

# Chapter 12

## Assessment and Characterisation of the Organic Component of Atmospheric Nitrogen Deposition

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**Abstract** The organic component of atmospheric reactive nitrogen is known to be important for biogeochemical cycles, climate and ecosystems, but it is still not routinely assessed in atmospheric deposition studies, and most worldwide air quality monitoring networks disregard it. The available jigsaw puzzle pieces of knowledge from diverse sources can now give a richer picture of global patterns of organic nitrogen deposition. This effort at data synthesis highlights the need for more data, but also suggests where those data gathering efforts should be focused. The development of new analytical techniques allows long-standing conjectures about the nature and sources of the organic matter to be investigated, with tantalising indications of the complex interplay between natural and anthropogenic sources, and links between the nitrogen and carbon cycles. Atmospheric emission and deposition models are needed, along with new chemical process models, to let us explore questions about the role and dynamics of organic nitrogen.

**Keywords** Anthropogenic global change • Atmospheric deposition • Biogeochemical cycles • Organic nitrogen • Pollution monitoring

### 12.1 Introduction

Organic nitrogen is something of a castaway in global biogeochemistry research. The global monitoring networks, model developments, and environmental policies created in response to the serious nitrogen (N) linked issues of acid rain, eutrophication and urban pollution in recent decades have focused on emissions and deposition of inorganic reactive N species and rather ignored the organic N component. Organic N has long been known to be a quantitatively significant component of atmospheric N deposition (reviewed in Neff et al. 2002; Cornell et al. 2003). Organic N is known to play a role in atmospheric particle formation, affecting atmospheric visibility, light-scattering, and climate. It is a component of polluted fogs and smogs,

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forms of atmospheric aerosol that are of environmental and public health concern. It is known to be bioavailable, a nutrient source to marine/aquatic and terrestrial environments, and to be important in the long-range transport of N. Given this knowledge of its implications for biogeochemistry and ecosystem and human health, the fact that organic N is still not routinely measured—or even roughly factored-in to quantitative evaluations of N fluxes—is something of an awkward anomaly. When it does get mentioned, it is with the caveat that it is “still poorly understood”.

Here, I trace the recent history of organic N research, trying to highlight the new research directions that offer promising ways to fill in the gaps in our nitrogen budgets and understanding of organic N behaviour.

## 12.2 Is Organic Nitrogen Really Important?

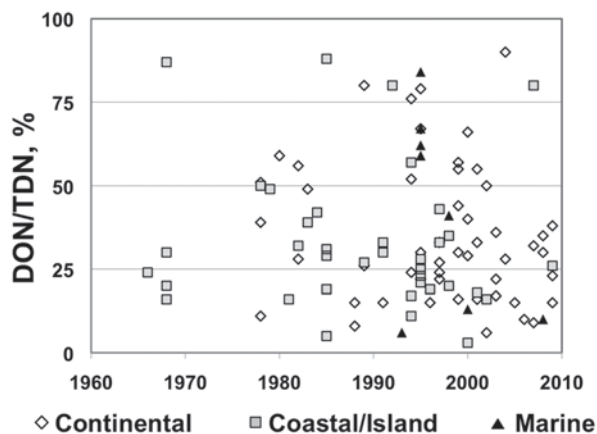
Neff et al. (2002) and Cornell et al. (2003) published reviews addressing the chemistry, deposition and analytical methods for determining atmospheric organic N, using essentially the same data drawn from nearly a century of literature. For the analysis presented here, that original database has been updated with reports published over the last decade of studies of organic N in rainwater.

The quantitative significance of the organic component of atmospheric N deposition has been recognised for a long time. The earliest reports relate to the Rothamsted Experimental Station’s long time-series of rainwater composition (Miller 1905; Russell and Richards 1919), where organic N (methods not described) ranged from 2 to 50  $\mu\text{mol N l}^{-1}$ , averaging 14  $\mu\text{mol l}^{-1}$  and contributed about a quarter of the total N deposited. This seems a substantial proportion of N deposition to disregard, but for several decades, organic N was only sporadically measured (e.g., Eriksson 1952; Brezonik et al. 1969). Growing concerns about air quality led to some renewed interest. Figure 12.1 shows that published studies of organic N in rainwater became more frequent and geographically widespread around the time of the 1977 Clean Air Act Amendment in the USA and the 1979 International Convention on Long-Range Transboundary Pollution.

Figure 12.1 also shows that organic N is consistently a significant component of total dissolved N in rain samples collected in all types of location—continental (shown in the graph as open diamond symbols), remote marine (filled triangles) and coastal or island (squares)—over the last 50 years. Miller’s first assessment in 1905 that “about a quarter” of total N deposited is organic still seems to hold true. However, the proportion that is organic is highly variable, ranging from mere traces up to nearly all of the N in rainwater. The kind of sampling location (continental, remote marine and mixed-influence) is not itself a determinant of the quantitative importance of organic N. This apparently random pattern may be part of the reason that organic N has not been systematically analysed and monitored.

However, the global data set is growing steadily. At the last count, there were 161 separate studies reporting organic N in wet deposition (including snow and bulk deposition, which include some dry deposition component). Data are now available

**Fig. 12.1** Reported organic nitrogen in rainwater and bulk deposition, as a proportion of total dissolved nitrogen (TDN), from studies in different types of location over the last 50 years. Reproduced with permission from Cornell (2011) *Environmental Pollution* 159, 2214–2222.



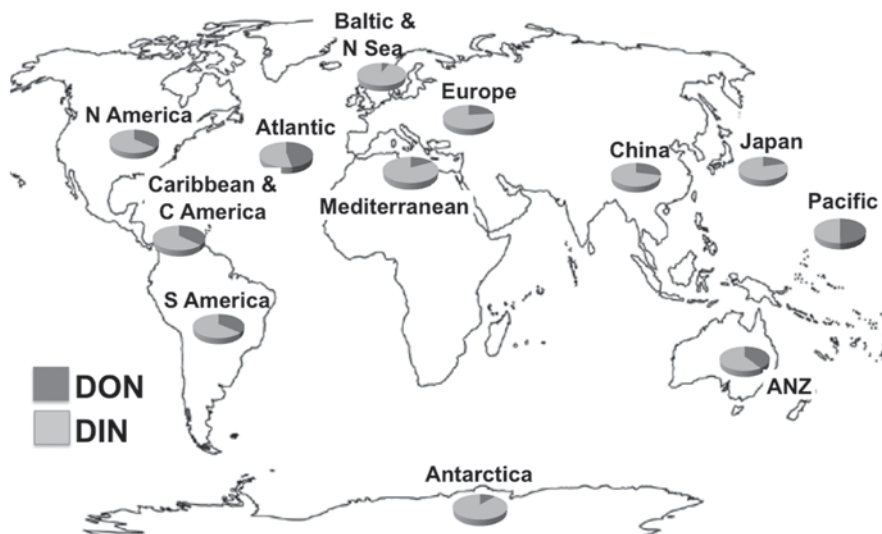
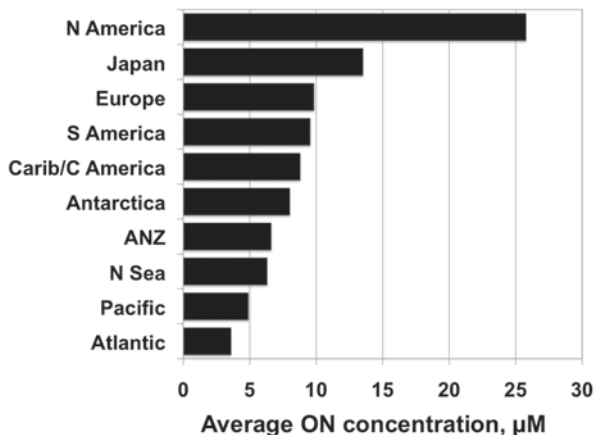
**Table 12.1** Numbers of published studies of atmospheric organic nitrogen deposition, by geographical location

Atlantic Ocean	7	Antarctica	1
Caribbean/Central America	9	Australia/New Zealand	8
Mediterranean Sea	1	China	2
North Sea	6	Europe	33
Baltic Sea	1	Japan	3
Pacific Ocean	1	N America	82
		S America	7

for most continents and marine environments (Table 12.1). Admittedly 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 data based on just a couple of samples); the sampling locations are very sparsely distributed; and information about sampling and analysis protocols is still woefully limited.

Figures 12.2 and 12.3 summarise the information from these studies. Organic N is globally ubiquitous. Average concentrations of rainwater organic N in marine locations are typically around  $5 \mu\text{mol l}^{-1}$ . Australasia and Antarctica samples are slightly higher. Northern hemisphere continental/land-influenced samples are generally about  $10 \mu\text{mol l}^{-1}$ , except for North America—the most studied region—where concentrations average about  $25 \mu\text{mol l}^{-1}$ . In Europe and Asia, up to a quarter of total N is organic. Across the Americas, the proportions seem systematically different: more like a third of total N is organic. A speculative hypothesis is that the Americas combine high biogenic gas emissions from the large forested areas (e.g., Wiedinmyer et al. 2006) with high levels of anthropogenic  $\text{NO}_x$  from car use and industry e.g., Benkovitz et al. 1996), providing precursors for the formation the organic N. In open ocean regions, organic N contributes a greater proportion of total N.

**Fig. 12.2** Organic nitrogen (ON) concentration in rainwater from different geographical regions (arithmetic averages of data from multiple studies). ANZ Australia and New Zealand



**Fig. 12.3** Proportions of dissolved organic (DON) and inorganic nitrogen (DIN) in rainwater or bulk deposition, by region. ANZ Australia and New Zealand

### 12.3 What is Organic Nitrogen?

Another reason organic N is left out of many assessments of impacts of biogeochemical perturbations is because it is so poorly characterised. Despite valiant efforts in various research groups worldwide, the overall picture of the composition of rain and aerosol organic N is still sketchy. It is evidently a “soup”:

- “mainly aliphatic oxygenated compounds, a small amount of aromatics” (Reyes-Rodriguez et al. 2009)
- peptides and dissolved free amino acids could be 20–50% of dissolved organic N (Kieber et al. 2005; Matsumoto and Uematsu 2005; Mace et al. 2003a, b; Spitzzy 1990)
- amines—but these 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), and at present, rain and aerosol data appear to show different patterns.

Perhaps as a result, there has been comparatively little consensus on *how* to measure it 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-destroying treatment; the differences in treatments—UV, chemical oxidation, and so on—are themselves “still poorly understood”. There is no simple, specific, field-deployable method for organic N (perhaps the third 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., Keene et al. 2002; Scudlark et al. 1998; Cape et al. 2001).

Observation networks for other atmospheric species have expanded steadily over the past 30 years. As part of the Global Atmosphere Watch 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, <http://nadp.sws.uiuc.edu>; and the European Monitoring and Evaluation Programme <http://www.nilu.no/projects/ccc>). Other GAW partners extend the worldwide sampling, analysis and data management 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 routinely. An exception to this general pattern is Fluxnet Canada, part of a worldwide programme to assess biosphere-atmosphere carbon fluxes. Its 2003 protocols (Fluxnet Canada 2003) propose analysing for dissolved organic and inorganic N in ~10% of the samples collected for dissolved organic carbon (C). Fluxnet links more than 10 national and regional networks, with over 540 sites, giving a fair global coverage ([http://en.wikipedia.org/wiki/File:Fluxnet\\_Map.jpg](http://en.wikipedia.org/wiki/File:Fluxnet_Map.jpg)). If all these partners followed 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 patterns to be established and more detailed characterisations to be made.

## 12.4 What Can We Say About Its Role?

In developing global N budgets and process understanding, we are often really only considering three-quarters of the real picture. As a result of data sparseness and poor characterisation, 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 multiphase behaviour. We have limited options for testing hypotheses about its sources, behaviour and consequences.

Understanding this invisible quarter 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. It is implicated in “renoxification” processes, where reservoir species such as peroxyacetyl nitrate (PAN) transport  $\text{NO}_x$ -derived anthropogenic N over long distances, extending the range of adverse impacts of pollution. Much more needs to be known about its behaviour in association with particulate matter, perhaps playing an important role in aerosol and cloud formation (e.g. Zhang and Anastasio 2001). Russell et al. (2003) and Sandroni et al. (2007) report significant deposition of “insoluble N” in atmospheric aerosol, strongly associated with anthropogenic emissions, raising new questions about bioavailability.

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, and they were focusing on known anthropogenic additions. The pattern that is emerging in the literature now is that organic N (as seen in rain and aerosol) is a nexus of biogenic and anthropogenic emissions. Contributory processes are the reactions of biogenic C compounds with  $\text{NO}_x$  (most recently, Goldstein et al. 2009); reactions of soot with  $\text{NO}_x$  and ammonia (Chang and Novakov 1975); and even the action of methane oxidiser bacteria on fossil fuel leaks (Davis et al. 1964). Isotopic studies so far (Cornell et al. 1995; Russell et al. 1998; Kelly et al. 2005; Chen 2008) have not untangled the pattern of sources; if anything, new results are adding to the perplexity. Huygens et al. (2005) describe method improvements for  $^{15}\text{N}$  analysis in total dissolved N in aquatic samples, using pre-combustion and an elemental analyser for sample introduction, but overall, robust separation methods for organic  $^{15}\text{N}$  analysis remain a challenge.

New analytical techniques are being applied to aerosol and rain analysis that will enrich this picture. Methods include Fourier Transform-Ion Cyclotron Resonance-Mass Spectrometry (Altieri et al. 2009; Koch and Dittmar 2006), giving elemental compositions of N-containing compounds with positive and negative ion detection. These studies confirm that much of what we see as organic-N are actually not N-rich compounds, and indicate that reduced N species, rather than oxidised forms, are important contributors. They offer scope for improved fingerprinting, say for thermogenic compounds. 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 (e.g., internally or externally mixed systems). Developments in nuclear magnetic resonance mean that bulk matter can be better characterised into known biogenic and anthropogenic compounds. For example, Herckes et al. (2007) show that in fog, biogenic organic C is important, while the organic N includes amines, nitrate esters, peptides and nitroso compounds—direct evidence of a complex, poly-disperse “soup”.

## 12.5 Next Steps

The indications in recent research that organic N 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) and representations of the dynamic coupling of nitrogen and other key elements with the C 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 seen as carbon issues. We need tools 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 constrained by a shortage of data and an unmet need for an overarching synthesis.

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