The Origin, Composition and Rates of Organic Nitrogen Deposition: A Missing Piece of the Nitrogen Cycle?

Article *in* Biogeochemistry · April 2002

DOI: 10.1023/A%3A1015791622742 · Source: OAI

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Biogeochemistry **57/58:** 99–136, 2002.

The origin, composition and rates of organic nitrogen deposition: A missing piece of the nitrogen cycle?

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Abstract. Organic forms of nitrogen are widespread in the atmosphere and their deposition may constitute a substantive input of atmospheric N to terrestrial and aquatic ecosystems. Recent studies have expanded the pool of available measurements and our awareness of their potential significance. Here, we use these measurements to provide a coherent picture of the processes that produce both oxidized and reduced forms of organic nitrogen in the atmosphere, examine how those processes are linked to human activity and how they may contribute to the N load from the atmosphere to ecosystems. We summarize and synthesize data from 41 measurements of the concentrations and fluxes of atmospheric organic nitrogen (AON). In addition, we examine the contribution of reduced organic nitrogen compounds such as amino acids, bacterial/particulate N, and oxidized compounds such as organic nitrates to deposition fluxes of AON. The percentage contribution of organic N to total N loading varies from site to site and with measurement methodology but is consistently around a third of the total N load with a median value of 30% (Standard Deviation of 16%). There are no indications that AON 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. Possible sources for AON include byproducts of reactions between NO_X and hydrocarbons, marine and terrestrial sources of reduced (amino acid) N and the long-range transport of organic matter (dust, pollen etc.) and bacteria. Both dust and organic nitrates such as PAN appear to play an important role in the overall flux of AON to the surface of the earth. For estimates of organic nitrate deposition, we also use an atmospheric chemical transport model to evaluate the spatial distribution of fluxes and the globally integrated deposition values. Our preliminary estimate of the magnitude of global AON fluxes places the flux between 10 and 50 Tg of N per year with substantial unresolved uncertainties but clear indications that AON deposition is an important aspect of local and global atmospheric N budgets and deserves further consideration.

Introduction

The first measurements of organic nitrogen in precipitation were made in the 1800s and have continued through the 20th century (Smith 1872; Fonselius 1954; Wilson et al. 1959). These early measurements and subsequent studies have shown that organic forms of nitrogen appear in both wet and dry deposition in many locations (Hendry and Brezonik 1980; Lewis 1981; Rendell et al. 1993; Cornell et al. 1995; Eklund et al. 1997). Despite the growing number of studies documenting organic N in deposition, its sources and magnitudes remain unclear. As a result, the role of organic N in atmospheric N deposition is not widely discussed and the majority of deposition measurements focus on inorganic N species. National deposition networks such as the National Acid Deposition Program (NADP) in the U.S. and the European Monitoring and Evaluation Programme (EMEP) in Europe have monitored ammonium and nitrate deposition in precipitation for many years but have little information on organic N deposition. As a result, it has been difficult to make quantitative evaluations of the role of AON in deposition budgets for large-scale compilations of atmospheric N fluxes due to limited data (Prospero et al. 1996).

Some of the functions of organic nitrogen in atmospheric chemistry are clearly established. Organic nitrate formation can be an important process in the nighttime boundary layer when NO_2 accumulates in the absence of sunlight (Munger et al. 1988). Organic nitrates such as PAN are also important to long range atmospheric N transport (Roberts 1990; Lelieveld and Dentener 2000). The role of organic N compounds in the total atmospheric N budget and deposition, however, is substantially less clear. A group of atmospheric chemistry models which all use similar reaction schemes suggest that, in many cases, peroxyacetyl nitrates (PAN) and the organic nitrates constitute more than 50% of NO_y (total odd nitrogen including NO_x, HNO_3, HONO, HO_2NO_2, NO_3, radical $NO_3^{\cdot}$, PAN, N_2O_2, organic nitrates) which is the primary source of N deposition of oxidized species (Hagulstaine et al. 1998; Klonecki, personal communication). But it is unclear how much these organic nitrates appear at the surface as wet or dry deposition or whether other processes/species are involved. The term atmospheric organic nitrogen includes a broad array of chemical compounds that differ widely in their function and reactivity. This complexity has hampered progress and complicated analysis of the role of AON in chemistry and deposition. There are also significant problems of contamination in AON measurements (Gorzelska et al. 1997; Church et al. 1999; Russell 1999). The chemical species that make up AON include compounds such as organic nitrates, amino acids and other organic acids with atmospheric lifetimes that range from seconds to weeks (Herlihy et al. 1987; Buhr et al. 1990; Gorzelska and Galloway 1990; Dentener and Crutzen 1994; Brassuer et al. 1998).

Conceptually, AON can be divided into three types of nitrogen: organic nitrates, reduced AON and biological/terrestrial AON. The first two categories are broad chemical descriptions but are useful because reduced and organic nitrate forms of AON can be thought of in conceptually distinct ways. Organic nitrates are the oxidized end products of reactions of hydrocarbons with NO_x ($NO + NO_2$) in polluted air masses. These forms of AON are generally formed *in situ* from the constituent molecules following reaction with light (Roberts 1990). The second category of AON primarily includes gas phase or aerosol amine N and urea that can be injected into the atmosphere in marine or agricultural environments but is not formed *in situ* due to the oxidizing conditions of the atmosphere (Milne and Zika 1993; Schade and Crutzen 1995). The last category of AON refers to biological and particulate forms of organic N including bacteria, dust particles and pollen all of which can be found in high concentrations in the lower levels of the atmosphere but have their sources in terrestrial environments (Bovallius et al. 1978; Lindemann et al. 1982; Jones and Cookson 1983; Littmann 1997).

Organic nitrate, reduced and biological/particulate contributions to AON have been reasonably well documented and, as a result, it is becoming increasingly apparent that organic N plays an important role in the chemistry of the atmosphere. Organic nitrates may also be an important input of N to ecosystems. This conclusion is further supported by an increasing number of detailed, analytically rigorous studies of nitrogen deposition that indicate significant organic contributions to deposited N (e.g. Gorzelska et al. 1992; Cornell et al. 1995). Despite the well-documented presence of AON in deposition, there remains substantial uncertainty regarding the quantitative role of AON in N deposition fluxes and in the global cycle of N. Are AON fluxes important contributors to atmospheric N loading in terrestrial and aquatic ecosystems? Are AON fluxes large enough to warrant routine analysis in deposition monitoring programs as these programs evolve to meet new challenges? Is AON a substantial global flux of N that should be considered in evaluations of the global N cycle? These questions remain difficult to answer but are important to developing a complete understanding of the N cycle at both small and large scales.

Methods

In this paper, we review published reports of all forms of organic N deposition including total organic N, oxidized forms of AON and reduced forms of AON. We discuss the implications of these results for estimates of N deposition and discuss the various pathways by which organic forms of N enter or are created in the atmosphere. We then evaluate the relationships between modeled and measured AON using the TM3 model of atmospheric chemistry and transport (Dentener et al. 1999) and use the model combined with our literature review to provide an estimated range of the organic nitrate and PAN contributions to global AON deposition.

Data selection and analysis

The measurement of AON involves many different sampling methods and multiple analytical techniques. The measurement of individual organic compounds such as amino acids or organic nitrates is too detailed to fully discuss here and has been addressed, at least in part, elsewhere (Roberts 1990; Russell 1999). In this review, we evaluate the potential contribution of reduced N, biological/particulate N and organic nitrates to the total organic N flux from the atmosphere. This differentiation is a conceptual simplification that provides insight into the possible controls over the total AON concentrations observed in deposition measurements. The biological and particulate N grouping may include both oxidized or reduced forms of N but is differentiated from the other two classes by the presence of a distinct biological form (e.g. bacteria) or particulate form that originates in terrestrial systems (e.g. dust, pollen). Sample molecules and definitions for these classifications are shown in Table 1. The biological AON definition is useful because of the established presence of organisms and dust in the atmosphere and in precipitation and the intriguing possibility that these materials could contribute to the net organic N flux from the atmosphere (Bovallius et al. 1978; Lindemann et al. 1982; Jones and Cookson 1983; Littman 1997). For each of these classes of organic N, we discuss the controls over the production and deposition of these compounds in order to better evaluate the regulation of the atmospheric organic N cycle.

We have compiled 41 measurements in which the total organic N concentrations in precipitation or wet/bulk deposition fluxes were presented. There are very few measurements of dry deposition of organic N containing gases, and so we cannot discuss these fluxes in detail here. However, we do discuss measurements of gas-phase organic nitrates such as PAN in order to examine the role that these gas phases organic nitrates may play in the deposition of organic N globally. It should be understood that the N wet deposition measurements presented in this paper represent the net flux of organic N from the atmosphere to ecosystems and contain a unspecified mixture of organic nitrates, amino acids, bacteria and other forms of organic N. One of the main goals of this paper is to link these N deposition measurements to the potential N deposition from the array of potential contributors to deposition.

Table 1. Examples of atmospheric organic nitrogen. Note that the bacterial and particulate N classes may also include reduced and oxidized N.

	General type of organic N	Example Molecules	Source
Bacterial nitrogen			
Reduced organic N larger than 0.2 microns	Multiple dissolved and particulate amine forms		Atmospheric Bacteria
Particulate nitrogen			
Particles larger than 0.45–1 micron	Multiple particulate organic nitrates or amine N forms		Atmospheric dust and organic debris
Reduced organic N			
Soluble N with sizes smaller than 0.45 microns	Amine N	Serine, Glycine, Alanine, Valine, Methylamine, Ethylamine and others	Oceanic aerosols, terrestrial emissions (agricultural sites or natural vegetation)
Oxidized organic N			
Soluble N with sizes smaller than 0.45 microns	Nitric acid esters	Methyl, ethyl, propyl and butyl nitrates	Atmospheric Reactions
	Nitric acid diesters	Ethylene & propylene glycol	Atmospheric Reactions
	Hydroxy nitric acid esters	Nitrooxy ethanol and propanol	Atmospheric Reactions
	Peroxynitric acid esters	Trifluoro methyl and dimethyl ethyl	Atmospheric Reactions
	Peroxycarboxylic nitric anhydrides	PAN	Atmospheric Reactions

For all the total organic N deposition measurements, the organic N (solution) concentration or flux data were presented alongside either total inorganic N or NH_4^+ and NO_3^- data. There are two types of organic N fluxes that we discuss in this review; total organic N (TON), which includes both particulate and dissolved forms of organic N and dissolved organic N (DON), which does not include the particulate component. The difference between TON and DON is operational and defined by the size of particle that will flow through a filter but both types of measurements are based on analyses performed on soluble (or at least filterable) material in deposition collectors. For the studies that reference DON, the samples have been filtered following collection. Because the pore size of the filter is not always provided in the referenced papers, we assumed DON represented the material that passed through a 0.45–1 micron filter (the most common size range). Unfiltered samples were assumed to contain both particulate and dissolved organic N and are represented as TON.

In addition to different definitions for the types of organic N in precipitation, there are multiple measurement techniques, sampling frequencies and field collection methodologies. DON (or TON) is measured as the difference between the total N in solution (determined via the oxidation or reduction of the organic compounds) and the sum of the initial NH_4^+, NO_2^- and NO_3^-. The conversion of organic N to inorganic N is generally carried out by chemical (persulfate), *uv* or high temperature oxidation of the solution. We also reference dissolved organic carbon concentrations and these measurements are generally made with high temperature oxidation techniques. These different approaches have varying oxidizing efficiencies but generally result in the conversion of at least 80% of the organic species to inorganic N in freshwater and seawater samples (Walsh 1989; Scudlark et al. 1998). The majority of the measurements described in this paper were made using persulfate oxidation-based conversion of organic N to nitrate or high temperature combustion.

As with analytical techniques, there are a variety of sampling approaches. Wet deposition measurements can be made for individual rain events on regular daily or weekly intervals. There are potential problems with storage of organic samples in field collectors in that organic N may be converted to inorganic N due to microbial decomposition or that organic N may be produced due to microbial activity. There is also substantial potential for contamination in samples that are left in the field for long periods of time. It is not readily apparent whether these post-deposition changes would lead to increased or decreased TON concentrations in collection devices. For event sampling of precipitation, where the potential for external contamination is minimized, organic N compounds may react with the materials in sampling equipment, storage containers or may volatilize from sampling vessels (Scudlark et al. 1998; Church 1999). For these reasons, there is potential for underestimation of organic N concentrations in event-based sampling. Most of the recent (after 1980) measurements discussed here were made either with event samples or with sub-weekly sampling intervals that should minimize the possibilities of N transformations or contamination post-collection. In some cases, samples were analyzed immediately following collection. The potential errors in DON deposition measurements, and options for mitigation have been discussed in more detail in Gorzelska et al. (1997), Russell (1999) and Church (1999). From the standpoint of this review, we note that measurement methodology does not appear to affect AON concentration measurements in a systematic manner. There were substantial, measurable quantities of DON in precipitation for every case study that we examined. We exclude some data points from analysis for reasons discussed below, but have maintained as large a data set as possible.

To examine the role of AON in total N fluxes, we analyzed published data for the fractional contribution of organic N to total N concentrations or fluxes. If both AON fluxes and solution concentration data were available, we use the flux data to estimate the proportional contribution of organic N to the total N concentration. However for Russell et al. 1998 and Malmquist 1978; we use concentration averages instead of fluxes because these particular data sets do not span an entire year. We also did not include the DON cloud deposition estimate for Chile (Weathers et al. 1998) and the DON dry deposition estimate for Canada (Simpson and Hemens 1978) because they are not directly comparable to wet or bulk deposition estimates compiled from other studies. We used the Statistica software package for Windows to carry out regression analyses and to estimate mean, median, standard deviation, and standard errors for the data (Statsoft Inc. Tulsa, OK, U.S.A.). For some analyses, we have classified a site as unpolluted or polluted. These classifications are based on the evaluation of the inorganic N flux for a site (Prospero et al. 1996) and/or the geographic location of a site (marine vs. continental).

Dry and wet deposition

AON can be deposited in both wet and dry forms. We discuss both types of deposition but there are some important distinctions in the two types of measurements. All but one of the flux measurements discussed here are made on soluble N from deposition collectors. These forms of deposition could include N deposited in either wet or dry form. In a bulk collector, for example, a certain amount of dry deposition will fall into the bucket and then be quantified as soluble N. Actual deposition rates of dry AON are difficult to obtain. Estimates of deposition can be made from measured atmospheric concentrations combined with deposition velocities but for most of the specific organic N species (e.g. amino acids or organic nitrates), it is difficult to find published deposition velocities, and therefore difficult to calculate a deposition rate (Dentener et al. 1999). Accordingly, we present data on the concentrations of specific dry AON species and discuss the ways that these dry AON species may contribute to the total N flux. We do not use any of these dry deposition calculations to estimate the fractional contribution of organic compounds to total N fluxes. For calculations of the average organic contribution to concentrations or fluxes, we present data summaries from the bulk or wet deposition collectors discussed above.

Modeled estimates of organic N fluxes

The deposition of organic nitrogen is strongly dependent on the distributions of sources, the lifetime and chemistry of N compounds and atmospheric transport. The lifetime of many reactive N compounds in the atmosphere is quite short. The global average lifetime of NO_x is on the order of one day while NH_x (NH_3 + NH_4^+) is between 1 and 5 days depending on NH_3 concentrations and other factors (Dentener et al. 1999). These global average lifetimes do not reflect the tremendous variability in lifetimes with season and height (Brasseur et al. 1999). For example, the lifetime of NO_x in the summer is on the order of a few hours to a day in the lower few kilometers of the troposphere, but extends to 4–7 days in the upper troposphere. The formation of organic nitrates provides a temporary reservoir of active nitrogen. Some of these organic nitrates have lifetimes of a week or more and so can be transported to the remote atmosphere where they can provide a source of NO_x. Peroxyacetyl nitrate (PAN) is the predominant organic nitrate produced in the atmosphere via NO_x, non-methane hydrocarbon reactions and has a much longer lifetime in the upper than in the lower troposphere (Bertman and Roberts 1992; Moxim et al. 1996; Nouaime et al. 1998; Roberts et al. 1998). Collectively, understanding the interaction between the lifetime of these compounds, their speciation and associated solubility are critical to understanding the spatial distribution of organic nitrate deposition. There are currently no atmospheric models that simulate the chemistry and transport of reduced or particulate AON. However, there are models that represent the chemistry of organic nitrates and these models may be useful tools for predicting the distribution and trends in this portion of the total AON flux.

Organic nitrate chemistry is represented in several models of global atmospheric chemistry (Stand and Hov 1994; Zimmerman 1987; Houweling et al. 1998). We use one of these models to provide insight into the potential transport and fluxes of the oxidized organic N species particularly as it relates to human activity and sources of precursor compounds. We use the TM3 model which is a 3D chemical transport model that includes representation of the atmospheric photo-oxidant, N and S cycles including NO_x, NO_y and reduced N (NH_3 and $(NH_4)_2SO_4$). The model incorporates globally-gridded source fields of NO_x and NH_3 and a series of detailed chemical reaction sequences (Dentener and Crutzen 1994; Houweling et al. 1998; Dentener et al. 1999; Lelieveld and Dentener 2000) including non-methane hydrocarbon and oxidized organic N reactions (Houweling et al. 1998) and NO_x source fields from Yienger and Levy (1995). The model has a resolution of 3.75 × 5 degrees and 19 vertical hybrid levels, 5 of which are located in the boundary layer. Dry deposition is parameterized following Ganzeveld and Lelieveld (1995), wet deposition using the parameterization of Guelle et al. (1999).

The deposition rates of organic nitrates, including PAN, are difficult to represent in models because uncertainty in NMHC reaction schemes, and the lack of published organic nitrate dry deposition rates and deposition velocities. One of the key uncertainties with regard to the wet deposition of organic nitrates is representation of their solubility and the efficiency of removal by precipitation. The solubility of individual organic nitrate compounds can span two orders of magnitude depending on the individual compound (Houewling et al. 1998). Uncertainties in wet and dry deposition parameters, such as surface characteristics, precipitation scavenging, and atmospheric stability limit the accuracy of simulation for even the better characterized compounds NO_x and HNO_3 . A detailed analysis of TM3 model errors in NO_x, NO_y and PAN representations is discussed in Houweling et al. (1998). In general, the model generally agrees within a factor of two with published PAN concentration data (Houweling et al. 1998). We present model based estimates of net global organic nitrate deposition as a comparison against our data compilation in order to evaluate the potential role of the organic nitrates and PAN in measured AON deposition. It is important to remember that these model-based estimates are preliminary and should be considered an upper limit on organic nitrate deposition.

Results and discussion

Reduced organic N compounds

The presence of reduced organic N in atmospheric aerosols and in deposition has been noted at multiple locations and like the distribution of oxidized organic N, appears to be a global phenomenon, albeit a poorly studied one. There are multiple types of reduced nitrogen that are found in the atmosphere or in deposition, including urea and amino acid N in aerosol and precipitation samples over oceans (Mopper and Zika 1987; Gorzelska and Galloway 1990; Spitzy 1990; Milne and Zika 1993; Cornell et al. 1998) and over continental environments (Fonselius 1954; Munczak 1960; Sidle 1964; Gorzelska et al. 1994). In contrast to the organic nitrates, considerably less is known about the mechanisms that lead to the production and emission of reduced N to the atmosphere or about the global transport patterns of this material. There is, however, enough information on the dynamics of these compounds to speculate on their role in the global AON cycle.

Unlike oxidized AON, reduced AON compounds are not produced *in situ* under the oxidizing conditions of the atmosphere. The most likely source of these compounds, which include urea, free amino acids and other methyated amines, is direct injection into the atmosphere from various sources. The types of reduced AON that may be expected in precipitation are shown in Table 1 and the potential sources of reduced AON include oceanic, agricultural and biomass burning emissions. The oceanic source of amino acid N to the atmosphere involves the direct injection of amino acid containing aerosols into the atmosphere during the bursting of bubbles at the air/sea interface (Mopper and Zika 1987; Milne and Zika 1993). The other potential source of amine compounds to the atmosphere is agricultural systems where a variety of aliphatic amines can be emitted from animal husbandry operations (Mosier et al. 1973; Hutchinson et al. 1982; Schade and Crutzen 1995) and from biomass burning (Lobert et al. 1991). The compounds that may be emitted from these sources include methylamine (MMA), dimethylamine (DMA) and trimethylamine (TMA) among others. In localized areas above animal feedlots, the concentrations of MMA, DMA and TMA can range from 20–280 pptv and may exceed NH_3 concentrations in the same air mass (Schade and Crutzen 1995).

Once in the atmosphere, many reduced N species react quickly. Compounds such as MMA and DMA are highly soluble and are very reactive with the OH radical (Schade and Crutzen 1995). Other radical species such as nitrate, perhydroxyl and superoxide molecules all may function as effective scavengers of reduced N compounds (Milne and Zika 1993). The general reactivity of these compounds suggests that they are not favorable candidates for long range atmospheric transport but are rather more likely to be locally emitted and deposited (consistent with the global lifetime of 1–5 days detailed by Dentner and Crutzen 1994). There is some indication of this type of behavior in comparisons of amino acid concentration in rains over the Gulf of Mexico where concentrations reached 13–15 μM compared to concentrations of 0.3 to 0.5 μM over Miami, Florida, further away from the presumed ocean source (Mopper and Zika 1987). The concentrations of amino acids in marine air range are generally in the low (1–10) pptv range but can range as high as 150 pptv (Mopper and Zika 1987; Gorzelska et al. 1994). In certain locations, such as the Gulf of Mexico, amino acid concentrations rival those of NH_4^+ and NO_3^- (Mopper and Zika 1987) but in other locations such as continental Canada, aerosol amine nitrogen concentrations were less than 5% of the sum of the inorganic N concentrations (Gorzelska et al. 1994). One pattern that is clear is that in most cases the concentrations of free amino acids in aerosol form are substantially less than PAN concentrations and more similar to the concentrations of the (non PAN) organic nitrates shown in

Table 2. The substantial variability in both aerosol amine content and amino N in rain samples in the above samples likely reflects the localized nature of these sources as well as short range transport of these compounds.

At the global scale there have been two estimates of global fluxes for reduced organic N compounds. Milne and Zika (1993) estimate an amine N flux to oceans at 0.6 Tg of N per year. Schade and Crutzen (1995) place the global MMA emission flux from animal husbandry operations at 0.15 Tg of N per year in comparison with a biomass burning source of 0.06 Tg N per year. If these two estimates are representative of the dominant reduced organic N fluxes, then the global deposition flux of reduced AON would be under 1 Tg of N per year. However, without additional information, it is premature to rule out additional sources or forms of reduced AON or to make more detailed estimates of the global reduced-AON flux. At local scales, however, the reduced AON contribution to N deposition may be substantial, particularly for areas influenced by marine air and areas downwind of agricultural operations.

Biological and particulate atmospheric N

The atmosphere contains not only aerosol and dissolved organic nitrogen but also airborne microorganisms, often associated with particulate material (Bovallius et al. 1978). This atmospheric flora contains N that could contribute to estimates of AON fluxes made from unfiltered samples of wet deposition or even to dry deposition measurements of total organic N. The role of bacteria in the AON budget is wholly unknown and there are no data on the N flux that might be associated with bacterial deposition. For dust deposition of N, there is not an extensive deposition data set, however there is enough information to evaluate the potential contribution of these materials to the AON deposition flux.

The concentration of bacteria in the atmosphere varies broadly between concentrations as low as 10 bacteria per m^3 over the open ocean to thousands of bacteria per m^3 in urban and agricultural environments (Bovallius et al. 1978; Lindemann et al. 1982; Jones and Cookson 1983). Concentrations of bacteria in the atmosphere increase with disturbances such as agricultural activity and dust storms and decline during rain events (Bovallius et al. 1978). Most airborne bacteria are associated with particles and may be transported long distances as a result (Bovallius et al. 1978). To make a preliminary estimate of how much N may be contained in airborne bacteria, we take a relatively high estimate of urban bacterial density of 3000 bacteria per m^3 of air. Assuming a radius of 0.5 microns, each bacterium would have a volume of approximately 5×10^{-19} m^3. With a solid to liquid ratio of 0.2, an average N content of 10%, and a density of 1000 kg m^{-3}, each bacterium would contain

Table 2. Concentrations of non-PAN organic nitrates for several sites and urban/non-urban PAN average concentrations for 48 studies contained in Roberts (1990). Standard Errors (SE) for the Roberts (1990) study means are shown. Concentration means are presented whenever possible with ranges presented when means were not available. Unpolluted (P) and Polluted (U) conditions were designated by the authors of this manuscript.

Site	Season (Sp, S, A, W)	Latitude, Longitude	Compound type	Concentration (pptv)	Unpolluted (U) Polluted(P)	Reference
North Pacific Ocean	Sp, S		C3–C7 alkyl nitrates	10	U	Atlas 1988
Alaska USA	Sp	64 N, 150 W	C2–C6 alkyl nitrates	34	U	Beine et al. 1996
Hawaii		20 N, 156 W	C3–C5 alkyl nitrates	7	U	Atlas and Schauffler 1991
South Africa	Sp	29 S, 24 E	C3–C5 alkyl nitrates	17	U	DeKock and Anderson 1994
Northwestern Canada	Sp	82 N, 62 W	C3–C7 alkyl nitrates	34–128	U	Muthuramu et al. 1994
Rural Ontario – Clean	S	45 N, 79 W	C3–C6 alkyl nitrates	8–50	U	O'Brien et al. 1995
			C2–C4 hydroxy nitrates & 1,2 dinitrooxybutane	5–20	U	

Polluted			C3–C6 alkyl nitrates	10–105	P	
			C2–C4 hydroxy nitrates & 1,2 dinitrooxybutane	1–35	P	
Alabama, USA	S	32 N, 86 W	C2-C5 alkyl nitrates	52	P	Bertman et al. 1995
Germany	Sp	51 N, 9 E	C1–C5 alkyl nitrates	1–230	P	Flocke et al. 1991
British Columbia	S	49 N, 123 W	C3–C6 alkyl nitrates	11–210	P	O’Brien et al. 1995
Rural Pennsylvania	S	40 N, 77 W	C2–C5 alkyl nitrates	2-200	P	Buhr et al. 1990
Urban Airmasses			PAN	780 140 SE		Roberts (1990)
Non-Urban Airmasses			PAN	380 50 SE		Roberts (1990)

1×10^{-14} g of N (Paul and Clark, 1996). With a boundary layer depth of 500 m, there would be 1.5×10^6 bacteria over a m^2 of land surface with a total N content of 1.5 10^{-8} g of N m^{-2}. Assuming a lifetime of 5 days and a removal coefficient of 2×10^{-6} s^{-1}, the annual flux of bacterial AON would be 9.5×10^{-6} kg of N ha^{-2}. Even with substantially higher bacterial densities, removal coefficients or bacterial N content, these hypothesized deposition rates appear to be inconsequential to the total N load to an ecosystem. While these calculations could certainly be improved upon with additional information, it does not appear that biological AON is a significant component of either local or global AON fluxes. It is also important to note that there are other forms of airborne biological N including insects. Given that precipitation-sampling equipment is open to the atmosphere, and the large amount of N that would be in an insect relative to precipitation, the possibility of organic contamination to sampling stations is significant. Techniques such as event sampling, filtration and visual inspection of precipitation samples will minimize this type of contamination, however both field studies and reviews such as this paper cannot rule out these forms of contamination at the present time.

The role of dust in the element cycling of ecosystems has received significant attention (c.f. Swap et al. 1992; Littmann 1997; Ramsperger et al. 1998a), however most of the discussion of element deposition in dust has focused on inorganic cations and anions. As with other forms of deposition, there appear to be significant organic matter inputs associated with dust deposition which may contribute to the organic N flux in certain types of measurements. The potential impact of dust to AON deposition measurements is limited to sampling designs that capture bulk (as opposed to wet only) deposition and to measurements made on unfiltered samples (although dust associated organic N could dissolve in contact with water). Dust particles can range in size from 0.1 to over 20 microns and as a result, they may fall into the operationally defined (filter pore size based) cutoff for dissolved organic nitrogen (Tegen et al. 1994; Ramsperger et al. 1998a). There is not sufficient published information to carry out a detailed evaluation of the role of different dust size classes in AON fluxes, however there are indications that there is substantial organic content on dust particles. In studies of the southwestern Argentinean Pampa, Ramsperger et al. (1998a) observed annual dust loading of 400–800 kg ha^{-1} yr^{-1}. Of this dust input, approximately 6–8% of the material was organic matter with a %N content of 0.5–0.8% for an annual deposition flux of 2 – 6.4 kg N ha^{-1} (Ramsperger et al. 1998b). In an Israeli sand dune ecosystem, Littman (1997) found total N loading rates of 0.48 kg N ha^{-1} yr^{-1} with only 5% of the flux attributed to inorganic N compounds and in dust samples from West Africa, Ramsperger et al. (1998b) observed % N contents (by mass) of 0.3–1.4.

The role of dust in the AON budget is particularly important because global dust emissions are increasing as the result of human disturbance (Tegen et al. 1995). These increases almost certainly lead to an increased organic N load in the atmosphere and likely contribute substantially to bulk TON loading in deposition measurements. There are both local and remote sources of dust for atmospheric transport and a complete review of this topic is impossible here but it is clear that dust could be a significant contributor toward AON deposition. Dust deposition estimates range between 100–2000 kg ha^{-1} yr^{-1} (Rabenhorst et al. 1984; Swap et al. 1992; Ramsperger et al. 1998a). Assuming small (2%) organic fractions and relatively low N content (1%), a conservative approximation of dust AON fluxes leads to an estimate of 0.02 to 0.4 kg dust AON ha^{-1} yr^{-1}. The studies mentioned above indicate that these numbers could be substantially higher.

Organic nitrates

Organic nitrates occur in both polluted and remote portions of the atmosphere. These compounds are produced through photochemically mediated reactions of non-methane hydrocarbons (NMHC) and NO_x (NO and NO_2). There are a variety of compounds and reaction sequences that are important in the formation of oxidized AON and a detailed review and discussion of these reactions is in Roberts (1990). A greatly simplified version of the NMHC/NO_x reactions is shown in Figure 1. There have been numerous field studies of the reactions of NMHC and NO_x focusing on the role of these compounds in photochemical reactions and the production of compounds such as PAN (Bertman and Roberts 1992; Williams et al. 1993; Nouaime et al. 1998; Roberts et al. 1998).

There are both natural and anthropogenic sources of NMHCs and NO_x which may contribute to the production of organic nitrates. Natural sources of NMHC's are dominated by plant production of isoprene which accounts for 40% or more of the global hydrocarbon emissions, but also includes a variety of additional higher molecular weight volatile organic carbon (VOC) compounds (Guenther et al. 1995). Isoprene and other plant emitted hydrocarbon emissions increase sharply with temperature and the correlation between temperature and production rates results in a global flux that is tropically dominated and which should be strongly seasonal in temperate climates (Sharkey et al. 1991; Guenther et al. 1995; Keller and Lerdau 1999). In northern latitudes the atmospheric NMHC budget is dominated by fossil fuel combustion (Guenther et al. 1995). Estimates of the pre-industrial NO_x budget place the pre-industrial global flux of NO_x from soils, biomass burning, lightning, NH_3 oxidation and stratospheric injection at approximately 12 Tg of N which is roughly 30 percent of the contemporary

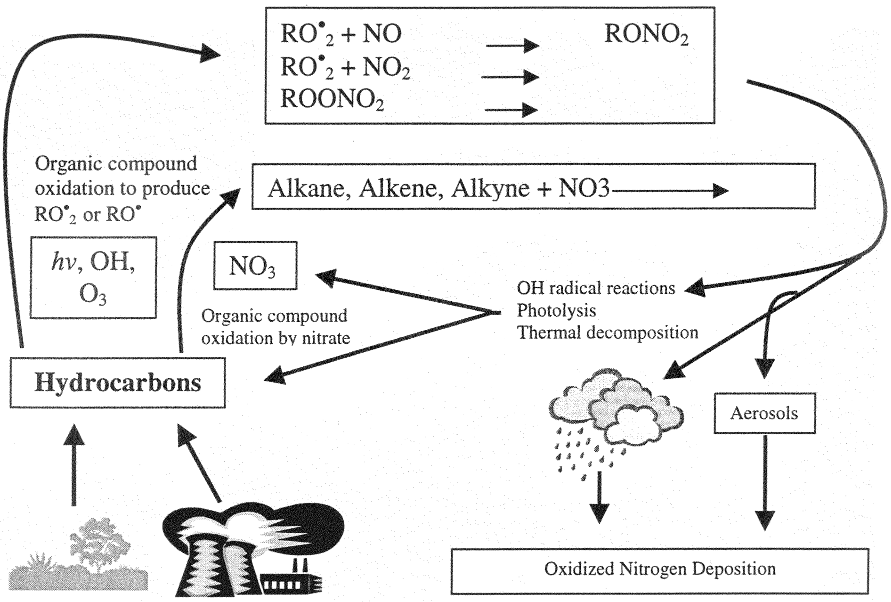


Figure 1. Simplified gas phase formation reactions and removal processes for organic, oxidized N species.

36 Tg NO_x budget (Holland et al. 1999). This three-fold increase in the global NO_x budget is due primarily to the combustion of fossil fuels. Once NMHC and NO_x compounds enter the atmosphere and begin the reaction sequences shown in Figure 1, there are additional factors that may influence organic nitrate deposition rates. The atmospheric lifetime of PAN is sensitive to temperature with longer PAN lifetimes at lower temperatures. This sensitivity should lead to longer transport distances of PAN in the northern latitudes relative to the tropics and during the winter relative to the summer (Houweling et al. 1998).

The large natural sources of NMHCs and NO_x suggest that there was a significant pool of oxidized AON in the pre-industrial world. In a review of the atmospheric cycle of organic nitrates, Roberts (1990) summarizes a series of PAN measurements from urban and non-urban air masses that we summarize with other non-PAN organic nitrates in Table 2. Concentrations of PAN in unpolluted sites are roughly 50 % of polluted sites (Table 2). This increase is generally consistent with the ratio of natural to anthropogenic fluxes of NMHCs and NO_x discussed above. In non-urban sites, there are a handful of measurements of the relative concentration of PAN to the total N concentration in the atmosphere with an average proportional PAN contribution of 15–30% for measurements in Colorado and Canada (Bottenheim et al.

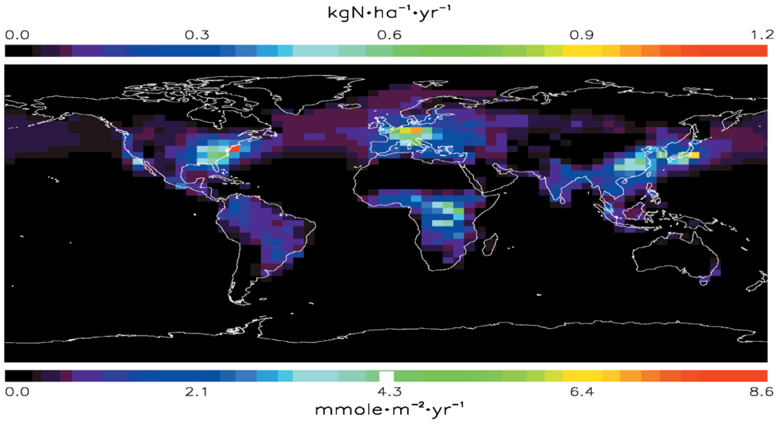
1984; Anlauf et al. 1986; Fahey et al. 1986; Pierson et al. 1987; Daum et al. 1989). The contribution of PAN to total atmospheric N is related to the age of the air mass and its distance from anthropogenic inputs that increase the overall contribution of inorganic N vs. PAN (Roberts et al. 1990).

There is substantially less known about other (non-PAN) organic nitrates but there are a number of compounds that, in addition to PAN, may contribute a sizable fraction to the total oxidized AON load. Table 1 shows the concentrations for several urban and non-urban sites with organic nitrate concentrations that range from the low part per trillion by volume (pptv) range to highs of 200 pptv. Like PAN, the concentrations of non-PAN organic nitrates are higher in polluted or urban areas and lower concentration in more remote areas. Without additional studies, it will remain difficult to evaluate the controls over the concentrations of these compounds in the atmosphere.

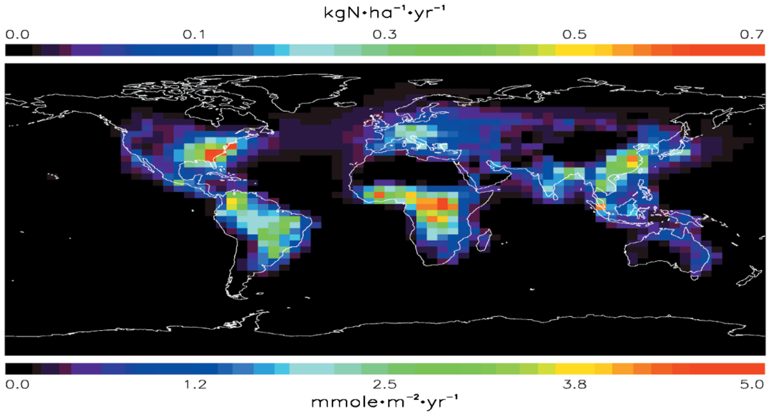
The evidence for the importance of chemical speciation is indicated by the contrasting spatial patterns of PAN and non-PAN organic nitrates deposition predicted from the TM3 model. PAN concentrations and deposition are highest in the industrialized Northern Hemisphere and the long distance transport of PAN over the Northern Atlantic Ocean is clearly shown (Figure 2(a)). PAN fluxes range between 0.1 and 2 kg N ha^{-1} yr^{-1} with average deposition between 0.3 and 0.6 kg ha^{-1} yr^{-1} for the north eastern U.S. and Europe and a global flux of 2.5 Tg (Table 3). For dry organic nitrate deposition, there are also high rates of deposition in North America and Europe but tropical regions in Africa and South America also show significant deposition (Figure 2(b)). In comparison to PAN, the dry organic nitrates deposition rates are approximately one half to two thirds of the PAN fluxes (Table 3). Of the three compounds shown in Figure 2, the wet organic nitrates have the most tropically oriented deposition pattern with peak deposition rates in the northwestern Amazon and the Congo region of Africa (Figure 2(c)). Interestingly, the highest of these deposition rates match PAN deposition in the northern hemisphere but the range of transport over the tropical regions is much shorter. The combination of warm temperatures and high rainfall appears to limit the transport of organic nitrate out of the tropical regions while PAN concentration are elevated in the entire 30–45 degree N band.

Globally, the TM3 model estimates that the sum of organic nitrates and PAN contributes 9.1 Tg of N to the total annual deposition flux of 92.9 Tg N. Our feeling is that this estimate represents an upper limit of organic nitrate deposition given the uncertainties in the model. However, there is also debate over the magnitude of terrestrial NO_x emissions and if higher terrestrial emissions fields were used in the model (e.g. Davidson and Kingerlee 1997) then higher organic nitrate deposition would follow. Modeled PAN concentration ranges roughly correspond with PAN data for urban and non-urban air masses

A. PAN Deposition (Dry)



B. Organic Nitrate Deposition (Dry)



C. Organic Nitrate (Wet)

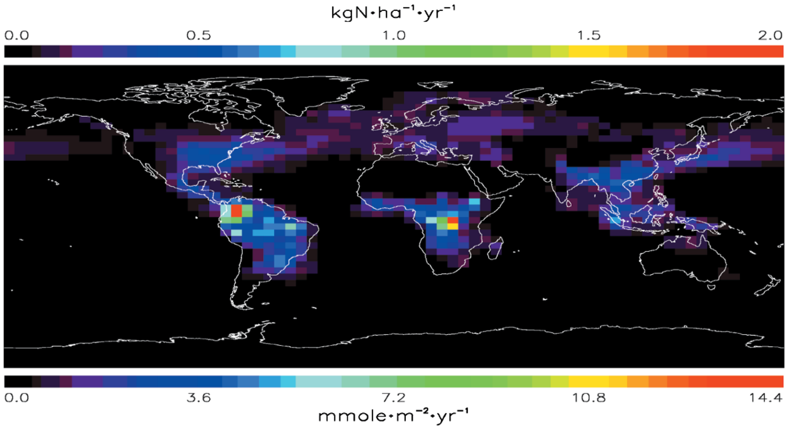


Figure 2. Annual deposition of organic nitrogen from the TM3 model. Panel A shows the PAN deposition (in dry form), panel B shows dry organic nitrates and panel C shows wet organic nitrate deposition.

Table 3. Annual global N fluxes from the TM3 Model and estimates of organic vs. inorganic loading in Teragrams of N (Tg).

	N Species	Global N deposition (Tg N)
Inorganic Species		
	NO_x (g)	6.4 Tg
	HNO_3^- (g)	10.6 Tg
	NH_4^+(g)	3.6 Tg
	NH_3 (g)	20.8 Tg
	HNO_3^-	20.3 Tg
	NH_4^+	13.6 Tg
	NH_3	8.5 Tg
Organic Species		
	Organic Nitrates (g)	2.7 Tg
	PAN (g)	2.5 Tg
	Organic Nitrates	3.9 Tg
Total Modeled Deposition		
	Inorganic	83.8 Tg
	Fraction Organic	9.8 %
Modeled organic flux estimate	Oxidized Species only	9.1 Tg

shown in Table 2. It is difficult to evaluate the non PAN, organic nitrate contribution to oxidized AON, however, both the model and the data summarized in Table 2, suggest that other organic nitrates may be sizable contributors to the total oxidized AON flux. These calculations also highlight the potential for oxidized AON to contribute significantly to global N deposition calculations. In a subsequent section, we compare these model estimates of organic nitrate loading to measured estimates of organic nitrogen in deposition fluxes.

Total AON deposition rates

In contrast to most measurements of atmospheric AON concentrations, most deposition measurements do not differentiate between different AON compounds and instead present a total TON or DON deposition rate. There have been a number of TON/DON deposition measurements made over a wide range of ecosystems and these studies show consistently large contributions of organic compounds to the total N deposition flux or concentration. These measurements are summarized in Table 4 and indicate that the organic

Table 4. Summary of AON and DIN fluxes. Bulk deposition is specified as B and Wet only measurements as W. TON is total organic nitrogen based on unfiltered samples. DON represented dissolved organic samples that are stated as filtered or presented as dissolved. Data presented as NH_4:NO_3:AON ratios (1 number = organic N, 2 numbers = inorganic N:organic N, 3 numbers = NH_4:NO_3:DON/TON). Percent composition is determined from fluxes wherever available and from concentration ratios if no flux data was presented.

Study	Site	Time	Latitude:Longitude	Meas Type	Concentration Ratios (mg/L)	Flux Ratios kg/ha/yr	% composition	Reference Number
1.	Minnesota	1971–1973	44 N, 93 W	B/TON		2.7:2.3:**2.3**	36:32:**32**	Verry and Timmons 1977
2.	Rhode River, Chesapeake Bay	1973–1991	38 N, 76 W	B/TON	0.28:0.47:**0.29**	3.12:5.18:**3.45**	27:44:**29**	Jordan et al. 1995
3.	Central Amazon Basin, Brazil	1983–1985	3 S, 60 W	W/DON		3.58:**2.45**	60:**40**	Williams et al. 1997
4.	Lewes, DE	1993–1994	38 N, 75 W	W/TON	0.19:0.30:**0.09**	14.8:23.5:**8.7***	32:50:**18**	Russell et al. 1998, Scudlark et al. 1998
5.	Gainesville, FL	1976–1977	29 N, 82 W	W/TON	0.1:0.19:**0.41**	1.2:2.3:**5.0**	14:27:**59**	Hendry and Brezonik 1980
		1976–1977	29 N, 82 W	B/TON	0.12:0.23:**0.47**	1.5:2.8:**5.7**	15:28:**57**	

Table 4. Continued

6.	Harp Lake, Ontario	1974	45 N, 79 W	Snow/TON	0.14:0.19:**0.16**		28:39:**33**	Nichols et al. 1978
				W/TON		10.1:**4.4**	70:**30**	
7.	Alberta, Canada	1975–1976	54 N, 113 W	W/TON	0.26:0.25:**0.15**	1.34:0.67:**1.11**	43:21:**36**	Caiaza et al. 1978
				D	0.19:0.03:**0.39**	5.56:0.48:**8.16**	40:3:**57**	
8.	New Zealand	1958	41 S, 175 E	Snow/TON	0.14:0.001:**0.11**	nd	56:0:**44**	Wilson 1959
9.	Taupo, New Zealand	1981	41 S, 174 E	W/DON	**0.13**	**2.2**		Timpereley et al. 1985
		1982				**1.0**		
	Japan		36 N, 138 E		**0.24**	**6.3**		
10.	Kampala, Uganda	≈1960	0 N, 32 E	W/TON	1.12:1.25:**2.73**	nd	22:25:**53**	Visser 1964
11.	Lake Valencia, Venezuala	1976–1978	10 N, 67 W	B/DON	nd	2.43:1.28:**1.33**	48:26:**26**	Lewis 1981
12.	Southern Chile	1987–1994	51 S, 71 W	Cloud/TON		1:1:**8****	10:10:**80**	Weathers et al. 1998
13.	Como Creek, CO	1975–1978	35 N, 105 W	B/DON	0.19:0.27:**0.18**	1.25:1.80:**1.22**	29:42:**29**	Grant and Lewis 1979

Table 4. Continued

Study	Site	Time	Latitude:Longitude	Meas Type	Concentration Ratios (mg/L)	Flux Ratios kg/ha/yr	% composition	Reference Number
14.	La Selva Biological Station, Costa Rica	1992–	10 N, 84 W	W/DON	0.12:0.07:**0.09**	3.6:2.4:**2.5**	42:28:**30**	Eklund et al. 1997
		1993–				2.6:1.8:**1.0**	48:33:**19**	
		1994–				5.0:6.6:**3.4**	33:44:**23**	
15.	UEA, United Kingdom	≈1994	54 N, 2 W	W/DON	0.97:**0.25**		80:**20**	Cornell et al. 1995
	Czech Republic		49 N, 15 E	Snow/DON	0.27:**0.1**		73:**27**	
	North Carolina		35 N, 79 W	W/DON	0.48:**0.13**		79:**21**	
	Maraba, Amazonia, Brazil		5 S, 49 W	W/DON	1.08:**0.31**		78:**22**	
	Recife, Brazil		8 S, 35 W	W/DON	0.13:**0.04**		75:**25**	
	Bermuda		32 N, 64 W	W/DON	0.15:**0.22**		41:**59**	
	Tahiti		17 S, 149 W	W/DON	0.04:**0.18**		16:**84**	
	NE Atlantic 50–80N		50–58 N, 20 W	W/DON	0.05:**0.11**		38:**62**	
	NE Atlantic 32–50N		32–50 N, 20 W	W/DON	0.04:**0.08**		33:**67**	
16.	Sweden, Goteborg	1977	57 N, 12 E	W/TON		**5.8:4.4:1.3*** **	50:38:**11**	Malmquist 1978
17.	Harvard Forest, MA	1993–1994	42 N, 72 W	W/DON		3.5:5.1:**0.6**	37:56:**7** 1996	Currie et al.
18.	SE Wyoming (pine forest)	1979–1982	41 N, 105 W	B/TON	0.2:0.3:**0.27**		26:39:**35**	Fahey et al. 1985

Table 4. Continued

19.	Sierra Nevada, California	1987–1993	36 N, 118 W	W/DON		1.11:0.94:**1.33**	33:28:**39**	Chorover et al. 1994
20.	Manaus, Brazil	≈1980	3 S, 60 W	W/DON		1.8:0.4:**3.9**	30:6:**64**	Brinkman 1983
21.	Central Amazon Basis Lake Calado	1984–1985	3 S, 60 W	W/DON		2.4:1.3:**2.5**	39:20:**41**	Lesack and Melack 1996
22.	Southern North Sea	1988–1989	50–55 N, 0–5 E	W/DON	0.52:0.77:**0.09**		38:56:**6**	Rendell et al. 1993
23.	South Africa, Durban	1976–1977	30 S, 31 E	W/DON	0.37:0.34:**0.57**	4.22:3.95:**10.79**	22:21:**57**	Simpson and Hemens 1978
24.	Emerald Lake, Sequoia Nat. Park, CA, U.S.A.	1985–1998	36 N, 118 W	B/DON		1.0:1.6:**0.7**	30:48:**21**	Sickman et al. *this issue*
25.	HJ Andrews Forest, OR, U.S.A.	1977–1998		B W		0.33:0.46:**0.64** 0.41:0.69:**0.16**	23:32:**45** 32:55:**13**	Vanderbilt et al. *in review*

Table 4. Continued

Study	Site	Time	Latitude:Longitude	Meas Type	Concentration Ratios (mg/L)	Flux Ratios kg/ha/yr	% composition	Reference Number
26.	Hubbard Brook, NH, U.S.A.	1995–1997	42 N, 72 W	B/DON		2.6:5.5:**1.9**	26:55:**19**	Campbell et al. 2000
	Cone Pone, NH, U.S.A.		42 N, 72 W	B/DON		3.0:3.9:**1.4**	36:36:**16**	
	Sleepers River, VT, U.S.A.		44N, 72 W	B/DON		3.1:4.3:**1.8**	34:47:**19**	
27.	Morehead City, NC, U.S.A.	1995	29 N, 82 W	W/DON	**0.08**	1.96:**0.69**	74:**26**	Peierls and Paerl 1997
	Total Number Studies				**26**	**31**	**41**	
	Mean Value				**0.30 mg/L**	**3.1 kg N/ha/yr**	**34.0 %**	
	Median Value				**0.17 mg/L**	**2.2 kg N/ha/yr**	**30.0 %**	
	Standard Error				**0.10 mg/L**	**0.5 kg N/ha/yr**	**2.6 %**	
	Standard Deviation				**0.51 mg/L**	**2.8 kg N/ha/yr**	**16.7 %**	

*Extrapolated from the average flux of 60 daily measurements.

**Estimated from a cloudwater deposition estimate of 10 kg N/ha/yr of total N loading and an average 80% contribution of organic N to deposited N.

***Annual flux estimated from the arithmetic mean of 5 months of sampling.

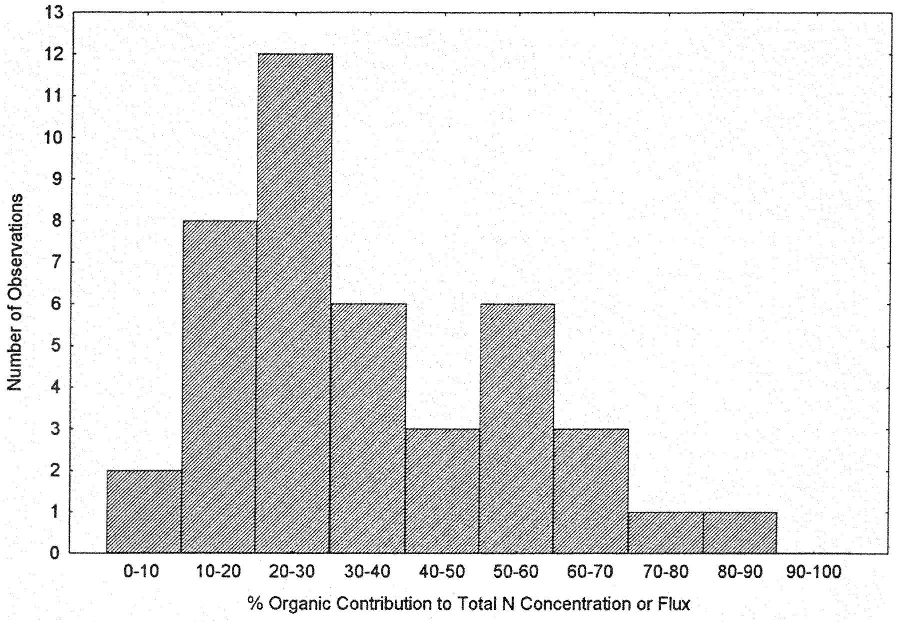


Figure 3. Histogram of the % organic contribution to deposition concentrations or fluxes from data listed in Table 4.

fraction of deposition can contribute between 7 and 80% of the total N in deposition. Although the range of the organic fraction in precipitation is quite large, 60% of the measurements in Table 4 have an organic fraction between 10% and 40%. Table 4 contains both TON and DON fractions and it would be reasonable to expect that unfiltered samples (TON) would contain a greater organic fraction than filtered samples (DON) due to the contribution of particulate organic N. On average the DON measurements in Table 4 have an organic fraction of 33% (plus/minus 19%) and TON measurements are 41% (plus/minus 18%) of total solution N. Although the mean contribution of TON to total N in deposition is higher than for DON, these two types of deposition samples are not different from one another statistically (t-test, t=1.24, p=0.21). The fractional distributions of percent organic N deposition are shown in Figure 3. Considering all the fractional organic contributions together, on average 34% of deposited N is in organic form globally with an average organic N concentration of 0.3 mg L^{-1} in deposition. Median, standard error, standard deviation values for the organic contributions to deposition are given in Table 4.

Fluxes of organic N in precipitation also show a large range of rates from 0.6 to 10.9 kg organic N ha^{-1} yr^{-1} with a median deposition rate of 2.2 kg organic N ha^{-1} yr^{-1} (Table 4). One significant and unanswered issue in understanding AON deposition is whether AON deposition is impacted by human activity. The deposition of inorganic N constituents has increased substantially in most areas of the industrial world (Prospero et al. 1996; Vitousek et al. 1997). N deposition may lead to increased productivity and substantially increased rates of C sequestration under certain conditions and these calculations are relatively sensitive to the amount of N deposited to ecosystems (Townsend et al. 1996; Holland et al. 1997). In addition, high rates of inorganic N deposition fluxes can lead to the acidification of streams and ecosystems and over time, may lead to declines in terrestrial productivity (Agren and Bosatta 1988; Aber et al. 1991). Over oceans, the role of both organic and inorganic N deposition has been evaluated and both types of N deposition may play important roles in the regulation of primary productivity (Paerl et al. 1990; Paerl 1995). There are some indications that the deposited DON in precipitation is relatively labile and in this sense, it would behave similarly to inorganic N in its effects on the biotic activity of an ecosystem (Timperley et al. 1985; Seitzinger and Sanders 1999; Paerl et al. 1990; Paerl 1995; Herlihy et al. 1997). However given the diversity of potential AON compounds, some deposition of recalcitrant compounds unlikely to be rapidly broken down by microbial activity is possible. In this case, the effects of AON deposition on short-term biotic activity would be less significant. Further investigations are needed to evaluate these possibilities and whether there are differences in the decomposability of marine and continental AON.

Anthropogenic Influences

If the patterns and flux estimates shown in Tables 2 and 4 are correct, then organic compounds contribute substantially to both local and global N deposition rates. Assuming this is true, the question becomes whether these fluxes have a distinct geographic distribution or have exhibited changes over time. Both questions speak to the issue of human influences on AON fluxes. This issue is important because the role of AON in the global atmospheric N budget and ecosystem dynamics is closely related to whether AON fluxes are a stable background component of the N cycle or are increasing alongside the inorganic N species. If AON fluxes are impacted by human activity, then the changing deposition rates will exacerbate the impacts of N deposition on the dynamics of ecosystems and represent a human perturbation to the N cycle that has not received attention in recent evaluations of the global N cycle (c.f. Vitousek et al. 1997).

From a theoretical perspective, AON concentrations should increase, at least in the industrialized world, in response to increased NO_x concentrations due to combustion and agricultural activities, and increased amine emissions from agricultural systems. In addition, AON fluxes may reflect the elevated

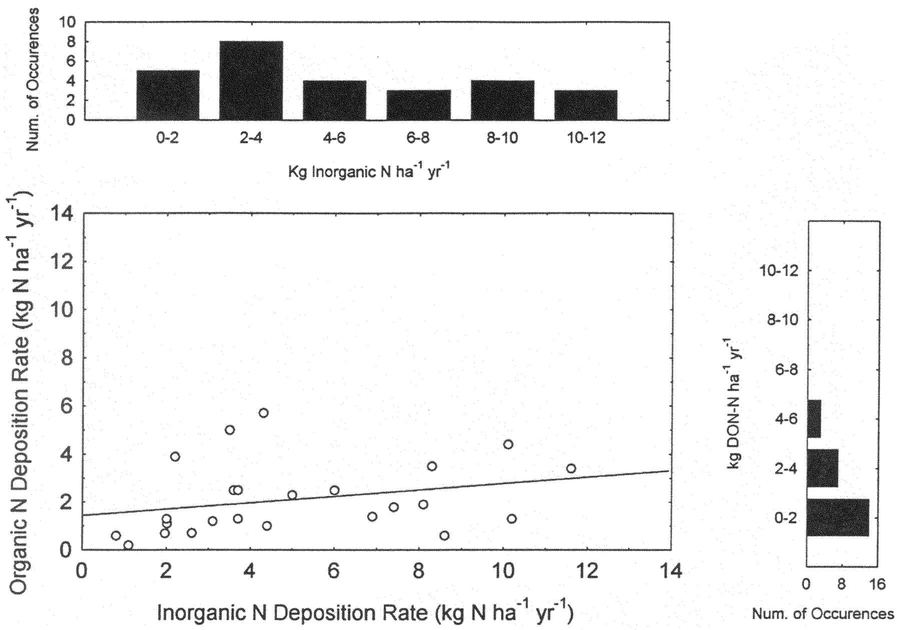


Figure 4. Inorganic vs. Organic N deposition regression and histograms based on the data in Table 4.

concentrations of atmospheric dust described above. For the organic nitrates, the work by Roberts (1990) and the data summarized in Table 2, indicate that organic nitrate concentrations are higher in urban vs. rural environments. Reduced forms of organic N should also be higher near agricultural areas. It is not as obvious, however, if these increased concentrations near areas of human activity will translate into higher concentrations of organic N in wet or bulk deposition.

To examine the relationship between inorganic and organic forms of N deposition, we evaluated the data listed in Table 4. Comparing AON and inorganic fluxes from Table 4, there is no correlation (at the $p < 0.05$ level) between DON flux and NH_4^+ flux (multiple regression analysis (MRA): $r^2 = 0.09$, $F = 2.1$, $P = 0.1$) and no correlation between DON flux and NO_3^- flux (MRA: $r^2 = 0.00$, $F = 0$, $P = 0.9$). In general, as the total deposition flux increases, the fractional contribution of DON to the total N flux decreases. This is shown in Figure 4 where DON fluxes generally remain below 4–6 kg N ha^{-1} yr^{-1} while inorganic N fluxes rise as high as 12 kg N ha^{-1} yr^{-1}. If the sources of AON are related to sources of inorganic N and affected by human activities such as industrial activities, then inorganic N and AON should follow similar long-term trajectories. But with currently available data, there is a discrepancy between patterns in AON fluxes in precipitation and the observed concentrations of gaseous and aerosol forms of organic N.

There is relatively little multi-year deposition data for AON. In a study at the Chesapeake Bay, inorganic N fluxes increased from 1979 to 1995 while TON showed a slight downward trend (Jordan et al. 1995). In a relatively unpolluted site in the Sierra Nevada of California, there were no suggestions of a temporal change in DON deposition rates between the mid 1980s and the present (Sickman et al. this issue). Similarly, long term (1983–1992) DON deposition rates at the H.J. Andrews Experimental Forest in Oregon have not increased over time, in contrast to NO_3^- deposition which shows increasing deposition rates in the same period (K. Vanderbilt, Pers. Com.). There also appear to be substantial interannual variations in DON rates in sites where multiple years of data are available and this year to year variation in organic N loads can be on the order of 200 to 300 percent for sites in Costa Rica and in the Eastern U.S. (Jordan et al. 1995; Eklund et al. 1997). These results suggest that AON fluxes have not increased during the past decade, at least not when considered as a bulk organic N in wet deposition. However, until there is more information on the flux rates and concentrations of both bulk AON and its underlying constituents, the long-term trajectory of organic N deposition and the impacts of humans on AON fluxes will remain unknown.

Spatial patterns

The modeled results shown in Figure 2, and the organic nitrate concentration data in Table 2 suggest that organic nitrates might be a likely candidates for the organic nitrogen commonly observed in precipitation. To evaluate whether modeled organic nitrates fluxes could account for the measured AON fluxes in Table 4, we carried out point comparisons of some of the more well documented studies in Table 4 against the results of organic N deposition from the TM3 model for the equivalent grid cell. While this is a very coarse comparison, it allows a rough assessment of the possibility that measured AON fluxes are made up primarily of oxidized AON compounds. For sites in the North-Eastern U.S., the TM3 model predicts organic nitrate loading rates of approximately 0.44 kg N ha−1 yr−1. In comparison, the fluxes for Cone Pond, NH, Sleepers River, VT, USA, Hubbard Brook and Harvard Forest DON deposition estimates are 0.6, 1.4, 1.8 and 1.9 kg N ha^{-1} yr^{-1} respectively (Campbell et al. 2000; Currie et al. 1996). For the La Selva research station in Costa Rica, the TM3 model prediction is 0.9 kg N $ha^{-1}yr^{-1}$ and the measured deposition values range between 1 and 3.4 kg DON-N ha^{-1} yr^{-1} (Eklund et al. 1997). For the Sierra Nevada in California, TM3 predicted oxidized AON fluxes are 0.05 kg DON-N ha^{-1} yr^{-1} compared to measured deposition fluxes of 0.7 to 1.33 kg DON-N ha^{-1}

yr^{-1} (Chorover et al. 1994; Sickman et al. this issue). In the Brazilian and Venezuelan studies listed in Table 4, measured DON fluxes ranged between 1.3 for the Venezuelan site (Lewis, 1982) and 2.5 – 3.9 kg AON-N ha^{-1} yr^{-1} for the Brazilian Amazon (Brinkman 1983; Lesack and Melack 1993) compared to model AON deposition estimates of 0.08 kg AON ha^{-1} $yr^{-1}$for Venezuela and 1.1 kg AON-N ha^{-1} $yr^{-1}$for the Brazilian Amazon. The large differences in modeled deposition fluxes between Brazil and Venezuela and between the western and eastern U.S. result from the transport patterns and source field distributions in the model. Because the Venezuelan and western U.S. sites primarily receive marine air (at the grid scale of the model), they are far from the source fields for NO_x and hydrocarbons that lead to larger deposition of organic nitrates in regions affected by either natural (Amazon) or industrial (eastern U.S.) emissions.

Based on the patterns in oxidized organic N as well as modeled emissions scenarios, we would expect to see the largest PAN deposition rates in continental environments near to large NO_x/hydrocarbon source areas. In contrast, other organic nitrates would be likely to dominate more remote continental sites, particularly in tropical regions. AON fluxes in marine air masses should be smaller than in continental environments due to distance from organic nitrate source fields. Over marine environments, it seems likely that the bulk of the organic species in precipitation would be in amine N form as the result of N fluxes associated with aerosol formation at the ocean/air interface. Particulate deposition could contribute substantially to certain types of measured fluxes but should not be a large factor in the wet only DON measurements in Table 4.

Regardless of the composition of AON, and assuming that the organic nitrate deposition estimates from the TM3 model are an upper bound on the possible flux, then there remains a missing organic N contribution to most measurements of organic N in precipitation or bulk deposition samples. There are several possibilities for what could lead to this missing contribution. First, the measurements may be in error. However, although the problems with AON measurements are significant, it is difficult to accept that out of 41 studies listed in Table 4, which span a range of both analytical and measurement approaches, each of the studies is systematically biased. On the contrary, the fractional contribution of AON to the total N load is surprisingly consistent across a range of sites and over many years. A second possibility is that there is a gap in our understanding of the potential sources of AON that leads to an underestimate of the role of reduced N species in the AON flux, particularly for more unpolluted or marine influenced areas. A third possibility is that there are other sources and types of organic compounds in the atmosphere that are simply not accounted for in existing studies. At this point, we cannot rule out either the second or third possibilities described here.

Organic C:N ratios:

The ratio of C:N in AON may help in identifying sources of AON. Of the various potential contributors to the atmospheric organic flux, many of the compounds have somewhat different C:N ratios. For example, bacterial C:N ratios generally vary between 5 and 10 while soils vary between 15 and 30 (Holland and Coleman 1987; Paul and Clark 1996). Amino acid C:N ratios vary from 3 (Glycine, Alanine & Valine) to higher numbers for aliphatic amino acids, which can have larger C:N ratios of 5–16 (Beyer and Walter 1997). For the organic nitrates such as nitric acid esters and hydroxy nitric acid esters C:N ratios vary between 2 and 12 with most compounds within the 2–6 range. PAN has a C:N ratio of 2 and the other peroxycarboxylic nitric anhydrides vary between 7 and 11 (Roberts 1990). Organic C:N ratios for several studies are shown in Table 5 and average 12.3. There is a large range in AON C:N ratios from 8.4 to 21.9 but the most notable feature of these values is that they are clearly higher than C:N ratios of free amino acids or PAN. These measurements are also higher than the majority of the C:N ratios of organic nitrates and higher than many of the aliphatic amino acid compounds. While AON deposition certainly contains a mix of compounds and could indeed contain some contribution of organic nitrates, PAN or amino acids, these data also suggest that there is a contribution of higher C:N ratio material such as that observed in soils or plant material or some other, as yet unidentified, contributor to the AON flux.

Conclusions

This data compilation suggests that fluxes of organic nitrogen in deposition may be substantial contributors to the total atmospheric N flux. There are high concentrations and fluxes of AON for a variety of measurements including bulk, wet and event collections and for both filtered and unfiltered samples. There are no clear indications that AON fluxes are related to inorganic N deposition rates. Nor do we find any obvious relationship between AON fluxes and the relative unpolluted or polluted, marine or continental nature of the deposition sites. On average AON fluxes or concentrations contribute one third of the total N in precipitation but the available data are skewed toward relatively clean regions of the atmosphere.

There are several possible sources of AON including organic nitrates, reduced organic N, dust and biological AON. Of these sources, only the

Table 5. Organic Carbon Fluxes and DOM C:N ratios

Site	Time	DOC Flux kg ha^{-2} yr-1	Organic C:N ratio	Reference
Gainesville, Florida, U.S.A.	1976–77	63.2	12.6	Hendry and Brezonik 1980
	1976–77	115.3	20.2	
Lake Valencia, Venezuela	1976–1977	13.4	10.1	Lewis 1981
Como Creek, CO, U.S.A.	6/75 – 10/78	10.29	8.4	Grant and Lewis 1981
Southeast WY, U.S.A.	1979–1982		10	Fahey et al. 1985
Rhode River, Chesapeake Bay, U.S.A.	1973–1991	39.9	11.4	Jordan et al. 1995
Harvard Forest, MA, U.S.A.	1993–1994	13.8	21.6	Currie et al. 1996
La Selva Research Station,	92–93	27.9	11.2	Eklund et al. 1997
Costa Rica	93–94	21.9	21.9	
	94–95	35.6	5.4	
Hubbard Brook, NH	1995–	15.5	8.1	Campbell et al.
Cone Pond, NH	1997	14.1	10	2000
Sleepers River, VT	17.2	9.5		
Mean DOM C:N Ratio			**12.3**	
Standard Deviation			**5.4**	

organic nitrates species, including PAN, and dust fluxes appear to have sufficient atmospheric concentrations or fluxes to account for a large portion of the observed AON flux at most sites. Amine forms of N are likely important to AON over marine environments but are unlikely to have sufficient concentrations to account for the deposition of AON, even in sites influenced by marine air. Our preliminary comparisons of modeled (organic nitrate and PAN) and measured AON deposition rates suggest that there are sources of AON that are not accounted for in current measurements of any of the AON classes described above. The C:N ratios of atmospheric organic deposition suggest that there is some contribution of material with C:N ratios greater than 10 to deposition fluxes which cannot be explained by either amine N or organic nitrate N. Possible sources of these higher C:N ratio material could include dust for bulk, unfiltered AON samples and other soil or plant based materials however, there is no data with which to evaluate this possibility.

The role of AON in the global N cycle and the atmospheric N budget appears to be significant. Preliminary model based estimates of the organic nitrate and PAN contributions to N deposition suggest that approximately 10 Tg of AON may be deposited annually. Model data comparisons and our data compilation suggest that this estimate may represent the low end of the total AON flux. Given contemporary reactive atmospheric N sources of 48–164 Tg of N (NH_3 + NO_x) and our data based median fractional AON contribution to deposition of 30%, we suggest that global AON fluxes could be as high as 14–50 Tg. While the results of this study indicate that the global AON fluxes are almost certainly higher than traditionally assumed, substantial work is needed before these flux estimates can be taken for anything other than a first order approximation. However, they highlight the need for increased attention to measurements and evaluations of organic N deposition.

Acknowledgements

This work was initiated as part of the International SCOPE N Project, which received support from both the Mellon Foundation and from the National Center for Ecological Analysis and Synthesis. The work was supported by the Mellon Foundation, the Max Planck Institute for Biogeochemistry and The National Center for Atmospheric Research (NCAR). NCAR is operated by the University Corporation for Atmospheric Research under the sponsorship of the National Science Foundation. T. Zbacnik was instrumental in the review of literature & J. Sultzman aided in model analysis. J. Baron and two anonymous reviewers provided helpful comments on an earlier version of this manuscript.

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