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Chemical Composition and Bioavailability of Dissolved Organic Nitrogen in Atmospheric Wet Deposition from Urban and Rural New Jersey Sites

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PROJECT DESCRIPTION

Project Overview

Atmospheric deposition is a major source of nitrogen to many ecosystems. Marked changes in both terrestrial and aquatic ecosystems are occurring as a result of increased nitrogen (N) deposition from anthropogenic sources. To date, most studies of the magnitude, sources and effects of atmospherically deposited N have only considered inorganic-N. However, a considerable portion of N in rainwater is in the form of organic-N, and almost nothing is known of the chemical composition, sources or ecosystem effects of the bulk of that organic-N.

The research that we are proposing will provide information that can be linked to the decision-making needs of environmental managers. Our long-term goal is to identify the current, and potentially future, processes (natural and anthropogenic) and technologies that are major contributors to atmospherically deposited organic-N compounds and to assess the effect of these specific chemicals on receptor ecosystems. The specific objectives of the studies proposed here are to:

1) characterize the chemical composition of total dissolved N, both inorganic and organic nitrogen, in atmospheric deposition in 2 urban and 2 relatively undisturbed sites in New Jersey;

2) begin to identify sources of organic nitrogen in atmospheric deposition at those sites; and

3) identify which of the compounds, and therefore which potential sources, are bioavailable and thus contributing to ecological changes in ecosystems.

This project will address the changing chemical composition of the atmosphere with regards to N containing compounds and potential ecosystem effects. It will provide a benchmark of N-chemical species concentration in wet deposition, including information on both the temporal (seasonal) and spatial characterization of the chemical composition of dissolved organic N. It will establish a baseline upon which to interpret future trends in dissolved organic N (both total DON deposition and chemical composition of the DON). Our collection procedures parallel those of NADP which are targeted at inorganic-N analyses (nitrate, nitrite and ammonium). The information provided by this project, therefore, will provide additional chemical detail within the framework of the NADP N-deposition program. The advanced DON measurements are a pilot for a possible chemical protocol for routine N-wet deposition monitoring studies. This project will interface and complement NJDEP's existing and/or planned field studies on funded terrestrial effects of atmospheric deposition (Dr. John Dighton) and air toxics deposition (Dr. Steve Eisenrich).

Table 1. *Summary of the major science questions, objectives of current study and proposed approaches for atmospheric organic nitrogen deposition in New Jersey.* ***(See Table 3 and Methods Section for detailed descriptions)***

Science Question	Objectives of Current Study	Approach Proposed for this Study
I. What are the sources of dissolved organic N deposited in rain, and how do they differ in undisturbed versus urban areas?	A. Determine the chemical composition of dissolved organic N (DON) in rain at two relatively undisturbed and two urban sites in NJ; use that information to obtain insight into: 1) the relative magnitude of biogenic sources, anthropogenic sources, and atmospheric photochemical reactions, and 3) long-range transport versus local sources.	1. Analyze chemical composition of organic compounds in rain collected over two complete annual cycles in: 1) Camden, 2) New Brunswick, 3) the Pinelands, and 4) northeastern NJ. Meteorology and storm origin are linked to precipitation chemistry. 2. Determine dissolved organic N compounds whose functional group composition is indicative of: 1) biogenic, 2) anthropogenic, and 3) photochemical processes. 3. Search for specific chemical molecular markers within each of the 3 source categories. This information will be used to link specific types of processes to atmospheric loadings (e.g., combustion, manufacturing processes, vehicular exhaust, landfill emissions, photochemical, natural vegetation).
II. What is the disruption to ecological systems from DON in rain, and how does that differ in relatively undisturbed and urban rain?	A. Determine how much of the DON in rain from relatively undisturbed and urban sites is utilized by aquatic microorganisms.	1. Examine stimulation or inhibition of aquatic microbial populations due to DON additions from rain collected at the 4 study sites to microcosms of aquatic microorganisms. Quantify total amount of DON utilized.
	B. Determine which of the DON compounds in rain from undisturbed and urban sites are utilized by receiving ecosystems.	1. Determine which of the DON compounds in rain decrease when subjected to degradation by aquatic microorganisms.
	C. Begin to relate bioavailable organic components to sources (biogenic, anthropogenic or photo-chemical)	1. Compare utilization of individual compounds with information linking specific types of processes to those chemical compounds (e.g., combustion, manufacturing processes, vehicular exhaust, landfill emissions, photochemical, natural vegetation).
III. How does the terrestrial vegetation change the chemical composition of DON deposited to soils?	A. Examine the difference in the chemical composition of DON in rain and through-fall at one site in the Pinelands.	1. Compare the detailed chemical composition of the DON in rain at the Pineland's site with that of through-fall at Dr. John Dighton's microrhizia study site during 3 rainfall events.

Background and Significance

Natural and anthropogenic N compounds are emitted to the atmosphere as oxides of N (NO_X, that is NO, NO2), ammonia, and organic-N (e.g., Graedel et al., 1986, Galloway et al., 1995, Finalyson-Pitts and Pitts, 1985, 2000). Anthropogenic activities are the main source of inorganic-N (e.g., NO_X and ammonia) to the atmosphere. For example, in North America the dominant sources of the NO_X compounds are from fossil fuel combustion in motor vehicles and electrical power generators, and from the manufacture of nitric acid or nitrated substances (Council of the Commission for Environmental Cooperation, 1997; U.S. EPA 1996, 1997; NARSTO 2000). These and other anthropogenic sources have increased the inorganic-N inputs to the atmosphere by 300% during the past 20 years and resulted in increased N deposition to many terrestrial and aquatic ecosystems (Fisher et al., 1988, Galloway et al., 1995; Munger et al., 1996, 1998). Shifts in plant and algal species composition, increased productivity, decreased species diversity, and changes in food web structure can result from these increased N inputs (e.g., Vitousek and Howarth, 1991; National Research Council, 1993; Wedin and Tilman, 1996; Paerl et al. 1990).

To date, inorganic-N has been the focus of most measurements (including NJ) and models of N emissions to the atmosphere. Similarly, inorganic-N has been highlighted as part of atmospheric deposition studies of N (wet and dry) and has been the dominant N form studied in relation to effects on ecosystems (e.g., NAPAP 1991; NADP/NTN 1996; Wedin and Tilman 1996; Paerl et al. 1990). However, data from a wide range of locations (urban, rural, and remote) demonstrate that organic-N comprises an additional important component of N in rainwater (Table 2). Hints of the importance of organic-N in precipitation trace back to studies as early as the mid-1800's in France and England (reviewed by Mazurek and Simoneit 1986). More recent studies demonstrate that atmospheric organic-N typically accounts for 20%-70% of the total N annually (Table 2). Neither the chemical forms, sources or the effects of this organic-N on ecosystems have been adequately identified and measured for any system.

Table 2. *Percent composition of inorganic (DIN) (ammonia plus nitrate) and organic N in precipitation from various locations.* (modified from Seitzinger and Sanders, 1999)

Source/Location	DIN %	Organic N %
Walker Branch, TN[1]	68	32
Coweeta, NC[2]	53	47
Coastal plain, FL[3]	57	43
Cascade Mtns., OR[4]	32	68
Coastal plain, SC[5]	51	49
Philadelphia, PA[6]	70	30
Chesapeake Bay[7]	43	57
Rhode River, MD[8]	55	45
Raritan Bay, NJ[9]	62	38
UK[10]	79	21
N. Carolina[10]	79	21
Amazonia[10]	78	22
Recife, Brazil[10]	75	25
Bermuda[10]	41	59
Tahiti[10]	16	84
NE Atlantic[10]	33	67

[1] Kelly and Meagher 1986; [2] Swank and Waide 1987; [3] Riekerk 1983; [4] Grier et al. 1974, Fredriksen 1983; [5] Richter et al. 1983; [6] Seitzinger unpubl. data; [7] USEPA 1982; [8] Peterjohn and Correll 1984; Jordan et al. 1995; [9] Seitzinger, unpublished data; [10] Cornell et al. 1995.

Policy Issues

As a result of the Clean Air Act, nitrogen oxide inputs to ecosystems are predicted to decrease in the US over the next 10 years (Periasepe 2000). EPA is undertaking a major, multifaceted nitrogen oxide initiative, including reducing emissions from power plants and

requiring cleaner cars, trucks and buses, and lower-sulfur fuel. When fully implemented, it is projected these programs will produce a significant reduction of NOx pollution in NJ, as well as nationwide. However, as noted above, a major component of N in rainwater is dissolved organic N (DON), and it is not known how these new management approaches will affect the amount or forms of DON in atmospheric deposition. For example, 1) if DON has no links to processes producing NOx, then the amount of DON in atmospheric deposition should stay constant; however, DON would become an increasingly higher percentage of the total N deposited, 2) if some DON compounds are from secondary reactions with NOx and ozone, total DON deposition would decrease, due to a decrease in the deposition of specific DON compounds; 3) similarly, if some DON compounds are more directly linked to primary emissions and atmospheric photochemical processes involving NOx, total DON may decrease due to a decrease in the emissions and secondary production of those specific compounds, and/or 4) DON may increase in amount due to other human activities. Thus, now is a critical time to begin monitoring the amount of DON in rain, changes in the chemical composition of DON compounds in rain, and utilization of DON by organisms in the environment.

Science Issues

I. What are the sources to the atmosphere of organic N compounds? (Table 1)

The chemical composition of dissolved organic nitrogen (DON) in rainwater has only been partially characterized (Gorzelska et al. 1997). However, the available data indicate a variety of sources, both natural and anthropogenic. Analyses of the ^{15}N content of bulk DON from a range of locations (Cornell et al., 1995) as well as variations in the C:N ratios of the bulk DON in urban sites (Seitzinger and Mazurek, unpublished data) indicates multiple sources. The range of different chemical compounds in the atmosphere and in precipitation also indicates a range of sources. Over 100 different organic-N containing compounds in the atmosphere have been reported, which are candidate chemicals to be included in rain DON (reviewed by Graedel et al. 1986).

From Graedel's (1986) review of the multitude of organic-N compounds in the atmosphere and from measurements of specific compounds in precipitation, we can see that they fall into three main functional classifications: 1) reduced N (e.g., nitriles, amines, amides); 2) aromatic N (N-heterocycles); and 3) oxidized N (alkyl nitrates, nitro-aromatics). These three classes can be used to begin to identify and quantify the major categories of sources contributing to atmospherically deposited organic-N (Table 3). For example, most amines have a biogenic source, while the heterocycles (aromatic species) mostly arise from combustion processes and are present in crude oil and refined petroleum products. Nitro compounds also would be primarily from combustion sources, although indirectly, through photochemical reactions in the atmosphere between NO_X (anthropogenic origin) and ozone (anthropogenic), to form nitro aromatic compounds with the nitro group attached at the 2-carbon position (Finalyson-Pitts and Pitts, 1997 and 2000). ***Thus, the chemical composition of DON can provide critical information to identify the general categories and specific sources of atmospheric organic-N substances.***

Anthropogenic sources are likely to be an important component of DON in rainwater based on a number of lines of evidence. For example, while amines, which generally indicate a

Table 3. *Summary of DON component groups, molecular compositions, and major sources.*

DON Component	Wet Deposition Field Study	Sources *(Major Sources)*
Reduced Species		
Amines	Semenov *et al.*, 1967a; Gorzelka *et al.*, 1990, 1992, 1994, 1997	*Biogenic* (primary emission); animal feedlots, biological decay processes *(1,2)*
Primary amines	Likens *et al.*, 1983; Mopper & Zika, 1987	
Secondary amines		
Tertiary amines		
Diphenylamine	Lunde *et al.*, 1977	*Industrial*, chemical manufacturing, combustion
Amino acids (bulk)	Fonselius, 1954; Semenov *et al.*, 1967ab; Rozinoyer *et al.*, 1973; Timperly *et al.*, 1985 Mopper & Zika, 1987; Gorzelska *et al.*, 1990, 1992, 1994, 1997	*Biogenic* (primary emission)
Amino acids (individual compounds)	Sidle, 1967; Mopper & Zika, 1987; Gorzelska *et al.*, 1990, 1992, 1994, 1997	*Biogenic* (primary emission)
Aromatic Species		
N-Heterocyclic compounds		*Diesel exhaust* (primary emission), tobacco smoke, coal combustion, animal waste, chemical manufacturing *(1,9)*
Nitro-PAH		*Diesel exhaust*, chemical manufacturing *(1,2);* Photochemical (secondary compound) *(2,9)*
Oxidized Species		
Amides		*Industrial, tobacco smoke*, animal waste *(1)*
Urea	Semenov *et al.*, 1967a; Timperly *et al.*, 1985	*Biogenic*, animal waste *(1)*
Nitrates		
Alkyl nitrates		*Photochemical (2-4,5)*
Hydroxy alkylnitrates		*Photochemical (2-4)*

biogenic and thus partially natural source, are a consistent component in precipitation, the total amount of amines often accounts for only a small fraction of the total DON. A number of organic-N compounds with anthropogenic sources have been reported in field studies (Table 3). Laboratory investigations have calculated significant wet removal rates for hydroxy organic nitrates (form of oxidized-N) from the atmosphere (Shepson *et al.,* 1996). Other water-soluble anthropogenic organic-N compounds found as atmospheric particulate matter that are likely to be found as DON in precipitation have been reported in a critical literature review (Saxena and Hildemann, 1996). However, previous studies have generally not taken a mass balance approach for total DON in rainwater, but rather have focused on a particular compound or group of compounds. A mass balance inventory that accounts for all organic-N in rainwater is a first step toward quantifying the relative contribution of different forms, and thus different sources, of organic-N to atmospheric deposition. A mass balance approach is central to our analytical scheme (Figure 1). We propose to quantify, to the maximum extent possible, the absolute and relative magnitude of reduced, heterocyclic and oxidized N compounds in atmospheric deposition at 4 sites in New Jersey. We propose to identify as many individual compounds as possible and to determine chemical properties of compounds that can not be specifically identified. The N functional group scheme will be used to classify broadly the molecular indicators according to sources from biogenic (reduced-N compounds) processes and anthropogenic processes (heterocyclic and oxidized organic-N compounds) (Tables 1 and 3). Detailed information on the chemical structure of specific compounds within each of these 3 categories will be used to further identify specific types of sources (combustion, vehicular exhaust, photochemical conversion, manufacturing, etc.) within each category.

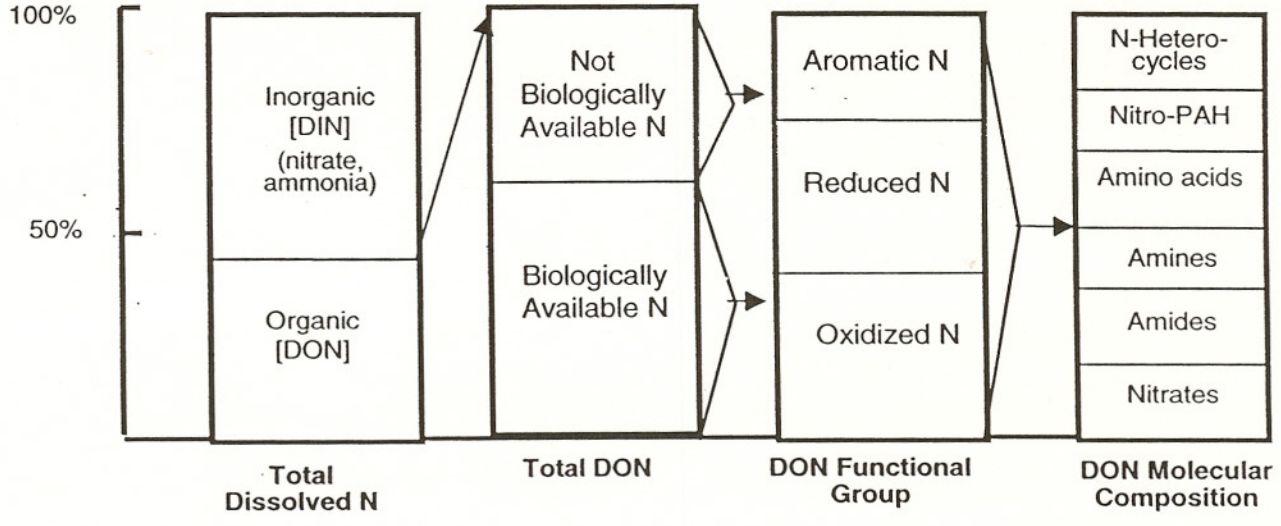


Figure 1. *Mass balance inventory for N chemical substances in wet deposition.*

We have developed an analytical approach for characterizing the chemical composition of DON in rainwater. It is a heirarchical approach that includes:

1. Determining the molecular weight of all major ionizable DON compounds in rain using mass spectrometry (atmospheric pressure electrospray ionization – APESI-MS)
2. For each compound (each molecular weight from 1. above)
    a) determine whether the compound has primarily basic or acidic functional groups
    b) identify the potential number of N atoms in the structure; "N rule"
3. Match, where ever possible, the above information on each compound with our atmospheric organic compound data base which contains detailed chemical information on specific organic N compounds reported in the atmosphere
    a) obtain authentic standards for as many compounds in the data base as possible
    b) analyze those standards with the same APESI-MS methods used for the rain samples
    c) compare APESI-MS results from standards and rain samples
    d) for compounds with a match (standard and rain) use liquid chromatography (HPLC) to determine if the standard and the compound in the rain sample show the same retention timecs
    e) for standard compounds without a match in rain, we also gain considerable important information concerning which compounds are not found in rain
4. For compounds that are not in our data base or that we can not find authentic standards for, we will use HPLC in combination with the mass spectrometry to determine additional chemical characteristics of those compounds using columns which select for compounds with different chemical characteristics (aromatics, reduced N, COOH groups, etc.).

An example of the above approach with rain from New Brunswick is shown in Figs. 2 & 3. The mass distribution of ionizable organic compounds was determined using atmospheric pressure-electrospray ionization mass spectrometry (APESI-MS) without LC column separation (Figs. 2-3). APESI is a soft ionization method and, as such, does not fragment compounds. The mass spectrometer scans over two mass ranges 50 to 500 molecular weight, and 500 to 3000 molecular weight. Analysis of samples from New Brunswick suggests that most of the compounds in rainwater have a molecular weight between 50 and 500 (Fig. 2A & B).

The APESI-MSD can be operated in two modes: a negative and a positive mode, providing substantial additional information on the potential chemical structure of each mass detected (Fig. 2B). In the negative mode, compounds that have acidic functional groups are detected, such as carboxylic acids and nitro-aromatics. In the positive mode, compounds that have basic functional groups are detected, such as amides, amines (primary, secondary, tertiary), and nitriles. Analysis of samples to date from New Brunswick indicate that there are substantial numbers of organic acids (negative mode detection: indicated by blue lines in Fig. 2B) and organic bases (positive mode detection: indicated by red lines).

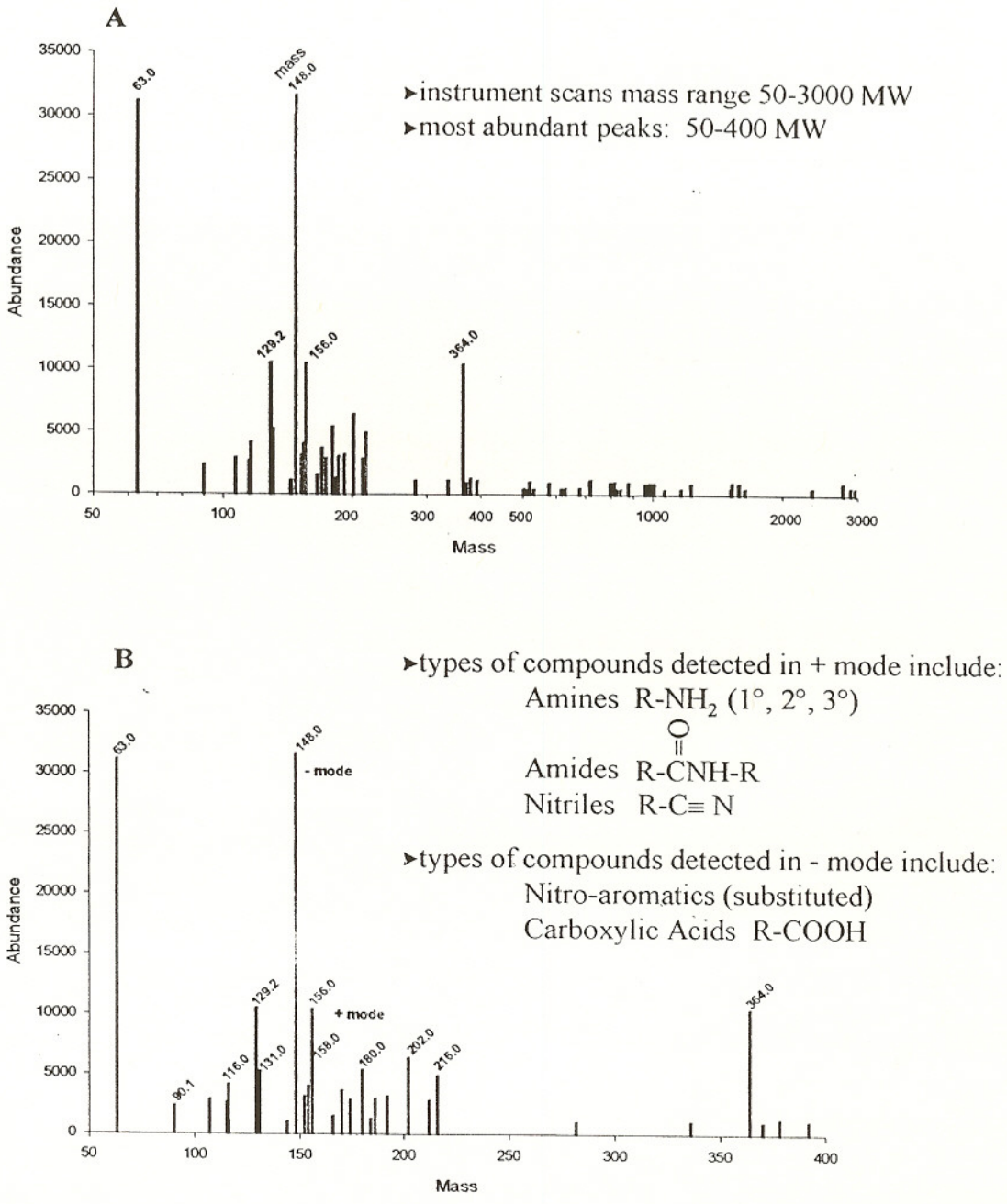


Figure 2 Example mass spectra from a rainwater sample collected May 11, 2000. A) Masses 50-3000 molecular weight, detected in both positive and negative modes. B) Masses 50-400 molecular weight detected in positive mode (red) and negative mode (blue). Abundance is an indicator of concentration. Numbers above individual bars indicate mass.

The potential number of N atoms in each compound is then evaluated by applying the "N rule" which says that if a compound has an odd mass it definitely has a N atom in its structure, and that it contains an odd number of N atoms (1,3,5 etc.). If a compound has an even mass, it has either no N or an even number of N atoms in its structure (0, 2, 4 etc.).

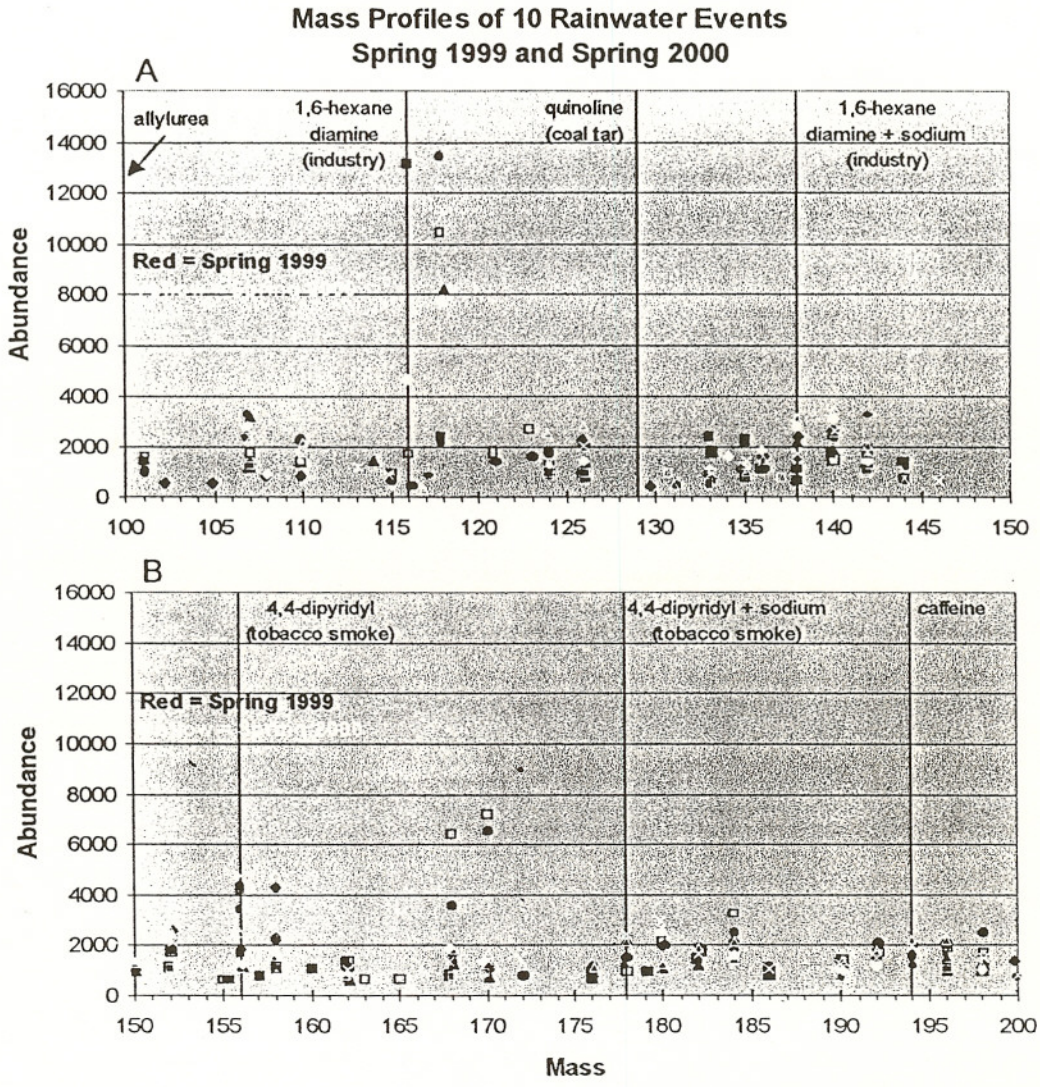
The APESI-MS analysis of twelve samples of rainwater collected in New Brunswick, during the spring of 1999 and 2000, all with a SSW storm trajectory, are shown in Fig. 3 (A &B) (only data for masses between 100 and 200 are shown in these figures). There is considerable constancy of composition among the 12 spring-time rain samples during the 2 years, both in terms of common masses and abundances of individual masses. There are also numerous masses (compounds) which only appear occasionally (e.g. 105, 121, 146, etc.), or which vary considerably in abundance (e.g. 116, 118, 170).

This information is then combined with information in our database of atmospheric organic compounds, which we are developing (Table 4), to begin to target specific organic compounds in the rain samples. This database includes a compilation of information from the literature on organic N compounds reported in atmospheric samples. It includes a range of information on each compound including chemical structure, pKa, water solubility, and known sources.

The APESI-MS approach not only is used to identify target compounds in the rain samples, but also provides concentration data for individual compounds. We have now obtained, analyzed with APESI-MS, and developed initial response factors for standards of approximately 20 compounds of potential atmospheric significance. We are currently in the process of comparing the APESI-MS data from our New Brunswick rain samples. The data suggest that many of these compounds consistently occur in the rain samples. A few such examples are: 4,4-dipyridyl (a product of tobacco smoke), 1,6-hexane diamine (from industrial processes), and caffeine (indicated by the blue lines in Figs. 3A & B). Other compounds which have been reported in the atmosphere, such as allylurea and quinoline (from coal tar), do not occur in these samples (indicated by the black lines in Fig. 3A).

We proposed to examine the chemical composition of DON in rainwater from 2 relatively undisturbed sites (Pinelands & northwestern NJ) and two urban sites (Camden & New Brunswick) over 24 months, using the above analytical approach (Table 1). This will provide information for each of these sites on specific DON compounds and their sources. In addition, by combining the detailed chemical composition data with environmental information such as storm trajectory, season and location, we can start to determine those DON components that are from natural, anthropogenic and photochemical sources, and from local versus long-range sources.

II. What is the disruption to aquatic and terrestrial systems from atmospheric organic N deposition? (Table 1) At the same time that we are developing and applying this new analytical approach to chemically characterize the DON compounds in rainwater, we are also developing new approaches to determine which of these compounds are biologically used once they are deposited to ecosystems. We know from the few studies conducted to date, that some portion, although not all, of the bulk (total) DON in rainwater is biologically available (Peierls and Paerl 1997). For example, between 40% and 70% of the bulk DON in rainwater collected from the Philadelphia, PA, area was utilized by coastal plankton (Seitzinger and Sanders 1999).

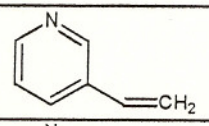
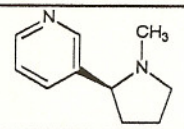
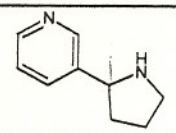
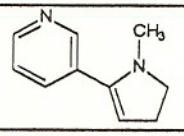
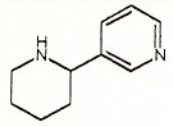
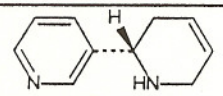
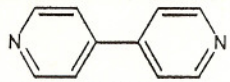
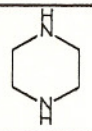


- some constancy in composition among 1999 and 2000 spring rain events
  - -masses similar
  - -abundance generally agree within a factor of two
- preliminary presence/absence of standards and target compounds

Figure 3 Mass spectra of ten rainwater samples collected in the spring of 1999 (red) and spring of 2000 (yellow). Data for mass ranges 100-150 (A) and 150-200 (B) shown. Vertical lines indicate the mass of standards. A blue line indicates the possible presence of a standard compound in one or more rainwater samples. A black line indicates the absence of a standard compound from all ten rainwater samples.

Table 4. Excerpt from atmospheric nitrogen compounds database showing some heterocyclic compounds.

Heterocyclic Nitrogen Compounds

Registry (CAS) Number	Name(from Graedel)	CAS Name(s)	Formula	M.W.	Structure	Solubility	Dissociation Constant in Aqueous Solutions pKa/T deg.C	Source G-Graedel M-Merck
26274-35-1	2, 4-Diphenylpyridine	2, 4-Diphenylpyridine	C17H13N	231.3				G-biomass combustion
1121-55-7	3-Vinylpyridine	3-Ethenylpyridine	C7H7N	105.14		very slightly sol in water		G-tobacco smoke
54-11-5	Nicotine	(S)-3-(1-Methyl-2-pyrrolidinyl)pyridine	C10H14N2	162.23		Misc with water below 60degrees	Step 1 8.02 / 25 Step 2 3.12 / 25	G-tobacco smoke
494-97-3	Nornicotine	3-(2-Pyrrolidinyl)pyridine	C9H12N2	148.21		Miscible with water.		G-tobacco smoke
525-74-6	N-Methylmyosmine	3-(4,5-Dihydro-1-methyl-1H-pyrrol-2-yl)pyridine	C10H12N2	160.22				
494-98-4	Nornicotyrine	3-pyrrol-2-yl-pyridine	C9H8N2	144.18				G-tobacco smoke
494-52-0	Anabasine	3-(2-Piperidinyl)pyridine; 2-(3-pyridyl)piperidine	C10H14N2	162.23		Sol in water		G-tobacco smoke
581-49-7	Anatabine	1,2,3,6-Tetrahydro-2,3prime-bipyridine	C10H12N2	160.22		Misc with water		G-tobacco smoke
581-50-0	2,3'-Bipyridyl	[2,3']bipyridinyl	C10H8N2	156.19				G-tobacco smoke
26844-80-4	5-Methyl-2, 3'-bipyridyl	5-methyl-[2,3']bipyridinyl	C11H10N2	170.21				G-tobacco smoke
553-26-4	gamma,gammaprime-Dipyridyl	4,4prime-Bipyridine	C10H8N2	156.19		slightly sol in water.		G-tobacco smoke
110-85-0	Piperazine	Piperazine	C4H10N2	86.14		Freely sol in water	Step 1 9.83 / 23.5 Step 2 5.56 / 23.5	
106-55-8	2, 5-Dimethylpiperazine	2,5-dimethyl-piperazine	C6H14N2	114.19			Step 1 9.66 / 25 Step 2 5.20 / 25	G-diesel

Experiments conducted with rainwater from New Brunswick, NJ, indicated that approximately 5% to 50% of the total DON was utilized by aquatic microorganisms, with different amounts of DON utilized in different rainfall events (Seitzinger, Mazurek, Styles, and Lauck, in prep.). Why do we see such variation among locations and rain events? The most likely explanation is because of differences in the chemical composition of the rain. The next step is to determine which components (compounds) of the DON in rain are utilized by organisms and thus causing changes to receiving ecosystems.

We propose to examine the utilization of the DON compounds in rainwater collected from four sites in NJ: two relatively undisturbed sites (Pinelands and northwestern NJ) and two urban sites (New Brunswick and Camden) (Table 1). This will be done by analyzing the detailed chemical composition of rain water (e.g., Figs. 2 & 3) before and after degradation by aquatic bacteria. A comparison of the chemical characteristics of the utilized (and un-utilized) compounds with authentic standards of atmospheric relevance will provide information on which specific types of processes (e.g., combustion, manufacturing processes, vehicular exhaust, photochemical, natural, etc.) are contributing biologically available organic-N. Such information is necessary to begin to develop models to predict changes in ecosystems due to changes in human activities that contribute organic-N to the atmosphere. It will also provide information that could be used to determine what sources would be the most effective to control in order to decrease effects on receiving ecosystems.

Approach

Precipitation Collection:

Atmospheric deposition of DON is expected to be influenced by both regional transport as well as local inputs and chemical reactions. Samples will be collected from 4 sites within New Jersey. Our sites include two relatively undisturbed forested sites and 2 urban sites. The two forested sites are: 1) in the Pinelands ecological preserve, and 2) in northwestern NJ. For the latter site we are considering either the Delaware Water Gap or Chester, NJ; the selection of one of these will depend on logistical factors such as availability of local personnel, and access to site. The two urban sites are: 1) Camden and 2) New Brunswick. All four sites are surface air quality and meteorological sites that are supported by the NJ Dept. of Environmental Protection and are co-located with Dr. Steve Eisenrich's toxics deposition sites. In addition, the New Brunswick site is part of a larger network, the North American Research Strategy for Tropospheric Ozone -- Northeast (NARSTO-NE) (NARSTO, 1996). Meteorological parameters, particulate matter, and chemical species data are measured routinely at the NJDEP locations. Our strategy for selecting existing air monitoring sites will allow us to couple simultaneously gathered ambient air data, chemical species data (ozone, NO_X, and reactive hydrocarbon concentrations), and meteorological information including storm trajectories, to our determinations of precipitation chemistry and bioavailability tests.

Samples will be collected from the 4 sites for a 24-month period (Table 5). Collecting rainwater from storm events during different seasons and with different air mass trajectories will

Table 5. Project schedule

Year 1	Year 2	Year 3
1. (Months 1-3) Establish personnel and sampling procedures at 3 sites (Pinelands, Camden, Delaware Water Gap/Chester), in addition to our current New Brunswick site. Collect and evaluate field blanks.	1. Items 2-6 (Year 1) for 12 months	1. Item 2-5 (Yr 1) for 6 months
2. (Months 4-12) Collect precipitation samples from the 4 NJ sites (New Brunswick, Pinelands, Camden, Delaware Water Gap/Chester)	2. Data processing and data interpretation, including multivariate statistical analyses to examine trends on several scales	2. Items 2-3 (Year 2)
3. Analyze precipitation samples for bulk constituents (inorganic N, bulk DON and DOC, etc.) (all rain samples and blanks)	3. Further develop and test conceptual model using Year 1 and 2 data.	3. Using HPLC separation, analyze a suite of rain samples from each site for: a) characterization of chemical properties and b) identification of specific compounds
4. Analyze selected precipitation samples for detailed dissolved organic matter chemical characterization (mass distribution, acid/bases) (5 samples per season per site)	4. Optimize and apply HPLC methods for selected compounds in rainwater to a) further characterize chemical properties and b) identify specific compounds	4. Conduct biological availability experiments on seasonally (summer) composited precipitation from 4 sites
5. Prepare and analyze, using APESI-MS, UV/VIS, and CLND, suites of authentic standard compounds (approx. 30 compounds) from the 3 source categories: biogenic, anthropogenic, secondary photochemical.	5. Conduct biological availability experiments on seasonally (spring) composited rain from 4 sites	5. Item 6 (Year 2) for winter bioavailability experiment.
6. APESI-MS data processing and initial data interpretation, including multivariate statistical analyses to begin to examine trends on several scales	6. Chemically characterize the BIOAVAILABLE components of the rainwater DOM including molecular weight, acid/base properties; compare with authentic standards.	6. Develop integrated analysis of results of chemical characterization of precipitation samples and biological availability experiments.
7. Begin to develop HPLC chromatographic separation of major compounds in precipitation samples.	7. Continue to develop database of atmospheric organic compounds	7. Submit manuscript for publication including Year 3 results and overall project synthesis.
8. Continue to develop database of atmospheric organic compounds	8. Collect throughfall (3 times) at Dighton's microrhizzae study site and analyze for detailed chemical composition	8. Submit final report to NJDEP
9. Begin to develop conceptual model for data interpretation.	9. Submit manuscript for publication including Year 2 results.	
10. Submit manuscript for publication that details Year 1 results.	10. Submit progress report to NJDEP	
11. Submit progress report to NJDEP		

allow us to begin to make associations between the chemical composition of DON and the air mass trajectory. During any one season, the sites receive precipitation from storms that are associated with synoptic air mass flow from three dominant directions: 1) northwesterly (Canadian subarctic airflow; background continental; 2) easterly (marine, remote Atlantic Ocean); and 3) southwesterly (VA/MD/PA/NJ corridor; polluted continental) transport. Additionally, the sites are influenced locally by ambient meteorological conditions, solar intensity (seasonal), and by local urban and/or natural sources of emissions that also may differ by season.

At the end of Year 1, we will develop a conceptual model (Table 5) based on the differences in DON chemical composition found among the 4 sites, among seasons and among storm trajectories, along with other potential factors. This conceptual model will be used to begin to interpret the chemical composition data with respect to the relative importance of natural, anthropogenic and photochemical processes as sources of DON, and the relative importance of local versus long-range sources. Data from Year 2 and 3 of the study will be used to test and further refine this conceptual model.

The overall project schedule is summarized in Table 5 with specific details described below.

I. What are the sources to the atmosphere of organic N compounds?

Objective I. A: (Table 1) Characterize the chemical composition of dissolved organic N (DON) in atmospheric deposition at 2 urban and 2 relatively undisturbed sites in NJ.

Precipitation volume will be measured at each site with a manual rain gauge. Samples for chemical analysis will be collected using a precipitation collector (fitted with a stainless steel liner) that opens only during wetfall events. Collection of samples within hours after the rain fall stops is important to minimize biological decomposition of DON. Samples will be immediately filtered at the end of a rainfall event (events over 0.5 cm) after temperature and pH are measured, and then will be frozen until analysis.

Bulk constituent analysis: All samples will be analyzed for: inorganic N (ammonium, nitrite and nitrate), phosphate, total dissolved organic N, and DOC. The following analytical methods will be used: ammonium (Lachat, Inc. QuickChem 31-107-06-1-A), nitrate plus nitrite (Lachat, Inc. QuickChem 31-107-04-1-A), total dissolved N (TDN) (Antek, Inc.), total DOC (Shimatzu 5000 high temperature combustion; Benner and Strom 1993; Sharp et al. 1993). DON is determined by the difference between TDN and DIN. TDN is analyzed by high temperature combustion followed by chemiluminescent detection of nitric oxide using an Antek Model 7000 Total N Analyzer (Antek, Inc.) equipped with a quartz combustion tube (1000 +/- 10 °C) and a ceramic insert (Seitzinger and Sanders, 1997). TDN samples will be preserved in capped autosampler vials with 3N HCL (7.5 µl acid per 1.5 ml sample). Blanks will consist of de-ionized water.

Detailed chemical characterization (without chromatographic LC separation): Samples from up to 5 events per season from each of the four sites will be analyzed for more detailed DON chemical characterization. The mass distribution of ionizable organic compounds will be determined using atmospheric pressure-electrospray ionization mass selective detection (APESI-MSD) without LC column separation. Analysis of rainwater samples from New Brunswick

suggests that the most abundant compounds have a molecular weight between 50 and 500 (Fig. 2). However, we do not know if that is typical for the chemical composition of rain from other sites. Therefore, we will initially scan samples from all 4 sites in the 500 and 3000 mass range in both the positive and negative modes to ensure that we are not missing compounds in that high molecular weight range. If needed, all samples will be scanned in this higher range.

All samples will be analyzed by APESI-MSD in both the negative and positive mode, to determine which compounds have primarily acidic functional groups (negative mode detection) and which basic functional groups (positive mode detection) (Fig. 2B). This considerably narrows the potential chemical identity of each compound. Four to six replicate injections of each sample will be analyzed in each mass range and mode.

Further characterization of the potential number of N atoms will be obtained by applying the "N rule." If a compound has an odd mass it definitely has a N atom in its structure, and contains an odd number of N atoms (1,3,5 etc.). If a compound has an even mass, it has either no N or an even number of N atoms in its structure (0, 2, 4 etc.). Each mass will be evaluated with this rule.

The combination of specific mass, positive or negative mode detection, the "N rule", and the database of atmospheric organic compounds (e.g., Table 4), will be used to begin to target specific potential organic compounds in the suite of rain samples. Authentic standards of approximately 20 compounds have been obtained and analyzed to date. We will obtain additional (30 or more) target marker organic compounds and determine their APESI-MS response factors. A comparison of the APESI-MS response to these standards with the detection of the same mass and mode (+/-) response from rain samples will be used to evaluate what specific compounds are in the rain samples as well as what the concentration is of each of these compounds.

Advanced chemical characterization - HPLC/MS analysis: The above approach reflects the status of our current chemical characterization approach for analyses of DON in rain samples. It provides detailed compound molecular weight information, acid/base functional group information, and insight into the number of N atoms (odd/even) in the structure. We can begin to identify potential compounds and their concentration based on the combined information from those analyses, the atmospheric organic compound data base that we will continue to develop, and the analysis of authentic standards of atmospheric significance. However, many compounds can potentially have these sample characteristics. In the current project we will undertake additional methods development by combining high pressure liquid chromatography (HPLC) with the APESI-MS and total N detection (CLND). Separation of the DON components of the samples by HPLC followed by APESI-MSD and CLND detection will further the identification of the compounds, including the amount of N in different compound groups. We will use HPLC in two basic ways: 1) specific compound identification, and 2) further chemical property characterization of compound groups. Specific compound identification will be based on a comparison of the behavior (e.g., retention time, different mobile phase conditions) on LC columns of the authentic compound standard and the target compound in the rain sample. To further characterize the chemical properties of compounds in the rain samples for which we are not able to obtain authentic standards, we will analyze rain samples using various HPLC columns that are selected for their known characteristics to retain compounds with selected properties (e.g., aromatic, amines, COOH groups, etc.). We have already explored the performance of a

number of different LC columns (e.g., ES Aquasep, Supelco CN, Zorbax Bonus RP) for different components of the DON in New Brunswick rainwater. Selection and testing of additional columns will be based on the specific project needs as identified above.

Molecular marker database: Understanding the composition and sources of organic compounds present as aerosol particulate matter has been a major research focus of ours for the past 17 years (Mazurek group). We have developed a unique molecular marker database for atmospheric organic compounds that contains over 500 compounds pertinent to carbonaceous particles including authentic emission sources (Hildemann et al., 1991) and aerosols from urban and remote locales (Mazurek et al., 1987, 1989; 1991; 1993; Rogge et al., 1993e) based on GC/MS analyses. We will use the IMCS/Rutgers molecular marker data base and considerably expand and enhance it for our current use as follows: 1) We will continue to compile information from the literature on organic N compounds reported in atmospheric samples. This will include a range of information on each compound including chemical structure, pKa, water solubility, and known sources. To date, we have assembled information on over 300 compounds (for example: Table 4); 2) We will add chromatographic and mass spectroscopic information from our HPLC/MS APESI-MS studies for the DON compounds identified in the rain samples from our 4 study sites and from the suite of authentic standards. This molecular database is key to identifying and quantifying sources of DON in rain.

Artifact Evaluation: Over the past 2 years we have established procedures that result in low blanks for: 1) sample collection, 2) sample handling and storage, and 3) laboratory analysis. During the first three months of the project, we will train field personnel at each site in the field collection procedures. We will then test their performance by analyzing numerous field blanks from each site before commencing collection of rain from those sites. Procedural blanks for field collections and sample processing will be collected regularly and analyzed throughout the project.

Data processing: Each sample analyzed by APESI-MSD provides over 1200 data points (~100 masses per mode, 2 modes (+ and -), 6 replicate injections per sample). Processing of this data into a format that can be analyzed statistically and interpreted is time intensive. It takes approximately 5 days to analyze 12 samples by APESI-MSD (high/low mass ranges, +/- modes); however, it currently takes two people approximately 6 weeks to do the initial data processing of those samples (before any data interpretation can begin). We have made considerable progress in developing computer programs to reduce the time needed for initial formatting and processing of data. We will continue to optimize data handling time.

II. What is the disruption to ecological systems from atmospheric organic N deposition?

Objectives II. A-C (Table 1): Determine how much of the total DON and which specific components of the DON in rainwater from urban and relatively undisturbed (forested) sites is biologically available to aquatic microbes.

Our bioavailability experiments are similar to those that we have developed and used previously to examine utilization and effects on aquatic organisms of DON inputs from a variety

of sources (rainwater, urban runoff, agricultural runoff, forest runoff, etc.) (Seitzinger and Sanders 1997; Seitzinger and Sanders 1999; Seitzinger et al. in prep.). The major pathway by which DON is first incorporated into the biological cycle in aquatic ecosystems is through bacteria. Bacteria can utilize the DON for growth (increase in biomass) or mineralized it to DIN (ammonia).

Table 5. *Analytical methods used to measure DON utilization and bacterial response. Certified standards are analyzed each day that samples are analyzed. DOC check samples (Jonathan Sharp, Univ. DE) are analyzed with each DOC run. For rainwater nitrate analyses, certified standards for acidic rainwater will be obtained from the National Institute of Standards and Technology. Matrix spikes will be analyzed for 10% of all samples.*

Parameter	Method	Ref.
DON		
Bulk (total)	Chemiluminescence (CLN)	1
Functional groups	HPLC/ APESI-MS/CLND	p.9-11
Specific compounds	APESI-MS	p. 9-11
Ammonium	Phenol hypochlorite	2
Nitrate, nitrite	Cd reduction	2
DOC	High temp. combustion	3
PO_4	Molybdate rx.	2
Bacterial production	^{3}H-Leucine incorporation	4

1. Walsh 1989; 2. Lachet Quick-Chem, 3. Benner & Strom 1993; Sharp et al. 1993; 4. Kirchman 1993

Experiments will be conducted using rainwater collected in spring (Year 2) and summer (Year 3) from each of the four sites (Table 5) to examine how much of the DON in the precipitation at each site can be readily utilized by aquatic microbial populations. Each experiment will consist of rainwater composited from storm events from the same trajectory, plus controls (rain from different sites will NOT be composited). There will be duplicate microcosms for each treatment or control. Previous experiments have demonstrated very close agreement between duplicates (Seitzinger and Sanders 1997, 1999 and Seitzinger et al., in prep). Controls will consist of de-ionized water that is treated and sampled exactly like the rainwater DON treatments. This approach is designed to capture differences in the biological availability of DON deposited from different storm trajectories within a season (i.e., different chemical composition and sources), as well as provide information on differences among the 4 sites.

The basic protocol involves inoculating rainwater with bacteria from an aquatic system (river or lake) and quantifying decreases in the bulk DON, DOC, DIN, and changes in the specific DON masses (APESI-MSD) (presence/absence as well as abundance) over time (Table 5). In addition, rates of bacterial production are measured. The total quantity of DON utilized (bioavailable component) will be determined based on the difference between the amount of total DON at the beginning of the experiment and the amount remaining over time. We will determine which of the organic compounds are refractory (not utilized by the microbes) and which are biologically available (utilized) and thus contributing to changes in ecosystems, by comparing the masses and their abundances in rainwater at the beginning of the experiment and at the end of the experiment after bacterial degradation. Integration of this data with information linking specific types of human activities/processes to those chemical compounds will be used to begin to link source categories/human activities to ecological changes.

III. ***How does the terrestrial vegetation change the chemical composition of DON deposited to soils?***

Objective III. A. (Table 1) Examine the difference in the chemical composition of DON in rain and through-fall at one site in the Pinelands.

In addition to increasing biological productivity in aquatic ecosystems, atmospheric deposition also can be a significant external source of N to terrestrial ecosystems. The current project provides an exciting opportunity to link to Dr. Dighton's proposed studies in the Pinelands examining mycorrhizae as bio-indicators of air pollution. The Pinelands is one of the sites that we will be analyzing rainwater for inorganic-N (nitrate, nitrite, ammonium) and total DON. Dr. Dighton also needs these measurements for his studies; we will provide those data. In return, we will ask him to provide field personnel to collect the routine rainwater samples from the Pinelands site for our project. We will also provide him with the detailed DON chemical characterization information which may provide some insights into changes he is observing in mycorrhizae populations. Furthermore, we will analyze samples of throughfall during three rain events collected at his study site. We will then compare the detailed DON chemical composition (APESI-MS) data of the throughfall with the bulk deposition collected from the same rainstorms at our Pinelands monitoring site. This will be the first detailed examination of how the DON chemical species composition is altered by vegetation. We will work with Dr. Dighton to coordinate sampling.

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SUMMARY
PROPOSAL BUDGET

Revised August 2001 - YEAR

ORGANIZATION
Rutgers, The State University of New Jersey

PRINCIPAL INVESTIGATOR/PROJECT DIRECTOR
Sybil Seitzinger and Monica A. Mazurek, Co-Investigators

A. SENIOR PERSONNEL: PI/PD, Co-PI'S, Faculty and Other Senior Associates (List each separately with title, A.7. show number in brackets)	Funded Person-months CAL	ACAD	SUMR	Funds Requested by Proposer
1. CoPI -- S. Seitzinger	1.3			n/c
2. CoPI -- M. Mazurek	0.7			$4,457
3. CoPI - H. Hartnett	1.0			n/c
4.				
5.				
6. ( ) OTHERS (LIST INDIVIDUALLY ON BUDGET EXPLANATION PAGE)				
7. (2) TOTAL SENIOR PERSONNEL (1-6)	3.0			$4,457
B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)				
1. (1) POST DOCTORAL ASSOCIATES	4.0			12,66
2. (1) OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ETC.)	12.0			40,00
3. ( ) GRADUATE STUDENTS				
4. (0) UNDERGRADUATE STUDENTS				
5. ( ) SECRETARIAL - CLERICAL (IF CHARGED DIRECTLY)				
6. (1) OTHER - hourly				1,25
TOTAL SALARIES AND WAGES (A + B)				58,37
C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS) A.2 = 26.0%; B.1 = 18.75%, B.2 = 26.0%; B.6 = 9%				14,04
TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A + B + C)				72,42
D. PERMANENT EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM EXCEEDING $5,000)				
TOTAL EQUIPMENT				
E. TRAVEL 1. DOMESTIC (INCL. CANADA, MEXICO AND U.S. POSSESSIONS)				8C
2. FOREIGN				
F. PARTICIPANT SUPPORT COSTS				
1. STIPENDS				
2. TRAVEL				
3. SUBSISTENCE				
4. OTHER				
( ) TOTAL PARTICIPANT COSTS				
G. OTHER DIRECT COSTS				
1. MATERIALS AND SUPPLIES -				12,68
2. PUBLICATION COSTS/DOCUMENTATION/DISSEMINATION				
3. CONSULTANT SERVICES				
4. COMPUTER SERVICES				
5. SUBAWARDS				
6. OTHER - LC/MS CLND, DON and DOC instrument Maintenance Contracts				5,0
TOTAL OTHER DIRECT COSTS				17,6
H. TOTAL DIRECT COSTS (A THROUGH G)				90,9
I. INDIRECT COSTS (SPECIFY RATE AND BASE) MTDC = Total Sum A-G 90,909 Rate: 10%				
TOTAL INDIRECT COSTS				9,0
TOTAL DIRECT AND INDIRECT COSTS (H + I)				100,0
RESIDUAL FUNDS (IF FOR FURTHER SUPPORT OF CURRENT PROJECTS SEE GPG II.D.7.j.)				
L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K)				100,0

Maryellen O'Brien 8/30/01

MARYELLEN O'BRIEN
RESEARCH CONTRACT/GRANT SPECIALIST

SUMMARY
PROPOSAL BUDGET

YEAR 1

ORGANIZATION
Rutgers, The State University of New Jersey

PRINCIPAL INVESTIGATOR/PROJECT DIRECTOR
Sybil Seitzinger and Monica A. Mazurek, Co-Investigators

A. SENIOR PERSONNEL: PI/PD, Co-PI'S, Faculty and Other Senior Associates (List each separately with title, A.7. show number in brackets)	Funded Person-months CAL	ACAD	SUMR	Funds Requested by Proposer
1. **CoPI -- S. Seitzinger**	2.0			n/c
2. **CoPI -- M. Mazurek**	2.0			$13,000
3.				
4.				
5.				
6. ( ) OTHERS (LIST INDIVIDUALLY ON BUDGET EXPLANATION PAGE)				
7. (2) TOTAL SENIOR PERSONNEL (1-6)	4.0			$13,000
B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)				
1. (1) POST DOCTORAL ASSOCIATES	6.0			19,000
2. (1) OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ETC.)	12.0			40,000
3. ( ) GRADUATE STUDENTS				
4. (1) UNDERGRADUATE STUDENTS				2,500
5. ( ) SECRETARIAL - CLERICAL (IF CHARGED DIRECTLY)				
6. ( ) OTHER				
TOTAL SALARIES AND WAGES (A+B)				74,500
C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS) A.2=25.0%; B.1=18.25%, B.2=25.0%; B.4=0%				16,718
TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A+B+C)				91,218
D. PERMANENT EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM EXCEEDING $5,000) 2 wet/dry precipitation collectors for the Camden and NW New Jersey sites -- 2@$3,000 pH meter + probe for each offsite ppt collection -- 3@$750 each= $2,250				
TOTAL EQUIPMENT				8,250
E. TRAVEL 1. DOMESTIC (INCL. CANADA, MEXICO AND U.S. POSSESSIONS)				3,000
2. FOREIGN				
F. PARTICIPANT SUPPORT COSTS				
1. STIPENDS _____				
2. TRAVEL _____				
3. SUBSISTENCE _____				
4. OTHER _____				
( ) TOTAL PARTICIPANT COSTS				0
G. OTHER DIRECT COSTS				
1. MATERIALS AND SUPPLIES -				20,000
2. PUBLICATION COSTS/DOCUMENTATION/DISSEMINATION				1,000
3. CONSULTANT SERVICES				
4. COMPUTER SERVICES				
5. SUBAWARDS				
6. OTHER - LC/MS CLND, DON and DOC instrument Maintenance Contracts				7,000
TOTAL OTHER DIRECT COSTS				28,000
H. TOTAL DIRECT COSTS (A THROUGH G)				130,468
I. INDIRECT COSTS (SPECIFY RATE AND BASE) **MTDC = T Total Sum A-G 130,468 Rate: 10%**				
TOTAL INDIRECT COSTS				13,047
J. TOTAL DIRECT AND INDIRECT COSTS (H+I)				143,515
K. RESIDUAL FUNDS (IF FOR FURTHER SUPPORT OF CURRENT PROJECTS SEE GPG II.D.7.j.)				
L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K)				143,515

SUMMARY
PROPOSAL BUDGET

Revised August 2001 - YEAR

ORGANIZATION
Rutgers, The State University of New Jersey

PRINCIPAL INVESTIGATOR/PROJECT DIRECTOR
Sybil Seitzinger and Monica A. Mazurek, Co-Investigators

A. SENIOR PERSONNEL: PI/PD, Co-PI'S, Faculty and Other Senior Associates (List each separately with title, A.7. show number in brackets)	Funded Person-months CAL	ACAD	SUMR	Funds Requested by Proposer
1. CoPI -- S. Seitzinger	1.4			n/c
2. CoPI -- M. Mazurek	0.6			$3,39
3. CoPI - H. Hartnett (n/c for 0.4 mo;$2,284 for 0.6 mo)	1.0			$2,28
4.				
5.				
6. ( ) OTHERS (LIST INDIVIDUALLY ON BUDGET EXPLANATION PAGE)				
7. (2) TOTAL SENIOR PERSONNEL (1-6)	3.0			$5,68
B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)				
1. (1) POST DOCTORAL ASSOCIATES	10.0			$31,66
2. (1) OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ETC.)	6.0			$20,00
3. ( ) GRADUATE STUDENTS				
4. (0) UNDERGRADUATE STUDENTS				
5. ( ) SECRETARIAL - CLERICAL (IF CHARGED DIRECTLY)				
6. (1) OTHER - hourly				1,2
TOTAL SALARIES AND WAGES (A+B)				58,5
C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS) A.2&3=26.0%; B.1=18.75%, B.2=26.0%; B.6=9%				12,7
TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A+B+C)				71,3
PERMANENT EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM EXCEEDING $5,000)				
TOTAL EQUIPMENT				
E. TRAVEL 1. DOMESTIC (INCL. CANADA, MEXICO AND U.S. POSSESSIONS)				8
2. FOREIGN				
F. PARTICIPANT SUPPORT COSTS				
1. STIPENDS				
2. TRAVEL				
3. SUBSISTENCE				
4. OTHER				
( ) TOTAL PARTICIPANT COSTS				
G. OTHER DIRECT COSTS				
1. MATERIALS AND SUPPLIES -				13,5
2. PUBLICATION COSTS/DOCUMENTATION/DISSEMINATION				2
3. CONSULTANT SERVICES				
4. COMPUTER SERVICES				
5. SUBAWARDS				
6. OTHER - LC/MS CLND, DON and DOC instrument Maintenance Contracts				5,0
TOTAL OTHER DIRECT COSTS				18,7
H. TOTAL DIRECT COSTS (A THROUGH G)				90,5
I. INDIRECT COSTS (SPECIFY RATE AND BASE) MTDC = T Total Sum A-G 90,909 Rate: 10%				
TOTAL INDIRECT COSTS				9,0
J. TOTAL DIRECT AND INDIRECT COSTS (H+I)				100,0
RESIDUAL FUNDS (IF FOR FURTHER SUPPORT OF CURRENT PROJECTS SEE GPG II.D.7.j.)				
K. AMOUNT OF THIS REQUEST (J) OR (J MINUS K)				100,0

Maryellen O'Brien/dg 8/30/0

MARYELLEN O'BRIEN
RESEARCH CONTRACT/GRANT SPECIALIST

SUMMARY
PROPOSAL BUDGET

YEAR 2

ORGANIZATION **Rutgers, The State University of New Jersey**				
PRINCIPAL INVESTIGATOR/PROJECT DIRECTOR **Sybil Seitzinger and Monica A. Mazurek, Co-Investigators**				
A. SENIOR PERSONNEL: PI/PD, Co-PI'S, Faculty and Other Senior Associates (List each separately with title, A.7. show number in brackets)	Funded Person-months			Funds Requested by Proposer
	CAL	ACAD	SUMR	
1. **CoPI -- S. Seitzinger**	**2.0**			**n/c**
2. **CoPI -- M. Mazurek**	**2.0**			**$13,650**
3.				
4.				
5.				
6. ( ) OTHERS (LIST INDIVIDUALLY ON BUDGET EXPLANATION PAGE)				
7. (**2**) TOTAL SENIOR PERSONNEL (1-6)	**4.0**			**$13,650**
B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)				
1. (**1**) POST DOCTORAL ASSOCIATES	**12.0**			**$39,900**
2. (**1**) OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ETC.)	**12.0**			**$42,000**
3. ( ) GRADUATE STUDENTS				
4. (**1**) UNDERGRADUATE STUDENTS				
5. ( ) SECRETARIAL - CLERICAL (IF CHARGED DIRECTLY)				
6. ( ) OTHER				
TOTAL SALARIES AND WAGES (A+B)				95,55
C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS) **A.2=25.0%; B.1=18.25%, B.2=25.0%; B.4=0% B.4=0%**				21,19
TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A+B+C)				116,74
D. PERMANENT EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM EXCEEDING $5,000)				
TOTAL EQUIPMENT				
E. TRAVEL 1. DOMESTIC (INCL. CANADA, MEXICO AND U.S. POSSESSIONS)				3,00
2. FOREIGN				
F. PARTICIPANT SUPPORT COSTS				
1. STIPENDS _____				
2. TRAVEL _____				
3. SUBSISTENCE _____				
4. OTHER _____				
( ) TOTAL PARTICIPANT COSTS				
G. OTHER DIRECT COSTS				
1. MATERIALS AND SUPPLIES -				20,00
2. PUBLICATION COSTS/DOCUMENTATION/DISSEMINATION				1,00
3. CONSULTANT SERVICES				
4. COMPUTER SERVICES				
5. SUBAWARDS				
6. OTHER - LC/MS CLND, DON and DOC instrument Maintenance Contracts				7,00
TOTAL OTHER DIRECT COSTS				28,00
H. TOTAL DIRECT COSTS (A THROUGH G)				147,74
I. INDIRECT COSTS (SPECIFY RATE AND BASE) **MTDC = T Total Sum A-G 147,744 Rate: 10%**				
TOTAL INDIRECT COSTS				14,77
J. TOTAL DIRECT AND INDIRECT COSTS (H+I)				162,5
K. RESIDUAL FUNDS (IF FOR FURTHER SUPPORT OF CURRENT PROJECTS SEE GPG II.D.7.j.)				
L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K)				162,5

SUMMARY
PROPOSAL BUDGET

YEAR 3

ORGANIZATION
Rutgers, The State University of New Jersey

PRINCIPAL INVESTIGATOR/PROJECT DIRECTOR
Sybil Seitzinger and Monica A. Mazurek, Co-Investigators

A. SENIOR PERSONNEL: PI/PD, Co-PI'S, Faculty and Other Senior Associates (List each separately with title, A.7. show number in brackets)	Funded Person-months CAL	ACAD	SUMR	Funds Requested by Proposer
1. **CoPI -- S. Seitzinger**	**2.0**			n/c
2. **CoPI -- M. Mazurek**	**2.0**			14,333
3.				
4.				
5.				
6. ( ) OTHERS (LIST INDIVIDUALLY ON BUDGET EXPLANATION PAGE)				
7. (**2**) TOTAL SENIOR PERSONNEL (1-6)	**4.0**			**$14,333**
B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)				
1. (**1**) POST DOCTORAL ASSOCIATES	**12.0**			41,895
2. (**1**) OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ETC.)	**6.0**			22,050
3. ( ) GRADUATE STUDENTS				
4. (**1**) UNDERGRADUATE STUDENTS				0
5. ( ) SECRETARIAL - CLERICAL (IF CHARGED DIRECTLY)				
6. ( ) OTHER				
TOTAL SALARIES AND WAGES (A+B)				78,278
C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS) **A.2=25.0%; B.1=18.25%, B.2=25.0%; B.4=0% B.4=0%**				16,741
TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A+B+C)				95,019
D. PERMANENT EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM EXCEEDING $5,000)				
TOTAL EQUIPMENT				
E. TRAVEL 1. DOMESTIC (INCL. CANADA, MEXICO AND U.S. POSSESSIONS)				3,000
2. FOREIGN				
F. PARTICIPANT SUPPORT COSTS				
1. STIPENDS _____				
2. TRAVEL _____				
3. SUBSISTENCE _____				
4. OTHER _____				
( ) TOTAL PARTICIPANT COSTS				
G. OTHER DIRECT COSTS				
1. MATERIALS AND SUPPLIES				17,500
2. PUBLICATION COSTS/DOCUMENTATION/DISSEMINATION				1,500
3. CONSULTANT SERVICES				
4. COMPUTER SERVICES				
5. SUBAWARDS				
6. OTHER - LC/MS CLND, DON and DOC instrument Maintenance Contracts				6,458
TOTAL OTHER DIRECT COSTS				25,458
H. TOTAL DIRECT COSTS (A THROUGH G)				123,477
I. INDIRECT COSTS (SPECIFY RATE AND BASE) **MTDC = T Total Sum A-G 123,477 Rate: 10%**				
TOTAL INDIRECT COSTS				12,34
J. TOTAL DIRECT AND INDIRECT COSTS (H+I)				135,82
K. RESIDUAL FUNDS (IF FOR FURTHER SUPPORT OF CURRENT PROJECTS SEE GPG II.D.7.j.)				
L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K)				135,82

Years 1-3 Cumulative
PROPOSAL BUDGET

ORGANIZATION **Rutgers, The State University of New Jersey**				
PRINCIPAL INVESTIGATOR/PROJECT DIRECTOR **Sybil Seitzinger and Monica A. Mazurek, Co-Investigators**				
A. SENIOR PERSONNEL: PI/PD, Co-PI'S, Faculty and Other Senior Associates (List each separately with title, A.7. show number in brackets)	NSF Funded Person-months			Funds Requested by Proposer
	CAL	ACAD	SUMR	
1. **CoPI -- S. Seitzinger**	6			n/c
2. **CoPI -- M. Mazurek**	6			40,983
3.				
4.				
5.				
6. ( ) OTHERS (LIST INDIVIDUALLY ON BUDGET EXPLANATION PAGE)				
7. (**2**) TOTAL SENIOR PERSONNEL (1-6)	12			40,983
B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)				
1. (**1**) POST DOCTORAL ASSOCIATES	30			100,795
2. (**1**) OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ETC.)	30			104,050
3. ( ) GRADUATE STUDENTS				
4. (**1**) UNDERGRADUATE STUDENTS				2,500
5. ( ) SECRETARIAL - CLERICAL (IF CHARGED DIRECTLY)				
6. ( ) OTHER				
TOTAL SALARIES AND WAGES (A+B)				248,328
C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS) **A.2=25.0%; B.1=18.25%, B.2=25.0%; B.4=0%**				54,653
TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A+B+C)				302,981
D. PERMANENT EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM EXCEEDING $5,000) 2 wet/dry precipitation collectors for the Camden and NW New Jersey sites -- 2@$3,000 pH meter + probe for each offsite ppt collection -- 3@$750 each= $2,250				
TOTAL EQUIPMENT				8,250
E. TRAVEL 1. DOMESTIC (INCL. CANADA, MEXICO AND U.S. POSSESSIONS)				9,000
2. FOREIGN				0
F. PARTICIPANT SUPPORT COSTS 1. STIPENDS _____ 2. TRAVEL _____ 3. SUBSISTENCE _____ 4. OTHER _____				
( ) TOTAL PARTICIPANT COSTS				0
G. OTHER DIRECT COSTS				
1. MATERIALS AND SUPPLIES				57,500
2. PUBLICATION COSTS/DOCUMENTATION/DISSEMINATION				3,500
3. CONSULTANT SERVICES				
4. COMPUTER SERVICES				
5. SUBAWARDS				
6. OTHER - LC/MS CLND, DON and DOC instrument Maintenance Contracts				20,450
TOTAL OTHER DIRECT COSTS				81,450
H. TOTAL DIRECT COSTS (A THROUGH G)				401,681
I. INDIRECT COSTS (SPECIFY RATE AND BASE) **MTDC = T Total Sum A-G 401,689** **Rate: 10%**				
TOTAL INDIRECT COSTS				40,169
J. TOTAL DIRECT AND INDIRECT COSTS (H+I)				441,850
K. RESIDUAL FUNDS (IF FOR FURTHER SUPPORT OF CURRENT PROJECTS SEE GPG II.D.7.j.)				
L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K)				441,850

Budget and Explanation

Item	*Description*	*Year 1*	*Year 2*	*Year 3*
A.0	**Senior Personnel**			
A.1	*Dr. Seitzinger's* salary is supported by the Rutgers/NOAA Cooperative Marine Education and Research Program; no funds are requested to support her time. She will co-direct and manage the project.	2 mo.	2 mo.	2 mo.
A.2	*Dr. Monica Mazurek* will require 2 months per year of salary support from NJDEP. She will co-direct and manage the project.	2 mo.	2 mo.	2 mo.
B.1	Funds are requested to support a postdoctoral research fellow for 2 full years over the 3 year grant. The fellow will contribute to the sample analysis, data interpretation and synthesis tasks of the project (rate= $3,167 per month).	6 mo.	12 mo.	6 mo.
B.2	Funds are required to cover an assistant to perform laboratory experiments (bioavailability tests), chemical analyses, and to assist with precipitation collection (rate= $3,333 per month).	6 mo.	12 mo.	12 mo.
C.0	**Fringe benefits** are calculated as follows: of base salary. **A.1, A.2=25.0%; B.1=18.25%, B.2=25.0%; B.4=0%**			
D.0	**Equipment**			
D.1	Two additional wet/dry deposition collectors will be needed for the Camden and the NW New Jersey sites (2@$3,000).	$6,000		
D.2	The 3 offsite locations will need a pH meter and probe to measure ppt pH (3@$750)..	$2,250		
	Subtotal	*$8,250*		
E.0	**Travel**			
E.1a	Domestic travel to and from field collection sites (3 sites) estimated at roughly 6 visits per site in Year 1, 12 visits per site in Year 2, and 6 visits per site in Year 3.	$1,200	$2,400	$1,100
E.1b	Partial travel support to one scientific meeting per year for one PI is planned in Years 1,2&3.	$1,800	$600	$1,900
	Subtotal	*$3,000*	*$3,000*	*$3,000*
G.0	**Other Direct Costs**			
G.1	Materials and Supplies			
G.1a	*General Supplies for Nutrient Analyses, Bulk DON, Bulk DOC* Reagents for nutrient analyses; Filters, pipettes, autoanalyzer cups, test tubes, tubing, etc.; for inorganic nutrient analyses; Filters, drying tubes, vials, etc. for high-temperature DON analyses; Compressed gases for DOC and DON analyses; General glassware; Cartridges for Nanopure water system	$10,000	$10,000	$8,400
G.1b	*HPLC columns*	$1,500	$1,500	$1,000
G.1c	*Laboratory glassware and supplies, chemicals for standards*	$2,500	$1000	$800
G.1d	*HPLC AP-ESI MS Instrument, expendable supplies* Includes: gases; autosampler vials; pump seals; filters; mobile phase solvents; plus other expendable parts	$4,650	$4,150	$4,000
G.1e	*Bioavailability experiment supplies including ^{3}H-[Leu]*		$2,000	$2,000
G.1f	*Computer software upgrades and expendable supplies*	$600	$500	$500
G.1g	*Office supplies, postage, photocopies, phone*	$750	$850	$800
	Total Materials and Supplies	*$20,000*	*$20,000*	*$17,500*

G.2	Publication costs/document dissemination	$1,000	$1,000	$1,500
G.6	Other			
G.6a	HPLC AP-ESI MS Instrument maintenance and repair	$4,000	$4,000	$4,000
G.6a.1	Shimatzu DOC analyzer maintenance and repair	$1,500	$1,500	$1,200
G.6a.2	Antek Instruments, Dissolved Organic Nitrogen analysis	$1,500	$1,500	$1,258
	Subtotal Other	*$7,000*	*$7,000*	*$6,458*

The above estimated costs are based on known expenditures from previous studies for similar analyses.

Sybil P. Seitzinger

Institute of Marine and Coastal Sciences

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Email: sybil@imcs.rutgers.edu

Citizenship: USA

Education: B.S. (Biology), Boston University, 1974; Ph.D. (Oceanography), University of Rhode Island, 1982.

Professional History: ***Director*** , Rutgers/NOAA Cooperative Marine Education and Research Program and Visiting Professor, Rutgers University, Institute of Marine and Coastal Sciences, 1994-present; ***Associate Curator***, Academy of Natural Sciences of Philadelphia, 1990-1994; ***Visiting Scientist***, University of Aarhus, Denmark, 1990; ***Assistant Curator***, Academy of Natural Sciences of Philadelphia, 1986-1990; ***Senior Scientist***, Academy of Natural Sciences of Philadelphia, 1984-1986; ***Distinguished Patrick Scholar***, Academy of Natural Sciences of Philadelphia, 1982-1984; ***Research Associate***, School of Oceanography, University of Rhode Island, 1981; ***Instructor in Marine Sciences***, International Sea Grant Program, University of Pertanian, Malaysia, 1980.

Professional Activities (selected) (+=Invited):

+Member, Editorial Board, ECOSYSTEMS (1999-2001)
+Member, Scientific Advisory Committee, Institute for Ecosystem Studies, Millbrook, NY (1998-2002)
+Elected Member, Governing Board, American Society of Limnology and Oceanography (1994-1997)
+Member, NOAA's Assessment Team for Nitrogen in Atmospheric Deposition (1997-present)
+Member, Scientific Committee on Problems in the Environment (SCOPE) Nitrogen Project, Nitrogen Transport Workgroup (1994 and 1999)
+Member, Scientific and Technical Advisory Committee, U.S. EPA National Estuaries Program, Barnegat Bay Program (1996-present)
+Advisory Panel, The Royal Swedish Academy of Sciences and Swedish Environmental Agency to provide advise on management and research options for the Baltic. (August 1997)
Special Symposium Volume Editor, Limnology and Oceanography, Effects of Multiple Stressors in Freshwater and Marine Ecosystems, vol. 44 (2) part 2 (co-edited with D.Breitburg and J. Sanders)
+Chair, American Society of Limnology and Oceanography, *Limnology and Oceanography* Journal Evaluation Committee (1997-present).
+Visiting Scholar, University Wageningen, Center for Global Change Research, The Netherlands, May 1997.
+Elected Member, Governing Board, Estuarine Research Federation (1992-1994)
+Member, Expert Group, United Nations, Organization for Economic and Cooperation and Development., Intergovernmental Panel on Climate Change. Nitrous Oxide and Carbon Dioxide in Agriculture Work Group. Workshop Meeting, Geneva, Switzerland, Dec. 1995.

Sybil P. Seitzinger

(continued)

B. Selected Publications

Seitzinger, S.P., R. Styles, R.W. Sanders. In prep. Seasonal pattern in the biological availability of dissolved organic matter from natural and anthropogenic sources.

Wiegner, T.N. and S.P. Seitzinger. Submitted. Photochemical and microbial degradation of external dissolved organic matter inputs to rivers. Aquatic Microbial Ecology.

Paerl, H.W., W.R. Boynton, R.L Dennis, C.T. Driscoll, H.S. Greening, J.N. Kremer, N. N. Rabalais, S. P. Seitzinger. 2000. Atmospheric deposition of nitrogen in coastal waters: biogeochemical and ecological implications. *In:* Valigura, R. (editor), Nitrogen Loading in Coastal Water Bodies: An Atmospheric Perspective, Coastal and Estuarine Studies, volume 57, AGU Press.

Seitzinger, S. P. 2000. Scaling up: Site specific measurements to global scale estimates of denitrification. Chapter 12. *In*: Hobbie, J. (editor), Estuarine Synthesis: The Next Decade. Island Press

Seitzinger, S.P. and R.W. Sanders. 1999. Atmospheric inputs of dissolved organic nitrogen stimulate coastal bacteria and algae. Limnol. Oceanogr. 44: 721-730.

Reysenbach, A.-L., S. P. Seitzinger, J. Kirshtein and E. McLaughlin. 1999. Molecular constraints on a high-temperature evolution of early life. Biol. Bull. 196:367-372.

Seitzinger, S.P. and R.W. Sanders. 1997. Biologically reactive dissolved organic nitrogen inputs from rivers to estuaries. Mar. Ecol. Progr. Ser. 159: 1-12.

Seitzinger, S.P. and C. Kroeze. 1998. Global distribution of nitrous oxide production and N inputs in freshwater and coastal marine ecosystems. Global Biogeochem. Cycles 12: 93-113.

Kroeze, C. and S. P. Seitzinger. 1998. Nitrogen inputs to rivers, estuaries and continental shelves and related nitrous oxide emissions in 1990 and 2050: a global model. Nutrient Cycling in Agroecosystems, 52: 195-212.

Seitzinger, S. P. and A. E. Giblin. 1996. Estimating denitrification in North Atlantic continental shelf sediments. Biogeochem. 35: 235-259.

Nixon, S. W., J. Ammerman, L. Atkinson, V. Berounsky, G. Billen, W. Boicourt, W. Boynton, T. Church, D. DiToro, R. Elmgren, J. Garber, A. Giblin, R. Jahnke, N. Owens, M. E. Q. Pilson, and S. Seitzinger. 1996. The fate of nitrogen and phosphorus at the land-sea margin of the North Atlantic Ocean. Biogeochem. 35: 141-180.

Seitzinger, S.P. 1994. Linkages between organic matter mineralization and denitrification in eight riparian wetlands. Biogeochem. 25:19-39.

C. Scientific Collaborators Within the Past Four Years: A.E. Giblin, S.W. Nixon, R. Sanders, C. Kroeze, L. Kerkhof, D. Breitburg, J. Sanders, D. Correll, C. Gilmour, S. Brandt, S. Bartell, T. Jordan, D. Weller, G. Riedel, K. Sellner, M. Mazurek, A.-L. Reysenbach.

D. Graduate Advisees: T. Weigner, S. Watts, Steve Litvin, Ji Yongcheng

Post-doctoral Scholars: Andrew Laursen, Hilairy Hartnett

Monica A. Mazurek

BIOGRAPHICAL SKETCH

A. Vita

Monica A. Mazurek

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Education: B.S. (Chemistry), University of California at Los Angeles, 1977; Ph.D. (Geochemistry), University of California at Los Angeles, 1985.

Professional History: ***Director of Academic Initiatives,*** *Office of the Dean, School of Engineering,* Rutgers University, 2000-to present; ***Associate Research Professor***, Rutgers University, 1995-present; ***Coordinator of Program Development in Science, Mathematics, Engineering, and Technology Education,*** *Office of the Vice President for Undergraduate Education*, Rutgers University, 1998-2000, ***Associate Program Director***, Atmospheric Chemistry Program, National Science Foundation, 1996-1998; ***Chemist***, Environmental Chemistry Division, Brookhaven National Laboratory, 1989-1995; ***Post-doctoral Research Fellow***, Environmental Engineering Science Department, California Institute of Technology, 1986-1989; ***Research Associate***, Environmental Geochemistry Group, Oregon State University, 1982-1985; ***Graduate Student***, University of California at Los Angeles, 1978-1985.

Professional Activities:

Member, Advisory Board for the Douglass Project for Women in Math and Science, Douglass College for Women, Rutgers University, January 1998 to present.

Member, Subcommittee on Air Quality, Committee for Environment and Natural Resources (CERN), Washington, D.C., February 1996 to present. Designated representative of the National Science Foundation, Atmospheric Sciences Division.

Member, Institutional Steering Committee for North Atlantic Research Strategy for Tropospheric Ozone (NARSTO), Washington, D.C., March 1996 to present. Designated representative of the National Science Foundation, Atmospheric Sciences Division.

Contributing author to "Radiative Forcing of Climate Change -- 1994," Report to the Intergovernmental Panel on Climate Change (IPCC) from the Scientific Assessment Working Group (WGI), sponsored by the World Meteorological Organization.

Editorial advisory board *Aerosol Science & Technology*, 1994 to 1996.

B. Five Publications Most Relevant to this Project

Mazurek, M. A., M. Mason-Jones, H. Mason-Jones, L. G. Salmon, G. R. Cass, K. A. Hallock, and M. Leach. 1997. Visibility-reducing organic aerosols in the vicinity of Grand Canyon National Park: 1. Properties observed by high resolution gas chromatography. JGR Atmospheres, 102 (D3), 3779-3793.

Hildemann, L. M., M. A. Mazurek, G. R. Cass, and B. R. T. Simoneit. 1991. Quantitative characterization of urban sources of organic aerosol by high-resolution gas chromatography. Environ. Sci. Technol. 25: 1311-1325.

Mazurek, M. A. and B. R. T. Simoneit. 1986. Organic components in bulk and wet-only precipitation. Critical Reviews in Environmental Control 16: 1-140.

Simoneit, B. R. T. and M. A. Mazurek. 1989. Organic tracers in ambient aerosols and rain, Aerosol Sci. Technol. 10: 267-291.

Rogge, W. F., M. A. Mazurek, L. M. Hildemann, G. R. Cass, and B. R. T. Simoneit. 1993e. Quantification of organic aerosols at a molecular level: Identification, abundance and seasonal variation. Atmos. Environ., 27A: 1309-1330.

Other significant publications:

Mazurek, M.A., Simoneit, B.R.T. (1998). Higher molecular weight terpenoids as indicators of organic emissions from terrestrial vegetation. *ACS Symposium Series 671*, 92-108.

Schauer, J.J., Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., and Simoneit, B.R.T. (1996). Source apportionment of airborne particulate matter using organic compounds as tracers. Atmos. Environ. 30:, 3837-3855.

Mazurek, M.A., Cass, G.R. and Simoneit, B.R.T. 1991. Biological input to visibility-reducing aerosol particles in the remote arid southwestern United States. Environ. Sci. Technol.: 25, 684-694.

Mazurek, M. A., G. R. Cass, and B. R. T. Simoneit. 1989. Interpretation of high-resolution gas chromatography and high-resolution gas chromatography/mass spectrometry data acquired from atmospheric organic aerosol samples. Aerosol Science Technology 10: 408-420.

Simoneit, B. R. T. and M. A. Mazurek. 1982. Organic matter of the troposphere. II. natural background of biogenic lipid matter in aerosols over the rural western United States. Atmos. Environ. 16: 2139-2159.

C. *Scientific Collaborators Within the Past Four Years:* Glen R. Cass, Peter H. Daum, Steve Eisenreich, Lynn M. Hildemann, Paul Lioy, Martin Leach, Leonard Newman, Wolfgang F. Rogge, James J. Schauer, Sybil P. Seitzinger, Bernd R. T. Simoneit, Laurel J. Standley, Barbara J. Turpin.

D.1 *Graduate Advisees:* none

D.2 *Post-Graduate Advisees:* Orest E. Kawka (DOE Alexander Hollaender Postdoctoral Fellow).

D.3 *Summary:*
Total number of graduate students advised: none

Total number of postdoctoral scholars sponsored: one

E.1 *Graduate Advisors:* Walter E. Reed (UCLA), Bernd R. T. Simoneit (Oregon State University)

E.2 *Postdoctoral Advisor:* Glen R. Cass (Caltech)

HILAIRY ELLEN HARTNETT
CURRICULUM VITAE

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EDUCATION

Ph.D. 1998	Oceanography. University of Washington, Seattle, WA Dissertation Title: *Organic carbon input, degradation and preservation in continental margin sediments: An assessment of the role of a strong oxygen deficient zone.*
M.S. 1995	Oceanography. University of Washington, Seattle, WA
A.B. 1990	Chemistry, with Honors. Vassar College, Poughkeepsie, NY

PROFESSIONAL EXPERIENCE

2001-present	Associate Director, Rutgers/NOAA Cooperative Marine Education and Research Program, Rutgers University
2000-present	Visiting Assistant Professor, Institute of Marine and Coastal Sciences, Rutgers University
1998-2000	Post-Doctoral Fellow, Institute of Marine and Coastal Sciences, Rutgers University
1990-1998	Research Assistant, University of Washington

TEACHING EXPERIENCE

2000, 2001	Instructor. Chemical Oceanography, Ocean 540. Rutgers University (50%)
1999, 2000	Instructor. Oceanographic Methods and Data Analysis, Marine Science 364. Rutgers University (50%)
2001	Instructor. Introduction to Marine Science, Marine Science 200. Rutgers University (25%)
1999	Guest Lecturer. Oceanography of Puget Sound, Ocean 485. University of Washington
1992, 1994	Teaching Assistant. Marine Chemistry, Ocean 520 and 527. University of Washington
1993	Teaching Assistant. Chemical Oceanography, Ocean 421. University of Washington

SUPERVISORY EXPERIENCE

2001-present	Manager of biogeochemistry research laboratory with two full-time technicians. Rutgers University

2001-present Advisor to 2nd-year graduate student in oceanography with a multidisciplinary project involving DOM and trace-metal/organic interactions. Rutgers University

1993-present Advisor for undergraduate summer interns. Mentored and advised undergraduates conducting summer projects in REU program in chemical oceanography. Rutgers University, and University of Washington.

OTHER TEACHING EXPERIENCE

2001 Instructor, Douglass College Science Institute, Rutgers University. Summer class in marine science for high-school aged girls in science and math with an emphasis on experimental design and hypothesis testing.

1994-1997 Coordinator, *University of Washington Oceanography Outreach Program.* Designed and presented lectures for middle schools, secondary schools, and community groups in the Seattle area. Lecture topics: Oceanography of Puget Sound; El Niño and Climate Change; Ecology of the Inter-tidal Zone.

1995-1996 Consulting Scientist, Curriculum Development Team. *Washington Initiative for Science Education – Science Teacher Enhancement Program (WISE-STEP).* Advised science teachers and designed a one-semester marine science curriculum for grades 4-6, based on national and state science curriculum standards.

PUBLICATIONS

Hartnett, H.E. (in preparation, manuscript available upon request) Denitrification in Antarctic Continental Shelf Sediments. To be submitted to *Deep-Sea Research.*

Hartnett, H.E. and S.P. Seitzinger (in preparation, manuscript available upon request) High-resolution nitrogen gas profiles in sediment porewaters using a new probe for membrane-inlet mass spectrometry (MIMS). To be submitted to *Marine Chemistry.*

Hartnett, H.E. and A.H. Devol. (in preparation, manuscript available upon request) Oxygen isotope fractionation during sediment respiration: oxidant stress vs. carbon limitation. To be submitted to *Limnology and Oceanography.*

Hartnett, H.E. and A.H. Devol. (in revision) The role of a strong oxygen deficient zone in the preservation and degradation of organic matter: a carbon budget for the continental margins of NW Mexico and Washington State. *Geochimica et Cosmochimica Acta.*

Devol, A.H. and **H.E. Hartnett** (in press) Role of the oxygen minimum zone in transfer of organic carbon to the deep ocean. *Limnology and Oceanography.*

Hedges, J.I., F.S. Hu, A.H. Devol, **H.E. Hartnett**, E. Tsamakis and R.G. Keil. (1999) Sedimentary organic matter preservation: A test for selective degradation under oxic conditions. *American Journal of Science.* **299**(7,8,9), 259-555.

Kristensen, E., A.H. Devol and **H.E. Hartnett.** (1999) Organic matter diagenesis in sediments on the continental shelf and slope of the Eastern tropical and temperate North Pacific. *Continental Shelf Research.* **19**(10), 1331-1351.

Hartnett, H.E., R.G. Keil, J.I. Hedges and A.H. Devol. (1998) Influence of oxygen exposure time on the preservation of organic carbon in continental margin sediments. *Nature.* **391,** 572-574.

Hartnett, H.E. and A.H. Devol. (1998) Isotopic fractionation of oxygen during sediment respiration. V.M. Goldschmidt Conference, Toulouse 1998. *Mineralogical Mag.* **62A**(1), 577-578.

A.H. Devol and **H.E. Hartnett.** (1998) The effect of the water column oxygen minimum zone on sedimentary organic matter diagenesis. V.M. Goldschmidt Conference, Toulouse 1998. *Mineralogical Mag.* **62A**(1), 377-378.

Beck, C.W. and **H.E. Hartnett**. (1990) Sicilian Amber. In: *Amber in Archaeology. (Proceedings of the Second International Conference on Amber in Archaeology, Liblice 1990)*. C.W. Beck and J. Bouzek (Eds.) Institute of Archaeology, Czech Academy of Sciences. Prague, pp. 36-47.

PRESENTATIONS AT PROFESSIONAL CONFERENCES

2001 ASLO Meeting. Nitrogen, oxygen and nutrient fluxes in continental shelf sediments from the western Antarctic peninsula. Albuquerque, NM.

2000 AGU Ocean Sciences Meeting. Oxidant availability as indicated by porewater oxygen and nutrient distributions in continental margin sediments. Invited talk. San Antonio, TX.

2000 AGU Ocean Sciences Meeting. Nitrogen gas profiles in sediment porewaters using membrane-inlet mass spectrometry. San Antonio, TX.

1999 Dissertation Symposium in Chemical Oceanography (DISCO). Organic carbon input, degradation and preservation in the continental margin sediments of NW Mexico. Honolulu, HI.

1998 8th Annual V.M. Goldschmidt Conference. Fractionation of oxygen during sedimentary respiration. Toulouse, France.

1998 AGU Ocean Sciences Meeting. DOC production in oxic and anoxic incubations of sediments from the oxygen minimum zones of Washington and Mexico. San Diego, CA.

1996 American Chemical Society Annual Meeting. Oxygen exposure time as a control on carbon preservation in continental margin sediments. Orlando, FL.

1995 AGU Fall Meeting. Organic carbon:surface area ratios for the Washington and Mexican Continental Margins. San Francisco, CA.

1994 AGU Ocean Sciences Meeting. Carbon burial efficiencies in the continental margin sediments of Washington and Mexico. San Diego, CA.

INVITED SEMINARS

2000 Princeton/Rutgers Biogeochemistry Seminar. Denitrification rates in Antarctic continental shelf sediments. New Brunswick, NJ.

1999 Institute of Marine and Coastal Sciences Departmental Seminar. Organic carbon input, degradation and preservation in the continental margin sediments of NW Mexico. New Brunswick, NJ.

1997 Chemical Oceanography Departmental Seminar. Mid-depth N_2/Ar anomalies in the Pacific and Indian Oceans. University of Washington. Seattle, WA.

1997 O_2 exposure time as a control on carbon preservation in continental margin sediments. Carnegie Geophysical Laboratory. Washington D.C.

1995 Biological Oceanography Departmental Seminar. What controls carbon preservation in continental margin sediments? A geochemist's perspective on some biological processes. University of Washington.

CRUISE/FIELD EXPERIENCE

Western Antarctic Peninsula (FOODBANCS II, V). *R/V L.M. Gould*, Mar. 2000; Feb. 2001. Chief Scientist: David DeMaster

Washington Margin. *R/V Wecoma*, August-September 1997. Chief Scientist: Allan Devol

Gulf of Mexico. *R/V Gyre*, June 1997. Chief Scientist: Gil Rowe

Vancouver Island Fjords. *R/V Barnes*, May 1997. Chief Scientist: Ellery Ingall

Mexican Margin (TTAN2). *R/V New Horizon*, Nov.-Dec. 1996. Chief Scientist: Allan Devol

Pacific Coast Transect (STUPEX 96). *R/V Thomas G. Thompson*, July 1996. Chief Scientist: **Hilairy Hartnett**

Washington Margin. *R/V Wecoma*, August-September 1994. Chief Scientist: Allan Devol

Mexican Margin (TTAN). *R/V New Horizon*, Nov.-Dec. 1993. Chief Scientist: Allan Devol

Bermuda Transect. *R/V Oceanus*, October 1989. Chief Scientist: Steve Emerson

Washington Margin. *R/V New Horizon*, June-July 1988. Chief Scientist: Allan Devol

RESEARCH TECHNIQUES AND ANALYTICAL METHODS

Mass Spectrometry (continuous flow, dual-inlet and quadrupole MS; $\delta^{18}O$, $\delta^{15}N$, $\delta^{13}C$, O/N/Ar gas ratios; APESI-MS, MIMS, EA-IRMS, GCMS), *In situ* benthic chamber techniques (design, construction and deployment), Microelectrode techniques (Solid-state voltammetric microelectrodes, O_2 microelectrodes), Sediment coring (box coring, gravity coring, piston coring), Sediment traps (moored and floating arrays), Solid-phase analyses (POC/N, surface-area, XRD), Seawater analyses (DOC, TDN, O_2, TCO_2, Alkalinity, Nutrients), Radiochemical techniques (^{210}Pb and ^{14}C accumulation rates, ^{35}S-labled $SO_4^=$ reduction rate assay)

PROFESSIONAL AFFILIATIONS

American Geophysical Union
The Geochemical Society (Organic Geochemistry Division affiliate)
American Society of Limnology and Oceanography
American Chemical Society, Geochemistry Division

GRADUATE ADVISOR

Allan H. Devol

POST-DOCTORAL ADVISORS

Sybil Seitzinger, Clare Reimers

Chemical Composition and Bioavailability of Dissolved Organic Nitrogen in Atmospheric Wet Deposition from Urban and Rural New Jersey Sites

Progress to Date (April – August 2001)

1. Establish personnel and sampling procedures at Pinelands site and Camden site. Collect and evaluate field blanks.

Rainwater collectors were installed at both the Pinelands and Camden sites. Personnel at both sites were trained for collection of the rainwater samples, sample filtering, and field and lab blank procedures. Small freezers were purchased and installed at both sites for use exclusively for storage of NJDEP samples until transfer to New Brunswick. Field blanks, filter blanks, and de-ionized water blanks at both sites have been repeatedly collected and analyzed for bulk constituents (DOC, DON, DIN). Initially there were some contamination problems at both sites. Those issues now have been resolved by purchasing a new vacuum pump for the Pinelands site and improving the de-ionized water source at the Camden site. We continue to routinely collect blanks (field and lab) at both sites.

2. Collect precipitation samples from the 2 NJ sites (Camden, Pinelands)

Beginning in June, precipitation samples were collected at both sites.

3. Analyze precipitation samples for bulk constituents (inorganic N, bulk DON and DOC, pH) (all rain samples and blanks)

Precipitation and blanks (field and lab) have been analyzed for bulk constituents. Concentrations of bulk constituents for blanks are now low at both sites. The concentrations of bulk constituents in precipitation at the two sites are within an expected range; no additional interpretation of these precipitation data can be made at this early stage of the project, given the limited number samples.

4. Analyze selected precipitation samples for detailed dissolved organic matter chemical characterization (mass distribution, acid/bases) (estimated 5 samples per season per site)

This task is currently in progress.

5. Prepare and analyze, using APESI-MS and CLND, suites of authentic standard compounds (approx. 20 compounds) from the 3 source categories: biogenic, anthropogenic, secondary photochemical.

Twelve (12) organic compounds have been analyzed to date. Additional standard compounds will be targeted and obtained for analysis in the upcoming months.

6. APESI-MS data processing and initial data interpretation, including multivariate statistical analyses to begin to examine trends on several scales

We have: a) explored the applicability of a number of multivariate statistical analyses and visualization techniques for the interpretation of the APESI-MS data, b) purchased additional software, and c) conducted an initial application of several statistical approaches using data previously collected from New Brunswick. We will continue this task with data from the Camden and Pinelands sites as sufficient data become available.

7. Continue to develop database of atmospheric organic compounds

We are continuing to develop this data base.

8. Begin to develop conceptual model for data interpretation.

This task will come on line as sufficient data from the two sites becomes available.

9. Collect preliminary throughfall samples at Dighton's microhizzae study site. Evaluate field blanks and conduct preliminary analyses.

We met with Dr. Dighton at his field site and discussed locations for throughfall collection, and collection procedures. Sample collection will be scheduled during the next few weeks.

10. Submit progress report to NJDEP

This report (submitted 23 August 2001)

Overview of Year Two Research

The following tasks will be conducted during Year 2. Please see the original proposal for more detailed information.

1. Continue with items 2-5 (Year 1) for 12 months.

We will continue to collect precipitation samples from the 2 NJ sites (Camden, Pinelands). Samples and blanks will be analyzed for bulk constituents (inorganic N, bulk DON and DOC, pH). Additional authentic standard compounds from the 3 source categories: biogenic, anthropogenic, secondary photochemical will be obtained and analyzed, using APESI-MS and CLND. Selected precipitation samples will be analyzed by APESI-MS for detailed molecular level dissolved organic matter chemical characterization (mass distribution, acid/bases) (estimated 5 samples per season per site). Data will be processed and prepared for interpretation.

2. **Examine trends in molecular level precipitation data on several scales.**

   Interpretation of the molecular level chemical composition data of dissolved organic matter in precipitation from the Camden and Pinelands sites will be conducted. This will include: a) searching the molecular level precipitation data for specific chemical molecular markers within each of the 3 sources categories (biogenic, anthropogenic, and photochemical); the database that we are developing of atmospheric organic compounds will be the basis of this task, b) using visualization and statistical approaches (univariate and multivariate) compare patterns in the organic matter composition between the 2 study sites, as a function of storm origin and meteorology.

3. **Further develop and test a conceptual model using Year 1 and 2 data.**

   Based on the results of task 2. (above) we will further develop and test a conceptual model, the overall aim of which is to understand the sources of dissolved organic matter deposited in precipitation. This will include furthering our understanding of the relative magnitude of biogenic sources, anthropogenic sources and atmospheric photochemical reactions, and long-range transport versus local sources.

4. **Conduct biological availability experiments on spring composited rain from the 2 study sites**

   We will examine stimulation or inhibition of aquatic microbial populations due to dissolved organic matter in precipitation from the Camden and Pinelands study sites.

5. **Chemically characterize the BIOAVAILABLE components of the rainwater DOM including molecular weight, acid/base properties; compare with authentic standards.**

   We will determine which of the organic compounds in the rainwater are utilized by the aquatic microbes, and the extent of utilization (partially, fully). This will be done by analyzing (using APESI-MS) the detailed chemical composition of

rainwater before and after degradation by aquatic bacteria. A comparison of the chemical characteristics of the utilized (and un-utilized) compounds with authentic standards of atmospheric relevance and with the results from tasks 2 and 3. will begin to provide information on the origin (long/short range) and types of processes that are contributing biologically available organic-N.

6. **Continue to develop database of atmospheric organic compounds**

7. **Collect throughfall (3 times) at Dr. Dighton's Pinelands microrhizzae study site and analyze for detailed chemical composition**

   The molecular level organic composition (determined by APESI-MS) of dissolved organic matter in direct fall and throughfall will be compared. We will work closely with Dr. Dighton on the ecological interpretation of this data within the context of his studies. We will also provide Dr. Dighton will our complete data set of bulk DON and DIN deposition at the Pinelands site.

8. **Submit manuscript for publication including Year 1 results.**

9. **Submit progress report to NJDEP**