



## Surface-atmosphere exchange of water-soluble gases and aerosol compounds above agricultural grassland

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The dry deposition of nitrogen and sulfur-containing reactive trace gases and aerosols provides an important sink of these compounds, and can impact ecosystem health. Agricultural surfaces in particular can act as an important source of nitrogen compounds such as ammonia ( $\text{NH}_3$ ) and nitrous acid ( $\text{HNO}_2$ ). Due to the difficulties in measuring fluxes of these reactive compounds, the understanding of the release rates is still limited. High temporal resolution measurements with low detection limits are therefore required in order to aid understanding of these processes.

In this study, the concentrations of selected atmospheric trace gases ( $\text{NH}_3$ ,  $\text{HCl}$ ,  $\text{HNO}_2$ ,  $\text{HNO}_3$  and  $\text{SO}_2$ ) and water-soluble reactive aerosol compounds ( $\text{NH}_4^+$ ,  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ ) were measured at two heights using the Gradient of Aerosols and Gases Online Registrator (GRAEGOR) (Thomas et al., 2009) over an agricultural grassland site near Edinburgh, United Kingdom from May to July 2016. This time period covered a fertilisation event at the site in mid-June. Using the hybrid Aerodynamic Gradient Method (Nemitz and Sutton, 2004) and the Modified Bowen Ratio Method (Meyers et al., 1996), fluxes for each species were determined from the concentration gradients measured by the GRAEGOR. From this, a detailed atmospheric flux profile was generated, which determined the net emission and deposition rates to and from the site for the chemical species measured. Deposition velocities for each species were derived and compared to theoretical maximum deposition velocities. Comparison studies with other instruments which were operated concurrent to the project, such as a Quantum Cascade Laser (QCL, Aerodyne), a Monitor for Aerosols and Gases in Ambient Air (MARGA, Applikon) and a  $\text{HNO}_2$  Long-Path Absorption Photometer (LOPAP), were also conducted.

The atmospheric acids  $\text{HNO}_3$  and  $\text{HCl}$  deposited at rates close to their transport maximum, i.e. with a near-zero canopy resistance for most of the time (the median canopy resistance value for  $\text{HNO}_3$  was  $5.71 \text{ s m}^{-1}$  and for  $\text{HCl}$  was  $3.24 \text{ s m}^{-1}$ ). The flux profile for several species showed a bi-directional pattern, with emissions of  $\text{NH}_3$  and  $\text{HNO}_2$  occurring after fertilisation, with the diurnal concentration pattern for  $\text{HNO}_2$  confirming the presence of a  $\text{HNO}_2$  daytime source. Evaporation of ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) was also inferred from deposition fluxes of  $\text{NO}_3^-$ .

The emission of  $\text{NH}_3$  after fertilisation suggests that targeted fertiliser application is required, particularly to reduce the incidence of  $\text{NH}_4\text{NO}_3$  formation.