



## Atmospheric nitrogen deposition in south-east Scotland: Quantification of the organic nitrogen fraction in wet, dry and bulk deposition

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### ABSTRACT

Water soluble organic nitrogen (WSO) compounds are ubiquitous in precipitation and in the planetary boundary layer, and therefore are a potential source of bioavailable reactive nitrogen. This paper examines weekly rain data over a period of 22 months from June 2005 to March 2007 collected in 2 types of rain collector (bulk deposition and “dry + wet” deposition) located in a semi-rural area 15 km southwest of Edinburgh, UK (N55°51'44", W3°12'19"). Bulk deposition collectors are denoted in this paper as “standard rain gauges”, and they are the design used in the UK national network for monitoring precipitation composition. “Dry + wet” deposition collectors are flushing rain gauges and they are equipped with a rain detector (conductivity array), a spray nozzle, a 2-way valve and two independent bottles to collect funnel washings (dry deposition) and true wet deposition. On average, for the 27 weekly samples with 3 valid replicates for the 2 types of collectors, dissolved organic nitrogen (DON) represented 23% of the total dissolved nitrogen (TDN) in bulk deposition. Dry deposition of particles and gas on the funnel surface, rather than rain, contributed over half of all N-containing species (inorganic and organic). Some discrepancies were found between bulk rain gauges and flushing rain gauges, for deposition of both TDN and DON, suggesting biological conversion and loss of inorganic N in the flushing samplers.

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### 1. Introduction

In recent years there has been a growing concern that dissolved organic nitrogen (DON) compounds can contribute significantly to the nutrient budgets of many ecosystems and, therefore, to eutrophication processes (Cornell et al., 2003). Organic nitrogen compounds also influence atmospheric chemistry and air quality (Nakamura et al., 2006) and, in water treatment, DON compounds are an emerging concern as precursors for carcinogenic disinfection byproducts such as haloacetonitriles and N-nitrosodimethylamine (Ambonguilat et al., 2006; Lee and Westerhoff, 2005; Westerhoff and Mash, 2002).

One of the main limitations in DON determination in water samples is that it is not possible to quantify directly (Cape et al., 2001; Jones and Willett, 2006; Vandenberg et al., 2007; Zhang et al., 2008). DON concentration is calculated by the subtraction of several independently measured concentrations, which leads to an important analytical uncertainty (Lee and Westerhoff, 2005;

Vandenberg et al., 2007). For this reason, and other difficulties associated with organic nitrogen species analysis, most of the studies regarding N budgets to date have been conducted only on the inorganic nitrogen species. In Europe, the reactive nitrogen compounds restricted under the Gothenburg Protocol (UN-ECE, 1999) and the EU Directive 2001/81/EC (EU, 2001), both aiming to limit emissions of acidifying and eutrophying pollutants and ozone precursors, only include nitrogen oxides (NO<sub>x</sub>) and ammonia (NH<sub>3</sub>) and their roles as precursors of inorganic N deposition in precipitation. However, atmospheric DON deposition has been estimated to represent on average 30% of the total dissolved nitrogen (TDN) in precipitation in the UK (Cape et al., 2004) and varying proportions (both higher and lower) elsewhere (Cornell et al., 1995, 2003; Cornell and Jickells, 1999; Neff et al., 2002).

The atmospheric organic nitrogen fraction is believed to include a large spectrum of natural compounds such as amino acids and urea, and small amounts of synthetic compounds such as atrazine (Ambonguilat et al., 2006), or reaction products from man-made emissions, such as nitrophenols (Luttke et al., 1997), but in spite of the importance of ON in the global N budget, the chemical forms and sources of ON are not yet sufficiently understood.

An important and yet unanswered question is the atmospheric ON origin: natural, anthropogenic or mixed? Due to the important

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contribution of the ON fraction to the total N budget, this is a key question when assessing the scale of the human perturbation of the N cycle. To date, investigations of individual compounds and isotopic analysis have been unable to provide conclusive results regarding the origin of atmospheric ON (Kelly et al., 2005). In a recent study over the East China Sea and western North Pacific it was suggested that water soluble organic nitrogen (WSON) compounds in marine aerosols were mainly from anthropogenic origin, as they were associated with continental materials of anthropogenic origin, particularly  $\text{NH}_4^+$  in fine particles (Nakamura et al., 2006). On the other hand, another study (Pacheco et al., 2004) claimed that WSON represents up to 90% of the total soluble nitrogen found in tropical continental rain in remote unpolluted sites, suggesting a natural origin.

Another crucial question is whether the main contributor to the ON fraction in terrestrial ecosystems is dry or wet deposition. Wet deposition denotes removal by clouds and falling precipitation, and dry deposition denotes the direct collection of gases and particulates on a surface. In this context, a number of methods and different designs have been described for rain sampling over the last 30 years (Dämmgen et al., 2005). However, despite several studies showing that dry deposition can contribute significantly to nitrogen in bulk precipitation (Cape and Leith, 2002), in many cases, precipitation composition is derived from measurements of bulk precipitation, i.e. the basic design comprises a funnel connected to a collecting bottle, and therefore does not discriminate between dry deposition to the surface of the funnel and nitrogen species dissolved in the rain. There have been many studies aimed at evaluating the contribution of dry deposition to bulk precipitation collectors (Cape et al., 2009; Lee and Longhurst, 1992) but none so far has explicitly considered the effect on water-soluble organic nitrogen.

In summary, very little is known with regard to organic nitrogen in the atmosphere and in precipitation, and to its source and sink budgets. To date very important questions such as deposition mechanisms remain unanswered: wet vs. dry deposition; natural, anthropogenic or mixed origin; composition and biological availability. The aim of the work presented in this paper is to measure the organic nitrogen fraction dissolved in precipitation, and to discriminate between what is coming from dry and wet deposition.

## 2. Experimental

### 2.1. Study site and collection methods

Precipitation was sampled weekly from June 2005 to April 2007 at the Centre for Ecology and Hydrology, in a 'science park' and within 1 km of mixed farming (arable and dairy) 15 km southwest of Edinburgh, UK (N55°51'44", W3°12'19"). Two types of rain collector were used in this study: standard rain collectors and flushing rain collectors. Three rain collectors of each type were mounted 1.5 m above ground, in a 5 m-side square, in the middle of a grass field. The standard rain collectors consisted of a polypropylene funnel diameter 152 mm mounted directly in a polypropylene collecting bottle, and is the design used in the UK national network for monitoring precipitation composition (Cape et al., 2001). The flushing rain collectors (Cape et al., 2009) are equipped with a rain detector (conductivity array), a spray nozzle, an identical polypropylene funnel to the standard collector, a 2-way PTFE motorised valve, and two independent collecting bottles at ground level, connected to the funnels by 1.5 m lengths of silicone tubing enclosed in an opaque flexible PVC tube (to exclude light and minimise biological activity). When a rain event is detected, the funnel is rinsed with a fixed volume of 10% methanol in distilled water and the washings are collected in one of the sampling bottles

as a measure of dry deposition on the funnel surface since the last precipitation event. One minute after the rinsing, the 2-way valve is switched to allow the subsequent rain, free from any contamination by prior dry deposition, to enter the second rain sample bottle. At the end of a rain event, signalled by the rain detector, the valve is switched again to the 'divert' position to seal the rain sample bottle from the atmosphere.

### 2.2. Sample preservation

Nitrogen containing compounds in precipitation are especially vulnerable to biological degradation (Cape et al., 2001; Hadi and Cape, 1995). For this reason there is a need for preservation of the sample during the processes of collection, transportation and storage. In this study, a small amount of a biocide solution was added to the collection bottles prior to sampling. Thymol (2-isopropyl-5-methyl phenol) was the biocide of choice in this study, as it is non-volatile, effective at low concentrations, and presents few toxicity problems for disposal. 100 mg L<sup>-1</sup> was previously determined to be the optimum concentration (Cape et al., 2001; Hadi and Cape, 1995). This was the target concentration when sample bottles for rainfall and washings were charged with 25 mg thymol per litre of capacity before use (1 mL and 0.5 mL of 50 g L<sup>-1</sup> methanol solution for rain and washings, respectively). The final thymol concentration in each sample was therefore variable, depending on the amount of rain during each particular week. However, the biocidal effect is not diminished greatly even if the sample bottle is filled (Cape et al., 2001). Collected rain samples were stored at 4 °C before analysis. Samples were filtered through a 0.2 µm pore-size inorganic membrane filter (Whatman, Anotop 10 IC) before chemical analysis.

### 2.3. Detection techniques & instrumentation

Dissolved organic nitrogen (DON) concentrations in water samples cannot be quantified directly. Analysis involves several steps: determination of the total dissolved nitrogen (TDN) concentration, determination of the dissolved inorganic nitrogen species (DIN) concentration, and finally subtraction of DIN concentrations from the TDN concentrations. TDN includes all nitrogen containing species (organic and inorganic) dissolved in the sample. DIN includes all the nitrates ( $\text{NO}_3^-$ ), nitrites ( $\text{NO}_2^-$ ) and ammonium ( $\text{NH}_4^+$ ) dissolved in the sample.

### 2.4. Total dissolved nitrogen (TDN) determination methods

TDN determination requires a preparatory digestion step, either chemical or by combustion. The main digestion methods available and in current use for total nitrogen determination in aqueous samples are: Kjeldahl digestion (Doval et al., 1997; Nozawa et al., 2005; Yasuhara and Nokihara, 2001), alkaline persulphate oxidation (Cape et al., 2001; Cornell et al., 2003; Scudlark et al., 1998) and high-temperature catalytic oxidation (Cape et al., 2001; Cornell et al., 2003; Keene et al., 2002).

High-temperature catalytic oxidation (HTCO) was the method of choice in this study. This method aims for the complete combustion of all organic material to  $\text{CO}_2$  and nitric oxide (NO), followed by quantitative detection of nitric oxide (NO) by chemiluminescence. The instrument used for this technique was a Nitrogen Specific HPLC Detector, ANTEK 8060-M, operated according to the manual. The analysis was conducted in flow-injection mode, with triplicate analysis of a 20 µL sample in a carrier of deionised water at a flow rate of 250 µL min<sup>-1</sup>. Typical detection limit for TDN was 1 µM N, based on independent calibration with standard solutions of ammonium sulphate and sodium nitrate. Prior tests had shown

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