



Supplement of

Reactive nitrogen fluxes over peatland and forest ecosystems using micrometeorological measurement techniques

Christian Brümmer et al.

Correspondence to: Christian Brümmer (christian.bruemmer@thuenen.de)

The copyright of individual parts of the supplement might differ from the article licence.

Table S1: Overview of literature presenting eddy-covariance measurements of reactive nitrogen compounds. Some additional flux campaigns are listed in the publication of Walker et al. (2020).

| Paper | Compound | Main aim of study | Dataset length | Flux uncertainty / detection limit | Vegetation type |
|-------------------------------------|---|--|--|---|--|
| Ammann et al. (2012) | ΣNr | Suitability of converter for EC measurements | Few weeks are shown for cross-validation with other techniques | ~5 ng N m ⁻² s ⁻¹ (upper flux detection limit) | Managed grassland |
| Brümmer et al. (2013) | ΣN_r | Temporal dynamics, controlling factors, and seasonal N budget | 11 months | ~6.6 ng N m ⁻² s ⁻¹ (upper flux detection limit) | Cropland (winter wheat) |
| Eugster and Hesterberg (1996) | NO ₂ | Deriving transfer resistances | Four different periods with a total of 68 days | Not explicitly given | Rural litter meadow |
| Famulari et al. (2004) | NH ₃ | Suitability of TDLAS system for EC; cross-validation with AGM | 2 months | Not explicitly given, only standard deviation of fluxes for entire campaign | Managed grassland |
| Farmer and Cohen (2008) | HNO ₃ , Σ AN, Σ PN and NO ₂ | In-canopy chemical analysis | 12 months | Not explicitly given | Ponderosa pine plantation |
| Farmer et al. (2006) | HNO ₃ , Σ AN, Σ PN and NO ₂ | Suitability of TD-LIF system for EC | 12 months; shorter periods are shown from different seasons | <1 ng N m ⁻² s ⁻¹ ; <20% relative errors at low wind speed (<1 m s ⁻¹) | Ponderosa pine plantation |
| Farmer et al. (2011) | Aerosols (NH4, SO4, NO3) | Suitability of HR-AMS system for EC | 15 days | ~0.4 to 6.4 ng m ⁻² s ⁻¹ depending on substance and mode; typical single flux measurement was below DL for NH ₄ fragments | Ponderosa pine plantation |
| Ferrara et al. (2012) | NH ₃ | Comparison of high-frequency correction methodologies using QC-TILDAS | 13 days | ~75 ng N m ⁻² s ⁻¹ (flux detection limit) | Cropland (sorghum) |
| Ferrara et al. (2016) | NH3 | Temporal dynamics of NH ₃ volatilization after slurry application using QC-TILDAS | ~14 days | Only MAE (4700 ng NH ₃ m ⁻² s ⁻¹) and RMSE (12000 ng NH ₃ m ⁻² s ⁻¹) given | Maize stubbles and Italian ryegrass |

| Ferrara et al. | NH ₃ | Evaluation of measurement | 21 days | 13.6 and 20.7 ng m ⁻² s ⁻¹ at 95 and | Cropland (faba bean) |
|----------------|-----------------------------------|--|------------------------------|---|------------------------|
| (2021) | | errors using QCL spectrometer | | 99% CI, respectively | |
| Horii et al. | NO, NO ₂ , | Impacts of temporal dynamics | 7 months, but no time series | Not explicitly given | Mixed deciduous |
| (2004) | O ₃ | on tropospheric chemistry and | shown | | forest |
| | | parameterizations | | | |
| Horii et al. | NO _x , NO _y | Concentration and flux budgets | 5 months, but only time | Not explicitly given | Mixed deciduous |
| (2006) | | of N _r , inferring HNO ₃ , | series of ~2 weeks are shown | | forest |
| | | validation of deposition | | | |
| | | velocities | | | |
| Marx et al. | ΣN_r | Suitability of converter for | 1-week validation, 11 months | Not explicitly given as aim was on | Managed grassland |
| (2012) | | capturing all N _r species at high | field campaign | concentrations and fast response | and cropland (winter |
| | | frequency | | | wheat) |
| Min et al. | NO, NO ₂ | Comparison of gradient and | 6 weeks, no time series | <8% for NO flux; <6% for NO ₂ flux; | Ponderosa pine |
| (2014) | | direct flux measurements; | shown | 0.08 ppt m s ⁻¹ (NO); 0.14 ppt m s ⁻¹ | plantation |
| | | within-canopy chemistry of | | (NO ₂) | |
| | | NO _x | | | |
| Moravek et | NH ₃ | Quantify impact of adsorption | 5 months | Median flux detection limit of 2.15 | Corn crop field |
| al. (2019) | | on time response of the system | | ng m ⁻² s ⁻¹ | |
| Munger et al. | NO _y , O ₃ | Response of NO _y deposition to | 5 years | Only given for concentrations (~50 | Mixed deciduous |
| (1996) | | environmental conditions | | ppt at the mixed forest site and | forest and spruce |
| | | | | <10 ppt at the spruce woodland) | woodland |
| Rummel et | NO | Flux pattern within the canopy | 3 months | 0.07 ng N m ⁻² s ⁻¹ | Amazonian rain forest |
| al. (2002) | | | | | |
| Sintermann | NH ₃ | Suitability of a CIMS (chemical | Few days | 5 ng N m ⁻² s ⁻¹ | Crop stubble field and |
| et al. (2011) | | ionization mass spectrometry) | | | cut grassland |
| | | instrument for EC | | | |
| | | measurements | | | |
| Sun et al. | NH ₃ | Suitability of the open-path | 2 weeks | 1.3 +/- 0.5 ng m ⁻² s ⁻¹ | Cattle feedlot |
| (2015) | | NH ₃ sensor for EC | | | |
| | | measurements and | | | |
| | 1 | 1 | | | |
| | | comparison to other | | | |

| Wang et al. | NH ₃ | Suitability of the open-path | 1 week | 7.1 ug N m ⁻² h ⁻¹ | Subtropical rice paddy |
|--------------|-----------------|-------------------------------|----------------------------|--|------------------------|
| (2021) | | NH ₃ sensor for EC | | | |
| | | measurements | | | |
| Whitehead et | NH ₃ | Suitability and inter- | 2 campaigns, only few days | Not explicitly given | Managed grassland |
| al. (2008) | | comparison of different | are presented | | |
| | | analyzers | | | |

References in Table S1:

Ammann, C., Wolff, V., Marx, O., Brümmer, C., and Neftel, A.: Measuring the biosphere-atmosphere exchange of total reactive nitrogen by eddy covariance, Biogeosciences, 9, 4247–4261, https://doi.org/10.5194/bg-9-4247-2012, 2012.

Brümmer, C., Marx, O., Kutsch, W., Ammann, C., Wolff, V., Flechard, C. R., and Freibauer, A.: Fluxes of total reactive atmospheric nitrogen (ΣNr) using eddy covariance above arable land, Tellus B, 65, 19770, doi:10.3402/tellusb.v65i0.19770, 2013.

Eugster, W. and Hesterberg, R.: Transfer resistances of NO2 derived from eddy correlation flux measurements over a litter meadow at a rural site on the Swiss Plateau. Atmos. Environ., 30, 1247–1254, 1996.

Famulari, D., Fowler, D., Hargreaves, K., Milford, C., Nemitz, E., Sutton, M. A., 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. and Cohen, R. C.: Observations of HNO3, ΣAN, ΣPN and NO2 fluxes: evidence for rapid HOx chemistry within a pine forest canopy. Atmos. Chem. Phys., 8(14), 3899–3917, doi:10.5194/acp-8-3899-2008, 2008.

Farmer, D. K., Wooldridge, P. J., and Cohen, R. C.: Application of thermal-dissociation laser induced fluorescence (TD-LIF) to measurement of HNO3, Σalkyl nitrates, Σperoxy nitrates, and NO2 fluxes using eddy covariance, Atmos. Chem. Phys., 6, 3471–3486, https://doi.org/10.5194/acp-6-3471-2006, 2006.

Farmer, D. K., Kimmel, J. R., Phillips, G., Docherty, K. S., Worsnop, D. R., Sueper, D., Nemitz, E., and Jimenez, J. L.: Eddy covariance measurements with high-resolution time-of-flight aerosol mass spectrometry: a new approach to chemically resolved aerosol fluxes, Atmos. Meas. Tech., 4, 1275–1289, https://doi.org/10.5194/amt-4-1275-2011, 2011.

Ferrara, R. M., Loubet, B., Di Tommasi, P., Bertolini, T., Magliulo, V., Cellier, P., Eugster, W., and Rana, G.: Eddy covariance measurement of ammonia fluxes: Comparison of high frequency correction methodologies, Agr. Forest Meteorol., 158–159, 30–42, 2012.

Ferrara, R. M., Carozzi, M., Di Tommasi, P., Nelson, D. D., Fratini, G., Bertolini, T., Magliulo, V., Acutis, M., and Rana, G.: Dynamics of ammonia volatilisation measured by eddy covariance during slurry spreading in north Italy. Agric. Ecosys. Environ., 219, 1–13, <u>https://doi.org/10.1016/j.agee.2015.12.002</u>, 2016.

Ferrara, R.M., Di Tommasi, P., Famulari, D., and Rana, G.: Limitations of an Eddy-Covariance System in Measuring Low Ammonia Fluxes. Boundary-Layer Meteorol 180, 173–186, <u>https://doi.org/10.1007/s10546-021-00612-6</u>, 2021.

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.

Horii, C. V., Munger, J. W., Wofsy, S. C., Zahniser, M., Nelson, D., and McManus, J. B.: Atmospheric reactive nitrogen concentration and flux budgets at a Northwestern US forest, Agr. Forest Meteorol., 136, 159–174, 2006.

Marx, O., Brümmer, C., Ammann, C., Wolff, V., and Freibauer, A.: TRANC – a novel fast-response converter to measure total reactive atmospheric nitrogen, Atmos. Meas. Tech., 5, 1045–1057, https://doi.org/10.5194/amt-5-1045-2012, 2012.

Min, K.-E., Pusede, S. E., Browne, E. C., LaFranchi, B. W., and Cohen, R. C.: Eddy covariance fluxes and vertical concentration gradient measurements of NO and NO2 over a ponderosa pine ecosystem: observational evidence for within-canopy chemical removal of NOx, Atmos. Chem. Phys., 14, 5495–5512, https://doi.org/10.5194/acp-14-5495-2014, 2014.

Moravek, A., Singh, S., Pattey, E., Pelletier, L., and Murphy, J. G.: Measurements and quality control of ammonia eddy covariance fluxes: A new strategy for high frequency attenuation correction, Atmospheric Measurement Techniques, 12, 6059–6078, https://doi.org/10.5194/amt-12-6059-2019, 2019.

Munger, J. W., Wofsy, S. C., Bakwin, P. S., Fan, S.-M., Goulden, M. L., Daube, B. C., Goldstein, A. H., Moore, K. E., and Fitzjarrald, D. R.: 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(D7), 12639–12657, doi:10.1029/96JD00230, 1996.

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.

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.

Sun, K., Tao, L., Miller, D. J., Zondlo, M. A., Shonkwiler, K. B., Nash, C., and Ham, J. M.: Open-path eddy covariance measurements of ammonia fluxes from a beef cattle feedlot, Agr. Forest Meteorol, 213, 193–202, <u>https://doi.org/10.1016/j.agrformet.2015.06.007</u>, 2015.

Walker, J. T., Beachley, G., Zhang, L., Benedict, K. B., Sive, B. C., and Schwede, D. B.: A review of measurements of air-surface exchange of reactive nitrogen in natural ecosystems across North America, Science of The Total Environment, 698, 133975, <u>https://doi.org/10.1016/j.scitotenv.2019.133975</u>, 2020.

Wang, K., Kang, P., LU, Y., Zheng, X., Liu, M., Lin, T.-J., Butterbach-Bahl, K., and Wang, Y.: An open-path ammonia analyzer for eddy covariance flux measurement, Agr. Forest Meteorol, 308–309, 108570, <u>https://doi.org/10.1016/j.agrformet.2021.108570</u>, 2021.

Whitehead, J. D., Twigg, M., Famulari, D., Nemitz., E., Sutton, M. A., Gallagher, M. W., and Fowler, D.: Evaluation of Laser Absorption Spectroscopic Techniques for Eddy Covariance Flux Measurements of Ammonia, Environ. Sci. Technol., 42, 2041–2046, 2008.



Fig. S1: Concentration time series of NH_3 at the peatland (WET) site. Horizontal red lines correspond to the exposition time of the DELTA denuders. For better comparability, averages of the QCL are shown in blue for the same periods.



*Fig. S2: Scatter plot of NH*³ concentration from QCL and DELTA denuders corresponding to identical periods at the peatland (WET) site.



Fig. S3: Concentration time series of NH₃ at the forest (FOR) site. Horizontal blue and red lines correspond to the exposition time of the DELTA denuders and passive samplers (PS), respectively. For better comparability, averages of the QCL are shown in black for the same periods.



*Fig. S4: Scatter plot of NH*³ concentration from QCL and DELTA denuders corresponding to identical periods at the forest (FOR) site.



Fig. S5: Scatter plot of NH_3 concentration from QCL and passive samplers (PS) corresponding to the same periods at the forest (FOR) site.



Fig. S6: Measured vs. modeled deposition data in half-hourly time resolution at the forest (FOR, left panel) and peatland site (WET, right panel). FOR data comprise the period mid-July to end of September 2016. For the WET site the entire campaign from February to May 2014 is shown.



Fig. S7: Time series (upper panel) and cumulative curves (lower panel) of measured vs. modeled deposition data in half-hourly time resolution at the peatland site (WET) from February to May 2014.



Fig. S8: Time series (upper panel) and cumulative curves (lower panel) of measured vs. modeled deposition data in half-hourly time resolution at the forest site (FOR) from mid-July to September 2016.