

FINAL REPORT

EPA Chesapeake Bay Program Workshop Meeting

"Atmospheric Organic Nitrogen Deposition"

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The Scientific and Technical Advisory Committee (STAC)
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I. ABSTRACT

Atmospheric organic nitrogen (AON) is an important nitrogen component with significant deposition to many natural waters. The range and quality of the data are varied, but deposited organic nitrogen (DON) is ubiquitous globally, both in extent and magnitude.

The Environmental Protection Agency's Chesapeake Bay Program (CBP) sponsored a workshop 20-21 May 1998 at the University of Maryland (College Park). The purpose was to (1) determine the current knowledge of organic nitrogen in atmospheric deposition, and (2) establish research priorities needed to obtain an adequate database for coastal waters such as Chesapeake Bay.

Workshop participants concluded that both the abundance of organic nitrogen in the atmosphere, and its proportional deposition is likely to have an effect on aquatic ecosystems. However, knowledge is deficient in the most critical areas, including the nature of atmospheric speciation, transformation, scavenging, sampling, analysis, and ecosystem response. This deficit can only be addressed by the careful design and execution of fundamental research in these areas, such as developing stable isotopic tools and adequate analytical methods, and designing joint intercalibration and field exercises.

II. EXECUTIVE SUMMARY

A. *Current Knowledge of Atmospheric and Deposited Organic Nitrogen*

1) Atmospheric Sources

Major sources of primary AON include both natural emission sources (such as soil humic substances, animals, and vegetation), and anthropogenic ones (such as combustion processes, manufacturing, animal husbandry, food processing, waste treatment, and landfills). The atmosphere also is a secondary source of AON when reactive inorganic forms of nitrogen oxidize vapor phase hydrocarbons to produce, for example, alkyl and substituted alkyl nitrates. The reaction pathways for photochemical conversion of individual, vapor phase organic compounds are complex and can produce many different N-containing products from a single organic reactant. As shown in Figure 1, the original composition and form (vapor, condensed phase) of the organic primary emission can be converted into N-containing material.

Much is known of industrial and vehicular emissions of N gases and particles to the atmosphere (primary emissions) since these are both regulated by and monitored for compliance with local, state, and federal ambient air quality standards. Primary emissions of N-containing gases and particles from biological sources are not well understood in terms of chemical composition or magnitude of a given source. However, photochemical sources of secondary AON are only well understood for simple gas phase species such as alkyl nitrates and for some aromatic nitrocompounds.

2) Atmospheric Processing

In a broad sense, the atmosphere can be regarded as a processing unit for organic nitrogen compounds that are distributed between the vapor and condensed phases, including particles and droplets (Figure 1). These compounds represent a wide cross section of nitrogen functional groups (for example, amines, amides, nitriles, nitrogen heterocycles, nitroaromatics, and alkyl nitrates) with both primary and secondary sources. Both seasonal and diurnal trends are observed in AON atmospheric concentrations, some of which are produced secondarily as a result of photochemical reactions within the atmosphere. The reported AON locations now include urban, rural, and remote sites in North American, European, Arctic, and open marine atmospheres.

It is expected that the inventory and occurrence of AON compounds will continue to expand rapidly as advances occur in both sampling technologies and molecular-level analytical techniques. We know more about oxidized N compounds (such as alkyl nitrates) than reduced N compounds (such as amines) because of emission control studies.

3. Deposition Modes

Organic nitrogen vapors and condensed phase species can deposit from the atmosphere via wet and dry depositional processes. However, no simple relationship exists between the sources of AON and how, where, and in what form (chemical or physical) the AON will be deposited as DON. In general, the chemical composition of AON material governs its solubility in aqueous media, where pH and temperature-dependent chemical

equilibria must also be considered for individual compounds. Flux determinations of AON as condensed phase species is further complicated by particle diameter considerations (in other words, gravitational settling, impaction and entrainment by falling raindrops, and condensation nuclei for water vapor).

Essentially, no direct measurement exists for that portion of AON removed by dry deposition mechanisms. Major species of AON must first be identified and then accommodation coefficients must be either determined experimentally for candidate AON compounds or inferred from inorganic analogues. Preferential scavenging of AON constituents by wet or dry mechanisms and the residence or transport times of AON compounds are also not well known.

4) Collection and Analysis

The speciation of both AON and DON is poorly characterized primarily because of limitations in available measurement techniques. However, on timescales corresponding to the collection of DON in precipitation, an important fraction can be labile and disappear from fresh samples within hours. The cause of these losses has not been determined, but it may involve postcollection chemical transformations in the aqueous phase. Available evidence suggests that losses from microbial uptake or surface absorption are probably of relatively minor importance.

The most widely used measurement techniques for DON involve conversion of all N species in precipitation to inorganic nitrogen (DIN) species, which are subsequently analyzed to yield total N. Thus DON is calculated as the difference between total N and the sum of DIN prior to treatment. Because calculated DON often represents the difference between two relatively large numbers, resulting data are associated with large uncertainties, which frequently approach or exceed the magnitude of the corresponding DON signal. Quantitative conversion of all N species to a labile analyte and accurate analytical techniques are needed to prevent large bias in the resulting data.

5) Biological Responses to DON

There is assumed to be some bioavailability and ecological consequences of AON externally derived and directly deposited as DON to both terrestrial and aquatic ecosystems. The impact of this deposition depends on transport and transformation processes that occur between systems, as well as physical and biological transformations within the receiving system. The role of DON can be as a nutrient source, an energy source, a toxicant, or all three depending on the compounds deposited, the rates of deposition, and the biota present.

Answers to how many AON components are in DON and which are biologically available are critical to begin to assess the impact on receiving ecosystems. While the chemical composition of DON is not well known, we do know that a number of bio-active types of organic nitrogen compounds are present in DON, including amino acids, phenylalanine hydroxylases and organo-nitrates. Bacteria are known to utilize each of these compound classes to a greater extent, as in the case of amino acids, or to a lesser extent, as in the case of PAHs.

Phytoplankton also can use some small molecular weight organic compounds (such as amino acids or urea) following decomposition by extracellular enzymes. Some of the compounds identified in atmospheric deposition have known toxic properties that could be

reached at typical atmospheric flux rates. To date, the bioavailability or toxicity of the identified DON compounds has been inferred mostly from laboratory studies using isolated cultures in controlled bioassays.

Variations in size, shape, geology, climatic regimes, hydrology, flora, and fauna in these ecosystems can lead to distinct differences in ecosystem "sensitivity" in terms of biotic responses to and ecosystem assimilation of DON. This information would be fundamental to evaluate the extent to which AON should be controlled and to determine which specific sources, if any, should be targeted for reduction in DON. To gather the data would involve field monitoring of chemical forms and target taxa or communities over a range of temporal and spatial scales, and conducting bioassays of either cultured "indicator" taxa or natural communities.

The contrasting physiographic, hydrodynamic, and biotic features among ecosystems can lead to a range of effects. These could be positive (for example, increased fertility and fisheries yields) or negative (for example, harmful algal blooms and toxicity) responses to atmospheric, as well as terrigenous, organic nitrogen loadings along geographic gradients. This necessitates comparative regional studies of the role of DON (and AON in general) in determining ecosystem structure and function.

B. Research Priorities for Atmospheric and Deposited Organic Nitrogen

1) Atmospheric Speciation Studies

Little is known about the magnitude of AON fluxes to the Earth's surface, or how major functional groups of AON species are removed by wet- or dry-deposition processes. Thus, there should be strong support for a series of field intensive experiments designed to understand the presence of organic nitrogen in the atmospheric budget and its role in the surface flux of DON (gases and particles) to the Earth's surface. Reliable, species-specific measurements of AON in all phases are limited and therefore needed. In precipitation these are often inconsistent and typically correspond only to minor fractions of estimated DON.

2) Intercomparison Studies

The highest priority is to compare available DON techniques including collection, preservation, handling, and analysis. Ideally, such comparisons should be conducted in the context of a mass balance based on parallel, species-specific measurements of constituent DON components. Sample stability and recovery must be rigorously tested, with immediate analysis or preservation of samples in the field during collection. Such intensive protocols make measurements over large spatial or temporal scales difficult and expensive. The effects of sample filtration on the DON composition in precipitation should also be examined.

3) Stable Isotope Studies

Stable isotopic measurements of deposited N should also be useful for identifying atmospheric sources and processes, as well as for assessing the distribution and biological effects of DON in aquatic and terrestrial ecosystems. Especially important will be new field studies, which incorporate in situ mass spectrometer instruments to analyze an ambient

isotopic sample without sample preconcentration and can produce molecular-level information at the low parts per billion level. However, the collection, preservation, and analytical techniques may alter nitrogen speciation and consequently isotopic composition.

4) Ecosystem Response Studies

Once the important compound classes have been identified, the fate of DON can be determined using combinations of bioassays, field measurements, and modeling. Most of what is known about organic N is based on experimental evidence for a few compounds and for isolated microbial communities. The complete effect of the total DON pool that reaches ecosystems will be more challenging to measure.

The separation techniques currently employed to isolate AON for use in biological response experiments may also significantly alter its composition and thus biochemical behavior. By necessity, such experiments preclude the use of biocides for preservation, and so associated implications must be considered when interpreting these results.

Clear knowledge is needed on which DON compounds are utilized within ecosystems and what impact the compounds have on ecosystems. But the effort required to determine the ecological impact of every DON compound would be considerable and probably unnecessary. Also, it would be difficult to isolate the impact of DON alone amid numerous other multiple stressors. Instead, information on the sources and identities of major AON compounds can be combined with knowledge on bioavailability and ecological significance in order to distinguish the critical compounds or their classes.

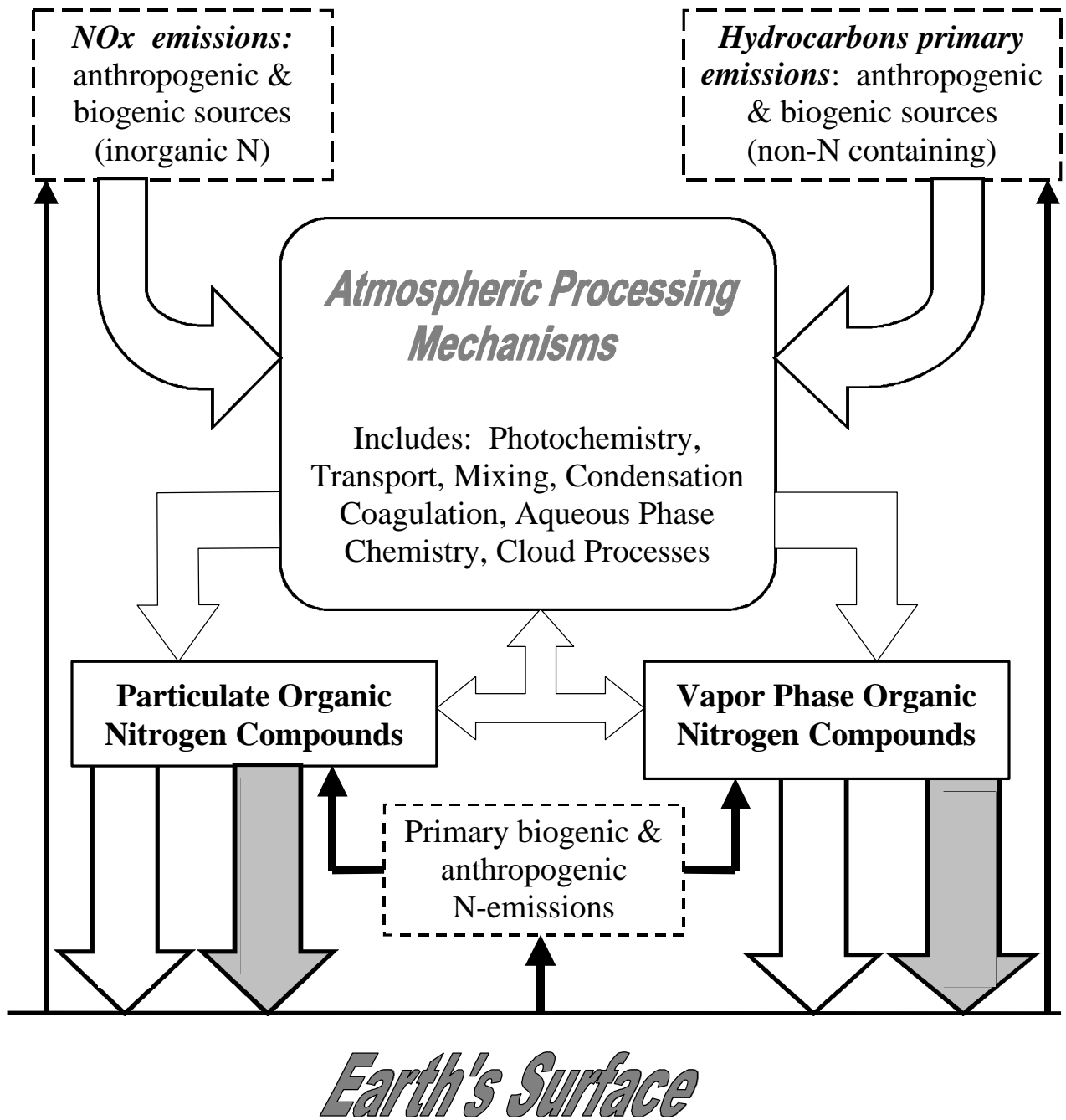


Figure 1. The atmosphere as a source and processing unit of organic nitrogen compounds to the Earth's surface.

IV. WORKING GROUP REPORTS

Working Group I: **Atmospheric Organic Nitrogen**

Group Members: Monica Mazurek (chair), Russ Dickerson (rapporteur), Robert Duce, James Galloway, Krystyna Gorzelska, Grant Gross, Bruce Hicks, Steve Macko, William Munger, Julie Thomas

The specific instructions for Working Group I were: (1) to assess the current state of knowledge concerning the sources, composition and atmospheric removal mechanisms for atmospheric organic nitrogen compounds (AON); and (2) to identify and prioritize a research agenda for organic nitrogen deposition and receiving ecosystems. The group considered these topics through a series of questions. How well each of these topics are currently understood is indicated in the subsection discussions. In addition, prior to answering the specific working group questions, members considered several fundamental issues dealing with: (1) the definition of nitrogen substances in the atmosphere and in dry and wet deposition; and (2) the use of literature reported values for nitrogen compounds measured in deposition samples.

State of the Science

The working group considered existing information reported in the open literature. Major questions addressed by the group focused on the composition of atmospheric organic nitrogen compounds, their sources, and their removal mechanisms via wet and dry deposition.

In a broad sense, the atmosphere can be regarded as a processing unit for organic nitrogen compounds that are distributed between the vapor and condensed phases (particles and droplet) (Figure 1). Direct emissions from anthropogenic and biogenic sources constitute two dominant sources of primary AON chemical substances. One other important source of AON species is through chemical reaction in the atmosphere itself. As shown in Figure 1 (top section), this process involves reaction of oxides of nitrogen (NO_x) with reactive hydrocarbons (as vapor phase or condensed phase substances) to form N-containing organic compounds (secondary AON). The photochemically derived AON is processed further within the atmosphere, and along with the primary nitrogen-containing substances, eventually is removed from the atmosphere as wet or dry deposition (Figure 1, bottom section). The chemical forms of AON that are deposited (wet or dry) to the Earth's surface are distributed as particle or vapor phase materials.

AON Chemical Composition. Understanding the chemical composition of AON is the first major question addressed by the working group. Specifically, available information was considered concerning AON in different atmospheres (urban, rural, remote), their species (gases, particles), and concentration ranges. Graedel et al. (1986) gives an extensive summary of atmospheric organic-N compounds. In this report alone, nearly 400 organic nitrogen chemicals are listed systematically by N-compound class and functional group category (nearly 20 major N categories). More recent reviews (Finalyson-Pitts and Pitts, 1986, 1997; Flocke et al., 1998; Seinfeld and Pandis, 1998) and individual field studies (e.g., Beine et al., 1996; Shepson et al., 1993; Rogge et al., 1993ab, 1994; Atlas et al., 1991, 1992, 1993; Buhr et al., 1990; Ridley et al., 1990; Muthuramu et al., 1993, 1994; Nielsen et al., 1995; Roberts et al., 1996; O'Brien et al., 1995, 1997; Bertman et al., 1995; Fraser et al., 1996; Flocke et al., 1991, 1998) have expanded the number of individual AON species identified, along with locations and ambient concentrations. The AON compounds (reported as gas and condensed phase species) represent a wide cross-section of chemical functional groups, including reduced nitrogen forms (e.g., amines), amides, nitriles, nitrogen heterocycles, nitro-aromatics, and alkyl nitrate compounds. Both seasonal and diurnal trends are observed in the atmospheric concentrations of alkyl nitrate compounds. This chemical form of AON is formed predominantly as a result of photochemical reactions within the atmosphere. The reported locations now include urban, rural and background sites in the North America and Europe, the Arctic and remote marine atmospheres. Surface concentrations and ambient concentrations aloft (e.g., aircraft sampling platforms) also comprise the AON observations. It is expected that the inventory and occurrence of AON compounds will continue to expand rapidly as advances occur in both sampling technologies and molecular level analytical methods techniques. Especially important will be new field studies that incorporate *in situ* mass spectrometer instruments which analyze an ambient sample without sample preconcentration and can produce molecular level information at the low parts per billion level (e.g., Eisele et al., 1992; Noble et al., 1996; Prather et al., 1994; Salt et al., 1996; Thomson et al., 1994; Johnston et al., 1995; Mansoori et al., 1994).

Summary. The issue of AON composition was considered to be the best understood topic for Working Group 1. In general, we know more about oxidized N compounds (e.g., alkyl nitrates) compared to reduced N compounds (e.g., amines). *A moderate level of confidence was attributed to the present state of AON chemical species data.* This level will likely increase rapidly as new molecular level field instruments are deployed routinely in future field studies.

Sources of AON. Organic nitrogen is emitted directly to the atmosphere from anthropogenic and biogenic sources as either vapors or condensed phase materials (Figure 1). Major sources of the primary AON are combustion processes, manufacturing, animal husbandry, food processing, waste treatment, landfill emissions, soil dust (humic substances), and direct biomass emissions from animals and vegetation (Graedel et al., 1986; Finlayson-Pitts and Pitts, 1997; Rogge et al., 1993a-c, 1994). The atmosphere also is a source of AON (secondary species). Reactive inorganic forms of nitrogen (NO_x) can oxidize vapor phase hydrocarbons to produce, for example, alkyl nitrates and substituted alkyl nitrates (*e.g.*, Shepson et al., 1993, 1996; O'Brien et al., 1995, 1997; Roberts, 1990; Ridley et al., 1990). The reaction pathways for photochemical conversion of individual, reactive vapor phase organic compounds are complex and can produce many different N-containing products from a single organic reactant (Fehsenfeld et al., 1992; Grosjean et al., 1992; Pandis et al., 1992; Paulson et al., 1990; Seinfeld et al. 1998; Roberts, 1990). As shown in Figure 1 (top), the original composition and form (vapor, condensed phase) of the organic primary emission can be converted into N-containing material. It is especially important to note the particular linkage between the carbon and nitrogen cycles as reactive NO_x species oxidize atmospheric organic matter to form AON compounds.

Summary. The issue of AON sources was considered to be a partially understood topic for Working Group 1. We have greatest confidence in the industrial and vehicular emissions of N gases and particles to the atmosphere (primary emissions) since these are both regulated by and monitored for compliance with local, state and federal ambient air quality standards. Primary emissions of N-containing gases and particles from biological sources are not well understood in terms of major biological sources, chemical composition, or magnitude of a given source. Photochemical sources of AON (secondary AON) is well understood for simple gas phase AON such as alkyl nitrates and for some aromatic nitro compounds. Laboratory and field studies are continuing to expand the list of identified AON gases and condensed phase species that are photochemically derived from anthropogenic and biogenic precursors. Continued efforts in this area particularly involving: (1) heterogeneous systems, and (2) emissions from specific ecosystems will help to establish important sources of AON and their relative importance. *A moderate/low level of confidence was attributed to the present state of AON source information.*

Removal Mechanisms from the Atmosphere. Organic nitrogen vapors and condensed phase species can deposit from the atmosphere via wet and dry depositional processes. However, there is no simple relationship between the sources of AON and how, where, and in what form (chemical and physical) they will be deposited as DON. At present, the magnitude of AON deposition has been measured principally as wet deposition. Very little is known about the dry deposition of N-containing gases and particles. Work by Huebert et al., (1985, 1988) provided early information on atmospheric N deposition. More recent studies by Munger et al., (1996, 1998) report the total N seasonal deposition (wet and dry, reactive vapor phase N-compounds) to a rural forested site in the northeastern U.S. In addition, the contribution of atmospherically reactive nitrogen to the N budget of sensitive watersheds, such as the Chesapeake Bay, is highly uncertain, but estimates based on a variety of theoretical and experimental techniques, center around 25% (Fisher and Oppenheimer, 1988; Doddridge et al., 1992; Valigura 1995; Valigura et al., 1994, 1996). For many of the sensitive pollution receptors, even information on the concentrations of the principal inorganic N species is

sparse and inadequate to determine N fluxes (Fahey et al., 1986. Emmons et al., 1997). As a result, little information exists about the actual chemical species composition of atmospherically derived TON in wet and dry deposition or how this TON is utilized by receiving ecosystems. These gaps in the scientific understanding of AON fluxes to the Earth's surface, its chemical composition, and the relative magnitude of its sources (e.g., biogenic and anthropogenic direct emissions, and *in situ* photochemical processes) limit efforts by watershed and air quality managers in controlling sources of AON to sensitive ecosystems.

Flux information is sparse for individual chemical constituents of AON. Flux measurements for amine N-compounds have been reported (Gorzelska et al., 1992, 1994, 1997; Likens et al. 1983; Mazurek and Simoneit, 1986). In general, the chemical composition of the AON material governs solubility in aqueous media, for which chemical equilibria (pH and temperature dependence) must also be considered for individual compounds. Flux determinations of AON as condensed phase species is further complicated by the particle diameter considerations (i.e., gravitational settling, impaction and entrainment by falling raindrops, condensation nucleus for water vapor). Essentially no information exists for directly measured AON that is removed by dry deposition mechanisms. There are two reasons for this lack of AON dry flux information. First, major species of AON must be identified chemically, and second, accommodation coefficients must be determined experimentally for candidate AON compounds or must be inferred from those determined for inorganic chemicals (e.g., HNO₃). Other issues such as preferential scavenging of AON constituents by wet or dry mechanisms, and the residence and transport times of AON compounds also are not well known understood at present.

Summary. The issue of AON removal mechanisms and fluxes was considered to be the least understood topic for Working Group 1. We know very little about the magnitude of AON fluxes to the earth's surface, or how major groups of AON chemical species are removed by wet- or dry-deposition processes. *A low level of confidence was attributed to the present state of AON chemical species data.* Accordingly, the Working Group members expressed strong support for a series of field intensive experiments designed to understand the role of organic nitrogen in the atmospheric budget and surface flux of reactive nitrogen (gases and particles). Such experiments should be designed to address the following research questions.

Outstanding Research Questions

Research priorities for AON characterization, source determinations, and flux measurements were identified by Working Group I. These priorities are listed in terms of importance to strengthening current scientific understanding of AON deposition:

- 1) Intercompare sampling and analytical methods for TON, filtered DON, and specific DON chemical species to provide accurate flux measurements of these AON components.
- 2) Conduct intensive field experiments in sensitive watersheds to determine the role organic nitrogen in the atmospheric budget and surface flux of reactive nitrogen. These experiments should address concentrations and wet and dry deposition of gas- and particulate-phases species as a function of season.

- 3) Develop an inventory of major AON constituents for key airsheds. (i.e., regional comparison).
- 4) Investigate the flux of nutrient N mass and the lifetime of this AON material.
- 5) Incorporate 15-N analysis as part of the suite of chemical characterization techniques for AON and TN, and TON. This additional quantitative N measurement is useful for identifying the sources of the N and their relative magnitudes and is an independent N mass determination that is critical for the intercomparison experiments as recommended in item (1) above.
- 6) What fraction of TON can be accounted for in terms of individual AON chemical groups?
- 7) What specific AON constituents are toxic to organisms at key receptor locations?
- 8) What is the range of influence for total AON that is deposited to ecosystems or its major N chemical groups (do transport and residence time within an air mass affect AON deposition mass and major chemical constituents, for example)?
- 9) Broaden current understanding of the atmospheric chemistry of photochemical AON, particularly for the class of hydroxy alkyl nitrates. It is important to account for the mass of hydroxy alkyl nitrates that are contributed by biogenic gas-phase precursors such as isoprene.
- 10) Improve DON chemical speciation in wet deposition samples using a variety of analytical measurement techniques that provide quantitative information about functional group and/or molecular compositions.

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Working Group 2:
Sampling, Preservation and Analysis of Organic Nitrogen

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Hypothesis

Our ability to provide reliable information about the concentration, deposition, sources, distribution and ecological effects of atmospheric organic nitrogen depends fundamentally on the use of reliable collection, preservation and analytical methods for DON.

State of the Science

A review of the most recent data on the concentration of organic nitrogen in precipitation, as presented by the workshop participants, reflect a rather wide range of values. One set of measurements for locations including Lewes, DE (Scudlark *et al.*, 1998), Charlottesville, VA (Keene *et al.*, in press; Russell *et al.*, 1998) and eastern North Carolina (Peierls and Paerl, 1997) indicates annual average concentrations in the 5-10 mole/L range. In contrast, mean concentrations reported for Philadelphia, PA (Seitzinger *et al.*, unpublished data), mid-Chesapeake Bay (Jordan *et al.*, 1995), Rhode Island (Nixon and Buckley, unpublished data), and several sites in Texas (Shon, 1994) are all in the 20-50 mole/L range.

While the significantly greater concentrations reported for urban sites (Philadelphia and Houston) could be explained by enhanced anthropogenic emissions, the broad range of concentrations at the rural locations is difficult to reconcile with spatial gradients reported for other chemical constituents measured in precipitation at these sites (*e.g.*, NADP, 1996). Thus, either AON concentrations strongly reflect local sources and are extremely heterogeneous, or there exist basic methodological differences in collection, preservation, handling and/or analytical techniques which cause either positive or negative bias in the resulting data. For example, other studies have demonstrated that inadequate preservation against microbial degradation prior to analysis results in significant negative bias in measured H^+ , associated carboxylic acids, and inorganic N species (*e.g.*, Keene *et al.*, 1983; Keene and Galloway, 1984).

Most of the data on AON have been generated within the past 5 or 6 years, and thus we are still at a fairly early stage in method development and validation. Parallels can be drawn to the learning curve for sampling and analysis of other precipitation constituents, where many of the initial collection and measurement techniques were subsequently demonstrated to be inappropriate. A prime example of this is the measurement of trace elements in precipitation, where much of the early data have been shown to be highly questionable (*e.g.*, Tramontano *et al.*, 1986; Barrie *et al.*, 1987).

Research Questions

1) *The highest priority should be given to inter-laboratory comparisons of measurement*

techniques (including collection, preservation, handling and analytical) for total N, DIN and (by difference) DON.

In the studies cited above, five different analytical techniques were employed to quantify ON in precipitation. Ideally, all of these would all be included in any methods intercomparison. In the first four techniques outlined below, ON is inferred from the difference between TN and DIN measured in sample splits. In using this approach, ON often represents a relatively small difference between two large numbers, and thus, small errors in either measurement translates into a comparatively large uncertainty in the calculated ON concentration. A brief description of the five techniques is as follows:

(1.) Kjeldahl Digest. The literature contains a number of variations on the Total Kjeldahl Nitrogen procedure. The method utilized for the analysis of precipitation (Jordan *et al.*, 1995), which is reported to be particularly effective towards refractory organic N, involves digesting the sample with H_2SO_4 , K_2SO_4 , Se as a catalyst, and H_2O_2 , which reduces all the organic N to NH_4^+ . The digested solution is neutralized with NaOH, the NH_4^+ produced is steam distilled, and is analyzed by standard aqueous chemical methods. ON is thus inferred as the difference in NH_4^+ between digested and undigested aliquots.

(2.) Persulfate Wet Oxidation. All N compounds are oxidized to NO_3^- under alkaline conditions and in the presence of $\text{K}_2\text{S}_2\text{O}_8$. NO_3^- is analyzed by standard colorimetry or ion chromatography, and ON is inferred from the difference in NO_3^- between digested and undigested aliquots.

(3.) UV Photo-Oxidation. All N compounds are oxidized to NO_3^- by exposure to UV radiation, with or without the addition of H_2O_2 . In some applications of this procedure, the oxidation to NO_3^- is reported to be incomplete, with some N species recovered in the form of NH_4^+ . NO_3^- (and NH_4^+ if present) are quantified using standard wet chemistry, and the ON is inferred as the difference between NO_3^- (or $\text{NO}_3^- + \text{NH}_4^+$) in irradiated and non-irradiated aliquots.

(4.) High-Temperature Combustion. All N compounds are oxidized to NO via high-temperature combustion in an O_2 -rich atmosphere. The NO is subsequently quantified using chemiluminescence, and ON is inferred from the difference between TN in combusted aliquots and DIN measured by standard aqueous chemical techniques in uncombusted aliquots.

(5.) Mass Spectrometry. The NH_4^+ is first extracted from the sample using a modified Kjeldahl distillation, and the NH_4^+ is removed by ion exchange using a molecular sieve. The remaining NO_3^- is reduced to NH_4^+ using Devarda's alloy (50% Cu, 45% Al, 5% Zn). The ON that remains is converted to NO_3^- by the UV method described above, then converted to N_2 gas which is measured by the ion beam of the mass spectrometer. An important distinction with the UV method described above, is that the ON concentration is measured directly, and not inferred by difference between TDN and DIN.

A small number of method comparisons within single laboratories have been reported in the literature, but the results are inconsistent and thus inconclusive. Scudlark *et al.*, (1998)

report poor agreement between persulfate oxidation and UV photo-oxidation, with the evidence suggesting that the persulfate method provides a greater oxidation efficiency. Conversely, analyses of rainwater and aerosol extracts reported by Cornell and Jickells (in press) indicate good correlation between results obtained by these two methods, with the persulfate technique yielding concentrations which were systematically *lower* than those obtained by the UV method. In a comparison of ON concentrations obtained using persulfate oxidation and mass spectrometry, Russell (1997) reports poor agreement, with the mass spectrometry method generating higher concentrations. The apparent inconsistencies between studies may simply be related to methodological differences between laboratories (with respect to sample collection, handling, storage, and analysis), but may also be due in part to fundamental differences in AON composition between locations.

Direct intercomparison and intercalibration of measurement and collection techniques for AON are required to resolve the nature of the apparent incongruity in reported results. Facing similar data inconsistencies, the oceanographic community has successfully carried out a method intercomparison for DOC; a similar exercise for DON is currently underway (Hopkinson *et al.*, 1993; Sharp, 1997). Unfortunately, the fundamental dissimilarities between seawater and precipitation, with respect to their chemical matrix and molecular composition of organic matter, preclude the possibility of extrapolating intercomparison results based on marine samples to the analysis of DON samples. However, this exercise may identify potential problems common to both fields, and can help identify the most effective format for how such inter-laboratory comparisons and intercalibrations can be effectively conducted for DON.

A reliable intercomparison must be based on representative samples. Unfortunately, the apparent instability of ON in precipitation reported by some groups (see below) complicates inter-laboratory comparisons. For example, the most commonly used approach involves the distribution of split aliquots from multiple samples to each participant for analysis. However, if a significant and perhaps variable fraction of the DON pool disappears from the splits during shipment or storage, intercomparison results would be misleading. A similar intercalibration approach would entail the analysis of synthetic precipitation samples which have been spiked with a range of known concentrations of a model DON compound or series of compounds. The current limitation to this approach is that very little is known about the specific species that comprise DON, and thus the choice of candidate compounds is uncertain.

Alternatively, researchers and instrumentation can be brought together at a common location, allowing for analysis of freshly-collected samples. This approach not only eliminates any uncertainty related to sample stability, it also presents the opportunity for researchers to work side-by-side, which greatly facilitates the exchange of ideas and direct comparisons of their methods. As demonstrated by the DOC inter-comparison (Sharp, 1997), analytical discrepancies can often be traced to subtle methodological differences, which are often more apparent when observing techniques first-hand. A definitive methods evaluation would be conducted in the context of a *closure* experiment, where the individual ON species are measured in parallel, and the sum of their concentrations compared with the coincidental measurement of total DON concentrations.

All of the above approaches require coordination by a central laboratory, which would be responsible for sample/standard preparation and shipment, compilation and dissemination of the data, and quality assurance/control procedures. In the case of the oceanographic exercise previously mentioned, this represented a large, multi-year effort funded by the National Science Foundation.

2) *The issue of sample stability and preservation needs to be further explored.*

Initial experimental evidence from two laboratories (Scudlark *et al.*, 1998; Keene *et al.*, in press) indicates that AON can be extremely labile. In some unpreserved samples stored at ambient temperatures, virtually all of the ON disappeared within 12 hrs. of collection. Interestingly, although these two studies provided the most attention to sample preservation, the ON concentrations are among the *lowest* reported, which is counter-intuitive to the microbial degradation theory.

It was the opinion of this working group that these experiments need to be reproduced at other locations to more firmly establish this behavior. If the preliminary evidence is borne out, the routine collection of samples for DON analysis will require the use of preservation techniques in the field. Accordingly, the efficacy and potential matrix interferences of various commonly-employed preservation techniques should be examined. Included in this list would be both chemical (*e.g.*, thymol, HgCl₂, chloroform) and physical (refrigeration at 4 degrees C, freezing at various temperatures, sterile filtration) preservation techniques.

3) *The effects of sample filtration on the ON composition in precipitation should be examined.*

Currently there is no experimental evidence on the effects of sample filtration. Although the common nomenclature refers to *dissolved* organic nitrogen, in reality most collection and analysis protocols currently do not employ filtration, and thus represent *total* organic nitrogen. The issue of filtration is both a practical question (*e.g.*, samples are essentially filtered by the ion chromatography columns which are routinely employed for NO₃⁻ analysis) as well as an academic one (*e.g.*, what is the soluble/insoluble phase distribution of DON in precipitation?). The latter point is particularly relevant when comparing DON concentrations from different locations, where reported concentrations can represent either total (unfiltered) or dissolved (filtered) ON.

Concerns with filtration include potential sample contamination at low DON levels, and the possibility of de-gassing volatile DON compounds from supersaturated solutions.

4) *Isotopic measurements may be useful for identifying atmospheric sources and processes, and for assessing the distribution and biological effects of AON in aquatic and terrestrial ecosystems.*

For isotopic collections of AON, three considerations are important: (1) the effect of sample preservation techniques (*e.g.*, biocides) on isotopic measurements should be thoroughly investigated. While sample preservation is a critical issue in quantifying the

inorganic and organic N pools, the use of chemical preservatives could offer N contamination or otherwise interfere with the isotopic measurement. (2) Collection and chemical preparation techniques could potentially bias results. Isotopic fractionation in sampling and processing is a more serious issue, as potential variations among laboratories are considerable. For example, similar chemical compounds can have substantially different isotope values depending on their chemical state, *i.e.*, gas phase *vs* particulate phase. Chemical isolation of AON for biological assays may also compromise the isotopic composition. For example, ion-exchange chromatography, a commonly employed technique, can substantially fractionate both C and N isotopes in amino acids (Macko *et al.*, 1987; Hare *et al.*, 1991). (3) Sufficient quantities of material for bulk and compound-specific analysis need to be considered.

5) *The separation techniques which are currently employed to isolate AON for use in biological response experiments may significantly alter its composition and biochemical behavior.*

Based on the preliminary evidence of DON stability in precipitation, it is quite possible that some fraction of the ON in precipitation may be lost or chemically altered by the sample manipulation used to isolate AON. The use of biocides must be totally avoided in rainwater collections for biological assays. Without further knowledge of the composition of ON in precipitation, it is impossible to predict what effect such sample processing may have.

6) *Some assessment of dry atmospheric deposition of AON requires an initial measurement of the concentrations, size distributions and speciation of AON in atmospheric aerosols, as well as vapor phase organic nitrogen.*

Very little is known about particulate-phase AON. It is likely that aerosol ON, like particulate organic carbon, originates from three major pathways: (1) direct injection in association with mechanically produced aerosol (*e.g.*, sea salt, mineral aerosol, biomass burning), (2) direct scavenging of primary or secondary volatile ON compounds and/or (3) chemical production from precursors within or on the surface of atmospheric aerosols (*e.g.*, Keene *et al.*, 1998 and references therein). Many of the methodological issues discussed above are also relevant for quantification of aerosol ON. A potentially important additional problem unique to aerosol chemistry involves artifact reactions resulting from mixing chemically distinct particles on sampling media. Problems of this nature may lead to significant bias in resulting data (*e.g.*, Keene *et al.*, 1990, 1998). However, such artifacts can be minimized by sampling aerosols as a function of particle size using cascade impactors. Since little is known about the speciation (and thus reactivity) of aerosol AON, the magnitude of potential artifacts associated with sampling aerosol in bulk cannot be reliably assessed at this time.

There are several additional advantages to measuring aerosol AON as a function of particle size. Atmospheric lifetimes against dry deposition vary from a few hours for particles > 10 μ m in diameter, to 5-10 days for particles 1 μ m in diameter. Thus, size-resolved data provide critical information with which to begin assessing associated dry deposition fluxes to ecosystems, and direct the choices of appropriate techniques for the estimation of dry

deposition (*e.g.*, the level of attention that must be directed towards the issues of surface roughness, fetch, and the effects of turbulent eddies on particle deposition). In addition, the size distribution of aerosol AON provides insight concerning the nature of its formation, atmospheric reactivity and chemical speciation.

The recent study of Cornell, *et al.* (1998) provide the only published data on the size distribution of aerosol-phase total organic nitrogen, based on analysis of size fractions obtained using a 6-stage cascade impactor. Although based on analysis of only 2 samples from a single location in the U.K., these data suggest a bimodal distribution. Approximately 40% of the aerosol organic nitrogen was encountered on particles with a diameter of $< 0.3\mu\text{m}$, and more than 50% was found on particles $> 1.5\mu\text{m}$.

Unlike the situation for precipitation and aerosols, no methods currently exist to measure the total concentration of vapor-phase organic nitrogen in air. Methods development and analysis is restricted to quantifying individual compounds or groups of compounds. Concentrations of several classes of volatile ON species in the atmosphere have been reported (see Group 1 report), but clearly additional work, including methods intercomparison and intercalibration, is needed in this area as well.

7) *A knowledge of the composition of specific AON chemical species is needed.*

There exist a number of studies which have quantified the atmospheric concentrations of specific classes of organic N in precipitation and atmospheric aerosols (*e.g.*, primary amines, urea). However, as reviewed by Gorzelska *et al.* (1997), the range of concentrations reported in such compound-specific studies are generally insufficient to account for the total organic-N concentrations observed in this and other studies. For example, many measurements of amine-N in precipitation (Gorzelska and Galloway, 1990; Gorzelska *et al.*, 1992, 1997) report total concentrations $1 \mu\text{M}$, which can account for only a small fraction of the organic-N that has been reported. Such data suggest that DON is primarily comprised of uncharacterized species. On the other hand, some of the highest reported values, in the 5-10 μM range (Galloway *et al.*, 1983; Mopper and Zika, 1987), begin to approach total DON concentrations reported at some locations.

The collective opinion of Working Group 2 is that DON is not dominated by a single compound or class of compounds, but rather is comprised of a *mélange* of compounds whose composition varies in space and time. It is also recognized that some fraction of DON may represent a by-product of secondary reactions involving primary atmospheric emissions (*e.g.*, NO_x and hydrocarbons), as hypothesized by Cornell *et al.* (1995). As discussed above, information on the specific DON compounds or functional groups is germane to a number of critical issues, including (1) generating a representative standard for inter-laboratory comparisons; (2) assessing chemical stability and preservation techniques; (3) evaluating the biological response to AON additions; (4) quantifying dry deposition; and (5) deconvoluting the biogeochemical cycles. It is recognized that such measurements are largely research-level tasks and are not easily addressed.

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Working Group 3:**Bioavailability and Ecological Consequence of Atmospheric Organic Nitrogen**

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Overview

Atmospheric organic nitrogen (AON) is deposited to both terrestrial and aquatic ecosystems. The impact of this externally derived organic matter depends on transport and transformation processes that occur between systems as well as physical and biological transformations within the receiving system. The role of AON can be as a nutrient source, an energy source, a toxicant, or all three depending on the compounds deposited, the rates of deposition, and the biota present. Once the important compound classes have been identified, then the fate of AON can be determined with a multimedia approach that includes bioassays, field measurements, and modeling. Most of what is known about organic N is based on experimental evidence for a few compounds and for isolated microbial communities. The complete effect of the total AON pool that reaches ecosystems is more challenging to measure.

Before the question of the bioavailability and ecological consequence of AON can be fully answered, it will be important to have at least partial answers to two questions addressed by the other two working groups. 1), *Do the measurements of AON in deposition collectors provide a good approximation of the actual AON input to terrestrial or aquatic systems?* 2), *What are the major compounds or compound classes that reach the receiving ecosystems?* We are gradually improving our ability to measure AON in wet and dry deposition from collectors. These collector measurements may differ from the actual deposition of AON to soil, vegetation or water surfaces; the magnitude of the difference will provide ecologists with a $A_{true} \cong$ flux estimate. The pool of AON has many, and probably variable components. The identification of the most important compound classes (based on flux and/or toxicity) will help direct current and future research needed for evaluating the ecological impact of AON.

Many questions were raised (with only a few answers) about the ecological impact of organic N and more specifically, AON on terrestrial and aquatic ecosystems. Here we present four prioritized topics that should be addressed to effectively quantify and qualify the bioavailability and consequences of AON deposition:

1. What DON compounds or compound classes are most and least biologically active (including nutritive or toxic effects) at natural deposition rates to the environment?

The question of which AON components are biologically available (and how much of those components are in DON) is critical in order to begin to assess the impact of DON on receiving ecosystems. While the chemical composition of DON is not well known, we do know that a number of different types of organic nitrogen compounds are present in atmospheric deposition (e.g., amino acids, PAHs, organo-nitrates, etc.). Bacteria are known

to utilize each of these compound classes to a greater (amino acids) or lesser extent (PAHs). Phytoplankton also can use some small molecular weight organic compounds (amino acids, urea, etc.) following decomposition by extracellular enzymes (Antia et al. 1991). Some of the compounds identified in atmospheric deposition have known toxic properties, although the threshold for toxicity may not be reached at typical atmospheric flux rates. The bioavailability or toxicity of the identified DON compounds is inferred mostly from laboratory studies using isolated cultures in controlled bioassays. We know little about which of the specific compounds in DON are available to organisms in the environment, or what their effects (e.g., as a nutrient or as a toxicant) are at the species, community or ecosystem level. There is a clear need for knowledge concerning which of the DON compounds are utilized within ecosystems and what impact DON compounds have on ecosystems.

2. What are the effects (nutrient or toxicity) of these DON compounds at community or ecosystem level?

There are a number of pathways by which organic nitrogen (ON) can be incorporated into biogeochemical cycles once it has entered a system. Typically, bacteria utilize ON for growth, mineralizing ammonia in the process. Protozoa and other microorganisms can feed on the bacteria, transferring the bacterial N to higher trophic levels which also regenerate readily available inorganic N (typically as ammonia). Phytoplankton and higher plants can assimilate the inorganic N to produce new biomass, but bacteria also compete for dissolved inorganic nitrogen (DIN). Phytoplankton also are able to use some DON compounds after mineralization by extracellular enzymes or by direct assimilation of the compounds for use as N or C in cellular metabolic pathways (Antia et al. 1991). An additional pathway of incorporation of ON into terrestrial and aquatic ecosystems is through utilization by fungi. Finally, non-biological pathways such as photochemical reactions may degrade DON to DIN.

The addition of new, biologically available N can increase primary and bacterial productivity especially in N limited ecosystems (e.g. marine). Changes in primary productivity can translate to positive changes at other trophic levels (e.g. increases in fishery yields). However, DON combined with other N sources could contribute to high N loading and the eutrophication of receiving ecosystems (Nixon 1995). In addition to changes in community and ecosystem functions such as primary productivity, heterotrophic activity, and net system metabolism, bioavailable N may also produce changes in community or ecosystem structure. For instance, certain species may have a competitive advantage in assimilating organic N forms leading to changes in dominant taxa (e.g. harmful algal blooms, Berg et al 1997)

Biological responses to AON inputs are assessed by an array of approaches and methods that measure community structure and function. Field monitoring of chemical forms and target taxa or communities usually encompasses a range of temporal and spatial scales, depending on the system size, morphometry, and complexity, and the event frequency and seasonality of DON inputs. Bioassays include either cultured "indicator" taxa or natural communities. They can be incubated under natural conditions (i.e., in situ) or defined laboratory conditions. Bioassay duration can range from hours to weeks, depending on research and management informational needs. Bioassay response parameters should reflect

both community composition (e.g. diagnostic algal photopigment measurements or microscopic, taxa-specific identification and enumeration) and function (e.g. primary productivity or enzyme-specific activity measurements). The extent of biotic utilization and degradability can be determined over time by sequentially subsampling the bioassay. Short-term (hrs to several days) bioassays are used to examine utilization of the most biologically-available ("reactive") fraction (cf. Peierls and Paerl 1998; Paerl, et al., 1999), with longer-term bioassays (days to weeks) used to examine biodegradation of more recalcitrant compounds (cf. Seitzinger and Sanders 1997; 1999).

3. How are the effects modulated by the hydrology, geology, and other physical characteristics of an ecosystem?

Once DON is deposited to a terrestrial or aquatic ecosystem system, its residence time within that system and its transport to other systems may change the potential impact on the biota. In watersheds, most of the DON will infiltrate into the soilwater or groundwater where its residence time is on the order of days to years. The DON may then be processed microbially or adsorbed to the soil matrix. Adsorption is typically stronger in high-clay soils and weaker in sandy soils, while microbial degradation is a more important process in warm, organic-rich ecosystems. Studies of DOC transport in terrestrial systems can be used as a first approximation for hypotheses about DON transport, since the nitrogen is bound up in the same organic molecules. Much of this organic matter is released from the soil, particularly during storm events, but its form is altered by in-system processing (Kaplan 1993), such that the stream DON characteristics are probably defined more by watershed soil properties than by the original DON properties. The amount of DON A_{signal} reaching a stream or river is a function of in-system residence time and in-system rate of processing. Both of these characteristics will differ from system to system, but are related to hydrologic pathways and levels of ecosystem productivity

In a given watershed, the temporal variability in the rate and flowpath of water delivery to a stream is likely to influence DON transport. Large storms tend to produce greater incidence of saturated overland flow, which allows more direct transport of DON components to aquatic systems. This same effect can be found in watersheds characterized by urbanized land use which tends to promote overland flow (i.e. over concrete). The timing and form of deposition may play a large role in determining the residence time of DON in terrestrial systems. In areas where a few large storms contribute most of yearly precipitation, or areas with a high proportion of precipitation as snow, followed by a rapid snowmelt season, DON is more likely to be transported directly to stream ecosystems and not subjected to soil system processing.

The effect of DON input depends also on the existing pools of N, C, and toxic compounds. In N saturated systems, for example, the addition of DON presumably will not have a significant effect as a N source. Terrestrial systems already contain large standing stocks of organic nitrogen in the form of soil organic material, although that organic matter may be more refractory than incoming AON. More information on the chemical characteristics of in situ organic matter relative to DON will be needed in order to assess the fate and transport of additional ON in each receiving ecosystem.

4. What are the differences in ecosystem responses over geographic regions?

Terrestrial and aquatic ecosystems under the influence of DON vary in size, shape, geology, climatic regimes, and hydrology. This variability, coupled with contrasting flora and fauna, can lead to distinct differences in ecosystem "sensitivity" in terms of biotic responses to and ecosystem assimilation of AON inputs. The size of the watershed and airshed relative to the receiving water body is likely to determine the role of AON in N budgets. Jointly, these physical features determine overall ecosystem trophic (e.g. productivity, food web structure and function) and biogeochemical (e.g. nutrient cycling, hypoxia/anoxia) responses to DON inputs. In addition, the quantity and "quality" of DON inputs may vary geographically, depending on location of sources, transport routes and proximity to receptor ecosystems.

These contrasting physiographic, hydrodynamic and biotic features lead to a range of positive (e.g., increased fertility and fisheries yields) and negative (e.g. harmful algal blooms, toxicity) responses to DON (as well as terrigenous organic nitrogen) loading scenarios along geographic gradients. This necessitates comparative regional studies of the role of DON in general in determining ecosystem structure and function. It is recommended that terrestrial and aquatic ecosystems varying in location, size, proximity to DON and other N inputs (i.e., anthropogenic vs. natural), retention time or flushing, trophic state, and fertility be included in a comparative evaluation. Prospective regions should include the Great Lakes, coastal Northeast (Narragansett Bay, Gulf of Maine), Mid-Atlantic (Chesapeake Bay, Barnegat Bay, Long Island Sound, Albemarle-Pamlico Sound System), Gulf Coast (Tampa/Sarasota Bay) and West Coast locations (Puget Sound, San Francisco Bay).

The effort required to determine the ecological impact of every DON compound would be considerable, and probably unnecessary. Also, it would be difficult to isolate the impact of DON alone amid numerous other multiple stressors. Instead, we can combine the information on the sources and identities of major DON compounds with the knowledge of bioavailability and ecological significance in order to distinguish the critical compounds or compound classes. This information will be fundamental in order to evaluate the extent DON should be controlled, and which specific sources, if any, should be targeted for reduction.

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APPENDIX A

Workshop Program

APPENDIX B

Participants/Workgroup Assignments

APPENDIX C

Workgroup Questions