8.1 MEASURING THE BIOSPHERE-ATMOSPHERE EXCHANGE OF TOTAL REACTIVE NITROGEN BY EDDY COVARIANCE USING A NOVEL CONVERTER

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1. INTRODUCTION

Because nitrogen availability is one of the key limiting factors for the productivity of ecosystems, it also has a strong influence on the greenhouse gas exchange. The joint monitoring of reactive nitrogen exchange is therefore essential for the interpretation of the greenhouse gas budget of ecosystems. However, the exchange of reactive nitrogen (rN) with the atmosphere includes various compounds (NO, NO_2, HNO_3, NH_3, NH_3^-, NH_4^+, etc.) and the long-term monitoring of all of them individually would be very expensive and seems unrealistic in practice. An alternative approach is the measurements of the exchange of the sum of all these rN species (total reactive nitrogen: TorN). For this purpose we tested a custom built converter system that thermally converts all reduced and oxygenated reactive nitrogen compounds.

2. METHODS

2.1 *Converter Principle*

A total reactive nitrogen converter ('TRANC') custom-built according to Marx et al. (2006) was used for fast response detection of all rN compounds. The basic principle of the converter is to thermally convert all reduced and oxygenated rN compounds to nitric oxide (NO), which is then analyzed by a commercially available NO detector. For this purpose, the sample air is first passing an alloy cell heated to 870°C followed by a gold cell heated to 300°C. Between the two cells, CO is added to the sample air as reducing agent. In the first part, nitrogen containing particles are vaporized and reduced nitrogen gases are oxidized. In the second part, all oxidized rN compounds are reduced by CO to nitric oxide (NO) on the gold catalyst.

2.2 *Eddy Covariance Setup*

The converter was combined with a fast response chemiluminescence NO analyzer (Eco-Physics CLD 780 TR, cf. Rummel et al., 2002), which provides a response time of <1 s. The fast response time allowed the utilization of the TorN detection system (TRANC + NO analyzer) for eddy covariance (EC) flux measurements. The EC approach determines the vertical flux of a trace gas in the air as the covariance of the (instantaneous) vertical wind *w* and the gas concentration *c* at a given point:

$$F_c = \sum_{i=1}^{n} \left[w(t) - \overline{w} \right] \cdot \left[c(t+\tau) - \overline{c} \right] \qquad (1)$$

w(*t*) and *c*(*t*) are the instantaneous values of vertical wind and scalar concentration (sampling interval <1 s), and the overbars indicate the mean over an integration interval of 10 min here. The range between about 1 s and 10 min covers the time scales of turbulent structures contributing to vertical mixing in the atmospheric boundary layer. The time lag τ is introduced to correct for the delayed detection of the trace gas concentration mainly due to the residence time in the converter and the sampling tube.

In order to measure the EC flux in the field, the fast TorN detection system was used in combination with a 3-dimensional ultrasonic anemometer ('sonic', Gill Instruments HS Research Anemometer) mounted at a height of 1.2 m above ground (due to the limited field size). According to the EC concept, the sample inlet of the trace gas analyzer was placed close to the sonic sensor (separation distance *c*. 0.25 m). Since most rN compounds may interfere with the sampling tube walls, the converter was positioned directly at the sample air inlet but without disturbing the wind flow through the sonic sensor head. Once the sample air has passed the converter, only NO is left which does generally not react with the tubing walls. Directly after the converter, a critical orifice restricts the flow to a constant flow rate and produces a strong pressure drop. In this way the residence time is kept small even if the tube between converter and NO analyzer is relatively long. In the present study, the NO analyzer was positioned in an air-conditioned trailer at 20 m distance from the actual EC measurement location.

The TorN detection system was regularly calibrated in the field with NO cylinder standard gas in combination with an automated gas dilution system.

2.3 *Field Site*

The TorN flux system was installed at the Swiss FLUXNET site Oensingen (7°44'E, 47°17'N, 450 m a.s.l.). The investigated grassland field has been

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established in 2001 and is intensively managed (clover-grass mixture, 4-5 cuts per year, total fertilizer input: c. 230 kgN ha^{-1} y^{-1}). The site is situated on the Central Swiss Plateau in a region with intensive agriculture and other strong local anthropogenic influence (highway, roads, villages). Oensingen has been a main experimental site of the European GreenGrass and CarboEurope networks and is presently one of 13 main sites of the Nitro-Europe project (see Ammann et al., 2007; 2009).

2.4 *Additional Measurements*

Carbon flux measurements and a large number of basic and specific meteorological parameters as well as soil and vegetation properties are monitored at the Oensingen site since 2002. Beginning in 2006, also fluxes and concentrations of the main reactive nitrogen species are measured by various systems.
Among these are dynamic chamber system measurements of NO_2 fluxes and concentrations. The system is operated continuously (half hour resolution) and consists of 3 automated chambers. NO_2 (and NO/O_3) are detected inside and outside the chambers by a chemiluminescence detector (ThermoEnvironment 42C trace level). The detailed design is described in Pape et al. (2009). Due to the modified air exchange within the dynamic chambers and with the ambient air, the chamber flux may deviate from the real flux for deposition processes. Therefore, the more representative surface resistance R_c for NO_2 deposition was derived from the measured chamber fluxes. Because of the considerable variability of the resulting individual R_c values, the following evaluation procedure was applied:

- rejection of cases with highly non-stationary ambient concentrations during the measurement
- averaging of chamber fluxes over the 3 chambers for every half hour
- calculation of R_c from average flux (according to Pape et al., 2009)
- parameterization (non-liner fit) of R_c as a function of leaf area index and global radiation
- calculation of aerodynamic resistances R_a and R_b for each half hour from sonic turbulence data
- calculation of deposition velocity from R_a, R_b, and parameterized R_c
- calculation of ambient (undisturbed) deposition flux from deposition velocity and ambient NO_2 concentration.

Ammonia concentrations and fluxes have been measured with a gradient system as described by Spirig et al. (2010). The system consists of two AiRRmonia analyzers (Mechatronics, Hoorn, NL). Two sample blocks with diffusion membranes are installed at two heights (ca. 0.4 m and 1.4 m above the surface). The system is operated semi-continuously (30 min resolution) from spring to fall and NH_3 fluxes are calculated by the aerodynamic flux-gradient method (Spirig et al., 2010).

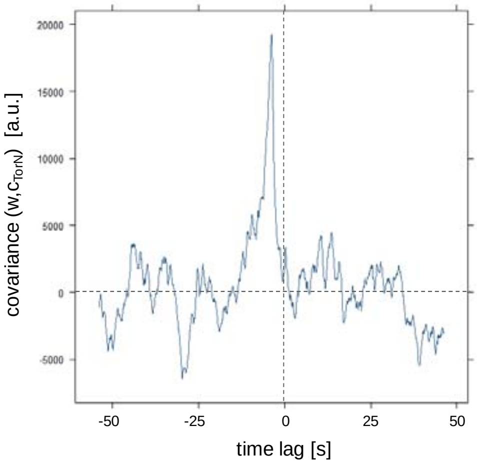

Figure 1: Exemplary cross-covariance function of vertical wind speed and TorN concentration obtained at the Oensingen site during a slurry application phase.

3. RESULTS

3.1 *Response Characteristics and Damping Correction of the EC fluxes*

A necessary pre-requisite of successful EC flux measurements is that the covariance between *w* and *c* (Eq. 1) is significant, i.e. that it can be clearly discerned from the noise in the covariance. This can be checked by the cross-covariance function. It corresponds to the covariance flux in Eq.1 evaluated for varying values of the lag time τ. An example for such a function is plotted in Fig. 1. It shows a clear peak at a time lag of -3.7 s. This corresponds to a plausible value of the residence time in the converter and sampling tube for the given volume and air flow.

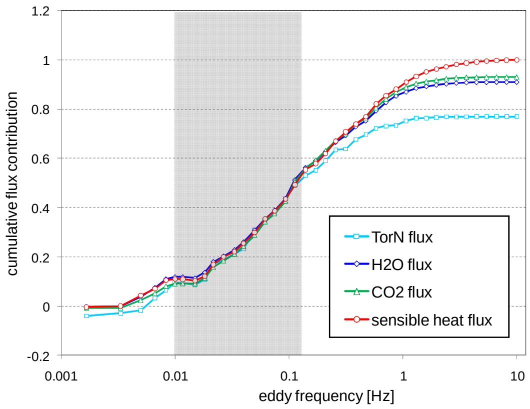

Figure 2: Exemplary case of normalized flux ogives (=cumulative cospetra) for the sensible heat flux and trace gas fluxes (CO_2, H_2O, TorN) at the Oensingen site. The sensible heat flux ogive was normalized to 1 and the trace gas ogives were scaled to the sensible heat ogive in the medium-low frequency range (light gray area). The cumulative value at the right end of the curves indicates the high frequency damping factor.

Despite the significant covariance peak, some high frequency damping of the TorN time series is likely to occur due to mixing effects during the sampling air flow through the converter and the tube. The total damping effect was determined empirically with the ogive method according to Ammann et al. (2006). An exemplary case of this method is illustrated in Fig. 2. The ogives (cumulative cospectra) of the trace gas fluxes are scaled to the corresponding sensible heat flux ogive (used as reference) in the medium-low frequency range, where no damping is supposed to occur. The resulting deviation of the trace gas ogives from the reference ogive in the high frequency range is a quantitative measure of the spectral damping. In the present case, the TorN ogive indicates a damping factor of 0.78 (loss of 22% of the flux). Overall an average damping factor of 0.77 was found and used for correction of the TorN fluxes.

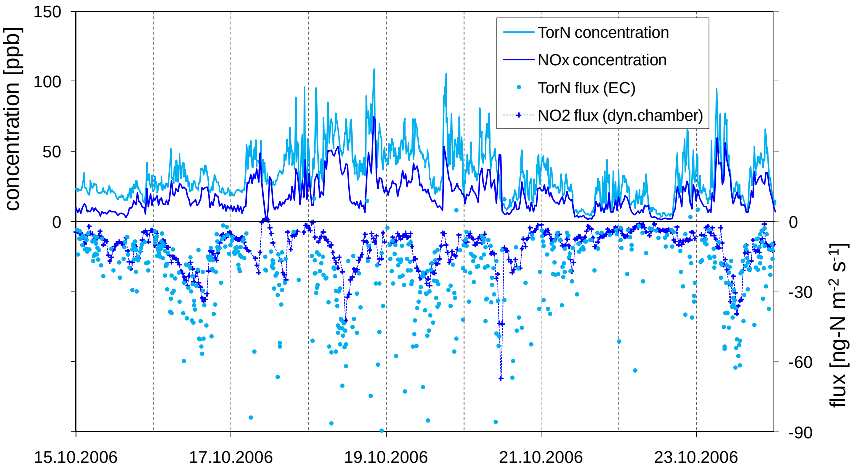

Figure 3: Nine days of flux and concentration measurements at the Oensingen grassland site during a growing phase in autumn 2006. TorN concentrations and fluxes result from the fast response converter/EC system (10 min data); NO_X concentration and NO_2 fluxes result from the dynamic chamber system (30 min data; see Sect. 2.4).

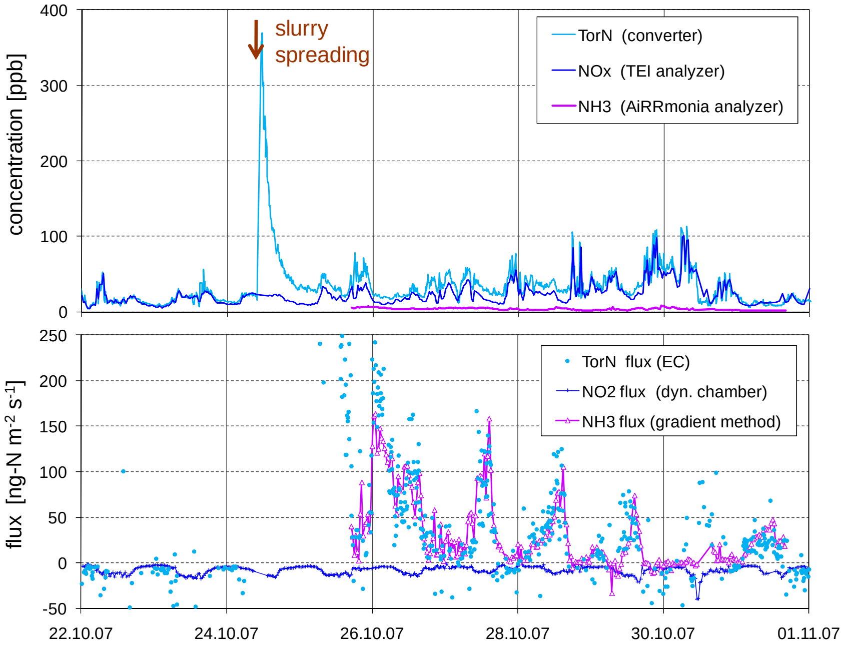

Figure 4: Ten days of flux and concentration measurements at the Oensingen grassland site during a slurry application event in autumn 2007. TorN concentrations and fluxes result from the fast response converter/EC system (10 min data). NO_X concentration and NO_2 fluxes result from the dynamic chamber system (30 min data; see Sect. 2.4). NH_3 concentration and fluxes result from the gradient system (30 min data; see Sect. 2.4).

3.2 *NO_X Dominated Phase*

Figure 3 shows field data during a growing phase. The concentration results show that the TorN is dominated by NO_X (=NO+NO_2) in this period. NO_X concentrations as detected by the slow response instrument of the dynamic chamber system were generally quite high and showed large and fast variations. TorN and NO_X concentration time series are highly correlated with TorN being always higher.

A similarly good correlation is found for the TorN and the NO_2 flux (Fig. 3), although the scatter of the TorN EC fluxes is relatively large. All fluxes are negative and show a clear diurnal cycle with largest deposition during daytime. This diurnal variation is not correlated with the corresponding concentration which indicates that nocturnal deposition is strongly limited by the weak aerodynamic mixing.

3.3 *NH_3 Dominated Phase*

The second phase of field results (Fig. 4) includes a slurry application event on the third day. Before this event and about 5 days afterwards, there is a very good agreement between the observed TorN and NO_X concentrations. However directly after slurry spreading, the TorN concentration jumps to much higher values and decreases again more slowly. The difference between TorN and NO_X can be attributed to NH_3 emitted from the spread slurry. Unfortunately no measurements from the gradient system are available for the application day, but only afterwards.

The flux intercomparison in Figure 4 shows a good agreement between the TorN fluxes and the gradient derived NH_3 fluxes for the days after the slurry application. During this phase, the NO_2 deposition flux was much smaller and played an almost negligible role for the total reactive nitrogen.

4. CONCLUSIONS

The present field measurements show that the applied detection system for total reactive nitrogen with the novel converter is able to measure EC fluxes of oxidized and reduced rN gases. The position of the converter at the sample inlet ensures a minimum interaction between the reactive rN compounds and the measurement system leading to a moderate average high-frequency damping loss and correction of 20-25%. It has to be noted that this damping was mainly a consequence of the very low measurement height of 1.2 m in the present experiment (due to the limited field size). For larger measurement heights commonly used above taller vegetation or more extended ecosystems, the EC cospectrum will shift to lower frequencies and thus the resulting damping effect would be significantly lower.

The relatively large scatter in the TorN fluxes mainly originate from the strongly varying concentrations of the main rN compounds at the measurement site. The large variation in the NO and NO_2 concentrations were due to the nearby highway and other anthropogenic sources, the variability of the NH_3 concentration after slurry application was due to the strong local source in combination with varying wind conditions. The ongoing activities include an optimization of the data evaluation aiming at a reduction to the corresponding noise effects.

Acknowledgements

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