Surface-Atmosphere Exchange of Ammonia in a Non-fertilized Grassland and its Implications for $PM_{2.5}$

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Abstract: A growing body of evidence suggests that the surface-atmosphere exchange of ammonia (NH_3) occurs in a bidirectional fashion governed by a compensation point (i.e. the atmospheric mixing ratio where flux changes direction). The compensation point represents an equilibrium between atmospheric NH_3 and dissolved NH_4^+ in soil water and/or plant tissues. Direct measurement of the compensation point is not trivial, due to its dependence on surface temperature, pH and the nitrogen distribution in the system. In particular, previous studies on bidirectional flux have been hindered by a lack of direct measurements of compensation point values and poor temporal characterization of surface nitrogen pools. Furthermore, few studies have explored bidirectional exchange in non-fertilized grasslands. An accurate understanding of the factors governing bidirectional flux is required in order for air quality models to accurately predict trace gas mixing ratios, aerosol composition and spatial patterns of nitrogen deposition.

To address these issues, a field study was conducted in southwestern Ontario during the summer of 2012 to simultaneously measure the atmospheric and surface components of this framework and provide observational constraints that test our understanding of the bi-directional exchange of NH_3. An Ambient Ion Monitor Ion Chromatograph (AIM-IC) was used to quantify the water-soluble trace gases (NH_3, SO_2, HNO_3, HCl, and HONO) as well as water-soluble ions in $PM_{2.5}$ with hourly time resolution. Similar IC methods were used in an offline fashion to periodically measure soil ammonium, nitrite and nitrate composition. Soil temperature and moisture were measured continuously with hourly time resolution. Using interpolated data for soil composition, diurnal and seasonal trends in the compensation point could be evaluated. The surface atmosphere exchange of NH_3 was calculated using an estimated exchange velocity, measured gas phase ammonia concentration and estimated compensation point. Back trajectories calculated throughout the campaign show that NH_3 is the only atmospheric constituent that does not exhibit a directional bias implying NH_3 concentrations are efficiently modulated by bidirectional exchange. In addition, there is evidence that dew evaporation contributes to a frequently observed yet unexplained morning spike of NH_3. Challenges in quantifying inorganic nitrogen speciation in soils are also discussed.

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