# Nitrogen Transport and Transformation in the Aberjona Watershed

by

Jongsok Choi

B.Eng. Civil and Environmental Engineering Chung Ang University 2001

Submitted to the Department of Civil and Environmental Engineering in partial fulfillment of the requirements for the degree of

### MASTER OF ENGINEERING IN CIVIL AND ENVIRONMENTAL ENGINEERING

#### AT THE

# MASSACHUSETTS INSTITUTE OF TECHNOLOGY

JUNE 2003

MASSACHUSETTS INSTITUTE OF TECHNOLOGY JUN 0 2 2003 LIBRARIES

©2003 Jongsok Choi. All rights reserved.

The author hereby grants to MIT permission to reproduce and to distribute publicly paper and electronic copies of this thesis document in whole or in part

	$\sim$		
Signature of	Ų		
2 101101			vironmental Engineering
	Dopart		May 16, 2003
	. /	~	
Certified			
by:		· · · · · · · · · · · · · · · · · · ·	
5	/ /		Harold F. Hemond
	William E. Leonhard Profe	essor of Civil and En	vironmental Engineering
	$\sim$ $\sim$	1	Thesis Supervisor
Accepted by:	L		
oy			Oral Buyukozturk
	Chairman, I	Departmental Comm	ittee on Graduate Studies

BARKER

# Nitrogen Transport and Transformation in the Aberjona Watershed

by

Jongsok Choi

Submitted to the Department of Civil and Environmental Engineering On May 17, 2003 in Partial Fulfillment of the Requirements for the Degree of Master of Engineering in Civil and Environmental Engineering

# Abstract

The Aberjona watershed has been subject to contamination by dense urbanization and industrial effluent. A large amount of nitrogen loading to watersheds nation-widely comes from agricultural areas, but the Aberjona watershed has a considerable nitrogen inflow from an industrial area. The nitrogen compounds in the Aberjona watershed might be delivered to the estuary near Boston, and could cause damage to the ocean environment.

With these concerns in mind, the Aberjona watershed research team measured three kinds of nitrogen compounds and evaluated nitrogen characteristics in different regions. Enormous amount of ammonium has leached to the Aberjona River, one of the tributaries, as the river passes by an industrial area and two superfund sites. Horn Pond Creek, another tributary, has a low level of ammonium and nitrate flux, and dilutes the high concentration of ammonium from the Aberjona River before the creek arrives at the USGS site. In the Aberjona River, nitrification, which is an oxidization reaction from  $NH_4^+$  to  $NO_3^-$ , would be expected due to a high concentration of ammonium. In the Horn Pond Creek, denitrification, which is reduction reaction from  $NO_3^-$  to  $N_2$ , seems to take place between Horn Pond and Wedge Pond. As for organic nitrogen, it comprises around 15 %~30% of total nitrogen through the watershed.

Thesis Supervisor: Harold F. Hemond Title: Professor of Civil and Environmental Engineering

# Acknowledgments

Thanks to all who helped, assisted, inspired, advised...

I deeply appreciate Professor Harry Hemond. You have guided me to escape from ignorance in environmental science. I will never forget your constant support, professional advice, and warm heartiness.

Also, I would like to thank to our Aberjona River team members Matthew S Orosz and Yi-ju Chou for our wonderful teamwork, cooperation, and friendship. With Matt, I will never forget the legend of how we walked two hours in a snowy mountain to find Horn pond inlet on the third sampling day, wearing waders. With Yi-ju, I will keep the special memory of sharing delicious food after every filtering session. I bless you guys to keep well always.

Finally, I would like to appreciate my family members:

my parents, Kwangnam Choi and Jungshin Park and sister and brother-in-law for their support and concern.

# **Table of Contents**

Abstract
Acknowledgements
Table of Contents   4
List of Figure and Table
1. INTRODUCTION
1.1Nitrogen in aquatic ecosystem       7
1.1.1 Nutrient enrichment
1.1.2 Health Concerns
1.2 Fate change and reactions of nitrogen
1.2.1 Ammonification
1.2.2 Nitrification
1.2.3 Denitrification
2. DESCRIPTION OF STUDY AREA
2.1 Location
2.2 Land use
2.3 Hydrology
3. AMMONIUM ANALYSIS
3.1 sample collection and filtering method
3.2 Solorzano method
3. 2. 1 Major Procedure
3. 2. 2 Standard Preparation
4. RESULTS AND DISCUSSION
4.1 The Aberjona River Branch
4.2 The Horn Pond Creek Branch
5. CONCLUSION

Appendix A: Spectrophotometric Measurement Standard	33
Appendix B: Ammonium Concentration & Flux	33
Appendix C: Nitrate Concentration & Flux	42
Appendix D: Organic N Concentration	. 48
Appendix E: Total N Concentration	. 49
References	

# **List of Figures**

Figure 1.1 Nitrogen transformation and removal	10
Figure 2.1 Location of the Aberjona Watershed, Massachusetts	7
Figure 2.2 Land Use of the Aberjona Watershed, Massachusetts	18
Figure 2.3 Discharge vs. Measurement Site	19
Fig 3-1 Location of Sampling Site	22
Figure 3.2 Ammonium Concentration vs. Spectrophotometric Absorbance	25
Figure 4.1 Dissolved NH <sub>4</sub> <sup>+</sup> Concentration vs. Measurement Date	29
Figure 4.2 Dissolved NH <sub>4</sub> <sup>+</sup> Flux vs. Measurement Date	29
Figure 4.3 Dissolved NO <sub>3</sub> <sup>-</sup> Concentration vs. Measurement Date	30
Figure 4.4 Dissolved NO <sub>3</sub> <sup>-</sup> Flux vs. Measurement Date	30
Figure 4.5 Average Dissolved $NH_4^+$ & NO <sub>3</sub> <sup>-</sup> Concentrations vs. Measurement Site	31
Figure 4.6 Average Dissolved NH4 <sup>+</sup> & NO3 <sup>-</sup> Fluxes vs. Measurement Site	31

# List of Tables

Table 1.1 Factors affecting the proportion of $N_2O$ and $N_2$ Pro-	duced during denitrification
Table 2.1 Land use in each basin of the Aberjona watershed	
Table 3-1 Sampling Site Description and Geographical Posit	ioning System Coordinaes
Table 3.2 Ammonium Concentration vs. Standard Dilutions	

# **1.1 Nitrogen in aquatic ecosystem**

#### **1.1.1 Nutrient enrichment**

The major sources of natural water pollution are nutrients, organic or inorganic chemical substances and pathogens. Eutrophication caused by excessive input of nutrients such as nitrogen and phosphates is a common and growing problem in lakes, rivers, estuaries, and coastal oceans (Smith 1998). Unlike phosphates, nitrogen, especially as nitrate, is quite mobile in soil and can easily reach groundwater. As nitrogen-loaded groundwater is added to surface water, it can lead to overgrowth of plant life and oxygen deficit in the water. In the USA, rivers that include a high concentration of nitrogen usually pass through agricultural and urban areas (Carpenter et al. 1998). This land typically has high rainfall, a large amount of organic matter in soils, and high productivity of agriculture. Eutrophication has many negative effects on aquatic ecosystems. The most significant issue of eutrophication is the increased growth of algae and aquatic weeds that interfere with use of the water for fisheries, recreation, industry, agriculture, and drinking. Oxygen depletion caused by decomposition of nuisance plants kills fish. Also, eutrophication causes the loss of habitats, including aquatic plant beds in fresh and marine waters, and coral reefs of coasts (Jeppesen et al. 1998). In fresh water, blooms of cyanobacteria are a prominent consequence of eutrophication. These blooms contribute to a wide range of water-related problems such as fish kills, foul odors, and unpalatablility of drinking water. Some eutrophic freshwater systems that are not enough buffered by surrounding soil can

be acidified. This water acidification decreases pH level and helps surface water have the tropic structure.

Nitrogen infiltrates streams and rivers, where it is delivered to estuaries and the coastal ocean, and consequently has an ecological impact on the ocean. The environmental impact of nitrogen contamination in the Aberjona Watershed directly affects the coastal environment, because the end of the watershed is located only 12 miles from Boston harbor. Nitrogen compounds from the Aberjona River watershed limit the productivity of salt marsh vegetation and phytoplankton and algae in the ocean near Boston. Excess nitrogen in the seawater increases plant biomass and oxygen demand. Also, nitrogen loads in coastal waters cause hypoxia or anoxia, and changes plankton community structure. As a result of excessive phytoplankton production in the ocean, turbidity increases and penetration of light decreases through water column, and consequently submerged aquatic vegetation may perish.

As I discussed above, excess nitrogen in waters is certainly unwelcome, and sources of nitrogen should be watched carefully.

### **1.1.2 Health Concerns**

Health concerns of nitrate in drinking water were raised in the middle 1940s. Because excessive exposure to nitrate can cause methemoglobinemia, or "blue baby" disease, drinking water standards to prevent high levels of nitrate were established by federal and state governments. The federal standard for nitrate in drinking water is 10 milligrams per liter nitrate as N, or 45 milligrams per liter nitrate as NO<sub>3</sub>.

Methemolglobinemia is the most crucial health problem associated with nitrate in

8

drinking water. Blood contains hemoglobin that carries oxygen in our body. When nitrate is present, hemoglobin can be changed to methemoglobin that cannot carry oxygen. In the adult body, enzymes convert methemoglobin to hemoglobin, and methemoglobin levels usually do not exceed 1 percent. However, newborn infants have lower level of these enzymes, so their ability to reduce methemoglobin is low and babies can easily suffer from oxygen deficit. Consuming drinking water with nitrate levels near the drinking water standard does not normally increase the methemoglobin level of humans beyond infancy.

Another health concern of nitrate-contaminated water is the possible formation of Nnitroso compound. The toxicity of nitrate greatly increases when bacteria commonly found in the upper gastrointestinal track reduce it to nitrite. Nitrite can undergo nitrosation reactions in the gastrointestinal track and bladder with amines and amides to give rise to N-nitroso compounds. N-nitro compounds are some of the most potent known carcinogens and can induce cancers in a variety of organs such as stomach, bladder, lymphatics, colon, and hematopoietic system in many different animal models.

# **1.2 Fate Change and Reactions of Nitrogen**

Nitrogen transformation in aquatic ecosystems is an intricate process that varies in rate and direction. The possible reactions of nitrogen transformation in a watershed are through mineralization, nitrification, and denitrification.

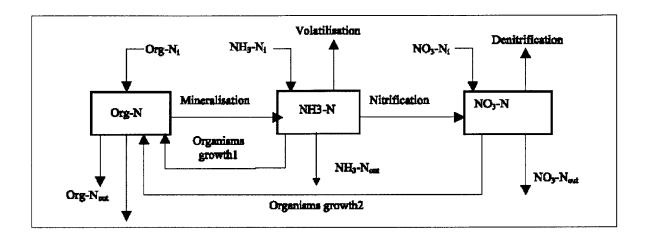


Figure 1.1 Nitrogen transformation and removal (Senzia, 2002)

Nitrogen cycling dynamics and pathways differ within terrestrial, freshwater, and ocean. However, some similarities persist and often dominate N dynamics in the environment. Natural and cultural characteristics of watershed affect temporal and spatial variations not only in the rate of mineralization, nitrification, denitrification, but also in the nitrogen storage and transport.

### **1.2.1 Ammonification**

Ammonification, a part of the mineralization process, is the decomposition of organic nitrogen to inorganic ammonium ion. On a global basis, ammonification is the major source of assimilable nitrogen owing to numerous bacteria, yeasts, and other microbes that utilize organic carbon as their energy source and carry on under aerobic as well as anaerobic conditions in virtually all environments (Vaclav 1985). Mineralization of OrgN was modeled using first order kinetics with respect to Org-N concentration (Di Toro et al., 1971)

$$r_m = 0.002 \text{ T} \times (\text{Organic Nitrogen})$$
 (1)

in which  $r_m =$  mineralization rate (mg/l d), T = water temperature (°C), Org-N = organic nitrogen concentration (mg/l).

This process depends on temperature and concentration of organic nitrogen in an aquatic system.

#### **1.2.2** Nitrification

Nitrification is the microbial oxidation of ammonium  $(NH_4^+)$  to nitrite  $(NO_2^-)$  and nitrate  $(NO_3^-)$ . From the nitrification reaction, a less mobile ammonium species changes to a highly mobile nitrate species. The first step of nitrification is processed by aerobic ammonia oxidizers (Muller 1995). *Nitrosomonas* is the most frequently identified genus associated with this step, and *Nitrosospira* and *Nitrosospira* take a small part.

$$NH_3 + O_2 + 2 H^{\dagger} + 2 e^{-} \rightarrow NH_2OH + H_2O$$
(2)

$$NH_2OH + H_2O \rightarrow NO_2^- + 5 H^+ + 4 e^-$$
(3)

Two electrons produced in the second reaction are utilized in the first step, and the terminal cytochrome c oxidise uses the other pair of electrons. This enzyme reduces oxygen according to:

$$0.5 O_2 + 2 H^+ + 2e^- \rightarrow H_2O$$
 (4)

In addition, electrons are used for the generation of reductant power via reversed electron flow, and might flow to a nitrite reductase (DiSpirito et al.).

Overall reaction is:

$$NH_3 + 1.5 O_2 \rightarrow NO_2^- + H^+ + H_2O$$
 (5)

Then, the second step of nitrification is transformation from nitrite to nitrate. *Nitrobacter* is a well-known nitrite oxidizer for this reaction, although other genera such as *Nitrospira*, *Nitrococcus*, and *Nitrospira* also autotrophically oxidize nitrite

$$NO_2^{-} + H_2O \rightarrow NO_3^{-} + 2 H^+ + 2 e^-$$
(6)

If electrons only flow to the terminal oxidise, as in equation (6), the net reaction is:

$$\mathrm{NO}_2^- + 0.5 \,\mathrm{O}_2 \,\rightarrow\, \mathrm{NO}_3^- \tag{7}$$

These nitrification reactions, which are needed for energy generation, are considered to be confined to oxic conditions as oxygen is consumed. (Muller 1995)

If there is not enough oxygen in the aquatic system, the nitrification reaction could be processed by anaerobic ammonium oxidizers according to:

$$NH_3 + 1.32 O_2 + H^+ \rightarrow 1.02 N_2 + 0.26 NO_3^- + 2 H_2O$$
 (8)

$$NH_3 + 0.85 O_2 \rightarrow 0.11 NO_3^{-} + 0.44 N_2 + 0.14 H^+ + 1.43 H_2O$$
 (9)

Since anammox-bacteria are reversibly inhibited by low concentrations of oxygen, the process described by equation (9) must occur under oxygen limiting conditions. At the optimum temperature, pH, and humidity, the nitrification reaction can process so rapidly that it takes only two weeks to convert all  $NH_4^+$  to  $NO_3^-$ .

#### **1.2.3 Denitrification**

Through the denitrification reaction, nitrate species is transformed to nitrogen gas to the atmosphere. The denitrifiers involved in this reaction are lots of heterotrophic bacteria that use an oxidized nitrogen source as an electron acceptor. The dinitrification reaction include four steps of processes by releasing electrons (Stouthamer, 1988).

 $NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O$  (10)

$$NO_2^- + 2H^+ + e^- \rightarrow NO + H_2O$$
(11)

- $2NO + 2H^{+} + 2e^{-} \rightarrow N_2O + H_2O \qquad (12)$
- $N_2O + 2H^+ + 2e^- \rightarrow N_2 + H_2O$  (13)

As oxygen level in the aquatic system or soil decreases, the potential for denitrification is increased. Through the reaction, the oxidation state of nitrogen is changed from +V for nitrate to O for nitrogen gas. The proportion of N<sub>2</sub>O and N<sub>2</sub> depends on the various

environmental conditions (Table 1.1)

Factor	Will increase N <sub>2</sub> O/N <sub>2</sub>	
[NO <sub>3</sub> <sup>-</sup> ] or [NO <sub>2</sub> <sup>-</sup> ]	increasing oxidation	
[O <sub>2</sub> ]	Increasing O <sub>2</sub>	
Carbon	Decreasing pH	
[H <sub>2</sub> S]	Increasing sulfide	
Temperature	Decreasing temperature	
Enzyme status	Low N <sub>2</sub> O reductase activity	

۰.

Table 1.1 Factors affecting the proportion of  $N_2O$  and  $N_2$  produced during denitrification

(Follett and Hatfield, 2001)

# **2.1 Location**

The Aberjona watershed is located northwest of Boston in eastern Massachusetts. The watershed is a 25 square-mile area and contains 44 small ponds and lakes. Within the boundary of the watershed, parts of 5 towns and 7 municipalities are located: the City of Woburn and the Towns of Winchester, Stoneham, Reading, Wilmington, Burlington, and Lexington. The average altitude of the watershed is 120 feet above mean sea level and the river water flows from northwest to southeast.

## 2.2 Land use and nitrogen loading

Historically, the Aberjona Watershed has been contaminated by industrial effluent and land disposal of toxic chemicals. The tanning industry around the watershed has harshly degraded the quality of water since the 1700's. Even though the tanning industry doesn't operate any more, the watershed still has a large amount of heavy metals, such as arsenic and chromium (Durant 1991). In the northern part of the Aberjona Watershed, the city of Woburn is located in the industrial area that includes two EPA Superfund sites: Industriplex and Wells G & H around Rt. 128 (figure 2.1). The Aberjona River, one of the tributaries, originates from that area, and is highly contaminated by industrial waste disposal. Horn Pond Creek, another tributary, flows through the west portion of the Aberjona Watershed where forest, residential areas, and playgrounds are mostly located. These two pivotal streams confluence in Winchester and flow into the Upper Mystic Lake. In general, nitrogen loading to the aquatic environment is highest from crop and pasture

area, lower for forest area, and urban areas (Puckett 1995b). As for the Aberjona Watershed, the industrial area in the northern position contributes a large part of nitrogen loading. Figure 2.2 shows land use in the Aberjona watershed. The whole watershed was divided into six sub-basins, the outlets of which correspond to the six sampling sites. Base on the land use graph, the ratio of land use was calculated (Table 2.1). Different land use patterns in each basin are assumed to affect different nitrogen influxes.

	Water	Area	Stream	Land Use (%)		
	Confluence Point	(mile <sup>2</sup> )	passed by	Industrial	Residential	Others
1	Horn Pond In	7.3	Horn Pond Creek	5	51	44
2	Horn Pond Out	2.7	Horn Pond Creek	2	29	69
3	Wedge Pond Out	0.8	Horn Pond Creek	0	20	80
4	UGGS Gage	5.8	Confluence	7	47	46
5	Montvale	3.5	Aberjona River	19	27	54
6	Road 128	4	Aberjona River	24	16	60

Table 2.1 Land use in each basin of the Aberjona watershed

(Adapted from Tufts University GIS Center)

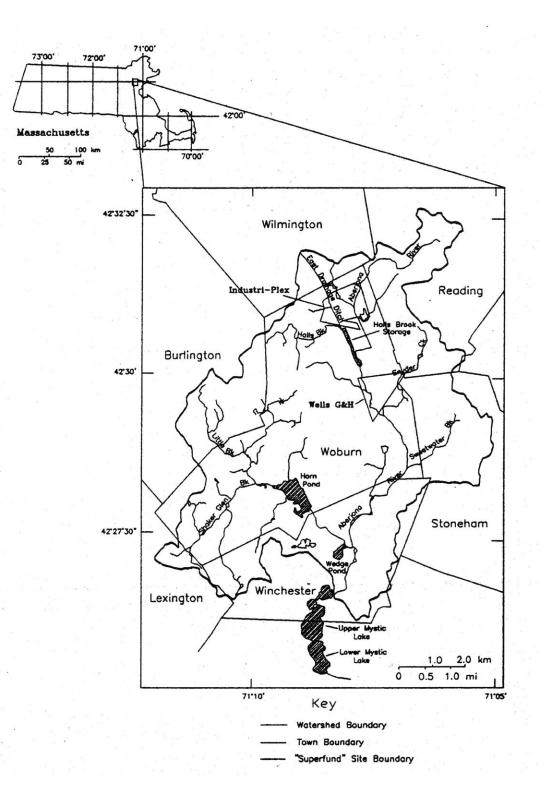


Figure 2.1 Location of the Aberjona Watershed, Massachusetts

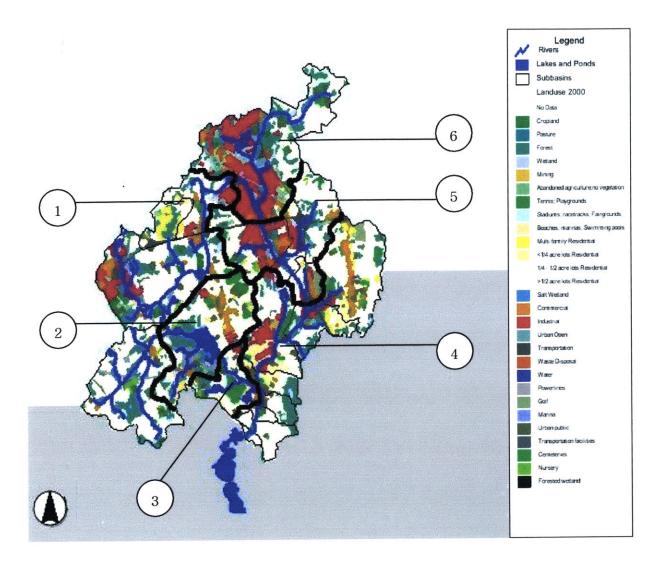


Figure 2.2 Land Use of the Aberjona Watershed (Tufts University GIS Center)

### 2.3 Hydrologic description

The major source of the water in the Aberjona Watershed is rainfall. Usually precipitation is filtered through soil, recharged to ground water, and ends up in the surface river (Cist, 1999). The basins have a rapid recharge and discharge response that affect the surface water flow pattern (Brainard, 1990). Groundwater and precipitation recharge the surface river, and flow downstream. The seasonal effect of the watershed is crucial because the temperature and the amount of rainfall in New England vary with the different seasons. During our research time when season changed from winter to spring, the discharge of all streams increased gradually due to thawing ground, snowmelt, and spring rains (figure 2.3). The lines in the figure 2.3 do not imply any interpolation, but are used to aid visual identification of data points.

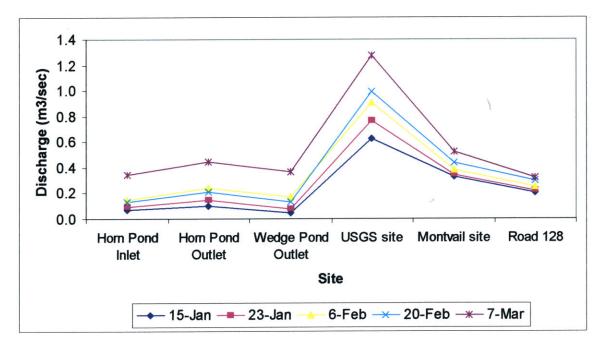


Figure 2.3 Discharge vs. Measurement Site

# **3 AMMONIUM ANALYSIS**

## **3.1** Sample collection and filtering method

Samples were collected at six locations (Fig 3.1) on January 16, January 24, February 07, February 21, March 07, and March 22, 2003. On the last sampling day, March 22, 2003, our project team added extra three sampling sites from the upper Mishawum Pond. Two 1-liter bottles were used per a site. The sampler dropped the bottles into the river for rinsing bottles three times, and drew a sample on the fourth time. The spot of sampling was 20 cm below the surface water and at the middle of the stream width. After sample

collection, the sampler measured the temperature, pH, and dissolved oxygen concentration at the same spot as sampling point. Then, the samples were kept in the ice cooler, and then moved for nitrogen analysis.

### Filtering

Collected waters were filtered prior to ammonia, nitrate and organic nitrogen measurement, using 0.45  $\mu$ m filters and 50cc cylinders. Filtered samples for ammonia were analyzed within 24 hours. Samples that could not be analyzed immediately were kept freezing in the refrigerator.

Site	Town	Coordinates
Horn Pond Inlet	Winchester	71 09 45 w
		42 28 11 n
Horn Pond Outlet	Winchester	71 09 17 w
		42 27 56 n
Wedge Pond Outlet	Winchester	71 08 19 w
		42 27 20 n
USGS gaging station	Winchester	71 08.22 w
		42 26.50 n
Montvale	Woburn	71 07.07 w
		42 28.46 n
Road 128	Woburn	71 08.09 w
		42 30 06 n

Extra Sampling (March 22, 2003)

Site	Town	Coordination
Mishawum pond	Woburn	71 08 w
		42 30 n

Table 3-1 Sampling Site Description and Geographical Positioning System Coordinaes

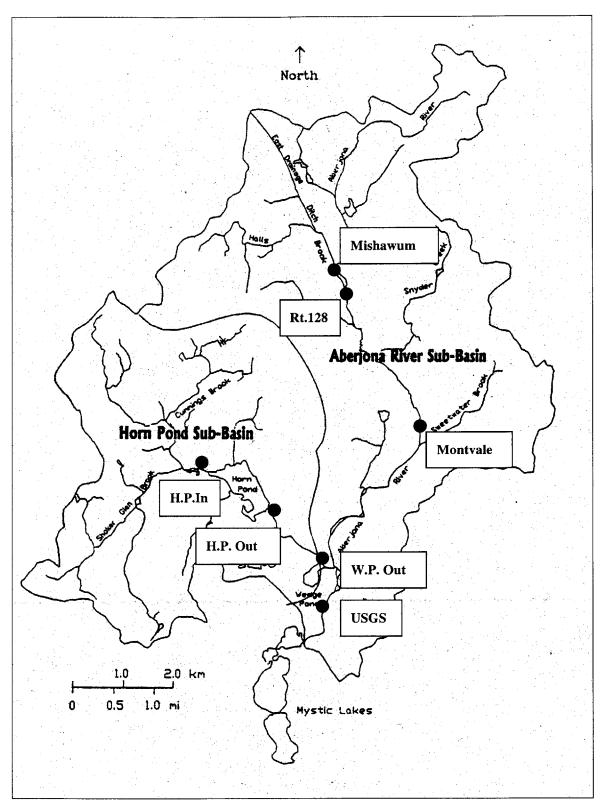


Fig 3-1 Location of Sampling Site

# 3. 2 Solorzano method analysis

### 3. 2. 1 Major Procedure

The solorzano method, or so-called indolphenol blue method, was used for determination of ammonium ion in the natural water. The resulting blue color is similar to that of indophenol dyes and its intensity of darkness is proportional to the ammonium concentration.

#### Preparation

• Regent 1 - Phenol Solution

Dissolve 10 g phenol in 100 ml 95% v/v ethyl alcohol (95 ml  $H_2O$  + 5ml ethyl alcohol)

• Regent 2 - Sodium Nitroprusside solution

Dissolve 0.5 g of sodium nitroprusside in 100 ml water (use an amber bottle or dark bottle)

• Regent 3 - Alkaline Regent

Desolve 5g sodium sitrate and 0.5 g sodium hydroxide in 50 ml water

Add 12.5 ml Chlorox

#### Procedure

Add all regents in the hood.

- 1. Add 0.2 ml Regent 1. Mix
- 2. Add 0.2 ml Regent 2. Mix
- 3. Add 0.5 ml Regent 3. Mix

The color is allowed to develop at room temperature (22~27°C) for one hour.

Reading on the Spectrophotometer

Turn on the spectrophotometer lamp, set wavelength to 640 nm.

Fill cuvette with deionized water, insert it into the instrument, and zero the reading. Fill cuvette with standard, and measure the absorbance. (Low standards are read first) Before re-zeroing, sip again to make sure all residual material is removed and reading is stable (Solorzano, 1969).

## 3. 2. 2 Standard Preparations

## Stock Solution- 200 µM NH<sub>4</sub><sup>+</sup> as N

1. Prepare a 200  $\mu$ M NH<sub>4</sub><sup>+</sup> standard (2 ml primary standard + 98 ml deionized water)

Concentration (µM)	Volume of 200 µM Standard (ml)	Volume of Water (ml)
100	10	10
75	7.5	12.5
50	5	15
25	2.5	17.5
10	1	19
5	0.5	19.5

2. Prepare additional standards by diluting the 200  $\mu$ M standard.

#### Table 3.2 Ammonium Concentration vs. Standard Dilutions

#### Spectrophotomatric Measurement

The concept of spectropohotometeric measurement is based on the quantification of light transmitted by the sample materials related to the intensity of light transmitted by the blank. The relationship of absorbance and ammonium concentration is calculated by plotting a standard curve. From the graph (Fig 3.2), ammonium concentration can be considered linearly proportional to the absorbance up to 200  $\mu$ M. For samples that had ammonium concentration over 200  $\mu$ M, I diluted samples with deionized water to 50:50 ratio.

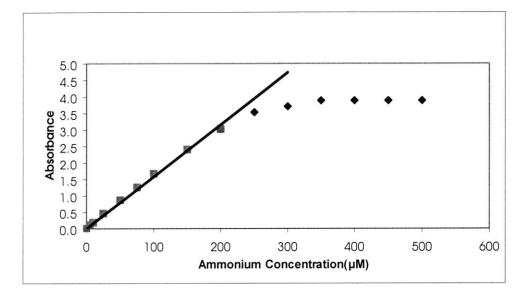


Figure 3.2 Ammonium Concentration vs. Spectrophotomatric Absorbance

## **4.1 The Aberjona River Branch**

Ammonium ion concentrations along the Aberjona River were generally higher than concentrations along Horn Pond Creek. The highest concentration of 3.97 mg/l-N was observed March 07, 2003 at Rt. 128, and the lowest concentration of 2.17 mg/l-N was measured March 07, 2003 at Montvale site (Fig 4.1). Ammonium concentration along the Aberjona River was reduced in the downstream direction. The concentration decreased from Rt. 128 to Montvale, and to USGS. However, when discharge effects at the three sampling sites were considered, the ammonium flux slightly increased as the river approached the end of the watershed (Fig 4.2). One explanation of this trend is that a source of ammonium-contaminated water was located in the sub-watershed near Rt. 128, and relatively clean inflows from several branches of the river diluted the ammonium contamination as the Aberjona River continued to run to downstream.

Nitrate concentrations did not vary much compared to the ammonium ion throughout the Aberjona River. The highest nitrate concentration of 2.3mg/l-N was measured at Montvale on January 24, 2003 (Fig 4.3). Except for that sampling, the nitrate concentration remained less than 2 mg/l-N for every sampling. As with nitrate, especially in the surface water, there is no state standard, but nitrate concentrations at all sampling sites were less than the drinking water regulations of USEPA. As opposed to the ammonium result, upstream of Rt. 128 did not have a large nitrate source and average nitrate concentration increased going downstream with no observed dilution effect (Fig

4.5)

As for the organic nitrogen, the data included broad error boundaries. Because three results from ammonia analysis, nitrate analysis, and total nitrogen analysis were used to calculate the organic nitrogen concentration, three different types of errors overlapped. Even though the organic nitrogen concentration has a large error boundary, one thing observed is that generally 15% of total nitrogen was organic nitrogen at almost all sites including Horn Pond creek (Appendix E).

#### Transformation

Nitrification was assumed to take place in the Aberjona River even though water dilution was a major means of decreasing ammonium concentration (Fig 4.5). Observations of the dissolved nitrogen species flux (Fig 4.6) support the notion that some amount of ammonium ion was transformed to nitrate while the ammonum flux was slightly rising with continuous ammonium additions from small branches of the river or some mineralization effect. The rate of nitrate flux increase is apparently bigger than the rate of ammonium flux increase. In other words, the nitrate flux increased more sharply possibly due to ammonium oxidation (Fig 4.6).

Also another possible reaction is mineralization in Mishawum Pond. It is difficult to diagnose the environmental situation in the pond with only ammomium concentration data. Mineralization of the vegetation in the swamp or contaminated ground water discharge is one of the possible explanations for the significant increase of ammonium concentration between the inlet and outlet of the pond (Appendix A),

27

# **4.2 The Horn Pond Creek Branch**

The analysis data of Horn Pond Creek shows that both concentrations of ammonium and nitrate were relatively stable throughout the tributary (Fig 4.1, 4.3). Ammonium concentration remained lower than 0.2 mg/l-N except for the fourth sampling at Wedge Pond. The branch of Horn Pond Creek passed by the area of forest, residences, and playgrounds. Even though commercial fertilizer and agricultural non-point sources were expected to increase the ammonium concentration in that tributary, the effect of these sources were small enough to be ignored compared to the result of the Aberjona River. Nitrate concentration varied from 0.64 mg/l-N to 1.84 mg/l-N. Horn Pond Inlet had results above 1.0 mg/l-N for all sampling events. The remaining sites had levels generally at or below 1.0mg/l-N (Fig 4.3). The nitrate concentration decreased from Horn Pond Inlet to Horn Pond Outlet, and to Wedge Pond. Organic nitrogen is composed of 15%~30% of total nitrogen and did not have any typical trend.

#### Transformation

Nitrogen measurement in the Horn Pond Creek tributary shows that nitrogen loading in the surface water was low compared with the Aberjona River tributary (Appendix E). Therefore, we anticipated only small chemical and biological reactions of nitrogen compounds. However, it is likely that denitrification occurred between the Horn Pond outlet and the Wedge Pond site. There was an average 36% decrease of nitrate flux in this section, and transformation from nitrate to other reduced nitrogen compounds is a possible explanation.

28

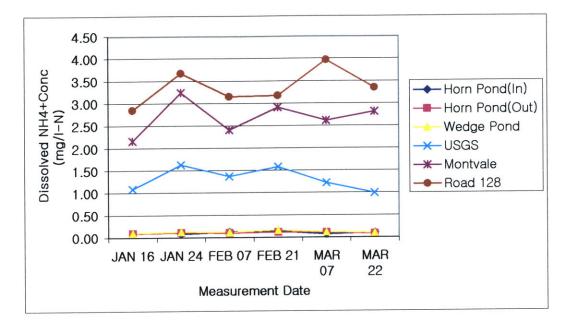


Figure 4.1 Dissolved NH4<sup>+</sup> Concentration vs. Measurement Date

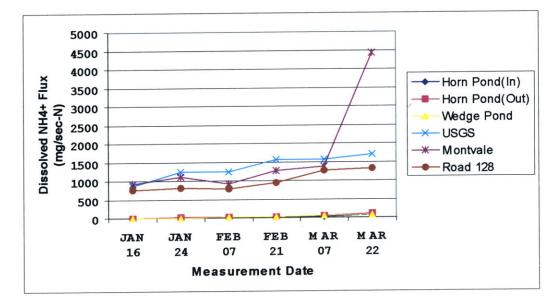


Figure 4.2 Dissolved NH4<sup>+</sup> Flux vs. Measurement Date

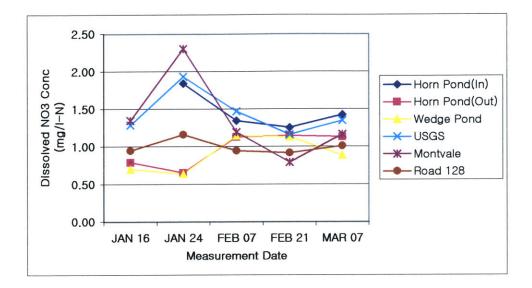


Figure 4.3 Dissolved NO<sub>3</sub><sup>-</sup> Concentration vs. Measurement Date

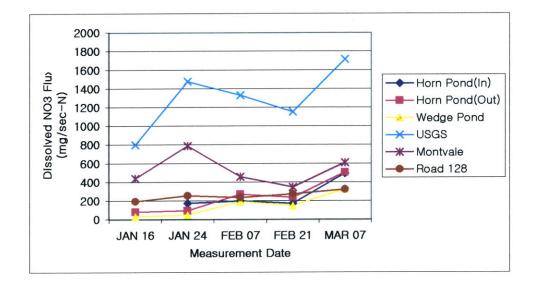


Figure 4.4 Dissolved NO<sub>3</sub><sup>-</sup> Flux vs. Measurement Date

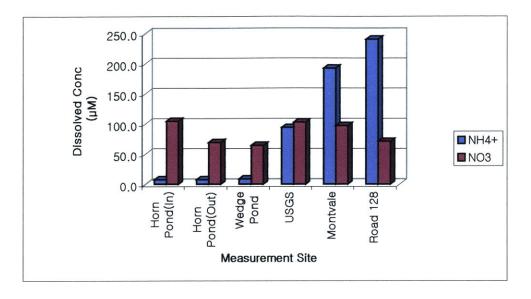


Figure 4.5 Average Dissolved NH4<sup>+</sup> & NO3<sup>-</sup> Concentrations vs. Measurement Site

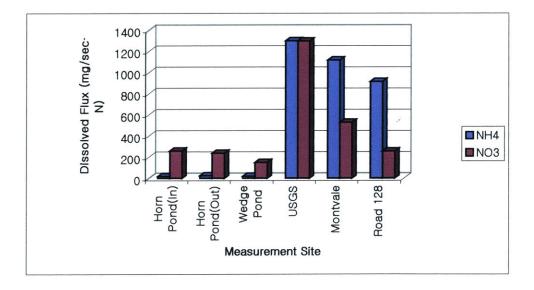


Figure 4.6 Average Dissolved NH4<sup>+</sup> & NO3<sup>-</sup> Fluxes vs. Measurement Site

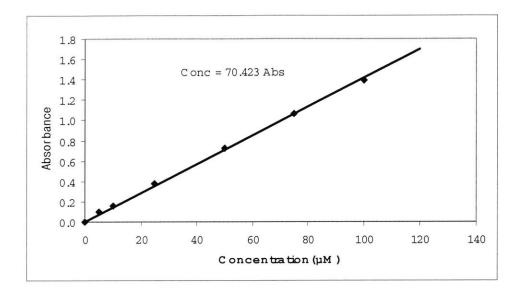
# **5. CONCLUSION**

The Aberjona watershed had different characteristics depending on which regions the streams passed by. Among ammonium, nitrate, and organic nitrogen, ammonium ion concentration shows the most significant difference between the Aberjona River tributary and Horn Pond creek tributary. Highly ammonium-contaminated water, which originates from industrial areas at the northern Aberjona River watershed, flows downstream increasing the risk of nitrogen loading problems. From our measurement data, some clues of possible nitrification reactions were discovered, but the ammonium flux is not much reduced due to the short residence time in the river, and low temperatures especially in winter. The major part of the ammonium flux was delivered to the Mystic Lake, from which it could pass down to the estuary near Boston. This situation is of great concern because nitrogen loading in the Aberjona Watershed causes potential problems such as oxygen deficits, algae blooms, and eutrophication in fresh water as well as the Boston coast.

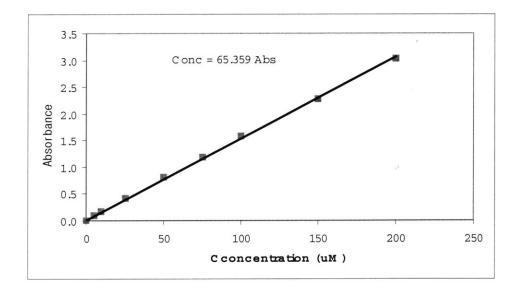
This study measured ammonium, nitrate, and organic nitrogen to assess the nitrogen behavior in the aquatic environment and define the nitrogen characteristics in the Aberjona watershed. For an accurate and specific evaluation, measurement of more biological, chemical, and geological conditions is required.

It is highly recommended to determine the relationship between land use and nitrogen loading in the watershed. Also, defining factors that make ammonium increase in the Mishawum Pond is suggested.

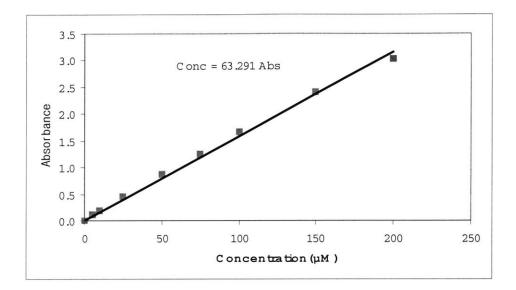
Appendix A: Spectrophotometric Measurement Standard



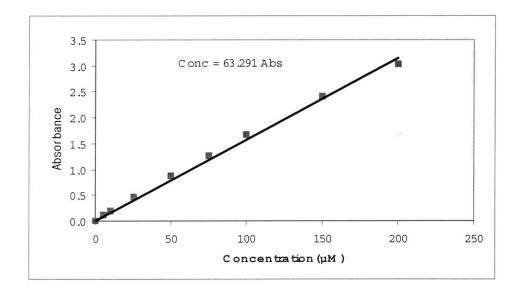
Spectrophotometric Measurement, January 16, 2003



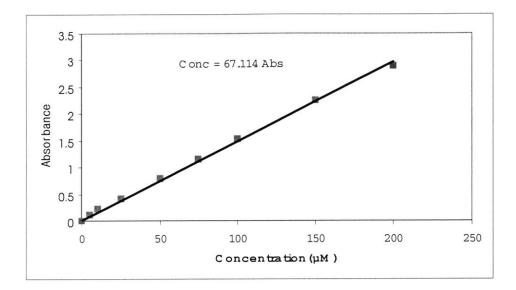
Spectrophotometric Measurement, January 24, 2003



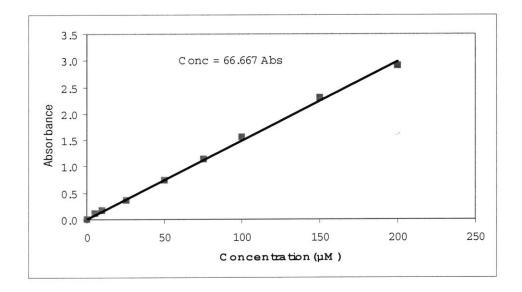
Spectrophotometric Measurement, February 02, 2003



Spectrophotometric Measurement, February 21, 2003

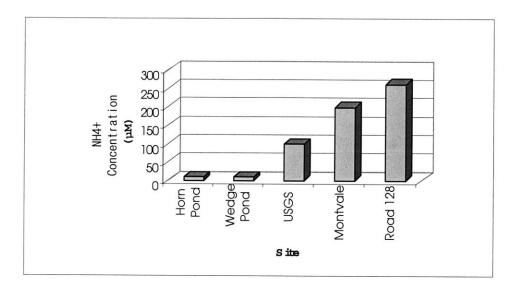


Spectrophotometric Measurement, March 07, 2003

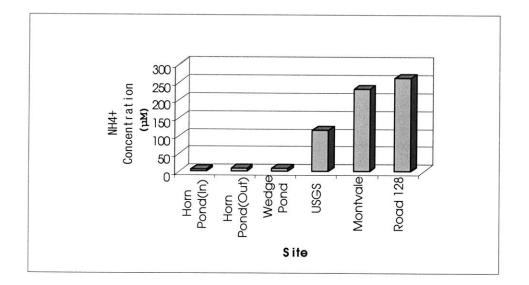


Spectrophotometric Measurement, March 22, 2003

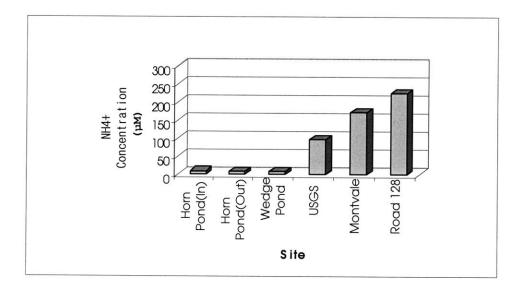
**Appendix B: Ammonium Concentration & Flux** 



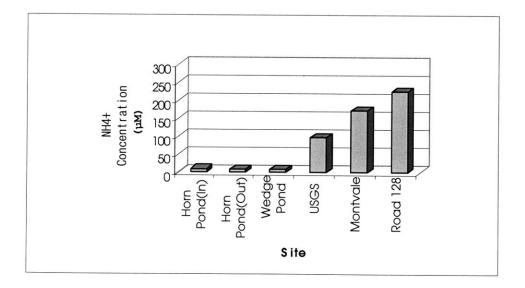
Ammonium Concentration vs. Measurement Site, January 16, 2003



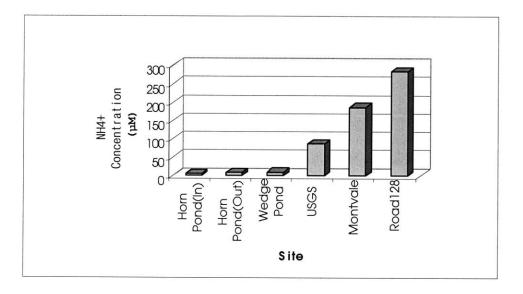
Ammonium Concentration vs. Measurement Site, January 24, 2003



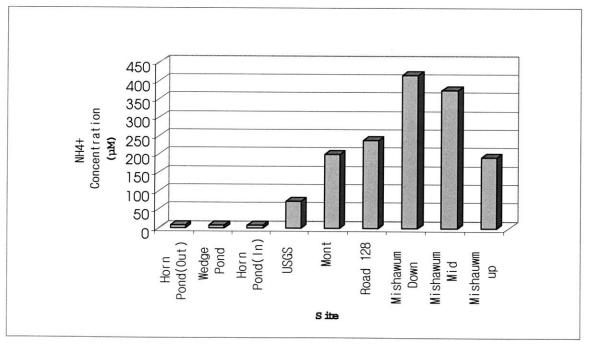
Ammonium Concentration vs. Measurement Site, February 02, 2003



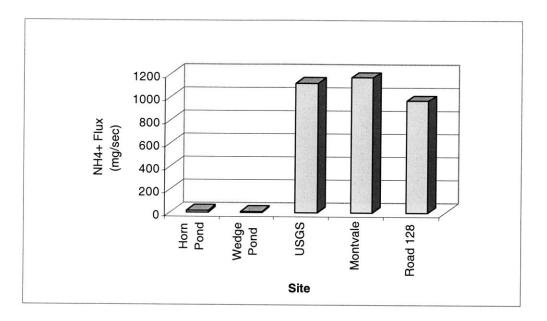
Ammonium Concentration vs. Measurement Site, February 21, 2003



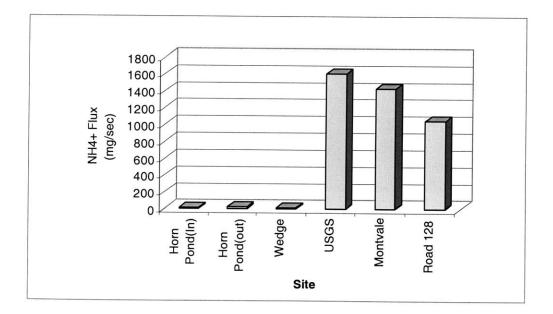
Ammonium Concentration vs. Measurement Site, March 07, 2003



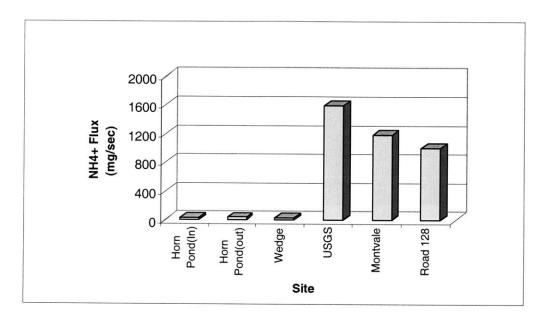
Ammonium Concentration vs. Measurement Site, March 22, 2003



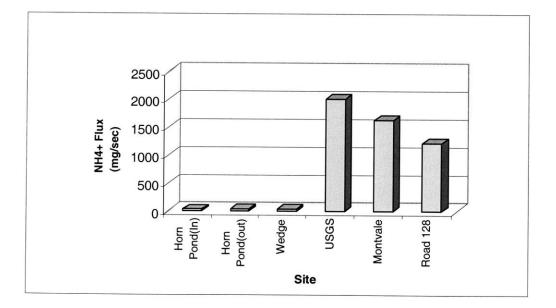
Ammonium Flux vs. Measurement Site, January 16, 2003



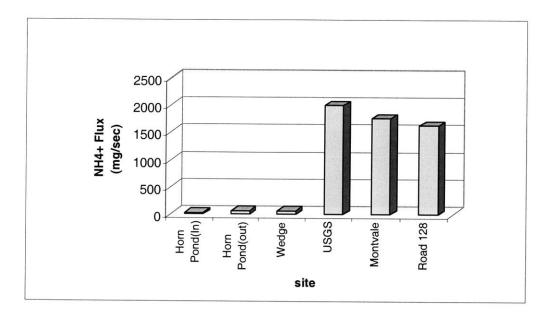
Ammonium Flux vs. Measurement Site, January 24, 2003



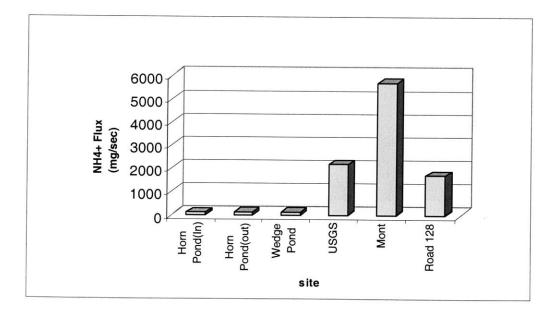
Ammonium Flux vs. Measurement Site, February 02, 2003



Ammonium Flux vs. Measurement Site, February 21, 2003



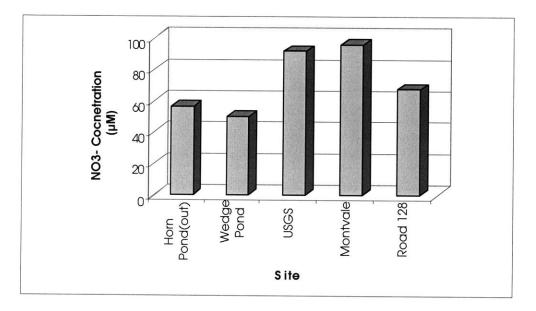
Ammonium Flux vs. Measurement Site, March 07, 2003



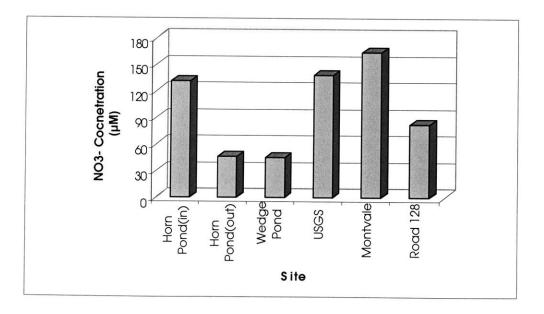
Ammonium Flux vs. Measurement Site, March 22, 2003

## **Appendix C: Nitrate Concentration & Flux**

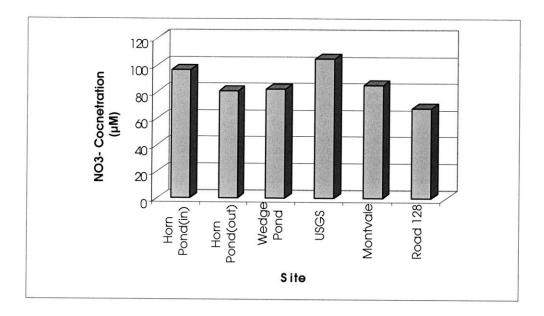
Nitrate measurements of the Aberjona Watershed samples performed at Parsons Laboratory by Yi-Ju Chou (2003).



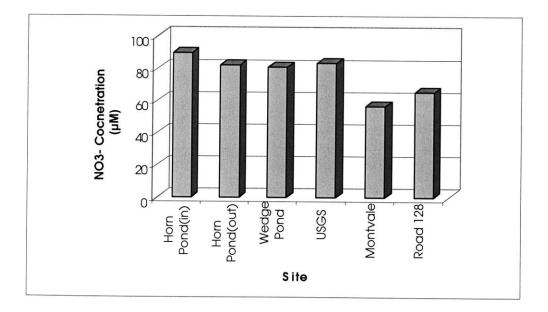
Nitrate Concentration vs. Measurement Site, January 16, 2003



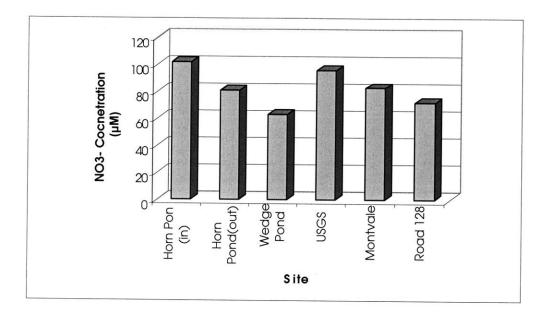
Nitrate Concentration vs. Measurement Site, January 24, 2003



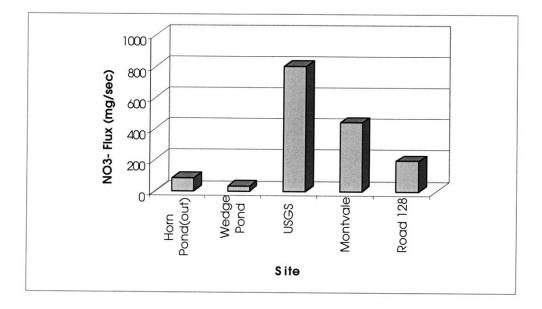
Nitrate Concentration vs. Measurement Site, February 02, 2003



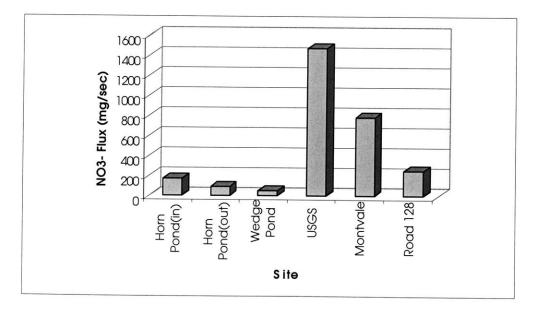
Nitrate Concentration vs. Measurement Site, February 21, 2003



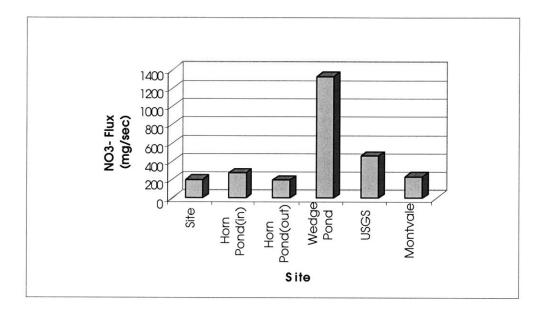
Nitrate Concentration vs. Measurement Site, March 07, 2003



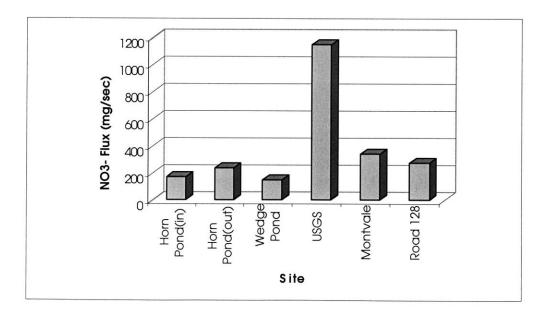
Nitrate Flux vs. Measurement Site, January 16, 2003



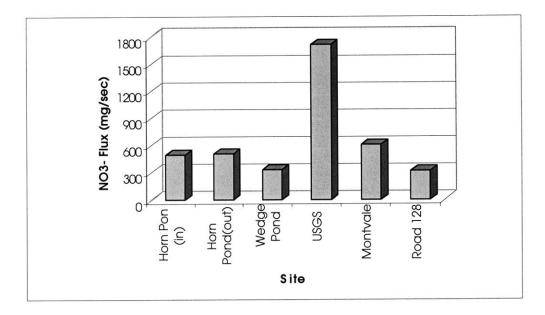
Nitrate Flux vs. Measurement Site, January 24, 2003



Nitrate Flux vs. Measurement Site, February 02, 2003



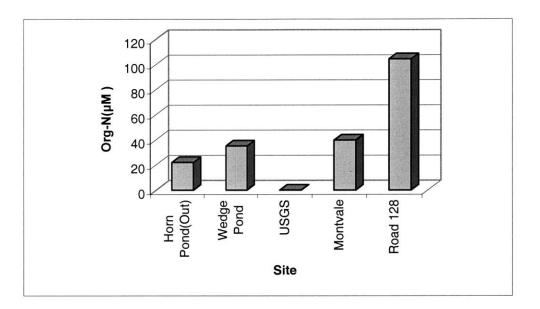
Nitrate Flux vs. Measurement Site, February 21, 2003



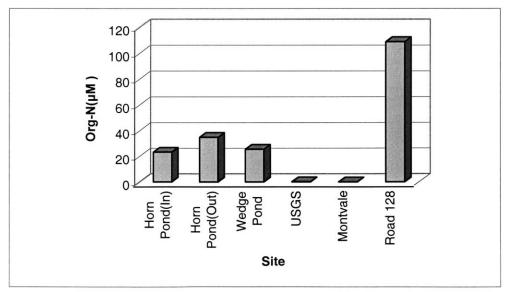
Nitrate Flux vs. Measurement Site, March 07, 2003

## **Appendix D: Organic N Concentration**

Organic N measurements of the Aberjona Watershed samples performed at Parsons Laboratory by Matthew S. Orosz (2003).



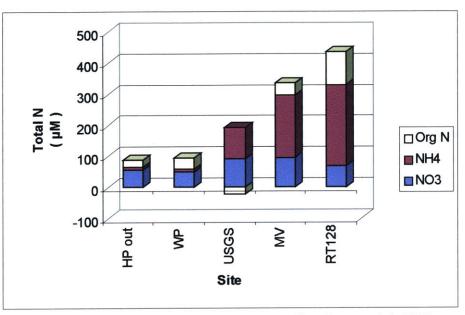
Org-N Concentration vs. Measurement Site, January 16, 2003



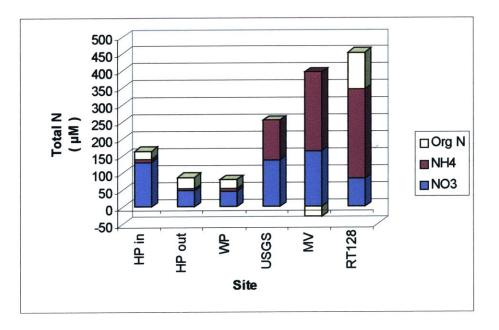
Org-N Concentration vs. Measurement Site, January 24, 2003

## **Appendix E: Total N Concentration**

Nitrate and Organic N measurements of the Aberjona Watershed samples performed at Parsons Laboratory by Yi-Ju Chou and Matthew S. Orosz (2003).



Total N Concentration vs. Measurement Site, January 16, 2003



Total N Concentration vs. Measurement Site, January 24, 2003

## References

Alexander, R. B., Smith, R. A. & Schwarz, G. E. 2000. "Effect of Stream Channel Size on the Delivery of nitrogen to the Gulf of Mexico." Nature. 403, 758-761.

Behar, S. 1997. "Testing the Waters: Chemical and Physical Vital Signs of a River." River Watch Network.

Bialon, J. L. 1995. "Characterization of The Physical and Engineering Properties of the Aberjona Wetland Sediment." Ph.D. Thesis. Massachusetts institute of Technology.

Brainard, E. C., 1990. "Ground Modeling of the Aberjona Basin." M.S. Thesis, Massachusetts institute of Technology.

Brion, N. et al., 2000. "Distribution of Nitrifying Activity in the Seine River (France) from Paris to the Estuary." Estuaries 23, 669-682.

Carpenter, S. R. et al., 1998 "Nonpoint pollution of Surface Waters with Phosphorous and Nitrogen." Ecological Application. 8(3), 559-568.

Caspers, H. 1981. "Seasonal Effects on the Nitrogen Cycle in the Freshwater Section of the Elbe Estuary." Verhandlungen Internationale Vereinigung fur Limnologie 21, 866-870.

Cist, D. B. 1999. "Ground penetrating radar characterization of geologic structure beneath the Aberjona wetland." Ph.D. Thesis. Massachusetts institute of Technology.

DeSimone, L. A., Howes, B. L.1998. "Nitrogen transport and transformation in a sallow aquifer receiving wastewater discharge: A mass balance approach." Water Resources Research. 30(2), 271-285.

DiSpirito, A. A., Taaffe, L. R., Lipscomb, J. D. & Hooper, A. B. 1985. "A blue Copper Oxidase form *Nitrosomonas eutropaea*." Biochem. Biophysics. Acta 827, 230-326.

Di Toro, D.M., O'Connor, D.J. & Thomann, R.V. 1971. "A Dynamic Model of the Phytoplankton Population in Sacramento-San Joaquin Delta." In non equilibrium systems in natural water chemistry. In: Adv. Chem. Ser, vol.106. American Chemical Society, Washington, DC, pp. 131-180.

Durant, J. L. 1991. "Industrial history, mutagenicity, and hydrologic transport of pollutants in the Aberjona watershed." Civ.E. Thesis. Massachusetts institute of Technology.

Eberhardt, A., Larson, L. 2000. "Water Quality Monitoring in the Mystic River Watershed: A Study of 10." Mystic Monitoring Network Coordinators and the Mystic Monitoring Network Mystic River Watershed Association.

Ellis, B. 1999. "Impact of Urban Growth on Surface Water and Groundwater Quality." IAHS Publication no. 259. IAHS Press, Wallingford, UK.

Follett, R. F., Hatfield, J. L. 2001. "Nitrogen in the Environment: Sources, Problems, and Management." Elsevier Science B.V. Amsterdam.

Garnier, J. et al., 2002. "Modelling the Transfer and Retention of Nutrients in the Drainage Network of the Danube River." Estuarine, Coastal and Shelf Science. 54, 285-308.

Herrmann, T., Klaus, U. 1997. "Fluxes of Nutrients in Urban Drainage Systems: Assessment of Sources, Pathways and Treatment Techno lodge." Water Science and Technolodge. 36(8-9), 167-172.

Jeppensen et al., "Cascading Trophic Ineractions from Fish to Bacteria and Nutrients after Reduced Sewage Loading: An 18-Year Study of a Shallow Hypertrophic Lake." Ecosystems (1998) 1: 250-267.

Lewis, W.M. 2002. "Yield of Nitrogen from Minimally Distribbed Watersheds of the United Stateds." Biogeochemistry. 57, 375-385.

McCasland, M. Trautmann, N. M. & Porter, K.S. 2002. Nancy M& Porter, Keith S. Natural Resource. Cornell Cooperative Extention. Nitrate: Health Effects in Drinking Water. From <u>http://pmep.cce.cornell.edu/facts-slides-self/facts/nit-heef-grw85.html</u>

McNeely, R.N., V.P. Neimanis and L. Dwyer. 1979. "Nitrogen-ammonia." In Water Quality Sourcebook. A Guide to Water Quality Parameters. Water Quality Branch. Inland WaterDistrectorate. Environmentat Canada. Ottawa. 22-27. En: CCME. Canadian Water Quality Guideline.

Puckett, L. J., 1995. "Identifying the major sources of nutrient water pollution." Environmental Science and Technology. 29, 408-414.

Rabalais, N. N. 2002. "Nitrogen in aquatic ecosystems." Ambio. 31(2) 102-112.

Reynolds, J. E. 1993. "Three-Dimensional, Transient Groundwater Model of the Aberjona Watershed." Ph.D. Thesis. Massachusetts institute of Technology.

Sawyer, C. N., Mc Carty, P. L., & Parkin, G. F. 1994. "Chemistry for Environmental Engineering." 4<sup>th</sup> Ed. McGraw-Hill, Inc. New York.

Senzia. M. A., Mayo. A. W., Mbwette, T. S. A., Katima. J.H.Y. & Jorgensen. S. E. 2002 "Modeling nitrogen transformation and removal in primary facultative ponds." Ecological Modelling. 154, 207-215.

Sliekers, A. O., Stouhamer, E. B. & van Verseveld, H. W. 2002. "Completely autotrophic nitrogen removal over nitrate in one single reactor." Water Research. 36, 2475-2482.

Smil, V. 1985. "CARBON-NITROGEN-SULFER." Human Interference in Grand Biospheric Cycle. Plenum Press. New York.

Solo-Gabriele, H. 1995. "Metal Transport in the Aberjona River System: Monitoring, Modeling, and Mechanism." Ph.D. Thesis. Massachusetts institute of Technology.

Solorzano, L. 1969. "Determination of ammonia in natural waters by the phenolhypochlorite method." Limnol. Oceanogr. 14:799-801.

Stanford, G. & Smith, S.J. 1972. "Nitrogen Mineralization Potentials of Soils." Soil Sci. Soc. Amer. Proc. 36, 465-472.

Stouthamer A. H. 1988. "Dissimilatory Reduction of Oxidized Nitrogen Compounds." In: Zehnder AJB (Ed) Biology of Anaerobic Micoorganisms. Jhon Wiley &Sons, Inc., New York, pp. 245-303.

Tufts University GIS Center. 2002. "The Mystic River Watershed: Interactive GIS Mapping" Tufts University. <<u>http://www.ase.tufts.edu/GIS/home.htm#</u>>.

Peterson, B. J., Bahr, M., Kling, G.W. 1997. "A tracer investigation of nitrogen cycling in a pristine tundra river." Can. J. Fish. Aquat. Sci. 54. 2361-2367.

Peterson, B.J., et al., 2001. "Control of Nitrogen Export from Watersheds by Headwater Streams." Science. 292, 86-90.

Pollice, A., Tandoi, V. & Lestingi, C. 2002. "Influence of Aeration and Sludge Retention Time on Ammonim Oxiditon to Nitrate and Nitrate." Water Research. 36, 2541-2546.

Puckett, L. J. et al., 1995. "Identifying the Major Sources of Nutrient Water Pollution." Environmental Science & Technolodge. 20(9), 408-414.

Tong, S.T.Y. & Chen, W. 2002. "Modeling the Relationship between Land Use and Surface Water Quality." Journal of Environmental Management 66. 377-393.

U. S. Environmental Protection Agency. 2002. Monitoring and Assessing Water Quality: Nitrates. From <u>http://www.epa.gov/owow/monitoring/volunteer/stream/vms57.html</u>

Wolfe, A. H. 2002. "Reactive Nitrogen and Human Health: Acute and Long-term Implications." Ambio. 31(2) 120-125.

٠