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Atmospheric nitrogen deposition: Revisiting the question of the importance of the organic component

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Routinely including the organic component of atmospheric deposition (known to be around 25–35% worldwide) would make the understanding and prediction of nitrogen biogeochemistry more robust. This paper makes a preliminary global synthesis based on literature reports.

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ABSTRACT

The organic component of atmospheric reactive nitrogen plays a role in biogeochemical cycles, climate and ecosystems. Although its deposition has long been known to be quantitatively significant, it is not routinely assessed in deposition studies and monitoring programmes. Excluding this fraction, typically 25–35%, introduces significant uncertainty in the determination of nitrogen deposition, with implications for the critical loads approach. The last decade of rainwater studies substantially expands the worldwide dataset, giving enough global coverage for specific hypotheses to be considered about the distribution, composition, sources and effects of organic-nitrogen deposition. This data collation and meta-analysis highlights knowledge gaps, suggesting where data-gathering efforts and process studies should be focused. New analytical techniques allow long-standing conjectures about the nature and sources of organic N to be investigated, with tantalising indications of the interplay between natural and anthropogenic sources, and between the nitrogen and carbon cycles.

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1. Introduction

The last forty years have seen substantial societal investment in response to the serious nitrogen (N) linked issues of acid rain, eutrophication, and urban pollution, with the establishment of monitoring programmes linking observational networks and modelling efforts, and steadily strengthened environmental policies. These have focused on emissions and deposition of inorganic N species, which are known to have anthropogenic sources. Although organic N has long been known to be a quantitatively significant component of atmospheric nitrogen deposition (reviewed in Neff et al., 2002 and Cornell et al., 2003), it is not routinely assessed, nor are best-estimates factored into quantitative evaluations of N fluxes. Here, the case for filling this knowledge gap is presented, together with a preliminary analysis giving an indication of priority studies.

There is already considerable knowledge of the implications of organic N for biogeochemistry and ecosystem and human health. Organic N is known to play a role in atmospheric particle formation (Zhang and Anastasio, 2001; Seinfeld and Pankow, 2003; Facchini et al., 2008), affecting atmospheric visibility, light-scattering, and climate. It is a component of polluted fogs and smogs, forms of atmospheric aerosol that are an environmental and public health concern (e.g., Harrison and Yin, 2000). Organic N compounds have been identified as important in the long-range transport of N (e.g., Singh and Hanst, 1981; Gorzelska and Galloway, 1990; Neff et al., 2002; Matsumoto and Uematsu, 2005) because their removal processes tend to be less effective than those for nitrate and ammonium, which are generally deposited closer to their sources. A fraction of organic N is known to be bioavailable (e.g., Timperley et al., 1985; Peierls and Paerl, 1997; Seitzinger and Sanders, 1999), providing a nutrient source to marine/aquatic and terrestrial environments; much less is known about its potential toxicity (Paumen et al., 2009). However, until recently the usefulness of this knowledge has been constrained because so little is known about the chemical composition of organic N, due to the limitations of available analytical methods, and about its spatial distribution.

In the context of recent environmental policy, the omission of organic N arguably may not have been problematic. First of all, natural variability in atmospheric N deposition is very high and sampling and monitoring density is generally much lower than ideal, so policy has had to be developed in ways that accommodate a high degree of uncertainty (e.g., Heywood et al., 2006). Empirical critical loads for nitrogen have been determined from a comparatively rich evidence base, drawing on field as well as experimental studies (e.g., Hall et al., 2007). In this sense, they are likely to reflect the real deposition to receiving habitats, regardless of what the measured deposition is.

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However, with the growing emphasis on modelled mass balance approaches to critical load determination, where inputs over an extended period are compared with the outputs from the ecosystem, the absence of organic-nitrogen data becomes a more serious issue, which has so far not featured in discussions of methods and uncertainty (e.g., Fenn et al., 2008; Li and McNulty, 2007; Skeffington et al., 2006). An underestimation of deposition leads to an underestimation of the nitrogen retention within the system. This becomes a more pressing problem as more of the world's ecosystems become nitrogen-enriched as a result of human activities (and thus potentially begin to approach critical thresholds). Evidence indicates that species change or losses can occur at early stages of N saturation of ecosystems, when N availability exceeds biotic and abiotic sinks (Emmett, 2007).

Disregarding organic N deposition is also potentially problematic as the critical loads approach is extended to other parts of the world: the composition of the organic matter and the relative contributions of organic and inorganic N to total deposition may be very different from the temperate environments of North America and Europe where the critical loads approach has been devised. Even in these regions, the context is changing: there has been a shift in European environmental protection policy away from fixed threshold values for pollutants towards a more dynamic objective of "good environmental status" (as in the European Commission's Marine Strategy Framework Directive; EC, 2008) or "good environmental quality" (as in the European Commission's Water Framework Directive; EC, 2000), evaluated in terms of ecosystem structure, function and process (e.g., Solimini et al., 2009). The signatories of the Convention on Biological Diversity are also moving towards the implementation of an "ecosystem approach" (UNEP-CBD, 2000) oriented towards the optimisation of the benefits that natural environments provide to humans, alert to the challenges of maintaining these ecosystem services in the context of a changing climate. Demand is growing for predictive dynamic tools to inform decision-making about land and marine ecosystems. All of this requires much deeper and more comprehensive process understanding about the nitrogen cycle. It is therefore timely to reflect on what is understood about organic N, and to use the current partial understanding to develop hypotheses to direct new scientific enquiry.

2. What is known about the global pattern of organic N deposition?

Neff et al. (2002) and Cornell et al. (2003) published reviews addressing the chemistry, deposition and methods for the analysis of atmospheric organic N, substantially drawing on the same data compiled from nearly a century of literature. For the analysis presented here, that original database has been updated with reports published over the last decade. Here, the focus is on studies of organic N deposition in rainwater (wet and bulk deposition). Additional studies have reported on organic N in atmospheric aerosol, which in principle present significant advantages in addressing the composition and sources of organic N because the formation processes of rain and its high dilution complicate analysis and interpretation. However, at present, there is still very great diversity in sampling and analysis methods for aerosol, making comparisons even more problematic than for rainwater. Furthermore, those studies tend not to have addressed the deposition of nitrogen, focusing more on elucidating the chemical composition of sampled aerosol. However, the exclusion of the aerosol literature from this report is not a comment on its importance. In their long-term (22-month) study in southern Scotland, Benitez et al. (2009) found that dry deposition exceeds rain-deposited N, for both organic and inorganic N, exposing yet another substantial knowledge gap in nitrogen assessment.

The quantitative significance of the organic component of atmospheric nitrogen deposition has long been recognized. The earliest reports relate to the Rothamsted Experimental Station's long time-series of rainwater composition (retrospectively reported by Miller, 1905, and Russell and Richards, 1919), which included organic N data spanning several years (methods not described). Concentrations ranged from 2 to 50 μmol N l^{-1}, averaging 14 μmol l^{-1}, and contributed about a quarter of the total N deposited. Although this seems a substantial proportion of N deposition to disregard, analysis ceased because the measured organic N was considered to be a natural background of locally-recycled material and the focus was on trends in anthropogenic N. This presumption may still be part of the reason that organic N is not systematically analysed and monitored. For several decades, organic N was only sporadically measured (e.g., Eriksson, 1952; Brezonik et al., 1969).

In the 1970s, growing policy concerns about air quality led to renewed scientific interest in organic N. A rapid rise in the frequency and geographic distribution of published studies of organic nitrogen in rainwater occurred around the time of the 1977 Clean Air Act Amendment in the USA and the 1979 International Convention on Long-Range Transboundary Pollution (Fig. 1).

The global dataset of organic N deposition is growing steadily, but in a piecemeal way. At last count, over 160 separate studies reported organic N in wet deposition (including snow and bulk deposition studies, which include some dry deposition component), with many other studies addressing atmospheric aerosol. Rainwater deposition data are now available for most continents and marine environments (Table 1). However, this collation of organic-nitrogen data still falls short of being a usable, investigable synthesis database. The list of caveats is long: entries may be concentrations determined on individual samples, or average values, or ranges. Sometimes, multiple samples have been bulked together for the organic N determination. In some cases, no concentration data are given, merely the percentage organic N contribution to total N deposition, and again these may be single values or ranges. These data sets are mostly very short term, typically reporting on rain events collected over a period of days to weeks (indeed some studies report on just a single sample); the sampling locations are very sparsely distributed and often not precisely specified; and information about sampling and analysis protocols is still woefully limited, even absent. With such a motley collection of studies, any statistical treatment of the data as they currently stand must be regarded as indicative at

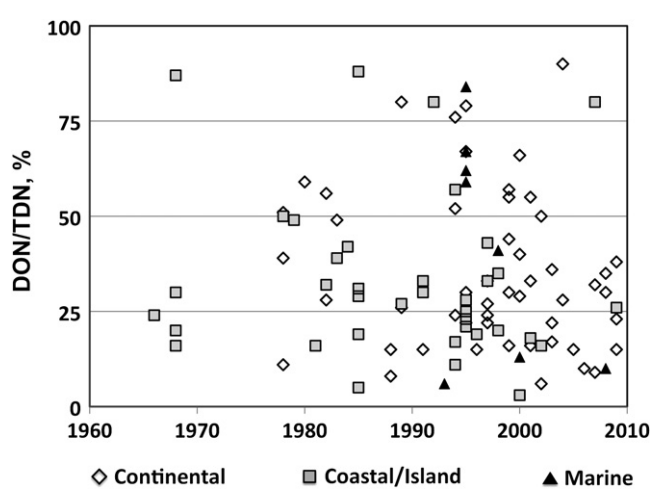

Fig. 1. Reported organic N in rainwater (including bulk deposition), as a proportion of total dissolved N, over the last 50 years. Data from publications up to 2000 have previously been collated, reported in Cornell et al. (2003). References for the sources are listed in Table 1.

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Table 1
Summary of published reports since 1950 of atmospheric organic N in rainwater, by region. Some publications report data for multiple sites.

Region	Organic N, as % of total N	Mean organic N concentration, μmol N l^{-1}	Reported range	Number of published studies	References
Antarctica	11	7.9	1.1–21	1	Downes et al., 1986.
Australia and New Zealand	40	7.2	2–14	9	Wilson, 1959; Timperley et al., 1985; Alongi et al., 1992; Crockford et al., 1996; Mace et al., 2003a; Vant and Gibbs, 2006.
North America	35	32	bd – 240	58	Eriksson, 1952; Williams, 1967; Tarrant et al., 1968; Brezonik et al., 1969; Bourne, 1976; Nicholls and Cox, 1978; Valiela et al., 1978; Valiela and Teal, 1979; Hendry and Brezonik, 1984; Grant and Lewis, 1982; Verry and Timmons, 1982; Correll and Ford, 1982; Richter et al., 1983; Jordan et al., 1983, 1991, 1995; Urban and Eisenreich, 1988; Shaw et al., 1989; Dillon et al., 1991; Jassby et al., 1994; Shon, 1994; Butler and Likens, 1995; Peters and Reese, 1995; Cornell et al., 1995; Prospero et al., 1996 (cites unpublished data for four sites); Valiela et al., 1997; Scudlark et al., 1998; Russell et al., 1998; Seitzinger and Sanders, 1999; Anastasio and McGregor 2000; Jordan and Talbot, 2000; Weathers et al., 2000; Whitall and Paerl, 2001; Zhang and Anastasio, 2001; Keene et al., 2002; Kieber et al., 2005; Hill et al., 2007; Calderon et al., 2007.
Caribbean, Central America	40	7.1	bd – 28.6	5	Mopper and Zika, 1987; Bowden, 1991; Eklund et al., 1997; Wanek et al., 2007; Reyes-Rodriguez et al., 2009.
South America	42	23	3–43	7	Lewis, 1981; Cornell et al., 1995; Williams et al., 1997; Weathers et al., 2000; Morales et al., 2001; Pacheco et al., 2005.
Europe	25	18	6–27	22	Carlisle et al., 1967; Allen et al., 1968; Gore, 1968; Persson and Bromberg, 1985; Emmett et al., 1991; Cornell et al., 1995, 1998; Reynolds and Edwards, 1995; Kopacek et al., 1997; Spokes et al., 2000; Roda et al., 2002; Rogora et al., 2006; Kram, 2008; Bencs et al., 2009: Benitez et al., 2009.
Asia (excluding China)	24	13	7–119	7	Eriksson, 1952; Timperley et al., 1985; Ham and Tamiya, 2007; Hayashi et al., 2007; Karthikeyan et al., 2009; Sundarambal et al., 2009; Hayashi and Yan, 2010.
China	33	117		3	Chen et al., 2008; Zhang et al., 2008, Hayashi and Yan, 2010.
Atlantic Ocean	41	7.9	1.7–16	8	Williams, 1967; Knap et al., 1986; Mopper and Zika, 1987; Cornell et al., 1995; Spokes et al., 2000.
Baltic Sea, North Sea	10	6.5		2	Rendell et al., 1993; Rolff et al., 2008
Mediterranean Sea	17			1	Mace et al., 2003c.
Pacific Ocean	40	5.5	1.7–13	5	Williams, 1967; Cornell et al., 1995, 1998, 2001; Carrillo et al., 2002.

best – but until a coordinated plan of action for organic N assessment is in place, these data are all we have to work with.

With these caveats in mind, Figs. 1–3 summarise the information from these studies. Organic N is globally ubiquitous. Fig. 1 shows that organic N is a significant component of total dissolved N in rain, for samples collected over the last 50 years in continental, remote marine, and coastal or island locations (defined as within 100 km of the sea). Miller's 1905 assessment that "about a quarter" of total N deposited is organic is not inconsistent with this collation of data (median of all studies is 29%, inter-quartile range is 17–43%), but the organic fraction is highly variable, ranging from mere traces up to nearly all of the N in rainwater.

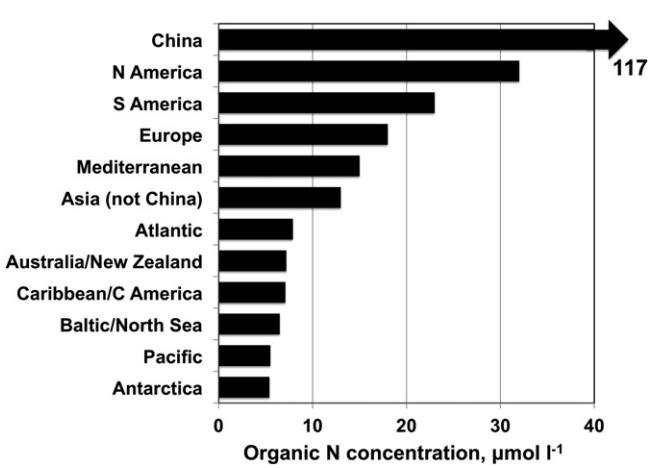

Fig. 2. Organic N concentration in rainwater from different geographical regions (arithmetic averages of data from multiple studies).

In the absence of more detailed information about the composition and sources of the organic nitrogen, a reasonable preliminary hypothesis could be that land-locked and remote marine samples would show systematically different behaviour. Emissions of N (Dentener et al., 2006) and of tropospheric particles and precursors (Heintzenberg et al., 2002) – both biogenic and anthropogenic – are generally higher over and near to land, so a land–sea gradient in absolute concentrations would be expected unless organic N has a primarily marine source. Removal processes for inorganic N are very effective, with concentrations declining rapidly with distance from source; if organic N has a longer atmospheric lifetime than inorganic N, as some studies have suggested, or if there is a marine source, then relative concentrations (organic N as a fraction of total N) might be expected to show less of a land–sea gradient. The available data are still not robust enough to address these questions adequately. There is weak support in the data for the hypothesis, in that the marine median ON as percent of TN is higher than for land-influenced samples, and marine median concentrations are lower, but the ranges for all three categories overlap almost completely. The kind of sampling location (continental, remote marine and mixed-influence) is no determinant of the relative importance of organic N: an analysis of variance of the ON fraction in these three categories returns a probability of 0.45 ($n = 47$). These apparently random patterns of geographical distribution may be a further part of the reason that organic N has not been included in N assessments.

However, apparently robust geographic patterns are emerging in this growing dataset (Figs. 2 and 3; in all regions, the standard deviation of the available measurements is a very similar magnitude as the mean concentration). Average concentrations of rainwater organic N in marine locations are typically around 5 μmol l^{-1} (Fig. 2). Australasian samples are slightly higher. Northern hemisphere continental/land-influenced samples are generally about

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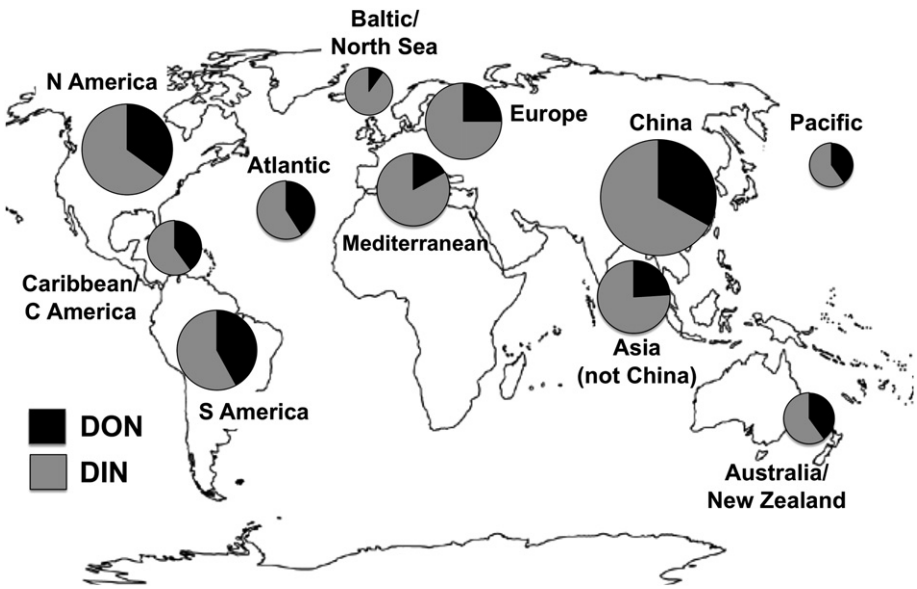

Fig. 3. Proportions of dissolved organic and inorganic N in rainwater or bulk deposition, by region. Areas of the pie charts are proportional to the mean concentration, with the exception of China, which is scaled down by a factor of two relative to the other regions in order to fit on the plot.

10 μmol l^{-1}, except for North America – the most studied region – where concentrations average about 25 μmol l^{-1}. The few studies from China are suggestive of a radically different environment, with apparently unprecedented high concentrations (>100 μmol l^{-1}) of both inorganic and organic N in rainwater. Rainwater data generally show log-normal distributions with drawn-out tails at higher concentrations (e.g., Seto et al., 1992), so these high values could be an artefact of the small and intermittent sampling effort in China to date. However, although the estimates shown here are based on a very limited set of observations, there is growing evidence that China is experiencing acute air quality problems (e.g., Galloway et al., 2009), so these few observations strongly suggest organic N should be a focus of future studies. The policy challenges China faces are likely to be different from those faced by other regions where N deposition has been a chronic problem.

In Europe and Asia, up to a quarter of total N deposited in rainwater is organic. Across the Americas, the proportions are somewhat different: 35–40% of total N is organic. In open ocean regions, organic N also contributes about two-fifths of total N, but the variability in the sparse marine dataset makes these estimates more uncertain than for other regions.

3. What is known about the composition and sources of organic N?

A further contributory factor in the omission of organic N from many assessments of impacts of biogeochemical perturbations is the fact that it is so poorly characterized. Despite valiant efforts in various research groups worldwide, the overall picture of the composition of rain and aerosol organic N in is still sketchy. Many different compound groups are known to contribute to bulk organic N, as a result of a set of studies that have tended to investigate one compound group at a time:

- Peptides and dissolved free amino acids could contribute 20–50% of dissolved organic N (Kieber et al., 2005; Matsumoto and Uematsu, 2005; Mace et al., 2003a,b; Spitzy, 1990);
- Amines have been detected, but probably contribute much less than 10% (Calderon et al., 2007; Gibb et al., 1999; Gorzelska et al., 1992; Mopper and Zika, 1987);
- Urea could account for anything from <10% to nearly all the organic N (Timperley et al., 1985; Cornell et al., 1998, 2001; Seitzinger and Sanders, 1999; Mace et al., 2003a,b,c);
- A ^{1}H nuclear magnetic resonance study of cloud water found that most of the organic matter consists of aliphatic oxygenated compounds, with "a small amount of aromatics" (Reyes-Rodriguez et al., 2009);

Perhaps as a result of this known complexity in chemical composition, there has been comparatively little consensus on *how* to measure organic N or what fractions or modes should be measured. Organic N techniques developed for river and seawater are used for rain and aqueous aerosol extracts, although matrix and concentration differences affect the efficiency and precision of the analysis. Organic N is still normally defined as the difference in total measurable N before and after some organic matter destroying treatment (Scudlark et al., 1998; Cornell et al., 2003); the exact nature of the transformations involved in the different treatments – UV, chemical oxidation, and so on – is a further aspect of organic N research that is "still poorly understood". There is not yet any simple, specific, field-deployable method for organic N (a fourth and perhaps the most constraining reason it is not included in deposition studies). Nevertheless enough meticulous investigation is emerging to inform a consensus on sampling and analysis protocols (e.g., Benitez et al., 2009; Keene et al., 2002; Cape et al., 2001; Scudlark et al., 1998). Improvements in analytical techniques and instruments, particularly total nitrogen analysers that ensure much more complete transformation and detection of the organic N, mean that data can be obtained at better resolution, precision, and sampling frequency than ever before.

In their 2002 review, Neff et al. stated that "there are no indications that AON [atmospheric organic nitrogen] is a proportionally greater contributor to N deposition in unpolluted environments and there are not strong correlations between fluxes of nitrate and AON or ammonium and AON." The present collation of rainwater analyses (Fig. 3) tends to confirm the former part of Neff et al.'s statement, but it does raise the logical sequitur question of how and why the overall ratios of organic to inorganic N can stay consistent across a very wide concentration range without there being any correlation between organic N and nitrate or ammonium.

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Some recent studies have explicitly sought out these correlations between organic N and known anthropogenic pollutants – and the picture is still murky. The data of Duan et al. (2009) show no correlation between organic and inorganic N in Beijing aerosol, nor between organic N and ammonium or nitrate ($n = 24$, samples collected over a four month period). Zhang et al. (2009), however, using a much larger and spatially more extensive data set of precipitation samples (from China and elsewhere) do observe strongly significant correlations between organic N and ammonium, nitrate and total dissolved nitrogen, concluding that these species have anthropogenic sources in common. Ham and Tamiya (2007) also see significant positive correlations with ammonium and total inorganic N in Japanese samples. Overall, there is evidence of a substantial anthropogenic source for some, if not most, of the organic N in rain and aerosol (Cornell et al., 1995, 2001; Russell et al., 1998; Seitzinger and Sanders, 1999; Cape et al., 2001; Mace et al., 2003a,c; Wanek et al., 2007; Sandroni et al., 2007; Lin et al., 2010). Lin et al. (2010) have looked at inter-correlations for multiple aerosol components, with back-trajectory analysis, in one of the most high-resolution studies to date. As perhaps should have been expected, organic N shows unusual behaviour – for example, non-linear relationships between organic N and organic carbon. Their analysis shows that there are multiple sources, natural and anthropogenic, some of which may dominate others at specific times of year or day.

Particular components of the "soup" of organic N compounds may show stronger correlations that help to elucidate sources, although the individual compound groups investigated to date are minor components of the bulk organic N. For example, Kieber et al. (2005) observed a positive relationship between amino acid and ammonium concentrations in coastal rainwater, and Gorzelska and Galloway (1990) saw a significant correlation between amines and ammonium in marine rain and aerosol. Many other studies have also provided evidence of a substantial natural (often marine) source for some of the organic N (e.g., Mace et al., 2003b; Reyes-Rodriguez et al., 2009; Miyazaki et al., 2010).

Isotopic studies so far (Cornell et al., 1995; Russell et al., 1998; Kelly et al., 2005; Rolff et al., 2008; Miyazaki et al., 2010) have not untangled the pattern of sources; if anything, insights from these studies may add to the perplexity. For example, Cornell et al. found isotopically light, anthropogenic signals in remote locations, while natural (soil and vegetation) signals dominated in the more polluted locations. Robust separation methods for organic ^{15}N analysis remain a challenge. Huygens et al. (2005) describe method improvements for ^{15}N analysis in total dissolved N in aquatic samples, using pre-combustion and an elemental analyser for sample introduction, but to date, the approach has not been applied to atmospheric samples.

4. What can we say about the ecological or biogeochemical role of organic N?

The analysis above indicates that we are often really only considering three-quarters of the real picture in our efforts to develop regional and global nitrogen budgets and increase fundamental process understanding. As a result of data sparseness and poor characterization, the role of organic N in ecosystems and Earth system processes remains much less clear than for other species. With the exception of the gas-phase organic nitrates, important in secondary organic aerosol formation processes, deposition and atmospheric chemistry models have only cursory representations of organic N and its multi-phase behaviour. We have very limited options for testing hypotheses about its sources, behaviour and consequences.

Understanding this invisible quarter –or more – of deposited N would help in understanding nutrient enrichment, especially for coastal zones and forest and bog ecosystems where concerns about exceedance of critical loads of atmospheric pollution are serious (e.g., Kram, 2008; Bowen and Valiela, 2001; Weathers et al., 2000; Paerl et al., 1999). Bronk et al. (2007) comment that compounds such as urea and amino acids, known to be significant components in rainwater, are the "doughnuts" of the organic nitrogen world – labile and easily taken up by the biota on very short timescales. It would also potentially illuminate other aspects of environmental degradation. Other compounds known to be present in rainwater, such as the azaarenes and other N-substituted polycyclic aromatic compounds (Chen and Preston, 2004), are toxic to plants and plankton (e.g., Paumen et al., 2009; Bleeker et al., 2002).

Much more needs to be known about the behaviour of organic N in association with particulate matter. It perhaps plays an important role in aerosol and cloud formation (e.g., Zhang and Anastasio, 2001; Facchini et al., 2008). Russell et al. (2003) and Sandroni et al. (2007) report significant deposition of "insoluble N" in atmospheric aerosol, strongly associated with anthropogenic emissions and assumed to be recalcitrant organic material, raising new questions about bioavailability. Cloud and aerosol organic nitrogen is implicated in "renoxification" processes (Zhang and Anastasio, 2003), where reservoir species such as peroxyacetyl nitrate transport NOx-derived anthropogenic N over long distances, extending the range of adverse impacts of pollution.

As outlined above, the question of the balance of anthropogenic and natural sources for organic N is still wide open. Part of the reasoning in the original Rothamsted studies for disregarding organic N was their assessment that it was likely to be from locally-recycled natural material (Russell and Richards, 1919), and they were focusing on known anthropogenic additions. A pattern that is emerging in the literature now is that organic N (as seen in rain and aerosol) could be the end result of interacting biogenic and anthropogenic emissions. Contributory processes include the reactions of biogenic carbon compounds with NOx (most recently, Goldstein et al., 2009); reactions of soot with NOx and ammonia (Chang and Novakov, 1975); and even the action of methane oxidiser bacteria on fossil fuel leaks (Davis et al., 1964).

5. Next steps

The indications in recent research that organic nitrogen is the product of mixed anthropogenic and biogenic sources may not be surprising from a chemical point of view, but it presents new challenges for global-scale assessment and any model-based projections. The impetus in modelling for improved understanding of the climate system is focusing attention on multi-phase atmospheric processes, particularly secondary aerosol formation (e.g., the UK's Chemistry–Aerosol Community Model, www.ukca.org; and the MEGAN biosphere–atmosphere and MOZART chemical transport models developed by the US National Center for Atmospheric Research, www.acd.ucar.edu/Models) and representations of the dynamic coupling of nitrogen and other key elements with the carbon cycle. A key challenge is the attribution of climatic changes, natural system variability and anthropogenic perturbation to the patterns and trends being observed. What we already know about organic N brings a different perspective to processes such as biomass burning, deforestation or afforestation, and changing energy sources, which are widely seen as "carbon issues" in the Earth system research community. We need tools to be developed that will enable us to explore climate and biogeochemical feedbacks, which in turn requires a rethink of research method design.

Organic N is one instance where model development and process understanding is still deeply constrained by a shortage of data and an unmet need for an overarching synthesis. Observation networks for other atmospheric species have expanded steadily

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over the past 30 years. As part of the Global Atmosphere Watch (GAW) programme, there is now good continental-scale coverage of North America and Europe (e.g., the US National Atmospheric Deposition Program and National Trends Network, nadp.sws.uiuc.edu; and the European Monitoring and Evaluation Programme, tarantula.nilu.no/projects/ccc/emepdata.html). Other GAW partners extend the sampling, analysis and data management into a worldwide infrastructure:

- Deposition of Biogeochemically Important Trace Species (DEBITS)
- US Global Precipitation Chemistry Program (GPCP)
- Canadian Air and Precipitation Monitoring Network (CAPMoN)
- Acid Deposition Monitoring Network in East Asia (EANET)

None of these address organic N deposition. An exception to this general pattern is Fluxnet Canada, part of a worldwide programme to assess biosphere–atmosphere carbon fluxes (daac.ornl.gov/FLUXNET). While most of the Fluxnet community is fully absorbed in carbon-related research, Fluxnet Canada proposed in its 2003 protocols (Fluxnet, 2003) the analysis of dissolved organic and inorganic N in ~10% of the precipitation samples collected for dissolved organic carbon. There appears to be no published data resulting from this analysis yet, but at present, the Fluxnet programme links more than 10 national and regional networks, with over 540 sites, giving acceptable global coverage (en.wikipedia.org/wiki/File:Fluxnet_Map.jpg). If all these partners were to follow Fluxnet Canada's example, using agreed protocols defined with the input of the organic N research community, the resulting organic N data would allow for clearer spatial and temporal patterns to be established, and more detailed characterizations to be made. More generally, the meta-analysis presented here suggests that there are differences in the patterns of N deposition between North America and Europe and the currently under-sampled areas of the world (South America and Asia). Effective observation of nitrogen deposition and changing processes, including human perturbations, may call for an extension of sampling protocols even for the GAW networks.

New analytical techniques are being applied to aerosol and rain analysis that should enrich the picture of the composition and behaviour of organic N. Methods include Fourier Transform-Ion Cyclotron Resonance–Mass Spectrometry (Altieri et al., 2009; Koch and Dittmar, 2006), which gives elemental compositions of N-containing compounds with positive and negative ion detection. It offers scope for improved chemical fingerprinting of the organic matter that can help in source attribution; for instance, it can be used to identify thermogenic aromatic compounds (products of fossil fuel combustion or biomass burning). Based on the relationships between series of compounds observed in their analysis of rainwater, Altieri et al. (2009) indicate that many of the reduced N compounds identified in their study could have been formed from amino acids through oligomerisation reactions in the atmosphere, providing one explanation for the persistent ~50% gap between known bulk organic N concentration and measured components. Time-of-Flight mass spectrometry (Bruns et al., 2010) enables steadily improved identification of multifunctional compounds, and single-particle methods (e.g., laser ablation) give information on composition and formation (for example, allowing for a distinction between internally or externally mixed aerosol systems). Developments in nuclear magnetic resonance spectroscopy mean that bulk matter can be better characterized, giving insights into the fates of known biogenic and anthropogenic compounds. For example, Herckes et al. (2007) has analysed the organic N in fog water, recovering and characterizing over 80% of the organic matter, and finding that it is indeed a complex, polydisperse "soup" that includes amines, nitrate esters, peptides and nitroso compounds. The detail of this chemical insight proved to be a vital factor in building a new understanding of the importance of biological sources of organic matter in atmospheric fog droplet formation.

5.1. To conclude, some specific recommendations

When organic N is determined in atmospheric samples, the data should be reported in research articles in ways that allow for a robust synthesis. This means that adequate summary statistics are needed: the number of samples; (volume-weighted) mean concentration; the range and median; and ideally also the interquartile range, since a normal standard deviation is not the best measure of variability for what is often a quasi-log-normally distributed component. Wherever possible, these summary statistics should be routinely provided for the full N speciation, that is, organic N *and* the inorganic species nitrate and ammonium. An important issue in all organic N datasets, given that organic N is necessarily determined as the difference between total N and inorganic N, is the occasional incidence of negative values for the difference. Published reports of organic N data therefore need to report both total and inorganic N so that the negative values can be dealt with systematically and transparently.

There is a pressing need for agreement on a set of protocols for sampling and analysis. In any case, researchers should routinely disclose whatever protocols were actually used in their study. Many publications reporting organic N deposition data fall short of providing sufficient information to allow the study to be reproduced.

What is ultimately needed is a real database, where atmospheric organic N data can be lodged, exchanged and investigated by a wider community. In the most impacted regions (China, Japan, Singapore, India), organic N is an emergent research focus, and their findings should inform the development of new protocols. Priority should also be given to observations in pristine regions (marine environment, Antarctica, Arctic), and areas where perturbation is projected to increase rapidly. Africa is currently entirely missing from the database, although substantial research investment is underway on the continent (e.g., the international Africa Monsoon Multidisciplinary Analysis programme, amma-international.org); and N deposition issues should be a priority in Latin America, because of the poor soils coupled with serious land-use change projections.

Improved engagement is needed across the various specialist groupings that have evolved in the atmospheric science community. These include the gas-phase, particulate, and wet/multi-phase sub-communities, and the field empirical, laboratory experimental, theoretical and modelling groups.

When all this is in place, programmes can be designed that will deliver more resolved measurements, which should begin to capture the dynamics and trends in the behaviour of organic nitrogen.

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