For more details on NO and N_2O producing processes see Butterbach-Bahl et al. (2013) and Pilegaard (2013). Firestone & Davidson (1989) introduced a conceptual model which describes NO and N_2O production by two factors: (1) the N-flux

through the “pipes” (nitrification and denitrification) and (2) the amount of N-trace gases “leaking” these pipes through holes of different sizes. This model, now known as the “Hole-in-the-pipe” model (Davidson et al. 2000), couples the two gases through their common processes of production and consumption. So basically determining the rate of gas production on the amount of available substrates for nitrification (ammonium) and denitrification (nitrate), respectively and other (abiotic) factors, like moisture, pH and O_2 presence (Firestone & Davidson 1989). Similarly to nitric oxide emissions, agricultural soils, influenced by fertilization, and natural soils are the main global sources of nitrous oxide (N_2O) emissions. The dominant processes are related to nitrification and denitrification processes in soils, which account for about 70 % of global emissions (Syakila & Kroeze 2011).

Nitric oxide and nitrogen dioxide have a large influence on the distribution of ozone in atmospheric chemistry. NO and NO_2 (NO_x) catalyze the decomposition of O_3 in the stratosphere, where at lower altitudes nitric oxide supports the formation of ozone through catalytic reactions (Crutzen 1979). In the troposphere nitric oxide reacts rapidly and therefore NO_x emitted from the earth’s surface does not reach the stratosphere. NO_x catalyzes photochemical tropospheric ozone production and usually leaves atmosphere as its principal end product of HNO_3 incorporated in wet or dry deposition (Williams et al. 1992). Furthermore NO may influence oxidizing capacity of the atmosphere by directly affecting the formation of OH (Steinkamp et al. 2009). Nitrous oxide (N_2O) is a very important potent greenhouse gas in the troposphere by itself with a calculated global warming potential 298 times that of CO_2 over 100 year (Forster et al 2007, IPCC). In the stratosphere N_2O is responsible for the decomposition of ozone and is considered the most important O_3 depleting substance in the atmosphere (Ravishankara et al. 2009).

Furthermore, deposition of N_y (all oxidized forms of nitrogen except for N_2O) has substantial effects, especially on semi-natural ecosystems (Galloway et al. 2003). In general N_r-input can lead to fertilization of sensitive ecosystems, subsequent eutrophication and loss of biodiversity (Erisman et al. 2008). Addition of N_r can in return lead to higher emissions of NO and N_2O and higher leaching to aquatic systems, especially as NO_3^- (Galloway et al. 2003). Sutton et al. (2011) estimates that emissions of NH_3 and NO_x have reduced forest diversity over two-thirds of Europe by 10 %.

Reduced nitrogen emission

Ammonia (NH_3) is the most abundant alkaline molecule of the atmosphere and one of the most important atmospheric pollutants (Singh et al. 2001). Through the reaction of NH_3 to NH_4^+(collectively termed NH_x), ammonia is a major component of atmospheric aerosols and precipitation. It can lead to the eutrophication of sensitive ecosystems, acidification of soils (Asman et al. 1998) and can have various impacts on human health (Townsend et al. 2003)

Ammonia emissions from the biosphere to the atmosphere depend on the difference in surface concentration compared to the overlying air's concentration. Emissions will usually occur at higher NH_4^+ concentrations at alkaline pH, as is the case after fertilizer or manure application respectively (Asman et al. 1998). Furthermore atmospheric turbulences stimulate convective mixing and generally favor NH_3 volatilization (Flechard et al. 2013). Ammonia flux is bi-directional and plants, soils and litter can essentially be a net source or sink depending on their nitrogen status through N_r input to the ecosystem (Massad et al. 2010).

Atmospheric turbulences through unstable conditions generally favor NH_3 volatilization (Flechard et al. 2013). Moreover, ammonia is the most abundant alkaline molecule of the atmosphere and thus is involved in a wide range of interactions with various substances in ecosystems and the atmosphere (Asman et al. 1998). NH_3 neutralizes a substantial part of acids in the atmosphere formed by the oxidation of SO_2 and NO_x. As a result of these processes aerosols are formed, with negative effects on human health (Townsend et al. 2003) and considerable impact on radiative forcing and visibility (Adams et al. 2001). Reduced nitrogen can be deposited in wet and dry forms; Dry gaseous NH_3 and particulate NH_4^+ is depositing on surfaces which is most important close to its emission source, whereas wet deposition of NH_4^+ in water droplets, is more important further away of its sources (Sheppard et al. 2011). NH_3 and NH_4^+ (NH_x) are valuable nutrients, but excessive deposition to sensitive ecosystems, like ombotrophic bogs, can lead to a species shift towards more neutrophile plant species and rapid carbon loss (Bragazza et al. 2006, Sutton et al. 2011). Dry deposition of ammonia promotes species change faster than wet deposition through direct leaf uptake (Sheppard et al. 2011). The deposition of NH_x to soils can lead to formation of nitric acid and consequently acidification of soils. Major nitrogen deposition is not only caused by NH_x but also by oxidized forms of N_r (Asman et al. 1998).

Ammonia exchange is bi-directional, which means unlike many other gases (e.g. O_3, SO_2) it can be emitted by, as well as deposited on plants and soils, which has only recently been included in

resistance models (Nemitz et al. 2000). Knowledge is lacking about bi-directional ammonia exchange to fully understand biogeochemical feedback mechanisms and their climatic impacts (Hansen et al. 2013). Data on natural NH_3 emissions is lacking, especially for bare soils and litter (Massad et al. 2010). Hansen et al. (2013) measured ammonia fluxes over a deciduous forest in Sweden and observed that flux rates change from a net uptake to net emissions after litter fall expecting soil and litter as the main sources.

The vital role of ammonia in many environmental problems is recently becoming more and more recognized and is seen as one of the major environmental concerns of the 21st century (Erisman et al. 2007, Sutton et al. 2011).

Litter decomposition

Litter decomposition is the counterpart of photosynthesis in terrestrial ecosystems. Together they can be considered as most important ecosystem processes. For various reasons, however, the process of decomposition is less well understood than that of photosynthesis. In principle, decomposition makes organically bound nutrients available again to plants and microorganisms and is thus closely associated with nutrient cycling. On the other hand, decomposition also transforms fresh litter into more recalcitrant forms, i.e. humus, influences soil fertility and long-term carbon storage (Berg & McClaugherty 2014).

The main drivers of litter decomposition are climatic factors and substrate quality (i.e. chemistry) (Meentemeyer 1978). For several decades researchers have looked for general patterns of litter decomposition and worked on developing models to predict mass loss rates of different litter types around the planet (Meentemeyer 1978, Zhang et al. 2008, Prescott 2005, 2010). On a global scale the most direct regulator is considered to be the litter quality (chemistry) (Zhang et al. 2008). Even though this idea is controversial in many cases, it is the predominant paradigm today (Prescott 1995, Brandstätter et al. 2013, Berg und McClaugherty 2014). By knowing the initial chemical composition of plant litter and its chemical transformations it will undergo, it is possible to predict mass-loss rate changes also for later stages of decomposition (Prescott 2010, Berg und McClaugherty 2014). Higher initial N content has been shown to accelerate decomposition, due to a smaller difference in C:N ratio at which decomposer-microbes need to immobilize less carbon in relation to nitrogen (Aber et al. 1991). According to Brandstätter et al. (2013) the importance of early stage litter decomposition dynamics has been commonly overlooked, even though more and more studies have focused on this topic in recent years (Prescott 2010).

Carbon and Nitrogen pulses after rewetting of dry soils

Several changes of the Earth's climate will affect humans in the future. While the Earth will continue spinning under new circumstances, humans will have to adapt to several new challenges and measures are being taken around the globe (Field et al. 2014, IPCC). Over 30% of the global landmass is considered to be in arid climate zones (Peel et al. 2007) and in a warming world, extreme weather events like drought- and heat-waves are expected to increase (Seager et al. 2007, Rahmstorf und Coumou 2011). Therefore also soils in many ecosystems will undergo drought and rewetting cycles more often and it is thus very important to understand ecosystem responses and formulate detailed models for future predictions and planning. The central role of litter decomposition in nutrient cycling and gas emissions, makes the understanding of the underlying processes urgent (Prescott 2010).

Rapid C and N mineralization after wetting of soils has often been observed and has been termed as "Birch Effect" after a classic publication of H. F. Birch (Birch 1958, Jarvis et al. 2007). The Birch effect has been intensively investigated ever since, and pulses of C and N emission peaking shortly after wetting have been observed in many ecosystems (Pulleman und Tietema 1999; McCalley und Sparks 2008). A reason for gas pulses was long believed to be the sudden release of osmolytic substances accumulated by microbes to combat drought stress (Schimel et al. 2007, Borken and Matzner 2008). However, Boot et al. (2013) have recently shown that the observed excretion of solutes in pure cultures might not be relevant in situ.

Motivation for the study

N containing trace gases have various effects on ecosystems and the atmosphere. Understanding the mechanisms and dynamics of the nitrogen cycle are not only vital for the understanding of ecosystem processes, but also to tackle future challenges in nutrition, pollution and climate change issues (Galloway 2003). To develop more detailed ecosystem models, high resolution litter emission data need to be included and data, especially for ammonia, are still rare (Massad et al. 2010). Although it is known that leaf litter contributes to NH_3 emissions (Nemitz et al. 2000, Hansen et al. 2013), due to a very limited number of studies, those emissions remain poorly understood and request further assessment (Massad et al. 2010). Emissions of plant litter from semi-natural ecosystems and forests remain almost unquantified, but are likely to depend on litter N content (Asman et al. 1998, Massad et al. 2010). A major part of this thesis was the construction of an

incubation device that, attached to an ammonia analyzer (Picarro G2103 CRDS), can reliably measure NH_3 emitted from leaf litter and soil samples, comparable to those of forests and semi-natural ecosystems. The detection of changes in mixing ratios in the range of 0.1 ppb from litter samples, as well as undisturbed soil cores, was our goal. After the incubation device was conceptualized and built at the Institute of Soil Research, at Boku Vienna and it had to be subsequently tested and used for first experiments. Uncertainties in emissions of reduced nitrogen had to be determined.

After the setup and testing of the new NH_3 – measurement device, two experiments have been conducted: (1) To examine the influence of different moisture levels on beech litter emissions of NH_3, NO and N_2O (2) to assess the effects of drying-rewetting on gas emissions from beech litter.

The following research questions were formulated:

1. What are challenges of incubation experiments for NH_3 measurements?
2. Are there detectable NH_3 emissions from beech litter samples?
3. What are the effects of different N contents (C:N ratio) and moisture levels on N gas emissions after a drought?
4. Is there a temporal emission cascade of beech litter emissions: from NH_3 to NO to N_2O?

Material & Methods

Sampling Sites

For the incubation experiments aiming at measuring NH_3, NO, N_2O and CO_2 emissions during early stages of litter decomposition beech litter samples (*Fagus sylvatica L.)* were collected in fall of 2008 at two Austrian deciduous forests sites: Ort, Gmunden, Upper Austria (OR) and Schottenwald, Vienna (SW). Ort is situated in a rural area with low pollution (atmospheric deposition), whereas Schottenwald is situated in Vienna with higher deposition from the city (Tab. 1). Samples were stored indoors at room temperature (~20°C) and dry litter was shredded to 0.5 – 1 cm². The shredded litter was then used for incubation experiments, determination of $NH_4^+$and NO_3^- concentrations as well as pH and water contents. The sites and samples were further specified by Kitzler et al. (2006), Wanek et al. (2010) and Schneider et al. (2012).

Experimental Set-up

Experiment 1 and 2 were conducted in spring of 2015 to improve our understanding of gas emissions during early stage litter decomposition: (1) The effects of litter stoichiometry and moisture on ammonia (NH_3), nitrous oxide (N_2O) and nitric oxide (NO) emissions were investigated during the incubation of two litter types, SW and OR, with different C:N ratios. The analyzed moisture contents were 20 w/w% and 80 w/w%. (2) Litter from site SW was used to investigate the effects of repeated short-term drought and rewetting cycles on NH_3, NO, N_2O and CO_2 emissions of beech litter with constant C:N stoichiometry.

Experiment 1 aimed at determining the moisture effects on gas emissions from decomposing beech litter with different C:N ratios. Litter samples from Schottenwald (SW) and Ort (OR) were rewetted (biologically activated) with deionized water to moisture levels of 20 w/w % and 80 w/w %, respectively, before incubation. Afterwards samples were incubated under stable temperature conditions in an air –conditioned laboratory at about 20°C for at least 80 hours with no additional water added. After the incubations, inorganic N concentrations in the form of NO3- and NH4+, as well as pH and water content of the samples were determined. Gas samples for N2O measurements were taken one hour after initial wetting and at the end of the incubation periods, i.e. two times per sample.

Experiment 2 was conducted to assess effects of drying-rewetting cycles on gas emissions from beech litter. Effects of extreme weather events on NH_3, NO, N_2O and CO_2 emissions were simulated by repeated drying and rewetting events. A stored litter sample (SW) was wetted (biologically activated) with deionized water to a moisture level of 60 w/w % H_2O and incubated for about 250 hours. After drying out for 72h, the samples were rewetted by adding 13ml of deionized water i.e. the same amount of water that has been added to adjust the water content to 60 w/w %. These drying-rewetting cycles were conducted three times. Gas samples for N_2O measurements were taken one hour after each rewetting-event and at the end of drying periods (in total six times).

DEMON - Device for soil **E**mission **M**easurements **O**f reduced **N**itrogen

To determine NH_3 fluxes, a customized device was built to efficiently measure low concentrations of ammonia emissions from soil cores and plant-litter samples: **D**evice for soil **E**mission **M**easurements **O**f reduced **N**itrogen (**DEMON**). The device was designed after a concept of Holtermann (1996) and Schindlbacher et al. (2004). The system essentially consists of six sample-holding chambers and a valve chamber attached to a Picarro G2103 CRDS NH_3/H_2O Analyzer (Fig. 2). The Picarro G2103 Analyzer is a field and laboratory deployable using cavity ring-down spectroscopy (CRDS) for measurements and is capable of parts-per-billion sensitivity.

Certain material requirements had to be met for NH_3 measurements due to the nature of this chemical compound. Ammonia is a highly polar molecule with a subtantial dipole moment resulting from the N-H bonds and its geometrical structure. The nitrogen atom on the peak of a pyramidal configuration with the hydrogen atoms at the base makes ammonia highly adsorbable to various surfaces (Appl 1999). Therefore Polytetrafluoroethylene (PTFE) was used for all parts of the system in direct contact with ammonia to minimize adsorption effects. PTFE is a polymere with high chemical stability and few reaction sites. However, adsorption of ammonia can still not entirely be ruled out (Kosmulski 2001, Mukhtar et al. 2001). Nevertheless, differences of less than one ppbv of emissions could be detected, thus confirming the high sensitivity of our device.

Incubation chambers were entirely made out of PTFE with a gas inlet and outlet on top. Gas-tight rubber septa were installed on top of the chamber, for adding or extracting liquids or removing gas-samples from the headspace using a syringe. The incubation chambers had an inner volume of 372.7 cm^3 and cylindrical shape (Fig. 2b). Compressed air was used as a carrier gas for emissions in this system. It is distributed to all six chambers, to flush head-spaces and subsequently to transport the

samples' emissions towards the valve chamber. There, emissions of one sample at a time were directed to the ammonia analyzer via a system of 12 valves. These valves were aligned in two parallel rows of six valves each, controlled by the integrated valve-sequencer of the Picarro G2103 CRDS NH_3/H_2O analyzer. If one valve of the top row was open to direct the flux from one chamber to the analyzer, its counterpart beneath was closed and vice versa. This meant that the gas flow of only one incubation chamber at a time was directed to the analyzer, while the flow of the other five chambers was released in the ambient air through the open valves in the bottom row. During the whole measurement period gas flows through the headspaces of the incubation chambers were never interrupted, thus minimizing the buildup of concentration gradients. Like the tubes channeling the gas, also the upper row of valves in touch with gas were composed of PTFE to avoid as much surface interaction of the device with ammonia as possible.

Nitric oxide - and carbon dioxide - flux measurements

NO and CO_2 emissions measurements were conducted in chamber incubation experiments with another fully automated measuring system based on a system by Holtermann (1996) and Schindlbacher et al. (2004). Litter samples were put in modified Kilner jars (Kilner, UK) of a volume of 685 cm^3 each and incubated in the dark for the various experiments (see 2.2.). Emissions were analyzed in an open flow set-up where gas flows were diverted by a Teflon valve system to two analyzers. A PP SYSTEMS WMA-2 (Amesbury, MA, USA) infrared analyzer was used to measure CO_2 emissions, a HORIBA APNA-360 (Kyoto, Japan) chemo luminescence NO_x analyzer was used to determine NO emissions. The incubation system consisted of 22 sample chambers assembled in two rows and two ambient air reference chambers (one on each row) to measure background concentrations of the target gases. The jars were placed in a temperature controlled closet and were connected to the analyzers by PTFE tubes of 5mm in diameter. The closet was flushed with compressed air at a rate of 1 l min^{-1} to maintain ambient air pressure. 6 min of measurements for samples and 4 min for reference chambers were shown to be sufficient for chambers to reach steady state concentrations (Schindlbacher et al. 2004). Measurements of sample chambers were followed by measurements of a reference chamber. The first third of measured values of each chamber were excluded to correct for possible gas accumulation within the chambers. For flux calculations, raw data from the analyzers for CO_2, NO, and NH_3 were obtained as mixing ratios in the sample chambers' headspaces (ppb). Those values were then further transformed to fluxes as described by Schindlbacher et al. (2004) to determine net flux in µg N m^{-2} h^{-1} (F) (see Formula 1).

$$F = \left(C_{eq} - C_0\right) * \frac{M * Q * 10^3}{V_m * A * 10^6} * 60$$

Formula 1: A formula for flux calculations from mixing ratios for "open flow" incubation experiments (Schindlbacher et al. 2004).

M stands for the relative atomic mass of the element of interest (N = 14.008 g mol^{-1}), V_m indicates the molar volume of a standard gas (24.055 10^{-3} m^3 mol^{-1}), C_{eq} is the equilibrated (steady state) mixing ratio of the gas under investigation in a chamber (ppb/Volume = 10^{-9} m^{-3}), C_0 is the ambient air mixing ratio of the gas measured through a reference chamber (blank), Q demonstrates the mass flow rate of air going through a chamber (~0.0015 m^3 min^{-1}), and A is the field surface area of the incubated sample 0.02 m^2 (calculated after Kitzler et al., 2006).

Nitrous oxide - flux measurements

For N_2O measurements, sample chambers were opened and flushed with synthetic air to avoid gas accumulation on the bottom of incubation chambers. Subsequently, the chambers were closed with rubber septa on one side and on the other side with a closable valve on each PTFE tube (see Schindlbacher et al. 2004 for details). After closing the jars, gas samples were taken with a gas tight glass-syringe at 0, 10, 20 and 30 minutes. The samples were transferred to 10ml pre-evacuated gas tight glass-vials and afterwards analyzed with a gas chromatography system (Agilent 6890N, Agilent, Santa Clara, California, USA) connected to an automatic headspace sampler (Agilent 7697A, Agilent, Santa Clara, California, USA) and detected by a ^{63}Ni electron capture detector (ECD) (detector temperature: 350°C). For more details on the Gas chromatography system used, see Gritsch et al. (2015). This technique has shown to produce reliable N_2O flux measurements for forest soils (Zechmeister-Boltenstern et al. 2002). Fluxes were determined as positive or negative by linear regression, if slopes were significantly different from zero ($p < 0.1$).

Ammonium and nitrate determination and pH - measurements

Shredded litter samples were extracted in 1 M KCl solution in a 1:20 w/v ratio and filtered through

Whatman cellulose filter paper. Ammonium concentrations were determined photometrically via Berthelot reaction (Schinner et al. (1996), n=4). Nitrate concentrations were determined photometrically with the vanadium chloride method (Hood-Nowotny et al. (2010), n=4). Absorbances of reaction products were determined with a plate reader photometer (PerkinElmer 2300 EnSpire, PerkinElmer, Whatham , MA, USA) at wavelengths of 660 nm for NH_4^+-N and 540 nm for NO_3^--N.

The potential acidity (pH) of the litter was determined in 1 M KCl-solution with a WTW InoLab pH level 2 pH - meter. The pH-meter was calibrated with a pH 4 and a pH 7 solution before analyses.

Results

A customized device was built with the aim to sensitively measure ambient ammonia concentrations and NH_3 emitted from soil cores and plant-litter samples. The design was made after a concept of Holtermann (1996) and Schindlbacher et al. (2004) (Fig. 2). After completing the construction, the device was tested with litter samples of different origins to see if small emission differences (< 0.1 ppb) could be detected. Initial test runs showed distinctions of very small differences in ammonia mixing ratios with very quick responses. The device showed a response within a few seconds to changes in ammonia concentrations as well as changes of sample chambers (attachment Fig. 1).

Furthermore two experiments were conducted to assess early stage beech litter ammonia emissions upon wetting. We used two types of litter samples from two different sites. Carbon (C) and Nitrogen (N) content of the litter samples were analyzed by Keiblinger et al. (2012). Both the sample SW and OR had the exact same C content (47.61%), however the N content of the litter varied and thus the C:N ratios (Table 2). SW had a C:N ratio of 52.02 (±2.22) as compared to 46.25 (±2.38) for OR. The inorganic N nutrients NO_3^- and NH_4^+ were in similar range for SW and OR (Table 2). NO_3^- concentrations showed no difference for OR with 0.22 (±0.02) µg g^{-1} dm as compared to 0.11 (±0.09) µg g^{-1} dm in SW, whereas NH_4^+ was slightly higher in SW with 52.01 (±2.22) µg g^{-1} dm as compared to 46.25 (±2.38) µg g^{-1} dm in OR. The moisture levels of samples SW and OR were around 9 w/w % and the pH around 5 (± 0.02).

Sudden pulses of gas emissions after wetting have been well documented for soils, but litter responses are less well known. Therefore we conducted Experiment 1: Moisture effects on gas emissions of beech litter with different C:N ratios. Periodic wetting of arid and semi-arid ecosystems might account for higher nutrient turnover and higher cumulative N gas release than constant moisture levels. Our interest were the gas dynamics of drying and rewetting cycles and the influence of and progression of NH_3, NO and N_2O releases, which we investigated in Experiment 2: Effects of short cycles of drying-rewetting on ammonia, nitric oxide and nitrous oxide emissions of beech litter.

Ammonia - emissions

Interestingly all samples produced considerable NH_3 emissions. Samples from Schottenwald with different water concentrations (i.e. SW 20 and SW 80) showed higher NH_3 emissions from the start to the end of the experiment, compared to samples OR 20 and OR 80. Water vapor emissions showed

the same pattern as NH_3 - emissions (Fig. 3). Emissions showed diurnal dynamics, where water emission peaks seemed to follow peaks of NH_3. The observed diurnal dynamics showed peaks during daytime, with dynamics more strongly developed in the samples with higher moisture levels (SW 80 and OR 80). In Experiment 2 with three consecutive wetting and drying cycles, NH_3 emissions were highest right after the initial wetting to 60 w/w % (SW 60) with about 7 µg NH_3 - N m^{-2} h^{-1} and were then decreasing continuously in periodic day and night cycles (Fig. 4). The course of temperature measured at a later time point showed major diurnal temperature variations in the incubation chambers with peaks during daytime due to direct sun irradiation (see attachment). Three wetting events (one initial wetting and two rewetting events) and three drought cycles, respectively, are indicated by the large water peaks on the bottom more curve in figure 4. Ammonia values seemed to show an immediate increase at initial wetting and to the wetting after the first drought phase. The third wetting had no clear effect on ammonia emission increase. In general ammonia emissions stayed rather constant after Rewetting 1 with cyclic highs and lows in diurnal intervals. Whether water pulses have a clear enhancing impact on microbial induced NH_3 emissions remains to be clarified. Cumulative ammonia emissions showed SW 60 and SW 80 to have highest cumulative emissions, with values after 80 hours with 380 µg NH_3 - N m^{-2} and 350 µg NH_3 - N m^{-2}. Cumulative emissions continued to rise for SW 60 (Experiment 2) and summed up to a total of 967 µg NH_3 - N m^{-2} after 250 hours, where wetting and drying presented no noticeable effects. SW 20 and OR 80 had almost the same course of cumulative emissions, which ended also in almost the same total emissions of 236 µg NH_3 - N m^{-2} for SW 20 and 204 µg NH_3 - N m^{-2} for OR 80 which with shorter incubation time due to technical reasons. Lowest total emissions were observed for OR 20 with 103 µg NH_3 - N m^{-2} (Fig 5). Average emissions rates followed cumulative fluxes with lowest rates for OR 20 around 1 µg NH_3 - N m^{-2} h^{-1}, followed by SW 20 and OR 80 with ~3 µg NH_3 - N m^{-2} h^{-1} and SW60 and SW 80 with ~4 µg NH_3 - N m^{-2} h^{-1} (Fig. 8 a). Interestingly NH_3 average flux rates from SW 60 (Experiment 2) are highest together with SW 80.

Nitric oxide - & carbon dioxide - emissions

Nitric oxide (NO) emissions started off highest and decreased for all samples alike. SW 80 and OR 80 seemed to reach zero emissions a bit earlier than the drier samples (SW 20 and OR 20) (Fig. 6b). The same pattern as in Experiment 1 was observed for NO emissions of incubations from Experiment 2 (SW). Nitric oxide emissions started off highest with about 17 µg NO - N m^{-2} h^{-1} and decreased linearly until stopping around 80h. Surprisingly drying and rewetting had no effects on NO emissions

(Fig. 7b). Cumulative NO emissions showed the same pattern for all samples and could not really be distinguished, as there was hardly any activity after 80 hours of incubation (Fig. 9b). This is confirmed by the average emission rates (Fig. 8b). SW 20, SW 80, OR 20 and OR 80 showed the same average hourly flux of around 6 µg NO - N m^{-2} h^{-1}, whereas SW showed a lower average flux because of hardly any addition after 80 hours (Fig. 8b) .

CO_2 emissions started after 24h for the two moister samples (80 w/w % H_2O). Emissions peaked at 580 µg CO_2 - C m^{-2} h^{-1} for OR 80 and about 550 µg CO_2 - C m^{-2} h^{-1} for SW 80 respectively and decreased afterwards, first for OR 80 and about 10 hours later for SW 80 as well. In the first 24 hours of measurements no activity was observed in all samples. Where this changed with exponential increase for SW 80 and OR 80 as well as SW 60, dryer samples SW 20 and OR 20 showed no CO2 emissions over the whole period of measurements (Fig. 6a & Fig. 7a). CO_2 emissions showed similar patterns for SW 60 as observed for moister samples in Experiment 1 (SW80 and OR 80) (Fig. 7 a), but lower in magnitude. For SW 60, CO_2 emissions started to increase exponentially after a lag phase of about 24 hours and peaked after about 70 hours, before decreasing. Rewetting boosted CO_2 emissions again shortly, before decreasing again until the next rewetting event. Rewetting events are signaled by gaps in the curve due to N_2O sampling by closed chamber method (see Material & Methods) and wetting with a syringe. The third drought cycle showed decreased emissions again but in small periodic cycles (Fig. 7a). Cumulative CO_2 emissions displayed almost identical total emissions for SW 80 and OR 80 of 21985 and 21879 µg CO_2 - C m^{-2}, respectively and cumulative emissions increased linearly from 50 hours for SW 60. Average flux rates were the same around 250 µg CO_2 - C m^{-2} h^{-1} for SW 80 and OR 80, where SW 60 showed clearly lower average CO_2 emissions with 67.12 (±9.53) µg CO_2-C m^{-2} h^{-1} (Fig. 8 c).

Nitrous oxide - flux

Nitrous oxide fluxes were determined by the closed - chamber method. In Experiment 1 there was an initial wetting event and then a subsequent drying period for about 80 hours; N_2O samples were taken an hour after wetting and at the end of incubations. Experiment 2 featured repeated wetting and drying cycles. After initial wetting there were no clear N_2O uptakes or emissions detected for none of the samples in Experiment 1 (SW 20, SW 80, OR 20 and OR 80) and Experiment 2 (SW 60) (Fig. 11 a & b). However 80 hours later, all samples from Experiment 1 showed a clear N_2O uptake of

~ 15 µg N_2O-N m^{-2} h^{-1} for SW 20, ~ 10 µg N_2O-N m^{-2} h^{-1} for SW 80 and OR 20 and ~ 5 µg N_2O-N m^{-2} h^{-1} for OR 80 (Fig. 11 a). A less clear picture was found in Experiment 2, where in contrast slight emissions of ~5 µg N_2O-N m^{-2} h^{-1} at the end of drying circle 1 were observed (Fig. 11 b). Uptake of N_2O increased after second wetting and emissions decreased at the end of the drying Cycle 2 compared to Cycle 1. This trend continued for Cycle 3 (Fig. 11 a).

Litter data

Litter nitrate disappeared completely during Experiment 1 as compared to already low initial values (SW 0.11 and OR 0.33 µg NO_3^--N g^{-1} dm, Table 2). Ammonium values decreased considerably for all samples, especially SW 80 in ammonia measurements. An exception was OR 80 in NO/CO_2 incubations, but could also be due to measurements uncertainties. Moister litter samples (i.e. SW 80 and OR 80) showed a tendency for slightly higher pH in NH_3 incubations, whereas overall pH stayed roughly the same (Table 3).

Samples incubated in the NH_3 measuring device dried out more strongly during incubations in the DEMON than during NO/CO_2 incubations (Tables 3 & 4). The pH values showed a slight tendency of decrease for samples of the NO/CO_2 incubation device, whereas nitrate concentrations increased slightly from 0.11 (± 0.09) µg NO_3^--N g^{-1}, to 0.53 (±0.05) µg NO_3^--N g^{-1} dm for NH_3 incubations (Table 4). NH_4^+-N decreased from 22.70 (±2.84) µg g^{-1} dm, to 8.18 (± 0.86) µg g^{-1} dm for NH_3 incubations and 1.79 (±0.37) µg g^{-1} dm during Experiment 2.

Discussion

In this study, I describe gaseous emissions of NH_3, CO_2 and NO during the early phase of leaf litter decomposition from open-flow chamber incubation experiments. Emissions of CO_2 and NO were measured with a system previously described by Gritsch et al. (2015) and based on Schindlbacher et al. (2004). In addition, we present here, to our knowledge, for the first time results of NH_3 emissions from decomposing leaf litter using a new device (see Material & Methods). The **D**evice for soil **E**mission **M**easurements **O**f reduced **N**itrogen (**DEMON**) showed quick responses within seconds even to very small changes in ammonia mixing ratios (see attachment Fig. 1). Due to the construction of the sample incubation chambers, samples were exposed to relatively high headspace airflows of about 1.5 standard liters per minute (slm) which contributed to the drying of the samples. Even though samples in the NO_x/CO_2-incubation device were exposed to air flows of similar magnitude (~1 slm), samples showed higher moisture after incubation (Table 3). The reason behind this difference in sample drying is most likely due to the use of compressed air which is actively supplied (blown in) to the sample chambers to transport NH_3 emissions to the analyzer. This procedure is more invasive than the passive air supply of the device for NO/CO_2 measurements, which is regaining air through the under pressure created by the pumps of the measuring devices (see Material & Methods). It is known that wind speed strongly affects ammonia volatilization (Flechard et al. 2013). Similarly, Hansen et al. (2013) reported high NH_3 emissions over a deciduous forest in Sweden and concluded friction velocity to be the main factor influencing NH_3 emissions. Besides atmospheric turbulences, ammonia volatilization is highly sensitive to climatic factors such as, precipitation, temperature and radiation (Flechard et al 2013). Thus, these factors need to be as tightly controlled as possible.

Fungal succession during incubation experiments

Litter samples were stored indoors under dry conditions. At moisture levels of less than 10 %, leaves were still intact and degradation was likely put on hold (Prescott 2010). A study conducted by (Schneider et al. 2012) investigated the metaproteome and the enzymatic activity of microorganisms responsible for the decomposition of beech litter from the same study sites (Schottenwald, SW and Ort, OR). Their study showed that cellulolytic enzymes were exclusively produced by fungi. *Ascomycota* was the most abundant phylum that also produced most of the cellulolytic enzymes especially in the early stage of decomposition, whereas only a small fraction of detected proteins originated from *Basidiomycota* and *Mucoromycotina*, respectively (Schneider et al. 2012). The three phase decomposition model as described in Berg and McClaugherty (2014) suggests an early phase

(Phase 1) of decomposition which is regulated by nutrient availability and readily available carbon. In this early phase high levels of nutrients stimulate degradation of cellulose and hemicellulose whereas more recalcitrant substances like lignin and holocellulose are then degraded at a later stage (Phase 2). *Zygomycetes*, also called sugar fungi, are among the first fungal colonizers as they are adapted to degrade soluble compounds and cellulose. *Ascomycetes* and *Basidiomycetes* follow later in succession as they are capable of degrading more recalcitrant substances (e.g. lignin). *Mucoromycotina* are representatives of *Zygomycetes* and were found on the litter of SW and OR by (Schneider et al. 2012), with their number decreasing over time, while the biomass of *Ascomycetes* increased. Because of the relatively short period of our experiment, we assume that decomposition processes observed were part of Phase 1 of decomposition with *Mucoromycotina* and *Ascomycetes* being the main degraders. In the initial phase of decomposition the microbial communities already present on the leaf surfaces are most prominent on the litter until soil organisms become more and more dominant in later stages (Torres et al. 2005).

Drying-rewetting cycles impose physiological stress on microbial communities during incubation experiments

Water potential is essential for soil microorganisms. As they live closely in touch with water films, they need to control the water household through their membranes. To cope with stress phases like droughts, microorganisms need to deal with hyperosmotic conditions (Harris 1981). While microorganisms in pure culture may react by dehydration and the accumulation of osmotically active substances, recent findings by Boot et al. (2013) suggest that *in situ* microbes are more likely to endure droughts in dormant stages. The wetting of dry soils and litter increases microbial activity within minutes to hours (Borken & Matzner 2008). Dead cells may get hydrated and subsequently lysed after diffusive inflow of water thus presenting a new pool of readily available C and N to get metabolized by other organisms (Schimel et al 2007, Borken & Matzner 2008). The lysed cells therefore present pools of easy available substrate which may trigger a sudden response of surviving microorganisms. Moreover aggregates may be broken up which makes easily decomposable C accessible for microbial exo-enzymes (Schimel et al. 2007).

Dry storage of our beech litter samples halted microbial activity. The asserted moisture level of an average of 9.3 w/w % (Table 2) is well beneath the threshold for decomposing activity of 30 % moisture suggested by Prescott (2010). Therefore decomposition is believed to have been put on hold and the remaining microbial community either dead or dormant (Boot et al. 2013).

Microorganisms show various adaptations to endure long periods of unfavorable conditions like droughts, especially fungi have been found to remain dormant for decades (Atlas & Bartha, 1998).

Even though the accumulation of N containing solutes as a mechanism to combat drought stress and the subsequent release after wetting is a well-known microbial response, they have usually been observed in vitro (Boot et al. 2013). Boot et al. (2013) have doubted this prevailing theory and found constant osmolyte concentrations in microbial biomass in a Californian grassland during seasonal drought. They concluded that microbes rather than using scarce resources may become dormant to combat drought stress.

Beech litter as ammonia - source

NH_3 emissions were observed in all incubations, starting immediately from the start of measurements. Ammonia emissions were in general higher from Schottenwald samples (SW 20 and SW 80, Fig. 3 a & b), which was partly expected due to higher initial NH_4^+ concentrations and differences in carbon to nitrogen ratios (C:N) because of higher N content of the leaves (SW 44.76 (±0.96), OR 66.18 (±1.12). The emission potential for the beech litter is primarily dependent on the bulk N content of the leaves. Leaves with high N content are more likely to release NH_4^+ through mineralization (Flechard et al. 2013). Differences in C:N ratios seemed to outweigh moisture effects in controlling ammonia volatilization. Emissions started off high and then gradually declined in all treatments. In Experiment 1, SW 80 showed a second emission peak after about 24 hours with emissions as high as at the start. This peak in NH_3 emissions matched the diurnal dynamic which was evident in all samples (Fig. 3 & 4). Most likely, the diurnal pattern was caused by temperature changes in the sample chambers. Diurnal variations of ammonia emissions, including maximum/minimum emissions during daytime as well as no diurnal effect, have been attributed to different reasons (Hansen et al. 2013) . Nevertheless, temperature has been proposed to be the main driver of diurnal patterns in NH_3 emissions (Flechard et al. 2013). NH_3 fluxes in our experiments, and partly also those of H_2O, showed diurnal dynamics with peaks during daytime and lows during night time. Temperature was measured in chambers after incubations and showed a high daily variability (higher temperatures during daytimes) in the (air-conditioned) laboratory (ø 22.32 °C ± 0.69) (see attachment Fig. 2). The large diurnal temperature differences are most probably the result of sun irradiation penetrating the glass-walls of the laboratory. Temperature, as one of the major controllers of gaseous NH_3 exchange, affects the equilibria of thermodynamic dissociation of

NH_4^+/NH_3 and the solubility of ammonia in water (Henry's law) (Farquhar 1980, Nemitz et al. 2001, Massad et al. 2010). Therefore, we stress that the lab temperature sensitivity needs to be taken more strictly controlled in future measurements. The diurnal dynamics are stronger for the moister samples (i.e. SW 80 & OR 80 and SW 60), where, for the aforementioned reasons, ammonia volatilization and solution are more strongly influenced. In Experiment 2 the aim was to observe influences of short-time drying and wetting cycles on NH_3 emissions. The observed stronger diurnal cycles of NH_3 emissions are expected to be due to stronger diurnal variations in temperature. Even though the outside temperature was generally higher during measurements for Experiment 1 (June 2015) as compared to Experiment 2 (May 2015) (Appendix Fig. 3 a & b), the day/night contrast is believed to be higher in Experiment 2 due to larger temperature fluctuations in the building. The influence of wetting events is not clear. At first Rewetting 1 seems to initiate an ammonia pulse, but the response is probably falling into a diurnal temperature cycle. Rewetting 2 is conforming this idea, as NH_3 rises before the water pulse sets in (Fig. 4).

Initial ammonia pulses are thought to result from the volatilization of accumulated NH_4^+ in the litter during drought, as well as of NH_4^+ from microbial origin released through the sudden change of osmotic potential and lysis of cells (Davidson et al. 1993, McCalley & Sparks 2008). The long prevailing theory of the active release of N containing solutes upon rewetting, accumulated by microbes to combat osmotic pressure during drought (Schimel et al. 2007), seems to be only relevant in pure cultures (Boot et al. 2013). However, N from intracellular solutes expelled by microbes are found after wetting (Fierer & Schimel 2002), so we believe this is mostly due to release of N containing solutes through cell lysis. It is uncertain if and when nitrification starts during our experiments. Substantial ammonia volatilization as observed in our experiments points against microbial nitrification in general, because findings of Praveen-Kumar & Aggarwal (1998) suggest either NH_3 volatilization or microbial nitrification occur at the same time, due to rapid microbial use of NH_4^+ if circumstances allow it. Cumulative NH_3 emissions presented SW 80 and SW 60 to have almost the same path with a slightly higher trend for SW 60, suggesting that an initial moisture level around 60 w/w % might be near an optimum for ammonia emissions. 80 w/w % is the moisture maximum for litter decomposition estimated in a meta-study by Prescott (2010).

Carbon dioxide - and nitric oxide - fluxes

CO_2 emissions started about 24 hours after wetting of the dry samples. This pulse of C mineralization indicated the start of heterotrophic respiration and thus the start of microbial heterotrophic activity.

The initial lag phase suggests that the initially present microbial community suffered from severe drought stress. In the first 20 hours of measurements (Fig. 6 a & 7 a), none of the samples showed any CO_2 emissions. This changed after about 24 hours when samples with higher moisture levels, SW 80 and OR 80 in Experiment 1 and SW 60 in Experiment 2, showed an exponential increase in CO_2 -emissions. SW 80 and OR 80 showed a CO_2-emission peak after about 60 hours, after which emissions declined and seemed to stabilize at the end of measurements. SW 60 in Experiment 2 showed a very similar pattern, although with a delay in peak emissions which was reached only after about 80 hours. Hart et al. (1994) suggested C availability to be an important control factor of N cycling and CO_2 –measurements a useful index of soil N cycling. Declining respiration rates correlated strongly with declining N mineralization rates and the initial nutrient pulse might slow down due to the decrease of easily decomposable material even under optimal moisture conditions (Hart et al. 1994).

No microbial activity was seen for both samples with the lower moisture level of 20 w/w% for the whole period of measurements (Fig. 1a). This was in accordance with threshold levels for litter decay of 30 – 80 w/w% suggested by Prescott (2010). Initial moisture levels of 20 w/w% were the constraining factors of decay and microbial activity, respectively, in this case, whereas an initial moisture level of 80w/w% was at the upper end of being a rate limiting factor. Further thresholds for decomposition of a mean annual temperature of 10°C and an AUR:N ratio of 40 were hypothesized by Prescott (2010) and were not a limiting issue in our experiments. SW and OR samples showed similar initial NH_4^+ concentrations with 52.01 (± 2.22) µg g^{-1} dm and 46.25 (± 2.38) µg g^{-1} dm, respectively, where the total C:N ratio was lower for samples from the SW site (Table 1). Nitrate concentrations were very low, 0.11 (± 0.09) for SW and 0.33 (± 0.02) for OR respectively, and showed no differences between the samples. Both sites showed very similar behavior for respiration and nitric oxide emissions. In general, there was neither a difference in the average CO_2 emission rates, nor in the total emissions between sites at the same moisture i.e. SW 20 & OR 20 and SW 80 and OR 80) (Fig. 8c & 9 b), suggesting that water was the main factor influencing decomposition rates. Also Gritsch et al. (2015) found a positive correlation of moisture levels and CO_2 – emissions in litter incubation experiments up until 90 w/w %. SW 60 had also a lower average emission rates than SW 80 and OR 80, as well as lower cumulative emissions, even though incubations lasted three times longer (Fig. 8 c & 9 b).

As seen in figures 6 b (Experiment 1) and 7 b (Experiment 2), NO emissions started with the beginning of measurements and showed the same pattern for both experiments. Since microbial

respiration started only after about 24 hours, these emissions are expected to occur either during nitrification through chemoautotrophic organisms or abiotic chemo-denitrification (Chapin et al. 2011, Paul 2015). However, chemoautotrophic microorganisms are considered to grow slowly which makes their immediate reaction improbable (Killham 1994). Furthermore, Pullemann & Tietema (1999) saw no quick increase in nitrification after wetting of litter even NH_4^+ being not limiting, emphasizing the slow response of autotrophic nitrifiers. Similarily, Praveen-Kumar & Aggarwal (1998) observed that either NH_3 volatilization or nitrification occurred at a time, meaning that if conditions are allowing nitrification to occur, ammonia emissions stopped soon, even if NH_4^+ was not limiting. We found NH_3-volatilization to occur (Fig. 3 & 4), which supports the assumption that immediate pulse of NO emissions is abiotic and caused by the chemical decomposition of accumulated inorganic nitrogen (mostly NO_2^-). The immediate release nitric oxide emissions could be due to the reduction of initially present nitrite, until it was used up or microbial nitrification set in (Pilegaard 2013, Butterbach-Bahl 2013). The chemical decomposition of nitrite (chemo denitrification) has been shown to be important under acidic conditions. NO_2^- could react with H^+ to form HNO_2, which can then either decompose under aqueous conditions or react with organic matter to form NO (Davidson 1992, McCalley & Sparks 2008). Interestingly Rewetting 1 & 2 in Experiment 2 had no effect on nitric oxide (NO) emissions (Fig. 7 b) for aforementioned reasons. Average flux rate did not differ in all incubated samples, but there was a trend for a slightly lower rate for SW 60 (Fig. 8 a).

Large pulses of NO emissions peaking within hours after wetting events have been well documented for soils in arid areas (Scholes et al.
1997(Scholes,M.C.,Martin,R.,Scholes,R.J.,Parsons,D.,&Winstead,E.Ç, Austin et al. 2004). It is thought, that the accumulation of nitrogen during drought and the inability of microbes to use nutrients effectively during the first few days after the wetting pulse contribute to this pulse emissions (Scholes et al. 1997). The release of labile C following cell lysis as well as the sudden release of protective solutes from osmotically stressed cells are both expected to be the main reasons for the immediate mineralization pulse of C and N. Contrasting evidence, however, comes from Boot et al. (2013) who quantified the release of osmotically active substances after wetting events by microorganism and saw now significant increases of those pools after drought periods. These findings are in stark contrast to the prevailing ideas for drought combatting from microorganisms through uptake of osmolytes to endure dry phases and subsequent release of osmotically active substances after rewetting (Schimel et al. 2007, Borken & Matzner 2008). Previous studies have

shown the release of solutes from microorganisms after wetting pulses, however those were mostly conducted in pure cultures and could have posed different circumstances and pressures on microbes and be less relevant for natural environments (Boot et al. 2013).

Nitrous oxide - fluxes

N_2O can be produced by the same processes as nitric oxides including microbial nitrification and denitrification as well as by a range of abiotic mechanisms, where higher moisture levels (i.e. lower O_2 diffusion) with an optimum at 70-80% favor N_2O emissions (Davidson et al. 2000, Butterbach-Bahl et al. 2013). After wetting there is a general trend to increased N_2O emissions in field and laboratory measurements. However, responses can be small and may not outweigh reduced emissions during the dry period (Kim et al. 2012).

We observed a clear nitrous oxide uptake at the end of the incubation periods in Experiment 1 regardless of litter type and moisture (Fig. 11 a). At the end of incubations, samples were expected to be well aerated. This matches the assumption that N_2O emissions are more likely to occur under low oxygen levels and also obligatory low oxygen concentration for microbial denitrification to occur (Paul 2015). Gritsch et al. (2015) did not find any N_2O emissions from litter incubation experiments below a moisture range of 70 – 80 w/w %. These moisture levels are as high as our initial values for the moister samples (SW 80 and OR 80) before drying out further, so no or very low N_2O were expected from our samples. However if oxygen is consumed at a higher rate than supplied, anoxic microsites can occur easily and the anaerobic community in leaf litter can be very quick to respond (Reith et al. 2002). A different picture was presented for Experiment 2, where we saw net emissions at the end of the drying cycles in Cycle 1 & 2 of about 5 $\mu g\ N_2O - N\ m^{-2}\ h^{-1}$ (Fig. 11 b). Because incubation chambers are only allowing gas emissions to exit, no leaching of water or nutrients occured in our experiments. It is possible for water to accumulate at the bottom of sample chambers to form anoxic microsites which favor N_2O formation. However as we expect observed nitric oxide (NO) emissions to occur due to abiotic processes (see above), we expect N_2O emissions to occur through similar processes (Butterbach–Bahl et al. 2013). Especially early after wetting the microbial community has yet to recover from severe stress imposed by litter storage, which supports our explanation of an onset of microbial activity and respiration after a lag – phase of 24 hours.

Conclusions

We clearly showed that NH_3 emissions from deciduous leaf litter can contribute substantially to natural ecosystem fluxes. NH_3 emissions were more strongly influenced by the C:N ratio rather than the moisture levels of the samples (Fig. 3 & 4). In experiments with arid soils Praveen-Kumar (1998) concluded that volatilization of NH_3 and nitrification did not occur at the same time above a threshold N concentration. This emphasizes our explanation of abiotic NO emissions; NH_3 emissions occurred from the start of measurements therefore it is unlikely that nitric oxide emissions resulted from the nitrification process. NO emissions peaked within an hour of initial wetting and likely resulted from volatilization of accumulated nitrogen through abiotic chemical decomposition. After the initial volatilization of NO which ended for both Experiments after about 90 hours, no further NO emissions were registered. This might be because conditions favored NH_3 volatilization over nitrification processes or microbes started to more efficiently use substrates. Soils are known to be major sources of NO and N_2O and litter can also contribute substantial to emissions (Pilegaard 2013). However we found mostly nitrous oxide uptake in our experiments, which we believe to be due to rather low moistures and well aerated samples.

The magnitude of NH_3-emissions from natural ecosystems, especially from leaf-litter is not yet well investigated, but has been suggested to be substantial. We found total NH_3-emissions (967 µg NH_3 - N m^{-2}) of SW 60 to be higher than those of total NO emissions (520 µg NO - N m^{-2}) over the incubation period of Experiment 2 (250 hours). NH_3 emissions continued over the whole course of our experiments whereas NO emissions stopped for all samples after about 80 hours. Ammonia volatilization is highly sensitive to climatic factors especially temperature and atmospheric turbulences, so these factors need to be well accounted for in future experiments. Our results lead us to conclude that NH_3 emissions from the litter layer are a potential major source of nitrogen gas in deciduous forests.

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Figures and Tables

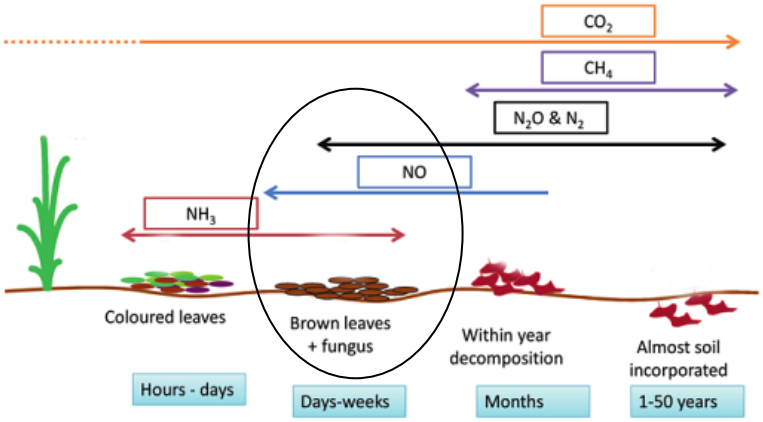

Figure 1: An idealized model scheme for simulation of trace gases exchange from litter with the atmosphere (after Massad et al. 2015). Black circle indicates expected stage of decomposition of the samples used for incubations.

Table 1: Characteristics of the sampling sites (Schneider et al. (2012), Wanek et al. (2010) and Kitzler et al. (2006)). Abbreviation: a.s.l, above sea level.

	Schottenwald (SW)	**Ort** (OR)
Location	48°14'N 16°15'E	47°51'N 13°42'E
Vegetation	beech	mainly beech (some conifers)
Stand age years	120	90
Exposition	SE	NE
Elevation (m a.s.l.)	370	700
Soil type	Dystric Cambisol over limestone	Cambisol
Soil texture	silty loam	loamy silt
Background N deposition	20 kg N ha^{-1} y^{-1}	< 10 kg N ha^{-1} y^{-1}
Litter C:N ratio	44	66
Litter-fall [kg N ha^{-1} y^{-1}]	4997 (see Kitzler et al. 2006)	4997 - Same litter-fall assumed as for SW

Table 2: Initial litter chemistry of the samples used for incubation experiments, Schottenwald (SW) and Ort (OR). Different letters indicate statistical differences between sites (T-test, $p < 0.01$)

	Schottenwald (SW)		**Ort (OR)**	
	mean	s.d.	mean	s.d.
C %	47.61	0.10	47.61	0.46
N %	1.06	0.02	0.72	0.01
C:N	44.76	0.96	66.18	1.12
dry mass %	90.78	0.15	90.59	0.57
pH	5.00	0.02	5.01	0.02
NO_3^--N [µg g^{-1} dm]	0.11[a]	0.09	0.33[b]	0.02
NH_4^+-N [µg g^{-1} dm]	52.01[a]	2.22	46.25[b]	2.38

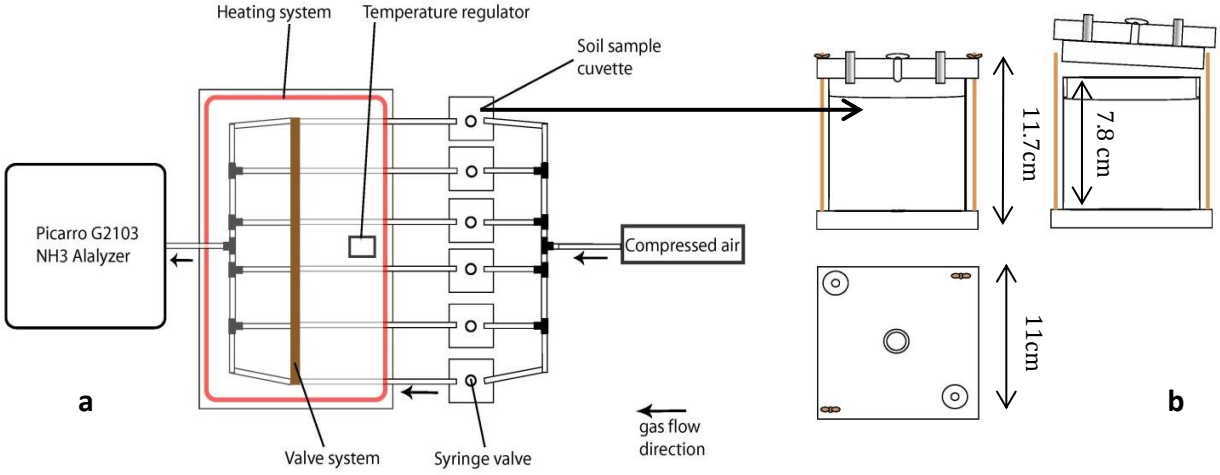

Figure 2: **a**: **D**evice for soil **E**mission **M**easurements **O**f reduced **N**itrogen (**DEMON**). Shown are the major compartments of the incubation device and the direction of gas flow. **b**: Scheme of an incubation chamber.

Table 3: Litter properties at the end of Experiment 1. Dry mass, pH, NO_3^- and NH_4^+ content of two litter types (SW and OR) with different initial moisture levels of 20% and 80% respectively are shown. Values are means and standard deviations (s.d.). (n = 5)

	sample	mean	s.d.	sample	mean	s.d.
NH_3 incubation device						
dry mass %	SW 20	91.62	±4.30	OR 20	96.07	±0.03
	SW 80	38.00	±1.92	OR 80	36.03	±3.81
pH	SW 20	4.89	±0.02	OR 20	4.98	±0.04
	SW 80	5.13	±0.19	OR 80	5.23	±0.28
NO_3^--N [µg g^{-1} dm]	SW 20	0.02	±0.00	OR 20	0.01	±0.00
	SW 80	0.02	±0.00	OR 80	0.01	±0.00
NH_4^+-N [µg g^{-1} dm]	SW 20	7.29	±0.19	OR 20	26.28	±2.44
	SW 80	11.92	±2.59	OR 80	18.97	±0.76
NO/CO_2 incubation device						
dry mass %	SW 20	86.29	±4.20	OR 20	84.77	±0.34
	SW 80	25.15	±3.44	OR 80	26.38	±2.32
pH	SW 20	4.87	±0.02	OR 20	4.85	±0.03
	SW 80	4.96	±0.07	OR 80	4.85	±0.04
NO_3^--N [µg g^{-1} dm]	SW 20	0.04	±0.00	OR 20	0.03	±0.00
	SW 80	0.01	±0.00	OR 80	0.01	±0.00
NH_4^+-N [µg g^{-1} dm]	SW 20	7.42	±0.71	OR 20	29.04	±4.53
	SW 80	18.25	±0.94	OR 80	44.25	±6.83

Table 4: Litter properties at the end of Experiment 2. Water content, pH, NO_3^- and NH_4^+ concentrations of SW 60. Values are means and standard deviations (s.d.). (n = 4)

Experiment	**NH_3 Incubation**	**s.d.**	**NO_x/CO_2 Incubation**	**s.d**
dry mass %	77.16	±9.61	50.13	±0.26
pH	5.01	±0.05	5.74	±0.07
NO_3^--N [µg g^{-1} dm]	0.53	±0.05	0.18	±0.19
NH_4^+-N [µg g^{-1} dm]	8.18	±0.86	1.79	±0.37

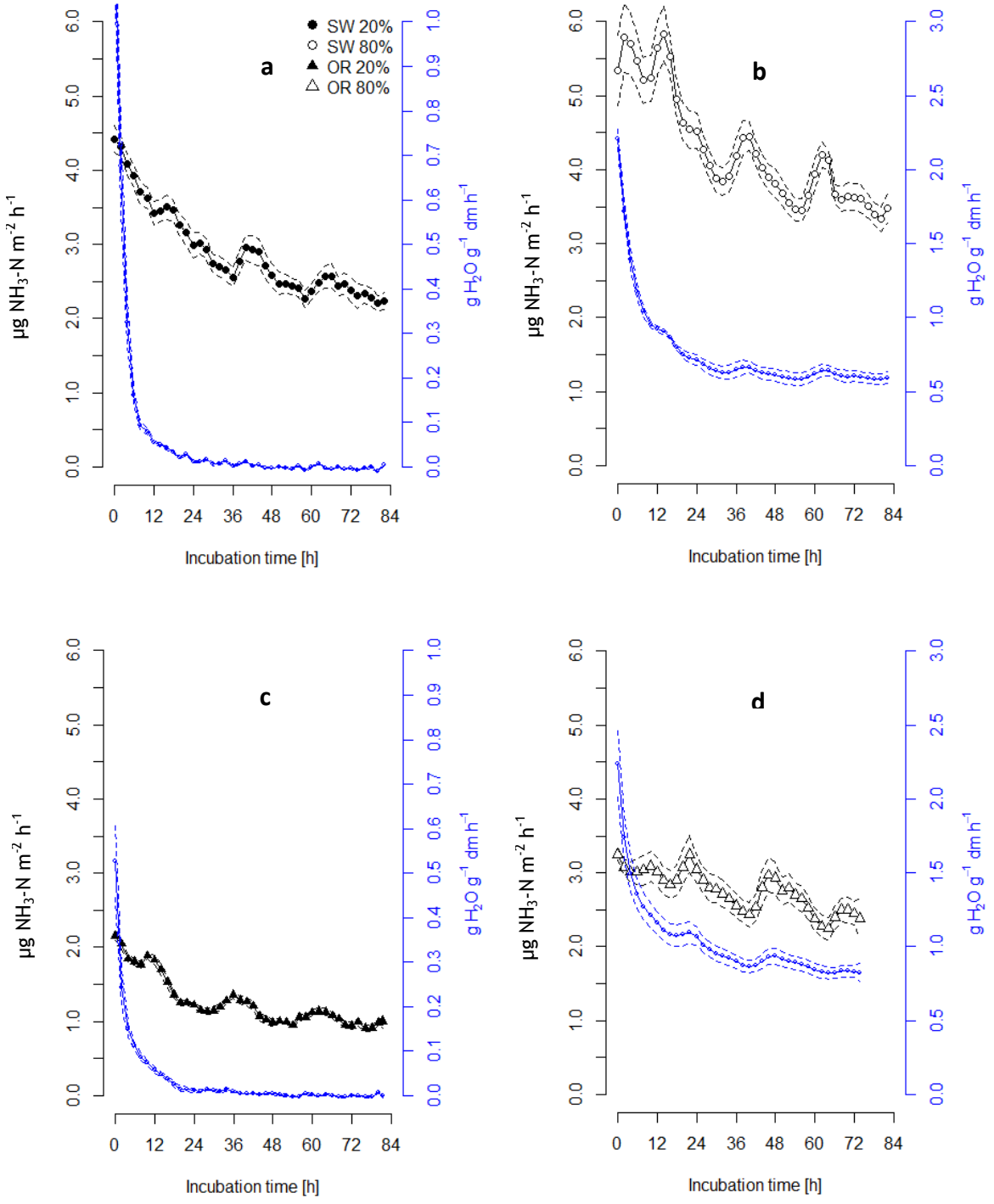

Figure 3: NH_3 and H_2O emissions of two beech litter types (SW and OR) over a period of about 80h and two different initial moisture levels of 20 w/w % and 80w/w % respectively. (a: SW 20%, b: SW 80%, c: OR 20%, d: OR 80%). Dashed lines represent standard error.

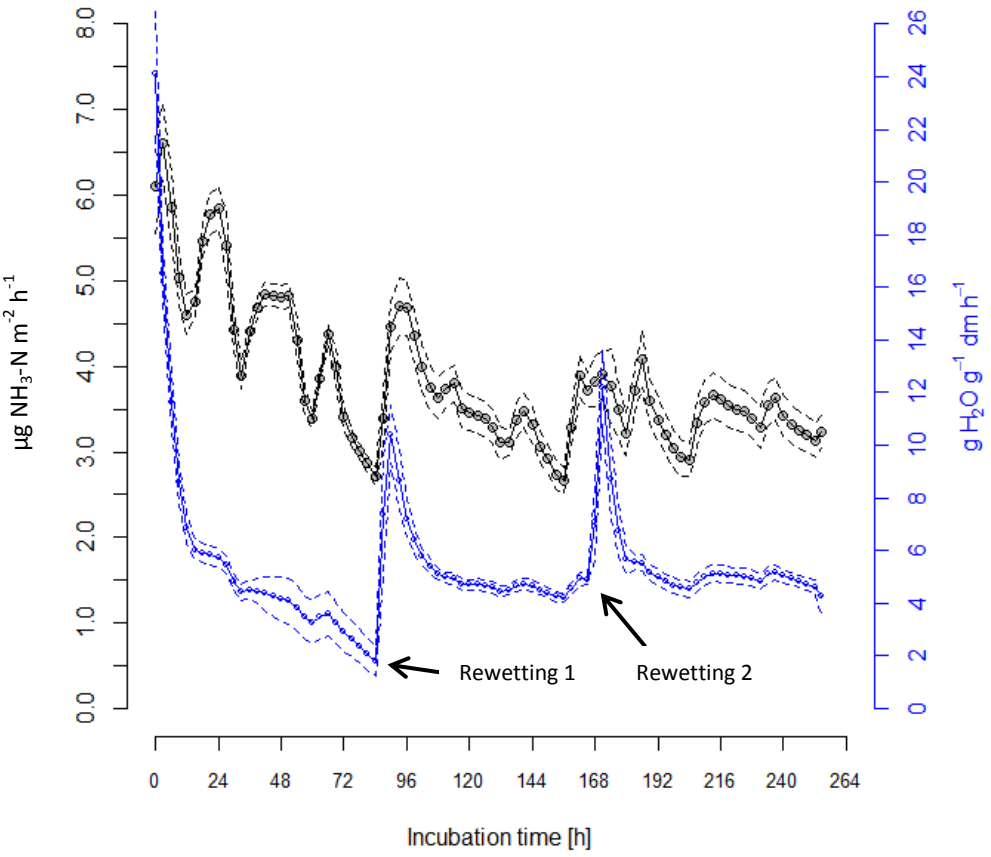

Figure 4: NH_3 emissions as well as water vapour emissions of beech leaf litter (SW) with the initial moisture level of 60 w/w%. During incubation three drought phases were simulated (~80h) with subsequent rewetting events of an equivalent of 750ml m^{-2} of deionized water. Water peaks after about 80h and 160h indicate the rewetting events. Dashed lines represent standard errors.

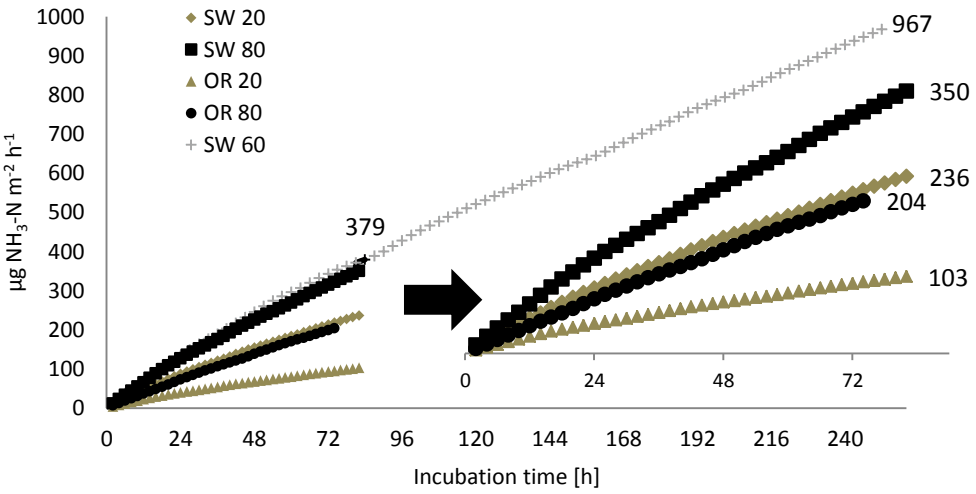

Figure 5: Cumulative NH_3 emissions over the course of Experiments 1 and Experiment 2. SW 20, SW 80, OR 20 and OR 80 indicate emissions from Experiment 1, SW 60 indicates cumulative ammonia emissions from Experiment 2. Black arrow indicates magnified area of Experiment 1 for better view. Standard deviations are smaller than symbols. Values at the end of the curves indicate magnitude of total emissions.

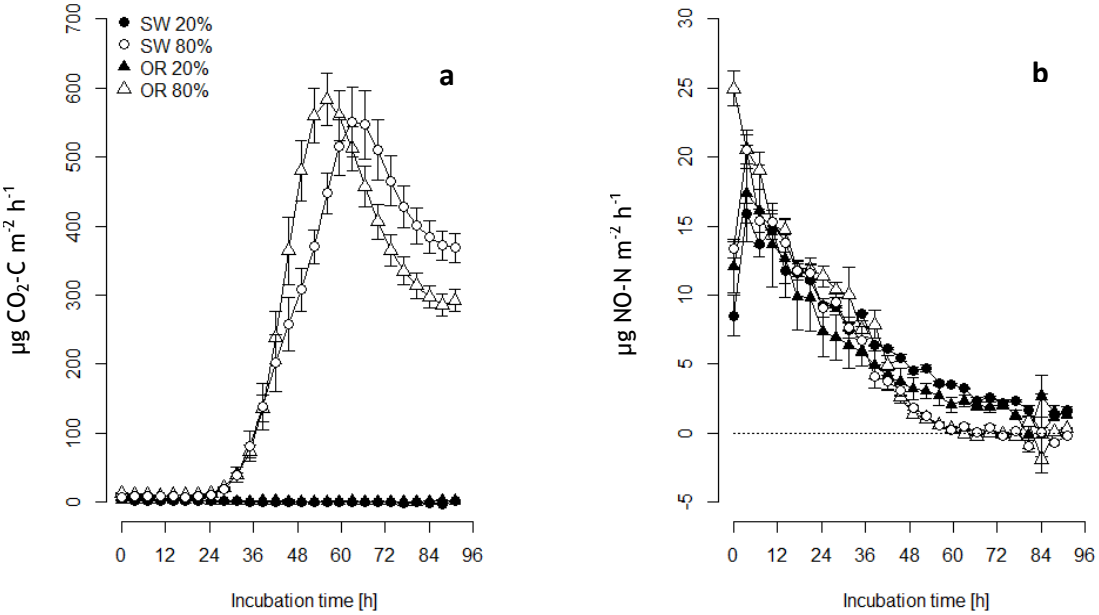

Figure 6: a) CO_2 emissions b) NO emissions of beech leaf litter with different initial moisture levels (20 and 80 w/w%)
over a period of 90h. Bars represent standard error.

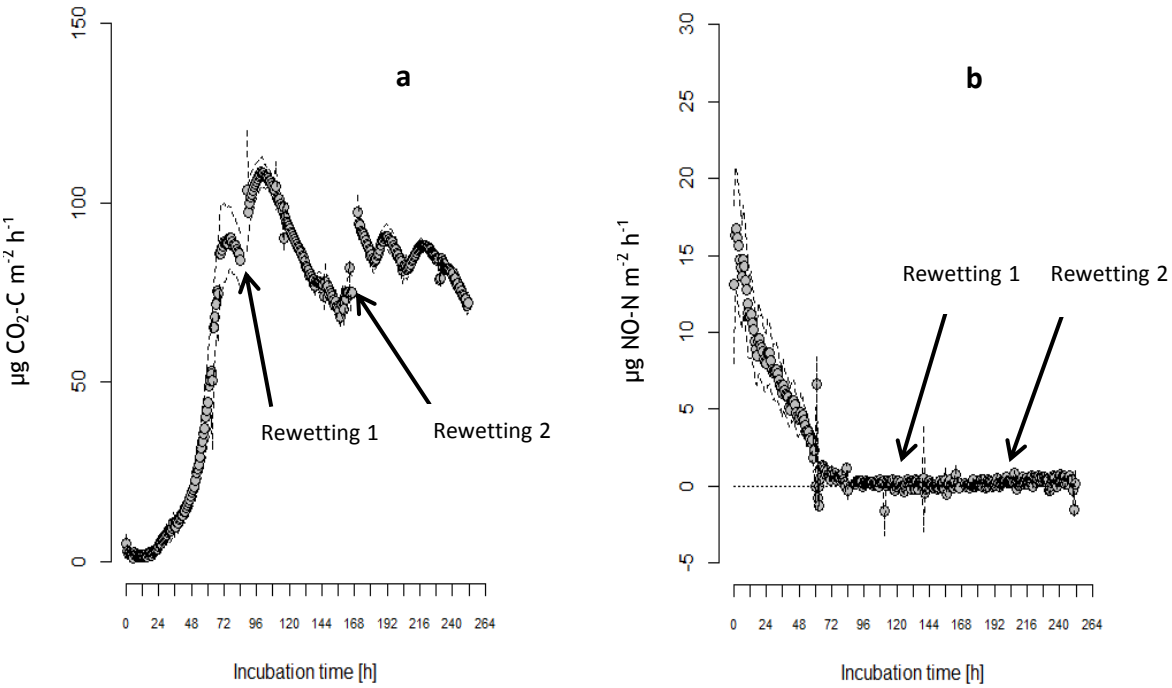

Figure 7: a) CO_2 b) NO emissions of beech leaf litter (SW, n=4) with the initial moisture level of 60 w/w%. During incubation three drought phases were simulated (~80h) with subsequent rewetting events of an equivalent of 750ml m^{-2} of deionized water. Dashed lines represent standard errors. Gaps in the emission curves after about 80h and 160h indicate interruptions of measurements for gas sampling regarding N_2O fluxes.

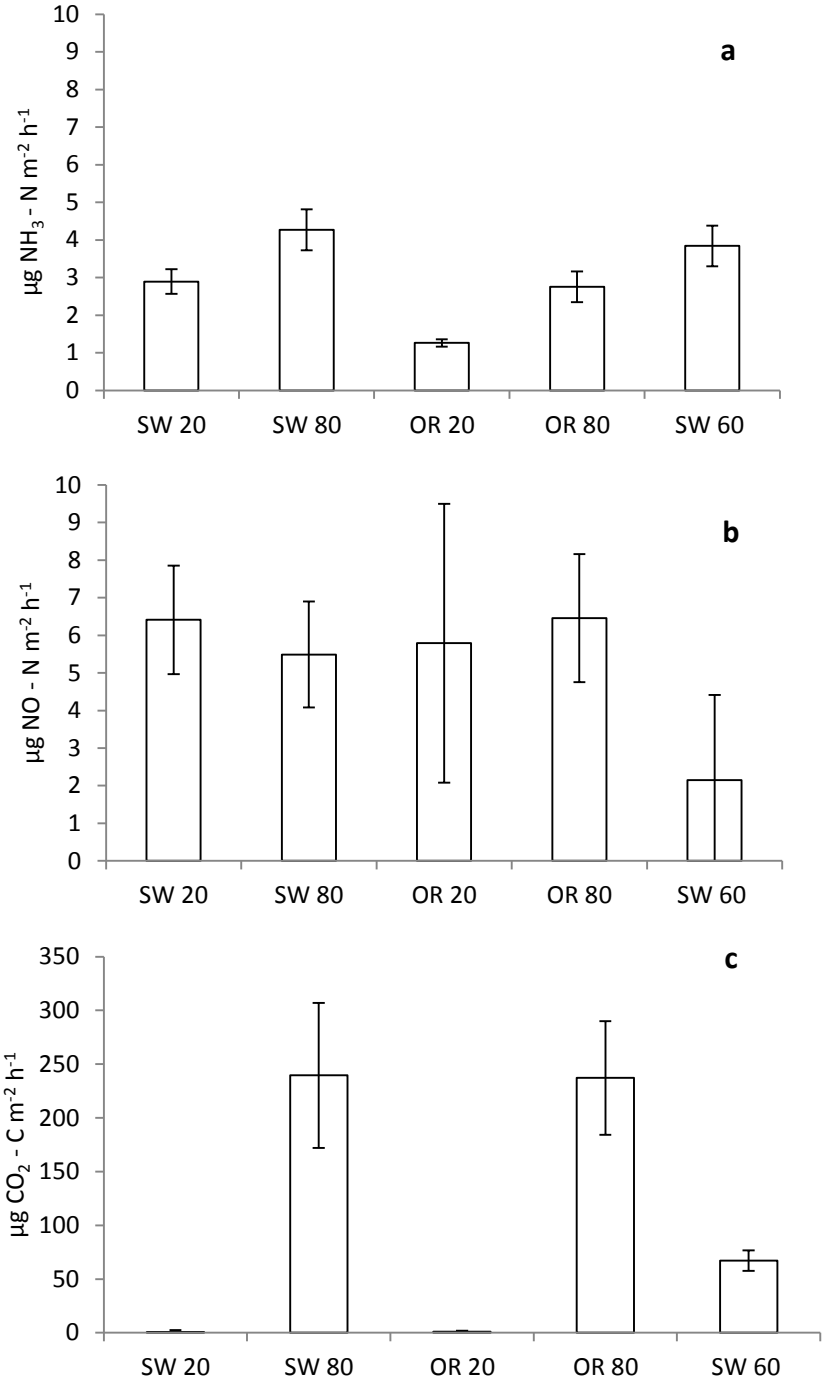

Figure 8: a) mean NH_3 flux b) mean NO flux c) mean CO_2 flux from different incubations of Experiment 1 and Experiment 2. SW 20, SW 80, OR 20 and OR 80 were incubated in Experiment 1 with initial wetting, whereas SW 60 was incubated in Experiment 2 with three repeated wetting and drying cycles. Error bars indicate standard deviation. Error bars indicate standard deviation. (n = 5)

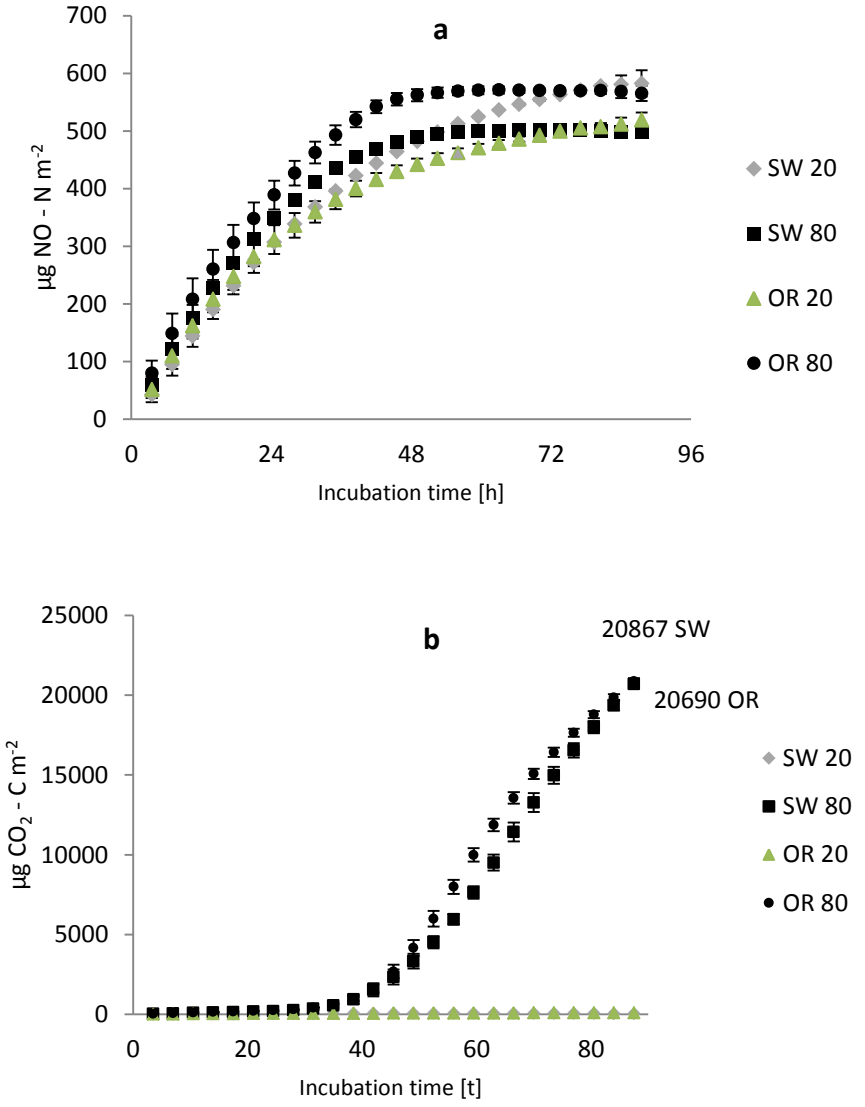

Figure 9: **a**) Cumulative NO emissions of four different incubated litter samples (i.e. SW 20, SW 80, Or 20 and Or 80, Experiment 1). **b**) Cumulative CO_2 emissions of four different incubated litter samples (i.e. SW 20, SW 80, Or 20 and Or 80, Experiment 1). Values at the end of the curves indicate magnitude of total emissions. Error bars indicate cumulative standard deviation. (n = 5)

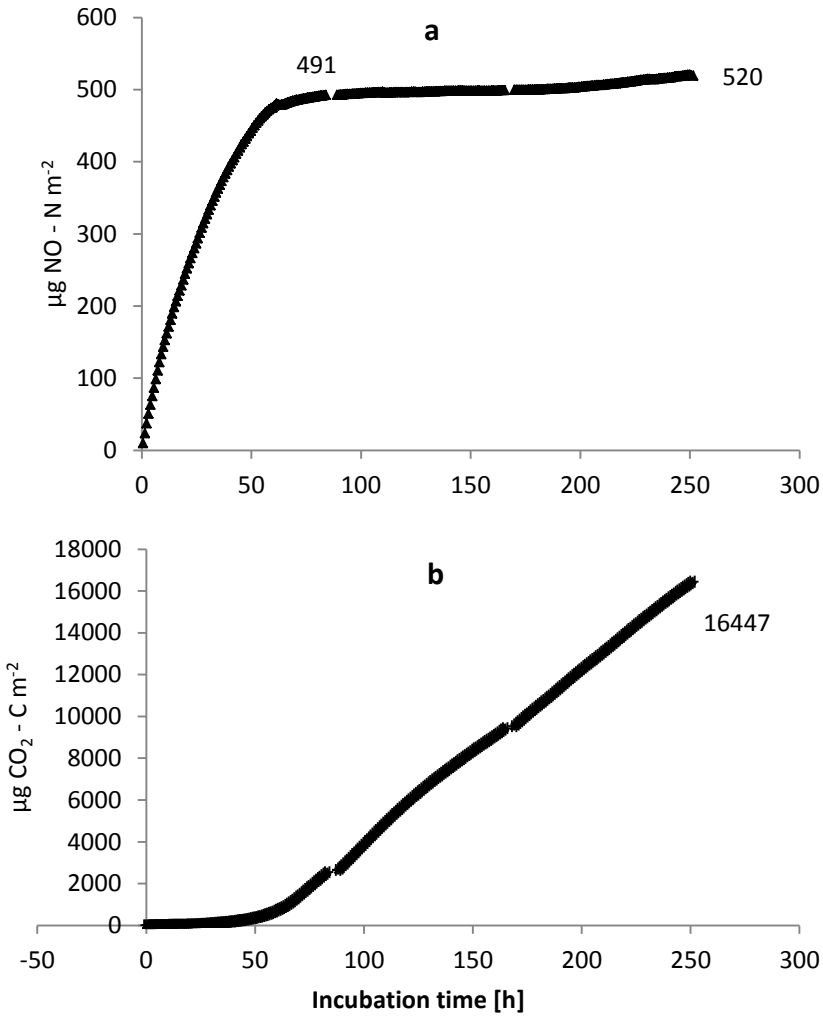

Figure 10: **a**) Cumulative NO emissions of SW 60 (Experiment 2). **b**) Cumulative CO_2 emissions of SW 60 (Experiment 2). Gaps in the curves indicate wetting events and nitrous oxide sampling by closed chamber method. Values at the end of curves indicate the magnitude of total emissions. Standard deviations are smaller than symbols. (n = 5)

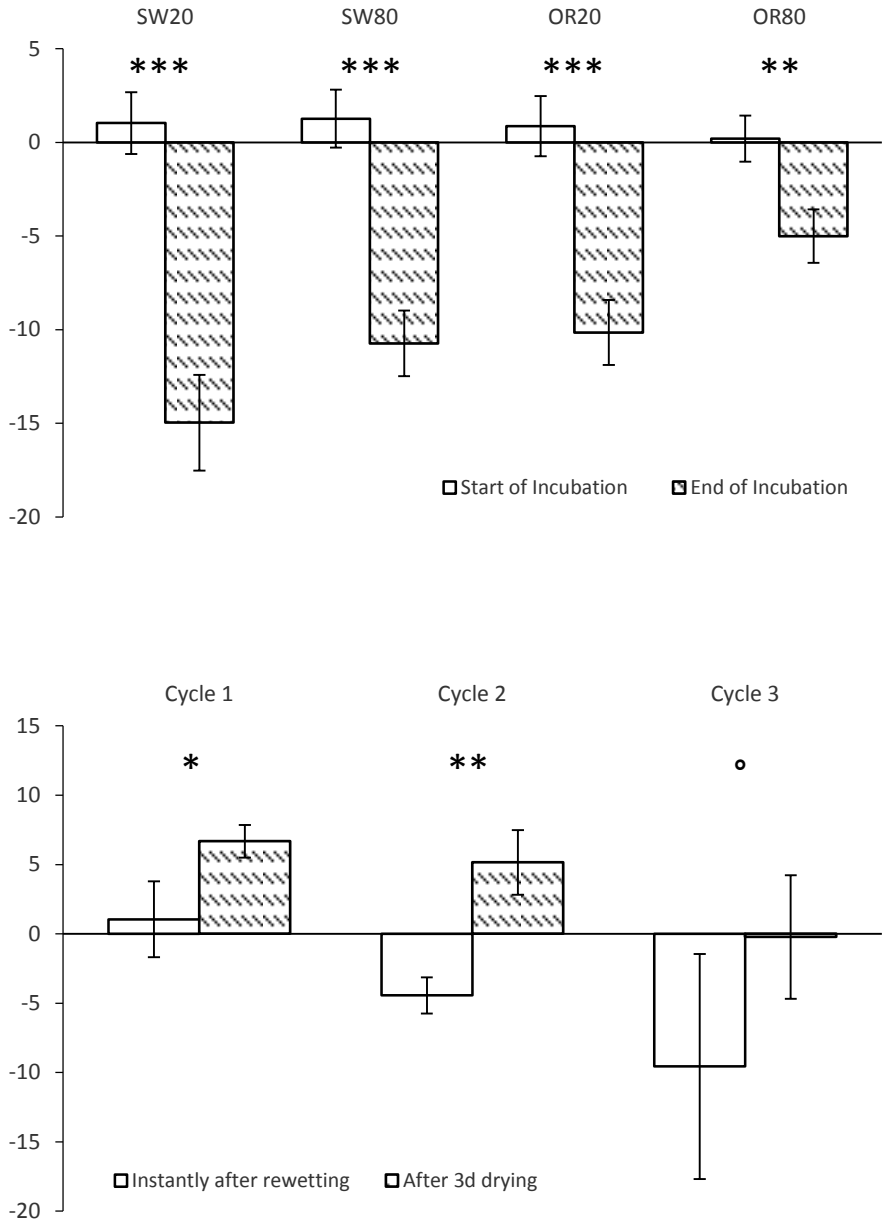

Figure 11: Nitrous oxide (N_2O) fluxes in (**a**) Experiment 1: initial wetting and subsequent drying for 80 hours of four incubated samples (SW 20, SW 80, OR 20 and OR 80, n = 5) and (**b**) Experiment 2: three cycles of wetting and subsequent drying of one sample SW 60 (n= 5). Symbols above bars indicate significant differences between time points (t-test); ° p = 0.1 – 0.05, * p = 0.05 – 0.01, ** p = 0.01 – 0.001, *** p = < 0.001. Error bars indicate standard deviation. (n = 5)

Appendix

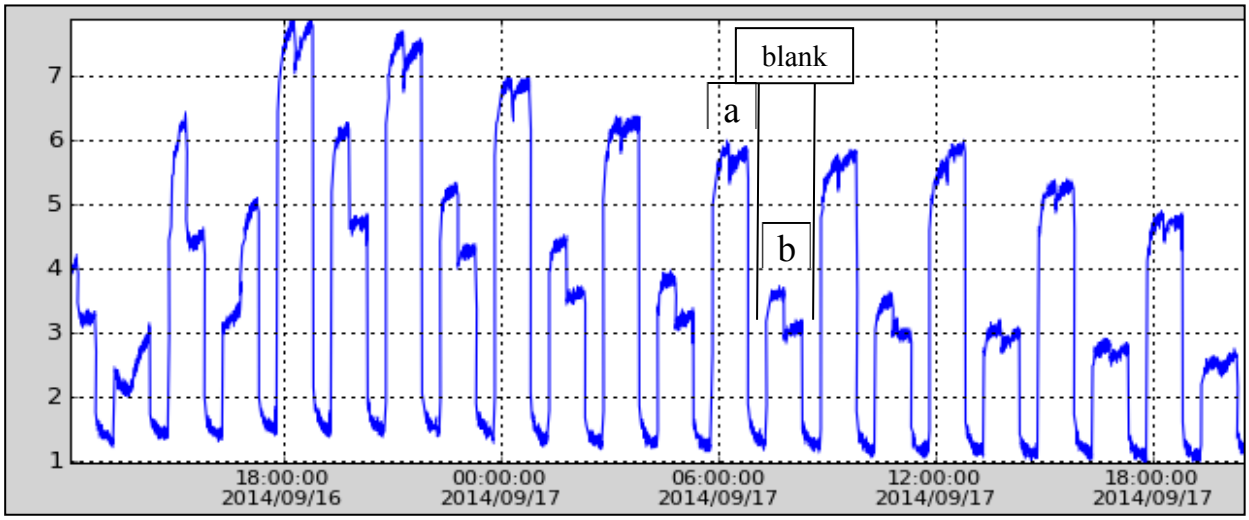

Figure 1: Initial test results of the newly built ammonia emission measuring device. Mixing ratios (ppb, 30s average) of litter ammonia emissions of samples SW (**a**) and OR (**b**) at same initial moisture levels. Curve indicates results of six incubation chambers: two for SW (**a**) and OR (**b**) each (indicated by the width of the measuring plateaus) and alternately a reference chamber.

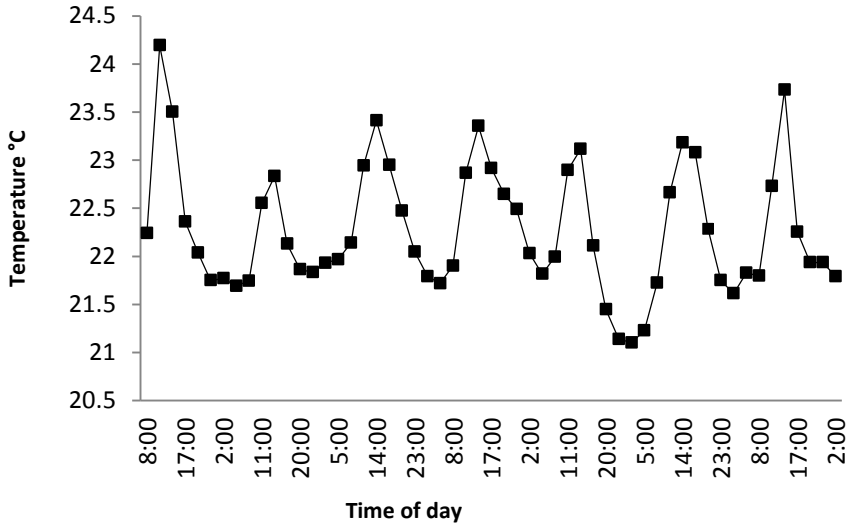

Figure 2: Diurnal temperature dynamic measured in two sample incubation chambers for ammonia measurements (n = 2).

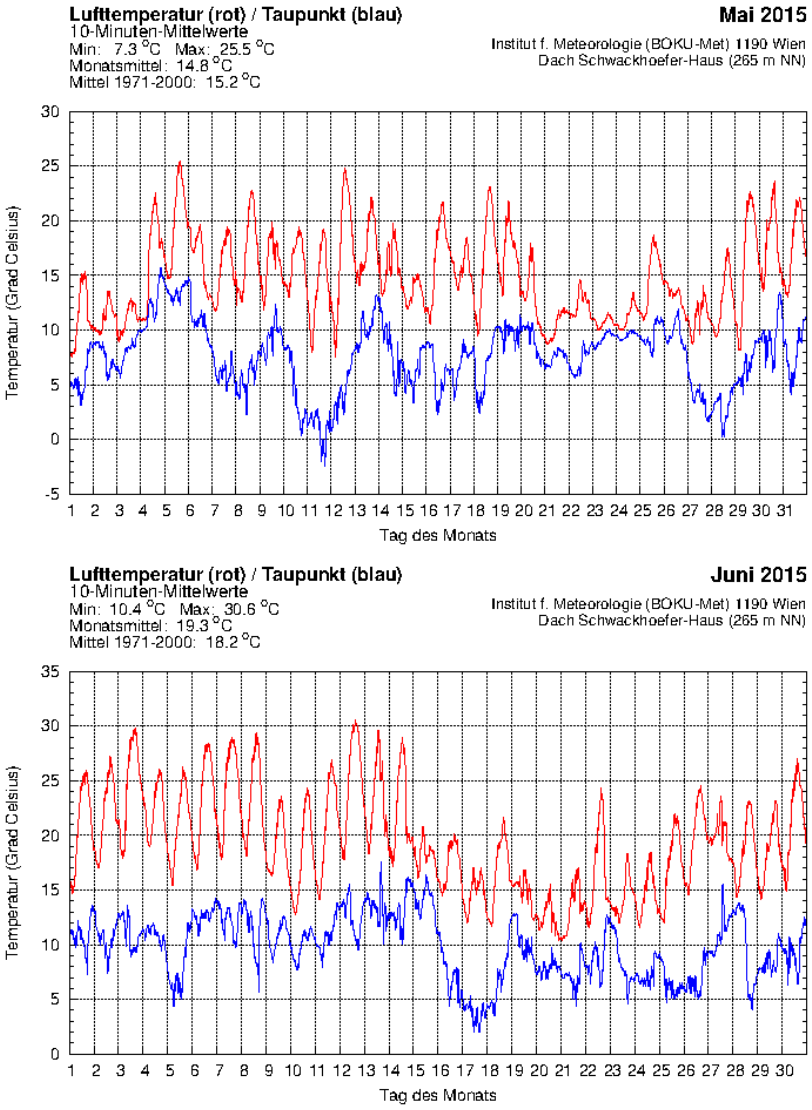

Figure 3: Ambient temperature fluctuations due to diurnal variation and sun radiation in incubation chambers for ammonia measurements. b) Ambient temperature for May 2015. Experiment 1: May 1st to May 11th c) Experiment 2: June 1st to June 11th. Ambient temperature for June 2015

Background Data

Ammonia data

Table 1: Average ammonia emissions, blank corrected, from measurements of Experiment 1 (SW 20, SW 80, OR 20, OR 80) (One run =3h = 6 chambers, 5 replicates 1 blank) with standard deviation (s.d.) in ppb per volume. The same is shown for water in per cent. Also shown are the calculated fluxes for ammonia in µg NH_3 – N $m^{-2}h^{-1}$.

Sample SW 20							
hours [h]	n	NH3_Raw_mean_korr_mean	NH3_Raw_mean_korr_sd	H2O_mean_korr_mean	H2O_mean_korr_sd	NH3_Raw_mean_korr_mean_flux	NH3_Raw_mean_korr_sd_flux
0	5	2.530924696	0.227047022	0.557648604	0.119406196	4.421516499	0.396650345
2	5	2.475023088	0.177224623	0.300625314	0.094348238	4.323856588	0.309610789
4	5	2.336008856	0.175743594	0.144939099	0.051755886	4.080999216	0.307023438
6	5	2.251019892	0.188513882	0.07133373	0.017957679	3.932523796	0.329333085
8	5	2.120670781	0.193927611	0.042083351	0.009731333	3.70480436	0.338790851
10	5	2.074086296	0.182186359	0.035308855	0.006253342	3.623421429	0.318278925
12	5	1.957898608	0.196423072	0.024255386	0.005132128	3.420441949	0.343150412
14	5	1.977632369	0.184860895	0.02209755	0.003423032	3.45491676	0.322951331
16	5	2.006050202	0.209947991	0.019066381	0.003440244	3.504562613	0.366778398
18	5	1.98034639	0.181200092	0.014836514	0.002985982	3.459658145	0.31655592
20	5	1.867759802	0.190147495	0.009405677	0.002509472	3.262969773	0.332187002
22	5	1.807110926	0.207377916	0.012796632	0.002477368	3.157016402	0.362288486
24	5	1.708724485	0.219873269	0.005563221	0.002325077	2.985135637	0.384117824
26	5	1.730016355	0.186778207	0.005506819	0.002831399	3.022332458	0.326300868
28	5	1.680631627	0.176087029	0.007807493	0.0032815	2.936057513	0.307623417
30	5	1.57327746	0.15765109	0.002634408	0.002820344	2.748510164	0.275415897
32	5	1.546115864	0.17424059	0.003032617	0.002588516	2.70105895	0.304397695
34	5	1.516843583	0.176869721	0.006173401	0.001548118	2.649920379	0.308990778

36	5	1.466151283	0.161419802	0.001323274	0.001941904	2.561361111	0.281999823
38	5	1.588005918	0.182487467	0.002788507	0.001832329	2.774240727	0.31880496
40	5	1.690008624	0.204313608	0.005716275	0.001005977	2.952439093	0.356935152
42	5	1.676624176	0.236060711	0.000846237	0.001760408	2.92905651	0.412397229
44	5	1.659940422	0.22937608	0.00167105	0.001315275	2.899910052	0.400719201
46	5	1.552819405	0.223892974	-0.000846046	0.001173677	2.712770014	0.391140235
48	5	1.479907576	0.204819752	-0.001203076	0.000973916	2.585393305	0.357819384
50	5	1.415193661	0.195535044	0.000191253	0.001458215	2.472338325	0.34159903
52	5	1.415008296	0.170228263	-0.000617886	0.002307882	2.472014493	0.297388174
54	5	1.39291173	0.140996212	-0.002132512	0.001914626	2.43341187	0.246319885
56	5	1.379197784	0.147754773	0.001269366	0.001699055	2.409453655	0.258127067
58	5	1.297164006	0.156320461	-0.003187631	0.002908005	2.266140934	0.273091293
60	5	1.352752389	0.137031017	-0.000276327	0.001770589	2.363253643	0.239392702
62	5	1.424871608	0.152035937	0.003666127	0.001199179	2.489245663	0.265606245
64	5	1.468024539	0.193905211	-0.00062902	0.002041332	2.564633681	0.338751718
66	5	1.474729932	0.207112515	-0.002592193	0.00123313	2.57634798	0.361824831
68	5	1.396924598	0.171333821	0.000389524	0.001622868	2.440422336	0.29931958
70	5	1.413207883	0.186944489	-0.002584725	0.001540526	2.468869176	0.326591362
72	5	1.365749574	0.216250547	-0.001293738	0.001261806	2.385959678	0.377788941
74	5	1.319177805	0.208158513	-0.003376769	0.001868679	2.304598963	0.363652187
76	5	1.335699753	0.153785611	-0.001015589	0.001238669	2.333462748	0.268662918
78	5	1.30909937	0.152549396	-0.000564966	0.002449132	2.286991973	0.266503256
80	5	1.264687735	0.137506763	-0.003926407	0.001981726	2.209405004	0.240223829
82	5	1.27823534	0.145063735	0.001806005	0.001449965	2.233072622	0.253425832
Sample SW 80							
hours [h]	N	NH3_Raw_mean_korr_mean	NH3_Raw_mean_korr_sd	H2O_mean_korr_mean	H2O_mean_korr_sd	NH3_Raw_mean_korr_mean_flux	NH3_Raw_mean_korr_sd_flux

0	5	3.060688673	0.609214008	0.984511738	0.060121065	5.347012296	1.06429472
2	5	3.31140763	0.604872025	0.765737935	0.062852342	5.785017427	1.056709289
4	5	3.262608418	0.538328998	0.619713895	0.062733928	5.699765375	0.940458858
6	5	3.129562038	0.466432826	0.525110823	0.047990302	5.467333821	0.814856499
8	5	2.980825667	0.393231146	0.46466908	0.037113618	5.207491906	0.686973422
10	5	2.996569841	0.403011118	0.424276839	0.021660293	5.234996923	0.704059
12	5	3.231478136	0.462375826	0.411149055	0.018288824	5.645380884	0.807768934
14	5	3.34253998	0.472038721	0.403552666	0.016716573	5.839405532	0.824649977
16	5	3.168577309	0.316146064	0.385587806	0.008296999	5.535493361	0.552306057
18	5	2.831832597	0.314976493	0.355042781	0.020256502	4.94720154	0.550262819
20	5	2.655075536	0.326425595	0.335608185	0.027814416	4.638407579	0.570264361
22	5	2.601737348	0.326664892	0.323097309	0.034061366	4.545225953	0.570682412
24	5	2.590460405	0.299930055	0.318645565	0.037832595	4.525525172	0.523976746
26	5	2.443781169	0.243131493	0.303630517	0.038265414	4.269277065	0.424749859
28	5	2.322009422	0.234312518	0.29253718	0.040798699	4.056542255	0.409343141
30	5	2.219996144	0.236834156	0.284445725	0.042641123	3.878325419	0.413748434
32	5	2.198927888	0.237650743	0.280577515	0.043738825	3.841519249	0.415175008
34	5	2.236551751	0.265974144	0.279910019	0.047306868	3.907248005	0.464655889
36	5	2.397204765	0.321376715	0.2879616	0.050585551	4.187908252	0.561443985
38	5	2.538755955	0.293728122	0.296433505	0.049516971	4.435197682	0.513141992
40	5	2.548940432	0.244526772	0.296903979	0.040483563	4.452989927	0.427187406
42	5	2.416615503	0.21145219	0.286303788	0.037853822	4.221818743	0.369406229
44	5	2.305287855	0.220504755	0.278774831	0.039574221	4.027329735	0.385221027
46	5	2.227517173	0.223908303	0.274923656	0.040162986	3.891464629	0.391167015
48	5	2.184784261	0.243538483	0.271854543	0.04235769	3.816810384	0.425460869
50	5	2.108714546	0.218104937	0.26561229	0.042177397	3.68391686	0.381028553
52	5	2.035371686	0.20015314	0.263077165	0.04120968	3.555787143	0.349666827

54	5	1.979622185	0.185851649	0.260273524	0.040116237	3.45839296	0.324682174
56	5	1.97665896	0.195085939	0.260312822	0.039906174	3.453216217	0.340814446
58	5	2.092079697	0.258746525	0.26624261	0.043945412	3.654855838	0.452029265
60	5	2.253820926	0.268854885	0.277552375	0.043588625	3.937417193	0.469688534
62	5	2.405423886	0.225717525	0.287227229	0.039717914	4.202267028	0.394327719
64	5	2.3596367	0.177311354	0.285906095	0.033412513	4.122276976	0.309762309
66	5	2.102137704	0.161433218	0.276218439	0.036864591	3.672427139	0.282023262
68	5	2.060876202	0.214996285	0.270920549	0.039085266	3.600343442	0.37559775
70	5	2.081766555	0.245828615	0.267825259	0.039812815	3.636838815	0.429461722
72	5	2.076800291	0.230407332	0.269095037	0.037649718	3.62816277	0.402520795
74	5	2.064232549	0.239616803	0.266148358	0.037956942	3.606206968	0.418609708
76	5	2.00609999	0.199186275	0.263520505	0.03769581	3.504649594	0.347977719
78	5	1.946150203	0.190936	0.260348715	0.036472175	3.399917527	0.333564517
80	5	1.907188351	0.215351878	0.260228581	0.038525038	3.33185131	0.37621897
82	5	1.987760491	0.251246079	0.264017125	0.040545193	3.472610553	0.438926012
Sample OR 20							
hours [h]	N	NH3_Raw_mean_korr_mean	NH3_Raw_mean_korr_sd	H2O_mean_korr_mean	H2O_mean_korr_sd	NH3_Raw_mean_korr_mean_flux	NH3_Raw_mean_korr_sd_flux
0	5	1.233216193	0.078232759	0.234108292	0.079818659	2.15442433	0.136672354
2	5	1.167973055	0.065038954	0.108012202	0.03985523	2.040444799	0.113622823
4	5	1.055561984	0.056460115	0.065969633	0.015164958	1.844063055	0.098635622
6	5	1.034423375	0.050297867	0.049879035	0.008299542	1.807133981	0.087870197
8	5	1.007975219	0.050139791	0.038872041	0.007726135	1.760929145	0.087594037
10	5	1.080676779	0.056691205	0.032877537	0.006522265	1.887938514	0.099039334
12	5	1.045804212	0.077465574	0.025665759	0.006304046	1.827016262	0.135332084
14	5	0.969290847	0.097004956	0.021465834	0.005464326	1.693347685	0.169467316
16	5	0.876671231	0.093198083	0.017073401	0.003989279	1.531541542	0.162816721

18	5	0.778519897	0.058150308	0.011487684	0.005430951	1.360071509	0.101588382
20	5	0.713377222	0.049409251	0.006877246	0.004897911	1.246267486	0.086317787
22	5	0.717931312	0.047801128	0.006274169	0.003957983	1.254223465	0.083508402
24	5	0.698413029	0.049955353	0.005212776	0.003779949	1.220125094	0.087271825
26	5	0.659345274	0.050488259	0.004586903	0.003118871	1.151873863	0.08820281
28	5	0.65012916	0.053297437	0.006765826	0.002299415	1.135773344	0.093110435
30	5	0.654396144	0.063352013	0.005494072	0.002127466	1.14322775	0.110675744
32	5	0.684646751	0.052695137	0.004146343	0.002500543	1.196075455	0.092058219
34	5	0.729546535	0.050748575	0.00591662	0.003153095	1.274515219	0.088657581
36	5	0.777329582	0.051550739	0.004620173	0.002922902	1.357992033	0.09005896
38	5	0.737665796	0.068661665	0.002621225	0.002252035	1.288699539	0.119951685
40	5	0.724100749	0.071694047	0.00160411	0.001924891	1.265001449	0.125249247
42	5	0.690334142	0.058743948	0.002346717	0.001546411	1.206011306	0.102625469
44	5	0.612697233	0.067864439	0.001322773	0.001328751	1.0703799	0.118558935
46	5	0.581892957	0.057326856	0.001644599	0.000908845	1.016564939	0.100149815
48	5	0.561183648	0.054116462	0.001911179	0.001759407	0.98038585	0.094541267
50	5	0.577061723	0.040907725	0.001136896	0.001993195	1.00812479	0.07146565
52	5	0.567506965	0.028556457	3.43E-05	0.002234281	0.991432663	0.04988803
54	5	0.539750527	0.03945649	-0.000739356	0.002710002	0.942942263	0.068930348
56	5	0.605230253	0.054232297	-0.000777986	0.001854304	1.057335113	0.094743632
58	5	0.603240935	0.043104246	0.001926305	0.002037312	1.053859781	0.075302965
60	5	0.638867857	0.044634827	0.001293787	0.001871754	1.116099888	0.077976885
62	5	0.654751417	0.055039372	-0.000465391	0.001702768	1.143848412	0.096153589
64	5	0.64619281	0.060959509	0.001321115	0.001556182	1.128896555	0.106496047
66	5	0.617687677	0.05109626	0.000157566	0.001306221	1.079098189	0.089264985
68	5	0.589212543	0.058443157	-0.00058043	0.00134293	1.02935223	0.102099989
70	5	0.543389929	0.052739746	-0.001329779	0.001160557	0.949300285	0.09213615

72	5	0.536180146	0.062326228	0.000159064	0.000822183	0.93670482	0.108883701
74	5	0.564396173	0.062597296	-0.000313828	0.001722087	0.98599812	0.109357255
76	5	0.521488403	0.050689658	-0.001146913	0.00200833	0.911038398	0.088554653
78	5	0.520995839	0.054624914	-0.000850879	0.001890226	0.910177889	0.095429532
80	5	0.562852179	0.03312431	0.003363333	0.001287213	0.983300767	0.057868053
82	2	0.570262407	0.072777281	-2.35E-05	0.00243726	0.99624641	0.127141653
Sample OR 80							
hours [h]	N	NH3_Raw_mean_korr_mean	NH3_Raw_mean_korr_sd	H2O_mean_korr_mean	H2O_mean_korr_sd	NH3_Raw_mean_korr_mean_flux	NH3_Raw_mean_korr_sd_flux
0	5	1.860828917	0.101918936	0.996785724	0.222838953	3.250861542	0.17805202
2	5	1.762559483	0.137287432	0.774237759	0.152050607	3.079185188	0.239840659
4	5	1.723303003	0.169619472	0.66462277	0.123537948	3.010604256	0.296324619
6	5	1.726098608	0.218615648	0.604947824	0.100353229	3.015488169	0.381920765
8	5	1.738674515	0.259792334	0.566638579	0.091913243	3.037458234	0.45385629
10	5	1.768149538	0.266823281	0.538989193	0.082990427	3.088950995	0.466139329
12	5	1.72191373	0.250419501	0.515655362	0.077009827	3.008177201	0.437481983
14	5	1.65782498	0.232265133	0.496225159	0.074094108	2.896214381	0.405766366
16	5	1.625608075	0.242275905	0.481386238	0.070376961	2.839931563	0.42325515
18	5	1.661279419	0.262502799	0.477134088	0.07183647	2.902249273	0.458591463
20	5	1.76183947	0.314748821	0.480466585	0.074195466	3.077927328	0.549865079
22	5	1.860623477	0.321257367	0.488222633	0.07297221	3.250502639	0.561235485
24	5	1.743259077	0.245870457	0.475675525	0.060807581	3.045467447	0.429534819
26	5	1.661957112	0.227413146	0.449303617	0.051005832	2.903433201	0.397289963
28	5	1.597643839	0.244865777	0.436609482	0.053165029	2.791078141	0.427779647
30	5	1.589271036	0.233233548	0.424410137	0.052196428	2.776450883	0.407458184
32	5	1.555417194	0.228098519	0.418097177	0.050771699	2.71730834	0.398487307
34	5	1.516061037	0.210491087	0.410376656	0.04793567	2.648553274	0.367727186

36	5	1.46192841	0.202143448	0.401294299	0.046620392	2.553983766	0.353143889
38	5	1.416649783	0.198330558	0.389248147	0.042805096	2.474882165	0.346482783
40	5	1.393893498	0.209360768	0.386220345	0.04388644	2.435127014	0.365752522
42	5	1.449254611	0.233123378	0.38884112	0.046088418	2.531842684	0.407265718
44	5	1.60454383	0.29545661	0.401878763	0.053000561	2.803132401	0.516161653
46	5	1.701419377	0.298318675	0.415279649	0.054660023	2.972373638	0.521161671
48	5	1.677832398	0.279667197	0.416977974	0.05278948	2.93116727	0.488577605
50	5	1.577570452	0.238215171	0.40712768	0.049542894	2.756010005	0.416161062
52	5	1.601607353	0.240708474	0.400127006	0.048886995	2.798002385	0.420516854
54	5	1.544868572	0.229621044	0.396843367	0.047611398	2.698879936	0.401147153
56	5	1.515006363	0.218894952	0.392102218	0.046086185	2.646710762	0.382408707
58	5	1.44530689	0.204184673	0.386146246	0.043667678	2.524946029	0.356709902
60	5	1.358970002	0.192958309	0.376864223	0.042043878	2.374115791	0.337097484
62	5	1.302392782	0.199700081	0.369204014	0.042428719	2.275275588	0.348875335
64	5	1.287425532	0.197300737	0.365028154	0.04098257	2.249127855	0.34468369
66	5	1.371612447	0.198245111	0.36611231	0.038462077	2.396202097	0.346333509
68	5	1.429740211	0.210554496	0.372184282	0.040193816	2.497751097	0.367837961
70	5	1.431553004	0.219175087	0.371765367	0.038799209	2.500918039	0.382898102
72	5	1.403784113	0.199780593	0.370853847	0.037000244	2.452405884	0.34901599
74	3	1.365657566	0.264882748	0.367264257	0.048661862	2.385798942	0.462749225

Table 2: Ammonia emission means, blank corrected, over three wetting/drying cycles of measurements for Experiment 2 (SW 60) (3h = 6 chambers, 5 replicates 1 blank) indicated in ppb per volume and standard deviations (s.d.). The same is displayed for water in per cent. Also shown are the calculated fluxes for ammonia in µg NH_3– N $m^{-2}h^{-1}$.

hours [h]	n	chamberid	NH3_Raw_mean_korr_mean	NH3_Raw_mean_korr_sd	H2O_mean_korr_mean	H2O_mean_korr_sd	NH3_Raw_mean_korr_mean_flux	NH3_Raw_mean_korr_sd_flux

0	5	12.4	3.49164857	0.713593537	1.072465512	0.238722073	6.099897712	1.246645387
3	5	12.4	3.785531575	0.560178151	0.735781643	0.106483414	6.613310284	0.978629249
6	5	12.4	3.353299597	0.562878212	0.519004436	0.103373145	5.858202545	0.983346246
9	5	12.4	2.885181308	0.358592293	0.382468107	0.074690853	5.040401549	0.626459469
12	5	12.4	2.634960688	0.298972904	0.305746926	0.055945701	4.60326701	0.522304607
15	5	12.4	2.718723358	0.182678792	0.268248921	0.036431937	4.749600099	0.319139204
18	5	12.4	3.128476147	0.23516693	0.26375762	0.035622573	5.465436773	0.410835795
21	5	12.4	3.304488329	0.306949204	0.260103582	0.036490198	5.772929432	0.536239174
24	5	12.4	3.350069214	0.311330362	0.25487569	0.034496264	5.852559078	0.543893042
27	5	12.4	3.10285997	0.481473032	0.243276204	0.033961149	5.420685402	0.841131686
30	5	12.4	2.532773454	0.310272195	0.214677787	0.031488787	4.424746274	0.542044428
33	5	12.4	2.228903945	0.211846735	0.196565975	0.028840245	3.893887315	0.370095498
36	5	12.4	2.525157177	0.137896632	0.200898546	0.034935657	4.411440664	0.240904929
39	5	12.4	2.680931516	0.15574495	0.198943211	0.048564726	4.683577884	0.272085878
42	5	12.4	2.772530044	0.176463629	0.194685892	0.065010067	4.843600189	0.308281336
45	5	12.4	2.762733864	0.167751547	0.189507656	0.076557418	4.826486296	0.29306136
48	5	12.4	2.754970605	0.179390873	0.185347732	0.082484193	4.812923911	0.313395222
51	5	12.4	2.760855373	0.180073006	0.181489974	0.0875427	4.82320458	0.314586905
54	5	12.4	2.461476714	0.307593894	0.169667876	0.08662094	4.300191121	0.537365446
57	5	12.4	2.056507548	0.205204528	0.154076536	0.081269413	3.592711419	0.358491585
60	5	12.4	1.938353737	0.1224049	0.146295404	0.079338476	3.386297128	0.213840928
63	5	12.4	2.20923772	0.110981602	0.155067684	0.082150342	3.859530489	0.193884467
66	5	12.4	2.500294121	0.137041682	0.159704255	0.084329037	4.368004994	0.239411335
69	5	12.4	2.285855975	0.262125775	0.144801003	0.078401952	3.993382309	0.457932803
72	5	12.4	1.954009039	0.172928214	0.129895816	0.071579036	3.413646885	0.302104979
75	5	12.4	1.809884362	0.121917657	0.117846696	0.067186567	3.161861584	0.212989716
78	5	12.4	1.72194406	0.115945409	0.105872624	0.063888576	3.008230188	0.202556221

81	5	12.4	1.640479408	0.119804291	0.092639157	0.059329746	2.865911728	0.209297673
84	5	12.4	1.555404427	0.126544146	0.080061943	0.054635995	2.717286037	0.221072175
87	5	12.4	1.937757546	0.416041375	0.326871924	0.224243354	3.385255585	0.726822812
90	5	12.4	2.55376439	0.350150148	0.4638876	0.108046597	4.461417365	0.61171107
93	5	12.4	2.690716437	0.430048641	0.386171449	0.115577797	4.700672106	0.751293456
96	5	12.4	2.685236198	0.424705389	0.321093399	0.068643491	4.691098148	0.741958814
99	5	12.4	2.494465321	0.392162411	0.284558267	0.046662414	4.3578221	0.685106347
102	5	12.4	2.283029918	0.350497132	0.258442689	0.032382337	3.988445199	0.612317252
105	5	12.4	2.143194509	0.345240031	0.240814435	0.027385313	3.744153233	0.603133114
108	5	12.4	2.079034469	0.302166313	0.22844867	0.021199541	3.632065871	0.52788348
111	5	12.4	2.137824569	0.286071192	0.22230249	0.020116109	3.734771968	0.499765362
114	5	12.4	2.173853041	0.278776195	0.220645685	0.021750267	3.797713579	0.487021027
117	5	12.4	2.010955121	0.295061652	0.209828853	0.021802544	3.51313149	0.515471663
120	5	12.4	1.980515132	0.26888974	0.209001762	0.020979713	3.459952936	0.469749425
123	5	12.4	1.959627511	0.26096654	0.209855814	0.020643449	3.423462336	0.455907622
126	5	12.4	1.937239705	0.256579004	0.207647818	0.02112124	3.384350918	0.448242613
129	5	12.4	1.88401189	0.253226064	0.205182155	0.021391162	3.291362114	0.442385038
132	5	12.4	1.780728111	0.251832124	0.19812222	0.020895496	3.110925717	0.439949831
135	5	12.4	1.778246173	0.187486598	0.199869595	0.018451594	3.10658978	0.327538425
138	5	12.4	1.932189414	0.262385773	0.207502083	0.023501967	3.375528079	0.458387019
141	5	12.4	1.993582148	0.260365761	0.210907554	0.023186515	3.482780967	0.454858064
144	5	12.4	1.898870295	0.282009298	0.206884275	0.02268463	3.317319695	0.492669247
147	5	12.4	1.75362664	0.226455555	0.20077571	0.019604673	3.063579543	0.395617054
150	5	12.4	1.677688625	0.238267599	0.195803716	0.020054725	2.930916099	0.416252653
153	5	12.4	1.567047475	0.21714543	0.189692892	0.018429365	2.737626401	0.379352299
156	5	12.4	1.529418603	0.184069475	0.187462142	0.018435168	2.671888895	0.321568723
159	5	12.4	1.876766288	0.229187227	0.202691977	0.022717231	3.278704072	0.400389275

162	5	12.4	2.225016106	0.325474103	0.219647246	0.024067083	3.887095275	0.568602107
165	5	12.4	2.128862467	0.254024098	0.217717207	0.017310413	3.719115207	0.443779202
168	5	12.4	2.190605894	0.38076035	0.315667572	0.141121106	3.826980756	0.665186986
171	5	12.4	2.237474012	0.361162815	0.542555275	0.141243015	3.908859191	0.630950161
174	5	12.4	2.153484807	0.56630622	0.388765648	0.139956132	3.762130347	0.989334964
177	5	12.4	1.995234536	0.417148581	0.299503398	0.095034015	3.485667683	0.728757097
180	5	12.4	1.839168155	0.319552681	0.251561583	0.053666569	3.213020266	0.558257404
183	5	12.4	2.13017419	0.330987923	0.247334227	0.029576255	3.721406783	0.578234733
186	5	12.4	2.335248506	0.418238673	0.246410406	0.030271667	4.079670887	0.730661483
189	5	12.4	2.059820203	0.339763283	0.230860177	0.027389538	3.598498616	0.593565255
192	5	12.4	1.934927088	0.316764303	0.221936237	0.029473411	3.380310784	0.553386118
195	5	12.4	1.827940335	0.288265618	0.214529356	0.029837792	3.193405305	0.503599015
198	5	12.4	1.742814879	0.279820044	0.208847279	0.030299388	3.044691434	0.488844629
201	5	12.4	1.679024622	0.269015542	0.204258519	0.030332702	2.933250081	0.469969202
204	5	12.4	1.662096586	0.249994753	0.201995942	0.02938661	2.903676861	0.436739949
207	5	12.4	1.907631567	0.334648212	0.213843134	0.033742447	3.332625607	0.584629244
210	5	12.4	2.045965002	0.335243901	0.223501796	0.033509529	3.574293627	0.58566991
213	5	12.4	2.099923784	0.336760328	0.228770675	0.03273475	3.668559429	0.588319102
216	5	12.4	2.067051837	0.334752335	0.227311154	0.031919086	3.611132254	0.584811146
219	5	12.4	2.024840312	0.319377853	0.225369879	0.030513775	3.537388869	0.55795198
222	5	12.4	2.004366423	0.315974364	0.224111908	0.0305395	3.501621058	0.552006097
225	5	12.4	1.990140121	0.314973354	0.223399968	0.030231098	3.476767759	0.550257337
228	5	12.4	1.944162866	0.295906753	0.221270099	0.029054435	3.396445657	0.516948051
231	5	12.4	1.88238002	0.304280292	0.215530369	0.029519819	3.288511242	0.531576594
234	5	12.4	2.031828279	0.316496269	0.226702722	0.029412122	3.549596824	0.552917863
237	5	12.4	2.078720367	0.320919221	0.230448626	0.028418082	3.631517134	0.560644745
240	5	12.4	1.96216252	0.309077163	0.224151361	0.02692561	3.427890989	0.539956712

243	5	12.4	1.900863523	0.293395164	0.219797434	0.025674728	3.320801857	0.512560314
246	5	12.4	1.863722819	0.280566772	0.215430079	0.024435481	3.255917178	0.490149158
249	5	12.4	1.836025638	0.277741812	0.210785399	0.024458921	3.207530301	0.485213964
252	5	12.4	1.795103672	0.257890785	0.204958755	0.029480609	3.136039772	0.450534291
255	3	4.666666667	1.850981258	0.190414643	0.189009588	0.050673972	3.233657717	0.332653708

Carbon Dioxide (CO_2) and Nitric oxide (NO) data

Table 3: Nitric oxide and carbon dioxide emission data in calculated mean fluxes, blank corrected, in µg CO_2-C m^{-2} h^{-1} and µg NO-N m^{-2} h^{-1}, respectively, for samples OR 20, OR 80, SW 20, SW 80 of Experiment 1. Values show average fluxes of replicates of one measurement run (3.5h). Also shown is standard error (s.e.).

No	Hours	Litter	Treatment	F_CO2_mean	F_NO_mean	F_CO2_se	F_NO_se	n
1	0.0	OR	20	2.963673784	12.0080474	0.394899	1.82333	5
2	3.5	OR	20	2.570024402	17.3632635	0.492901	3.506433	5
3	7.0	OR	20	2.607356799	16.1005882	0.149752	3.319926	5
4	10.5	OR	20	2.531758695	13.63275412	0.442825	3.044445	5
5	14.0	OR	20	2.049341171	12.63105322	0.159287	2.846518	5
6	17.5	OR	20	1.588286073	9.865154662	0.124927	2.367889	5
7	21.0	OR	20	1.524302493	9.808444469	0.363143	2.420435	5
8	24.5	OR	20	1.205525307	7.305939223	0.403919	1.795382	5
9	28.0	OR	20	0.18168433	6.928319217	0.324857	1.65418	5
10	31.5	OR	20	-0.253134389	6.339178255	0.216296	1.679308	5
11	35.0	OR	20	0.55635641	5.901085295	0.330249	1.044128	5
12	38.5	OR	20	1.286515867	4.907984996	0.23274	0.999054	5
13	42.0	OR	20	1.2896269	4.129899647	0.156092	0.958502	5
14	45.5	OR	20	0.773713919	3.707932808	0.234307	0.98844	5

15	49.0	OR	20	0.077672125	3.190284316	0.269102	0.821936	5
16	52.5	OR	20	0.262260086	3.055899973	0.255744	0.549601	5
17	56.0	OR	20	1.223569298	2.671829519	0.713746	0.70876	5
18	59.5	OR	20	1.10700926	2.034578962	0.31766	0.514114	5
19	63.0	OR	20	1.376424722	2.310066866	0.35065	0.399881	5
20	66.5	OR	20	0.452551608	1.964161566	0.308071	0.273944	5
21	70.0	OR	20	0.661405626	1.861760696	0.279551	0.384406	5
22	73.5	OR	20	-0.158973789	2.049630008	0.46382	0.307713	5
23	77.0	OR	20	-0.34076182	1.285789399	0.412532	0.336109	5
24	80.5	OR	20	-0.401530666	-0.166636586	0.239239	0.98544	5
25	84.0	OR	20	1.149630413	2.64898418	0.200364	1.510831	5
26	87.5	OR	20	2.105028662	1.494085132	0.502975	0.517335	5
27	91.0	OR	20	1.351640159	1.307559663	0.224057	0.24646	5
28	0.0	OR	80	13.02537687	24.95651644	1.223223	1.273095	5
29	3.5	OR	80	11.02508632	20.53150878	1.37657	1.388789	5
30	7.0	OR	80	10.54899456	19.0000648	1.443164	1.381448	5
31	10.5	OR	80	9.17049582	14.96047143	1.335669	0.917758	5
32	14.0	OR	80	9.910817985	14.71105409	0.370013	0.861992	5
33	17.5	OR	80	9.75692555	11.86882522	0.55266	0.555751	5
34	21.0	OR	80	10.64274036	11.9008087	0.492575	0.769337	5
35	24.5	OR	80	12.46632423	11.35843349	0.221769	0.744876	5
36	28.0	OR	80	21.12567732	10.37823409	1.059243	0.578887	5
37	31.5	OR	80	38.58220227	9.989594564	3.525865	2.057731	5
38	35.0	OR	80	73.19856331	7.465319054	8.604191	0.648381	5
39	38.5	OR	80	135.3927805	7.861752868	20.02146	1.022823	5
40	42.0	OR	80	237.7100947	4.910672683	37.89901	0.714802	5
41	45.5	OR	80	364.1106415	2.603562272	48.54741	0.418528	5

42	49.0	OR	80	479.9590828	1.324223322	44.02337	0.104638	5
43	52.5	OR	80	560.0279478	1.04416635	39.93311	0.172693	5
44	56.0	OR	80	583.450086	0.578658983	37.60486	0.126626	5
45	59.5	OR	80	560.0611322	0.288926339	35.48608	0.177994	5
46	63.0	OR	80	511.8890668	-0.113420386	32.44458	0.289447	5
47	66.5	OR	80	457.3674867	-0.216090024	29.09273	0.137984	5
48	70.0	OR	80	406.0224788	-0.039777766	25.87633	0.080002	5
49	73.5	OR	80	365.0161596	-0.059666649	22.87475	0.123746	5
50	77.0	OR	80	334.613278	-0.222540473	20.00291	0.078211	5
51	80.5	OR	80	313.2850724	0.79636162	18.62303	0.362918	5
52	84.0	OR	80	297.2389861	-1.900732155	16.41224	0.194588	5
53	87.5	OR	80	285.9158629	0.050259744	15.79774	0.143441	5
54	91.0	OR	80	292.0741528	0.35611851	16.01126	0.046746	5
55	0.0	SW	20	5.027256572	8.507872792	4.168726	1.486216	3
56	3.5	SW	20	2.092688231	15.92346964	0.850823	0.699485	5
57	7.0	SW	20	1.844635196	13.66285621	0.84244	0.138962	5
58	10.5	SW	20	2.091132715	14.73094297	0.839874	0.042921	5
59	14.0	SW	20	1.65486218	11.75406099	1.125918	0.883068	5
60	17.5	SW	20	1.76592606	11.62236434	0.822004	0.263901	5
61	21.0	SW	20	1.785214465	11.06332547	0.638788	0.147461	5
62	24.5	SW	20	1.225747021	9.258543735	0.464675	0.181883	5
63	28.0	SW	20	0.947620667	9.126040772	0.472079	0.080318	5
64	31.5	SW	20	1.753793031	7.429572819	0.471107	0.032722	5
65	35.0	SW	20	0.481173112	8.681766132	0.336821	0.024648	5
66	38.5	SW	20	0.396034507	6.328158739	0.624167	0.078618	5
67	42.0	SW	20	0.585289018	6.123356999	0.661072	0.065019	5
68	45.5	SW	20	0.542149359	5.443372221	2.21719	0.242228	5

69	49.0	SW	20	0.175773367	4.514507638	0.229194	0.22098	5
70	52.5	SW	20	-0.270970979	4.689476053	0.660368	0.229479	5
71	56.0	SW	20	-0.648442989	3.610369774	0.135389	0.138537	5
72	59.5	SW	20	0.129730078	3.49668062	0.404262	0.089667	5
73	63.0	SW	20	0.301873907	3.232749769	0.378332	0.041221	5
74	66.5	SW	20	0.066472406	2.292328133	0.016387	0.303847	5
75	70.0	SW	20	0.556460111	2.563784507	0.169594	0.089242	5
76	73.5	SW	20	0.306333054	2.174338679	0.181777	0.21673	5
77	77.0	SW	20	-1.784695959	2.317861158	0.566776	0.082017	5
78	80.5	SW	20	-0.430359572	1.610999511	0.596648	0.413487	5
79	84.0	SW	20	-2.240773404	-0.005106605	0.597898	2.874434	5
80	87.5	SW	20	-2.748805101	1.213490622	0.258868	0.330619	5
81	91.0	SW	20	1.614626153	1.681954444	0.620174	0.222254	5
82	0.0	SW	80	6.335964475	13.34346942	0.481528	0.683009	6
83	3.5	SW	80	8.649190382	20.55856483	0.477575	1.042199	6
84	7.0	SW	80	8.426751519	15.41321229	0.444853	0.851267	6
85	10.5	SW	80	8.227386152	15.25889426	0.327344	0.849474	6
86	14.0	SW	80	7.813013833	13.75894102	0.195429	0.641138	6
87	17.5	SW	80	7.2875085	11.80073716	0.351563	0.716326	6
88	21.0	SW	80	8.005120124	11.62536559	0.38745	0.53318	6
89	24.5	SW	80	10.81066701	9.050337592	1.320096	0.64864	6
90	28.0	SW	80	18.14129789	9.501421038	3.727237	0.654211	6
91	31.5	SW	80	39.28733519	7.647589019	10.41974	0.761058	6
92	35.0	SW	80	80.85134165	6.672182658	22.04606	1.08061	6
93	38.5	SW	80	138.0548569	4.112160913	33.9717	0.850875	6
94	42.0	SW	80	201.4647967	3.760745855	41.00499	0.717081	6
95	45.5	SW	80	257.4582065	3.080313129	38.9329	0.458849	6

96	49.0	SW	80	307.9074098	1.812620821	31.04179	0.159723	6
97	52.5	SW	80	369.9178168	1.208115249	24.59734	0.200485	6
98	56.0	SW	80	447.3903173	0.544704539	28.99744	0.231852	6
99	59.5	SW	80	515.7817988	0.20874368	41.80499	0.147627	6
100	63.0	SW	80	551.1279736	0.450635499	50.21877	0.229944	6
101	66.5	SW	80	546.9143386	0.034044034	50.19041	0.158177	6
102	70.0	SW	80	510.7331106	0.353430824	43.77872	0.221197	6
103	73.5	SW	80	465.5266894	-0.195305246	36.56272	0.099411	6
104	77.0	SW	80	428.5130873	0.107507475	30.37828	0.147807	6
105	80.5	SW	80	400.3316216	-0.996683881	26.34882	0.418034	6
106	84.0	SW	80	383.9247246	0.013886382	23.53393	0.358626	6
107	87.5	SW	80	371.4334084	-0.721867899	21.49299	0.182247	6
108	91.0	SW	80	368.6697741	-0.204936124	21.1924	0.102158	6

Table 4: Nitric oxide and carbon dioxide emission data in calculated mean fluxes, blank corrected, in µg CO_2-C m^{-2} h^{-1} and µg NO-N m^{-2} h^{-1}, respectively, for Experiment 2 with drying and rewetting cycles. Values are chamber means blank corrected per run of incubations (~50min). Gaps in the table indicate measuring breaks due to gas sampling and rewetting and beginning and end of one Cycle. Also shown is standard error (s.e.).

No	Hours	Litter	Treatment	F_CO2_mean	F_NO_mean	F_CO2_se	F_NO_se	n
Start Cycle 1								
1	0	SW	60	4.914913712	13.11389617	2.693471761	5.11887542	3
2	0.666666667	SW	60	2.902723461	16.32870563	0.562090511	4.107289258	4
3	1.5	SW	60	2.165408629	16.70263006	0.508484423	4.034761359	4
4	2.333333333	SW	60	2.479882219	16.15165425	0.793378069	4.054054577	4
5	3.166666667	SW	60	2.32458982	15.59496711	0.669614247	3.940829221	4
6	4	SW	60	1.64547723	14.71340582	0.433663815	3.814391026	4
7	4.833333333	SW	60	1.193729306	14.16746942	0.540412338	3.509244186	4
8	5.666666667	SW	60	2.368662788	13.58592117	0.34164421	3.37014904	4
9	6.5	SW	60	1.791566157	14.66872302	0.532956575	3.607303799	4
10	7.333333333	SW	60	2.070133242	14.24474042	0.481257354	3.515768143	4
11	8.166666667	SW	60	1.70847565	13.39274368	0.51145636	3.262296089	4
12	9	SW	60	1.592200789	12.77020821	0.281181191	3.109610285	4
13	9.833333333	SW	60	1.545405667	11.87655232	0.401969226	2.8643882	4
14	10.66666667	SW	60	1.701735078	11.25502473	0.379608476	2.780466806	4
15	11.5	SW	60	1.90952616	10.99499103	0.549692435	2.685870961	4
16	12.33333333	SW	60	1.704716485	11.00238217	0.603714296	2.679669024	4
17	13.16666667	SW	60	1.465685445	11.12836749	0.578367515	2.826981051	4
18	14	SW	60	1.796880839	10.60594836	0.762443463	2.542084793	4
19	14.83333333	SW	60	1.334114673	10.17927806	0.560861023	2.444492147	4
20	15.66666667	SW	60	1.415649664	9.404888285	0.57872439	2.263299134	4

21	16.5	SW	60	2.28881294	8.909010057	0.628525102	2.051926958	4
22	17.33333333	SW	60	2.347792941	8.514256048	0.689757166	1.963782155	4
23	18.16666667	SW	60	2.355570524	9.398505029	0.87290954	2.200663625	4
24	19	SW	60	1.929099743	9.6064648	0.853921175	2.336555454	4
25	19.83333333	SW	60	2.680154972	9.10957869	0.980527275	2.016234179	4
26	20.66666667	SW	60	2.765967634	8.947981517	0.980087359	2.236175132	4
27	21.5	SW	60	3.284084263	8.731958684	1.055720963	1.990489946	4
28	22.33333333	SW	60	3.18077204	8.190053819	1.102473539	1.936189539	4
29	23.16666667	SW	60	3.582873062	8.040887198	1.168625427	1.935346063	4
30	24	SW	60	4.464980558	7.989485186	1.347218313	1.897793832	4
31	24.83333333	SW	60	4.864877931	8.675181299	1.627694229	2.15451714	4
32	25.66666667	SW	60	5.206054555	8.642929057	1.696617443	2.132595276	4
33	26.5	SW	60	6.075199413	8.67551726	1.812316067	2.042613034	4
34	27.33333333	SW	60	6.335489178	8.139995651	1.954301858	1.889190605	4
35	28.16666667	SW	60	6.863457412	7.585660234	2.514811386	1.889994112	4
36	29	SW	60	7.359537557	7.362582223	2.459205333	1.719884829	4
37	29.83333333	SW	60	7.503422836	7.43548573	2.705198405	1.772903581	4
38	30.66666667	SW	60	8.249941141	7.448924164	2.641707968	1.901473607	4
39	31.5	SW	60	8.802797639	7.518132101	2.800995566	1.863813434	4
40	32.33333333	SW	60	8.498564532	7.253058983	2.94396797	1.730680874	4
41	33.16666667	SW	60	8.598895348	6.87241533	2.683642975	1.562474849	4
42	34	SW	60	9.2532493	6.503866268	2.773407853	1.563122255	4
43	34.83333333	SW	60	10.85322767	6.492107638	2.957004001	1.506366402	4
44	35.66666667	SW	60	9.729237356	5.994549606	2.813271417	1.503199234	4
45	36.5	SW	60	9.893085097	6.566354988	2.764923741	1.652726616	4
46	37.33333333	SW	60	11.00268688	6.197134004	2.863775731	1.432384289	4
47	38.16666667	SW	60	10.64426995	5.931724925	2.815109961	1.358100536	4

48	39	SW	60	11.87922045	5.840007611	2.902005793	1.408624821	4
49	39.83333333	SW	60	12.42274384	5.747954335	3.083054579	1.389999847	4
50	40.66666667	SW	60	12.84351106	5.134489807	3.048305657	1.296204184	4
51	41.5	SW	60	13.00113674	4.923506388	2.967848137	1.108824755	4
52	42.33333333	SW	60	14.09323897	5.52286056	3.198848129	1.247189646	4
53	43.16666667	SW	60	14.01896305	5.532603425	3.331124604	1.35182596	4
54	44	SW	60	15.2335622	5.544698016	3.499440907	1.362094078	4
55	44.83333333	SW	60	15.98461743	5.286344115	3.850895748	1.29429307	4
56	45.66666667	SW	60	16.41575476	4.746790976	3.853854097	1.197193907	4
57	46.5	SW	60	17.32625044	4.483397662	4.014462621	1.189952628	4
58	47.33333333	SW	60	18.23000554	4.350021201	4.138371968	1.148476327	4
59	48.16666667	SW	60	19.33377414	4.403774939	4.419456701	1.051814848	4
60	49	SW	60	20.06629279	4.773331884	4.68714119	1.225682038	4
61	49.83333333	SW	60	20.80036697	4.512290296	5.029098647	1.15009394	4
62	50.66666667	SW	60	22.86233375	4.632900245	5.642429075	1.141779416	4
63	51.5	SW	60	24.9762807	4.224035879	6.077095308	1.068985473	4
64	52.33333333	SW	60	25.79914895	3.95829084	6.23596914	1.069941041	4
65	53.16666667	SW	60	27.22413171	3.502727915	6.644529603	0.898040834	4
66	54	SW	60	29.26367313	3.555809731	7.044016867	0.888877594	4
67	54.83333333	SW	60	31.58242976	3.506087524	7.648378002	0.69786399	4
68	55.66666667	SW	60	33.56856511	3.08983202	8.240417673	0.767173518	4
69	56.5	SW	60	35.68990077	2.803929329	8.982766588	0.82518725	4
70	57.33333333	SW	60	37.27717575	2.984676271	9.305543654	0.70683827	4
71	58.16666667	SW	60	40.38678291	1.838713781	10.33095319	0.936684132	4
72	59	SW	60	42.36410367	2.310066866	11.12366974	1.270325575	4
73	59.83333333	SW	60	44.50501291	-0.006719217	11.72996525	1.524872461	4
74	60.66666667	SW	60	49.08523132	6.589536287	13.17434532	1.777752902	4

75	61.5	SW	60	50.53808375	-0.789508018	13.60098861	0.692758036	4
76	62.33333333	SW	60	53.00707736	-1.272955694	14.32683879	0.339252803	4
77	63.16666667	SW	60	52.32770551	0.003695569	11.49738167	0.358305241	4
78	64	SW	60	50.41830898	0.437085077	19.3852082	0.201959427	4
79	64.83333333	SW	60	65.31821289	1.190981245	11.15494572	0.226313219	4
80	65.66666667	SW	60	68.07951398	1.319990215	11.32278755	0.231124386	4
81	66.5	SW	60	72.00006375	1.246414787	11.1831571	0.278688257	4
82	67.33333333	SW	60	75.41844094	1.094224518	12.22760445	0.151944837	4
83	68.16666667	SW	60	74.7302545	0.731050829	13.80345462	0.427627367	4
84	69	SW	60	86.07165511	0.981341669	8.794377108	0.274951689	4
85	69.83333333	SW	60	85.78336605	0.761287306	13.333818	0.237020803	4
86	70.66666667	SW	60	86.88778278	0.578524599	11.75243905	0.300376565	4
87	71.5	SW	60	88.03043929	0.402145148	11.44583924	0.047850939	4
88	72.33333333	SW	60	89.03050679	0.877865724	11.03975333	0.422524755	4
89	73.16666667	SW	60	88.77617984	0.682336504	10.87091866	0.214018318	4
90	74	SW	60	88.95610125	0.52006741	9.979745906	0.205959808	4
91	74.83333333	SW	60	88.80171624	0.772709976	9.568097442	0.206068652	4
92	75.66666667	SW	60	89.94968743	0.412895896	9.181010933	0.196772804	4
93	76.5	SW	60	90.24964287	0.54358467	8.792380463	0.203020084	4
94	77.33333333	SW	60	90.12416454	0.518387605	8.661509896	0.321582406	4
95	78.16666667	SW	60	89.09713475	0.521075292	8.362671797	0.075672775	4
96	79	SW	60	88.22773064	0.280191356	8.190265628	0.140254706	4
97	79.83333333	SW	60	88.32806146	0.736762164	8.087864469	0.258821812	4
98	80.66666667	SW	60	88.11469644	0.4068486	7.574885846	0.163108103	4
99	81.5	SW	60	86.87209799	0.205944007	7.47803465	0.217534851	4
100	82.33333333	SW	60	86.09200645	-0.039643381	7.612217984	0.312202674	4
101	83.16666667	SW	60	85.85958636	1.147306333	7.268116638	0.295922022	4

102	84	SW	60	84.08746416	-0.326217994	7.405237279	0.875021887	4
End Cycle 1								
Start Cycle 2								
103	84.83333333	SW	60					
104	85.66666667	SW	60					
105	86.5	SW	60					
106	87.33333333	SW	60					
107	88.16666667	SW	60					
108	89.16666667	SW	60	103.4383922	0.112434901	16.8527421	0.038749428	3
109	89.83333333	SW	60	97.41862965	0.171004077	7.871082322	0.084914841	4
110	90.66666667	SW	60	100.1122658	0.316475129	6.611905461	0.183961401	4
111	91.5	SW	60	101.6067283	0.317483012	6.178937789	0.199213458	4
112	92.33333333	SW	60	102.3741164	0.334281055	6.09023185	0.101633389	4
113	93.16666667	SW	60	103.4141088	0.329913563	5.78618936	0.102383027	4
114	94	SW	60	104.6353189	0.30102093	5.380694845	0.190329067	4
115	94.83333333	SW	60	105.5416666	-0.048042403	5.100644434	0.162784853	4
116	95.66666667	SW	60	106.279111	0.121617831	4.812009558	0.199587143	4
117	96.5	SW	60	106.8424673	0.194521337	4.527363758	0.068182399	4
118	97.33333333	SW	60	107.4209898	0.321178581	4.537398411	0.188929126	4
119	98.16666667	SW	60	108.0113083	0.250626801	4.491105708	0.162201494	4
120	99	SW	60	108.5321471	0.19149769	4.255003381	0.170367603	4
121	99.83333333	SW	60	108.2775609	0.259361783	4.846954049	0.076094455	4
122	100.6666667	SW	60	108.2779498	0.188138081	4.020179	0.138446314	4
123	101.5	SW	60	107.5779673	0.186122316	3.365673559	0.063643674	4
124	102.3333333	SW	60	107.3264922	0.043338951	3.438842603	0.21341978	4
125	103.1666667	SW	60	107.2274576	0.103811905	2.873622245	0.062834262	4
126	104	SW	60	106.8446709	0.10549171	3.248647331	0.132123914	4

127	104.8333333	SW	60	106.2489081	0.31681109	3.012196165	0.104063842	4
128	105.6666667	SW	60	106.0276359	0.201576515	3.004290313	0.156061443	4
129	106.5	SW	60	105.4811311	-0.001007883	2.828082122	0.146978812	4
130	107.3333333	SW	60	104.748742	0.364853493	2.890080978	0.230756284	4
131	108.1666667	SW	60	104.1317205	0.224085893	2.847142613	0.149675621	4
132	109	SW	60	103.4981067	0.228117423	2.706406686	0.181613182	4
133	109.8333333	SW	60	104.7305943	0.278175591	6.70279483	0.098129714	4
134	110.6666667	SW	60	101.5652478	-1.663006252	3.001374105	1.576935092	4
135	111.5	SW	60	101.2323673	0.065512367	2.74839276	0.151965635	4
136	112.3333333	SW	60	101.0830377	0.336968742	2.588740241	0.075591193	4
137	113.1666667	SW	60	99.7644782	0.199896711	2.694566398	0.276352602	4
138	114	SW	60	98.95301708	0.127665126	2.627512081	0.163685242	4
139	114.8333333	SW	60	97.80608289	0.162605056	2.614501239	0.268725569	4
140	115.6666667	SW	60	90.36980652	-0.016126121	4.051663061	0.165522929	4
141	116.5	SW	60	98.92683255	0.033260125	2.473802507	0.118808446	4
142	117.3333333	SW	60	95.83887299	0.394082088	2.332049307	0.236529409	4
143	118.1666667	SW	60	94.64345855	-0.218710519	2.33632824	0.249501327	4
144	119	SW	60	94.22372834	-0.30135689	2.394065627	0.105058386	4
145	119.8333333	SW	60	93.49341333	-0.028892634	2.605862327	0.205005874	4
146	120.6666667	SW	60	92.66237863	0.252642566	2.461988939	0.258797754	4
147	121.5	SW	60	91.69821763	0.269440609	2.371821926	0.056030644	4
148	122.3333333	SW	60	91.25308065	0.056105463	2.439388544	0.118465948	4
149	123.1666667	SW	60	90.61168934	0.231812993	2.400461131	0.102550459	4
150	124	SW	60	90.01748203	-0.151518347	2.3819119	0.224169154	4
151	124.8333333	SW	60	89.19759519	-0.034603968	2.669578245	0.200768122	4
152	125.6666667	SW	60	88.32715407	-0.343351998	2.446662916	0.231089955	4
153	126.5	SW	60	87.77507533	0.05073009	2.477632291	0.062975413	4

154	127.3333333	SW	60	87.21366349	0.209639576	2.588186686	0.093430145	4
155	128.1666667	SW	60	86.56125394	0.388370753	2.564695634	0.125053279	4
156	129	SW	60	86.1104134	0.243571623	2.324490027	0.22208978	4
157	129.8333333	SW	60	85.22415786	0.137743952	2.588225275	0.238956437	4
158	130.6666667	SW	60	84.66533855	-0.210647459	2.339916199	0.246969014	4
159	131.5	SW	60	83.90157993	0.264065235	2.338854794	0.180145625	4
160	132.3333333	SW	60	82.41891343	0.206615928	2.172437649	0.157379286	4
161	133.1666667	SW	60	81.94720305	-0.18780212	2.464252373	0.289741586	4
162	134	SW	60	81.190185	0.368885023	2.298429481	0.16512012	4
163	134.8333333	SW	60	79.8677367	0.2738081	3.269131419	0.133959662	4
164	135.6666667	SW	60	80.02315873	-0.167980429	2.428852541	0.156661062	4
165	136.5	SW	60	79.3846192	0.218710519	2.607206549	0.084059842	4
166	137.3333333	SW	60	78.72741347	0.179403099	2.372658009	0.318282209	4
167	138.1666667	SW	60	78.52791847	0.069879859	2.412397873	0.157754284	4
168	139	SW	60	76.83175733	0.10179614	3.357582778	0.135474455	4
169	139.8333333	SW	60	78.25401794	0.497893993	2.596262423	3.512354716	4
170	140.6666667	SW	60	77.81147349	-0.444140256	2.626413212	0.148579806	4
171	141.5	SW	60	77.99308004	-0.179067138	2.887658822	0.220786275	4
172	142.3333333	SW	60	77.99787622	-0.094405001	2.723443427	0.080185865	4
173	143.1666667	SW	60	77.54742456	0.209975537	2.814064617	0.106087588	4
174	144	SW	60	77.20715532	0.314459364	2.756825193	0.154007428	4
175	144.8333333	SW	60	77.40133563	0.116242457	2.771561316	0.124422897	4
176	145.6666667	SW	60	74.07875233	0.060136994	3.536891278	0.138942597	4
177	146.5	SW	60	77.97739525	-0.108515357	5.629213877	0.184679796	4
178	147.3333333	SW	60	76.41656404	-0.115234575	3.095110084	0.151795206	4
179	148.1666667	SW	60	76.73363016	0.051737972	3.036671079	0.08883354	4
180	149	SW	60	74.79416031	-0.001679804	2.943281134	0.174087275	4

181	149.8333333	SW	60	75.30385122	-0.173691764	2.873236573	0.306378805	4
182	150.6666667	SW	60	74.80751182	-0.119266105	2.639357873	0.196152333	4
183	151.5	SW	60	74.16145396	0.275487904	2.902117815	0.251512425	4
184	152.3333333	SW	60	73.03253784	0.076263115	2.991897038	0.04574129	4
185	153.1666667	SW	60	71.46341055	0.096420767	2.443118756	0.079118366	4
186	154	SW	60	72.61747418	-0.230133188	3.180779203	0.197015098	4
187	154.8333333	SW	60	70.92520183	-0.211655341	2.966844768	0.226355857	4
188	155.6666667	SW	60	70.77755739	0.366197336	3.074380934	0.903846108	4
189	156.5	SW	60	69.93070827	-0.556015222	3.088110408	0.144492205	4
190	157.3333333	SW	60	68.33098915	0.094740962	3.264008885	0.143347324	4
191	158.1666667	SW	60	71.82429038	0.09373308	2.886765415	0.086280915	4
192	159	SW	60	72.53101339	0.354438706	4.583652525	0.125106669	4
193	159.8333333	SW	60	70.24920027	0.065512367	4.111343418	0.159811346	4
194	160.6666667	SW	60	73.95482952	-0.103811905	2.983874131	0.104393046	4
195	161.5	SW	60	73.24136594	-0.075927154	3.841345467	0.15242062	4
196	162.3333333	SW	60	75.10772651	0.295309595	3.720759335	0.196747564	4
197	163.1666667	SW	60	75.14441078	0.687711878	4.313371485	0.711989418	4
198	164	SW	60	82.07488503	-0.017805926	1.659997961	0.053510666	4
199	164.8333333	SW	60	74.87478791	0.208631693	5.433161112	0.229909433	4
200	165.6666667	SW	60	74.90071319	-0.087349823	4.873709319	0.112151229	4
End Cycle 2								
Start Cycle 3								
201	166.5	SW	60					
202	167.3333333	SW	60					
203	168.1666667	SW	60					
204	169	SW	60					
205	170	SW	60	97.43807361	0.171004077	4.756523579	0.069233754	4

206	170.8333333	SW	60	94.07971343	-0.020493612	4.083872561	0.109499706	4
207	171.6666667	SW	60	93.92675431	0.0154542	3.499532473	0.178992429	4
208	172.5	SW	60	92.03433883	0.036955694	3.175411435	0.038919293	4
209	173.3333333	SW	60	91.59697943	-0.08231041	3.116389816	0.060334367	4
210	174.1666667	SW	60	91.4435018	0.086677902	3.428499051	0.167505381	4
211	175	SW	60	90.59159725	0.0154542	3.099895139	0.096671922	4
212	175.8333333	SW	60	89.53527191	0.366533297	3.47278107	0.080438834	4
213	176.6666667	SW	60	88.60857294	0.003359609	3.211078046	0.131863959	4
214	177.5	SW	60	87.90586835	-0.005711335	3.1817435	0.027085336	4
215	178.3333333	SW	60	86.94092959	0.058121229	3.125763857	0.062133385	4
216	179.1666667	SW	60	86.68945442	0.158237565	3.274058002	0.137380608	4
217	180	SW	60	85.2867674	0.054425659	3.148133164	0.062172429	4
218	180.8333333	SW	60	85.58763022	0.023853221	2.994517099	0.092659239	4
219	181.6666667	SW	60	84.31016227	0.009070943	3.118135657	0.054524767	4
220	182.5	SW	60	83.80073061	0.37929981	3.177954454	0.160861647	4
221	183.3333333	SW	60	84.23821963	-0.052073933	2.728814783	0.175177415	4
222	184.1666667	SW	60	84.36395722	0.347719489	2.557932763	0.077268806	4
223	185	SW	60	85.48755866	0.122625714	2.537806031	0.100422329	4
224	185.8333333	SW	60	85.92815871	-0.120945909	2.749276977	0.128296586	4
225	186.6666667	SW	60	87.01442775	-0.018477847	3.054747551	0.291747334	4
226	187.5	SW	60	88.35411636	0.360821962	3.154312406	0.215216781	4
227	188.3333333	SW	60	89.39631243	0.319834738	3.217176823	0.100583487	4
228	189.1666667	SW	60	89.51660571	0.336968742	3.090034127	0.187947106	4
229	190	SW	60	90.2458837	0.232148954	3.136100495	0.187734796	4
230	190.8333333	SW	60	90.54570951	-0.001007883	3.37639164	0.041264875	4
231	191.6666667	SW	60	90.73172337	0.009406904	3.299937716	0.102168932	4
232	192.5	SW	60	90.58848622	0.034939929	3.424166116	0.111605098	4

233	193.3333333	SW	60	90.04729609	0.32453819	3.333574264	0.079428044	4
234	194.1666667	SW	60	89.30531471	0.500245719	3.450770212	0.230921143	4
235	195	SW	60	89.43416333	0.16025333	3.260563642	0.228440456	4
236	195.8333333	SW	60	89.07172798	-0.033260125	3.358312148	0.223703434	4
237	196.6666667	SW	60	87.98545894	0.165628703	3.246354695	0.125795249	4
238	197.5	SW	60	87.5061006	0.189481924	3.251370586	0.111764101	4
239	198.3333333	SW	60	87.14172085	0.331929329	3.312215489	0.263770713	4
240	199.1666667	SW	60	85.97080579	0.402481109	3.321623947	0.044911655	4
241	200	SW	60	85.41535676	0.372244632	3.288687076	0.132342995	4
242	200.8333333	SW	60	84.51847186	0.517043762	3.508558347	0.152288134	4
243	201.6666667	SW	60	84.36214245	0.194185376	3.33177162	0.171448038	4
244	202.5	SW	60	83.75652802	0.22307801	3.110357885	0.234534369	4
245	203.3333333	SW	60	81.2275174	0.200232672	3.705908998	0.201415937	4
246	204.1666667	SW	60	82.42902429	0.389714596	3.082095954	0.166936153	4
247	205	SW	60	82.70499885	0.339656428	3.489476329	0.066049996	4
248	205.8333333	SW	60	82.12971698	0.244243544	3.217247063	0.184481672	4
249	206.6666667	SW	60	81.63856264	0.777749388	2.836303603	0.194284454	4
250	207.5	SW	60	82.0393674	0.237860288	2.47235114	0.155256088	4
251	208.3333333	SW	60	82.39869172	-0.189817885	2.25459102	0.181912077	4
252	209.1666667	SW	60	83.18124615	0.134720304	2.479202274	0.151594807	4
253	210	SW	60	84.25234891	0.048378364	2.50665673	0.225904305	4
254	210.8333333	SW	60	84.3319395	0.423310682	2.508427362	0.197163709	4
255	211.6666667	SW	60	85.23997227	0.408864365	2.634973109	0.134804059	4
256	212.5	SW	60	85.61951831	0.556351182	2.25639189	0.124706209	4
257	213.3333333	SW	60	86.32040813	0.159581408	2.459610944	0.295941855	4
258	214.1666667	SW	60	87.11579558	0.245923349	2.472825897	0.297702018	4
259	215	SW	60	87.2564402	0.486135363	2.377545014	0.199223279	4

260	215.8333333	SW	60	87.64609709	0.112882849	2.19774956	0.233647835	4
261	216.6666667	SW	60	88.1297331	0.331593368	2.170904496	0.33865449	4
262	217.5	SW	60	88.05792009	0.424990487	1.955221942	0.165944601	4
263	218.3333333	SW	60	88.02279134	0.49688611	1.931036727	0.224383879	4
264	219.1666667	SW	60	88.02914303	0.615144333	1.731267147	0.255296286	4
End Cycle 3								

Table 5: N_2O fluxes calculated for Experiment 1 from closed chamber method (time points (TP) 0, 10, 20, 30 min) at 20°C for samples SW 20, SW 80, OR 20, OR 80, n =5.

Molvolume [L mol-1]	Molare mass N [g mol-1]	Area in the field [m²]				Molvolume [L mol-1]	Molare mass N [g mol-1]	Area in the field [m²]		
22.414	14.0067	0.02				22.414	14.0067	0.02		
After wetting						**After drying out**				
µg N2O-N m-2	TP 0	TP 1	TP 2	TP 3		µg N2O-N m-2	TP 0	TP 1	TP 2	TP 3
SW 20	0	0.166667	0.333333	0.5		SW 20	0	0.166667	0.333333	0.5
SW 20aX1	-2.12271	0.00063	-4.05221	-0.27897		SW 20bX1	1.895821	6.762688	-2.11799	-4.30507
SW20aX2	-0.20037	-0.13875	0.0469	1.008906		SW20bX2	2.839488	7.557061	-0.45465	-4.70889
SW 20aX3	-0.30033	-0.28994	-0.15746	-1.10187		SW 20bX3	0.188303	6.940126	-1.36601	-3.61791
SW 20aX4	-1.2176	0.128121	0.349923	0.295152		SW 20bX4	0.263777	8.773085	-1.46328	-4.44455
SW 20aX5	0.052614	0.641692	0.290718	0.445837		SW 20bX5	0.296135	6.807911	-1.63188	-4.38477

After wetting						**After drying out**				
µg N2O-N m-2	TP 0	TP 1	TP 2	TP 3		µg N2O-N m-2	TP 0	TP 1	TP 2	TP 3
SW 80	0	0.166667	0.333333	0.5		SW 80	0	0.166667	0.333333	0.5
SW 80aX1	-0.99948	-0.69431	0.299247	0.594348		SW 80bX1	1.26171	7.473523	-1.27407	-2.05504
SW 80aX2	-0.09099	-0.07831	0.898543	-0.31503		SW 80bX2	-0.04621	7.688333	-0.47777	-2.48097
SW 80aX3	-0.49277	-1.13192	-0.40999	-0.50274		SW 80bX3	0.045172	7.635372	-0.08797	-2.80139
SW 80aX4	0.111873	-0.31797	-0.28959	0.077752		SW 80bX4	0.643052	8.036529	-0.26878	-2.04073
SW 80aX5	-0.24402	-1.31179	-0.04005	0.622632		SW 80bX5	0.920159	7.757957	-1.17958	-3.64905
After wetting						**After drying out**				
µg N2O-N m-2	TP 0	TP 1	TP 2	TP 3		µg N2O-N m-2	TP 0	TP 1	TP 2	TP 3
OR 20	0	0.166667	0.333333	0.5		OR 20	0	0.166667	0.333333	0.5
OR 20aX1	-0.39082	-0.39727	1.162159	-0.27808		OR 20bX1	0.464769	7.287851	-1.17666	-3.32606
OR 20aX2	-1.07268	-0.71744	0.39629	0.179402		OR 20bX2	0.253518	6.794533	-1.51819	-3.13123
OR 20aX3	0.097147	0.129897	0.804592	-0.70938		OR 20bX3	-0.85884	6.897342	-1.06022	-4.0928
OR 20aX4	-0.32812	-0.26819	0.249593	-0.73062		OR 20bX4	0.093798	7.044341	-1.3976	-1.17605
OR 20aX5	-0.89943	0.207867	-0.16741	0.181254		OR 20bX5	-0.4555	6.871979	-1.41938	-3.14984
After wetting						**After drying out**				
µg N2O-N m-2	TP 0	TP 1	TP 2	TP 3		µg N2O-N m-2	TP 0	TP1	TP 2	TP 3

OR 80	0	0.166667	0.333333	0.5		OR 80	0	0.166667	0.333333	0.5
OR 80aX1	-0.58365	0.295806	0.258275	-1.14531		OR 80aX1	-0.89469	-	-0.51818	-2.69957
OR 80aX2	-0.53427	0.40608	0.203449	-0.13071		OR 80aX2	-0.45477	-	-0.39568	-4.20986
OR 80aX3	0.276477	-0.00039	0.035846	-0.35498		OR 80aX3	-0.72684	-	-0.54693	-3.36972
OR 80aX4	0.286938	-0.02268	2.469693	0.37553		OR 80aX4	-0.54269	-	0.021567	-3.5785
OR 80aX5	-0.3867	-0.60696	0.395307	-0.2157		OR 80aX5	-0.62666	-	-1.0001	-4.19305

Table 6: N_2O fluxes calculated for Experiment 2 from closed chamber method (time points (TP) 0, 10, 20, 30 min) at 20°C for three cycles of wetting and drying, n=5.

C1 after wetting		**20°C**				**after drying**	20°C			
µg N2O-N m-2	TP 0	TP 1	TP 2	TP 3		µg N2O-N m-2	TP 0	TP 1	TP 2	TP 3
SW 60 0h after Rewet	0.000	0.167	0.333	0.500		SW 60 3h after Rewet	0	0.167	0.333	0.500
A2a1		-0.069	0.896	-0.461		A1b1	-3.69829	-1.408	-1.955	0.132
A2a2	1.985	0.697	0.029	1.482		A1b2	-3.33526	-0.149	-1.598	0.983
A2a3	0.368	0.767	0.931	1.380		A1b3	-2.60003	-1.445	1.720	1.083
A2a4	1.367	-0.026	0.580	1.438		A1b4	-1.68725	0.282	0.891	1.184
A2a5	-0.773	-0.452	1.039	1.687		A1b5	1.169556	2.429	4.536	3.717
C2 after wetting						**after drying**				
µg N2O-N m-2	TP 0	TP 1	TP 2	TP 3		µg N2O-N m-2	TP 0	TP 1	TP 2	TP 3
SW 60 0h after Rewet	0.000	0.167	0.333	0.500		SW 60 3h after Rewet	0	0.167	0.333	0.500
B1a1	-1.374	0.636	0.528	-2.553		B1b1	-0.69938	**0.341**	0.842	1.131
B1a2	0.204	2.130	-0.315	-1.779		B1b2	1.339364	0.052	1.450	3.096
B1a3	1.042	1.110	0.713	-1.824		B1b3	-0.04945	2.205	0.259	5.497

B1a4	1.325	1.029	1.660	-1.358		B1b4	-1.35648	4.271	1.995	1.205
B1a5	1.413	4.358	1.683	-0.541		B1b5	3.431364	4.199	5.247	6.482
C3 after wetting						**after drying**				
µg N2O-N m-2	TP 0	TP 1	TP 2	TP 3		µg N2O-N m-2	TP 0	TP 1	TP 2	TP 3
SW 60 0h after Rewet	0.000	0.167	0.333	0.500		SW 60 3h after Rewet	0	0.167	0.333	0.500
C1a1	-0.658	7.074	-2.807	1.185		C1b1	1.533708	1.633	2.746	-1.433
C1a2	8.560	4.221	1.511	0.208		C1b2	1.106649	3.161	2.983	-1.636
C1a3	10.417	9.220	2.273	1.783		C1b3	-0.20468	0.565	2.224	-0.039
C1a4	1.474	6.062	3.173	1.172		C1b4	0.501477	2.700	2.201	3.479
C1a5	3.776	6.282	1.691	1.666		C1b5	1.222694	**2.679**	4.675	1.798

Litter data

Table 7: Initial Ammonium concentrations of samples used; Schottenwald (SW) and Ort (OR) with standard deviations (s.d.), n=4.

Sample	adsorpt values	cs	mean cs	V ml	Einwaage	NH_4^+-N [µg g-1 dm]dm	NH_4^+-N [µg g-1 dm]	mean	s.d.	
Ort 1	1.485	1.96584591	1.9592269	60.0	2.7353	43.12	42.98	46.251	2.380	Ort
Ort 1*	1.475	1.95260789		60.0	2.7353	42.83				
Ort2	1.698	2.24781573	2.19883505	60.0	2.7353	49.31	48.23			
Ort 2*	1.624	2.14985438		60.0	2.7353	47.16				
Ort3	1.623	2.14853058	2.17765422	60.0	2.7353	47.13	47.77			
Ort3*	1.667	2.20677787		60.0	2.7353	48.41				
Ort4	1.581	2.0929309	2.09822611	60.0	2.7353	45.91	46.03			
Ort 4*	1.589	2.10352131		60.0	2.7353	46.14				
SW 1	1.813	2.40005295	2.35835319	60.0	2.7296	52.76	51.84	52.007	2.218	SW
SW1*	1.75	2.31665343		60.0	2.7296	50.92				
SW2	1.876	2.48345248	2.47352396	60.0	2.7296	54.59	54.37			
SW2*	1.861	2.46359545		60.0	2.7296	54.15				
SW3	1.685	2.2306063	2.232592	60.0	2.7296	49.03	49.08			
SW3*	1.688	2.23457771		60.0	2.7296	49.12				
SW4	1.809	2.39475774	2.39939105	60.0	2.7296	52.64	52.74			
SW4*	1.816	2.40402436		60.0	2.7296	52.84				

Table 8: Ammonium concentrations in NH4-N [µg g-1 dm after Experiment 1 (Dry-Out) and Experiment 2 (Dry-Rewet) with standard deviations (s.d.), n=4.

DRY-OUT	abs value	cs	mean cs	V (ml)	dry weight (g)	NH_4^+-N [µg g-1 dm]			Times 10
SW 20 Nox	0.20300	0.03126	0.032186	60	2.602	0.721	1:10 verdünnt!	s.d.	Real conc
SW 20 Nox	0.20500	0.03157		60		0.728	0.742	0.07122733	7.42

SW 20 Nox	0.19050	0.02934		60		0.677			
SW 20 Nox	0.23750	0.03658		60		0.844			
OR 20 Nox	0.19850	0.03057	0.037037	60	0.765	2.397	1:10 verdünnt!	s.d.	Real conc
OR 20 Nox	0.22000	0.03388		60		2.657	2.904	0.45270432	29.04
OR 20 Nox	0.26550	0.04089		60		3.206			
OR 20 Nox	0.27800	0.04281		60		3.357			
SW 20 NH3	0.19850	0.03057	0.031166	60	2.567	0.715	1:10 verdünnt!	s.d.	Real conc
SW 20 NH3	0.21000	0.03234		60		0.756	0.729	0.01861145	7.29
SW 20 NH3	0.20050	0.03088		60		0.722			
SW 20 NH3	0.20050	0.03088		60		0.722			
OR 20 NH 3	0.25450	0.03919	0.034958	60	0.798	2.946	1:10 verdünnt!	s.d.	Real conc
OR 20 NH3	0.23250	0.03581		60		2.691	2.628	0.24387804	26.28
OR 20 NH 3	0.21000	0.03234		60		2.431			
OR 20 NH3	0.21100	0.03249		60		2.443			
				60			1:10 verdünnt!	s.d.	Real conc
SW 80 Nox	0.58450	0.09001	0.084546	60	2.780	1.942	1.825	0.09377305	18.25
SW 80 NOx	0.54350	0.08370		60		1.806			
SW 80 Nox	0.51600	0.07946		60		1.715			
SW 80 NOx	0.55200	0.08501		60		1.834	1:10 verdünnt!	s.d.	Real conc
OR 80 Nox	0.53250	0.08201	0.084546	60	1.146	4.292	4.425	0.68276733	44.25
OR 80 NOx	0.54900	0.08455		60		4.425			
OR 80 Nox	0.66000	0.10164		60		5.320			
OR 80 NOx	0.45450	0.06999		60		3.664	1:10 verdünnt!	s.d.	Real conc
SW 80 NH3	0.43600	0.06714	0.057365	60	2.886	1.396	1.192	0.2589885	11.92
SW 80 NH3	0.40500	0.06237		60		1.296			
SW 80 NH3	0.39500	0.06083		60		1.264			
SW 80 NH3	0.25400	0.03912		60		0.813	1:10 verdünnt!	s.d.	Real conc

OR 80 NH 3	0.21600	0.03326	0.034246	60	1.083	1.843	1.897	0.07569332	18.97
OR 80 NH3	0.23550	0.03627		60		2.009			
OR 80 NH 3	0.21950	0.03380		60		1.873			
OR 80 NH 3	0.21850	0.03365		60		1.864			

Table 9: Ammonium concentrations in NH_4^+-N [µg g-1 dm after Experiment 2 with standard deviations (s.d.), n=4.

Dry-Rewet	abs value	cs	mean cs	V (ml)	dry weight (g)	NH_4^+-N [µg g-1 dm]	1:10 verdünnt!		
DRewNOx	0.048	0.00739		60	2.32	0.19			
DRewNOx	0.057	0.00878		60	2.32	0.23			
DRewNOx	0.038	0.00585		60	2.32	0.15			Times 10
DRewNOx	0.037	0.00570		60	2.32	0.15	s.d.		Real conc
		Mean	0.00693	60	2.32	0.18	0.04		1.79
DRewNH3	0.128	0.01964		60	1.51	0.78			
DRewNH3	0.127	0.01948		60	1.51	0.77			
DRewNH3	0.127	0.01956		60	1.51	0.78			
DRewNH3	0.155	0.02387		60	1.51	0.95	s.d.		Real conc
		Mean	0.021	60	1.51	0.82	0.09		8.18

Table 9: Initial Nitrate concentrations in NO_3^--N [ug g-1 dm]of samples used; Schottenwald (SW) and Ort (OR) with standard deviations (s.d.), n=4.

Initial	abs value	cs	mean cs	V (ml)	dry weight (g)	NO_3^--N [µg g-1 dm]		
OR 1	0.087	0.016		60	2.730	0.358		
OR 2	0.077	0.015		60	2.730	0.319		
OR 3	0.077	0.015		60	2.730	0.319		
OR 4	0.076	0.014		60	2.730	0.313		s.d.
		mean	0.015	60.000	2.730	mean	0.33	0.02

SW 1	0.058	0.011		60	2.735	0.238		
SW 2	0.014	0.003		60	2.735	0.056		
SW 3	0.023	0.004		60	2.735	0.094		
SW 4	0.012	0.002		60	2.735	0.048		s.d.
		mean	0.005	60.000	2.735	mean	0.11	0.09

Table 10: Nitrate concentrations of samples after Experiment 1; Schottenwald (SW) and Ort (OR) with standard deviation (s.d.), n=4.

DRY-OUT	abs value	cs	mean cs	V (ml)	dry weight (g)	mean DW	NO_3^--N [µg g-1 dm]		
SW 20 NOx 1	0.095	0.0187	0.0189	60	3.004	2.602	0.022	1:2 diluted	s.d.
2	0.0945	0.0186		60	3.003		0.021	0.022	0.000516
3	0.095	0.0187		60	3.020		0.022		
4	0.0985	0.0194		60	3.033		0.023		
SW 80 Nox 1	0.009	0.0018	0.0012	60	3.055	0.765	0.007	1:2 diluted	s.d.
2	0.006	0.0012		60	3.045		0.005	0.005	0.001637
3	0.006	0.0012		60	3.057		0.005		
4	0.004	0.0008		60	3.014		0.003		
OR 20 NOx 1	0.0625	0.0123	0.0122	60	3.015	2.567	0.014	1:2 diluted	s.d.
2	0.0485	0.0095		60	3.026		0.011	0.014	0.002456
3	0.0735	0.0145		60	3.063		0.017		
4	0.0625	0.0123		60	3.008		0.014		
OR 80 Nox 1	0.005	0.0010	0.0007	60	3.033	0.798	0.004	1:2 diluted	s.d.

2	0.003	0.0006		60	3.056		0.002	0.003	0.002537
3	0.007	0.0014		60	3.008		0.005		
4	-0.001	-0.0002		60	3.004		-0.001		
SW 20 NH3 1	0.0985	0.0194	0.0189	60	3.054	2.780	0.021	Mean	s.d.
2	0.0925	0.0182		60	3.015		0.021	0.021	0.0023
3	0.092	0.0181		60	3.040		0.021		
4	0.1	0.0197		60	3.029		0.023		
SW 80 NH3 1	0.0335	0.0066	0.0081	60	3.033	1.146	0.017	Mean	s.d.
2	0.046	0.0091		60	3.010		0.024	0.020	0.004645
3	0.042	0.0083		60	3.010		0.022		
4	0.044	0.0087		60	3.013		0.023		
OR 20 NH3 1	0.0665	0.0131	0.0138	60	3.003	2.886	0.014	Mean	s.d.
2	0.066	0.0130		60	3.007		0.014	0.013	0.004053
3	0.069	0.0136		60	3.007		0.014		
4	0.079	0.0156		60	3.001		0.016		
OR 80 NH3 1	0.0125	0.0025	0.0023	60	3.007	1.083	0.007	Mean	s.d.
2	0.009	0.0018		60	3.009		0.005	0.006	0.001232
3	0.0135	0.0027		60	3.008		0.007		
4	0.0115	0.0023		60	3.001		0.006		

Table 11: Nitrate concentrations of samples after Experiment 2 (SW 60) for the two different incubation devices (NH_3 and NO/CO_2). With standard deviation (s.d.), n=4.

Dry_Rewet	abs value	cs	mean cs	V (ml)	dry weight (g)	NO_3^--N [µg g-1 dm]	

DRew NH3	0.101	0.023		60	2.325	0.58	
DRew NH3	0.085	0.019		60	2.325	0.49	
DRew NH3	0.084	0.019		60	2.325	0.49	
DRew NH3	0.099	0.022		60	2.325	0.57	s.d.
		mean	0.021	60	2.325	0.53	0.05
DRew Nox	0.051	0.011		60	1.513	0.45	
DRew Nox	0.007	0.002		60	1.513	0.06	
DRew Nox	0.016	0.004		60	1.513	0.14	
DRew Nox	0.005	0.001		60	1.513	0.05	s.d.
		mean	0.004	60	1.513	0.18	0.19

Dry weight

Table 12: Indicated are dry mass (DM), standard deviation (s.d.) and water content (%water).

Initial DW											
						net DW	% DM	s.d.	% water	sample	
	SW 1	49.43	2.00	51.44	51.25	1.82	90.61	0.15	9.39	SW 1	
	SW 2	54.97	2.00	56.97	56.79	1.82	90.82		9.18	SW 2	
	SW 3	59.50	2.00	61.50	61.32	1.82	90.91		9.09	SW 3	
		54.63				Mean	90.78	Mean	9.22		
	OR 1	47.65	2.00	49.65	49.47	1.82	90.76	0.57	9.24	OR 1	
	OR 2	47.28	2.00	49.28	49.08	1.80	89.96		10.04	OR 2	
	OR 3	46.73	2.00	48.73	48.55	1.82	91.06		8.94	OR 3	
		47.22				Mean	90.59	Mean	9.41		
After Experiment 1		**NH_3 – Incubation**					**NOx – Incubations**				

		SW 20	net dw	%DM		%WC	**SW 20**	net dw	%DM		% WC
		1	1.76	86.70		13.30	1	1.83	91.04		8.96
		2	1.93	94.61		5.39	2	1.72	84.73		15.27
		3	1.89	93.56	s.d.	6.44	3	1.67	83.08	s.d.	16.92
		SW 80	mean	91.62	4.296	8.38	**SW 80**	mean	86.29	4.20	13.71
		1	0.79	39.11		60.89	1	0.51	24.88		75.12
		2	0.73	35.78		64.22	2	0.58	28.71		71.29
		3	0.79	39.11	s.d.	60.89	3	0.45	21.84	s.d.	78.16
		OR 20	mean	38.00	1.919	62.00	**OR 20**	mean	25.15	3.44	74.85
		1	1.97	96.10		3.90	1	1.69	84.50		15.50
		2	1.96	96.08		3.92	2	1.71	84.65		15.35
		3	1.94	96.04	s.d.	3.96	3	1.72	85.15	s.d.	14.85
		OR 80	mean	96.07	0.030	3.93	**OR 80**	mean	84.77	0.34	15.23
		1	0.67	33.33		66.67	1	0.53	25.85		74.15
		2	0.79	38.73		61.27	2	0.49	24.38		75.62
		3	-5.29		s.d.		3	0.59	28.92	s.d.	71.08
			mean	36.03	3.813	63.97		mean	26.38	2.32	73.62
After Experiment 2		**NH_3 – Incubations**					**NOx – Incubations**				
			net dw	%DM	%WC			net dw	%DM	%WC	
		1	1.46	72.81	27.19		1	1.01	50.45	49.55	
		2	1.55	77.02	22.98		2	1.05	50.20	49.80	
		3	1.65	81.99	18.01		3	0.88	50.16	49.84	
		4	1.80	89.78	10.22		4	0.80	50.13	49.87	
		5	1.29	64.21	35.79		5	0.79	49.72	50.28	
			mean	77.16	22.84			mean	50.13	49.87	
				s.d.					s.d.		
				9.61					0.26		

pH

Table 13: initial pH for samples SW and OR in 0.1M $CaCl_2$ and 1M KCl.

initial						
Sample	Extract 25ml	weight g	Sample T°C	pH	mean pH	s.d.
SW1	0.01M $CaCl_2$	2.01	22.9	5.03	5.075	0.05
SW2	0.01M $CaCl_2$	2.01	22.9	5.11		
SW3	0.01M $CaCl_2$	2.00	22.9	5.13		
SW4	0.01M $CaCl_2$	2.01	22.9	5.03		
Ort1	0.01M $CaCl_2$	1.99	23.3	5.17	5.130	0.03
Ort2	0.01M $CaCl_2$	2.02	23.3	5.11		
Ort3	0.01M $CaCl_2$	2.02	23.3	5.14		
Ort4	0.01M $CaCl_2$	2.00	23.3	5.11		
Blank	0.01M $CaCl_2$	2.02	23.7	6.15	6.147	
Sample	ectract	0.06			mean pH	s.d.
SW1	1M KCL	3.01		5.03	5.005	0.02
SW2	1M KCL	3.01		5.00		
SW3	1M KCL	3.01		4.99		
SW4	1M KCL	3.01		5.00		
Ort1	1M KCL	3.01		5.03	5.010	0.02
Ort2	1M KCL	3.01		4.99		
Ort3	1M KCL	3.01		5.03		
Ort4	1M KCL	3.01		4.99		
Blank	1M KCL	3.00		6.55	6.55	
Blank	1M KCL	2.99		6.54		

Table 14: pH after Experiment 1 and Experiment 2 for samples of NO_x / CO_2- Incubations and NH_3- Incubations in 1M KCl

Experiment 1	After							
	NO_x	pH	mean	s.d.	NH_3	pH	mean	s.d.
	SW 20	4.85	4.87	0.02	SW 20	4.88	4.89	0.02
	SW 20	4.87			SW 20	4.92		
	SW 20	4.89			SW 20	4.89		
	SW 20	4.85			SW 20	4.88		
	SW 80	4.94	4.96	0.07	SW 80	5.02	5.13	0.19
	SW 80	4.88			SW 80	5.09		
	SW 80	5.05			SW 80	5.41		
	SW 80	4.99			SW 80	5.01		
	OR 20	4.89	4.85	0.03	OR 20	4.94	4.98	0.04
	OR 20	4.85			OR 20	4.98		
	OR 20	4.86			OR 20	4.97		
	OR 20	4.82			OR 20	5.03		
	OR 80	4.80	4.85	0.04	OR 80	5.20	5.23	0.28
	OR 80	4.82			OR 80	4.85		
	OR 80	4.88			OR 80	5.42		
	OR 80	4.89			OR 80	5.46		
Experiment 2	After	pH	mean	s.d.		pH		s.d.
	NO_x 1	5.66	5.74	0.07	NH_3 1	4.99	5.01	0.05
	NO_x 2	5.80			NH_3 2	5.04		
	NO_x 3	5.79			NH_3 3	5.06		
	NO_x 4	5.71			NH_3 4	4.94		

Manual - Incubation device for continuous NO_x - and CO_2 - measurements

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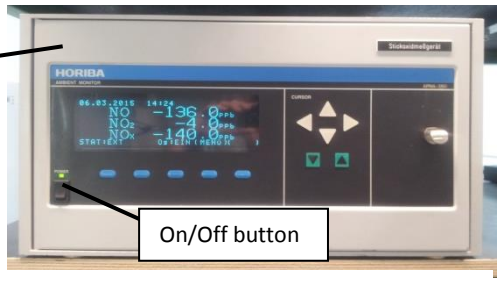
The following is a practical guide aimed at giving a quick overview and introduction for the use of the NO_x & CO_2 measuring device as planned and built by Dr. Christian Holtermann in 2011 at the Institute for Soil Research Boku.

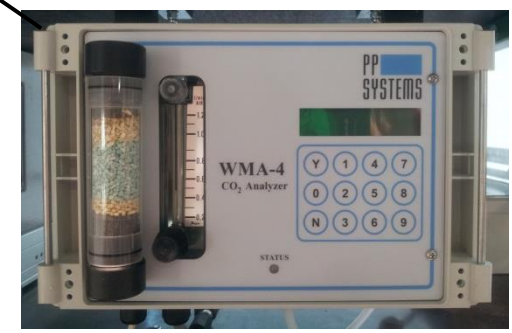
Introduction

The unit is a fully automated temperature controlled incubation measurement system with open flow technique. It consists of a temperature closet (Memmert) with 24 adapted jars (volume 685 cm^3 / jar) (Kilner, Liverpool, United Kingdom) (Fig.1 & 2) that serve as sample incubation chambers. The system is designed to measure carbon dioxide (CO_2) and nitrogen oxides (NO & NO_2 hereafter termed NO_x) fluxes of soil and litter samples. For each of the two floors, one empty chamber is used as a reference chamber (Fig. 2) to measure background gas concentrations to subtract. Schindlbacher *et al.* (2004) described the measuring system in detail. To measure flux rates, air from inside the incubator is sucked through open chambers to the CO_2 and NO_x analysers with a constant flow rate of 1.0 l min^{-1}. For the NO_x determination a HORIBA APNA-360 (Kyoto, Japan) chemo luminescence NO_x analyser is attached and CO_2 is measured with a PP Systems WMA-2 (Amesbury, Massachusetts, USA) infrared CO_2 analyzer. The current program measures each chamber for six min followed by a blank chamber for four minutes and so on.

Figure 1: NO_x & CO_2 measuring device. The main compartments are described below.



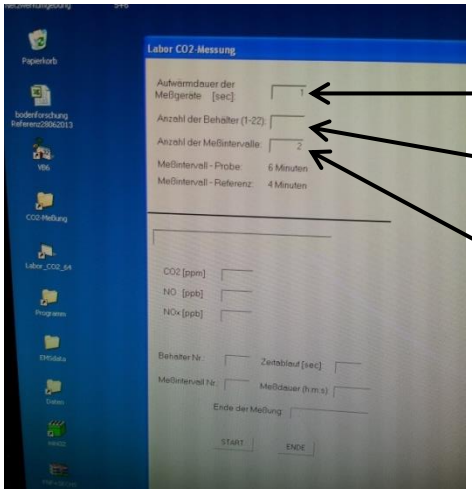
HORIBA APNA-360 (Kyoto, Japan) chemo luminescence NO_x analyser. On/Off button marked.



PP Systems WMA-2 (Amesbury, Massachusetts, USA) infrared CO_2 analyzer. Turns on automatically.

The CO_2 – measuring device needs to be turned on via the attached Compouter. To start the program find the icon on the desktop “Labor_CO2_64”. The valve sequencer can be adjusted depending on how many sample chambers are in use. The sample chamber of which gas concentration is currently measured is signalled with a glowing LED under the number (Fig. 3). There is a computer attached

with a software for the valve sequencer installed (Fig. 3 & 8). There are **THREE** that can be changed in the software (Fig. % below). [1] Warm-up time for CO_2 – device [2] Number of meaured chambers (WITHOUT reference chambers).



Warm up time [s] for the CO_2 measuring device can be as much as 600 (before you get random values around 0).

Number of incubation chambers planning to measure. Reference chambers (Nr. 12 & 24) are not included!

Number of measuring cycles. e.g. 6 Chambers, 2 Cyles => 6 * Sample Chambers + 6 * Reference Chamber (automatically) *2 Cycles of measurement.

Figure **%**: Valve sequencing software. Adjustment of warm-up time for CO_2 – measurements, number of sample chambers and number of measuring cycles possible .

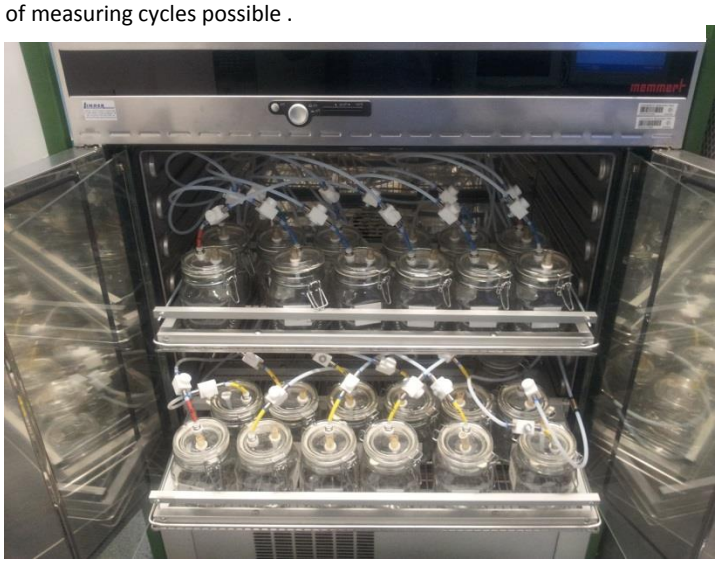


Figure 2: The heating closet (Memmert) is shown open with the two levels of 12 sample chambers each. On each level there is at least one blank (empty sample chamber) to measure background gas cponcentrations (CO2 etc.) and measure temperature in the sample chambers.

LED signalling which sample chamber is measured. In this case number 18.

Figure 3: LEDs signalling which sample chamber is measured.

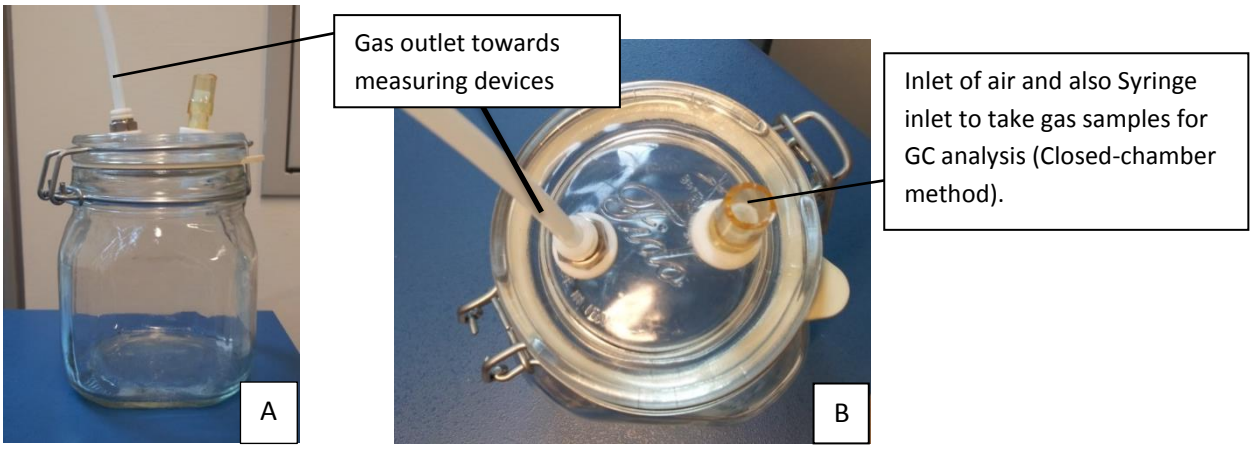


Figure 4: Sample chambers (one of 24) as positioned in the temperature closet. A is the a frontal view, B is the view from the top.

Sampling & handling of samples

Soil cores collected according to ÖNORM L 1051 (Österreichisches Norminstitut, 2005) with a stainless steel cylinder (diameter: 7.2 cm; height 7 cm), sharpened at the bottom end fit in the incubation chambers fit in the incubation chambers (Fig. 2). Such cylinders are stored at the IBF, they are all marked with numbers (Fig. 2B). They are each marked and their weight measured, an Excel-file with the weight is available (see attachment).

Figure 5: soil core cylinders which fit in the glass sample chamber. (Fig. 1). **A:** stainless steel cylinder with sharpened edge on top. **B**: Cylinder and closing cap. **C**: Cylinder closed with cap.

Before putting the samples or cylinders with samples temperature closet, heat or cool the closet to the temperature of choice.

Figure 6: Stainless steel sample cylinder in sample chamber (labelled with number 11).

The compressed air from the lab needs to be turned on, supplying air to the temperature closet (Fig. 7). The pump from the NO_x measuring device sucks in air from the sample chambers which in return flows in from the temperature closet naturally. To avoid under pressure compressed air is supplied.

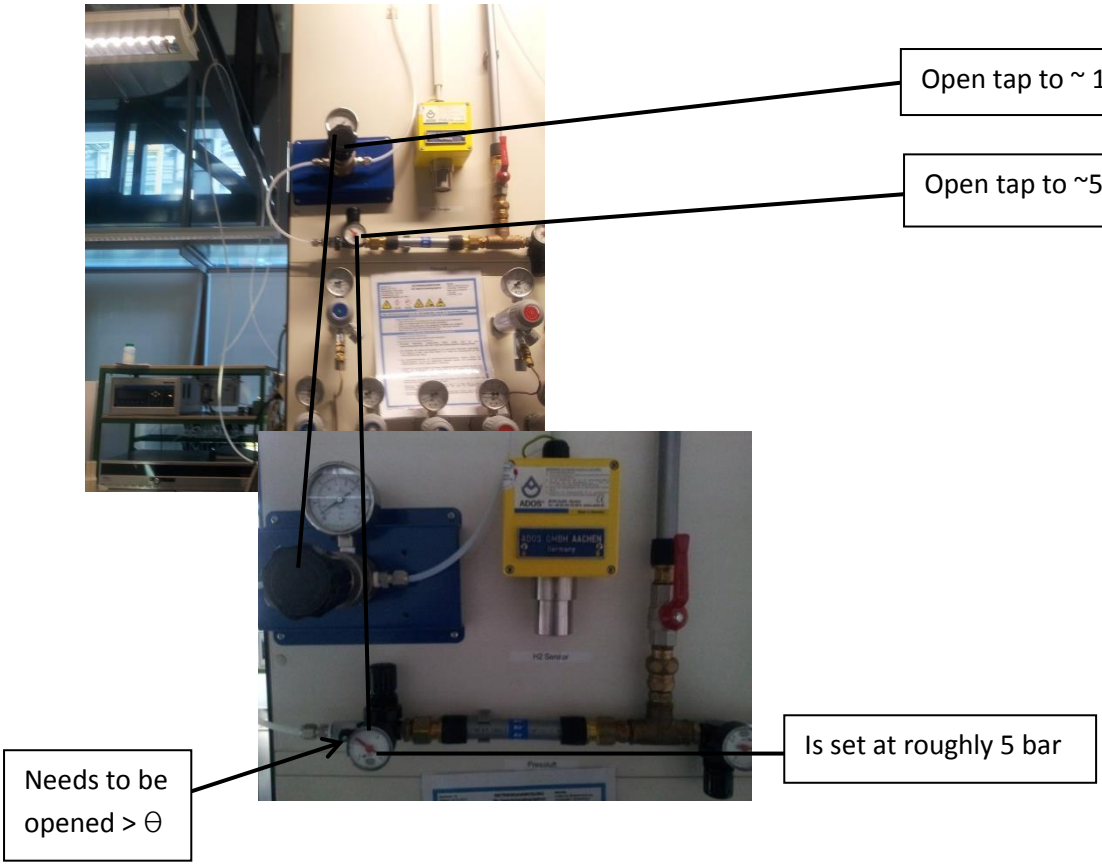


Figure 7: Shown are the armatures for various gases in the GC lab at the Institute of Soil Research. The once for compressed air (at the time this manual was made March 2015!!) are marked. Double check if it´s the right valves you change!! Each tap is labeled and you can see the tubes going towards the different devices

Start of Measurements:

Checklist for NO_x and CO_2 incubation measurements:

- Temperature of the temperature - closet needs to be adjusted before samples are brought in the closet.
- NO_x measuring device needs to be turned on (bottom left of NO_x device).
- CO_2 measuring device turns on automatically with start of measurements through the software on the attached computer.
- Air supply to the temperature closet needs to be provided with compressed air (or synthetic air) from the lab.
- Valves of tubes going away from the sample chambers need to be open.
- Start software ***Labor_CO_2_64*** on computer.
- Set warm – up time for CO_2 measurements device (~600s).
- Set valve sequencer on the computer and adjust number of sample chambers that are supposed to be measured.
- Set measurement intervals (number of repeating measurement cycles of samples).

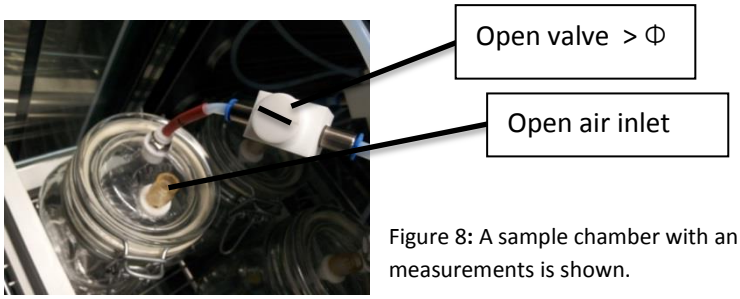


Figure 8**:** A sample chamber with an open valve of the gas flux tube necessary for measurements is shown.

Checklist for closed chamber method:

- Valves of tubes going away from the sample chambers need to be closed.
- The other inlet on tip of the sample holding chambers need to be closed with a rubber septum.
- Prepare evacuated glass vials for GC analysis.
- Prepare gas tight glass syringe for gas sampling.

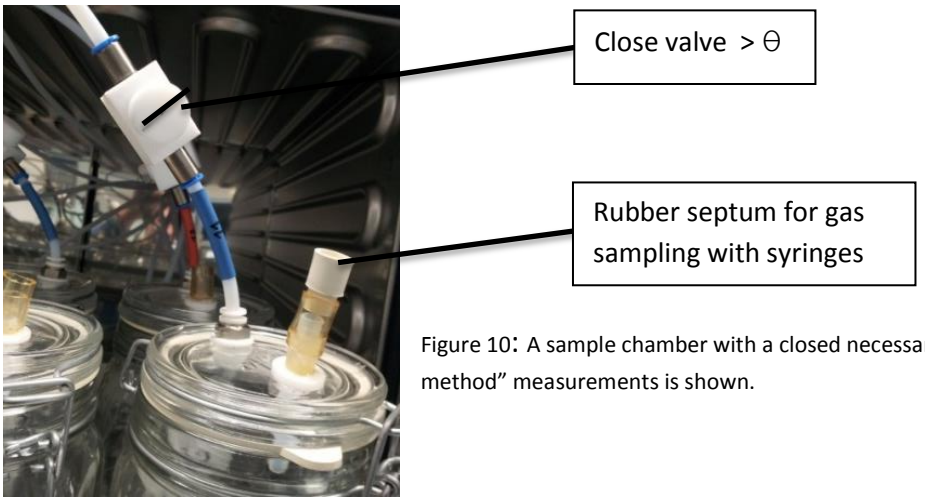


Figure 10: A sample chamber with a closed necessary for the "closed chamber method" measurements is shown.

Data output and calculations

Figures 9 Aa, Ab and B show where to find the program icon for the valve sequencer on the desktop of the attached computer, as well as the look of the program and an example data output file and where it is stored.

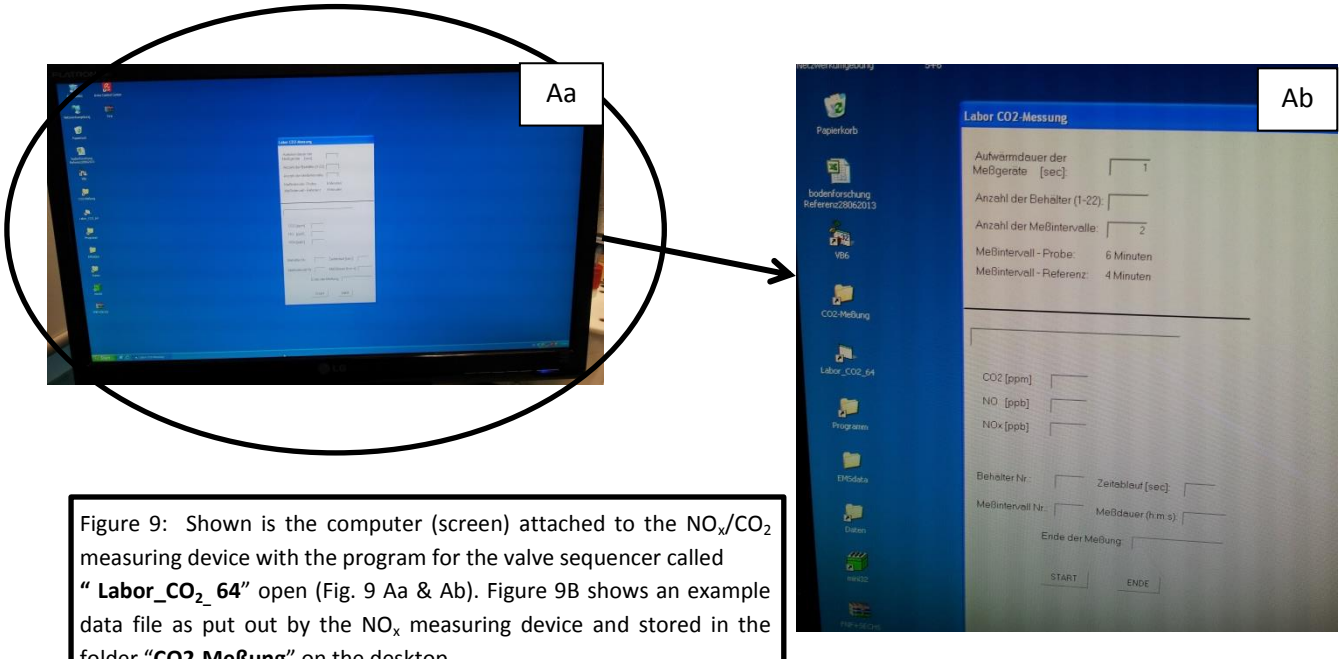
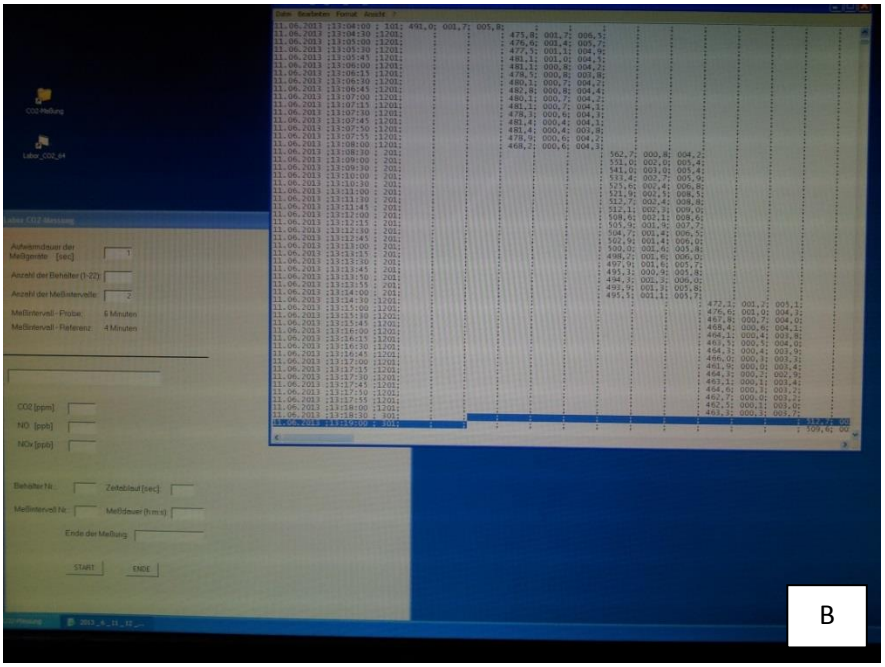


Figure 9: Shown is the computer (screen) attached to the NO_x/CO_2 measuring device with the program for the valve sequencer called **" Labor_CO_2_ 64**" open (Fig. 9 Aa & Ab). Figure 9B shows an example data file as put out by the NO_x measuring device and stored in the folder "**CO2-Meßung**" on the desktop.



The output file is in *.text* format and can be used for further evaluation.

Flux determination

The flux rates of NO and CO_2 were calculated using the following *equation 1*

(Schindlbacher *et al*., 2004):

Equation 1: Flux determination for incubation experiments from deceived mixing ratios.

$$F = (C_{eq} - C_0) * \frac{M*Q*10^3}{V_m*A*10^6} * 60$$

where *F i*s the net flux (µg NO-N m^{-2} h^{-1} and mg CO_2-C m^{-2} y^{-1}), *M* is the atomic weight of the element (N= 14.008 g mol^{-1}; C= 12,0107 g mol^{-1}), V_m is the standard gaseous molar volume (24,055*10^{-3} m^3 mol^{-1}), C_{eq} is the mixing ratio of the gas when the chamber under investigation has reached steady state, C_0 is the mixing ratio of the gas in the reference chamber, *Q* is the mass flow rate of air through the chamber (0.0015 m^3 min^{-1}) and *A* is the soil surface area of the soil core (0.0041 m^2) (Schindlbacher *et al.*, 2004).

Nitrous oxide and methane flux measurements

For the methane (CH_4) and nitrous oxide (N_2O) measurements, all jars with a volume of 685 cm^3 are opened and flushed with compressed air to avoid accumulation of gases at the bottom (not directly in the samples to avoid disturbance of samples). Valves on tubes going from sample chambers towards CO_2 & NO_x detecting devices are to be closed that line on the valve looks like this > θ instead of this > Φ when valve is open allowing gas flow. Afterwards the other inlet on the sample chambers (Fig. 2B) are closed with rubber septa making the sample chambers gas tight. Subsequently 35 ml of compressed air are injected with a syringe into the jars to avoid low pressure in the following samples. Four gas samples (each 10ml + 2ml more as buffer) are taken at four time points (e.g. 0, 15, 30 and 45 minutes, or similar regular time points) with a glass gastight syringe and injected into evacuated gastight 10 ml glass vials (for GC), closed with a rubber stopper and an aluminium cap. The prepared vials have to be evacuated in advance to produce a slight under pressure (ask lab personal for details).

Analyse samples as soon as possible! Storage should be at constant conditions (e.g. drawer in the GC lab.)

Schaufler *et al.* (2010) explains the gas measurements in detail.

For more details on Gas Chromatography and measurements' analysis ask experts at the Institute.

Excel files or other instructions for the following are available;

- Weight of stainless steel soil core cylinders.
- Instructions for soil core sampling (WHIM bog).

References:

Schaufler, G., Kitzler, B., Schindlbacher, A., Skiba, U., Sutton, M. A., and Zechmeister-Boltenstern, S. (2010). Greenhouse gas emissions from European soils under different land use: effects of soil moisture and temperature. In: *European Journal of Soil Science*, *61*(5), 683-696.

Schindlbacher, A., Zechmeister-Boltenstern, S. and Butterbach-Bahl, K. (2004). Effects of soil moisture and temperature on NO, NO_2, and N_2O emissions from European forest soils. In: *Journal of Geophysical Research: Atmospheres (1984–2012)*, *109*(D17).

Abstract

Gas and nutrient release during litter decomposition are important processes in element cycles. Early stage decomposition has recently seen increasing attention. Moreover the magnitude of ammonia (NH_3) emissions from beech litter is not well known. Therefore a new device for automatic soil emission measurements of reduced nitrogen was constructed and tested to assess ammonia fluxes from beech litter.

Subsequently two experiments were conducted to examine the influence of beech litter (*Fagus sylvatica L.*) stoichiometry (C:N ratio) and moisture levels on gaseous emissions of NH_3, NO, N_2O and CO_2. In particular we were interested in the temporal dynamics of emissions and whether these follow the nitrogen cascade ($NH_3 \rightarrow NO \rightarrow N_2O$). For this purpose samples from two Austrian deciduous forests exposed to different nitrogen pollution (Schottenwald (SW), Vienna and Ort (OR), Gmunden) were examined. Two experiments were performed; first to detect NH_3 emission of the two litter types under different moisture levels over a period of ~ 80 hours (Experiment 1) and another Experiment to simulate three consecutive wetting and drying cycles for 80 hours each with one litter type (Experiment 2). Furthermore accompanying litter parameters (i.e. NH_4^+, NO_3^- concentrations, moisture, and pH were assessed.

In Experiment 1 we could clearly distinguish higher NH_3 emissions from samples with higher nitrogen content (SW) regardless of moisture levels. Furthermore, emissions decreased with progressing drying of the samples, and higher initial moisture levels promoted higher NH_3 emissions within the same litter types. NO emissions decreased with decreasing moisture until zero. Carbon dioxide emissions started only 24 hours after wetting for the moister sample (80 %), peaked after 60 hours and then declined again. No CO_2 – emissions were registered for the drier samples (20 %) which were believed to be under the threshold of microbial decomposition (30%). Uptake of N_2O was registered at the end of the drying period for all samples.

In Experiment 2 NH_3 emissions started out highest after initial wetting and then decreased until rewetting, which seemed to boost emissions strongly. However, in spite of air conditioning we observed diurnal temperature variations in the chambers due to sun irradiation which likely amplified the wetting effects. Nitric oxide emissions decreased exponentially until emission stopped after 80 hours. After a lag phase of 24 hours CO_2 emissions increased exponentially. Carbon dioxide emissions were boosted by rewetting events but declined over time.

We found total NH_3-emissions (967 µg NH_3 - N m^{-2}) of SW (60 % moisture) exceeded those of total NO emissions (520 µg NO - N m^{-2}) over an incubation period of 250 hours. Concerning the nitrogen cascade we observed simultaneous emissions of both reduced (NH_3) and oxidized (NO) nitrogen

compounds shortly after litter wetting. Whereas NH_3 emissions lasted throughout our experiments NO emissions declined before the onset of microbial respiration. Higher leaf litter N-concentration resulted in higher ammonia emissions, where higher moisture contents of samples may enhance ammonia volatilization through increased mineralization and amplified effects through evaporation. Within this thesis we clearly showed that NH_3 emissions from deciduous leaf litter can contribute substantially to natural ecosystem fluxes.

Zusammenfassung

Ammoniak (NH_3) gilt als einer der wichtigsten Luftverschmutzer des 21. Jahrhunderts und Messdaten von natürlichen Emissionen werden benötigt um detailliertere Ökosystmenmodelle zu entwickeln. Gasemissionen und Nährstofffreisetzung während des Abbaus von Pflanzenmaterial sind wichtige Prozesse der Stoffkreisläufe in Ökosystemen. Als Gegenpol zur Photosysnthese erfahren auch die Frühphasen des Pflanzenstreuabbaus immer mehr Beachtung, gerade der bidirektionale Fluss von Ammoniak ist dabei noch kaum untersucht. Um Ammmoniakemissionen aus Pflanzenstreu (und Bodenproben) in geringen natürlichen Konzentrationen (< 1 ppb) zu messen, wurde ein neues, voll automatisiertes Messsystem entwickelt.

Im Anschluss wurden zwei Experimente durchgeführt um den Einfluss unterschiedlicher Stickstoffgehalte (C:N-Verhältnisse) und Feuchtigkeit von Buchenstreu (*Fagus sylvatica L.*) auf die Gasmissionen von NH_3, NO, N_2O und CO_2 zu untersuchen. Hierfür wurden Buchenstreuproben aus zwei österreichischen Laubwäldern (Schottenwald (SW), Wien und Ort (OR), Gmunden) verwendet. Ziel war es, die zeitliche Dynamik von Stickstoffemissionen zu untersuchen und diese mit theoretischen Mustern entlang der Stickstoff-Kaskade ($NH_3 \rightarrow NO \rightarrow N_2O$) zu vergleichen. In Experiment 1 wurden die Proben der zwei Standorte nach anfänglicher Befeuchtung auf jeweils 20 und 80 % Wassergehalt einer 80-stündigen Austrocknungsphase ausgesetzt. Bei Experiment 2 wurde eine Probe (SW) nach anfänglicher Befeuchtung (60 % WG) 80 Stunden lang ausgetrocknet, dieser Zyklus wurde danach zweimal wiederholt. N_2O – Gasproben wurden jeweils nach einer Befeuchtung und am Ende einer Austrocknungsperiode genommen. Als Begleitparameter wurden NH_4^+-, NO_3^--Konzentrationen, Feuchtigkeit und pH-Wert analysiert.

In Experiment 1 waren die NH_3-Emissionen der SW Proben mit dem höherem N-Gehalt höher als die des weniger belasteten Standorts OR. Außerdem waren Emissionen aus feuchteren Proben (80 %) höher als die von trockeneren Proben (20 %), was vermutlich auf höhere Mineralisierungsraten nach ursprünglicher Befeuchtung zurückzuführen ist. Weder für Stickstoffmonoxid- (NO) noch für CO_2– Emissionen konnten signifikanten Unterschiede zwischen den zwei Laubtypen festegestellt werden. Der Verlauf der CO_2 – Emissionen zeigte für die Proben mit höheren Feuchtegehalten nach ~ 24 Stunden ohne Aktivität, exponentiellen Zuwachs und Emissionspeaks nach ~ 60 Stunden. Die trockeneneren Proben (20 %) zeigten über den gesamten Zeitverlauf keine CO_2 – Emissionen, vermutlich da ein postulierter Schwellenwert für Streuabbau von 30 % Feuchtigkeit unterschritten wurde. Bei allen Proben wurde eine deutliche Lachgasaufnahme (N_2O) am Ende des Trockenzyklus verzeichnet.

Bei Experiment 2 wurden die höchsten Ammoniakwerte aller Messungen zu Beginn verzeichnet. Danach nahmen diese kontinuierlich ab und zeigten dabei einen starken Tag-/Nachtverlauf. Die höheren Werte am Tag wurden durch höhere Temperaturen aufgrund von Sonneneinstrahlung erklärt. Die Erhöhung durch Befeuchtung dürfte daher mit eine Verstärkung der Ammoniakverdampfung durch Wasserverdunstung einhergehen. Ähnlich wie im 1. Experiment waren NO – Emissionen waren anfänglich am höchsten, bis diese nach ~ 80 Stunden ganz aufhörten. Auch CO_2 – Emissionen zeigten anfangs einen ähnlichen Verlauf, allerdings mit niedrigeren Werten, was auf die niedrigeren Feuchten zurückzuführen ist. Lachgasaufnahme war am Ende der Trockenzyklen zu beobachten.

Insgesamt waren die NH_3-Emissionen (967 µg NH_3 - N m^{-2} h^{-1} bei 60% WG) fast doppelt so hoch wie die NO-Emissionen (520 µg NO - N m^{-2} h^{-1}) über eine Inkubationszeit von 250 Stunden. In Bezug auf die Stickstoffkaskade beobachteten wir die gleichzeitige Emission von sowohl reduzierten (NH_3) als auch oxidierten (NO) Stickstoffverbindungen. Während jedoch die NH_3-Emissionen während der Inkubationszeit anhielten, sanken die NO-Emissionen ab, bevor die mikrobielle Atmung einsetzte. Höhere N-Konzentration in der Laubstreu führte zu höheren Ammoniakemissionen, auch die Feuchtigkeit hatte eine verstärkende Wirkung. Im Rahmen dieser Arbeit konnten wir deutlich zeigen, dass NH_3-Emissionen aus Laubstreu ganz wesentlich zu den Stoffflüssen in natürlichen Ökosystemen beitragen.

Curriculum Vitae

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