

This discussion paper is/has been under review for the journal Atmospheric Measurement Techniques (AMT). Please refer to the corresponding final paper in AMT if available.

TRANC – a novel fast-response converter to measure total reactive atmospheric nitrogen

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Received: 9 November 2011 – Accepted: 10 December 2011 – Published: 19 December 2011

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

The input and loss of plant available nitrogen (N) from/to the atmosphere can be an important factor for the productivity of ecosystems and thus for its carbon and greenhouse gas exchange. We present a novel converter for the measurement of total reactive nitrogen (TRANC: **T**otal **R**eactive **A**tmospheric **N**itrogen **C**onverter), which offers the opportunity to quantify the sum of all airborne reactive nitrogen (N_r) compounds in high time resolution. The basic concept of the TRANC is the full conversion of total N_r to nitrogen monoxide (NO) within two reaction steps. Initially, reduced N compounds are being oxidised, and oxidised N compounds are thermally converted to lower oxidation states. Particulate N is being sublimated and oxidised or reduced afterwards. In a second step, remaining higher N oxides or those originated in the first step are catalytically converted to NO with carbon monoxide used as reduction gas. The converter is combined with a fast response chemiluminescence detector (CLD) for NO analysis and its performance was tested for the most relevant gaseous and particulate N_r species under both laboratory and field conditions. Recovery rates during laboratory tests for NH_3 and NO_2 were found to be 95 and 99 %, respectively, and 97 % when the two gases were combined. In-field longterm stability over an 11-month period was approved by a value of 91 % for NO_2 . Effective conversion was also found for ammonium and nitrate containing particles. The recovery rate of total ambient N_r was tested against the sum of individual measurements of NH_3 , HNO_3 , $HONO$, NH_4^+ , NO_3^- , and NO_x using a combination of different well-established devices. The results show that the TRANC-CLD system precisely captures fluctuations in N_r concentrations and also matches the sum of all N_r compounds measured by the different single techniques. The TRANC features a specific design with very short distance between the sample air inlet and the place where the thermal and catalytic conversions to NO occur. This assures a short residence time of the sample air inside the instrument, and minimises wall sorption problems of water soluble compounds. The fast response time (half-value periods of 0.30 s were found during concentration step changes) and high accuracy in

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capturing the dominant N_r species enables the converter to be used in an eddy covariance setup. Although a source attribution of specific N_r compounds is not possible, the TRANC is a new reliable tool for permanent measurements of the net N_r flux between ecosystem and atmosphere at a relatively low maintenance and reasonable cost level allowing for diurnal, seasonal and annual investigations.

1 Introduction

1.1 Reactive nitrogen

Nitrogen is an essential nutrient for all living organisms. Beside dinitrogen (N_2), being practically inert and constituting 78 % of the earth's atmosphere (Seinfeld and Pandis, 2006), the important nitrogen-containing trace species are nitric oxide (NO, also nitrogen monoxide), nitrogen dioxide (NO_2), nitric acid (HNO_3), ammonia (NH_3), and nitrous oxide (N_2O) (Sutton et al., 2011). The sum of NO and NO_2 , the former emitted by both natural and anthropogenic sources, the latter formed in the atmosphere by oxidation of NO and emitted in small quantities from combustion processes along with NO, is usually designated as NO_x . Reactive odd nitrogen, denoted NO_y , is defined as the sum of NO_x and all compounds that are products of the atmospheric oxidation of NO_x . These include among others HNO_3 , nitrous acid (HONO), and peroxyacetyl nitrate (PAN). HNO_3 is rapidly deposited on surfaces and in water droplets and – in the presence of NH_3 – can form ammonium nitrate (NH_4NO_3) aerosols. Significant sources of NH_3 are animal waste, ammonification of humus followed by emission from soils, losses of NH_3 -based fertilizers, and industrial emissions. In this paper, we define reactive nitrogen (N_r) as all nitrogen-containing trace species except for N_2 and N_2O with the latter being inert in the troposphere (Seinfeld and Pandis, 2006). The oxidation states of the main N_r compounds range from +5 for HNO_3 to –3 for NH_3 .

The input of N_r into an ecosystem through atmospheric dry deposition is an important factor for its productivity and thus for its exchange of carbon dioxide (CO_2) and



other greenhouse gases. The dry deposition of N_r typically contributes between one third and two thirds to the total atmospheric N deposition (Simpson et al., 2006). The environmental effects of excess atmospheric N_r deposition to ecosystems may include soil acidification, eutrophication of water bodies, nutrient imbalances, leaching of base cation and nitrate, loss of biodiversity, direct toxicity to plants, increased N_2O emissions, and inhibition of soil methane (CH_4) oxidation (Galloway et al., 2003; Erisman et al., 2007; Flechard et al., 2011).

1.2 Exchange measurements of reactive nitrogen compounds

Unlike wet deposition, which is widely monitored in regional networks of wet-only or bulk precipitation collectors, measurements of dry (turbulent) N_r exchange fluxes have largely remained experimental and were limited to selected research sites and to measurement campaigns of typically a few days to a few months due to technical complexity and to the large equipment and operational costs involved (Flechard et al., 2011). This is due to the fact that dry N_r exchange constitutes a variety of compounds with different exchange patterns and that in general, concentration and flux measurements of N_r species are challenging from a metrological point of view (e.g. von Bobruzki et al., 2010; Wolff et al., 2010). Well-established measurement techniques (e.g. using chemiluminescence detectors CLD, molybdenum converter, denuder/impinger/filter sampling with ion chromatography analysis) are usually limited to single compounds (e.g. Sutton et al., 2007) or provide concentration values and flux rates in poor time resolution and require labour and cost-intensive lab analyses (Dämmgen and Zimmerling, 2002; Zimmerling et al., 1997).

Additionally, reliable, robust, interference-free, fast and precise detectors suitable for long-term micrometeorological flux measurements are available only for few N_r compounds. These are, however, essential for permanent monitoring of the N_r exchange between ecosystems and the atmosphere within an eddy-covariance (EC) setup. EC is the currently preferred method to measure continuously the exchange of CO_2 , water vapour and sensible heat over time scales of hours to decades, thus enabling the

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evaluation of seasonal and interannual variability in these exchanges and the elucidation of their climatic controls (Baldocchi et al., 2001; Coursolle et al., 2006; Brümmer et al., 2011a). In the last decade, substantial progress has been made in the use of tunable diode laser absorption spectroscopy (TDLAS) and quantum cascade lasers (QCL) as well as devices originating from individual applications such as Fourier transform infrared (FTIR) spectrometers. The precision and fast response of these approaches has allowed first EC measurements of field scale N_2O and CH_4 fluxes (Rinne et al., 2005; Denmead et al., 2010; Kroon et al., 2010; Neftel et al., 2010; Tuzson et al., 2010), whereas measurements of NH_3 fluxes by EC have been extremely limited (Famulari et al., 2004; Sutton et al., 2007; Sintermann et al., 2011), and are subject to substantial uncertainty (e.g. Shaw et al., 1998). Beside the necessity of a fast response detection of the desired N compound, additional issues regarding inlet design, sampling losses and air column chemical reactions for highly reactive and soluble N_r species have been identified, making the establishment of large-scale dry deposition monitoring networks of N_r nearly impracticable.

Chemiluminescence detectors (CLD) allow fast and reliable measurements of NO and – in combination with commercially available converters – of NO_2 , NO_x and NO_y , respectively. These instruments are either using a graphite, a molybdenum oxide (MoO) or a gold (Au) converter operating at temperatures between 275 and 390 °C, whereas Au converters need a reducing agent like CO or H_2 . Using fast-response NO detection by CLD, some approaches of long-term NO_y measurements using EC have been conducted. For example, Munger et al. (1996), report on five years of NO_y eddy flux data measured at Harvard forest, where NO_y was determined following reduction to NO by H_2 on a Au catalyst.

EC-based measurements of N_r compounds other than NO_x are extremely limited. Day et al. (2002) and Farmer et al. (2006) present the application of a thermal dissociation laser-induced fluorescence (TD-LIF) instrument suitable for the measurement of NO_2 , HNO_3 , alkyl (ΣAN) and peroxy nitrates (ΣPN). In this approach, each class of compounds thermally dissociates to NO_2 and an accompanying radical (RO_2 , RO, OH)

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in separately thermostatted ovens at temperatures of 180, 330, and 550 °C for ΣPN , ΣAN , and HNO_3 , respectively. Sintermann et al. (2011) use a system for fast NH_3 measurements with chemical ionisation mass spectrometry (CIMS) based on a commercial Proton Transfer Reaction-Mass Spectrometer (PTR-MS) within an EC setup over two agricultural fields in Oensingen, Switzerland, whereas the EC fluxes of NH_3 measured by Famulari et al. (2004) during a two-month field campaign were conducted by the use of a TDLAS system.

In the absence of fast-response instruments suitable for EC measurements, the aerodynamic gradient method is frequently applied for N_r compounds such as NH_3 , HNO_3 , HONO, and aerosol particles. It infers the flux from concentration measurements at several heights and measured turbulence characteristics. Concentration measurements are frequently performed by denuder or filter-pack sampling in combination with on- or offline analysis by ion-chromatography and/or flow injection analysis, e.g. for NH_3 in the AMANDA system (Wyers et al., 1993), or for HNO_3 and aerosol particles in the GRAEGOR system (Thomas et al., 2009; Twigg et al., 2011). However, this method has proved to be relatively labour and cost intensive, often shows limited time resolution and brings along method-linked limitations. Only very few long term measurements are published (Flechard and Fowler, 1998; Flechard et al., 2010).

Measurements of total N_r have been reported by McCalley and Sparks (2009) using selective thermal and chemical decomposition converters to reduce or oxidise all N_r trace gases to NO. However, their setup was applied for relatively slow enclosure measurements over short experimental periods to determine the soil-atmosphere exchange of NO, NO_y , and NH_3 differentially by switching between different converter configurations. No information is given on the influence of the enclosures and sampling tubes in the field configuration on the performance of the system.

Although the knowledge of total N_r exchange is of major importance for the compilation of matter flux balances on ecosystem level, none of the above-mentioned methods is capable of determining total N_r in high time resolution within longterm monitoring setups. The reasons for this limitation are (a) the wide range of N_r containing

compounds, their different molecular and exchange characteristics and thus different sampling and measuring approaches, (b) the interactions between different N_r compounds and therefore the necessity to measure several parameters simultaneously due to gas phase reactions and gas-aerosol particle interactions, and (c) the complexity and labour-intensity of flux measurements of the individual compounds.

1.3 Motivation and objectives of present study

In this study, we present a novel converter named TRANC (**T**otal **R**eactive **A**tmospheric **N**itrogen **C**onverter), which, in combination with a fast-response analyser (CLD), offers the opportunity to quantify the sum of all airborne N_r compounds in high time resolution. The design of the TRANC is supposed to fulfil the requirements needed for an operation within an EC setup. These requirements are an instantaneous oxidation and reduction of all N_r compounds in the sample air to NO with the conversion occurring close to the air inlet, thereby reducing errors due to chemical reactions, particularly of NH_3 , in the sampling tube. To our knowledge, this is the first approach that is on the one hand not limited to a single or a few N compounds, but provides the quantification of the sum of all N_r compounds, and that is on the other hand fast enough to be used for EC measurements if combined with a fast-response NO analyser, thus presenting a new methodology for permanent net exchange measurements of N_r at a relatively low maintenance level. The purpose of this paper is the presentation of the converter, its characteristics and results of performance tests. Validation and long-term application of the converter for EC flux measurements is presented in companion papers by Ammann et al. (2011) and Brümmer et al. (2011b).

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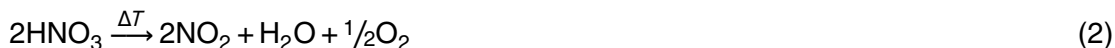
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2 Experimental setup

2.1 Converter principle and design

The basic concept of the TRANC is the full conversion of all N_r compounds in the sample air to NO in two reaction steps. Initially, reduced N compounds are being oxidised, whereas oxidised N compounds are thermally converted to compounds of lower oxidation states. Particulate N is being sublimated and oxidised or reduced afterwards. The conversions in the first reaction step, i.e. the thermal conversions, occur at temperatures $\geq 870^\circ\text{C}$. In a second step, i.e. the catalytic conversion, remaining higher N oxides in the sample air or those originated in the first reaction step are converted on a Au surface ($\geq 300^\circ\text{C}$) to NO with carbon monoxide (CO) used as reduction gas and by installing a platinum (Pt) gauze ensuring a complete catalytic conversion of NH_3 to NO. The main conversions resulting under these conditions are as follows:



Finally, the NO concentration in the gas sample leaving the converter towards a CLD represents the initial total N_r concentration that entered the converter through the sample air inlet. Regarding decomposition temperatures of the most abundant N_r compounds being significantly lower than 870 and 300°C during the thermal and catalytic reaction steps, respectively, we assume a full conversion of total N_r in the sample air to

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NO. The conversion efficiency of single N_r compounds was tested in several laboratory and field experiments and is described in Sects. 3.1 and 3.2.

A schematic overview of the TRANC is presented in Fig. 1. Core piece of the converter is a high-temperature resistant metal tube consisting of an iron-nickel-chrome (FeNiCr) alloy. The tube is encapsulated in a double-walled, weather-sealed aluminium housing. The inner box is filled with high-temperature resistant concrete granulate assuring effective heat insulation. Outside the outer housing, the FeNiCr tube is connected to a Pt gauze followed by a tee junction serving as gas inlet for CO and a stainless steel loop leading the sample air back to the inside of the TRANC. Here, the Au tube, i.e. the location where the catalytic conversion occurs, is mounted. Another loop at the back end of the Au tube leads the stainless steel pipe outside the converter, where a 4 µm filter and a critical orifice assure the desired pressure drop (see Sect. 2.2) before the sample air passes through lightproof tubing and enters the CLD for NO analysis.

An operating temperature of >800 °C is needed to fully oxidise the reduced N compounds (McCalley and Sparks, 2009, suppl.). Such high temperatures also convert oxidised N compounds like HNO₃ to lower oxidation states (Reaction 2; see e.g. Day et al., 2002). These conditions for the thermal conversion are implemented by the resistance-heated FeNiCr tube. A current of 80 A at a voltage of 5 V is fed to the tube over brass blocks at the two end fittings. Provision of electricity is effected by a switch-mode power supply with the temperature of the tube being regulated by a universal modulator and controlled by a thermocouple (see Fig. 1). The Au tube is indirectly warmed up to approximately 300 °C by the waste heat of the FeNiCr tube. The tube lead-throughs of both the inner and outer housing are electrically insulated by ceramic material except for two small additional inlets that are connected over flexible tubes with two pumps assuring permanent ventilation and removal of hot air between the inner and the outer housing at a flux rate of 5 l min⁻¹ each (not shown in Fig. 1).

Figure 2 shows the temperature distribution inside the FeNiCr and the Au tube during different experimental runs. The target temperature of the heating modulator was

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set to 895 °C to ensure temperatures above the desired values of 870 and 300 °C over a significant part of the FeNiCr and the Au tube, respectively. The relatively low temperatures (between 100 and 500 °C) of the FeNiCr tube within the first 20 cm after the sample air inlet represent the non-insulated tube part outside the housing.

2.2 Combination of TRANC with fast-response NO analysis

The TRANC is the key part of a comprehensive measuring system consisting of a CLD connected to a dry vacuum scroll pump (BOC Edwards XDS10, Sussex, UK) and a calibration unit (see Sect. 3.1) with a multi-gas calibrator and specific reference gases. In our setup, we used a commercial CLD (780 TR, ECO PHYSICS, Dürnten, Switzerland) for NO analysis. The measurement principle of this instrument is based on gas phase titration, i.e. the reaction of NO with O₃. It generates electronically excited NO₂^{*} molecules, which rapidly decay to their ground state in a reduced pressure regime by emitting photons. The total light intensity in the reaction chamber, detected by a photomultiplier tube (PMT), is proportional to the NO mixing ratio (Fontijn et al., 1970; Rummel et al., 2002). To minimise electrical noise, the temperature of the PMT is held constant at –18 °C. Flushing with oxygen or dry air avoids condensation. An ozone generator supplies the main chamber of the CLD with O₃-enriched air, where it reacts with NO to NO₂^{*} and O₂.

To reduce the probability of energy loss of NO₂^{*} molecules by collision with others, the gas phase titration in the main chamber occurs under low pressure, i.e. <20 hPa. This is effected by the critical orifice located at the back end of the stainless steel tube that is leaving the TRANC towards the CLD (Fig. 1) and restricts the flow to 2.7 l min^{–1}. In our setup, the instrument was running in a continuous mode, integrating the photons over 0.05 s. In the standard operation procedure, the CLD 780TR uses so-called pre-chamber measurements in order to correct for interferences which might be caused by e.g. hydrocarbons in the sample air that react with O₃ in a similar way like NO and are therefore detected as NO in the main reaction chamber. For fast response measurements this option is disabled. Frequent calibration aims at minimising related

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errors. Furthermore we estimate that the relative contribution of possible interferences is small in comparison to a total N_r concentration. As O_3 is completely destroyed in the TRANC (thermal decomposition and reduction by CO), chemical NO loss by gas phase reaction ($NO + O_3 \rightarrow NO_2 + O_2$) could also be neglected. Even if a small amount of O_3 would pass the TRANC, the influence on concentration changes are expected to be lower than the detection limit of the CLD according to Rummel et al. (2002). A schematic overview of the TRANC-CLD system in an EC-setup is given in Fig. 3.

3 Results of performance tests

3.1 Calibration and conversion of individual N_r compounds

3.1.1 General calibration and NO_2 conversion

The TRANC-CLD unit was calibrated by regularly feeding calibration gas with different NO and NO_2 concentrations through the system (Fig. 3). In our setup, we used a multi-gas calibrator (S6100, Environics Inc., Tolland, USA) connected to two different reference gas cylinders containing 10 ppm NO and 10 ppm NO_2 each as well as a pure air generator (PAG 003, ECO PHYSICS, Dürnten, Switzerland). The calibrator mixed the desired gas concentration by dilution of the cylinder standard with zero air.

We used gas concentrations of 6, 10, 20, and 50 ppb NO as well as pure air to calibrate the CLD. Additionally 50 ppb NO_2 and 50 ppb NO mixed with O_3 (<50 ppb) was given into the system to determine the conversion efficiency of NO_2 . During a typical calibration procedure, the calibrator started mixing the target concentration 3.5 h prior to the actual calibration run when the reference gas was fed into the system. At this time, the calibration valve near the TRANC inlet (Fig. 3) was still shut and the calibration gas was vented directly from the calibrator unit. After activating the TRANC valve, the system was calibrated for 30 min with one specific gas concentration. As the reference gas was fed into the tubes with a higher flow rate (approximately 5 l min^{-1}) than

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that established by the vacuum pump and the critical orifice (2.7 l min^{-1}), the excess gas was leaving the system through the sample air inlet at the front side of the TRANC. After 30 min the TRANC valve was switched off to set the system back to the measurement mode for ambient air. To assure a clearly stable signal of the CLD, only data of the 10-min period from 15 to 25 min after the initial switch were taken to calculate the NO concentrations. If necessary, spikes were removed and the 10-min window was shifted to the most stable interval during the respective half-hour calibration period. Over an 11-months measurement period, not a single calibration run was observed, where the 30-min interval had to be extended and data were not discarded due to other system instabilities.

For optimal data coverage during long-term measurement campaigns, the system was configured to calibrate for 30 min with only one gas concentration once a night, in this case from 3:30 to 4 a.m. The data obtained in these eight consecutive nights were used for the calibration regression of this time period. With a new calibration interval starting on day nine, the regression was updated with the data recorded from day 9 to 16, accordingly. These steps with the respective regression update were repeated for all following 8-day periods.

A low positive NO signal slightly different from zero (Fig. 4) was found while calibrating with pure air. Beside the interference with hydrocarbons in the sample air (see Sect. 2.2) or impurities in the added CO (Hegglin et al., 2006), this could have been induced by the pure air generator through a small contamination with any other N_r compound. The overall calibration performance of an 11-month observation period is given in Fig. 4. These data were taken from a field campaign conducted at an agricultural site in Gebesee, Germany, which will be described in more detail in Brümmer et al. (2011b). R^2 values from the correlation between the given calibration gas concentration and the corresponding CLD signals of single 8-day periods were ranging between 0.81 and 0.99 with $R^2 = 0.98$ for the averaged fit ($n = 30$ for each gas concentration). In most cases, intercepts were found to be slightly positive (Fig. 4).

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Over the same 11-month observation period, we found a mean conversion efficiency for NO₂ of 91 % (Fig. 5) with a standard deviation of ±9 %. It has to be considered that cylinder calibration standards for NO₂ are generally less accurate than for NO, because of possible non-ideal mixing in the gas cylinder over longer periods. The conversion rate for in-situ produced NO₂, resulting from 50 ppb NO mixed with O₃, was found to be 105 %. We observed no correlation between any of the conversion efficiencies and meteorological parameters like air temperature, relative humidity, wind speed and direction, or precipitation events as an effect of possibly poor heat insulation.

3.1.2 Recovery rates of NH₃ and mixed sample gas (NO₂ and NH₃)

Since the preparation of reliable and accurate calibration gas mixtures for reactive nitrogenous gases is generally difficult, we concentrated the conversion efficiency tests for the TRANC on NO₂ and NH₃, the most abundant oxidized and reduced N_r compounds, respectively, in central Europe (see e.g. Hesterberg et al., 1996; Flechard et al., 2011). The conversion of NH₃, NO₂ and a mixture of both gases was tested by parallel sampling of calibration gases by the TRANC-CLD system and specific NH₃ and NO₂ analysers. The NH₃ analyser (Picarro G1103, Sunnyvale, CA, USA) was calibrated prior to the measurements using a permeation oven manufactured by LN Industries (Geneva, Switzerland) equipped with a NH₃ permeation tube (VICI, Metronics Inc., Poughkeepsie, NY, USA). The permeation system was calibrated by directing the gas mixture through an impinger containing acidic solution (H₂SO₄, 0.01 M) and subsequent analysis by ion chromatography. The NO₂ analyser (Thermo Environment chemiluminescence NO-NO₂-NO_x analyser, 42C Trace Level, called TEI hereafter), a chemiluminescence detector, in principle operating identical to the CLD described earlier but containing an additional channel for NO₂ measurements making use of a NO₂ specific photolytic converter (blue light converter BLC, Air Quality Design Inc., Wheatridge, USA; see e.g. Pollack et al., 2010) was calibrated with a NO standard parallel to the CLD. Both instruments thus agreed in NO mixing ratios. The conversion efficiency of the build-in NO₂ converter of the TEI was determined during an instrument

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service just after the conversion tests.

Conversion tests for NH_3 were performed by comparing the TRANC-CLD signal to NH_3 mixing ratios as determined by the NH_3 analyser. Both instruments sampled at the overflow of the same calibration tube which was flushed with the calibration gas for 48 h to ensure a stable NH_3 mixing ratio. The TRANC-CLD system found 112.6 ± 0.7 ppb N_r , which corresponds to a conversion efficiency of 95 % compared to NH_3 mixing ratios of 118.8 ± 0.6 ppb. Using the same setup for NO_2 , the conversion efficiency was observed to be larger than 99 % with 45.3 ± 0.4 ppb detected by the TRANC-CLD system in comparison to 45.5 ± 0.3 ppb NO_2 . Finally, a mixture of NH_3 and NO_2 calibration gas was fed to the analysers (see Fig. 5). To ensure excellent conditioning of the calibration tube, it was flushed with NH_3 calibration gas for 3 days, adding the NO_2 calibration gas after 2 days. The calibration gas mixture showed a NO_2 mixing ratio of 88.8 ± 0.4 ppb and an NH_3 mixing ratio of 69.7 ± 0.4 ppb (mean values \pm standard deviation after 1 and 3 days of tube conditioning). The TRANC-CLD system found 154.0 ± 0.9 ppb corresponding to a recovery rate of 97 %. The uncertainty of the TRANC conversion efficiency not only depends on the precision of the individual measurements (indicated by the standard deviations) but also on the absolute accuracy of the independent measurement systems. The latter is limited by the absolute uncertainty of the calibration gas source and dilution leading to total absolute (2σ) errors in the order of 10 % (see error bars in Fig. 5).

3.1.3 Aerosol particle conversion tests

Aerosol particle conversion efficiency of the TRANC was tested in cooperation with the Institute for Tropospheric Research (IfT), Leipzig, Germany. Aerosol particles were generated using a collision-type atomizer (TSI, St. Paul, USA) with a 0.3 mm nozzle sequentially from aqueous solutions of NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, and NaNO_3 (1 g l^{-1} , 0.5 g l^{-1} , 1 g l^{-1} , respectively), the three most common nitrogen containing aerosol compounds (e.g. Wexler and Seinfeld, 1991; Nemitz et al., 2009). The aerosol particles were dried and flushed into a stainless steel chamber of 1 m^3 , which was kept at

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ambient pressure. From this chamber, samples were taken in parallel by the TRANC-CLD system and a twin differential mobility particle sizer (TDMPS, Birmili et al., 1999), consisting of a differential mobility analyser combined with a condensational particle counter (UCPC3025 and CPC3010, TSI, St. Paul, USA). The recorded particle size and number distribution were used in combination with the known salt solid state densities to derive salt mixing ratios and consequently particle-bound N_r mixing ratios in the chamber air. The latter were compared to the N_r measured by the TRANC-CLD system (Fig. 6). The results indicate apparent conversion efficiencies between about 80 % and 150 %. The deviations (especially the overestimation) may be due to uncertainties in the aerosol measurements and in the assumptions for particle shape and density. Additionally, for flushing the chamber and transporting the generated aerosol, ambient air was used. This led to a relatively high and variable N_r background (20 to 39 ppb) in the TRANC-CLD measurements, which could only be corrected for by approximation.

3.2 Field test with ambient N_r composition

In summer 2006, an intensive field campaign within the NitroEurope project allowed an in-field comparison between the concentrations of a variety of N_r compounds and the total N_r concentration measured by the TRANC-CLD system. The study took place in Central Switzerland, close to the village of Oensingen at an intensively managed grassland site. A detailed site description can be found in Ammann et al. (2009).

During this study NO and NO₂ were measured by a TEI chemiluminescence analyser in combination with a BLC photolytic converter (see Sect. 3.1.2), and gaseous NH₃, HNO₃, and HONO as well as particulate NH₄⁺, and NO₃⁻ were measured using the GRAdient of AErosol and Gases Online Registrator (GRAEGOR, Thomas et al., 2009) – a wet chemical instrument, sampling with a wet annular denuder – steam jet aerosol collector combination, coupled to online analysis by ion-chromatography (HNO₃, HONO, NO₃⁻) and flow injection analysis (NH₃, NH₄⁺). Furthermore, NH₃ was measured additionally by a wet chemical AiRRmonia instrument (Erisman et al., 2001;

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Spirig et al., 2010; Flechard et al., 2010) (Table 1). Time series of NH_3 measured by the AiRRmonia system, gap-filled HNO_3 , HONO , NH_4^+ , NO_3^- data of the GRAEGOR, and NO , NO_2 data of the TEI are shown in Fig. 7.

The time series reveals distinct fluctuations of the different N_r compounds as well as the large dominance of NH_3 and NO_2 , accounting for more than 75 % of the site's ambient N_r concentration. The TRANC-CLD system compares very well to the sum of the individual measurements, capturing its fluctuations independently of the driving compound, indicating near-complete conversion of the various N_r species under variable ambient conditions.

3.3 Time response

An important feature for a converter designed for EC measurements is the fast detection of rapidly changing gas concentrations. Thus, we checked the TRANC-CLD system for time response characteristics during the calibration periods (Sect. 3.1.1) to make sure that even fast variations are clearly determined by the CLD without major attenuation effects. Figure 8a shows the time response of the NO signal in ppb recorded at a rate of 20 Hz after switching the TRANC valve from the calibration mode back to ambient air, which in that case was about 5 ppb. The course of the curve can be best approximated by an exponential decay function in the form of $c(t) = \Delta c \cdot e^{-t/\tau} c_{\text{final}}$ with a response (e-folding) time of $\tau = 0.30$ s. The full step change was completed within about 1 s after switching the valve. Figure 8b and c shows the time response of the NO signal recorded after switching the TRANC valve from the NO_2 and the NO plus O_3 calibration mode, respectively, back to ambient air. Here, τ values of 0.30 s were found as well. These numbers demonstrate the fast conversion and time response of the TRANC-CLD system. In another experiment (data not shown), two different NO concentrations were prepared and alternately fed into the system, one by the multi-gas calibrator and the other directly from the gas cylinder. In this test, we found half-value periods of 0.35 s. Given the fact, that the average residence time of air in the CLD reaction chamber ($V = 0.7$ l) at a pressure of 20 mbar and a flowrate of 3 l min^{-1}) is

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0.28 s, the reaction time is largely limited by the flushing of the CLD reaction chamber with probably some additional longitudinal mixing due to the flow velocity profile within the tube.

4 Discussion and conclusions

5 High-frequency measurements of N_r species have been rarely conducted in land-atmosphere exchange research and were usually limited to selected sites and short field campaigns. Neither a robust measurement technique for the long-term monitoring of the sum of all N_r compounds nor a technique that is fast enough to be applicable for EC measurements has been engineered and field-tested up to now. With the develop-
10 opment of the TRANC, we present a unique methodology for both quantifying the sum of all N_r compounds and a device being robust and fast enough to be usable in an EC setup when combined with a fast response NO detector (CLD).

The specific design of the TRANC which features fast and strong heating of the sample gas and quick conversion of N_r compounds to NO allows the detection of polar, water soluble and sticky substances like NH_3 , avoiding e.g. water surface effects (Kita et al., 2006; Sintermann et al., 2011). As the NO resulting from the conversion is relatively inert (in the absence of NO_2 and O_3) it permits the use of long tubing between the TRANC and the analyser system and thus an installation of the TRANC on masts and towers for micrometeorological measurements. Other arising problems
15 when using long tubing such as the correct determination of the lag time (to maximise the covariance), i.e. the time the air sample needs from entering the converter until it reaches the analyser, or possible high-frequency damping will be addressed in Ammann et al. (2011).

Testing recovery rates for single N_r compounds during laboratory tests, we found
25 values of 95 and 99 % for NH_3 and NO_2 , respectively, and 97 % when the two gases were combined. In-field longterm stability was approved by repeated conversion tests for NO_2 with an average value of 91 %. These conversion efficiency results were not

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significantly different from 100 %. For particulate mineral N, the laboratory conversion tests showed a less clear picture with more uncertain conversion efficiencies. The results in Fig. 6 nevertheless indicate an effective conversion of the aerosol particle N to NO in the TRANC.

5 The conversion efficiencies of the TRANC are comparable to values observed in other studies. McCalley and Sparks (2009), for example, report on 86 % for NH_3 measured with their converter system and 100 % for NO_2 . Horii et al. (2004) compared concentrations of NO_2 obtained by TDLAS versus photolysis-chemiluminescence (P-C) instruments and found a slope of 1.1 ± 0.2 with a R^2 of 0.91. The TD-LIF instrument presented by Farmer et al. (2006) was tested by Thornton et al. (2003) and Rosen et al. (2004) with a conversion efficiency of >95 % for NO_2 and >94 % for $\sum \text{PN}$ using P-C and gas chromatographs equipped with electron capture detectors, respectively, for comparative measurements. McCalley and Sparks also found a 100 % transformation for HONO, however only 78 to 99 % for NO_y (PAN, alkyl nitrate, HNO_3 and other forms of NO_y). In our tests, we performed an in-field comparison between the sum of individually measured NO , NO_2 , NH_3 , HNO_3 , HONO, NH_4^+ , NO_3^- by commercially available systems and the N_r concentration by TRANC-CLD. Excellent agreement was found in the temporal course ($R^2 = 0.96$) with the TRANC showing on average slightly (7 %) higher values. This small systematic difference might be due to minor N_r compounds not measured individually (e.g. organic compounds like PAN) or small errors in the calibration of any of the used analysers. The concentrations of HONO and HNO_3 , for which we did not explicitly check the conversion efficiency, were very small during the field experiment and thus their contribution to the total N_r measurements by the TRANC was not statistically significant. However, based on previous reports in the literature (e.g. Fahey et al., 1985; McCalley and Sparks, 2009) we assume that they were nearly fully converted under the conditions in the TRANC.

Regarding the response time for step concentration changes, we determined half-value periods of ≤ 0.35 s during different laboratory and field tests. As this value is in large part influenced by the flushing of the CLD chamber, it demonstrates that the

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TRANC is able to quickly and accurately detect the variability in N_r concentrations. For a similar system that was used for NO_y deposition measurements over a 24-m high forest, Munger et al. (1996) found half-value periods of 1 s.

The usage of the TRANC-CLD system within an EC setup allows for the determination of the net ecosystem exchange of total N_r , thereby providing a parameter of major interest when assessing the productivity of ecosystems by its nutrient N input. Also, there is no need to correct for chemical interactions and phase changes of the N_r compounds, keeping the measurements at a relatively low maintenance and reasonable cost level. However, one of the major benefits of the TRANC is at the same time one of its biggest constraints, i.e. the fact, that it can only measure total N_r (or net N_r exchange) and a differentiation into single N_r compounds is not possible with one converter system. But even for process studies and mechanistic modeling, the total N_r measurement can provide important constraints and validation data. A quantitative partitioning of the total N_r results may be achieved by combination with additional selective converters or detectors.

Acknowledgements. This work was supported by the EU project NitroEurope-IP (Contract 017841) under the EC 6th Framework Program for Research and Technological Development and by the Swiss State Secretariat for Education and Research (Project No. C09.0028) under the framework of the COST action ABBA (ES0804). We would like to thank the Max Planck Institute (MPI) for Biogeochemistry in Jena, Germany, the MPI for Chemistry in Mainz, Germany, the University of Bayreuth, Germany, and the Institute for Tropospheric Research, Leipzig, Germany for supporting lab and field tests during the development of the TRANC within their experiments. We also gratefully acknowledge the technical support by Dirk Lempio and Catharina Don.

References

Ammann, C., Spirig, C., Leifeld, J., and Neftel, A.: Assessment of the nitrogen and carbon budget of two managed temperate grassland fields, Agr. Ecosyst. Environ., 133, 150–162, 2009.

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Ammann, C., Wolff, V., Marx, O., Brümmner, C., and Neftel, A.: Measuring the biosphere-atmosphere exchange of total reactive nitrogen by eddy covariance, Biogeosciences Discuss., in preparation, 2011.

Baldocchi, D. D., Falge, E., Gu, L., Olson, R., Hollinger, D., Running, S., Anthoni, P., Bernhofer, C., Davis, K., Evans, R., Fuentes, J., Goldstein, A., Katul, G., Law, B. E., Lee, X., Malhi, Y., Meyers, T., Munger, W., Oechel, W., Paw U, K. T., Pilegaard, K., Schmid, H. P., Valentini, R., Verma, S., Vesala, T., Wilson, K., and Wofsy, S. C.: FLUXNET: A new tool to study the temporal and spatial variability of ecosystem-scale carbon dioxide, water vapor and energy flux densities, B. Am. Meteorol. Soc., 82, 2415–2434, 2001.

Birmili, W., Stratmann, F., and Wiedensohler, A.: Technical note – Design of a DMA-based size spectrometer for a large particle size range and stable operation, J. Aerosol Sci., 30, 549–553, 1999.

Brümmner, C., Black, T. A., Jassal, R. S., Grant, N. J., Spittlehouse, D. L., Chen B., Nesic, Z., Amiro, B. D., Arain, M. A., Barr, A. G., Bourque, C. P. A., Coursolle, C., Dunn, A. L., Flanagan, L. B., Humphreys, E. R., Lafleur, P. M., Margolis, H. A., McCaughey, J. H., and Wofsy, S. C.: How climate and vegetation type influence evapotranspiration and water use efficiency in Canadian forest, peatland and grassland ecosystems, Agric. For. Meteorol., in press, doi:10.1016/j.agrformet.2011.04.008, 2011a.

Brümmner, C., Marx, O., Kutsch, W., Amman, C., Wolff, V., and Freibauer, A.: Fluxes of total reactive atmospheric nitrogen using eddy covariance above arable land, in preparation, 2011b.

Coursolle, C., Margolis, H. A., Barr, A. G., Black, T. A., Amiro, B. D., McCaughey, J. H., Flanagan, L. B., Lafleur, P. M., Roulet, N. T., Bourque, C. P. A., Arain, M. A., Wofsy, S. C., Dunn, A., Morgenstern, K., Orchansky, A. L., Bernier, P. Y., Chen, J. M., Kidston, J., Saigusa, N., and Hedstrom, N.: Late-summer carbon fluxes from Canadian forests and peatlands along an east-west continental transect, Can. J. For. Res., 36, 783–800, 2006.

Dämmgen, U. and Zimmerling, R.: Vertical fluxes of air-borne acidifying and eutrophying species in the Schorfheide Nature Reserve in Brandenburg, Germany, J. Appl. Bot., 76, 190–202, 2002.

Day, D. A., Wooldridge, P. J., Dillon, M. B., Thornton, J. A., and Cohen, R. C.: A thermal dissociation laser-induced fluorescence instrument for in situ detection of NO₂, peroxy nitrates, alkyl nitrates, and HNO₃, J. Geophys. Res., 107, D6, doi:10.1029/2001JD000779, 2002.

Denmead, O. T., MacDonald, B. C. T., Bryant, G., Naylor, T., Wilson, S., Griffith, D. W. T., Wang,

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W. J., Salter, B., White, I., and Moody, P. W.: Emissions of methane and nitrous oxide from Australian sugarcane soils, *Agric. For. Meteorol.*, 150, 748–756, 2010.

Erismann, J. W., Otjes, R., Hensen, A., Jongejan, P., van den Bulk, P., Khlystov, A., Mols, H., and Slanina, S.: Instrument development and application in studies and monitoring of ambient ammonia, *Atmos. Environ.*, 35, 1913–1922, 2001.

Erismann, J. W., Bleeker, A., Galloway, J., and Sutton, M. A.: Reduced nitrogen in ecology and the environment, *Environment. Pollut.*, 150, 140–149, 2007.

Fahey, D. W., Eubank, C. S., Hubler, G., and Fehsenfeld, F. C.: Evaluation of a catalytic reduction technique for the measurement of total reactive odd-nitrogen NO_y in the atmosphere, *J. Atmos. Chem.*, 3, 435–468, 1985.

Famulari, D., Fowler, D., Hargreaves, K., Milford, C., Nemitz, E., Sutton, M., and Weston, K.: Measuring eddy covariance fluxes of ammonia using tunable diode laser absorption spectroscopy, *Water Air Soil Pollut., Focus* 4, 151–158, 2004.

Farmer, D. K., Wooldridge, P. J., and Cohen, R. C.: Application of thermal-dissociation laser induced fluorescence (TD-LIF) to measurement of HNO_3 , Σ alkyl nitrates, Σ peroxy nitrates, and NO_2 fluxes using eddy covariance, *Atmos. Chem. Phys.*, 6, 3471–3486, doi:10.5194/acp-6-3471-2006, 2006.

Flechard, C. R. and Fowler, D.: Atmospheric ammonia at a moorland site. II: Long-term surface-atmosphere micrometeorological flux measurements, *Q. J. Roy. Meteorol. Soc.*, 124, 759–791, 1998.

Flechard, C. R., Spirig, C., Neftel, A., and Ammann, C.: The annual ammonia budget of fertilised cut grassland – Part 2: Seasonal variations and compensation point modeling, *Biogeosciences*, 7, 537–556, doi:10.5194/bg-7-537-2010, 2010.

Flechard, C. R., Nemitz, E., Smith, R. I., Fowler, D., Vermeulen, A. T., Bleeker, A., Erismann, J. W., Simpson, D., Zhang, L., Tang, Y. S., and Sutton, M. A.: Dry deposition of reactive nitrogen to European ecosystems: a comparison of inferential models across the NitroEurope network, *Atmos. Chem. Phys.*, 11, 2703–2728, doi:10.5194/acp-11-2703-2011, 2011.

Fontijn, A., Sabadell, A. J., and Ronco, R. J.: Homogeneous chemiluminescent measurement of nitric oxide with ozone, *Anal. Chem.*, 42, 575–579, 1970.

Galloway, J. N., Aber, J. D., Erismann, J. W., Seitzinger, S. P., Howarth, R. W., Cowling, E. B., and Cosby, B. J.: The Nitrogen Cascade, *BioScience*, 53, 341–356, 2003.

Hegglin, M. I., Brunner, D., Peter, T., Hoor, P., Fischer, H., Staehelin, J., Krebsbach, M., Schiller, C., Parchatka, U., and Weers, U.: Measurements of NO , NO_y , N_2O , and O_3 during SPURT:

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implications for transport and chemistry in the lowermost stratosphere, *Atmos. Chem. Phys.*, 6, 1331–1350, doi:10.5194/acp-6-1331-2006, 2006.

Hesterberg, R., Blatter, A., Fahrni, M., Rosset, M., Neftel, A., Eugster, W., and Wanner, H.: Deposition of nitrogen-containing compounds to an extensively managed grassland in central Switzerland, *Environ. Poll.*, 91, 21–34, 1996.

Horii, C. V., Munger, J. W., and Wofsy, S. C.: Fluxes of nitrogen oxides over a temperate deciduous forest, *J. Geophys. Res.*, 109, D08305, doi:10.1029/2003JD004326, 2004.

Kita, K., Morino, Y., Kondo, Y., Komazaki, Y., Takegawa, N., Miyazaki, Y., Hirokawa, J., Tanaka, S., Thompson, T. L., Gao, R. S., and Fahey, D. W.: A chemical ionization mass spectrometer for ground-based measurements of nitric acid, *J. Atmos. Ocean. Tech.*, 23, 1104–1113, 2006.

Kroon, P. S., Schuitmaker, A., Jonker, H. J. J., Tummers, M. J., Hensen, A., and Bosveld, F. C.: An evaluation by laser Doppler anemometry of the correction algorithm based on Kaimal co-spectra for high frequency losses of EC flux measurements of CH₄ and N₂O, *Agric. For. Meteorol.*, 150, 794–805, 2010.

McCalley, C. K. and Sparks, J. P.: Abiotic Gas Formation Drives Nitrogen Loss from a Desert Ecosystem, *Science*, 326, 837–840, 2009.

Munger, J. W., Wofsy, S. C., Bakwin, P. S., Fan, S.-M., Goulden, M. L., Daube, B. C., and Goldstein, A. H.: Atmospheric deposition of reactive nitrogen oxides and ozone in a temperate deciduous forest and a subarctic woodland, 1. Measurements and mechanisms, *J. Geophys. Res.*, 101, 12639–12657, 1996.

Neftel, A., Ammann, C., Fischer, C., Spirig, C., Conen, F., Emmenegger, L., Tuzson, B., and Wahlen, S.: N₂O exchange over managed grassland: Application of a quantum cascade laser spectrometer for micrometeorological flux measurements, *Agric. For. Meteorol.*, 150, 775–785, 2010.

Nemitz, E., Dorsey, J. R., Flynn, M. J., Gallagher, M. W., Hensen, A., Erisman, J.-W., Owen, S. M., Dämmgen, U., and Sutton, M. A.: Aerosol fluxes and particle growth above managed grassland, *Biogeosciences*, 6, 1627–1645, doi:10.5194/bg-6-1627-2009, 2009.

Pollack, I. B., Lerner, B. M., and Ryerson, T. B.: Evaluation of ultraviolet light-emitting diodes for detection of atmospheric NO₂ by photolysis – chemiluminescence, *J. Atmos. Chem.*, 65, 111–125, 2010.

Rinne, J., Pihlatie, M., Lohila, A., Thum, T., Aurela, M., Tuovinen, J., Laurila, T., and Vesala, T.: Nitrous oxide emissions from a municipal landfill, *Environ. Sci. Technol.*, 39, 7790–7793,

2005.

Rosen, R. S., Wood, E. C., Wooldridge, P. J., Thornton, J. A., Day, D. A., Kuster, W., Williams, E. J., Jobson, B. T., and Cohen, R. C.: Observations of total alkyl nitrates during Texas Air Quality Study 2000: Implications for O₃ and alkyl nitrate photochemistry, *J. Geophys. Res.*, 109, D07303, doi:10.1029/2003JD004227, 2004.

Rummel, U., Ammann, C., Gut, A., Meixner, F. X., and Andreae, M. O.: Eddy covariance measurements of nitric oxide flux within an Amazonian rain forest, *J. Geophys. Res.*, 107, 8050, doi:10.1029/2001JD000520, 2002.

Seinfeld, J. H. and Pandis, S. N.: *Atmospheric Chemistry and Physics – From Air Pollution to Climate Change*, Second Edition, John Wiley and Sons Inc., 1232 p., 2006.

Shaw, W. J., Spicer, C. W., and Kenny, D. V.: Eddy correlation fluxes of trace gases using a tandem mass spectrometer, *Atmos. Environ.*, 32, 2887–2898, 1998.

Simpson, D., Butterbach-Bahl, K., Fagerli, H., Kesik, M., Skiba, U., and Tang, S.: Deposition and Emissions of Reactive Nitrogen over European Forests: A Modelling Study, *Atmos. Environ.*, 40, 5712–5726, 2006.

Sintermann, J., Spirig, C., Jordan, A., Kuhn, U., Ammann, C., and Neftel, A.: Eddy covariance flux measurements of ammonia by high temperature chemical ionisation mass spectrometry, *Atmos. Meas. Tech.*, 4, 599–616, doi:10.5194/amt-4-599-2011, 2011.

Spirig, C., Flechard, C. R., Ammann, C., and Neftel, A.: The annual ammonia budget of fertilised cut grassland – Part 1: Micrometeorological flux measurements and emissions after slurry application, *Biogeosciences*, 7, 521–536, doi:10.5194/bg-7-521-2010, 2010.

Sutton, M. A., Nemitz, E., Erisman, J. W., Beier, C., Butterbach-Bahl, K., Cellier, P., de Vries, W., Cotrufo, F., Skiba, U., Di Marco, C., Jones, S., Laville, P., Soussana, J. F., Loubet, B., Twigg, M., Famulari, D., Whitehead, J., Gallagher, M. W., Neftel, A., Flechard, C. R., Herrmann, B., Calanca, P. L., Schjoerring, J. K., Dämmgen, U., Horvath, L., Tang, Y. S., Emmett, B. A., Tietema, A., Peñuelas, J., Kesik, M., Brüggemann, N., Pilegaard, K., Vesala, T., Campbell, C. L., Olesen, J. E., Dragosits, U., Theobald, M. R., Levy, P., Mobbs, D. C., Milne, R., Viovy, N., Vuichard, N., Smith, J. U., Smith, P., Bergamaschi, P., Fowler, D., and Reis, S.: Challenges in quantifying biosphere-atmosphere exchange of nitrogen species, *Environ. Pollut.* 150, 125–139, 2007.

Sutton, M. A., Billen, G., Bleeker, A., Erisman, J. W., Grennfelt, P., van Grinsven, H., Grizzetti, B., Howard, C. M., and Leip, A.: *Technical Summary of The European Nitrogen Assessment*, edited by: Sutton, M. A., Howard, C. M., Erisman, J. W., Billen, G., Bleeker, A., Grennfelt, P.,

AMTD

4, 7623–7655, 2011

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van Grinsven, H., and Grizzetti, B., Cambridge University Press, 2011.

Thomas, R. M., Trebs, I., Otjes, R., Jongejan, P. A. C., Ten Brink, H., Phillips, G., Kortner, M., Meixner, F. X., and Nemitz, E.: An automated analyzer to measure surface-atmosphere exchange fluxes of water soluble inorganic aerosol compounds and reactive trace gases, *Environ. Sci. Technol.*, 43, 1412–1418, 2009.

Thornton, J. A., Wooldridge, P. J., Cohen, R. C., Williams, E. J., Hereid, D. P., Fehsenfeld, F. C., Stutz, J., and Alicke, B.: Comparisons of in situ and long path measurements of NO₂ in urban plumes, *J. Geophys. Res.*, 108, 4496, doi:10.1029/2003JD003559, 2003.

Tuzson, B., Hiller, R. V., Zeyer, K., Eugster, W., Neftel, A., Ammann, C., and Emmenegger, L.: Field intercomparison of two optical analyzers for CH₄ eddy covariance flux measurements, *Atmos. Meas. Tech.*, 3, 1519–1531, doi:10.5194/amt-3-1519-2010, 2010.

Twigg, M. M., House, E., Thomas, R., Whitehead, J., Phillips, G. J., Famulari, D., Fowler, D., Gallagher, M. W., Cape, J. N., Sutton, M. A., Nemitz, E.: Surface/atmosphere exchange and chemical interactions of reactive nitrogen compounds above a manured grassland, *Agric. For. Meteorol.*, 151, 1488–1503, 2011.

von Bobruzki, K., Braban, C. F., Famulari, D., Jones, S. K., Blackall, T., Smith, T. E. L., Blom, M., Coe, H., Gallagher, M., Ghalaieny, M., McGillen, M. R., Percival, C. J., Whitehead, J. D., Ellis, R., Murphy, J., Mohacsi, A., Pogany, A., Junninen, H., Rantanen, S., Sutton, M. A., and Nemitz, E.: Field inter-comparison of eleven atmospheric ammonia measurement techniques, *Atmos. Meas. Tech.*, 3, 91–112, doi:10.5194/amt-3-91-2010, 2010.

Wexler, A. S. and Seinfeld, J. H.: Second-generation inorganic aerosol model, *Atmos. Environ.*, 25, 2731–2748, 1991.

Wolff, V., Trebs, I., Ammann, C., and Meixner, F. X.: Aerodynamic gradient measurements of the NH₃-HNO₃-NH₄NO₃ triad using a wet chemical instrument: an analysis of precision requirements and flux errors, *Atmos. Meas. Tech.*, 3, 187–208, doi:10.5194/amt-3-187-2010, 2010.

Wyers, G. P., Otjes, R. P., and Slanina, J.: A continuous-flow denuder for the measurement of ambient concentrations and surface-exchange fluxes of ammonia, *Atmos. Environ.*, 27, 2085–2090, 1993.

Zimmerling, R., Dämmgen, U., Grünhage, L., Haenel, H.-D., Küsters, A., Max, W., and Jäger, H.-J.: The Classifying Ratiometric Method for the Continuous Determination of Atmospheric Flux Densities of Reactive N- and S-Species with Denuder Filter Systems, *J. Appl. Bot.*, 71, 38–49, 1997.

Table 1. Overview of the instruments used for concentration measurements of nitrogenous compounds during the field inter-comparison in Oensing, August 2006.

Quantity	Oxidation level	Instruments	Detection principle	Observed concentration range
NO	+2	ThermoElectron 42C	Chemiluminescence	0–28 ppb
NO ₂	+4	ThermoElectron 42C +blue light converter	Photolytic conversion + chemiluminescence	1–22 ppb
NH ₃	–3	AiRRmonia	Membrane scrubber + conductivity cell	1–19 ppb
pNH ₄ ⁺	–3	GRAEGOR	Mist chamber + flow injection/conductivity	0–1.9 ppb
HNO ₃	+5	GRAEGOR	Rotating denuder + ion chromatography	0–0.8 ppb
pNO ₃ [–]	+5	GRAEGOR	Mist chamber + ion chromatography	0–1.7 ppb
HONO	+3	GRAEGOR	Rotating denuder + ion chromatography	0–0.8 ppb

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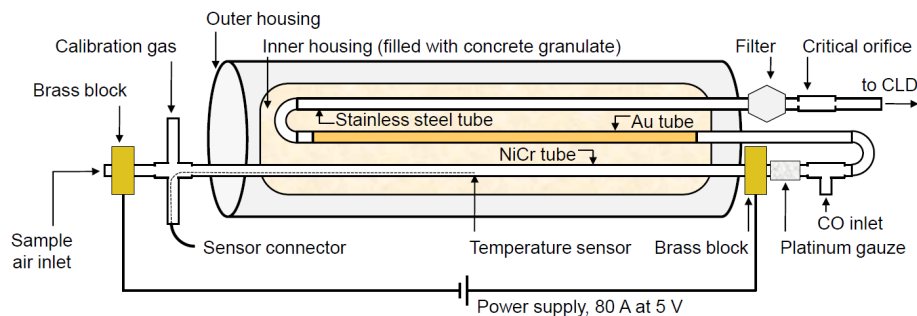


Fig. 1. Design of the total reactive atmospheric nitrogen converter (TRANC) (not true to scales).

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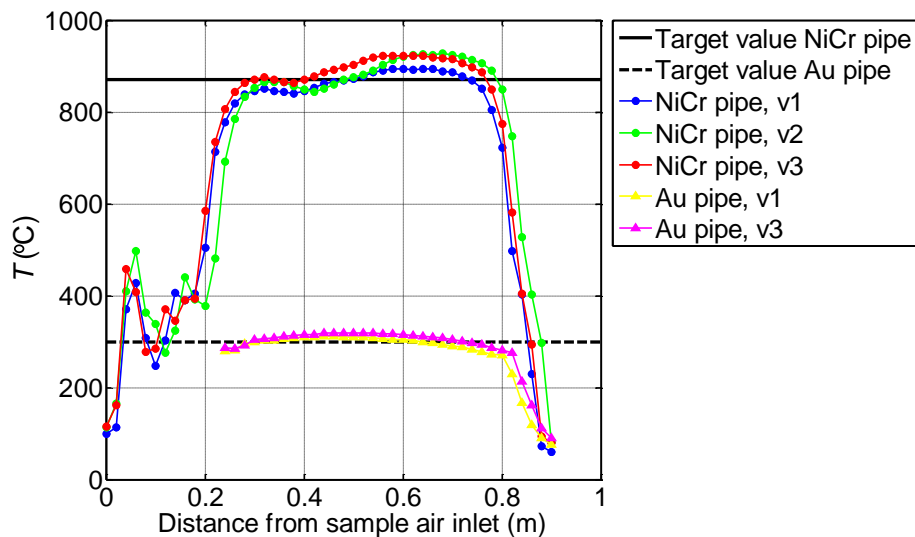


Fig. 2. Temperature distribution inside TRANC during different experimental runs with “v1”, “v2”, and “v3” indicating that the target temperature for the heating power modulator was set to 870, 880, and 895 °C, respectively.

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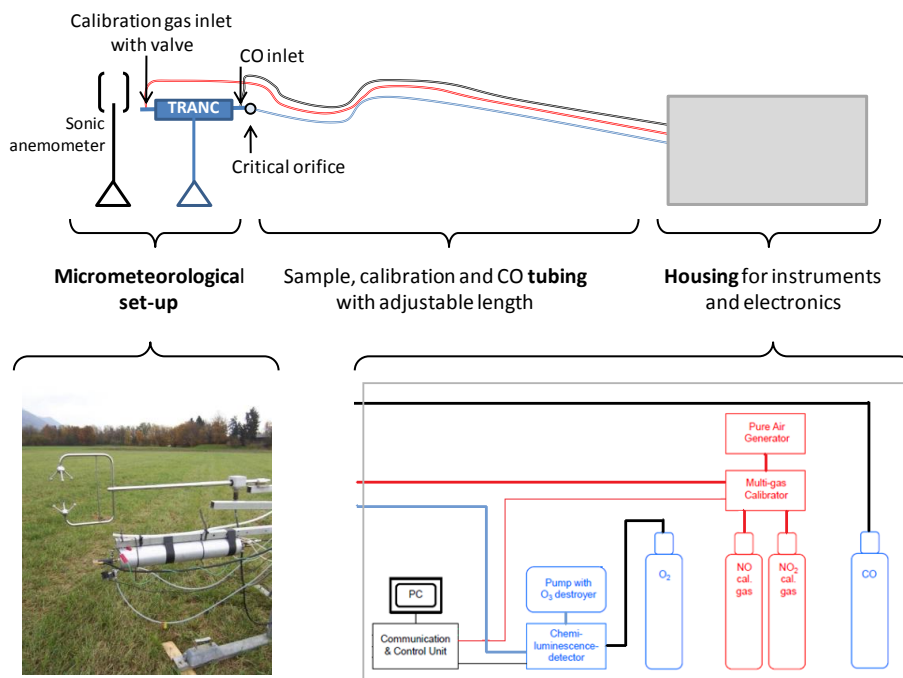


Fig. 3. Schematic overview of the TRANC-CLD system (blue) in an eddy-covariance setup. Elements of the calibration unit are shown in red. Bold lines indicate tubing. The photo shows the field-setup at the Oensingen site.

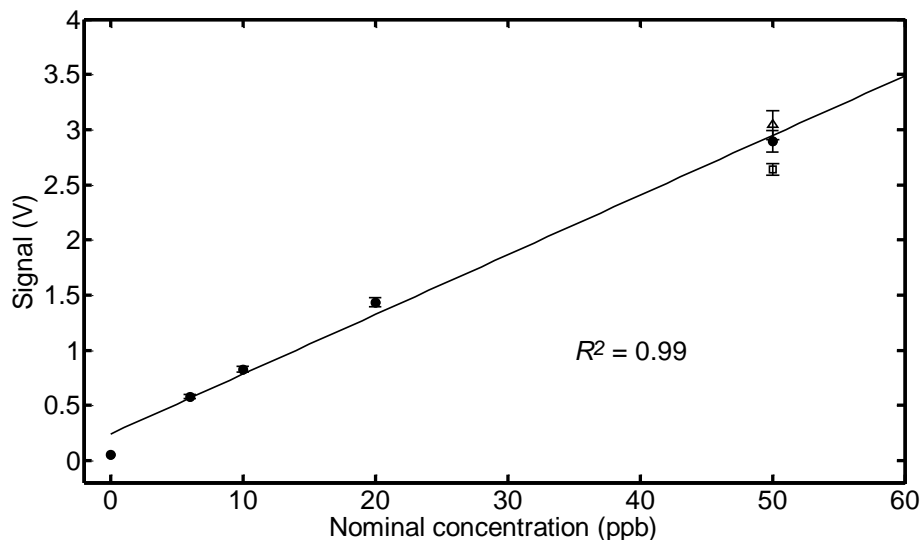


Fig. 4. Averaged signal response of the CLD coupled to the TRANC after calibrating with seven different concentrations, i.e. 0, 6, 10, 20, 50 ppb NO, 50 ppb NO₂, and 50 ppb NO + O₃. Data were taken from an 11-month field campaign conducted at an agricultural site in Gebesee, Germany. Each data point represents the mean of 30 calibration runs of the respective gas concentration. Error bars indicate the standard error of the mean. Filled symbols are NO calibrations, open square and open triangle are NO₂ and NO + O₃ calibration runs, respectively.

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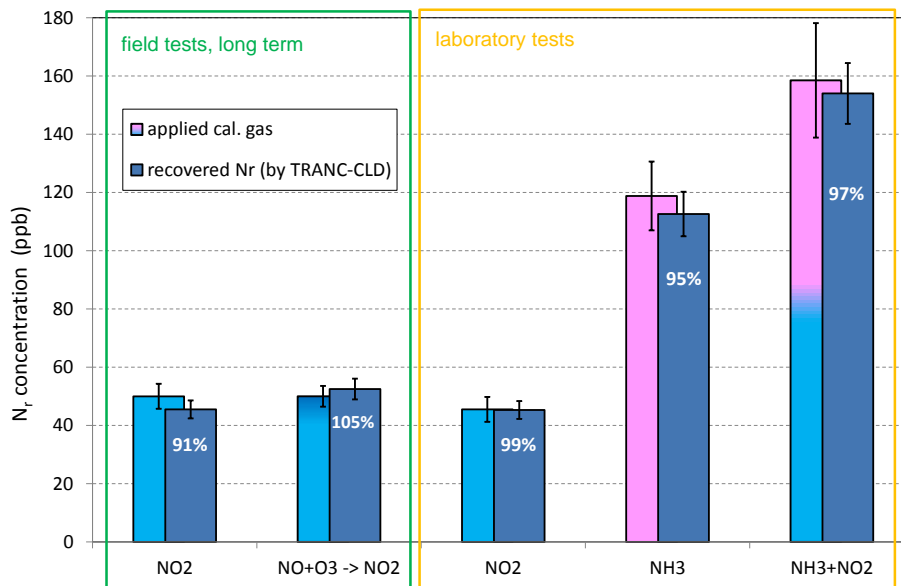


Fig. 5. Conversion efficiency tests with applied calibration gas concentrations and resulting measurements (recovered N_r) by the TRANC-CLD system under laboratory and field conditions. Error bars (2σ) were estimated from uncertainties in calibration (gas standards, mass flow controllers used for dilution, etc.) of the different instruments and signal noise.

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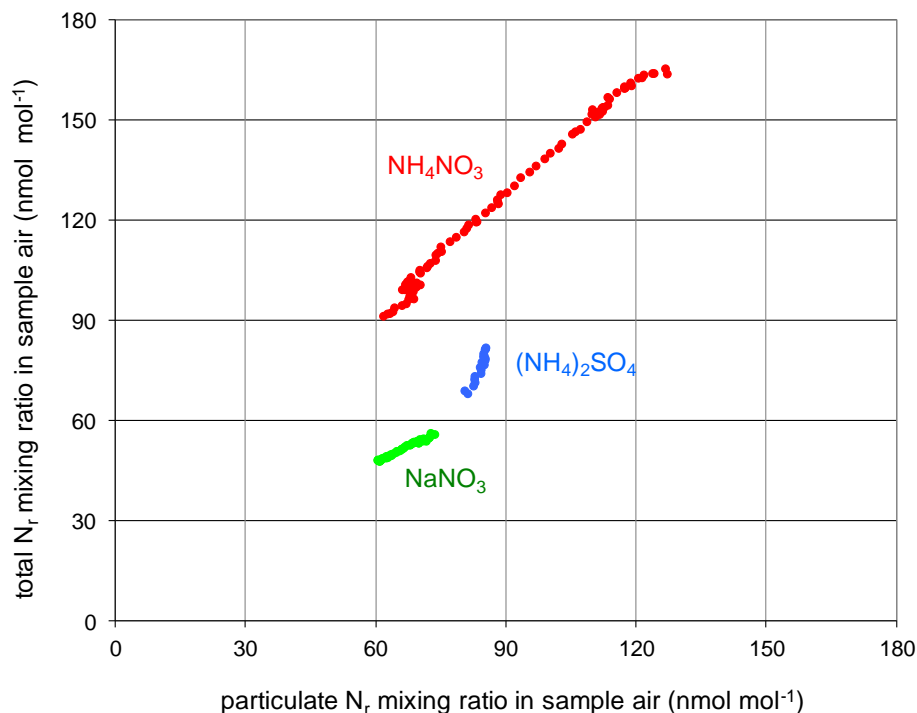


Fig. 6. Conversion tests of particulate N_r -compounds (NH_4NO_3 in red, $(NH_4)_2SO_4$ in blue, $NaNO_3$ in green): total N_r on y-axis as measured by the TRANC-CLD is plotted vs. particulate N_r mixing ratio derived from aerosol number concentration and size distribution measurements. Each dot represents an 8-min scan of the TDMPS; TRANC values were aggregated accordingly.

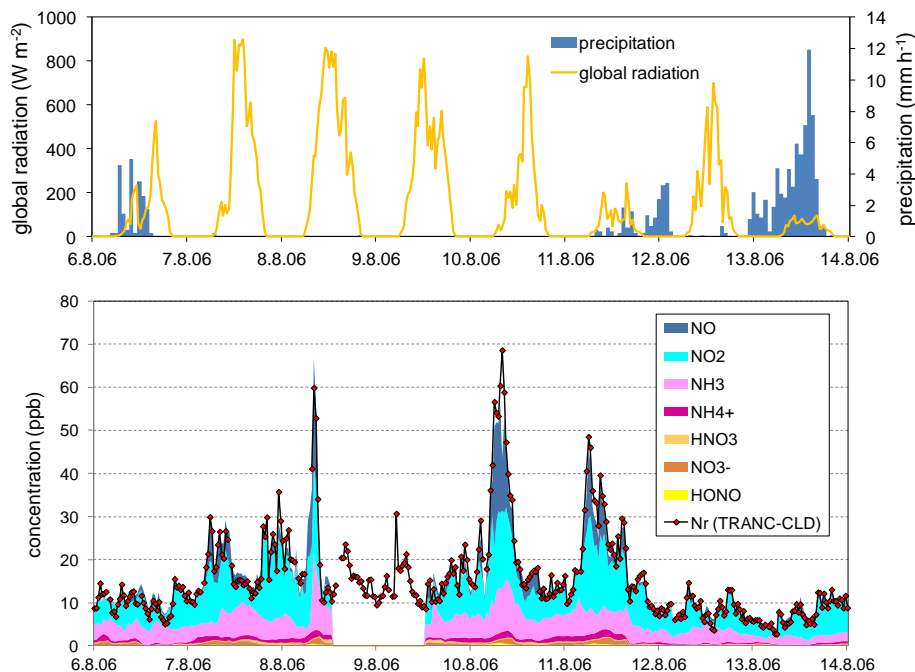


Fig. 7. Time series of **(a)** global radiation and precipitation and **(b)** concentrations of individual N_r compounds (cumulative) at the Oensingen site and of the total N_r concentration detected by the fast response TRANC-CLD system. All values were aggregated to 30 min means. For the minor compounds NH₄⁺, HNO₃, NO₃⁻, and HONO, few data gaps of 0.5 to 4 h length have been filled by linear interpolation.

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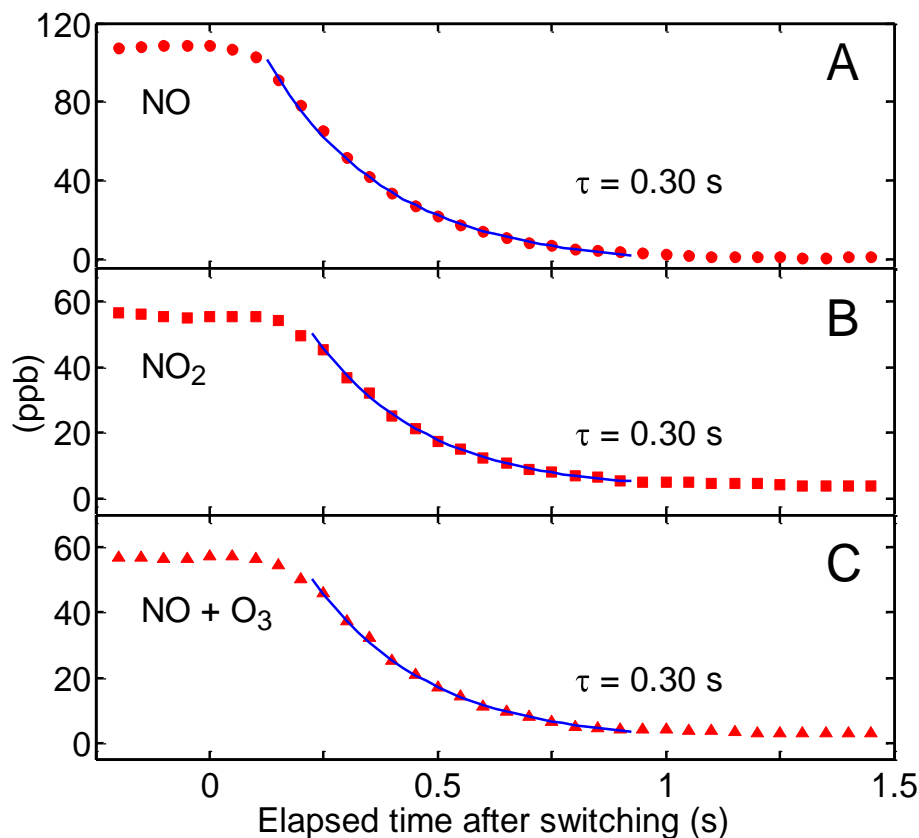


Fig. 8. Time response of the TRANC-CLD system characterising rapid step concentration changes. The course of the curve can be best approximated by exponential decay functions in the form of $c(t) = \Delta c \cdot e^{-t/\tau} c_{\text{final}}$ with response (e-folding) times of $\tau = 0.30$ s for NO, NO₂ and NO + O₃.