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Organic nitrogen in the atmosphere — Where does it come from? A review of sources and methods

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ABSTRACT

This review considers the ways in which atmospheric organic nitrogen has been measured and linked to potential sources. Organic N exists in gas, particle and dissolved phases and represents a large (ca. 30%) fraction of total airborne nitrogen, but with large variability in time and space. Although some components (e.g. amines) have been the subject of several studies, little information is available for the many other components of organic N that have been identified in individual measurements. Measurements of organic N in precipitation have been made for many decades, but both sampling and chemical analytical methods have changed, resulting in data that are not directly comparable. Nevertheless, it is clear that organic N is ubiquitous and chemically complex. We discuss some of the issues which have inhibited the widespread adoption of organic N as a routine analyte in atmospheric sampling, and identify current best practice. Correlation analysis is the most widely used technique for attributing likely sources, examining the co-variation in time and/or space of organic N with other components of precipitation or particulate matter, yet the shortcomings of such simple approaches are rarely recognised. Novel measurement techniques which can identify, if not yet quantify, many of the components of particulate or dissolved organic N greatly enhance the data richness, thereby permitting powerful statistical analyses of co-variation such as factor analysis, to be employed. However, these techniques also have their limitations, and whilst specific questions about the origin and fate of particular components of atmospheric organic N may now be addressed, attempts to quantify and attribute the whole suite of materials that comprise atmospheric organic N to their sources is still a distant goal. Recommendations are made as to the steps that need to be taken if a consistent and systematic approach in identifying and quantifying atmospheric organic N is to progress. Only once sources have been recognised can any necessary control measures to mitigate adverse effects of atmospheric organic N on human health or ecosystem function be determined.

1. Introduction

The atmospheric deposition of nitrogen is a focus of both scientific and policy concern, because of the importance of nitrogen (N) in acidification of soils and aquatic systems, nutrient enrichment, tropospheric ozone processes, and particulate matter. The role of inorganic N (nitrate and ammonium) is well understood in these contexts, and is probably dominant in the first two of these. Although organic N is known to be important, the details of the role of organic N are less well understood, especially in the latter two contexts.

Eriksson (1952) provided an early but comprehensive assessment of the scope of research into atmospheric deposition, and traced the history of nitrogen deposition studies. The

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more recent history of organic N measurement, focused on studies of rainwater, has been outlined by Cornell (in press). Early on, the deposition of organic N compounds was recognised as quantitatively significant (Eriksson reports studies from the United Kingdom, North America, India and New Zealand), but assumptions about its source – locally recycled dust – and a focus on agricultural productivity meant that its role in the 'nitrogen economy of soil' was regarded as negligible at that time.

Eriksson wrote at a time of growing awareness of N pollution in Europe, which led to the inception of atmospheric measurement and monitoring programmes, notably the European Air Chemistry Network for air and precipitation chemistry established in 1955. A rapid increase in studies of atmospheric nitrogen deposition, including studies of organic N, was a response to the requirements of the 1979 UNECE Convention on Long Range Transboundary Air Pollution (http://www.unece.org/env/lrtap/). The US National Atmospheric Deposition Program (NADP, http://nadp.sws.uiuc.edu/) was established in 1977, with a parallel organisation in Europe, the European Monitoring and Evaluation Programme (EMEP, www.emep.int), both with a remit of monitoring air quality for the management of acidification and eutrophication, but in both cases the monitoring programmes addressed only inorganic N. Since the 1980s, studies have extended beyond a focus on local pollution and agriculture, and paid more attention to N deposition in the marine environment, and its role in natural biogeochemical cycles. A 'third wave' of organic N deposition studies has recently become apparent in the last 1–2 decades, as Asia and Latin America become more concerned about anthropogenic pollution.

This paper fills a gap — other studies have confirmed the quantitative importance, ubiquity, and global distribution of organic N, but have largely left open the question of sources, except for rather speculative attention.

2. What is 'organic nitrogen'?

Atmospheric organic N exists in gaseous, particulate and aqueous phases, and has become of increasing scientific interest as its quantitative importance to total airborne nitrogen has been appreciated. In part, the lag in addressing the organic N, compared with the inorganic species, has been because of a lack of consistency in sampling and measurement methods and because of the large number of different compounds that contribute to the total organic N. This has led to an understandable caution in attributing measured organic N in precipitation to material actually deposited from the atmosphere, rather than formed in rain collectors by biological transformations of inorganic N, or other artefacts of sampling. However, careful attention to sampling protocols, including storage conditions and chemical analytical methods, has demonstrated that water-soluble organic N (WSON) measured in precipitation can be demonstrated to constitute a significant proportion (typically around 30%) of total water-soluble N (Cape et al., 2001; Cornell et al., 2003; Keene et al., 2002; Neff et al., 2002; Scudlark et al., 1998; Zhang et al., 2008). Measurements from a review of recent data (Cornell, in press) suggest that the absolute concentrations of organic N in precipitation may be increasing (Fig. 1), but this apparent trend may simply represent the number of recent measurements in areas of the world (such as China) where concentrations of all forms of atmospheric N are large, typically over 10 times greater than those observed in Europe or North America (Zhang et al., 2008).

A major difficulty with addressing the biogeochemical and ecological role of atmospheric organic N is that there has been little practical consensus to date on how to define and measure it. Two strategies have been applied to its analysis, largely in parallel — bulk analysis, and the analysis of specific compounds in precipitation or aerosol, similar to the issues faced when measuring carbonaceous compounds, cf. Fig. 4 in Hallquist et al. (2009). Molecular or functional group analysis allows for particular components to be investigated, but there remains a concern that this approach is not a representative sampling of the organic matter present in the bulk samples, and given the diversity of possible compounds to analyse in this approach, there are few comparable studies of any given compound group. In general, analysis of specific compounds in rain or aerosol has only been able to account for a small proportion of the total organic N (Shi et al., 2010; Zhang et al., 2002a). Bulk analysis gives the total concentration of the rain or aerosol organic N, so it can only give insights into the 'collective behaviour' of the organic matter. It has proved important in assessing global budgets, but the value of these budget assessments is now constrained by the paucity of knowledge about what the organic matter is, where it comes from, and what it does in the environment. The categories within bulk analysis are operationally defined. For precipitation organic N, 'dissolved' material is what passes through a filter. For aerosols, 'particulate' material is the organic matter that is retained on a filter through which air is sampled. Different studies have used different kinds of filter, and different extraction and dissolution treatments, with or without pre-denuder sampling to minimise gas-phase artefacts, raising issues even about the representativeness and comparability of bulk analysis. Aerosol samples are usually extracted into water to obtain water-soluble organic N (WSON); the interest in the water-soluble component arises from the assumption that solubility and bioavailability are linked, although some studies have noted that there may be a significant component of organic N that is collected by a particulate filter which is not readily water soluble (e.g. Miyazaki et al., 2010; Russell et al., 2003). Water-soluble organic N is regarded as bio-available (Lipson and Näsholm, 2001; Paerl, 1997; Peierls and Paerl, 1997; Seitzinger and Sanders, 1999; Timperley et al., 1985; Wedyan et al., 2007). Very little is known about the biological effects of the insoluble component.

Where deposition of inorganic N to terrestrial ecosystems exceeds the 'Critical Load' (Achermann and Bobbink, 2003) the additional input of organic N, which is not included in the risk evaluation, may provide even greater pressures towards eutrophication or species composition change than predicted, and may pose a threat to systems where the Critical Load does not appear to be exceeded.

2.1. Chemical analytical methods for organic N

Despite much recent measurement activity, the chemical composition of WSON is still very poorly understood; 'organic N' in this context is usually defined as the difference between some measure of the total dissolved N in a sample (or the