TOTAL AND DISSOLVED ORGANIC NITROGEN ANALYSIS IN AN URBAN WATERSHED

by

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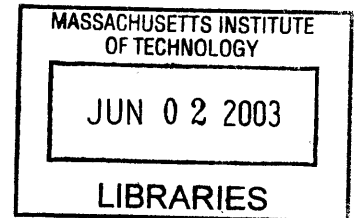
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ABSTRACT

An analysis of total nitrogen speciation in the Aberjona River (ABJ) was conducted using time-composite sampling in a spatial distribution along the watershed for the purpose of establishing patterns of organic and inorganic nitrogen concentrations and fluxes. A Total Nitrogen analysis (NO_3^-, NH_4 and organic N) was undertaken to determine the relevance of potentially labile organic nitrogen as a constituent of ABJ river water both in dissolved and particulate form, as well as to differentiate nitrogen species by source and provide the basis for an estimation of transformations and a correlation of fluxes to land use patterns. The laboratory approach for TN and TDN included modified versions of peroxidisulfate digestion derived from Solorzano et al. (1980), followed by a comparative analysis of two measurement techniques based on an ion selective electrode method and ion chromatography. In the context of this study ion chromatography proved to be the more effective means to measure TN; however significant differentiation between TN and TDN was not obtained, possibly due to varying levels of denitrification in the filtered and unfiltered samples.

Concentration of organic nitrogen ranged from non-detected to over 100 μM, and was not significantly differentiated by site. The average concentration of organic N in ABJ river water was approximately 15% of TN, a significant and potentially reactive flux whose quantification is important for complete analysis of N cycling in an urban watershed. Measured levels of TN in ABJ river water ranged from 1-6 mg/L over the sampling sites. Based on an average flux of 2.66 g/sec at the USGS site above the Upper Mystic Lake the Aberjona watershed as a whole exhibits a yield of 12.45 kg ha^{-1} yr^{-1}, with more than 60% of the mass flux originating in the industrial region around Rt. 128, which accounts for only 40% of the watershed surface area. TN concentrations in the water draining this sub basin were dominated by NH_4 and reached levels higher than 450μM (6 mg/L). TN measured in the sub watershed basin enscribing the area around Horn Pond were dominated by NO_3^- at concentrations around 60 μM. Despite the observable difference in fluxes among the three sub watershed basins defined in a GIS analysis, correlation with categories for residential and industrial land use derived from the LU 21 code revealed only a weak relationship between N yield and land use (R^2=.65). The lack of correlation could be attributed to limitations in the methodology or to similarity in the average loading of residential and industrial land uses. Extrapolation of the N retention capacity of the Charles River basin (Boyer et. al 2002) to Aberjona N yield data would result in an estimation of nitrogen loading to the watershed in excess of 31 kg ha^{-1} yr^{-1}, ranking it amongst the most polluted rivers in North America.

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I.   INTRODUCTION

1.1   Statement of Problem and Objectives of Study

The analysis of nitrogen in the Aberjona River was conducted for the purpose of quantifying the total fluxes and speciation of the constituents nitrate, ammonium and organic nitrogen. Collecting information on the movement of these compounds through the watershed is essential to completing a picture of the anthropogenically modified nutrient cycling regime and its important ramifications for water quality, public health and riverine ecological status. As the result of a "Total Nitrogen" study which accounts for all of the major components of nitrogen found in the river, the data and analysis presented here is intended to inform a growing body of knowledge of the relationship between types of land use and nutrient loading in the context of an urban watershed, which is currently poorly understood. Specifically the objective is to produce data describing the yield of nitrogen (total and broken down by species) for each sub-watershed area in terms of kilograms per hectare per year.

1.2 Relevance of Total Nitrogen Study

In the past nitrate received preferential attention as an indicator of N saturation due to its overall significance in terms of percentage of Total Dissolved Nitrogen, relative bioavailability, role in episodic acidification and its comparative ease of analysis.[1] Since the 1980's however organic nitrogen, in addition to ammonium, has been found to play a significant role in the interactive processes governing dissolved nitrogen concentrations in surface waters. This is in part a response to the increased availability of improved analysis methods such as persulfate digestion and high temperature combustion, which are less time and resource intensive than the Kjeldahl method and more reliable than earlier methods used in the 70s that produced controversial results. With the advent of rapid and cost-effective conversion methods demonstrating high recovery rates the quantification of Dissolved Organic Nitrogen (DON) can be obtained as the difference between Total Dissolved Nitrogen (TDN) and Dissolved Inorganic Nitrogen (DIN), and the relative importance of DON in the N cycle can be routinely evaluated.[2]

For the most part studies that examine TDN have mainly focused on rural, forested and agricultural watersheds, which differ significantly from urban watersheds in terms of biological activity, soil substrate (including capacity of soils to adsorb organic matter) and sources of nitrogen inputs. In forested watersheds, nitrification is considered the dominant source of nitrate whereas the NO_3 pollution in urban watersheds originates mainly from industrially fixed nitrogen. Given the relative lack of data on

TDN in urban watersheds there is significant potential for increasing the knowledge base concerning the interactions between nitrogen and other watershed parameters.

Measurements of DON as a component of total nitrogen in forested watersheds such as Hubbard Brook have revealed significant in-stream concentrations. This indicates that organic nitrogen could potentially provide a significant pool of potentially labile nitrogen that can be transformed in-situ first to NH_4^+, then to NO_3^- through microbial mineralization and can even become directly bioavailable. While the stream fluxes of organic nitrogen are typically small compared to the overall storage capacity of organic nitrogen in soil and biota, the concentration of organic nitrogen can reach levels twice as high as twice the amount of nitrate. In forested watersheds the sources of DON are numerous, including throughfall, leaching, decomposition of litter and soil organic matter, waste products of macro and microorganisms, amino acids, DNA fragments etc. In an urban watershed such as the one drained by the Aberjona River, one might expect to encounter additional loads from atmospheric deposition, precipitation and wastewater, with the anthropogenic component competing for a higher fraction of the Total Nitrogen budget. Inputs of fertilizer-derived inorganic nitrogen from surface runoff would most likely tend to increase the ratio of DIN to DON in the total nitrogen budget. However, given the limited amount of studies on urban watersheds it remains unclear as to the extent to which organic nitrogen contributes to N saturation and loading and whether or not it should be routinely analyzed as part of monitoring programs which evolve to address the challenges of nutrient loading. Is organic nitrogen substantial on the scale of global fluxes of nitrogen, and what considerations should be given to its role in the future? Answers to questions such as these are the rationale behind undertaking a total nitrogen analysis in an urban watershed.

1.3 On Going Research in the Watershed

Researchers at MIT's Ralph M. Parson's lab and TUFTS university have been collaborating in an interdisciplinary study of the Aberjona and Mystic River Watershed for over a decade, through sponsorship by the National Institute of Environmental Health Sciences Superfund Basic Research Program and the EPA and in partnership with the grassroots based Mystic River Watershed Association. The overarching goal of the research has been to identify the major reservoirs and human exposure pathways of chemical contaminants, to understand their interactions in-situ and the transport regime of the watershed as whole and to bring that knowledge to bear on the decision making process within the relevant communities and state agencies. On-going work includes surface water sampling and water balance studies focusing on microbial degradation, toxic metals, solvents, and nutrient cycling. Recent findings have shown that sediment processes and plant uptake governing the mobility of arsenic play an important role in this contaminant's movement through the watershed.[3] Public outreach is a prominent feature of this program, with researchers and faculty from MIT and TUFTS participating in municipal planning sessions, town meetings, education and awareness programs and discussions with public officials on the issues of chemical fate and transport and environmental health as they are affected by watershed.[4]

II.   NUTRIENT LOADING IN URBAN WATERSHEDS

2.1 Overview of Nutrient Pollution Issues

Human activity has modified the nitrogen cycle in numerous ways, most dramatically by doubling the rate of transfer of nitrogen from the abundant but biologically unavailable dinitrogen reservoir in the atmosphere to available forms such as ammonium (NH_4^+), nitrate (NO_3^-) and nitrite (NO_2^{-1}).[5] The global input of anthropogenic labile nitrogen into the biosphere has increased to approximately 150 Tg per year, as a direct result of the need to feed and provide energy for the growing world population.[6] Industrially fixed nitrogen used mainly for fertilizer (fixed from the unreactive atmospheric N_2 through the Haber

process) accounts for 100 Tg per year, with the balance emitted from the combustion of fossil fuels and the cultivation of legumes such as soybeans and alfalfa. The fact that these amounts are expected to increase into the foreseeable future, especially in developing countries which are also experiencing rapid rates of urbanization, has led to concern of the possible detrimental effects to global society.

The sources and mechanisms of anthropogenic perturbation of nutrient cycling have been extensively researched due to its deleterious effects including increased health risks, eutrophication and accelerated succession in watershed ecosystems. Elevated levels of nitrate in water supplies have been linked to conditions such as methoglobinemia (blue baby), impaired neurological development in children, non-Hodgkin's lymphoma and gastrointestinal cancers. Nitrate loading in surface waters results in a loss of recreational use, impacts species composition, mineralization rates, changes in leaching rates and causes eutrophication and algal blooms which accelerate oxygen depletion and alter the biochemistry of rivers, lakes and estuaries.[7] Recent research has also linked nitrogen levels and its effects on phosphorous and iron concentrations to the mobilization of trace metals such as arsenic. Ultimately these mobilized reactive nitrogen species will by cycled back to the atmosphere through denitrification; however one possible pathway is through N_2O emissions, which contributes to climate change as a greenhouse gas.[8]

The current and potential impacts of excessive reactive nitrogen pollution constitute serious threats to human quality of life and as such are being addressed through political and technical schemes aimed at reducing sources and or remediating *in-situ* nitrate levels. However the efficacy of these schemes depends on a knowledge of the complex and as yet poorly understood interactions between nutrient sources, transport, chemical reactions, biological uptake and in-stream transformations. Current conventional wisdom suggests that nitrate levels in urban watersheds are correlated to land use, which is a geographically variable amalgamation of industry, residential, agricultural and commercial and natural areas producing animal wastes and industrially fixed point sources over a range of runoff, atmospheric deposition and groundwater conditions. An effective response to Nitrogen saturation in urban surface waters critically depends on a systematic interpretation of these factors.

2.2 Composition of Organic Nitrogen

In general nitrogen compounds can be considered reactive or unreactive, with the latter types being of lesser interest for the most part. Reactive nitrogen consists of all oxidized forms of nitrogen, such as NO, NO_2, N_2O, N_2O_5, NO_3, HNO_2, HNO_3, and peroxy-acetyl-nitrate (PAN) and all reduced forms of nitrogen such as NH_3, NH_4 and amines.[9] While in the past the perception has been that organic nitrogen tends towards the unreactive end of the spectrum there are in fact an array of reactive organic nitrogen species.

Reactive organic nitrogen species are derived from a variety of sources, which can be broadly classified into three categories: organic nitrates, reduced organic compounds and biological organic nitrogen. For the most part organic nitrates are composed of the oxidized end products of photochemically mediated reactions of hydrocarbons and NOx in polluted air masses, but there are both natural and anthropogenic sources of NOx and non-methane hydrocarbons (NMHC) which contribute to their production.[10] Natural sources of NHMC are dominated by plant production of isoprene. The reaction between NMHCs and NOx can produce nitrates accounting for up to 12 Tg of nitrogen out of the contemporary 36 Tg NOx annual budget.[11] In northern latitudes atmospheric NOx and NMHC budgets are dominated by fossil fuel combustion, which releases nitrogen both as an unintentional product of the combustion of dinitrogen in the air and through the release of nitrogen sequestered in hydrocarbon fuels.

Reduced forms of organic nitrogen such as urea, amino acids and other methylated amines can also have a variety of sources, including direct oceanic injection through bursting of bubbles at the air/sea interface, aliphatic amine emissions from animal husbandry operations and biomass burning.[12] Compounds emitted from these sources, such as methylamine, dimethylamine, and trimethylamine are injected rather than formed in the atmosphere because they are highly soluble and react fairly quickly

with radical species such as the hydroxyl, nitrate, perhydroxyl, and superoxide molecules such that their global lifetime under oxidizing conditions is on the order of 1-5 days.[13] Milne and Zika (1993) estimate a global atmospheric flux of these reduced organic nitrogen compounds of around 1 Tg per year; however at local scales the contribution of these species to N loading may be substantial, particularly for areas influenced by marine air or agricultural operations.

Lastly, biological organic nitrogen consists of a host of compounds whose precise identity and nature are not yet fully catalogued, inclusive of bacteria, dust particles, pollen, proteins, DNA fragments, lysed cells, plant exudates, waste products of macro and microorganisms, humic and fulvic acids and other products of living matter. The reactivities of these compounds are not well known and depending on their particular chemical structures they could be as labile as inorganic nitrate or highly recalcitrant or somewhere in between.

2.3 General Sources of Pollution

In the pursuit of increased supplies of food and energy to support the growing population, industrialized societies have directly and indirectly modified the cycling of nitrogen through a variety of specific practices. While nitrogen is ultimately derived from atmospheric sources, it can take several routes through the biosphere before returning, with varying effects depending on the pathway. The principal vectors for nitrogen loading are through atmospheric deposition, the application of fertilizers, and the disposal of wastewater.[14]

The expansion of cities, towns and populations has been underpinned by the rapid growth of industry over the past two centuries, which has as one of its facets widespread use of internal combustion engine technologies for transportation and coal-fired thermal energy production.[15] These processes historically disposed of all waste products in the airshed (until the more recent developments of scrubber technology and innovations such as the catalytic converter). As mentioned above, the combustion of fossil fuels results in the emission of reactive nitrogen both as a by product of the oxidation of dinitrogen in air and by releasing nitrogen compounds found in hydrocarbon fuels. Thermal NO_x emissions are dominant for fuels with low nitrogen content such as natural gas and petroleum distillates, conversely heavier fuels such as oil and coal which contain 0.3 –3.0% nitrogen by weight emit NO_x from fuel as 50-90% of aggregate NO_x emissions.[16] Globally the combustion of fossil fuels causes the flux of about 20-25 million metric tons of nitrogen into the atmosphere per annum.[17] These aerosol nitrogen compounds eventually find their way to terrestrial systems through dry and wet atmospheric deposition. Pre-industrial rates of nitrogen deposition are not precisely known but were likely to be less than 2 kg N ha^{-1} year^{-1} compared to modern deposition rates which have been measured in some places as high as 90 kg N ha^{-1} year^{-1}.[18]

The industrial production of fertilizer was one of the fundamental engineering achievements enabling the growth of the food supply, which continues to fuel global population growth. Because nitrogen is often the major nutrient limiting plant growth, it was long ago identified as a means to enhance the primary productivity of agriculture, with the consequence that industrially fixed reactive N has become almost universally applied to agricultural operations. A small but significant fraction of agricultural N applied to fields is in excess of plant requirements for growth, and this surplus nitrogen will either accumulate in soils, move into surface waters, migrate into ground waters or enter the atmosphere via ammonia volatilization and nitrous oxide production.[19] The nitrogen effectively stimulates plant growth to the point where inputs of another nutrient (most likely phosphorous) become limiting, whereupon additional N inputs will not be assimilated until they are transported off site to a nitrogen limited ecosystem. In this way the application of agricultural fertilizer is a major cause of inadvertent nitrogen addition to non agricultural ecosystems. Of the anthropogenic inputs of nitrogen to the biosphere, fertilizer is by far the most substantial in absolute and relative terms at around 125 Tg yr^{-1} (more than two thirds of the total output).[20] However, not all fertilizer is industrially fixed through the Haber process; in fact a greater portion is derived from the application of animal manures and other organic residues and the planting of leguminous crops such as soybeans and alfalfa, which support

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symbiotic N-fixing organisms.[21] Galloway et al. (1995) estimated that between 32 and 53 Tg N is fixed by crops annually. Regardless of the whether the source represents the recycling of previously fixed nitrogen or new fixation, the outcome for watersheds has been an overall increase in nitrogen loads. A study by Howarth et al. (1996) revealed that inputs to 13 north Atlantic watersheds have increased several fold from pre-industrial times.[22]

Nitrogen from animal wastes can also be introduced to natural environments directly and through the effluent water of septic systems and wastewater treatment facilities. Waterways which have historically been used as convenient sinks for waste and sewage treatment effluent are increasingly overburdened with nitrogen and phosphorous loads, leading to a decrease in water quality which closely correlates to increasing population densities in a watershed. While the exact composition of wastewater organic nitrogen is variable and unknown, it is generally considered to be more labile than soil-derived DON and hence more likely to be mineralized or directly assimilated in the stream.[23]

Land use changes are also very important in determining the level of nutrient pollution in a watershed. Vitousek et al (1997) estimated that humans mobilize more than 50 million metric tons of N via land transformation alone.[24] The general global trend has been a transition from watersheds with naturally vegetated tesserae to human urban and agricultural land uses. Within this trend there is a tendency for urban sprawl to be the dominant land use trajectory in coastal areas. Human populations have increased dramatically in the near shore of every estuary around the world.[25] There is also the potential for regional shifts, such as are occurring in New England. In the past ammonia emissions in the northeastern United States were apparently dominated by emissions from livestock and natural vegetation.[26] Today livestock and agricultural land use is declining while reforestation is increasing the amount of natural vegetation. At the same time there is a continual accrual of urban sprawl. Emissions from livestock have decreased by about half a kilogram per hectare per year over the past century, and the region has undergone substantial reforestation since the 1800's.[27] The extent to which increased vegetation mediates the load of nitrogen in watersheds is difficult to predict, since microbially mediated emissions of NH_3 are dependant on a variety of factors including temperature, pH and quality of vegetative cover. Measurements of nitrogen fluxes from natural lands have thus been extremely variable, ranging from 0 to 100 kg N ha^{-1} yr^{-1} depending on ecological conditions.[28] While it may not be easy to ascertain the net effect of reforestation supplanting agricultural land in the northeast, it seems likely that a conversion from either type to an urban land use would result in increased nitrogen loads, for at least two reasons: insertion of more wastewater and loss of the retentive subsidy of atmospheric nitrogen furnished by natural vegetation.[29] The complex arrangement of various land use categories within urban watersheds would contribute to these effects through the introduction of fertilizer intensive turf associated with lawns, parks and golf courses and the proliferation of impervious surfaces such as roads, parking lots and roofs which enhance runoff.[30]

Of course in addition to anthropogenic sources of nitrogen pollution there is a pool of naturally fixed N that continually cycles through the biosphere at various "background concentrations" in atmospheric deposition, surface waters and to subsurface environments. While approximately 80% of the earth's atmosphere is composed of molecular nitrogen (N_2) this largest reservoir is not directly available to plants and animals. Biological nitrogen fixation is confined to specialized groups of auto and heterotrophic prokaryotes that possess the enzyme nitrogenase. Since the N-N bond is extremely stable the biological reduction of dinitrogen to ammonia is a fairly energy intensive process requiring a minimum of 16 ATP per molecule of N_2 fixed.[31] The ability to fix nitrogen is found in all major groups of marine cyanobacteria and a variety of chemoautotrophic bacteria. In studies of predominantly forested watersheds the pool of nitrogen was found to be mainly derived from nitrification processes in soils and the breakdown of litter and soil organic matter, fine-root and mycorrhizal turnover as well as through nitrosomes and other microbes capable of directly fixing dinitrogen.[32] In agricultural and urban watersheds it seems likely that anthropogenic inputs of fertilizers and wastes dominate over ecosystem nitrification as a source of reactive nitrogen.

2.4 EPA Criterion and Minimum Contaminant Levels

The minimum quality criteria set by the EPA for drinking water mandates that concentrations of nitrate must be less than 10mg/L. Natural background levels of nitrate are typically less than 1mg/L in undisturbed watersheds.[33] Beyond drinking water standards however there is no state or federal standard for nitrogen concentrations regarding the quality of surface waters as regards fishing or swimming.

Because the degree of nutrient loading control required to maintain satisfactory water quality is variable depending on site characteristics and usage, it is difficult to establish objective criteria to use in judging acceptable versus unacceptable water quality. Flowing waters in general have received less attention than lakes and reservoirs in determining critical loads. A critical load is an index of ecosystem susceptibility to changes in structure and function; essentially it is the amount of nitrogen input that an ecosystem can tolerate without damage.[34] From a large comparative analysis of stream ecosystems Dodds et al. (1997) estimated that total stream concentrations of less than 350 mg N m^{-3} would be necessary to keep benthic algal biomass below nuisance levels.[35]

Under the Clean Water Act Congress acknowledged two different sources of pollution: point source pollution which is discharged from a "discernable, confined and discrete conveyance such as a pipe [or] ditch;" and non-point source pollution which is runoff from a variety of sources including urban areas and agriculture or forestry sites. Under the legislation point source dischargers are required to obtain permits if they discharge waste into any U.S. water, and each state, subject to EPA supervision and approval, is authorized to regulate non-point source pollution as deemed necessary.

Section 303(d) of the Act also requires states to adopt water quality standards for impaired rivers and waters, without distinguishing between point and non-point sources, in the form of Total Maximum Daily Loads (TMDLs) which establish the maximum levels of various pollutants that can be allowed into specific rivers and waters to maintain certain water quality standards and allocates that level to the sources.[36] Under section 303(d) of the Clean Water Act each state must prepare a list of waters that do meet standards for water quality (i.e. they are not fishable or swimmable). The U.S. EPA approves and maintains this list of impaired waters according to the type and level of pollution as an index of the appropriateness of certain uses (drinking water, fishing, swimming recreation etc.) but it leaves enforcement of specific remedial action in the hands of the states. States, territories, and authorized tribes are responsible for developing schedules for establishing TMDLs (generally within 8-13 years of being listed) and providing reasonable assurances that load allocations will be achieved using incentive-based, non-regulatory or regulatory approaches. As constituted in 1972 and amended in 1985 section 303(d) does not mandate an aggressive response to evaluating and remediating pollution in flowing waters and consequently few states have progressed very far in terms of listing impaired waters, calculating TMDLs or designating specific action towards limiting point and non-point sources of pollution. Numerous complaints against the EPA have arisen due to the relative inaction of the agency in cleaning up polluted waterways since the Act became law. Partially in response to this the EPA generated new legislation to strengthen the current TMDL program and issued an updated rule in July of 2000. These new regulations were strongly opposed by agriculture and forestry industries and as result congress attached a "rider" to one of their appropriations bills that prohibited the EPA from spending FY2000 and FY2001 money to implement this new rule.[37] The EPA subsequently withdrew the new rule, leaving the former legislation in place.

2.5 The Effects of Nitrogen Saturation

As in the case of fertilizer application, natural ecosystems limited by another nutrient (often phosphorous) can become N saturated. One expectation of ecosystems saturated with nitrogen is a relative increase in the export of DIN versus DON due to the much larger capacity of mineral soils to adsorb and store organic matter.[38] From a mass balance point of view this characteristic of a system that

is approaching N saturation is of interest due to the increased leaching of nitrate to waterways.[39] This effectively alters the watershed level role from that of a nitrogen sink to a nitrogen source. The leaching of excess nitrate could also have the effect of attenuating seasonal patterns in stream water NO_3 concentrations, which would otherwise result from biological controls.[40]

From the standpoint of ecological health, an increase in acidic NO_3 deposition can also result in a base cation depletion in the soils of the watershed (particularly Ca^{2+} and Mg^{2+}), thus altering the acid-base balance.[41] Leachate from N-Saturated parts of the sub watershed would travel through the vadose zones and aquifers before flowing into lakes, ponds and estuaries where the harmful effects of nitrogen loads is most evident. For many years ecologists held the view that rivers were themselves relatively insensitive to nutrient inputs, under the assumption that other physical, chemical and biotic factors restricted the effects of nutrient enrichment of algal growth and the biomass accumulation of benthic algae. In low order streams where light penetration is reduced by forest canopies and suspended solids the growth of benthic and suspended algae is inhibited, just as phytoplankton growth is restricted in turbid reservoirs. In addition herbivore grazing and the hydraulic flow regime can limit the extent of periphyton standing crops in flowing waters, muting any potential algal responses to nutrient enrichment. A growing body of evidence however is now suggesting that algae are in fact responsive to nutrient additions despite these constraints. Corell (1998) and Elwood et al. (1981) found significantly increased benthic algal biomass, increased rates of detritus decomposition and increased abundances of macro-invertebrate consumers in phosphorous enriched oligotrophic streams.[42]

Perhaps the most important factor impacting the ecology of the watershed is the shift in primary productivity and succession of species that can result from N additions. Every living species in the watershed has physiological, reproductive, and adaptive traits that enable it to be a superior competitor at a certain point or region along a primary productivity gradient. These characteristics explain the shift in flora composition that occurs along major natural environmental gradients such as from rich to poor soils, elevational and latitudinal gradients and so forth. The adaptive mechanisms that allow a given species to obtain in an ecosystem (i.e. greater height, faster reproductive rates, tissue allocation of nutrients, photosynthetic pathways etc.) will be specific to a given nutrient regime, which, once altered, will give way to a shift in the species composition of the ecosystem. Shifts in the species diversity and composition of an ecosystem due to the addition of N and alterations in the soil chemistry would have impacts that ramify throughout the entire food chain.[43] This can be readily observed in the proliferation of once rare species, which tend to be non-native weeds. A well documented phenomenon in coastal estuaries fed by N saturated watersheds is the dieback of meadow eelgrass.[44] Ultimately the current widespread alteration of the structure and dynamics of riverine and coastal ecosystems will have far-reaching and difficult to predict consequences.

2.5.1 Eutrophication

One of the more commonly discussed consequences of N loading and the principal concern of many environmentalists is eutrophication of waterways and algal blooms. In essence the problem is that high production of plankton algae and excessive growth of weeds and microalgae leads to oxygen deficiency, fish kills, reduced biodiversity and bottom death. The Redfield atom ratios of 106C:16N:1P:16Si are typical for algal biomass. Assuming adequate light penetration and that CO_2 is never limiting in coastal waters, these ratios suggest that any N:P ratio greater than about 16:1 indicates potential limitation of algal growth by phosphate, while ratios less than 16:1 indicate potential limitation of algal biomass production by N. Whereas freshwater plankton generally tend to be limited by phosphate availability, primary production in estuaries and coastal waters is often N limited.[45] The problem of recurring toxic phytoplankton blooms in coastal waters has recently drawn considerable attention from academic and political circles in communities across the globe. The exceptional blooms which occurred in 1988 of the toxin-producing prymnesiophycean flagellate Chrysochromulina polyepsis in the Baltic Sea caused kills of large numbers of macroalgae, invertebrates and fish and was popularly called a 'silent spring in the sea'. Many estuaries along the Atlantic coast of the United States have had similar experiences with fish kills attributed to the toxic dino-flagellate Pfisteria piscicida.[46] In addition

to influencing entire ecosystems, these events have had a direct effect on fisheries and the economic benefits derived therefrom, and for that reason have attracted the interest of the fishing industry and policy makers.

2.5.2   Anoxia

Another well studied facet of nitrogen saturation and eutrophic conditions is the tendency to lead to anoxic conditions. The excessive primary production and increased pool of autochthonous particulate matter produced in eutrophic systems results in intense microbial activity when it is deposited at the sediment-water interface. As a result of high decomposition rates oxygen demand in the sediments increases and potentially utilizes all of the dissolved oxygen in the overlying water column while releasing toxic sulfide. This dystrophic crisis can cause pandemic mortality of the benthic macrofauna and fish stocks in rivers, lakes, estuaries and enclosed coastal lagoons.[47] A more subtle dissolved oxygen limiting can occur with shifting of species composition due to N saturation. As rooted phanerogams and seagrass give way to opportunistic communities of phytoplankton and macroalgae, gas transport and hence oxygenation of the surficial sediment is diminished.[48] Anoxic conditions can be detected in many seasonally stratified eutrophic lakes as well as in portions of the ocean. Macroalgal blooms have contributed to the development of a region of water column anoxia in the Gulf of Mexico that at times exceeds 6000 square miles in surface area (Tyson, 1997; Malakoff, 1998).[49] On this scale anoxia can result in significant losses to commercial finfish and shellfish operations.

2.6 Natural Attenuation

For all of the potential harmful effects of increased anthropogenic nutrient loads, there remain a variety of natural mechanisms for the removal of nitrogen. According to mass balances, less than 30% of the anthropogenic N inputs to large watersheds are exported to the oceans in surface runoff (Howarth et al. 1996).[50] Thus it can be inferred that more than 70% of manmade N loads are stored, denitrified or volatilized in the watersheds. The main processes which remove nitrogen are uptake by biota, burial in sediments, leakage into underground aquifers and microbial denitrification. The relative significance of these processes depends on the nitrogen species in question and on the various factors characterizing the ecology and hydrology of the watershed.

The transformation of unreactive to reactive nitrogen and the interconversions between mineral and organic species are governed by the chemical energetics of the system. The mineralization of organic matter is primarily mediated by bacteria and microflora and proceeds via a sequence of metabolic steps involving coupled fermentation and anaerobic respiration processes, each of which completes a partial oxidation of the organic matter. In the process oxygen and alternative e^- acceptors such as nitrate, manganese and ferric oxides are depleted in a spatial and temporal succession via thermodynamically favorable reactions.[51] Organic nitrogen is mineralized principally by deaminitive fermentation in a series of steps that remain poorly understood. The basic sequence in the degradation of these complex polymers is nucleophilic hydrolysis to their monomeric components, and then hydrolysis by proteinases and peptidases to the constituent amino acids which are then deaminated to release ammonium.[52]

Through nitrification, ammonium itself plays a pivotal role as a source of nitrate for denitrifying bacteria. The coupling of this necessarily aerobic process with anaerobic denitrification ultimately leads to the loss of nitrogen to the atmosphere as nitrous oxide or dinitrogen. In the latter process heterotrophic bacteria such as those belonging to the genus *Pseudomonas* utilize nitrate as a terminal e^- acceptor in respiration and reduce it to gaseous nitrogen which then diffuses to the atmosphere:

$$5CH_2O + 4NO_3^- + 4H^+ \rightarrow 2N_2 + 5CO_2 + 7H_2O$$
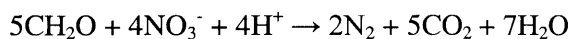
While Robinson et al. (1998) found benthic N_2O production to be less than 2% of denitrified nitrate it nonetheless represents a significant export of N_2O to the atmosphere.[53] Denitrification occurring in anoxic groundwater and riparian zones exhibits a distinct seasonal pattern linked to the supply of nitrate,

temperature and availability of organic carbon.[54] Increased temperatures tend to correspond with elevated dinitrifier activity and depressed dissolved oxygen levels.[55]

Although denitrification plays a dominant role in the recirculation of nitrogen to the atmosphere, it accounts for only a small proportion of the attenuation of NO_3 fluxes during transport through a watershed. An extensive 3 year study of denitrification in Boston Harbor and Massachusetts Bay undertaken by Nowicki et al. (1997) using the N_2 flux method recorded denitrification rates (which correlated with phytoplankton densities) that accounted for only 8% of the annual total nitrogen load.[56] In fact the dominant loss mechanism for most watersheds appears to be the conversion of inorganic to organic nitrogen through plant assimilation and algal and bacterial uptake.[57] Numerous studies have concluded that the majority of inorganic N removal during stream transport is result of plant uptake.[58] On the other hand DON, while being directly assimilated in some cases, has as its primary long term removal mechanism storage within mineral soils, which hold the largest pool of nitrogen in a watershed.[59] Finally, a fraction of nitrogen loads can migrate into the groundwater and be stored there or reduced to gaseous forms which eventually return to the atmosphere.

Evaluating the relative importance of these various transformations and sinks of nitrogen is extremely difficult to accomplish given current analysis methods, and while much work has been done on pristine and model watersheds such as Hubbard Brook, a comprehensive model describing N fluxes within an urban watershed such as the Aberjona does not yet exist.

III. BACKGROUND AND HISTORY OF THE ABERJONA RIVER

The Aberjona River Basin is located to the north of Boston, Massachusetts and comprises the largest tributary to the Mystic River watershed, which ultimately merges with the Charles River as it flows through Boston to the ocean. The Mystic River basin includes an area of about 70 square miles and is home to a population of more than 450,000 people, with more than 50% of the watershed surface in some form of urban land use.[60] The Aberjona River has its headwaters in Reading, Massachusetts and flows in a southerly direction through Wilmington, Woburn and Winchester draining a watershed of approximately 23 square miles which also includes parts of Burlington and Stoneham.[61] The two largest towns in the Aberjona sub-basin are Winchester and Woburn, which underwent tremendous urban expansion during the two decades from 1950 to 1970.[62] However the history of human development on the watershed extends back centuries, to colonial times and beyond.
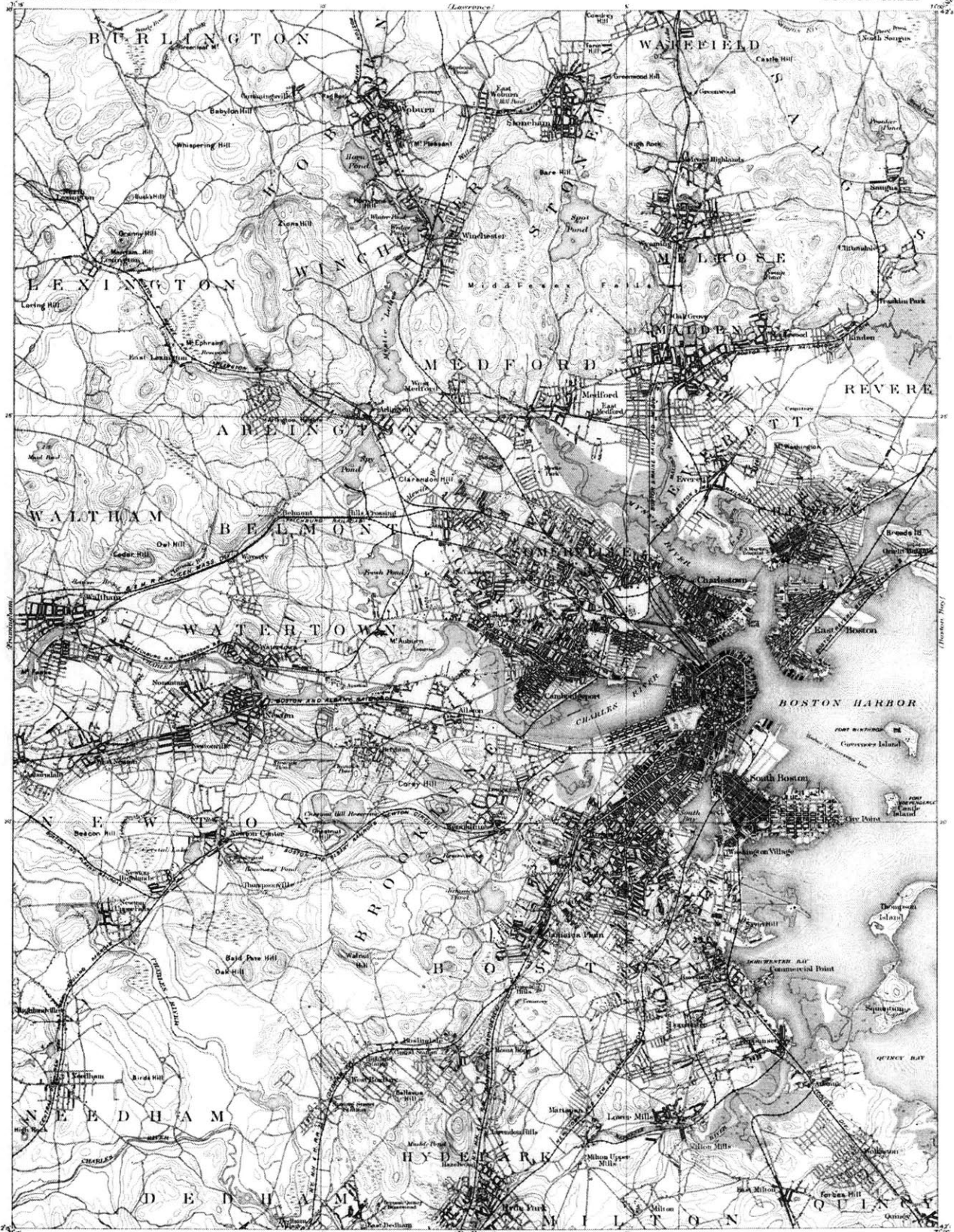
Figure 1 USGS Map of Charles River Basin (1883)

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Three hundred years ago European settlers began to use the resources of the Aberjona and Mystic rivers in much the same way as Native Americans had before them: for travel and as a source of freshwater and fish. In the spring Alewife, a type of herring, swam up the Mystic River to spawn beneath the cathedral-like canopy of old growth forest. Today the Aberjona and its tributaries flow largely unnoticed through culverts and besides parking lots, underneath Route 128 and alongside abandoned railroad tracks though a landscape of industrial parks, strip malls and fast food restaurants before draining into the Upper Mystic Lake. The river, with its rusting and corroded freight of shopping carts, throw-away packaging and plastic bags might have receded into complete obscurity but for the buildup of a more invisible cargo of industrial, human-produced wastes which finally accumulated to the point where the Aberjona and the communities it drains became seriously poisoned. Like many places in the northern Atlantic where Europeans settled, the areas along the river were home to a variety of tanneries, factories, munitions makers and chemical works which provided jobs and prosperity to the growing towns. In addition to wealth and progress the legacy of industrial activity in the watershed is polluted soils and surface waters which are unfit for drinking, fishing and swimming, and a national controversy over human health problems surrounding a leukemia cluster in Woburn.[63]

3.1 Historical Industry and Pollution

The first tannery to set up shop in Woburn opened in 1648; by 1865 there were 21 tanning and currying shops in operation. As early as 1871 the Department of Public Health conducted surveys which described contamination of Horn Pond and Russell Brook by tannery wastes and sewage.[64] The Upper Mystic Lake was used for public water supply until 1895, at which time it still supported outdoor contact recreational activities such as swimming and boating.[65] In the wake of the Civil War and up to 1929 Woburn Chemical Works built one of America's largest industrial complexes alongside the Aberjona River with 90 buildings spread over 417 acres. One of the many products produced here were the arsenic-based insecticides in common use throughout the country.[66] Over the 20th century countless industries emerged along the river, developed to a peak and then eventually closed, and the historical record of these companies and the characteristics of their operations are incomplete, making it difficult to form a whole picture of industrial use of the watershed. At one point it was recognized that pollution from National Polychemical Inc. in Wilmington and the drainage from two piggeries was compromising the water quality of the Aberjona.[67] While efforts have been made to catalogue historical industries and potential contamination (see Appendix A) in many cases the existence of polluting operations can only be inferred from the traces of man made chemicals buried in sediments.

From among the host of riparian industries near Woburn the historical operation of a handful of companies has stood out as the focus of much heated debate; these include the John J. Riley Tannery established in 1910 (purchased by Beatrice in 1978) and the Washington Street machine shop opened by W.R. GRACE & Co. in 1960. The activities of these and other companies in the watershed allegedly led to the presence of chlorinated solvents in the water supply which resulted in the closure of the Woburn municipal wells "G and H" in 1979 and subsequently became the subject of personally injury litigation and the designation of "Industriplex-128" as a Superfund site.

3.2 The Woburn Story

In the late 1950's the City of Woburn, seeking to further develop groundwater resources, hired an engineering consultant to locate potential sources of public water supply. The consultant made a survey of existing public water supply wells and those owned and operated privately by the Atlantic Gelatin Division of General Foods Corporation, John J. Riley Co. Tannery, Consolidated Chemical Industries, Independent Tallow Company, and Sylvania Electric Products Inc. Based on indications of pollution (high chloride and/or iron content) the consultant reported that "The Aberjona River valley still has a potential for ground water supply for certain industrial uses, but the ground waters of this valley are, in general, too polluted to be used for a public water supply."[68] Despite this warning, chronic water

shortages brought about by low flow conditions during summer droughts eventually persuaded the City of Woburn to sink Well G in 1964 and Well H 1967. During the summer of 1967 the Massachusetts State Department of Health recommended that both wells be taken out of service "due to the poor bacterial quality of the water supplied therefrom". The MSDH required that these wells not be used as sources of public water supply "without continuous chlorination to assure the safety of the water".[69] Chlorination facilities were installed in 1968 and residents promptly complained about the odor and chemical taste of the treated drinking water.

In the 1970's the State warned the Woburn Board of Water Commissioners that water in Wells G & H was of poor quality, exhibiting "elevated levels of nitrates, ammonia nitrogen, chlorides, sulfates, sodium, manganese and hardness and has poor physical characteristics … for color, odor, turbidity and sediment."[70] Well G was shut down in the fall of 1969. Meanwhile another potential threat to Woburn's water supplies developed as plans were announced for the construction of a new industrial park to be called "Industriplex-128" at the junction of Routes 128 and

Figure 2. Map of Wells G and H

93, at a site formerly occupied by the Stauffer Chemical Company. This site, located just north of wells G and H in the flood plain of the Aberjona river was found to contain hazardous waste from an arsenic pit, chromium lagoons, 200 acres of soil contaminated with heavy metals, 44 acres of buried animal hides and groundwater contaminated with benzene, toluene, dissolved arsenic and chromium.[71] The State Division of Environmental Health warned that "the proposed filling and drainage may adversely affect the City of Woburn's public water supply during high flows and flood conditions of the Aberjona River".

Due to drought conditions in the spring of 1970 the City of Woburn again began pumping from Well G in order to meet increased water demands. Despite continued complaints from residents during summer months water quality concerns in Woburn were focused on problems in Horn pond rather than wells G and H up through the mid 1970's. An extensive survey by Habitat, Inc. identified high counts of chlorides, nitrates, phosphates and coliform bacteria, all above the standards for class B ponds. The report noted that the most critical problem affecting the watershed was the "rapid accumulation of nutrients, particularly phosphates and nitrates, which stimulate the growth of aquatic weeds and algae."[72] This growing awareness of the nutrient-saturated conditions emerging in the watershed was eclipsed by the development of improved water quality analysis that could detect the presence of chlorinated solvents. On May 22, 1979, the Massachusetts Department of Environmental Quality Control informed the Woburn Board of Water Commissioners that analysis of water samples from Wells G and H revealed trichloroethylene concentrations of 117.6 ppb in Well G and 267.4 ppb in Well H.[73] The maximum guidelines for TCE in drinking water at the time were 10ppb (the enforceable MCL is now 5ppb).[74] Tetrachloroethylene (PCE) was later discovered in Wells G and H, a water emergency was found to exist in Woburn, and both wells were shut down.

In the 1970's a leukemia cluster was observed among the children in the eastern wards of Woburn which were directly supplied by the wells in question.[75] Given the carcinogenic properties of the TCE and PCE, Woburn became a National Priority List site (Superfund) and was the subject of much study by the EPA, USGS and environmental consultants hired to explore the liability of the various industries involved. Over 100 monitoring wells were installed in the Aberjona aquifer and extensive analysis were undertaken. Even before the hydrogeologic studies were completed a civil suit was brought against
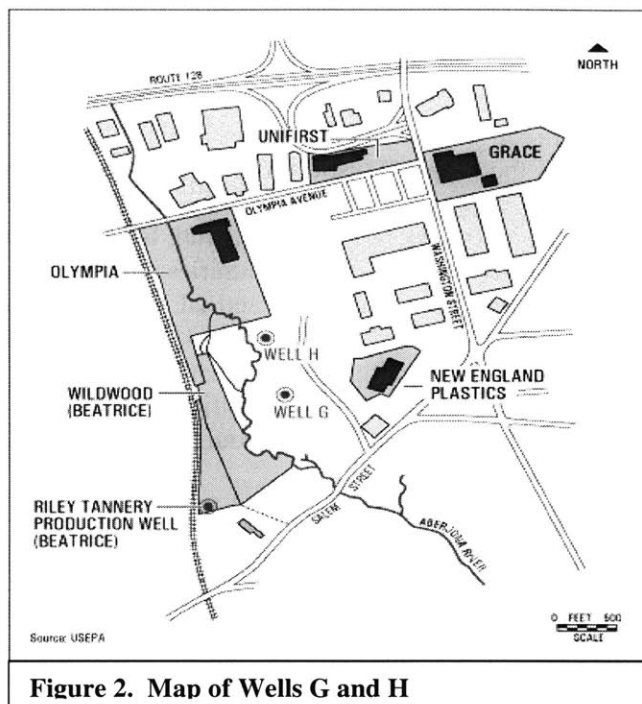
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Beatrice Co., W.R. GRACE & Co. and Unifirst by the law firm of Jan Schlictman, which was the popularized by the book and movie "A Civil Action". Eventually it was determined that the incidence of leukemia in Woburn between 1964 and 1986 was four times greater than would be expected for a such a community.[76] There were 28 cases of childhood leukemia identified in addition to elevated rates of kidney cancer, immune and nervous system disorders and birth defects. Of the leukemia cases sixteen children died.[77] Superfund is a "no fault" statute and the EPA is not required to make any findings regarding negligence; as a result the EPA has never made any findings or conclusions regarding the source of contamination in the Wells G & H Superfund Site. The convolutions of the legal process ended when the judge threw out the verdict in the civil trial and W.R. GRACE & Co. settled out of court for $8 million (Unifirst had settled for $1 million pretrial and Beatrice Co. ultimately eluded any real remunerations).

3.3 Status of the Watershed Today

Throughout the period when the Wells G & H Superfund issue dominated public discourse on pollution and water quality in Woburn, the tendrils of urban residential, commercial and industrial land uses were incrementally encroaching upon the surface of the watershed, modifying the hydrologic regime and increasing runoff and nutrient pollution. The population and its infrastructure and wastes grew considerably. During storm events and flooding in the 70's and 80's the combined sewage outflow (a system where stormwater and sewage from homes and businesses flows together) deposited millions of gallons of raw sewage into the Aberjona River. Even after closure of the CSO the floods of spring 2001 resulted in 50 million gallons of raw sewage spilled into Horn Pond which led to a temporary moratorium on municipal well usage in the area.[78] The amount of turf (including Winchester Country Club and Woburn Country Club) and pavement are increasing in proportion to the decrease in natural vegetation.

Extensive surveys of the watershed have revealed a number of areas of environmental concern. Discharge from the Aberjona River is responsible for the eutrophic conditions existing in the Upper Mystic Lake (UML). In the main body of the lake stratification causes near zero dissolved oxygen levels in the hypolimnion.[79] Nitrogen concentrations are approaching toxicity levels for fish and other aquatic organisms and previous attempts to stock the lake with trout have failed. While phosphorous is less abundant than nitrogen and probably the limiting nutrient for algal growth the overall level of N and P is sufficient to consider the lake eutrophic. Concentrations of zinc, arsenic and other trace metals are also of concern.[80] While the current nitrogen loading to the UML indicate eutrophication the high levels of ammonia nitrogen and low transparency apparently preclude severe algal blooms. One problematic aspect of plans for attenuating nitrogen loads is the potential for lower ammonium concentrations to actually enable conditions for algal blooms.[81]

While concern for water quality problems and a recognition of the watershed's value has inspired numerous studies and pollution abatement plans at the local state and federal level, a complete assessment of urban runoff via direct stormwater discharge and overland flow has yet to be completed.[82] Of the complex pollution problems existing in the basin, it is currently hypothesized that none of the significant nutrient sources are due to point inputs. The most likely sources of pollution are non-point seepage from old industrial waste, disposal areas and urban runoff, and there is an inherent difficulty in separating the effects of industrial and urban runoff pollution. As part of the ongoing research into pollution issues in the watershed, the joint MIT/TUFTS collaborative study will attempt to address the need for a comprehensive understanding of the runoff dynamics of the Aberjona sub-basin and the relationship between land uses, sources, sinks and transformations of nutrients. This understanding will be crucial in any attempt to model the characteristics of the watershed with the intent of informing policy on the control of water quality and the maintenance of environmental health of natural areas.
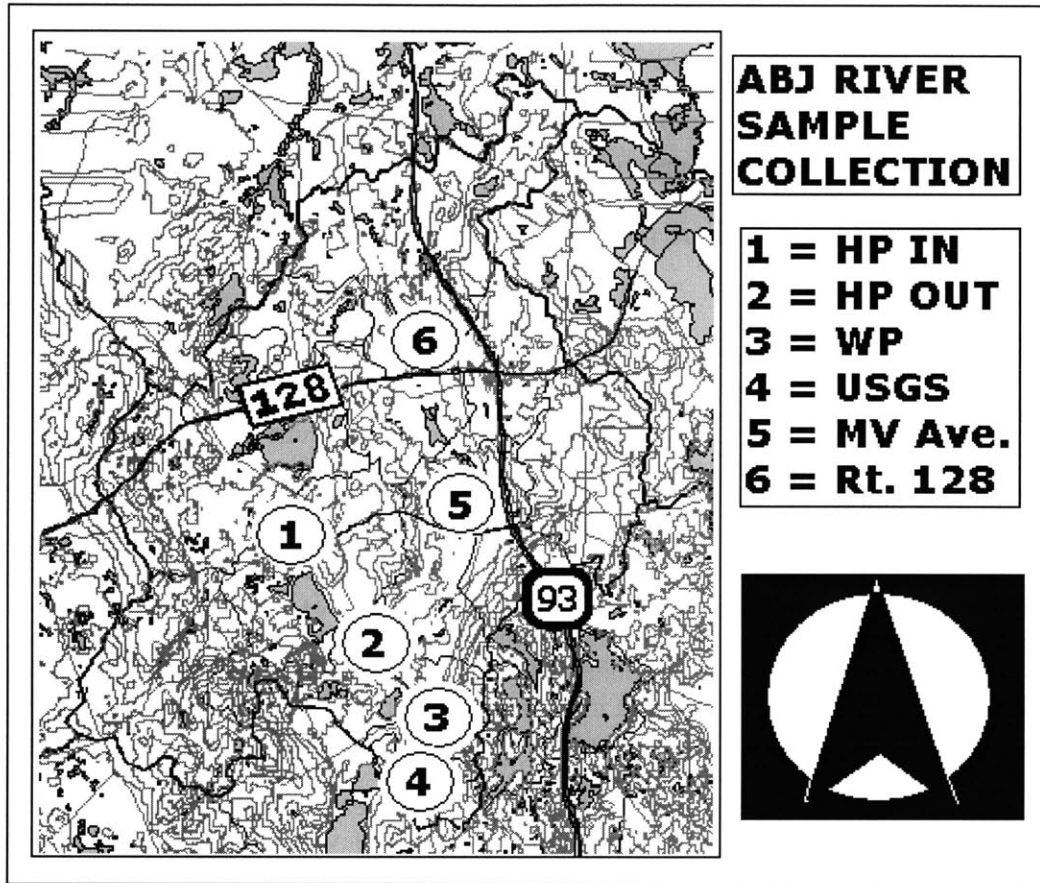
IV. SAMPLING METHODOLOGY

ABJ RIVER SAMPLE COLLECTION

1 = HP IN
2 = HP OUT
3 = WP
4 = USGS
5 = MV Ave.
6 = Rt. 128

Figure 3 Sampling Locations

4.1 Location of sampling sites and materials used

The sampling approach consists of the collection of data from a number of specific sites around Woburn and Winchester north of Boston. These sites provide coverage of two main reaches of the Aberjona River watershed and their confluence prior to emptying into the Upper Mystic Lake: Horn Pond Outlet, Horn Pond Inlet, Wedge Pond, USGS gauging station, Montvale Avenue, and Route 128. These river water samples are collected bi-weekly and analyzed for nitrogen composition, using Ion Chromatography for Nitrate, Spectroscopy for Ammonium and Peroxidisulfate Digestion for Organic Nitrogen (see individual methods sections). Samples are "grab" samples taken in clean 1 Liter plastic bottles, rinsed three times and filled normal to the direction of flow approximately 15 cm under the surface in the center of the respective channels. Sample bottles are capped under water and stored in a cooler for transport to the lab, where samples are separated and filtered for the respective analysis methods into 125mL or 60mL bottles which are first rinsed and capped three times before filling to ensure that any bonding sites in the plastic walls are saturated.

4.2 Time-composite samples

The samples are taken at locations that are relatively evenly distributed around the watershed every two weeks for the purpose of establishing a picture of the average loading of the river across space and time. Since it is not practical to obtain real time data for every location at every moment in time, the

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spatial distribution of sampling sites is intended to portray average concentrations down the length of the Hall's Brook and Horn Pond reaches of the Aberjona river. The sampling sites are spaced between 800 to 3000 meters apart. Likewise with respect to time the average composition of river water at the sampling sites is measured with a resolution of two weeks. While these time composite samples enable a fairly detailed picture of the spatial and temporal variation of Nitrogen concentrations in the watershed using a collection scheme which is feasible to implement, the averaging of levels across space and time will miss spatial or temporal variations too localized to be measured under the given sampling resolution. These could include variable or irregular discharges such as those associated with storm events, whose extent, frequency and duration would be difficult to capture.[83]

4.3 Hydrolab data collection

In addition to taking samples for lab analysis, the general characteristics of the river at the time and location of sampling are measured and documented using a Hydrolab Series 4 Datasonde Microprobe. The parameters recorded are specific conductance, pH, temperature and dissolved oxygen, and the Sonde was calibrated for each measurement at the MIT Parsons Laboratory prior to use. Specific conductance is a measure of the ability of the water to pass an electrical current, which is a function of the ions present. It is a general indicator of water quality, with high measurements corresponding to a source of excess dissolved solids such road salt used in deicing. Comparisons with baseline or background levels can be used to indicate a discharge of pollution.[84] pH is a logarithmic measure of hydrogen ion activity (i.e. acidity). Water which is too acidic or basic can be toxic to aquatic biota, and different pH regimes affect the speciation and behavior of many dissolved compounds of concern, including heavy metals. Temperature is a measure of the thermal activity of the water; rivers and streams must remain cool in order for fish and other aquatic life to survive. Water temperatures can get too warm from a lack of shade in the summertime, discharges of cooling water and water running off hot pavement, etc. Dissolved oxygen (DO) is the amount of oxygen that is dissolved in the water, which is typically around 9.6 mg/L at 25°C. DO must be present in the water at concentrations above about 5.0 mg/L for most fish and aquatic organisms to survive. Low DO values indicate a high rate of oxygen consumption relative to the rate of oxygen replenishment from the atmosphere (which is approximately 20% O_2). Low DO correlates with excess amounts of readily degradable organic matter which create biological oxygen demand (BOD) both in-situ and in river sediments. DO is dependant on temperature and can be viewed as a percentage of oxygen saturation relative to the total amount of oxygen the water can hold at a given temperature.[85] In addition to collecting hydrolab data, the stage (water level) was recorded at each sampling site where a staff gage was available for correlation to flow using stage-discharge curve data generated at TUFTS university.

4.4 Filtration

The filtration method uses Whatman .45 micron Nuclepore® polycarbonate membrane filters in reusable nalgene cartridges. The filtrate is pumped manually through the cartridges using 50cc glass syringes. Between samples the filters are replaced and the cartridges and syringes are washed with Milli-Q water. Before filling the sample bottles the filtering apparatus is rinsed three times. For the organic N analysis the sample is separated into both filtered and unfiltered categories to distinguish between Total Dissolved Nitrogen (TDN) which includes sorbed and particulate N and Dissolved Organic Nitrogen (DON). The filtered DON sample is prepared as above; the unfiltered TDN sample is supplied by an aliquot directly from the 1 L bottle of river water. All of the samples are labeled with date, location of sampling site, type of analysis to be performed, and regarding filtration before being stored in a freezer prior to analysis.

4.5 Preservation

Both filtered and unfiltered samples were placed in cold storage in a front loading freezer. Due to the lack of available freezer space the samples were sometimes stored in the bottom of a front loading refridgerator which was cold enough to keep them frozen. However it seems probable that at some points

during storage, which was anywhere between one week and a month, the samples may have been subjected to thawing and refreezing temperatures. In addition none of the samples were spiked with acid, which is recommended for nitrogen analysis by Standard Methods for the examination of water and wastewater(16th edition).[1] The preservation of the samples may have been somewhat compromised by these procedures, which could be rectified in the future by ensuring that acid addition is performed and the samples are consistently frozen prior to timely analysis.

V. COMPARISON OF LABORATORY METHODS

Given that organic nitrogen concentrations in river water can be a substantial percentage of the TDN (see results), and given the possibility that this pool of organic nitrogen can be potentially labile and/or converted to more labile forms it is appropriate and necessary to routinely make measurements of this species to complete an analysis of N budgets in a watershed.[86] Attempts to measure DON date back at least a century to Putter (1909).[87] However procedures using modern analytical chemistry began with ultraviolet (UV) light oxidation in the 1960's, which gave way to the introduction of strong oxidants in the 1970's due to problems with incomplete oxidation of recalcitrant organic compounds.[88] Until fairly recently difficulties in analysis of organic N persisted; the standard method for determination of total "Kjeldahl nitrogen" (organic N and NH_4 combined) is a rather unwieldy and expensive digest which uses a potassium sulfate (K_2SO_4) catalyst and introduces a mercury ammonium complex (decomposed by sodium thiosulfate), requiring a complex sealed apparatus for distillation.[89] In addition Kjeldahl digestion has high blanks and resulting low precision and has been found inappropriate for analysis of some natural waters.[90] D'Elia et al (1977) and Solorzano and Sharp (1980) developed a peroxidisulfate (PO; $K_2S_2O_8$) oxidation method that gave better recovery and slightly higher values for DON in natural marine samples than UV oxidation.[91] Currently three groups of methods are pursued to calculate DON concentrations: ultraviolet oxidation, high temperature oxidation (HTO) including high temperature catalytic oxidation (such as with PO) and Kjeldahl digestion using sulfuric acid. There is no consensus as to which is the superior method in terms of accuracy and precision of measurements. The methods utilized here have been variations of the Solorzano persulfate digestion, modified to cope with the proposed measurement using of an ion selective electrode (ultimately chromatographic analysis was used).

5.1 Overview of Persulfate Digestion (adapted from Solorzano 1980)[92]

Samples were run with the persulfate digestion method at the Massachusetts Institute of Technology's Parsons Laboratory. All glassware used in the analysis were washed with 1 M HCL, rinsed with copious amounts of Milli-Q water and autoclaved for 25 minutes at 250°C. In this study TN is total nitrogen while TDN is defined as all N species which pass through a 0.45 micron Whatman nuclepore filter. Organic N is defined as TN minus the combined concentration of NH_4^+ and NO_3^-, measured independently (See Appendix B). It should be noted that nitrite is nowhere accounted for in these measurements, and any concentration would be attributed to DON. However it is expected that nitrite concentrations would be two orders of magnitude lower then average nitrate concentrations, which would amount to less than 1-2 micromole in most cases.

5.1.1 Recrystallization of $K_2S_2O_8$
To ensure the purity of the peroxidisulfate Solorzano recommends recrystallizing twice. Despite the assurance from the manufacture that the contents are 99.99% pure, experiments using $K_2S_2O_8$ directly

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[1] Standard Methods recommends the acidification of Nitrate, Ammonia and organic nitrogen samples with H_2SO_4 to pH < 2, with analysis as soon as possible and refrigeration for ammonia nitrate and organic nitrogen and freezing for nitrate. (16th edition, pg 42-34)

without recrystallizing have confirmed the necessity of this procedure; the difference between one and two recrystallizations is perhaps precautionary.

To recrystallize:

a. Dissolve 32g. of $K_2S_2O_8$ in 200-ml of distilled water
b. Heat and stir on a hot plate until 75C temperature is obtained (all of the $K_2S_2O_8$ will be dissolved.)
c. Place in ice water to induce the reformulation of crystals
d. Filter using vacuum pump and #40 Whatman disc filters
e. Rinse the crystals with with distilled water
f. Collect the crystals in a beaker and dry in an oven for 10-20 minutes
g. Store crystals in a desiccator

5.1.2 *Preparation of reagents*

1.5 M Sodium Hydroxide

Dissolve 120 g NaOH in 2 liters of distilled water. The solution is stable for months when stored in a tightly closed polypropylene or nalgene bottle (glass is not suitable). Use low nitrogen (<.001%) analytical grade NaOH to ensure low blanks.

Oxidizing solution

Dissolve 6.0 g of twice recrystallized $K_2S_2O_8$ in 100 ml of 1.5 M NaOH, stirring with a Teflon coated magnetic stirring bar to aid solution. The reagent is stable for up to a week in a pyrex bottle stored in the dark.

Other reagents - used in some variations (See Appendix C)

5.1.3 *Peroxidisulfate Digestion*

Measure 20 ml of sample into a 50 ml capacity glass beaker or jar to be used for the PO digestion. Add 3 ml of the oxidizing solution to the digest container. Prepare reagent blanks by adding 3 ml of oxidizing solution to 20 ml of Milli Q water. Cover the beakers loosely with a cap or using tin foil. Autoclave for 35 minutes at 121°C and 15 pounds pressure. After cooling prepare the digested samples for measurement.
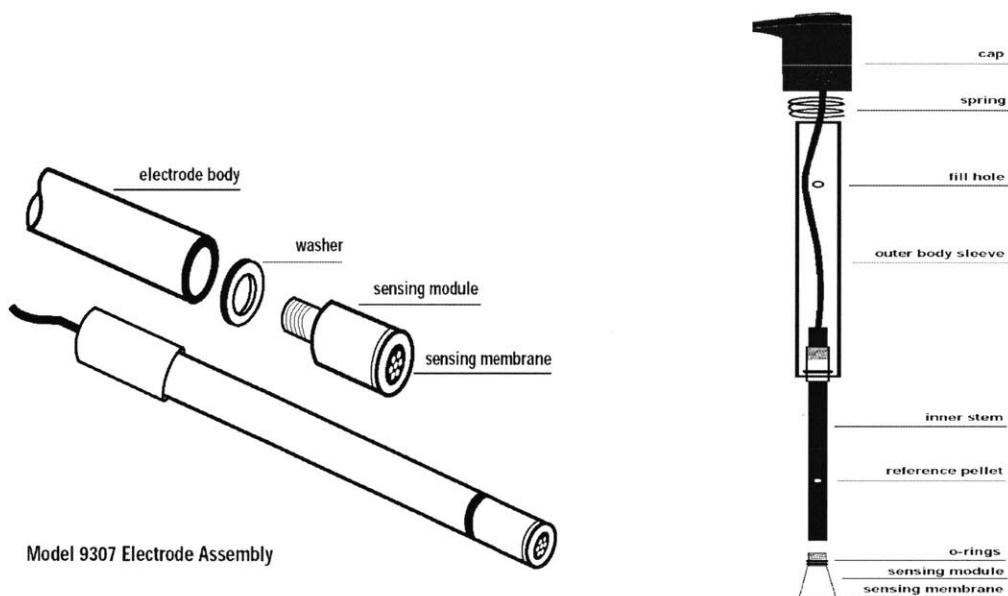
5.2 Ion Selective TOT N Electrode Measurement

The proposed method for measuring DON involves the oxidation of all species of nitrogen to nitrate using PO digestion, and subtracting the predetermined amount of nitrate and ammonium in the original sample. The measurement of total nitrogen as nitrate is accomplished by a Thermo Orion ion selective electrode model number 93-07 plastic membrane half cell. The process is as follows:

1) Assemble the ion plus electrode and reference electrode and fill with the appropriate filling solutions as per instructions in the ion plus users manual. Before use the nitrate electrode should be immersed in a 0.1M solution of nitrate standard. Connect to a standard Millivolt/pH meter.
2) Calibrate the nitrate electrode using nitrate standards (5, 15, 25,50, 75, 100, 150, 300, 500 μM). Measurement is taken by immersing the sensing membrane of the electrode in a container along with the reference electrode and reading the number from the millivolt meter display. The reading will fluctuate at first but should become stable within a few minutes at most. The known amount of nitrogen in the standards will be graphed logarithmically against the corresponding millivolt value

and used as a reference for concentration. Between each measurement the sensing membrane and reference electrode should be cleaned with Milli Q water and gently blotted dry with Kimwipes®. The range of standards used should be chosen to bracket the range of expected values in the sample. Because at low concentrations the operation of the electrode is non-linear, a calibration curve must be generated with an adequate number of standards to define the non-linear portion of the curve. After about 250 micromole the curve becomes linear according to the Nernst equation whereby a 56 Mv change corresponds to a logarithmic change in concentration.

3) An initial nitrate concentration of ABJ river sample could measured by ion specific electrode, or by ion chromatography.

4) A separate calibration is necessary to measure the recovery efficiency of the digest. Organic N standards and blanks run through the digest (see above) are measured and compared with the inorganic nitrate standards. Organic N standards using sulfanilamide, urea and ammonium should be used to compare efficiencies of various types of organic N. If the recovery efficiency of the digest is determined to be, for example, 90%, all measurements of digested samples would be multiplied by 1.11, and so forth.

5) Org N = TOT N $[NO_3]$ − (initial $[NO_3]$ + NH_4)

electrode body

washer

sensing module

sensing membrane

Model 9307 Electrode Assembly

cap

spring

fill hole

outer body sleeve

inner stem

reference pellet

o-rings

sensing module

sensing membrane

5.2.1 Ion interference

Ultimately this method proved unsuccessful in the determination of TN and DON, although it may still be viable for the measurement of NO_3 in ABJ river water samples. After many trials and iterations, including various alterations of the digest method the conclusion was reached that the extent of ion interference introduced by the reagents rendered the nitrate electrode inoperative for the purposes of measuring PO digested samples. While the river water itself contains significant amounts of sulfate, chloride and phosphate ions the reagents and standards used in calibrating the recovery efficiency introduce sulfate and potassium at millimole levels. The impediment of the normal operation of the nitrate electrode is twofold, in that the process both adds high levels of interfering ions and results in a pH outside of the range of the electrodes ability to measure nitrate (2-10). In general the electrode would function normally, obtaining a reasonable calibration curve for inorganic nitrate standards with a blank reading of approximately +183 mV.
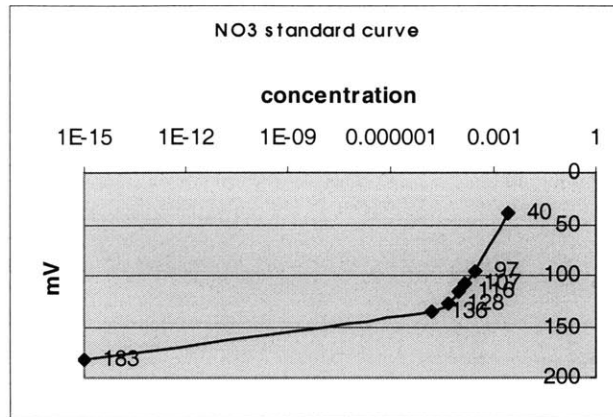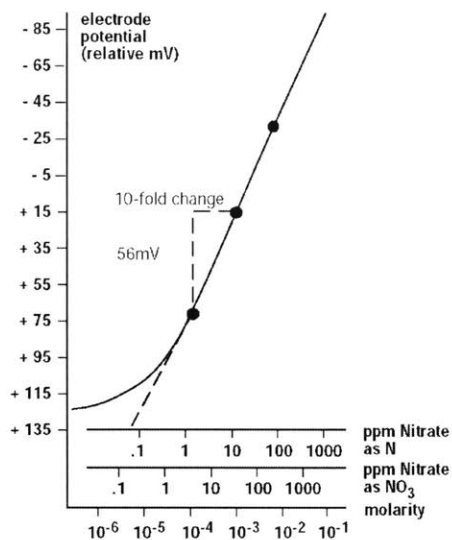
Figure 4 Example vs. Experimental Calibration Curve

However upon measurement of digested standards and blanks the bench meter would read anywhere from +60 to −60, which, if taken to represent an actual nitrogen concentration would be several orders of magnitude greater than was initially present. Subsequent measurements of Milli-Q water would range from +380 to +100 and exhibit drift. The electrode would fail to measure blanks and would not resume normal operation until after cleaning and refilling the reference electrode inner and outer solution. In some cases normal operation would not resume until after several cleanings. Merely switching out the sensor membranes on the ion plus electrode would not suffice; the problem would be rectified only after changing out the filling solution.

Several approaches were taken to attempt to ameliorate the extent of ion interference The following variations were attempted (including combinations) none of which proved satisfactory:

- The addition of ion suppressing solution – this proved ineffectual
- Switching from KCl to AgCl outer reference electrode filling solution to attenuate K interference
- Variation on PO for Phosphorus using Ammonium Persulfate, Ammonium Molybdate, Potassium Antimony Tartrate, Ascorbic Acid, and sulfuric acid reagents. In all likelihood this spiked the samples with NH4 nitrogen in addition to ion interference.
- Peroxidisulfate digest with phosphorous PO method reagents
- Use full Solorzano 1980 method with peroxidisulfate in 1.5M NaOH and including pH buffering with NH_4Cl and HCl titration[93]
- Variation of Solorzano with attenuated pH buffering
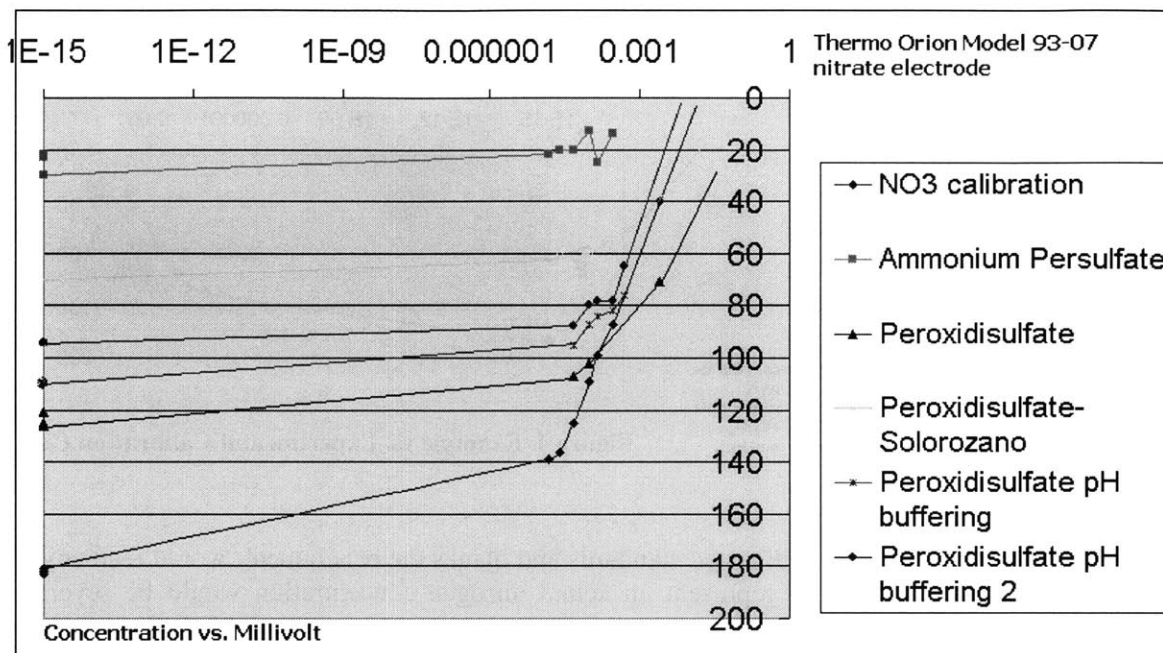- Peroxidisulfate digest using 50% oxidizing agent and no reagents

Figure 5 Results of Method Modifications

What emerged from these trials was the fact that the digest reagents, even the peroxidisulfate alone, deposited significant amounts of ions which interfered with the electrode. Attempts to buffer the solution and control the pH resulted in the addition of more ions and persistent interference. If a smaller amount of oxidizing reagent was used, the pH was more easily controlled and a signal would emerge from the 'noise' of ion interference above approximately 50 μM. At this point it became a tradeoff, using smaller quantities of reagents and managing the pH reduced the overall ion interference but also consequently reduced the recovery efficiency of the digest. To obtain a digest with greater than 90% recovery, which is necessary for precision, requires an amount of reagent which produces too many ions for the operation of the nitrate electrode. The optimum tradeoff obtained in this study was an ability to measure above 50 μM standards with a recovery efficiency of about 60%. This is inadequate for the purposes of conducting a Total nitrogen analysis. The nitrate electrode was abandoned after preliminary ion chromatographic measurements revealed both the extent of interfering ions present and the presence of a well defined peak for nitrate.

5.3 Ion Chromatography TOT N Measurement

Once the presence of a well defined nitrate peak was established measurements proceeded using ion chromatography. Due to the relative insensitivity to pH and the fact that the serial dilution involved (1/5) attenuated the alkalinity of the digested samples, the ion chromatograph was well suited to measure the converted TN. Whereas successful measurement of digested nitrogen samples using ion selective electrodes has not been reported in the literature, the procedure for ion chromatography is well established.

5.3.1 IC Method

To protect the column, the samples were diluted to one fifth with distilled water: The standards or samples were diluted in two steps to minimize volumetric error; first by addition of 20ml Milli-Q water to the beaker, and then by pipetting 3 ml into a 10 ml beaker and adding 7 ml distilled water. This amounts to a one fifth dilution. The IC is operated according the specifications of the manufacturer, with

the appropriate procedure for turning on pumps and air, adjusting pressure, ensuring proper eluent flow and chart recorder sensitivity.

5.3.2   Calibration using inorganic standards

The ion chromatograph was calibrated for the determination of recovery efficiency by running a set of prepared inorganic nitrate standards (50, 100, 400, 500 µM) and blanks against a set of digested sulfanilamide standards and blanks.

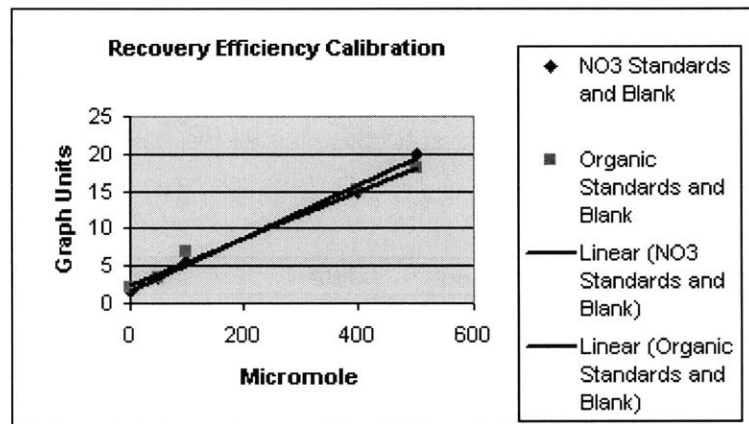| Inorganic	
0	1.5
50	3.4
100	5.5
400	15
500	20
Digest	
0	2
50	3.5
100	6.8
400	15.1
500	18

Figure 6. Recovery Efficiency of PO Digest

From the calibration above it was assumed that the digest obtained about 100% recovery within the range of concentrations used in this study. It appears that above 400 µM the digest began to lose some of the recovery efficiency, however the two linear regressions are highly correlated within the range of interest and provide sufficient basis for assuming near perfect recovery of sulfanilamide. In addition, the trailing off of recovery efficiency above 400 µM would be accounted for in the calibration of each sample set using organic standards. That is, every set of samples run will be run against a digest calibration curve, not an inorganic nitrate curve assuming 100% recovery, so that a measurement of 18 graph units for example would correspond to a measurement of 500 µM rather than be underestimated by an NO_3 curve. This does not, however, ensure the similitude of the dissolved organic matter with sulfanilimide. Even if similar results are achieved with urea and ammonium, there may be more recalcitrant components of DOM which fail to get oxidized in the PO digest. Thus the measurement of organic nitrogen using this method would represent a lower bound of the total organic nitrogen, inclusive of the most the labile species. Actual organic nitrogen concentrations may in fact be somewhat higher.

5.4   Determination of Organic N by Difference

The concentration of organic nitrogen is found by subtracting the measurement of ammonium and nitrate from the TN (unfiltered) measurement of the digest.   Org N = TOT N [NO_3] − (initial [NO_3] + NH_4). See Appendix B for independent lab results for NO_3 and NH_4 (Choi and Chou 2003).

VI.   DATA AND FINDINGS

6.1   Stage, Discharge and Hydrolab Data

(For stage/discharge curve data see Appendix D)

TABLE 1.

1/16/2003						
	HP in	**HP out**	**WP**	**USGS**	**MV**	**RT128**
Stage	28	27	19		19	29
discharge (m³/s))	0.0739	0.1046	0.046	0.62297063	0.3264	0.2058

1/24/2003						
	HP in	**HP out**	**WP**	**USGS**	**MV**	**RT128**
Stage	29	30	21		23	30
discharge (m³/s))	0.0945	0.146	0.0782	0.76455486	0.3424	0.2209

2/7/2003						
	HP in	**HP out**	**WP**	**USGS**	**MV**	**RT128**
DO	13.7	12.9	13	13.1	12.66	11.3
pH	6.81	6.88	6.97	6.7	6.86	6.5
SpC	1915	597	630	9.55	1264	1316
T	-0.1	2.19	1.14	0.94	0.09	0.55
Stage	31.5	36	26		28	32
discharge (m³/s))	0.14775	0.2396	0.1692	0.90613909	0.3849	0.2493

2/21/2003						
	HP in	**HP out**	**WP**	**USGS**	**MV**	**RT128**
DO	13.18	12.95	12.8	13.1	11.9	10.29
pH	6.95	6.93	6.98	6.75	6.77	6.6
SpC	1326	621	909	1744	1797	1636
T	3.03	1.74	2.49	2.13	1.33	2.2
Stage	31	34	24		32	36
discharge (m³/s))	0.1369	0.2068	0.131	0.99108963	0.4369	0.2989

| 3/8/2003						
	HP in	**HP out**	**WP**	**USGS**	**MV**	**RT128**
DO	13.5	12.8	12.69	13.52	12.5	11.74
pH	6.6	6.6	6.79	6.68	6.35	6.44
SpC	729	589	624	1218	12.51	1022
T	3.94	2.17	2.82	3.13	2.8	2.73
Stage	40	47	35		37	38
discharge (m³/s))	0.3475	0.4486	0.3708	1.2742581	0.5244	0.3201

6.2 Total Nitrogen and Total Dissolved Nitrogen

The following data represent lab analysis results using PO digestion and measurement of TN and TDN using Ion Chromatography as described above for the specified sampling sites in the watershed on

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three separate occasions. TN measurements are taken from unfiltered samples and TDN is measured from filtered samples. All sets of analysis were calibrated according to a run of sulfanilamide standards.

1/16/2003

Standard	Graph Units
40	2.8
100	5.3
200	9.1
400	15.6

IC Calibration Curve

$y = 0.0353x + 1.6767$
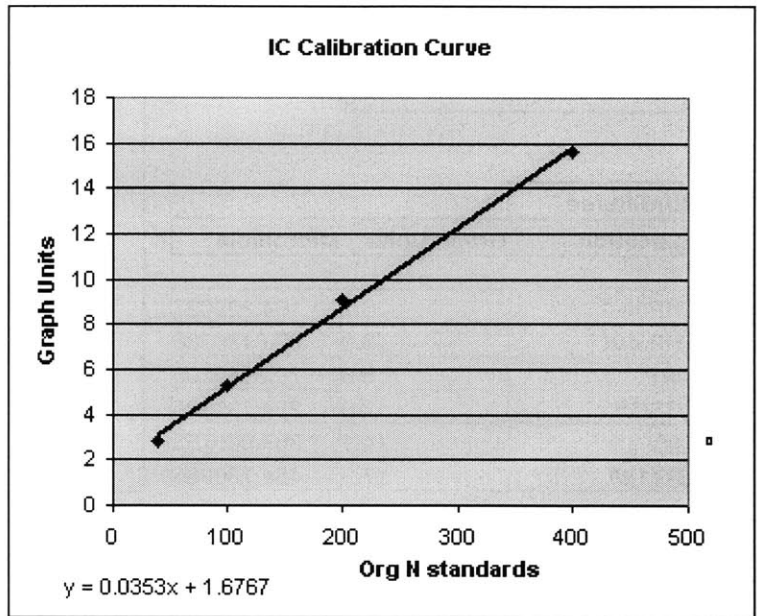
Unfiltered

Location	Graph Units	Micromole
HP out	4.8	88.4787535
WP	5	94.1444759
USGS	7.7	170.631728
MV	13.5	334.937677
RT128	17	434.087819

Filtered (.45micron)

Location	Graph Units	Micromole
HP out	4	65.815864
WP	4.5	79.98017
USGS	9.8	230.121813
MV	13.2	326.439093
RT128	17.5	446.517808

TOTAL NITROGEN 1/16/03

27
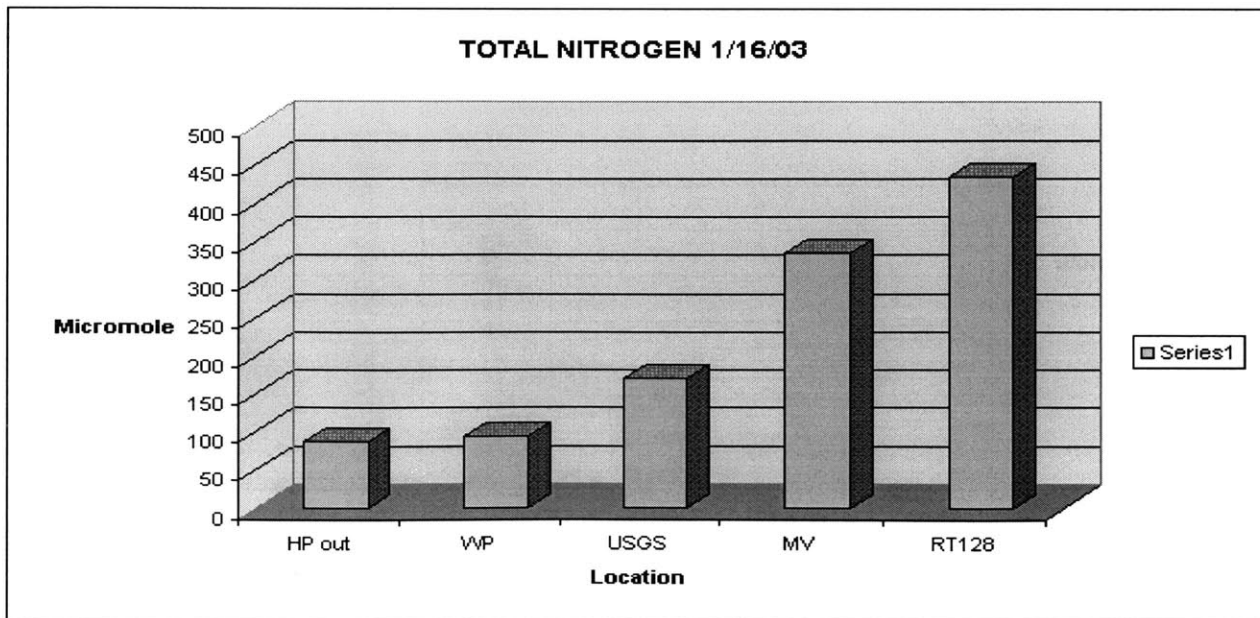
1/24/2003

Standard	Graph Units
50	2.3
100	4.6
500	18.9
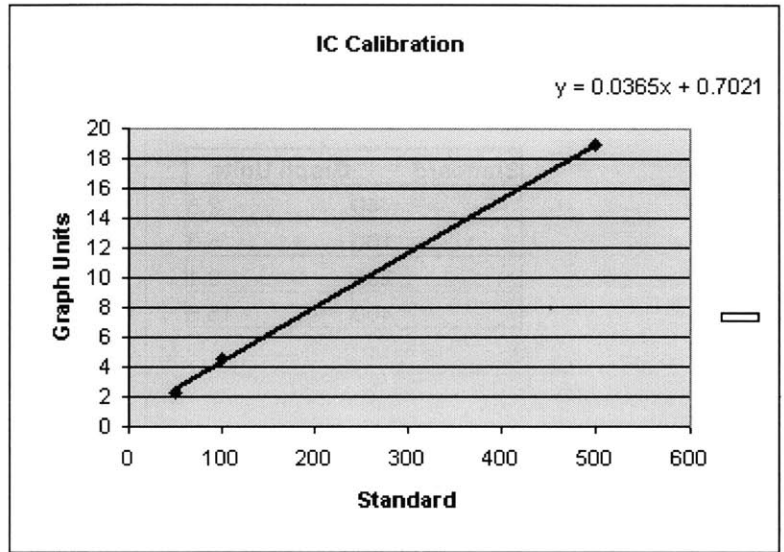
Unfiltered

Location	Graph Units	Micromole
HP in	6.7	164.326027
HP out	3.9	87.6136986
WP	3.6	79.3945205
USGS	10	254.736986
MV	14.1	367.065753
RT128	17.3	454.736986

IC Calibration

$y = 0.0365x + 0.7021$

Filtered (.45 micron)

Location	Graph Units	Micromole
HP in	4.8	112.271233
HP out	6.8	167.065753
WP	3.8	84.8739726
USGS	10.4	265.69589
MV	8.5	213.641096
RT128	17	446.517808

TOTAL NITROGEN 1/24/03

28
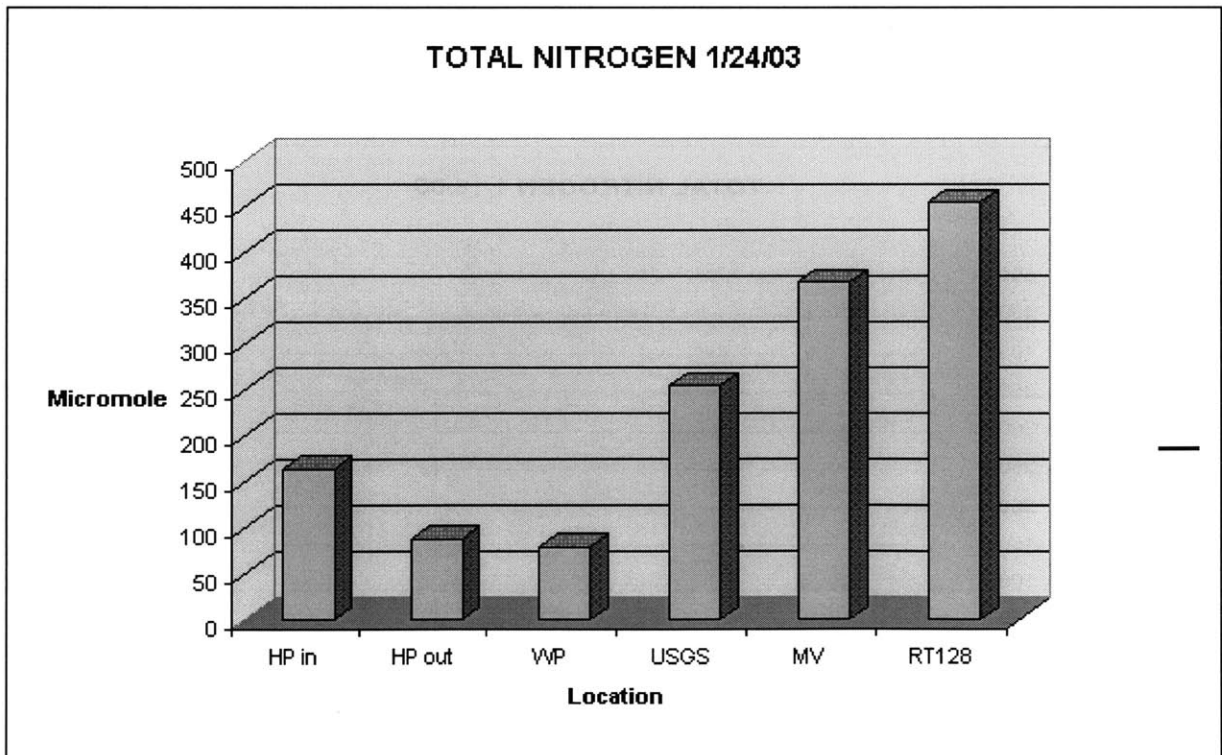
2/72003

Standard	Graph Units
50	6.1
100	10.1
300	21.4
500	32

Unfiltered

Location	Graph Units	Micromole
HP in	10.9	123.014085
HP out	8.2	75.4788732
WP	11	124.774648
USGS	20.8	297.309859
MV	21	300.830986
RT128	22.6	329
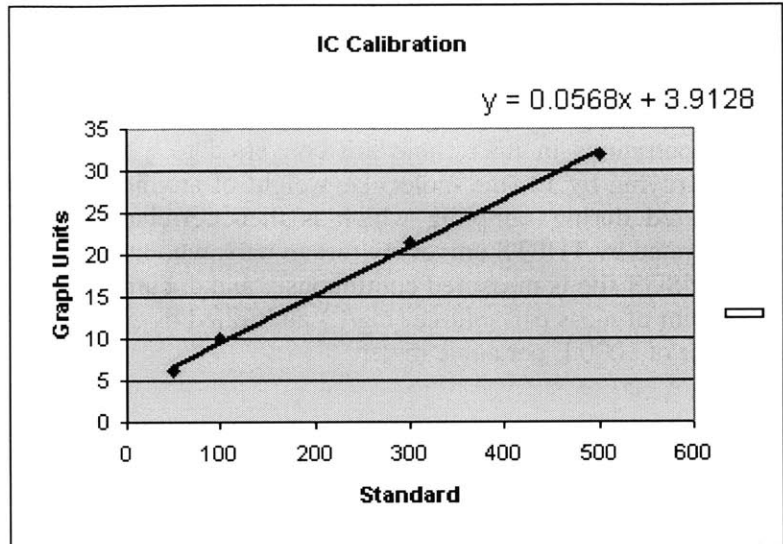
Filtered (.45 micron)

Location	Graph Units	Micromole
HP in	10	107.169014
HP out	14.1	179.352113
WP	10	107.169014
USGS	17.5	239.211268
MV	20	283.225352
RT128	25	371.253521

IC Calibration

$y = 0.0568x + 3.9128$

TOTAL NITROGEN 2/7/03
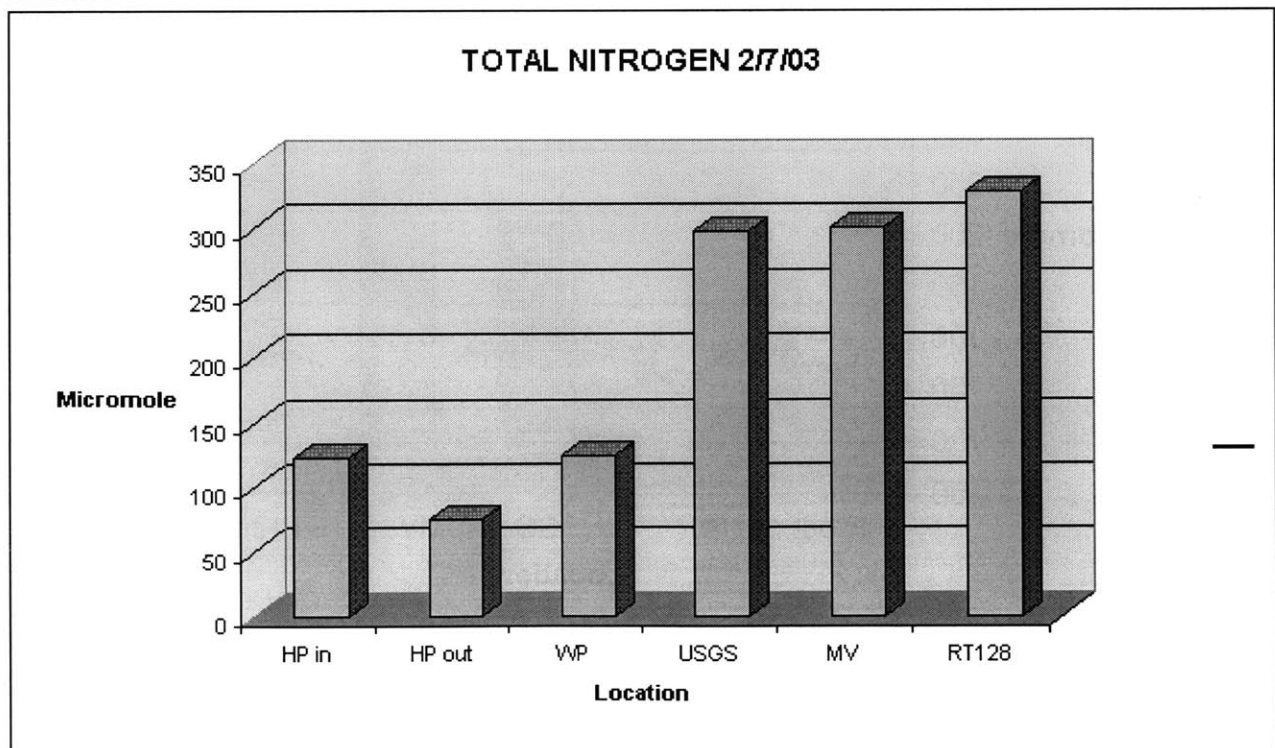
6.3 Nitrogen Speciation and Fluxes

The breakdown of TN by species was determined from prior analysis of nitrate and ammonium and the amount remaining after subtracting those measurements is attributed to organic nitrogen. The concentrations in micromole are converted to a mg/liter basis as nitrogen by dividing by 1000 and multiplying by 14 (the molecular weight of atomic nitrogen). Discharge is determined from stage data gathered during sampling which is then correlated to discharge through the stage-discharge curves generated by TUFTS university researchers, who installed the staff gages (see Appendix D). Discharge at the USGS site is measured continuously and documented on the USGS website. Flux is calculated as the amount of mass per volume (mg/L) multiplied by the volume per time discharge (m^3/s) with a conversion factor of 1000 L per cubic meter.

	TOT N	NO3	NH4	ORG N	TOT N mg/L	Q m^3/sec	Flux mg/sec
HP out	88.48	56.64	9.7	22.14	1.23872	0.1046	129.570112
WP	94.14	50.04	9	35.1	1.31796	0.046	60.62616
USGS	170.63	91.82	100.15	-21.34	2.38882	0.623	1488.23486
MV	334.94	96.22	198.93	39.79	4.68916	0.3264	1530.54182
RT128	434.09	67.63	261.9	104.56	6.07726	0.2058	1250.70011
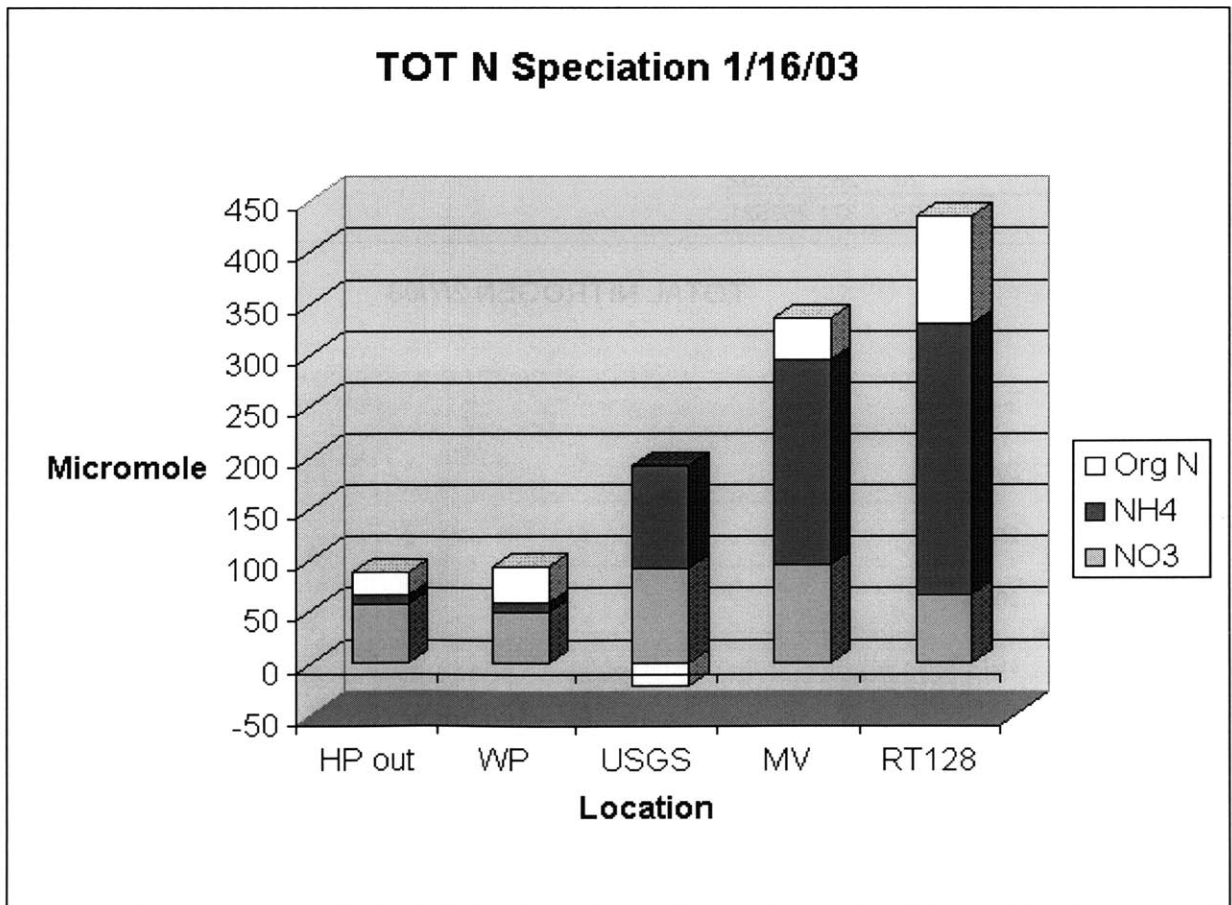
Figure 7.   N Speciation 1/16/03

	TOT N	NO3	NH4	ORG N	TOT N mg/L	Q m³/sec	Flux mg/sec
HP in	164.32	131.4	9.6	23.32	2.30048	0.0945	217.39536
HP out	87.61	46.74	5.9	34.97	1.22654	0.146	179.07484
WP	79.39	45.6	8.2	25.59	1.11146	0.0782	86.916172
USGS	254.73	138.01	116.56	0.16	3.56622	0.7646	2726.73181
MV	367.06	164.4	231.5	-28.84	5.13884	0.3424	1759.53882
RT128	454.73	83.03	262.68	109.02	6.36622	0.2209	1406.298
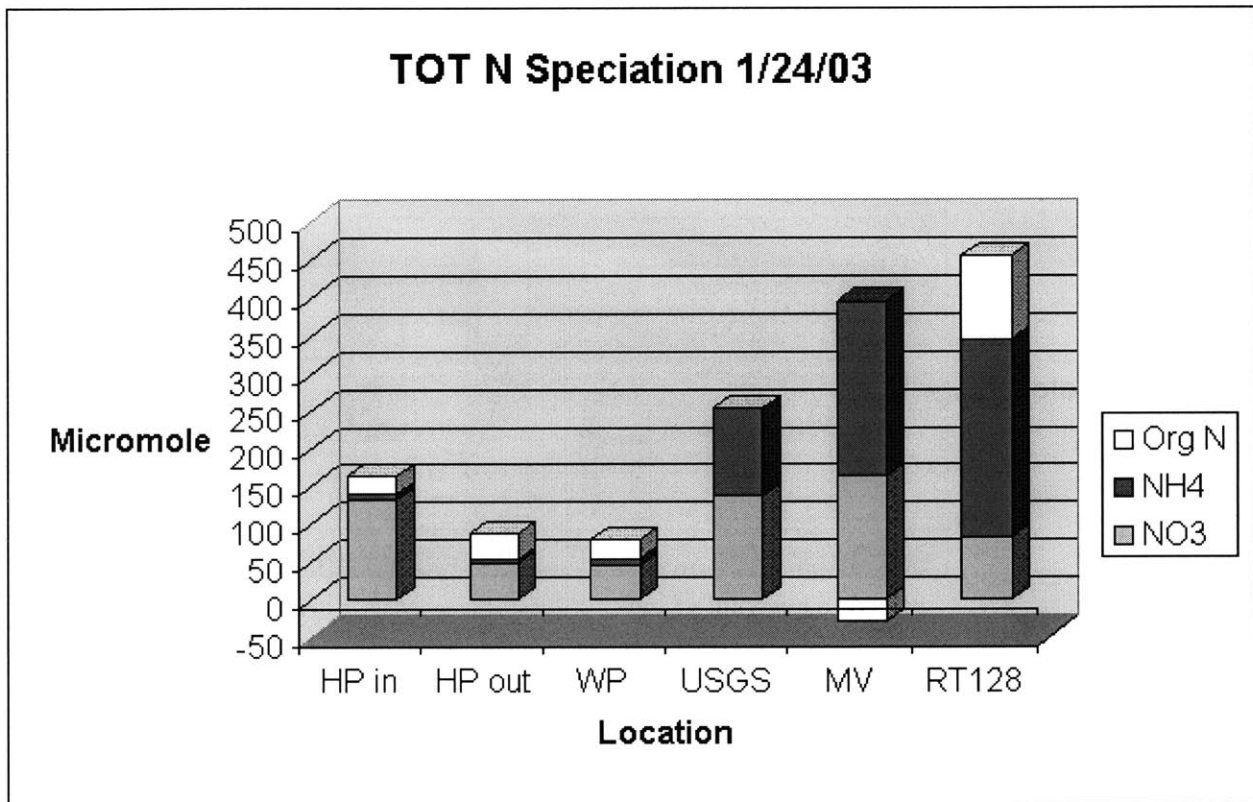
Figure 8.   N Speciation 1/24/03

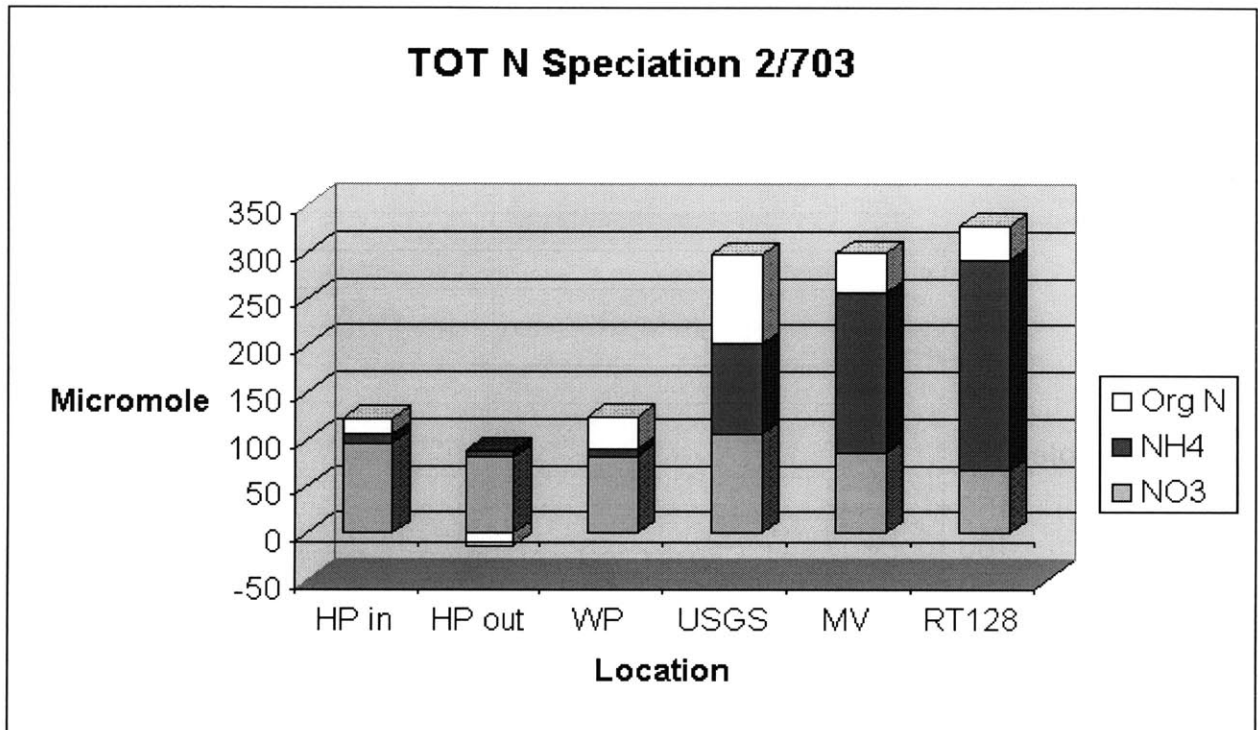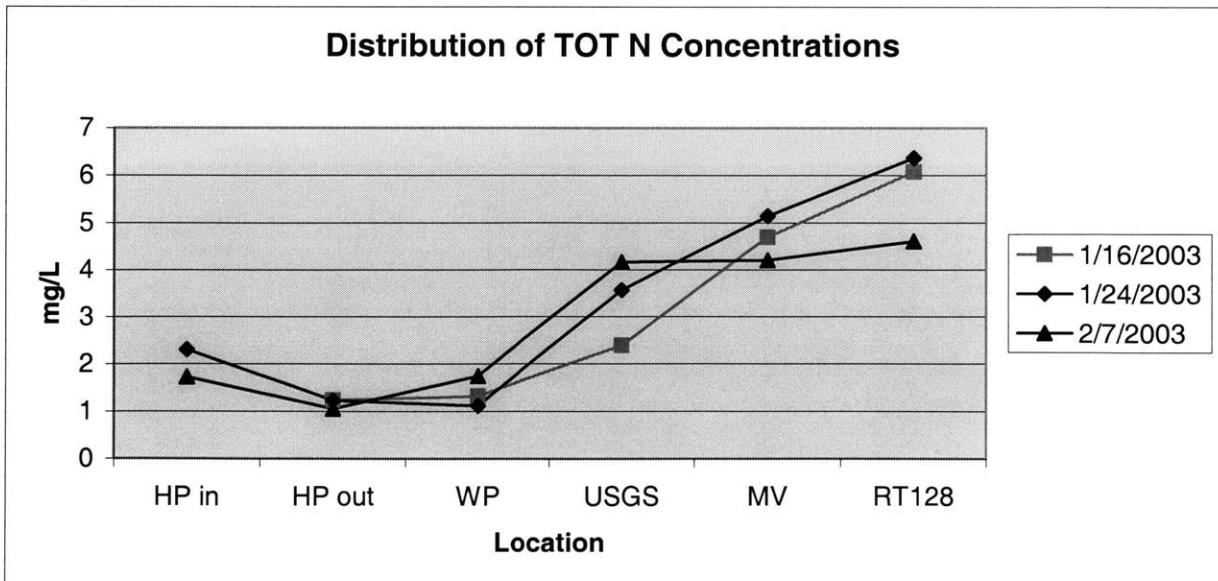|	TOT N	NO3	NH4	ORG N	TOT N mg/L	Q m³/sec	Flux mg/sec
HP in	123	96.22	9.3	17.48	1.722	0.147	253.134
HP out	75.4	80.83	7.5	-12.93	1.0556	0.239	252.2884
WP	124.7	81.9	8.7	34.1	1.7458	0.169	295.0402
USGS	297.3	105.02	98.1	94.18	4.1622	0.906	3770.9532
MV	300	85.23	172	42.77	4.2	0.384	1612.8
RT128	329	67.63	225.3	36.07	4.606	0.249	1146.894

Figure 9.   N Speciation 2/7/03

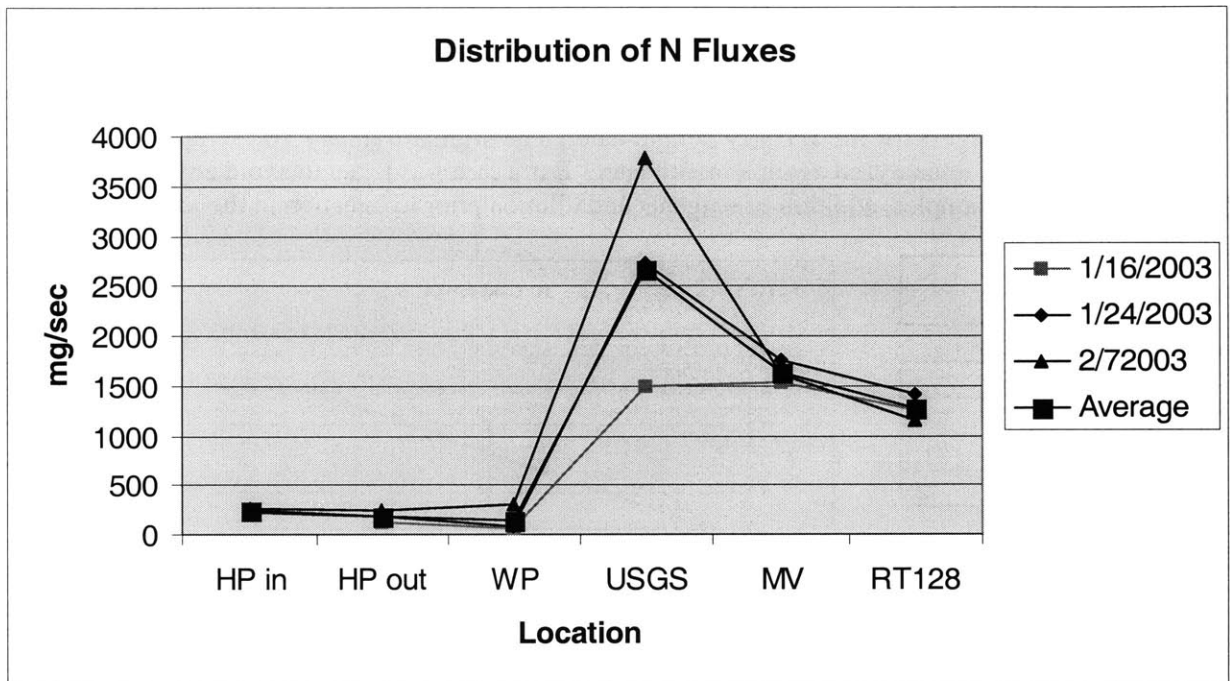**Figure 10. Concentration Distribution (note: lines are a visual guide, not an interpolation)**

Figure 11. Flux Distribution

|	Flux mg/sec			
	1/16/2003	1/24/2003	2/7/2003	Average
HP in		217	253	235
HP out	126	179	252	186
WP	60	86	295	147
USGS	1488	2726	3771	**2662**
MV	1530	1759	1613	1634
RT128	1251	1406	1147	1268

Table 2.

6.4 Quality Assurance/Quality Control

To determine the variance involved in the TN and TDN measurements a replicate sample was run through a PO digest for the 1/16/03 sample date. The original January 16th sample was analyzed in mid march and then re-analyzed again a month later. Extra care was taken to avoid any volumetric error in the preparation of samples, addition of reagents and dilution prior to injection in the ion chromatograph.

1/16/03 Replicate	

Standard	Mv
50	5.25
400	21.1
500	25

IC Calibration

$y = 0.0443x + 3.103$
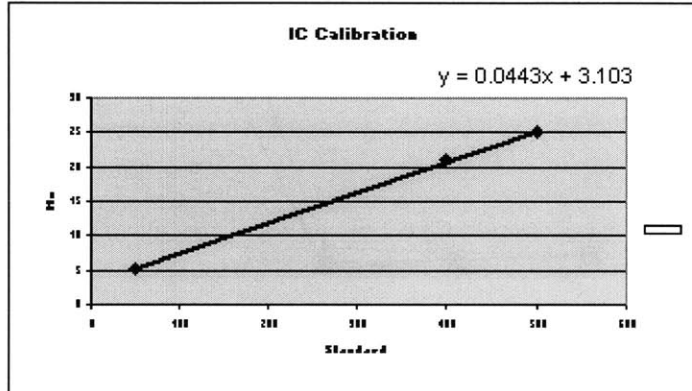
Replicate				Original				Difference
Unfiltered				**Unfiltered**				
Location	Mv	Micromole		Location	Mv	Micromole		
HP in								
HP out	5	42.82167		HP out	4.8	88.47875		45.65708
WP	4.75	37.17833		WP	5	94.14448		56.96615
USGS	11.5	189.5485		USGS	7.7	170.6317		-18.9168
MV	15.4	277.5847		MV	13.5	334.9377		57.35303
RT128	21	403.9955		RT128	17	434.0878		30.09233

Filtered (.45 micron)				Filtered (.45micron)				
Location	Mv	Micromole		Location	Mv	Micromole		
HP in								
HP out	6.1	67.65237		HP out	4	65.81586		-1.83651
WP	4.8	38.307		WP	4.5	79.98017		41.67317
USGS	14	245.9819		USGS	9.8	230.1218		-15.8601
MV	18	336.2754		MV	13.2	326.4391		-9.8363
RT128	19	358.8488		RT128	17.5	446.5178		87.66905

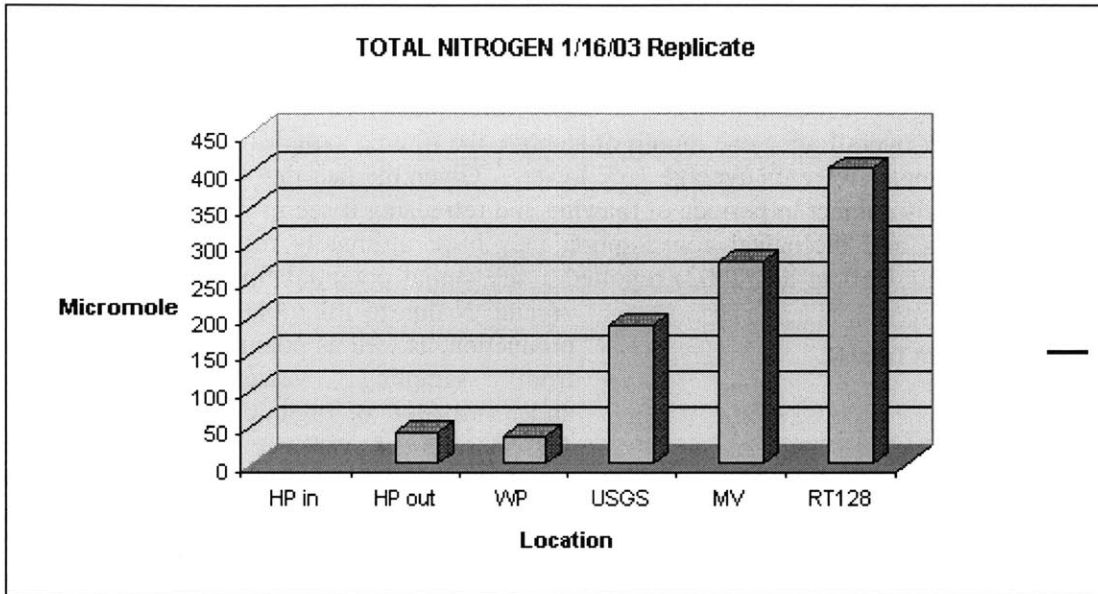**TOTAL NITROGEN 1/16/03 Replicate**

Figure 12. Replicate Results

VII. INTERPRETATION OF RESULTS

7.1 Evaluation of Analytical Methods

While the measurement of TN using PO digestion and ion chromatograph is highly correlated with the independent measurements of NO_3 and NH_4 there remain certain problems with the data. The foremost problem is that whatever variance is involved in the three separate methods is additive in the measurement of organic nitrogen, regardless of the fact that nitrate and ammonium are subtracted from total nitrogen. QA/QC data for the nitrate and ammonium methods are not available, so their contribution to variance is not known. The results of the January 16th replicate do not demonstrate satisfactory precision in the total PO analysis method, however they do shed some light on a possible mechanism corrupting the sample levels. A disconcerting phenomenon in the data occurs when the subtotal of NO_3 and NH_4 concentrations exceed the measured TN concentration, resulting in an effectively 'negative' organic nitrogen measurement. This could be attributed to three factors or a combination of them:

- Lab error in any of the three methods due to contaminated glassware, volumetric mistakes etc. (where the three variances are compounded).
- Incomplete digestion resulting in only partial recovery of organic nitrogen components.
- Degradation of the samples over time

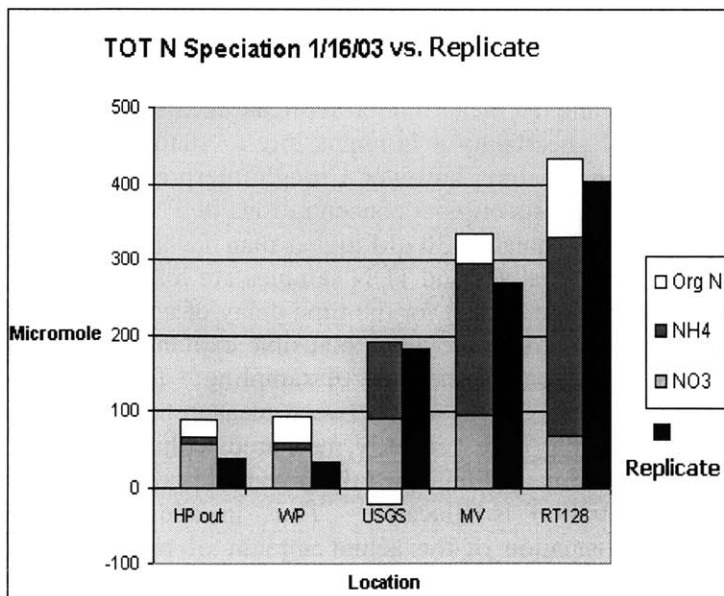While the extent of variance in the three methods has yet to be determined, the

TOT N Speciation 1/16/03 vs. Replicate

Figure 13. Initial Measurement vs. Replicate

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results of the replicate PO digestion tend to corroborate a degradation of the samples over time, which would in turn help to explain the relative statistical similarity of the TN and TDN samples and the potential for underestimating TN concentrations. The concentration analysis of the January 16th samples were on average 13% lower overall after one month of storage; the filtered samples were on average 9% lower and the unfiltered samples were on average 16% lower. Given the fact that the samples were not acidified and were potentially subject to periods of thawing and refreezing it seems reasonable to suggest that in-situ transformations and biological consumption may have ultimately resulted in the loss of nitrogen to the atmosphere. Neff et al. (2002) rep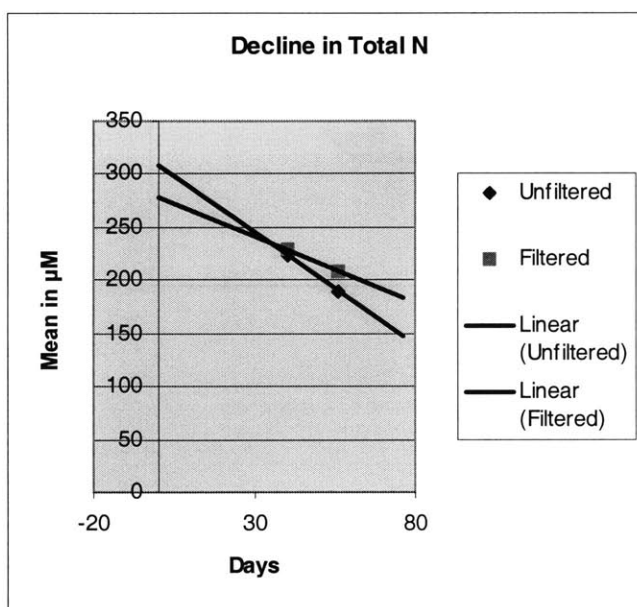orted a substantial potential for interconversions of organic N due to microbial decomposition and production, as well as potential for volatilization from sampling vessels resulting in underestimation of organic N concentrations.[94] An analysis of variance (ANOVA) of the unfiltered and filtered concentration distributions confirms that there is no significant difference between the filtered and unfiltered samples. The mean of unfiltered concentrations is 222.39 μM with SE 31.89, (though this distribution was not entirely normal) while the mean of filtered concentrations is 219.20 with SE 30.11. This gainsays the conventional wisdom which would predict that unfiltered samples, by including both dissolved and particulate organic matter, would have a higher concentration of nitrogen (or in any case should not contain any less). In a few instances however, the measurements for TDN were indeed significantly higher than for TN. A proposed explanation is that the unfiltered samples had a more robust community of

Figure 14. Degradation of Samples during Storage

microorganisms capable of consuming labile nitrogen and transforming it into more recalcitrant forms and/or denitrifying to gaseous N_2 or N_2O. The TDN samples, by virtue of being passed through a .45 micron filter, would have experienced less microbial activity. A one way ANOVA of the filtered and unfiltered replicate versus the original January 16th set corroborates this interpretation by showing that the concentration in the unfiltered samples diminished at faster rate then the filtered. The mean unfiltered replicate is 190 μM compared to an original of 224 μM and the mean filtered replicate is 209 μM against an original 229 μM. Within the bounds of statistical uncertainty it is impossible to state that such a decline is definitely occurring or that it should be linear in nature; however a rough interpretation of the trajectory change in concentration over change in time suggests original concentrations of TN could have been as much as 50 μM higher than the replicate and approximately 30 μM higher than TDN. Obviously a much larger data set is needed to support the hypothesis that TN and TDN samples are losing nitrogen over time at differential rates, and no attempt will be made to correct for the time delay of analysis using these linear regressions. However the available information does provide a plausible explanation for the similarity in TN and TDN samples analyzed over a month after the time of sampling. The potential degradation of samples would help to explain the occasional discrepancy between measurements of NO_3 and NH_4 and the total N measurements. While the former were generally measured within a week of sampling, the delay in measurement of TN and TDN could have diminished the potential pool of nitrogen from whose difference an organic nitrogen concentration is allocated. Thus in addition to the compounded variance of any laboratory errors an attenuation of the actual amount of total nitrogen present in the samples would have the effect of consuming from the organic nitrogen budget and possibly, as observed in some cases, reducing it to negative terms.

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Overall, given the uncertain level of analytical accuracy in the determination of total and organic nitrogen concentrations, a conservative approach would interpret the TN, TDN and organic N measurements as lower bounds representing an actual nitrogen concentration, but with a resolution insufficient for distinguishing between DON and particulate organic N. Since the blanks are consistently low, it can be said with reasonable confidence that the nitrogen 'seen' by the method exists at the time of measurement; whether higher concentrations are present in an unmeasured, recalcitrant form or whether concentrations diminished during storage is open to speculation. For the purposes of this study the measured concentration of unfiltered TN will be taken as a conservative estimate to be used in determining loads in the water column and runoff yields of the watershed.

7.2 Nutrient Loads and Speciation

Even with the potential underestimation of TN the presence of organic nitrogen in the water column is large enough to suggest that it cannot be overlooked in any analysis of N loading impacts. The average measured TN concentration is 3.11 mg/L (SE=.45) and of the total 15.86% (SE=4.14%) is organic nitrogen even accounting for instances of 'negative' organic nitrogen. In reality the percentage and absolute values of organic N would probably be higher. At places such as Rt. 128 and Montvale Avenue where concentrations reach as high 450 µM, the measured organic N constituent is above 100 µM. Even though the qualification of organic N as to its reactivity is not well understood, this quantity amounts to a substantial pool of N which could be potentially available directly or through transformations and its measurement is essential to complete an understanding of watershed N budgets.

In general the results of this study concur with past analysis and common knowledge that the Aberjona river is a heavily polluted waterbody. Concentrations of nitrate in the water column fell within the range measured in 2000 by volunteers of the Mystic River Watershed Association in collaboration with TUFTS researchers.[95] However, while their study reported only nitrates at concentrations between 1 and 3 mg/L this study measured total nitrogen levels ranging from 1 to 6mg/L with an average concentration of above 3 mg/L entering the Upper Mystic Lake. Average TN concentrations were remarkably high in the more urban industrialized branch of the watershed reaching 6 and 5 mg/L at Rt 128 and Montvale avenue respectively. At these heavily loaded locations the TN content is dominated by what could possibly be a lingering point source of NH_4. A 1980 preliminary study by CDM indicated the presence of a large ammonium source emanating from somewhere "in the vicinity of the Stepan Chemical waste dump site near Hall's Brook." It is not known whether or not this source was subsequently remediated, but the current data show that the high NH_4 levels persist more than two decades later. Given the range of values measured for DO, pH and temperature at the time of sampling the un-ionized Ammonia concentration could reach as high as .01 mg/L, within an order of magnitude of the .06 mg/L toxicity threshold for fish.[96] Nitrate concentrations are also within striking distance of the 3 mg/L level harmful to fish. Hydrolab measurements also reveal that DO levels dip the lowest beneath saturation at the Rt. 128 and Montvale sites, indicating that oxygen is being consumed *in-situ*, mostly likely in the service of nitrification of the abundant NH_4. Correspondingly, nitrate fluxes increase down the watershed from Rt. 128 to the USGS gage station beyond the confluence with the Horn Pond tributary while Ammonium levels decline. The driving mechanism behind nitrification in natural waters is the activity of microbial bacteria such as *nitrosomonas* and *nitrobacter* according to the reaction:
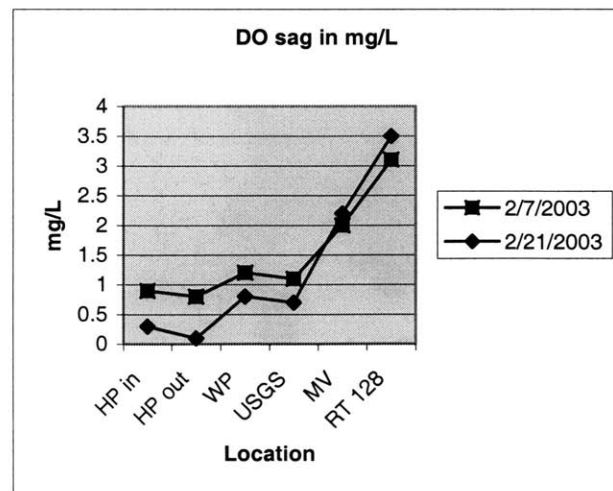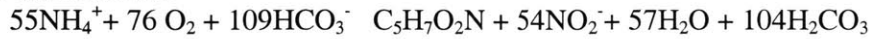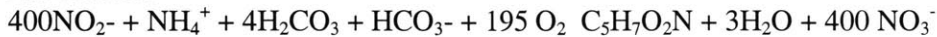

Figure 15. Oxygen Consumption in ABJ samples

Nitrosomonas:

$$55NH_4^+ + 76 O_2 + 109HCO_3^-\quad C_5H_7O_2N + 54NO_2^- + 57H_2O + 104H_2CO_3$$

Nitrobacter:

$$400NO_2^- + NH_4^+ + 4H_2CO_3 + HCO_3^- + 195 O_2\quad C_5H_7O_2N + 3H_2O + 400 NO_3^-$$

The process does not remove any nitrogen, but rather transfers N from an ammonium reservoir to a nitrate reservoir while providing bacterial cell mass and consuming O_2 and alkalinity in the process. Approximately 4.3 mg O_2 are consumed for every mg of ammonia-nitrogen oxidized to nitrate-nitrogen, while 8.64 mg of alkalinity in the form of HCO_3^- are consumed per mg of ammonia-nitrogen oxidized. Despite indications of the occurrence of in-stream transformations actual quantification of these processes are difficult due to a lack of suitable techniques for tracking N transformations. While isotopic analysis provides important insights into in stream processes there remain difficulties in isolating denitrification fractionation from non-fractionating processes. Whereas the preferential bacterial reduction of $^{14}NO_3^-$ over $^{15}NO_3^-$ leaves a pool of enriched $^{15}NO_3^-$, biological assimilation and dilution with low NO_3^- groundwater are non-fractionating and potentially difficult to quantify with a stable isotope approach.[97]

Extensive studies of the groundwater hydrology in relating to the Wells G and H Superfund site have indicated a fairly high amount of connectivity between the Aberjona river and the aquifer of the Aberjona river valley, but the impacts this has on the transfer of nitrogen pools is unknown. The amount of dilution occurring along the tributary from Horn Pond is probably not very high, given the decrease in the flow from HP in to the outlet of Wedge Pond. However from Rt. 128 to Montvale Avenue (MV) and from Montvale to the USGS site significant amounts of flow are accumulating. It is not known to what extent the accumulation of flow down the length of the Hall's brook tributary to the USGS site is attributable to surface runoff as opposed to groundwater inflow, but in either case dilution is potentially partly responsible for the decrease in TN concentration from Rt. 128 to USGS (Figure 10). Future research objectives should include the quantification of groundwater inflow relative to surface runoff and the variable contributions of each to N loads. On average the river flow swells by more than 200% from MV Ave. to the USGS station, yet the average concentration does not decrease by a factor of two. On the contrary, flux is increasing down the length of the river (Figure 11), indicating that elevated concentrations of nitrogen are contained in the lateral inflow.

Finally there is a degree of uncertainty introduced in the extrapolation of the results over a whole year, during which there may be shifts in sources and seasonal controls on nitrogen yields such as biological uptake or fertilizer application. To track these phenomena would require the observation of the speciation of total N over the course of at least one full year. Seasonal trends may exist within the watershed that are not captured in the current data set which covers only the early winter months of 2003.
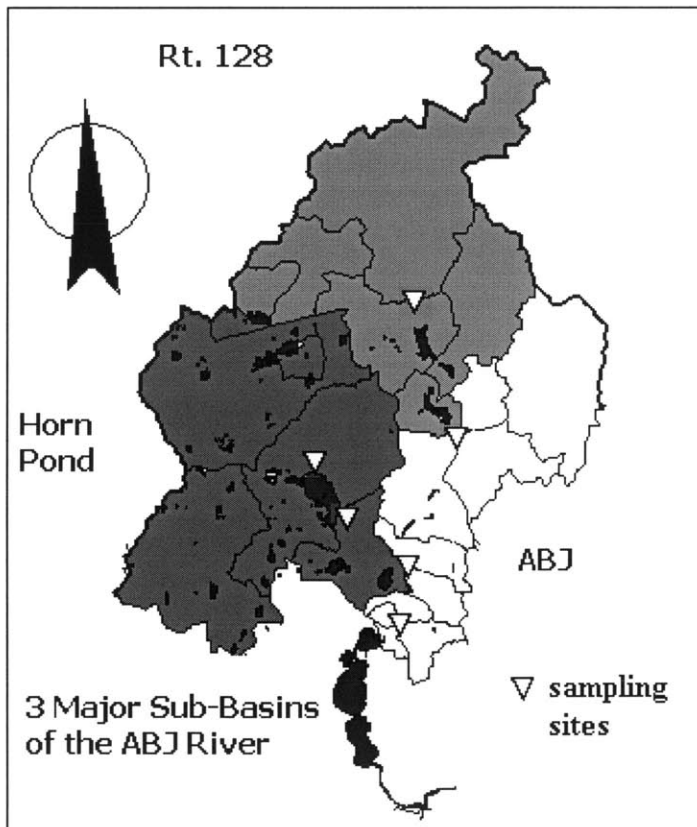

Figure 16 Sub-watershed areas of the Aberjona River

7.3 Nitrogen Yields in the watershed sub-basins

The most striking feature of the nitrogen distribution in the watershed is the large fluxes originating from the approximately 8.9 square mile sub-watershed basin passing through Rt. 128 and the Montvale Ave. sampling sites. The high numbers contrast starkly with the low fluxes emanating form the Horn Pond sub watershed basin. Overall the flux of nitrogen emitted from the 26 square mile Aberjona River watershed represents one of the highest nitrogen yields of any watershed in the world at 12.45 kg ha^{-1} yr^{-1}, estimated from average flux passing through the USGS gage station. This accounts for the transport of about 90 tons of nitrogen into the Upper Mystic Lake annually. Of an extensive analysis of North American basins conducted by Boyer et al (2002) only two watersheds exported more nitrogen per hectare; the Schuylkill and the Charles River (at around 17 kg ha^{-1} yr^{-1}) which of course the Aberjona itself merges with prior to draining into Boston Harbor.[98] What is even more remarkable about these results is the fact that the flux is averaged over the entire 6734 ha area of the watershed despite the fact that a majority of the mass is flowing from the 2304 ha area draining through Montvale Ave. The flux of the sub-watershed comprising the areas upgradient of Montvale Ave is a massive 21.9 kg ha^{-1} yr^{-1}. Numerous studies have documented the considerable retention of nutrients in the watershed (usually in excess of 70%) due to plant uptake, denitrification, mixing with ground water and incorporation into soil organic matter pools.[99] Boyer's study calculated the relative capacity of 16 watersheds to absorb nitrogen loads, and reported one of the lowest retentive capacities for the Charles River basin, where only 60% of N inputs are immobilized.[100] Extrapolating this finding to the sub-watershed of the Aberjona River, and calculating that river yields are 40% of N loads, the burden on the watershed is approximated at 31 kg ha^{-1} yr^{-1} for the entire watershed and an astonishing 55 kg ha^{-1} yr^{-1} for the sub-watershed area containing the industrial parks of Woburn.

7.4 Correlation with land use

Given the disproportionate contribution of the Rt. 128/Montvale sub-watershed to the overall N budget the obvious question to ask is what activities in that area may be responsible for the difference. All areas of the Aberjona watershed receive approximately equal amounts nitrogen by atmospheric deposition (possibly ranging up to 6 kg ha^{-1} yr^{-1}) and in precipitation (an additional 1-2 kg ha^{-1} yr^{-1}) per unit area, so the difference must result from a combination of topography, soil and vegetation type and land use.[101] While land use is an elusive attribute to define, in general the infrastructure associated with urban population density results in an increase in the impervious surface area due to pavement and roofs. This in turn affects the hydrogeologic characteristics of the surface flow regime by reducing percolation and competing with natural vegetation as a land cover. In addition to population density the activities of commerce and industry can
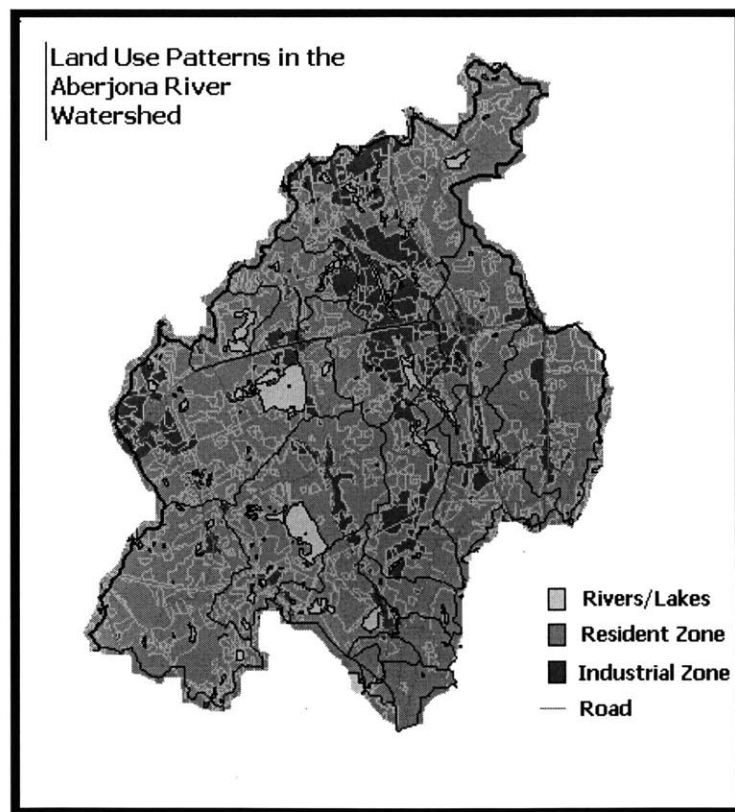

Land Use Patterns in the Aberjona River Watershed

Rivers/Lakes
Resident Zone
Industrial Zone
— Road

Figure 17 Land Use in Woburn and Winchester

result in an increase in the discharges of pollutants to the environment. To examine the relationship between landuse and watershed N yield a hydrologic model in ArcView GIS was used. This model applied a multi-layered approach to mapping land use and surface hydrology by combining a Digital Elevation Model (DEM) layer (to generate flow direction and accumulation data for use in estimating runoff and sub-watershed delineation) and polygon attribute layers describing categories of land use. The 21 category classification of land use was used with the aim of identifying spatial patterns in roughly two classes: urban commercial/industrial and residential/rural.

CODE	ABBREV	CATEGORY	DEFINITION
1	AC	Cropland	Intensive agriculture
2	AP	Pasture	Extensive agriculture
3	F	Forest	Forest
4	FW	Wetland	Nonforested freshwater wetland
5	M	Mining	Sand; gravel & rock
6	O	Open Land	Abandoned agriculture; power lines, areas of no vegetation
7	RP	Participation Recreation	Golf; tennis; Playgrounds; skiing
8	RS	Spectator Recreation	Stadiums; racetracks; Fairgrounds; drive-ins
9	RW	Water Based Recreation	Beaches; marinas, Swimming pools
10	R0	Residential	Multi-family
11	R1	Residential	Smaller than 1/4 acre lots
12	R2	Residential	1/4 - 1/2 acre lots
13	R3	Residential	Larger than 1/2 acre lots
14	SW	Salt Wetland	Salt marsh
15	UC	Commercial	General urban; shopping center
16	UI	Industrial	Light & heavy industry
17	UO	Urban Open	Parks; cemeteries; public & institutional greenspace; also vacant undeveloped land
18	UT	Transportation	Airports; docks; divided highway; freight; storage; railroads
19	UW	Waste Disposal	Landfills; sewage lagoons
20	W	Water	Fresh water; coastal embayment
21	WP	Woody Perennial	Orchard; nursery; cranberry bog
22	-	No Change	Code used by MassGIS only during quality checking

Figure 18. LU 21 Land Use Codes

For the purposes of analyzing the runoff regime Codes 15, 16, 18 and 19 were considered "Urban industrial" land areas and the rest are considered "Residential/Forested". While this amounts to a gross oversimplification of the LU21 code (which is itself a generalization of a complex suite of land use practices) and their impact on vegetation, ecology, nutrient cycling and so forth, it may be useful as a tentative predictor of N yields. All of the area within the sub-watersheds (as identified in the count attribute of the Land Use GIS layer merged from the towns of Woburn, Winchester, Reading, and parts of Stoneham and Lexington) was designated according to one of these binary values (See Appendix E). For the sub-watershed basin draining from Wedge Pond outlet and including Horn Pond it was found that 6.4% of the land use could be described as urban industrial; for the sub watershed basin including the Hall's brook, Mishuwam pond and Rt. 128 and Montvale Ave. sampling sites the percent urban industrial land use is 31% while in the balance of the watershed (including Sweetwater Brook) 15.8% of the land is urban industrial.

Table 3. Land Use, Flux and Yield for 3 Sub-Watersheds

Sub watershed	Sub Watershed Area (ha)	Industrial LU (percent)	Ave Flux g/sec	Yield kg ha-1 yr-1
Horn Pond	2586	6.4	0.14	1.7
RT128	2304	31	1.6	21.9
ABJ	1840	9.9	0.92	15.8
TOTAL	6730	15.8	2.66	12.5

40
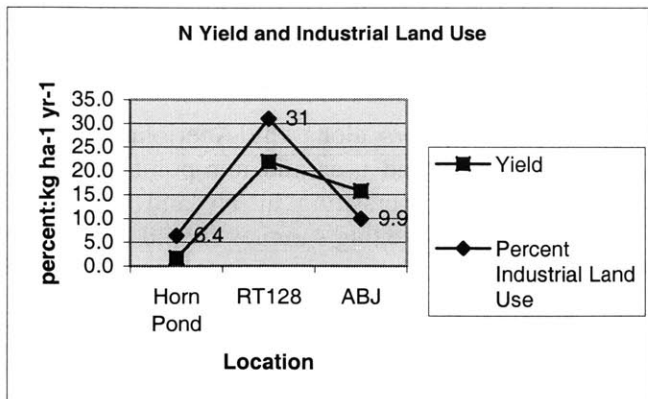
Figure 19 Nitrogen Yield and Industrial Land Use for 3 Sub-watershed Areas

Using this percentage land cover for industrial categories within the runoff defined sub-watershed basins it was found that percent industrial land use and yield in kg ha^{-1} yr^{-1} were not significantly correlated (R^2=.65), although a discernable positive trend exists. Thus while it cannot be stated with certainty that the source of non-point pollution resides in the industrial activities clustered around Rt. 128, the trend in the data does tend to support that hypothesis.

Linear Fit
% Industrial land use = 3.7662547 + 0.8477471 yield

Summary of Fit

RSquare	0.649642
RSquare Adj	0.299284
Root Mean Square Error	9.121953
Mean of Response	14.9
Observations (or Sum Wgts)	3

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	154.28997	154.290	1.8542
Error	1	83.21003	83.210	**Prob > F**
C. Total	2	237.50000		0.4033

Table 4. Statistical Analysis of Land Use compared to N Yield

Part of the difficulty in making this correlation is the fact that the Horn Pond and Rt. 128 sub watersheds represent two extremes of land use. In addition to residential areas large tracts of the Horn Pond watershed are covered with woodlands, in addition to the surface areas of the lakes themselves, whereas the area around Rt. 128 is almost completely built up except for a narrow corridor along lake Mishuwam. The balance of the watershed after subtracting those two basins comprises a less well defined admixture of commercial, industrial and residential lands uses. A positive correlation between percent industrial land and N yields would have predicted a greater percentage of industrial land within the balance of the Aberjona watershed in Woburn and Winchester. In other words, given the percentage of industrial land use in this area, N loads were higher than a correlation between Horn Pond and Rt. 128 would suggest. One possible interpretation of this information is that residential and industrial land uses are not that differentiated in terms of nitrogen loads, as compared to woodlots, possibly due to the application of lawn fertilizers. Perhaps a better indicator of nitrogen loads could be found by comparing them to the percentage of industrial land use categories relative to the percentage of truly naturally vegetated areas as opposed to created space such as lawns, parks, recreational fields and so forth.

7.5 Challenges and opportunities for future research

While this ongoing study samples and analyzes surface waters along the Aberjona River to develop a flux model and correlate concentrations and fluxes with land uses and non-point sources a primary consideration should be rectifying the level of uncertainty persisting in TN and organic N measurements. Presently implemented procedures for acidifying and freezing samples should ameliorate biological processes that may have resulted in denitrification and/or conversion to recalcitrant organic forms during storage. The samples should be analyzed within a week or two of collection. Additionally the ability of the PO digest to convert recalcitrant forms should be gauged by running standards of sulfanilamide, NH_4 and urea as well as various concoctions of the three. If possible an attempt should be made to qualitatively assess the organic N for lability and differentiate between sources (i.e. analysis of DON in precipitation, runoff and in stream).

Due to the compounding of variances among the three laboratory procedures which contribute to organic nitrogen measurement, a thorough replicate analysis must be run to ensure that reasonably tight error bars can be obtained. In addition the nitrate electrode method for determining inorganic nitrate concentrations in ABJ river water should be cross checked with ion chromatography to identify whether or not this simpler and less time consuming method can be used for NO_3 in place of chromatography.

One of the most serious shortcomings of the results presented so far is the relative lack of them. Due to the laboratory intensive methodology of PO digest and ion chromatograph measurement only 3 sample dates plus one replicate were measured. The average TN flux from the watershed of 2.66 g/sec is taken from only three measurements at the USGS gauging station, and this could be either higher or lower than the yearly average due to seasonal variation and the effects of storm event flushing. At least one full year cycle of measurements is required to account for seasonal patterns and an attempt should be made to accumulate a sufficient data set of storm event measurements to determine the extent to which precipitation alters river concentrations and whether or not TN and TDN are correlated with flow. Furthermore a detailed picture of N pools, sinks and transformations in the watershed must account for the role of the lakes and processes whereby N inputs may be denitrified or impounded in sediments. On going research in the Upper Mystic Lake should provide a data set which could be linked to a complete model of throughput in the watershed that examines the impacts of Horn and Wedge pond. An important indicator of the capacity of watersheds to immobilize N into the soil N pool is the DOC: DON ratio. Forested watershed studies have shown that riparian areas where the supply of N exceeds biological demand the reduction in the C:N ratio corresponds to higher DIN losses through nitrate leaching.[102] Since the export of DIN is negatively correlated with DOC:DON ratios it follows that organic carbon content should also be a useful index of N status in a watershed. Determinations of organic carbon in ABJ river samples should be compared with nitrogen speciation data in an attempt to gauge the relative N saturation of the watershed soils.

VIII. CONCLUSIONS

Compared with previous watershed studies of nutrient cycling, the bulk of which analyzed forested or agricultural watersheds, the results of the Aberjona River study to date are differentiated in a number of ways. In terms of average loads and concentrations the Aberjona is found to contain far more nitrogen then the values typically reported for forested and minimally disturbed watersheds.[103] At approximately 12.45 kg ha^{-1} yr^{-1} the watershed exhibits a yield more than three times that of typical undisturbed catchments.[104] This is not too surprising since it is well known that the Aberjona is an urban watershed with a long history of pollution. While concentration levels of nitrate in ABJ river water are much higher than in either forested or undisturbed watersheds, they are within the range of the few studies conducted in urban watersheds (Fong and Zedler 2000). In terms of Total N measurements however, which reached almost 500 μM (7 mg/L) at some sampling stations, the Aberjona ranks higher

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than many of the most heavily loaded agricultural watersheds.[105] Like an agricultural watershed with high fertilizer inputs, the Aberjona N fluxes are dominated by high levels of NH_4. However, this ammonia is most likely not fertilizer derived; rather it originates as a fairly defined non-point source in the industrial sub-watershed basin around Mishuwam pond.[106] This characteristically high ammonium content has been observed for more than 20 years, and poses a complicated problem in that it contributes to the nutrification of the watershed but at the same time inhibits the growth of algae. Remediation of this source beneath the tolerance threshold for microalgae without concomitantly reducing nitrate and labile organic nitrogen loads in the water column could potentially result in an exacerbation of eutrophication by introducing algal blooms.

Despite the potential for underestimation in the method used, the organic nitrogen content of ABJ river water was found to be significant. Approximately 15 percent of the total nitrogen in the water column is present as organic nitrogen compounds, with concentrations ranging as high as 100 μM (1.4 mg/L). This is considerably higher in absolute terms than organic nitrogen concentrations found in forested watersheds where DON can actually account for more than 50% of exported nitrogen.[107] While the Aberjona River is clearly dominated by inorganic nitrogen species, and in particular NH_4, organic nitrogen still accounts for a significant fraction of Total N and its relevance in future urban watershed studies should not be ignored.

Based on the results of this study it can be estimated that the Aberjona river deposits more than 80,000 kg of nitrogen into the Upper Mystic Lake annually. Of this amount over 60% is originating from the more urbanized reach of the watershed draining through Montvale Ave. and including the industrial complexes around Rt. 128. This region, which accounts for around 35% of the total watershed surface area, is exporting almost twice as much nitrogen as the rest of the watershed combined. The mass of nitrogen emanating from the Rt. 128 area is an order of magnitude higher than the N exported from the Horn Pond sub-watershed, which is of comparable area. Despite these obvious differences the flux of nitrogen from the sub-watersheds was only weakly correlated to land use patterns. While an observable trend was present, the relationship failed to correlate statistically, perhaps due to the relatively few numbers involved in comparing only three sub watershed basins. In addition the low R^2 may be a function of the failure of the basic categories derived from the LU 21 code used in the GIS analysis to encompass the complexity of land use impacts on the N loading regime. It may simply be the case, however that yield is only minimally correlated with percent cover by industry and commerce because residential N loads from lawn fertilizers themselves represent significant contributions to river nitrogen.

While the results presented here can provide a basis for discussing the nitrogen cycling regime in the Aberjona River watershed, further study including additional sampling and lab analysis is necessary to establish longer term trends and provide a more comprehensive data set for the determination of nitrogen yields as a function of urban land use patterns.

APPENDIX A

Partial catalogue of the historical pollution of the Aberjona River (Defeo, 1972)[108]

TABLE I

SOURCES OF POLLUTION ALONG THE ABERJONA RIVER EXAMINED DURING SUMMER 1970*

No.	Source	Pollutants	Flow	Pollution Abated	Comments
1	Walter and Bills Inc. Winchester	Caustic Rinse Water	Nil	No	Firm awaiting permission to tie into sewerage
2	General Foods-Atlantic Gelatin-Woburn	Thermal	Variable	Yes	Sweetwater Brook is monitored 24 hours by TV.
3	Anderson Foreign Motors Building #5-Woburn	Soap, oil and grease	Variable	Yes	Operation moved to main shops
4	Brodie Industial Trucks, Inc.-Woburn	Soap and oil	Variable	No	Firm awaiting city approval of oil trap
5	Stauffer Chemicals-Mark Phillip Trust-Owner (abandoned chemical pits and lagoons)	Abandoned filled chemical pits Intermittent leaching into drainage Some Cr^{+6}	Intermittent	No	Method of disposal of pit contents to be determined and approved by Division and MDPH
6	Woburn Dump-Woburn	Dump drainage containing assimilative organics and fecal bacteria	Variable	No	Landfill needs attention to lessen pollution to drainage into Michawum Lake
7	Whitney Barrel Company-Wilmington	Spillage and drainage	Nil	Yes	Owner will provide better storage procedures
8	NationalPolychemicals-Wilmington	Salts, acids, amines, oil, grease	Considerable	No	Discharge will terminate during Spring 1971
10	International Minerals-Woburn	Fertilizer piles and bags-drainage is intermittent	Nil	No	Owner will remove piles from near small pond
11	International Salt Co.-Wilmington	Salt Piles	Runoff	No	Future surveillance will determine action
12	J. O. Whitin Co.-Winchester	Thermal condensate	168 gpm	No	Writer will meet with plant engineer to reduce temp. of effluent

* Taken from report by Robert Cady of the Division of Water Pollution Control (See reference 3 in Bibliography)
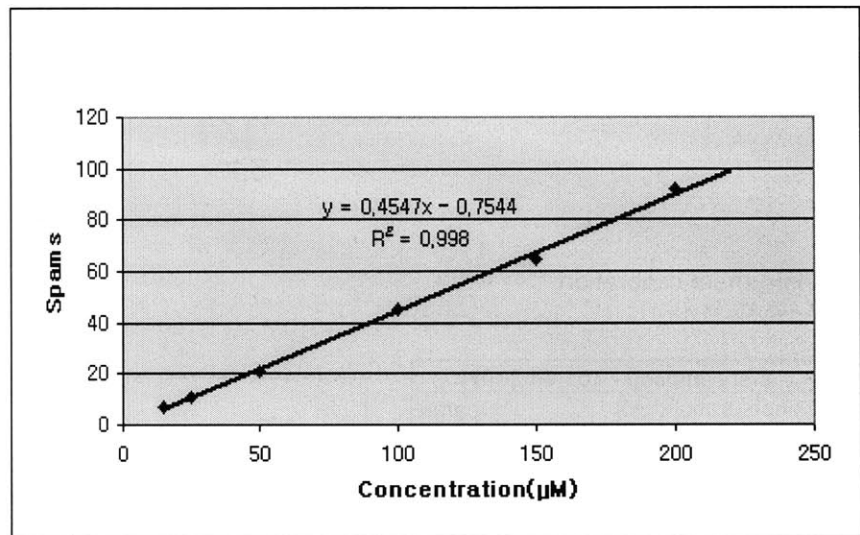
Nitrate and Ammonium measurements of ABJ river samples performed at Parsons Laboratory by Yi-Ju Chou and Jongsok Choi (2003).

NITRATE

Instrument calibration
Analysis Date:

first sampling	(01.16.2003)	
Concentration(µM)		Spams
15		7
25		11
50		21
100		45
150		65
200		92

$y = 0.4547x - 0.7544$
$R^2 = 0.998$

slope	0.4547
intercept	-0.7544

Results

sampling date: 01/16/03					
Site	Spams	Concentration(µM)	(mg/L)	m^3/sec	mg
Horn Pond	25.0	56.6404	0.792966	0.1046	82.94423
Wedge Pond (out)	22.0	50.0427	0.700597	0.046	32.22748
USGS	41.0	91.8285	1.285598	0.62297	800.8892
Montvale	43.0	96.2270	0.946914	0.3264	309.0726
#128	30.0	67.6367	1.347177	0.2058	277.2491

out

HP in	HP out	WP	USGS	MV	RT128
28	27	19		19	29
0.0739	0.1046	0.046	0.622971	0.3264	0.2058

45
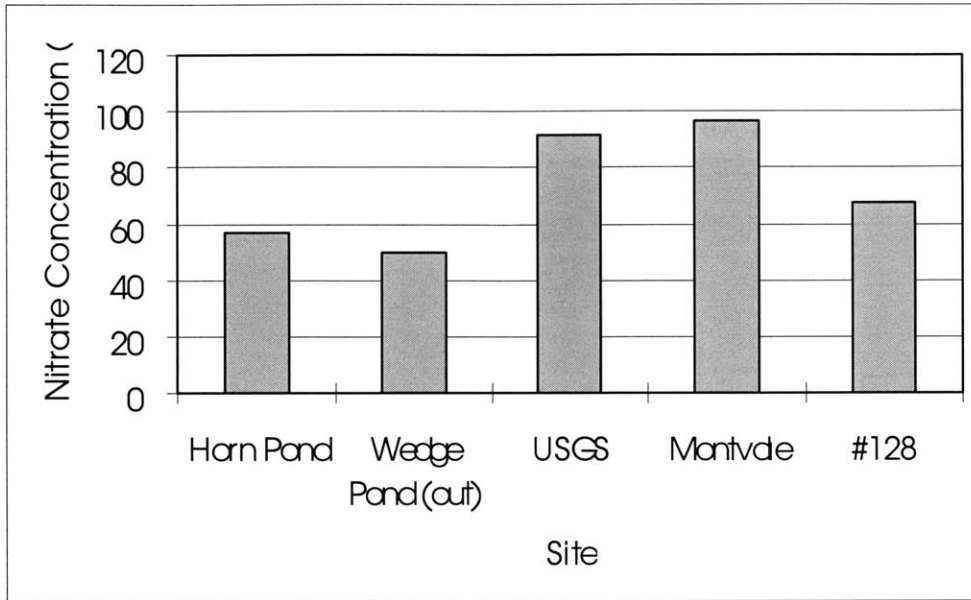
Instrument calibration
Analysis Date:

first sampling	(01.24.2003)	
Concentration(μM)		Spams
15		7
25		11
50		21
100		45
150		65
200		92

$y = 0.4547x - 0.7544$
$R^2 = 0.998$
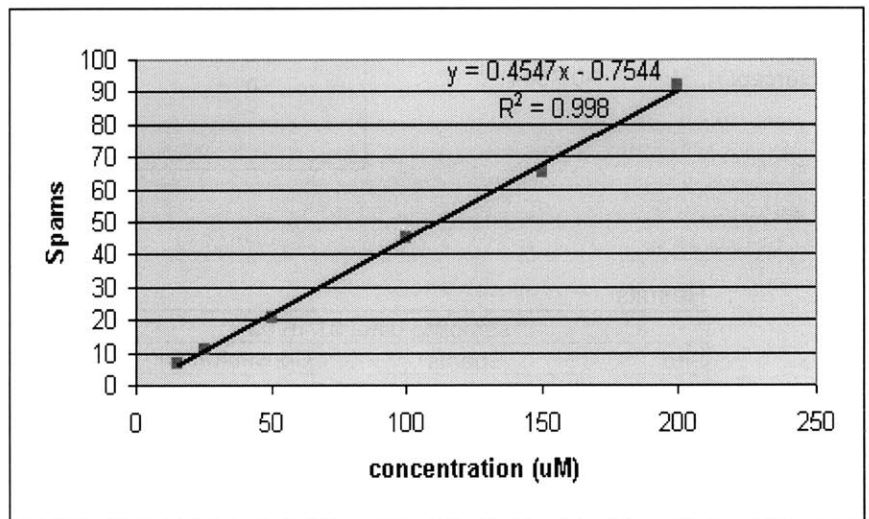
slope	0.4547
y-intercept	-0.7544

Results

sampling date: 01/24/03					
Site	Spams	Concentration(μM)	(mg/L)	m^3/s	mg
Horn Pond (in)	59.0	131.4150	1.83981	0.0945	173.862
Horn Pond (out)	20.5	46.7438	0.654413	0.146	95.5443
Wedge Pond	20.0	45.6442	0.639018	0.0782	49.97123
USGS	62.0	138.0128	1.932179	0.7646	1477.344
Montvale	74.0	164.4038	2.301653	0.3424	788.086
#128	37.0	83.0314	1.16244	0.2209	256.7831

46
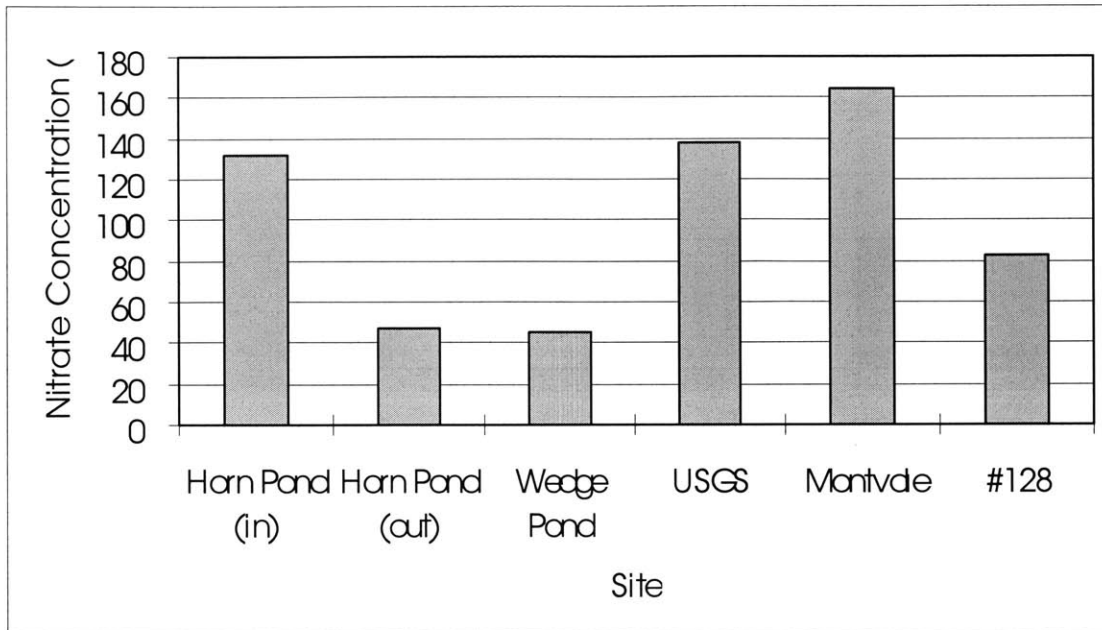
Instrument calibration
Analysis Date:

first sampling	(02.07.2003)	
Concentration(μM)		Spams
15		7
25		11
50		21
100		45
150		65
200		92

$y = 0.4547x - 0.7544$
$R^2 = 0.998$
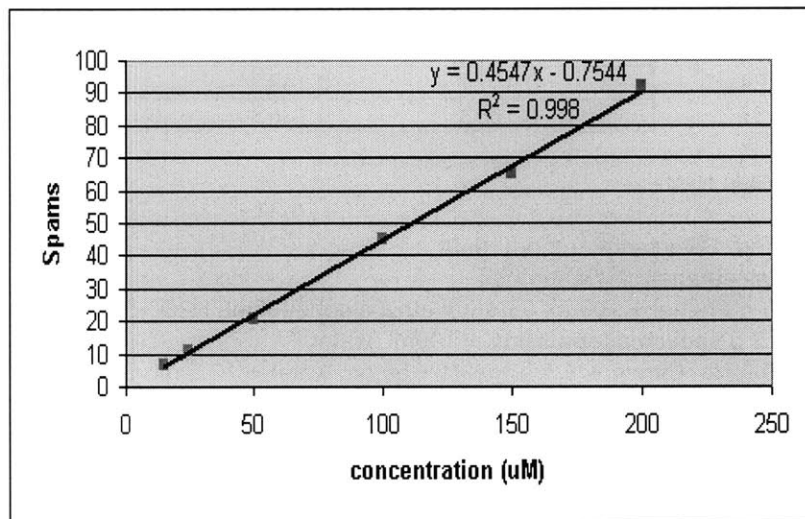
slope	0.4547
y-intercept	-0.7544

Results

sampling date: 02/07/03					
Site	Spams	Concentration(μM)	(mg/L)	Q (m^3/s)	mg
Horn Pond (in)	43.0	96.2270	1.347177	0.1478	199.1128
Horn Pond (out)	36.0	80.8322	1.131651	0.2396	271.1435
Wedge Pond	36.5	81.9318	1.147046	0.1692	194.0801
USGS	47.0	105.0240	1.470336	0.9061	1332.271
Montvale	38.0	85.2307	1.19323	0.3849	459.2742
#128	30.0	67.6367	0.946914	0.2493	236.0656
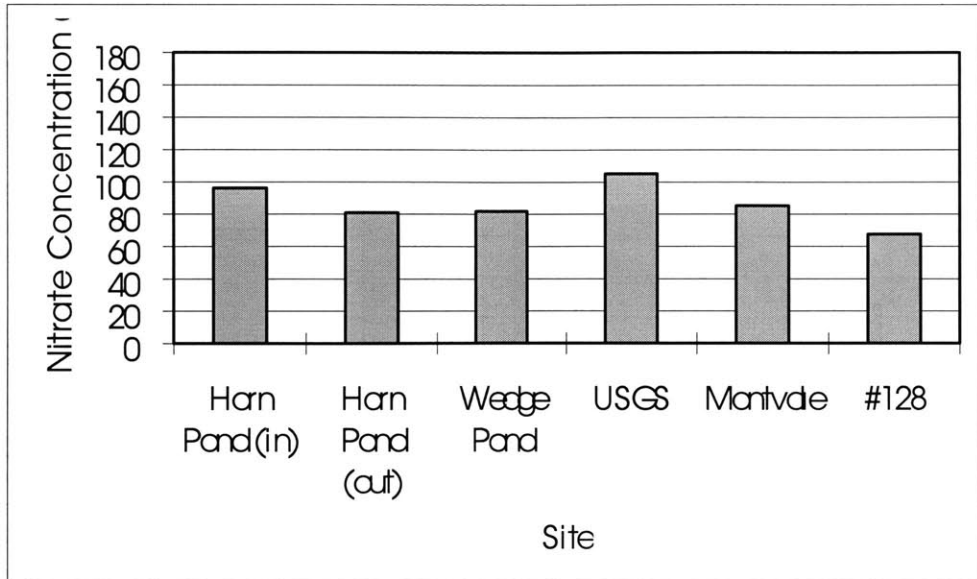
AMMONIUM

NH4 +(mg/L)

Day	Horn Pond(In)	Horn Pond(Out)	Wedge Pond	USGS	Montvale	Road 128
JAN 16		0.1262	0.1358	1.4022	2.7851	3.6665
JAN 24	0.1074	0.1493	0.1729	2.0982	4.1669	4.7284
FEB 07	0.1683	0.1363	0.1567	1.7661	3.0976	4.0570

Species: NH4+

Method: Solorzano Method(1969)
A. Making analysis Reagents
a) 10 g Phenol + 100 ml 95% v/v ethyl alcohol(95mL H2O +5mL ethyl alcohol)
b) 0.5 g sodium nitoprusside + 100mL water
c) 10 g Na-Citrate + 0.5 g NaOH + 50 mL water + 12.5 mL Chlorox(at least 1.5N)
B. Mix : for 5mL sample
1) Add 0.4 mL Reagent a
2) Add 0.4 mL Reagent b
3) Add 1.0 mL Reagent c
C. Allow 12 hours for color formation
D. Measuring absorbance using spectrometer(wavelength: 640 nm)

QA/QC
A. Collecting samples
Fivetimes rinses and get sample at the sixth
Place: middle of stream and 30 cm below the surface
B. Filtering
Filtering: 0.45 μ m filter
Three times rinces with filtered water and store sample at the fourth
C. Standard
I regard absorbance linear with concentration up to 200 μ M of NH4+
From 4th sampling, I diluted 50% for samples over 200μ M NH4+

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Instrument calibration: Spectrophotometer
Analysis Date: 01.18~19.2003

first sampling	(01.16.2003)
Concentration(μ M)	Absorbance
0	0.004
5	0.0972
10	0.1605
25	0.3789
50	0.7216
75	1.0668
100	1.3953

slope   0.0142
intercept   0

First sampling

$y = 0.0142x$
$R^2 = 0.9986$
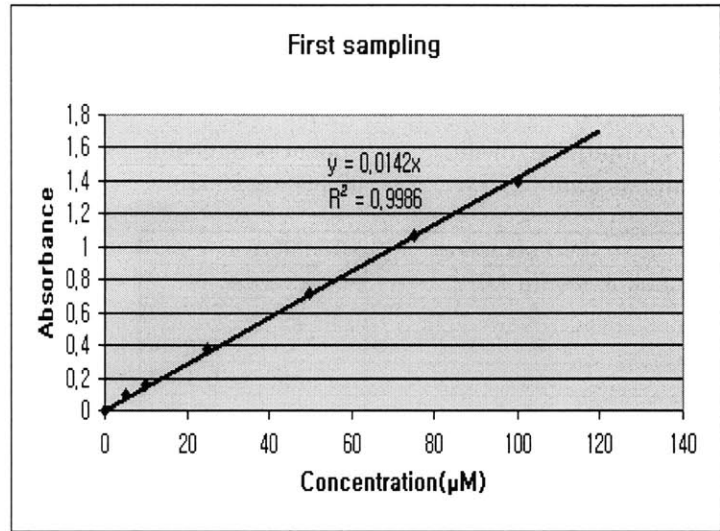
Results

sampling date: 01/16/03		
Site	Absorbance	Concentration(μ M)
Wedge Pond	0.1377	9.6972
Horn Pond	0.1280	9.0141
USGS	1.4222	100.1549
Montvale	2.8249	198.9366
#128	3.7189	261.8944
UML	1.6703	117.6268

First sampling
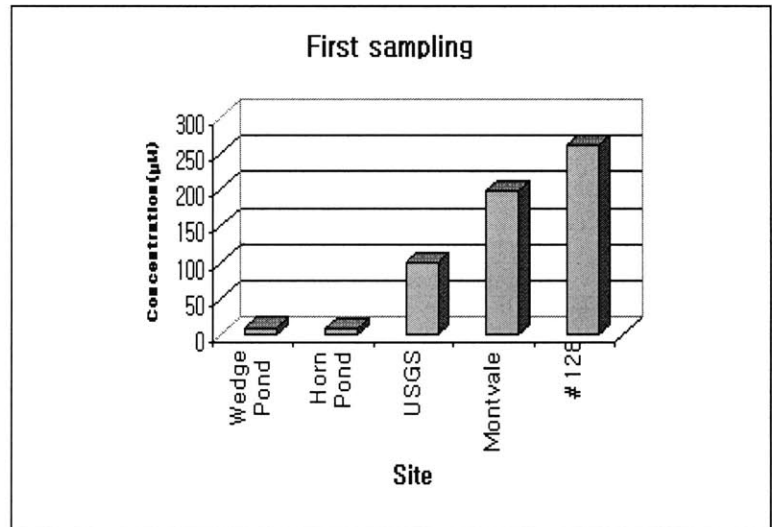
Instrument calibration Spectrophotometer
Analysis Date: 02.01~02.2003

second sampling	(01.24.2003)	
Concentration(μ M)		Absorbance
0		0
5		0.0928
10		0.1759
25		0.4092
50		0.8041
75		1.1883
100		1.5771
150		2.2787
200		3.0338

Second sampling

$y = 0.0153x$
$R^2 = 0.9991$
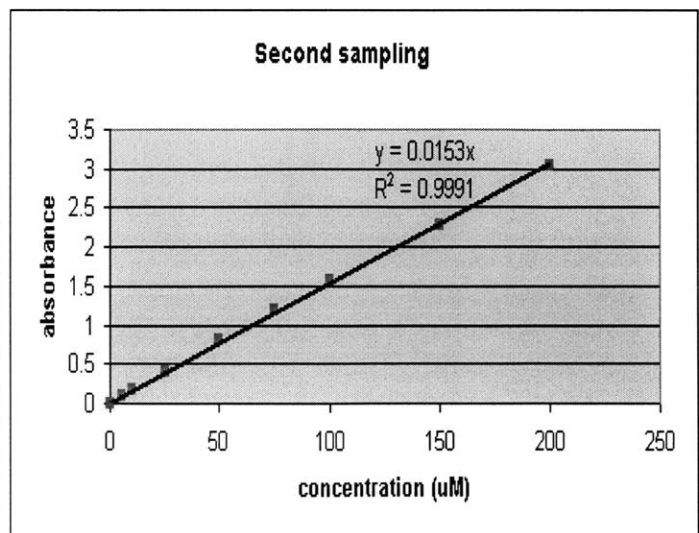
slope	0.0153
y-intercept	0

Instrument calibration   Spectrophotometer
Analysis Date: 02.08~09.2003

third sampling		(02.07.2003)
Concentration(μ M)		Absorbance
0		0
5		0.0708
10		0.1439
25		0.352
50		0.699
75		1.075
100		1.5585
150		2.3966
200		3.0955

Third sampling

$y = 0.0158x$
$R^2 = 0.9952$
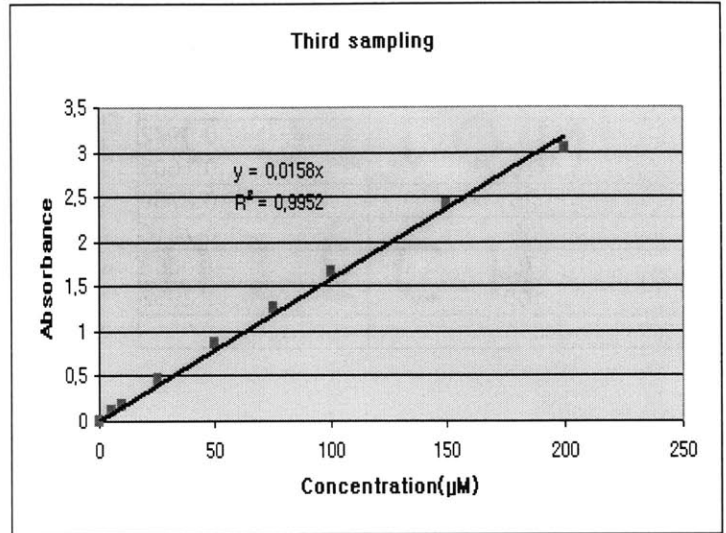
slope	0.0158
y-intercept	0

Result

sampling date: 02/07/2003		
Site	Absorbance	Concentration(μ M)
Wedge Pond	0.1349	8.7032
Horn Pond(In)	0.1449	9.3484
Horn Pond(Out)	0.1174	7.5742
USGS	1.5208	98.1161
Montvale	2.6674	172.0903
#128	3.4935	225.3871

Third sampling

50
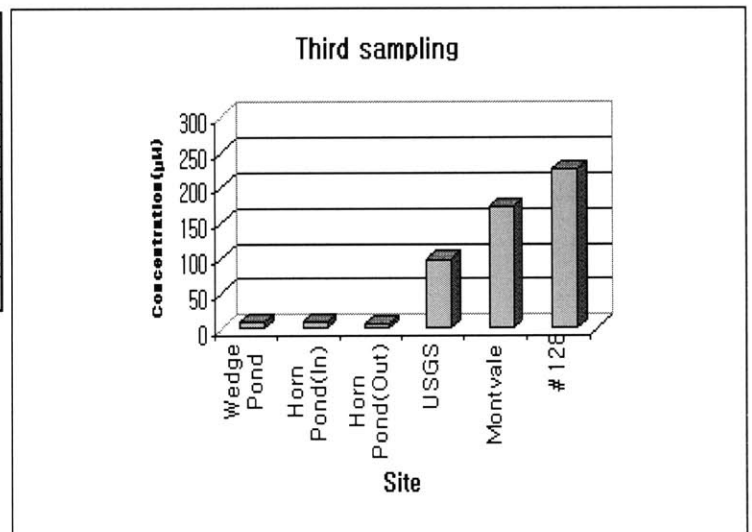
APPENDIX C

These reagents were used in method variations.

Ammonium Molybdate Solution

Dissolve 15g of ammonium molybdate poweder ($[MH_4]_6MO_7O_{24}\cdot4H_2O$) in 500 ml of distilled water. Store in a polyethylene or polypropylene bottle out of direct sunlight. Solution is stable for many months.

Sulfuric Acid Solution

Add 140 ml of concentrated sulfuric acid to 900 ml of distilled water. Store the solution in a glass bottle. This reagent is stable.

Ascorbic Acid Solution:

Dissolve 27 g of good quality ascorbic acid in 500 ml of distilled water. Keep the solution in a polyethylene or polypropylene bottle in the refrigerator. Solution must be prepared monthly.

Potassium Antimonyl Tartrate

Dissolve 0.34 g of AR grade potassium antimonyl tartrate in 250 ml of distilled water, warming if necessary. Solution is stable for many months.

NH_4 Buffer

Dissolve 75g of NH_4Cl in 400 ml of distilled water. Adjust the pH to 8.5 with concentrated NH_4OH and dilute to 500 ml with distilled water. It is stable for months when stored in a tightly capped glass bottle.

APPENDIX D STAGE DISCHARGE DATA

(TUFTS University 2003)[109]

Date   Minutes   Stage   Q (m^3/s)

Montvale Ave

1/6/2003	780	46	0.73		23	0.43
1/24/2003	720	23	0.43		23.5	0.24
2/10/2003	720	23.5	0.24		27	0.38
2/19/2003	660	27	0.38		29.5	0.33
2/22/2003	600	29.5	0.33		40	0.56
2/24/2003	660	84	2.36		41	0.52
3/7/2003	840	40	0.56		46	0.73
3/17/2003	600	41	0.52		84	2.36
3/31/2003	660	89				

Rt 128

2/3/2003	840	57	0.29		24	0.11
2/10/2003	720	28	0.16		28	0.16
2/19/2003	720	24	0.11		30	0.20
2/22/2003	600	30	0.20		41	0.29
3/7/2003	900	41	0.29		42	0.32
3/17/2003	660	42	0.32			
3/31/2003	660	75				

Fowl Brook

2/3/2003	840	37.5	0.23		29.5	0.18
2/10/2003	780	33.5	0.23		33.5	0.23
2/22/2003	660	29.5	0.18		37.5	0.23
2/24/2003	720	50	0.73		40	0.51
3/7/2003	960	41	0.51		41	0.51
3/17/2003	660	40	0.51		50	0.73
3/31/2003	720	62				

Horn Pond

2/3/2003	840	37	0.18		28	0.09
2/10/2003	840	32.5	0.13		32.5	0.13
2/19/2003	720	28	0.09		34	0.15
2/22/2003	720	34	0.15		37	0.18
2/24/2003	720	68	0.77		48	0.38
3/17/2003	720	48	0.38		68	0.77
3/31/2003	720	91				

Wedge Pond

1/6/2003	780	37.5	0.48		22	0.12
2/3/2003	840	28.8	0.13		23	0.12

2/10/2003	840	23	0.12		28.5	0.14
2/19/2003	780	22	0.12		28.8	0.13
2/22/2003	720	28.5	0.14		33	0.30
2/24/2003	780	51	0.76		37.5	0.48
3/17/2003	780	33	0.30		51	0.76
3/31/2003	720	69				

Montvale Ave

$y = 0.0005x^2 - 0.017x + 0.4689$
$R^2 = 0.9928$

$y = 0.0025x^{1.4695}$
$R^2 = 0.8874$

Rt. 128

$y = -0.0003x^2 + 0.0328x - 0.4981$
$R^2 = 0.9886$

$y = 0.0004x^{1.7797}$
$R^2 = 0.9499$

HP inlet

$y = 0.0002x^2 + 0.0092x - 0.3405$
$R^2 = 0.8871$

$y = 9E\text{-}06x^{2.9067}$
$R^2 = 0.8571$

HP outlet

$y = 0.0002x^2 + 0.0024x - 0.106$
$R^2 = 0.9987$

$y = 3E\text{-}05x^{2.4454}$
$R^2 = 0.9955$

Wedge

$y = 0.0003x^2 + 0.0041x - 0.1402$
$R^2 = 0.949$

$y = 5E\text{-}05x^{2.4687}$
$R^2 = 0.8937$
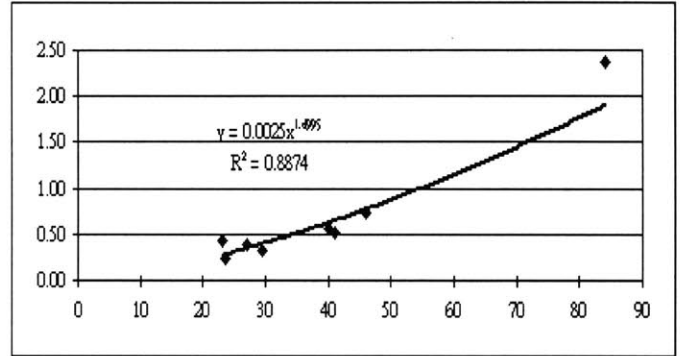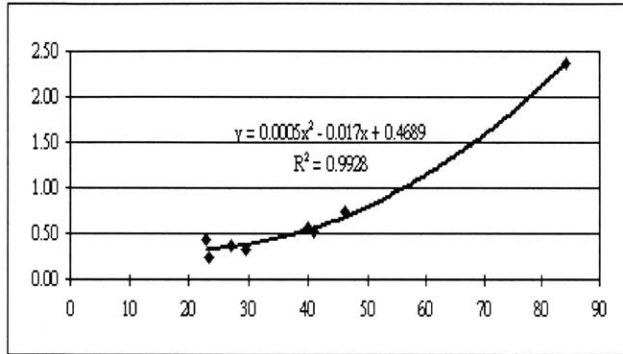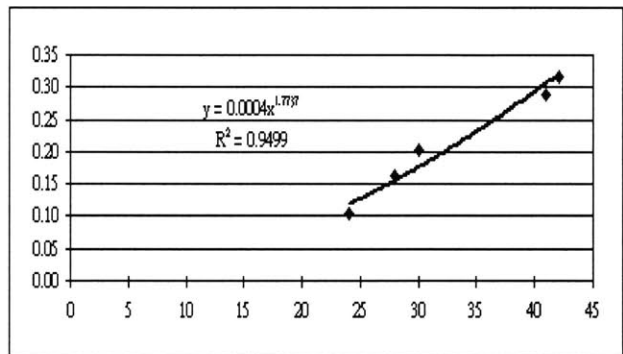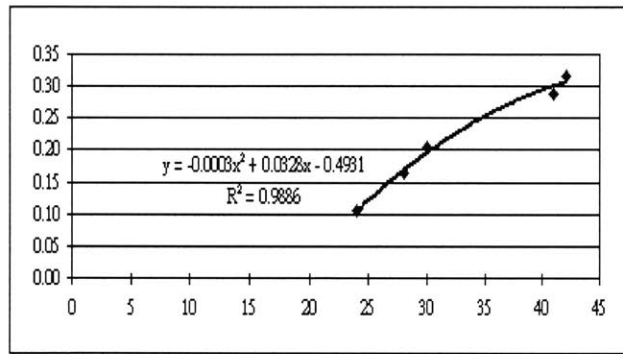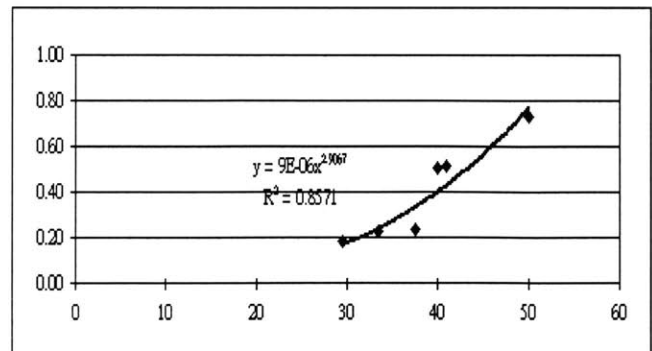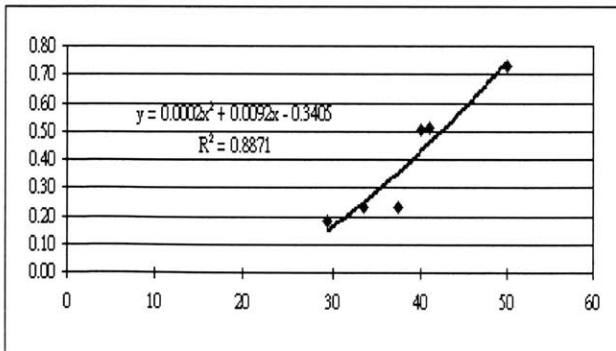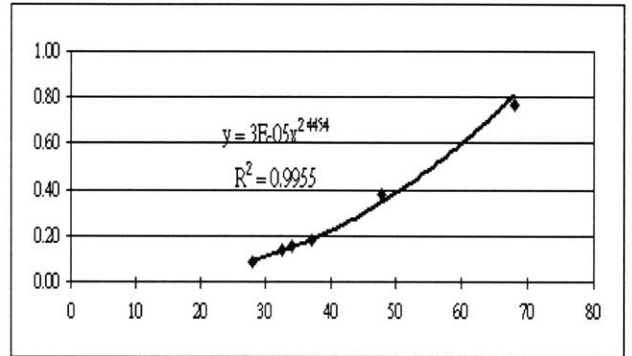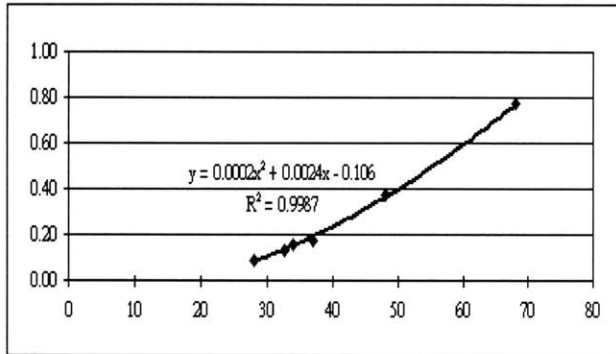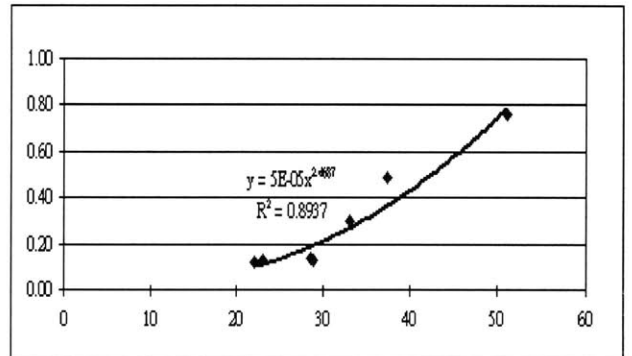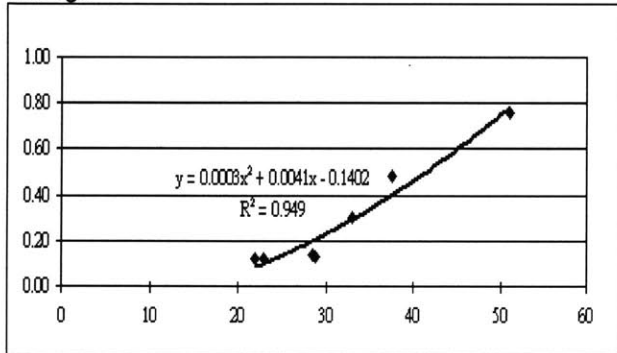
Percentage of Industrial Land in Sub Basins
% = (Total units in Sub Basin) / (Industrial units)

Land use	Area 1	Area 2	Area 3	Area 4	Area 5	Area 6	Area 7: HP	128	B
Total units	122.15	209	15.4	272	131	90	310.5	310.5	69
Industrial Units	23.33333	23	14	32	5	1	17.4	139.2	17.4
Percent Com/Ind	19.10%	11.00%	90.91%	11.76%	3.82%	1.11%	5.60%	44.83%	25.22%

Area 7: Sub Basin	HP:	128 MV:	Balance:
% Area 7	45%	45%	10%
% Total Industrial	10%	80%	10%

Area Key	
Area 1	Burlington
Area 2	Winchester
Area 3	Wilmington
Area 4	Stoneham
Area 5	Reading
Area 6	Lexington
Area 7	Woburn

HP:
6.41%

128MV:
31.11%

Balance:
9.94%

Relative % of Sub Basin
50% Area 7   20% Area 1   20% Area 2   10% Area 6

60% Area 7   8% Area 3   9% Area 4   33% Area 5

50% Area 4   33% Area 2   17% Area 7

Data derived from MASSGIS land use layers as described below:[110]

OVERVIEW

The MassGIS Land Use datalayer has 37 land use classifications interpreted from 1:25,000 aerial photography. Coverage is complete statewide for 1971, 1985, and 1999. Additionally, more than half the state was interpreted from aerial photography flown during 1990, 1991, 1992, 1995 or 1997. The 15 towns on Cape Cod also contain land use data for 1951. Please see the Land Use Status Map, which displays the years for which land use data were interpreted for each town. This datalayer is stored in the TOWN library; the layer is named LANDUSE and the individual community coverages are named LUS.

The year of most recent photography used for land use data interpretation is stored in a single statewide coverage called LUSTAT. This layer was necessitated because some towns contain partial coverage for a certain year, which eliminated the one-to-one link between town-ID and year.

PRODUCTION

Photointerpretation and automation were done by the Resource Mapping Project at the University of

Massachusetts, Amherst. The RMP staff aggregated the 104 classes of their original 1971 interpretation into 21 categories and digitized the data into individual community digital coverages using a PC version of Arc/INFO software. The RMP staff then visually compared the 1971 photography and 1985 photography and produced a digital map of only 1971-85 change for each community. Interpretation was made from 1:40,000 9"x 9" color infrared photos flown in Summer 1985. Southeastern Mass was flown in September 1984. The flight and photography were funded by the Massachusetts Dept. of Environmental Management for another project. Several additional categories of land use were added for parts of Massachusetts. Ten communities in the Southeastern Regional Planning & Economic Development District (SRPEDD) west of Buzzards Bay plus Bourne and Falmouth have a total of 28 land use classes. The 28 classes include the original 21 categories plus 23,24,25,26,27,28 and 29 (see Code Definitions below).

In 1990, the Cape Cod Commission funded an update of Cape Cod. These data are categorized into 26 land use classifications, expanding the original codes to include 23,26,29 and 30. These additional codes, along with the original 21, are listed in LU37_CODE. The Massachusetts Water Resources Authority (MWRA) funded land use interpretation in 1991 for 14 towns. The 33 code scheme for this update includes codes 23,24,29,30,31,32,33,34,35,36 and 37 in addition to the original 21 codes. The Executive Office of Transportation and Construction (EOTC) also funded a 1991 update for 113 towns using the same set of codes as the MWRA except for code 37. The UMass RMP staff updated some other towns not included in the 1990-1991 update based on digital orthophotography flown during 1992, 1995, and 1997. The towns that have been updated between 1985 and 1999 are listed below. The minimum mapping unit used was one acre.

Each land use coverage was plotted at a scale of 1:25,000 by the RMP before delivery to MassGIS. MassGIS used a workstation version of Arc/INFO to combine data from different years. Each coverage, therefore, may contain many small polygons that may have been one land use type in, say, 1971. Over the years the land may have been split up for different uses, and the linework in the coverage reflects the land use boundaries for all these uses during the many years of interpretation. Because MassGIS maintains only one coverage per town, the most recent land use code (for 1999) is stored in the polygon's attribute table and the older codes are stored in a "polygon history table". The process of combining the data from different years created some 'sliver polygons'. These result when a theoretically coterminous line in each coverage is actually offset due to it having been digitized twice, e.g. the shore of a lake. Many of these slivers were eliminated by screening for an area/perimeter ratio beyond normal limits.

REFERENCE:

[1] McHale et al. "Nitrogen solutes in an Adirondack forested watershed: Importance of dissolved organic nitrogen" Biogeochemistry 48 (2000) pg. 166

[2] Campbell et al. "Dissolved organic nitrogen budgets for upland, forested ecosystems in New England" Biogeochemistry 49 (2000) pg 124

[3] Katja Knauer, Renata Behra and Harry Hemond, "Toxicity of inorganic and methylated arsenic to algal communities from lakes along an arsenic contamination gradient" Aquatic Toxicology, Volume 46, Issues 3-4, August 1999, Pages 221-230

[4] "Aberjona River Project" webpage, http://web.mit.edu/civenv/html/student_profiles/superfund_cleanup.html

[5] Mosier et al. "Policy implications of human-accelerated nitrogen cycling" Biogeochemistry 57/58 (2002) pg. 478

[6] Ibid. pg. 477

[7] Valiela, I., Bowen J.L. "Nitrogen Sources to watershed s and estuaries: role of land cover mosaics and losses within watersheds" Environmental Pollution 118 (2002) pg 239

[8] Erisman et. al. "An outlook for a national integrated nitrogen policy" Environmental Science & Policy 4 (2001) pg 87

[9] Ibid. pg. 88

[10] Neff, J.C. et al (2002) "The origin, composition and rates of organic nitrogen deposition: A missing piece of the nitrogen cycle?" Biogeochemistry 47/58: pg 113

[11] Ibid. pg 113

[12] Ibid. pg. 108

[13] Ibid

[14] Valiela and Bowen (2002) pg 240

[15] Nedwell et al. "Variations of the nutrient loads to the mainland U.K. Estuaries: Correlation with Catchment Areas, Urbanization and Coastal Eutrophication" Estuarine, Coastal and Shelf Science 54 (2002) pg 951

[16] Mosier et al. "Policy implications of human-accelerated nitrogen cycling" Biogeochemistry 57/58 (2002) pg 495

[17] Smith et al. "Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems" Environmental Pollution 100 (1999) pg. 180

[18] Ibid pg. 187

[19] Ibid pg. 180

[20] Mosier et al. (2002) pg. 477

[21] Ibid pg. 479

[22] Smith et al. (1999) pg. 185

[23] Valiela and Bowen (2002) pg 240

[24] Smith et al. (1999) pg. 179

[25] Valiela and Bowen (2002) pg. 240

[26] Bowen, Jennifer and Valiela, Ivan "Historical changes in atmospheric nitrogen deposition to Cape Cod, Massachusetts, USA" Atmospheric Environment 35 (2001) pg 1046

[27] Ibid

[28] Ibid pg 1043

[29] Valiela and Bowen (2002) pg. 243

[30] Ibid pg. 241

[31] Herbert, R.A. "Nitrogen cycling in coastal marine exsystems" FEMS Microbiology Reviews 23 (1999) pg. 566

[32] Campbell et al. (2000) pg. 138

[33] Eberhardt, Alyson and Larson, Libby "Water quality monitoring in the Mystic River Watershed: A Study of 10 Sites (July-December 2000) pg. 35

[34] Smith et al. (1999) pg. 189

[35] Ibid pg. 185

[36] US EPA homepage "Total Maximum Daily Loads"   http://www.epa.gov/owow/tmdl/intro.html

[37] US EPA homepage "Overview of Current Total Maximum Daily Load - TMDL -Program and Regulations" http://www.epa.gov/owow/tmdl/overviewfs.html

[38] Campbell et al. (2000) pg. 124

[39] Ibid pg. 124

[40] McHale et al. (2000) pg. 166

[41] Bowen and Valiela (2001) pg. 1048

[42] Smith et al. (1999) pg. 184

[43] Ibid pg. 188

[44] Valiela and Bowen (2002) pg. 239

[45] Nedwell et al. (2002) pg. 951

[46] Smith et al. (1999) pg. 186

[47] Herbert (1999) pg. 579

[48] Ibid pg. 580

[49] Smith et al. (1999) pg. 186

[50] Mayer et al. "Sources of nitrate in rivers draining sixteen watersheds in the northeastern U.S.: Isotopic constraints" Biogeochemistry 57/58: (2002) pg 172

[51] Herbert (1999) pg. 564

[52] Ibid pg. 569

[53] Robinson, et al. "Hypernutrified estuaries as sources of N2O emissions to the atmosphere: the estuary of the River Colne, Essex U.K." Mar. Ecol. Prog. Ser. 156, 59-71 (1998)

[54] Herbert (1999) pg. 574

[55] Kellman, Lisa; Hillaire-Marcel, Claude (1998) "Nitrate cycling in streams: using natural abundances of NO3 15N to measure in-situ denitrification. Biogeochemistry 43 (1998) pg 275

[56] Nowicki et al. "Nitrogen losses through sediment denitrification in Boston Harbor and Massachusetts Bay" Estuaries 20 (1997) pg 626-639

[57] McHale et al. (2000) pg. 175

[58] Kellman and Hillaire-Marcel (1998) pg. 275

[59] McHale et al. (2000) pg. 166

[60] "Work Plan for the Mystic River Watershed Urban Runoff Project" (1979) prepared by CDM/Resource Analysis, Waltham Massachusetts for the Department of Environmental Quality Engineering, pg II.1

[61] Defeo, Fred L. "The Establishment and Operation of the Aberjona River Commission" (1972) pg. 13

[62] CDM (1979) pg I.1

[63] "Aberjona River Project" MIT webpage http://web.mit.edu/civenv/html/student_profiles/superfund_cleanup.html

[64] Durant, et al. "The history of leather industry waste contamination in the Aberjona watershed: A mass balance approach" Civil Enginnering Practice, Fall 1990 pg 41-66

[65] CDM (1979) pg II.3

[66] "Beyond a Civil Action" W.R. GRACE Webpage http://www.civil-action.com/facts/timeline.html

[67] Defeo (1972) pg. 14

[68] "Report on Improvements to the water system of the City of Woburn, Massachusetts" Whitman & Howard, Inc. Engineers August 1958

[69] Tarr, Joel A "History of Pollution in Woburn, Massachusetts" GeoTrans, Inc. July 1987 pg B-19

[70] Ibid B-23

[71] Latowsky, Gretchen P. "Meeting Community Needs: Lessons Learned from Health Studies Conducted in Woburn, MA" Lessons from Woburn Project webpage http://cyber.law.harvard.edu/acivilaction/MCN.htm

[72] Tarr (1987) pg B-19

[73] Ibid

[74] "Consumer Fact sheet on Trichloroethylene" U.S. EPA website http://www.epa.gov/safewater/dwh/c-voc/trichlor.html

[75] Woburn, Massachusetts Case Study http://www.geology.sdsu.edu/classes/geol351/woburn.htm

[76] Ibid

[77] Latowsky, Gretchen P

[78] "What is a Combined Sewer Overflow?" Mystic River Watershed Association webpage http://www.mysticriver.org/cso.shtml

[79] CDM (1979) pg. III.6

[80] Ibid

[81] Ibid pg. III.7

[82] Ibid pg. II.4

[83] Greenberg, et. al Standard Methods American Public Health Association, 16th Edition 1985 pg 39

[84] Eberhardt and Larson (2000) pg. 24

[85] Ibid pg. 26

[86] Neff et al. (2002) pg. 124

[87] Sharp et al. "A preliminary methods comparison for measurement of dissolved organic nitrogen in seawater" Marine Chemistry 78 (2002) pg 172

[88] Ibid pg. 172

[89] Standard Methods pg. 408

[90] Bronk et al. "Total dissolved nitrogen analysis: comparisons between the persulfate, UV and high temperature oxidation methods" Marine Chemistry 69 (2000) pg. 164

[91] Solorzano and Sharp "Determination of total dissolved nitrogen in natural waters" Limnology and Oceanography 25 (4) (1980) 751-754

[92] Ibid

[93] Ibid

[94] Neff et al. (2002) pg. 104

[95] Eberhardt and Larson (2000) pg. 22

[96] "Un-ionized Ammonia Concentration Calculation" AquaNIC webpage http://aquanic.org/images/tools/conversi.htm

[97] Kellman and Hillaire-Marcel (1998) pg. 277

[98] Boyer, et al "Anthropogenic nitrogen sources and relationships to riverine nitrogen export in the northeastern U.S.A" Biogeochemistry 57/58 (2002) pg. 159

[99] McHale et al. (2000) pg. 166

[100] Boyer et al. (2002) pg. 159

[101] Bowen and Valiela (2001) pg. 1045

[102] Campbell et al. (2000) pg. 124

[103] Campbell et al. (2000), 15

[104] Lewis, William M. "Yield of nitrogen from minimally disturbed watersheds of the United States" Biogeochemistry 57/58 (2002) pg. 381

[105] Mayer et al. (2002) pg. 182

[106] Choi 2003 unpublished

[107] Campbell et al. (2000) pg. 124

[108] Defeo (1972) pg. 16

[109] Shuman, Katherine, Tufts University Unpublished Data 2003

[110] MassGIS Datalayers – Land Use http://www.state.ma.us/mgis/lus.htm

Bibliography

Aberjona River Project MIT webpage http://web.mit.edu/civenv/html/student_profiles/superfund_cleanup.html

Alexander et al. "A camparison of models for estimating the riverine export of nitrogen from large watersheds" Biogeochemistry 57/58 (2002) 295-339

AquaNIC webpage "Un-ionized Ammonia Concentration Calculation" http://aquanic.org/images/tools/conversi.htm

Aurilio, Anna Clara. Unpublished data, 1992, Department of Civil and Environment Engineering, Massachusetts Institute of Technology, Cambridge, MA

Beyond a Civil Action W.R. GRACE Webpage http://www.civil-action.com/facts/timeline.html

Bowen, Jennifer and Valiela, Ivan "Historical changes in atmospheric nitrogen deposition to Cape Cod, Massachusetts, USA" Atmospheric Environment 35 (2001) pg 1046

Boyer, et al "Anthropogenic nitrogen sources and relationships to riverine nitrogen export in the northeastern U.S.A" Biogeochemistry 57/58 (2002) pg. 159

Bronk et al. "Total dissolved nitrogen analysis: comparisons between the persulfate, UV and high temperature oxidation methods" Marine Chemistry 69 (2000) pg. 164

Buffam, Ishi et al. (2001) "A stormflow/baseflow comparison of dissolved organic matter concentrations and bioavailability in an Appalachian stream" Biogeochemistry 53: 269-306

Campbell et al. "Dissolved organic nitrogen budgets for upland, forested ecosystems in New England" Biogeochemistry 49 (2000) 123-142

Choi, Jongsok "Nitrogen Transport and Transformation in the Aberjona Watershed" M.Eng Thesis (2003) Massachusetts Institute of Technology

Consumer Fact sheet on Trichloroethylene U.S. EPA website http://www.epa.gov/safewater/dwh/c-voc/trichlor.html

Cornell, S.E. and Jickells, T.D. "Water soluble organic nitrogen in atmospheric aerosol: a comparison of UV and persulfate oxidation methods" Atmospheric Environment 33 (1999) 833-840

Defeo, Fred L. "The Establishment and Operation of the Aberjona River Commission" (1972) pg. 13

Durant, et al. "The history of leather industry waste contamination in the Aberjona watershed: A mass balance approach" Civil Enginnering Practice, Fall 1990 pg 41-66

Eberhardt, Alyson and Larson, Libby "Water quality monitoring in the Mystic River Watershed: A Study of 10

Erisman et. al. "An outlook for a national integrated nitrogen policy" Environmental Science & Policy 4 (2001) pg 87

Fong, Peggy and Zedler, Joy "Sources, sinks, and fluxes of nutrients (N+P) in a small highly modified urban estuary in Southern California" Urban Ecosystems, 4: 125-144

Frankovich, Thomas, and Jones, Ronald "A rapid, precise and sensitive method for the determination of total nitrogen in natural waters" Marine Chemistry 60 (1998) 227-234

Garcia, J et al. (2000) "High rate algal pond operating strategies for urban wastewater nitrogen removal" Journal of Applied Phycology 12: 331-339

Greenberg, et. al Standard Methods American Public Health Association, 16th Edition 1985

Herbert, R.A. "Nitrogen cycling in coastal marine exsystems" FEMS Microbiology Reviews 23 (1999)

Hill, Alan R. (2000) "Subsurface denitrification in a forest riparian zone: Interactions between hydrology and supplies of nitrate and organic carbon" Biogeochemistry 51: 193-223

Katja Knauer, Renata Behra and Harry Hemond, "Toxicity of inorganic and methylated arsenic to algal communities from lakes along an arsenic contamination gradient" Aquatic Toxicology, Volume 46, Issues 3-4, August 1999, Pages 221-230

Kellman, Lisa; Hillaire-Marcel, Claude "Nitrate cycling in streams: using natural abundances of NO3 15N to measure in-situ denitrification. Biogeochemistry 43: (1998) 273-292

Latowsky, Gretchen P. "Meeting Community Needs: Lessons Learned from Health Studies Conducted in Woburn, MA" Lessons from Woburn Project webpage http://cyber.law.harvard.edu/acivilaction/MCN.htm

Lewis, William M. "Yield of nitrogen from minimally disturbed watersheds of the United States" Biogeochemistry 57/58 (2002) pg. 381

MassGIS Datalayers – Land Use http://www.state.ma.us/mgis/lus.htm

Mayer, Bernhard et al. "Sources of nitrate in rivers draining sixteen watersheds in the northeastern U.S.: Isotopic constraints" Biogeochemistry 57/58: (2002) 171-197

McHale et al. "Nitrogen solutes in an Adirondack forested watershed: Importance of dissolved organic nitrogen" Biogeochemistry 48 (2000) 165-184

Mosier et al. "Policy implications of human-accelerated nitrogen cycling" Biogeochemistry 57/58 (2002) 477-516

Nedwell et al. "Variations of the nutrient loads to the mainland U.K. Estuaries: Correlation with Catchment Areas, Urbanization and Coastal Eutrophication" Estuarine, Coastal and Shelf Science 54 (2002) pg 951

Neff, J.C. et al "The origin, composition and rates of organic nitrogen deposition: A missing piece of the nitrogen cycle?" Biogeochemistry 57/58: (2002) 99-136

Nowicki et al. "Nitrogen losses through sediment denitrification in Boston Harbor and Massachusetts Bay" Estuaries 20 (1997) pg 626-639

Robinson, et al. "Hypernutrified estuaries as sources of N2O emissions to the atmosphere: the estuary of the River Colne, Essex U.K." Mar. Ecol. Prog. Ser. 156, 59-71 (1998)

Scudlark, et al. "Organic nitrogen in precipitation a the mid-atlantic U.S. Coast – Methods evaluation and preliminary measurements" Atmospheric Environment 32 (1998) 1719-1728

Shuman, Katherine, Tufts University Unpublished Data 2003

Senn, David and Hemond, Harold F. (2002), "Nitrate Controls on Iron and Arsenic in an Urban Lake", Science

Senn. David (2002), "Coupled Arsenic, Iron, and Nitrogen Cycling in Arsenic-Contaminated Upper Mystic Lake " PhD Thesis, Department of Civil and Environment Engineering, Massachusetts Institute of Technology, Cambridge, MA

Sharp et al. "A preliminary methods comparison for measurement of dissolved organic nitrogen in seawater" Marine Chemistry 78 (2002) pg 172

Smith et al. "Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems" Environmental Pollution 100 (1999) pg. 180

Solorzano and Sharp "Determination of total dissolved nitrogen in natural waters" Limnology and Oceanography 25 (4) (1980) 751-754

Solorzano, L «Determination of ammonia in water by the phenolhypochlorite method» Limnology and Oceanography 14 (1969) 799~801

Tarr, Joel A "History of Pollution in Woburn, Massachusetts" GeoTrans, Inc. July 1987 pg B-19

US EPA homepage "Overview of Current Total Maximum Daily Load - TMDL -Program and Regulations" http://www.epa.gov/owow/tmdl/overviewfs.html

US EPA homepage "Total Maximum Daily Loads" http://www.epa.gov/owow/tmdl/intro.html

Valiela, I., Bowen J.L. "Nitrogen Sources to watershed s and estuaries: role of land cover mosaics and losses within watersheds" Environmental Pollution 118 (2002) pg 239

What is a Combined Sewer Overflow? Mystic River Watershed Association webpage http://www.mysticriver.org/cso.shtml

Whitman & Howard, Inc. Engineers «Report on Improvements to the water system of the City of Woburn, Massachusetts» August 1958

Woburn, Massachusetts Case Study http://www.geology.sdsu.edu/classes/geol351/woburn.htm

Work Plan for the Mystic River Watershed Urban Runoff Project (1979) prepared by CDM/Resource Analysis, Waltham Massachusetts for the Department of Environmental Quality Engineering, pg II.1