



Title :	Organic Nitrogen - Synthesis of Special Topic Working Group	
Time :	09:00 – 12:00, 14 th March 2006	
Venue :	Hotel am Badersee, Grainau, Germany	
Chair :	J Neil Cape	NERC
Rapporteur :	Geeta Wonnacott	Scottish Executive
Attendees :		
1.	Lutz Breuer	JLU
2.	Raia Massad	INRA
3.	Marta Mitosinkova	SHMU
4.	Lech Szajdak	RCAFE
5.	Sonja Vidic	MHSC

Introduction

'Organic nitrogen' comprises a wide mixture of different compounds, from small molecules to macromolecules. As controls on emissions of inorganic N (ammonia, nitrogen oxides) take effect, the relative importance of organic N will increase. However, even now it appears that organic N can contribute around 30% of wet deposited nitrogen – yet is usually ignored in terms of policy, because its sources and fate are not well understood.

What is known about organic nitrogen

Organic nitrogen compounds exist in all media – air, precipitation, soils, biota and surface waters. Usually they are not measured directly (with some exceptions), but as the difference between 'total N' and inorganic N (the sum of ammonium, nitrite and nitrate ions).

Air and precipitation

Individual organic N compounds have been measured in air and precipitation, but their individual concentrations generally contribute a small proportion of the difference between 'total N' and inorganic N; 'organic N' is a complex mixture of different types of chemical compound.

The literature on 'organic N' in precipitation (water soluble organic N, or WSON) has been reviewed recently (Cornell et al., 2003; Neff et al., 2002). The proportion of total N contributed by WSON is greatest for marine samples and least for continental samples, although there is a large variability, both across different sites and between years. Over the UK, the long-term average contribution of WSON to total N in precipitation was 10-40%. Annual average concentrations of WSON were linearly correlated with ammonium concentrations, but the seasonal patterns were different, with peak in ammonium and nitrate concentrations in spring, and peak WSON in summer (Cape et al., 2004).

Although WSON has been reported in the literature for many years, doubts exist over whether it is a real component of precipitation, or an artefact of the sampling or analytical methods used. Recent research has shown that WSON in chemically sterilised bulk precipitation

samples did not arise from biological transformation of inorganic N during sampling or storage (Cape et al., 2001). Different analytical techniques, however, can cause artefacts; the colorimetric indophenol blue method for measuring ammonium concentrations responds positively to other compounds with an amino group, such as amines and amino acids (Rowland, 1983). Reporting indophenol blue measurements as ‘ammonium’ therefore overestimates the true ammonium concentration. Comparison of indophenol blue data with analysis by ion chromatography suggests that ammonium concentrations may be biased (upwards) by 10% for UK conditions – but this result also indicates that a significant proportion of WSON is contributed by compounds that contain amino groups. Similarly, methods for assessing total N in water samples may give different results – the widely used persulphate digestion technique recorded values on average 14% lower than a high temperature combustion / chemiluminescence technique. These data suggest that a significant proportion of WSON is relatively unreactive (at least to persulphate digestion) (Cape et al., 2004).

Measurements of WSON in air, using a recirculating mist sampler, show that WSON in air exists in both the gas and particle phases, operationally distinguished by passage through a 0.45 µm PTFE membrane filter (Fig.1). These data again show that WSON is not simply an artefact of biological activity within rain samples during sampling or storage.

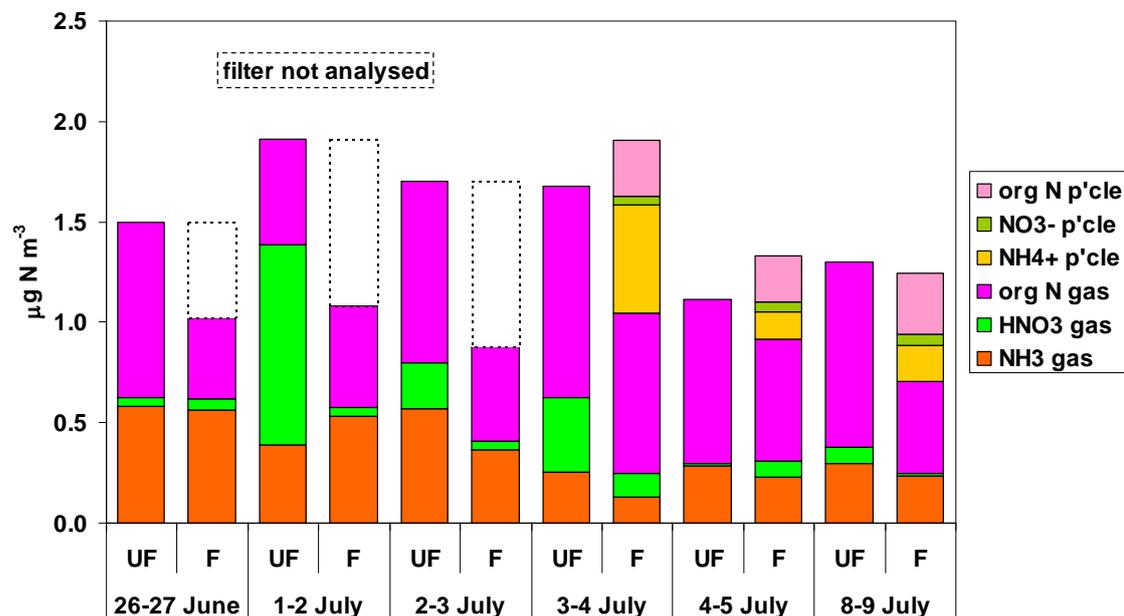


Fig. 1. Chemical composition of air sampled using a recirculating nebulizer, with (F) or without (UF) a PTFE membrane filter on the inlet. ‘Organic’ N is defined as the difference between total N (high T/chemiluminescence) and inorganic N (NH₄⁺ + NO₃⁻). (Cape, pers. comm..)

Interactions of organic N in deposition with foliage

Inorganic N compounds are known to be retained by plant canopies (e.g. throughfall under trees is often depleted in inorganic N, compared with incident rainfall) (Crockford et al., 1996; Ferm, 1993). Organic N compounds may also be retained by trees, in conditions where

the concentrations of inorganic N are low, but may also be enhanced in throughfall. Fumigation of canopies with ammonia gas, or treatment with solutions containing ammonium ions, leads to enhancement of organic N in throughfall (Cape, unpublished).

Interactions of organic N in soils

Soils contain very large amounts of organically-bound nitrogen, but most of this is chemically and biologically unreactive on time-scales of a year. However, some organic N in soils is labile, water-soluble, and available for use by microbes and by plants. WSON may provide a large proportion of the N uptake by plant roots. WSON is also leached from soils into freshwaters, and then be transported to the oceans. Although measured as WSON in streams and rivers, the overall chemical composition is not well defined, and usually determined simply as 'total N' minus inorganic N.

Organic N in drainage waters

Data from undeveloped parts of the world show that the N content of river outflows is dominated by WSON (Perakis and Hedin, 2002); only in areas heavily affected by man's activities does nitrate play a role, becoming the major contributor to soluble nitrogen (Fig. 2). Even in Europe, organic N content may be a marker for catchments affected by man's activities. WSON concentrations have been shown in a restricted number of studies to be strongly related to dissolved organic carbon (DOC) concentrations (Fig. 3).

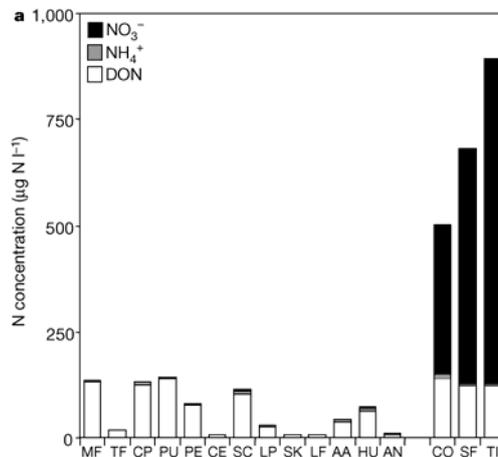


Fig. 2. Hydrologic nitrogen losses from temperate forest watersheds in 3 areas from eastern North America (CO, SF, TI) and 13 areas of South America (MF-AN) (Perakis and Hedin, 2002).

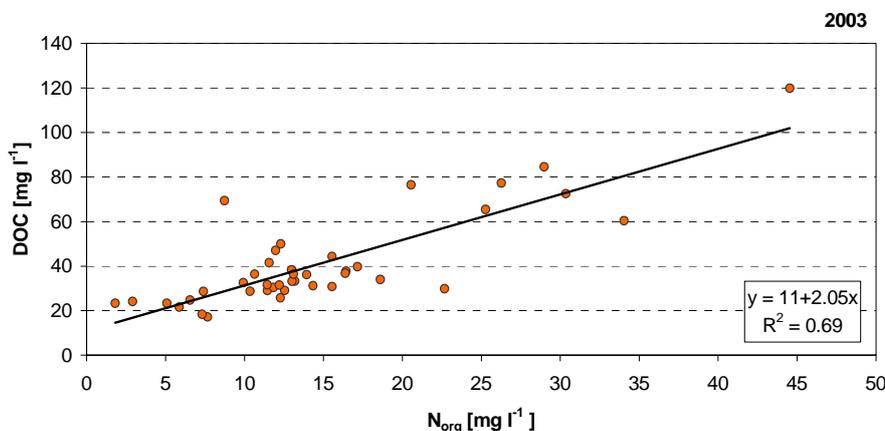


Fig. 3. Relation of dissolved organic N and C across 64 catchments within Hesse, Germany. Catchments investigated comprise streams of several orders that are dominated by natural as well as heavily human impacted ecosystems (Breuer, pers. comm.).

Organic N and greenhouse gases

Greatly enhanced emission of nitrous oxide is known to occur from animal urine patches, which contain large concentrations of organic N. However, it is not known whether it is the inorganic or organic components of urine which stimulate N_2O emission. First results of N_2O emission measurements from grassland soils amended with a variety of organic N substrates indicate the potential source strength of these compounds (McLain and Martens, 2005).

Organic N and plant growth

The commonly known pathway of plant nitrogen uptake is by nitrate and ammonium. Recent research though indicates that plants are not only capable of uptaking organic nitrogen, but that in many cases organic nitrogen proved to be the even more important way for plant nutrition. This pattern was not only shown for plants growing in nitrogen poor ecosystems with dominating organic soils, but also for cropland systems (Jones et al., 2005; Lipson and Näsholm, 2001).

What is not known

Air and precipitation

The presence of WSON in air as gases and particles suggests that bulk deposition may include a component of WSON dry-deposited to the sampling surface (Scheller, 2001). Although this would overestimate the role of WSON in wet deposition, it indicates (if real) the potential for a significant contribution of WSON to dry deposition, which is not currently considered in estimating total N deposition. The chemical composition of WSON is still largely unknown, although there are clues to potential contributory compounds, such as those with amino groups, from the different results found when using different chemical analytical techniques.

In general, the methods for air and rain sampling and analysis have not been standardised. Consequently, it is difficult to compare different studies quantitatively, to estimate the more widespread contribution of WSON to total N deposition. However, the likely contribution of organic N to the total amount of N deposited could be as great as 30%, which is currently ignored.

Interaction of organic N with vegetation

It is not known whether the transformation of inorganic N to organic N in plant canopies occurs as a result of plant (leaf) processing, or whether it is a surface phenomenon, controlled by leaf surface microbes. The chemical composition of WSON in throughfall (modified by the canopy) is not known, so neither is the input to the soil surface. Consequently, it is not known whether the interaction with a plant canopy makes deposited organic N more or less available to soil microbes and plant roots.

Interaction of organic N with soils

Although some studies have used stable isotopes to measure root uptake from model organic N compounds, the precise route of uptake is uncertain for field soils, because it is not known whether organic N is processed by microbes before uptake by plant roots. Moreover, the possibility of additions to soil of WSON from root exudates has been suggested, but not demonstrated. Once in soil, the fate of WSON is not known – it could be degraded by microbes, taken up by plant roots, adsorbed onto humic materials or clays (and thereby ‘fixed’ as part of the long-term soil N pool), or pass through into drainage water chemically unchanged.

Organic N and drainage waters

In general, the chemical composition and source of WSON is not known. It could come from percolation of wet deposition (without modification), abiotic or biotic solubilisation of the organic N pool in soil, or exudates from plant roots or animal excreta. Once in a water course, it can be degraded to simpler molecules (including gases) or taken up by higher plants, algae or benthic micro-organisms.

Organic N and greenhouse gases

It is not known whether organic N in soil is preferentially converted to nitrous oxide or nitrogen, or whether the availability of organic N changes the pattern of gaseous emissions from soils.

Opportunities for NitroEurope

As future reductions of inorganic N will increase the relative importance of organic N in the overall N cycle, organic N compounds should be considered in the investigation of the atmosphere, hydro-, bio-, and pedosphere within NitroEurope. Consequently, organic nitrogen fluxes and relevant (but so far broadly unknown) processes should be also implemented in the models used in WP3 Plot-Scale Modelling, WP4 Landscape Analysis and WP5 European Integration. A better understanding of the underlying processes will help to answer the questions, whether human impacts alter ecosystems from being organic to inorganic nitrogen controlled (van Breemen, 2002).

The wide range of measurements to be made as part of NitroEurope provide an opportunity to address our lack of knowledge of the sources, distribution and fate of organic N. Possible additional measurements include:

- Analysis of precipitation samples for total N – this could be done by any laboratory with appropriate equipment, but samples would need to be stabilised (using a biocide) before shipping to other laboratories.



- Analysis of denuder and/or filter samples for total N – volumes of available extract solutions may be small, but the partitioning between acid-coated and base-coated denuders may give information on the nature of airborne WSON.
- Analysis of freshwaters and leachates for WSON and DOC – to improve the understanding of the correlation between these parameters at different sites so that WSON may be predicted from DOC. There is scope here for looking at DON:DOC ratios as a marker for N loss in different ecosystems
- Use of organic N substrates in experimental manipulations, ideally using isotopically labelled material, to investigate the role of WSON in the production of greenhouse gases.
- Use of isotopically labelling to investigate the interaction of organic N with soils, including outputs to drainage waters.

The availability of several investigations at the same time at the same site (integrated measurements) should permit a more complete understanding of the role of WSON in the budgets and fluxes of N across Europe.

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