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Development of a relaxed eddy accumulation system for the determination of biosphere-atmosphere exchange fluxes of peroxyacetyl nitrate

Alexander Moravek (1), Ivonne Trebs (1), Michael Welling (1), and Thomas Foken (2)

(1) Max Planck Institute for Chemistry, Biogeochemistry Department, P. O. Box 3060, 55020 Mainz, Germany, (2) Department of Micrometeorology, University of Bayreuth, Universitätsstr. 30, 95447 Bayreuth, Germany

We have developed a flux measurement system based on the relaxed eddy accumulation (REA) method using a commercially available gas chromatograph with electron capture detection (GC-ECD). We made flux measurements of peroxyacetyl nitrate (PAN) over the largest continuous nutrient-poor steppe-like grassland ecosystem in Rhine Hessen (region of Rhineland-Palatinate, Germany) during selected days in 2010 and 2011. The PAN measurements were conducted on the estate of the Mainz Finthen airport (Mainz, Germany (49.969° N, 8.148° E)) together with measurements of other atmospheric compounds, which included vertical profiles of NO, NO₂, O₃, CO₂, H₂O and eddy covariance fluxes of O₃, CO₂ and H₂O as well as soil biogenic NO emission fluxes.

The use of the commonly applied REA sampling bags resulted in an unexplained PAN loss. Hence, conditional sampling was realized by trapping PAN onto two pre-concentration columns, one for updraft and one for downdraft events. Subsequent analysis of PAN was done online by a GC-ECD (Meteorologie Consult GmbH, Germany) located downstream of the splitter valves. The GC was modified for consecutive analysis of PAN accumulated in both reservoirs resulting in a total analysing time of 15 min. The GC-ECD was calibrated as a function of PAN mixing ratio and sample mass trapped onto the pre-concentration columns.

We will present the setup of the PAN-REA system and the quality assurance related to the application of the REA method. This mainly involves timing considerations and a quality assessment of PAN measurements. The design ensures constant flow and pressure conditions in the intake tubes and reservoirs. Special emphasis was given to the determination of the lag time between the vertical wind speed signal and the splitter valves. The wind vector is adjusted online using the double rotation method and a fixed deadband for vertical wind speeds around zero was tested. Finally, the use of high frequency O_3 measurements as a proxy for both deadband and *b*-value calculations will be discussed.