Application of common and new techniques for measuring air-surface exchange of reactive nitrogen

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For ecosystems, the availability of (reactive) nitrogen is one of the key limiting factors for the productivity and the competition success of individual species, thereby influencing the biodiversity and the exchange of greenhouse gases. Thus the quantification of the reactive nitrogen (N_r) exchange is essential for the interpretation of ecosystem behavior. Since the N_r exchange includes various inorganic as well as organic compounds that can undergo fast chemical reactions and have differing chemical and physical characteristics, a variety of detection techniques is usually necessary to measure all relevant compounds.

For dry deposition monitoring purposes, weekly or monthly integrating methods using denuders, filter packs, passive sampler or bulk sampler techniques may often be sufficient, but they depend on assumptions and generic parameterizations. In order to investigate specific surface exchange processes and improve the mechanistic parameterization schemes in models, direct measurement methods with high temporal resolution (one hour or better) are necessary. A number of online detection methods (incl. chemiluminescence, fluorescence, laser absorption, electrochemical techniques, online ion chromatography, mass spectroscopy etc.) have been developed or optimized for nitrogenous compounds in recent years.

For the observation of deposition processes or bi-directional exchange, micrometeorological methods are preferable since they do not modify the environmental conditions of the ecosystem and are less prone to wall effects than chamber methods. We show different applications of micrometeorological flux measurement systems for N_r compounds and discuss their advantages and disadvantages. Gas-phase chemiluminescence detectors for NO were used for eddy covariance (EC) flux measurements. In combination with inlet converters ('blue-light' converter for NO_2, gold catalyst converter for NO_y, and total N_r converter) this system allowed to measure lumped fluxes of a group or the total sum of N_r compounds. Specific EC flux measurements for the highly soluble and adsorbing NH_3 required the use of a strongly heated (>100°C) inlet tube. For all these EC systems the damping of high-frequency fluctuations in the inlet system is potentially problematic and needs to be quantified.

If no fast response detector is available, the gradient or relaxed eddy accumulation method can be a valuable alternative (e.g. for the NH_3-HNO_3-NH_4NO_3 triad). They need only slow but still very accurate detection of two inlet lines. Thus a careful assessment of error sources (especially biases between the inlets) is very important. For NO and NO_2 exhibiting fast gas-phase reaction within the canopy and in the surface layer (with chemical time scale similar to the turbulent transport time scale), micrometeorological measurements above the canopy may be less suitable to investigate the respective source/sink processes, because the fluxes often show a strong vertical divergence. In such cases, the use of (dynamic) chamber and cuvette systems is often a necessary complement or alternative.

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