The Science and Politics of Increasing Nitrogen Pollution from Human Activity: case study of the Aberjona watershed

by

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Abstract

The biogeochemical cycling of nitrogen has critical implications for all life on earth. The Haber-Bosch process (1909) paved the way for the industrial fixation of NH_3 from unreactive atmospheric dinitrogen, a phenomenon previously restricted to the enzyme nitrogenase and to a lesser extent lightning. Perhaps the most profoundly catalytic invention of the 20th century, Haber-Bosch has greatly increased the global anthropogenic throughput of nitrogen that now rivals the 160 million metric tons fixed annually via nitrogenase. Notably 40% of the world's 6 billion people alive today owe their body's kilogram of nitrogen to synthetic fertilizer created via the Haber-Bosch process (Smil 2001). The intensification of agriculture and the growth of urban centers during the 20th century has also resulted in substantive increases in nitrogen loads to the environment. Nitrogen transported by surface and groundwater is ultimately concentrated in rivers and coastal areas, with consequences such as eutrophication and the "dead zones" of hypoxia found throughout the world. Microbial metabolism of nitrogen via the nitrification and denitrification pathways also produces N_2O, a potent greenhouse gas currently responsible for 5% of total atmospheric radiative forcing.

This thesis examines the environmental implications of increased nitrogen throughput and the regulatory frameworks that are evolving to cope with nitrogen pollution. A case study of the Aberjona river, draining a heavily polluted urban watershed north of Boston, is examined in terms of the correlation between urban intensity and nitrogen yields ($r^2=0.79$), the internal processing of nitrogen via major biological pathways, and the role of legacy pollutants as a source of nitrogen. The high fraction of organic nitrogen (34% of TOT N export) suggests that the effects of urban intensification are not limited to the export of inorganic species, and should be included in urban nitrogen budgets for effective watershed management.

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THE SCIENCE AND POLITICS OF INCREASING NITROGEN POLLUTION FROM HUMAN ACTIVITY

CASE STUDY OF THE ABERJONA RIVER WATERSHED

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CHAPTER I
NITROGEN SCIENCE REVIEW

INTRODUCTION

The biogeochemical cycling of nitrogen has critical implications for all life on earth. Nitrogen in amino and nucleic acids is essential for the functionality of all living things, and is frequently a limiting nutrient for terrestrial systems. The Haber-Bosch process (1909) paved the way for the industrial fixation of NH_3 from unreactive atmospheric dinitrogen, a phenomenon previously restricted to the enzyme nitrogenase (and to a lesser extent lightning once the earths atmosphere became oxidizing). Perhaps the most profoundly catalytic invention of the 20th century, Haber-Bosch has greatly increased the global anthropogenic throughput of nitrogen that now rivals the 160 million metric tons fixed annually via nitrogenase.[1] Notably 40% of the world's 6 billion people alive today owe their body's kilogram of nitrogen to synthetic fertilizer created via the Haber-Bosch process.[2]

Naturally and industrially fixed nitrogen cycles through the environment in different redox states primarily as the result of microbial energetic and biosynthetic processes, and the relative concentration of these species has significant ramifications for soil and aquatic environments and atmospheric chemistry. Of particular interest are the effects of dissolved inorganic and organic nitrogen in watersheds and effluviums, and the capacity of nitrous oxide (N_2O) gas to trap outgoing long-wave radiation in the troposphere and produce the ozone-destroying radical NO in the stratosphere. As NO_3^- rich aerobic surface and groundwater enters the reduced riparian zones of polluted rivers, the dynamic redox zone of sediments can promote high rates of N_2O formation. N_2O is an intermediate product in nitrification, the conversion of NH_4 to NO_3, and an obligate

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[1] Jenkinson, D.S. "The impact of humans on the nitrogen cycle, with focus on temperate arable agriculture" Plant and Soil vol. 228 pg. 3 (2001)

[2] Smil, Vaclav, "Enriching the Earth, Fritz Haber, Carl Bosch, and the Transformation of World Food Production" MIT press, Cambridge Massachussetts, 2001 pg. 159

intermediate in denitrification, the process which re-forms stable N_2 gas and completes the nitrogen cycle.

NITROGEN CYCLE DYNAMICS

The key to understanding the environmental role of nitrogen lies in having a conceptual framework for its storage compartments and fluxes, from the global to the microbial scale. The largest pool of nitrogen (1.9×10^{17} tons) is found in sedimentary rocks, where it becomes bioavailable via weathering over geological time. Of more immediate relevance to organisms is the 4×10^{15} tons of molecular N_2 that comprises 79% of the earth's atmosphere, 2×10^{12} tons of which are assimilated in the machinery of life.[3] The gatekeepers of this essential building block are the few specialized prokaryotic bacteria capable of converting unreactive N_2 into labile forms.[4] In most terrestrial systems Nr is in short supply and is considered the "limiting" nutrient; for this reason bioavailable nitrogen is a particularly useful agricultural fertilizer.

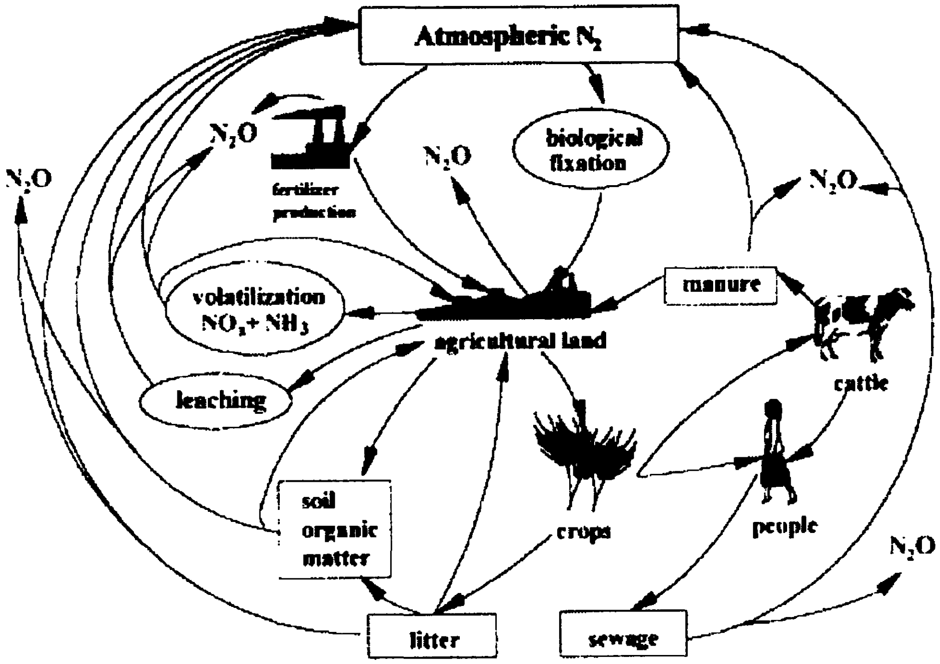

Figure 1 Box diagram of the Nitrogen cycle[5]

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[3] Finan, et. al "Nitrogen Fixation: Global Perspectives" CABI Publishing New York, NY 2002 pg 297

[4] Leigh, G. Jeffrey "Nitrogen Fixation at the Millennium" Elsevier 2002 pg. 4

[5] Mosier, Arvin, et. al "Closing the global N2O budget: nitrous oxide emissions through the agricultural nitrogen cycle" Nutrient Cycling in Agroecosystems 52:225-228 1998 pg. 227

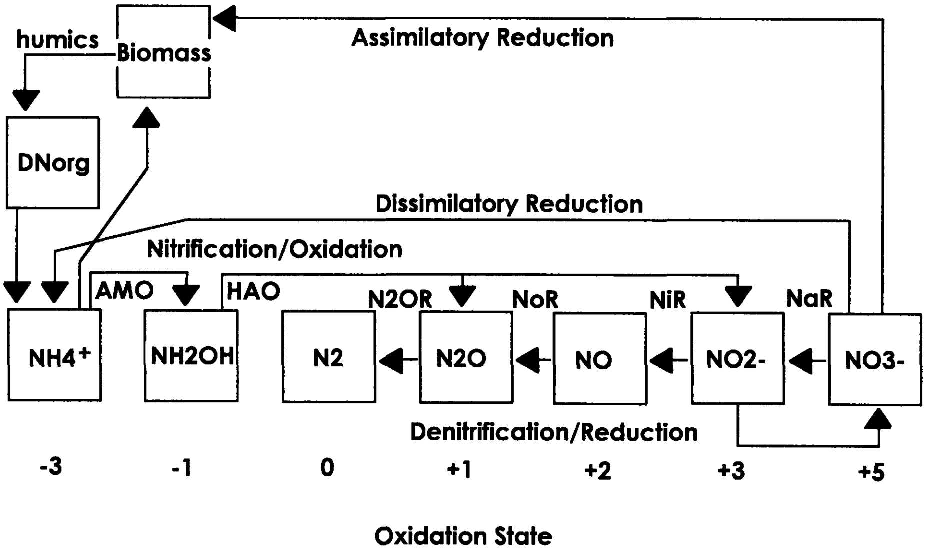

Figure 2 Oxidation State and Metabolic Pathways of Nitrogen Species[6]

NITROGEN FIXATION

Biological breaking of the stable N≡N by nitrogenase provides the main natural input of reactive nitrogen into the biosphere (about 160 million metric tons annually).[7] The primary source of this biologically fixed nitrogen is the range of free living bacteria such as *azobacter* and cyanobacteria (aerobic), *clostridium* and purple and green bacteria (anaerobic) and the *Rhizobium* (and related genera) found in legume symbiosis.[8] In the latter situation legumes provide bacteria with protected root nodule environments containing a supply of energy rich compounds and a modulated O_2 content in return for access to fixed nitrogen. A special O_2 transporting protein called leghemoglobin supplies a carefully controlled amount of O_2 at levels that enable bacteria to respire without denaturing nitrogenase.[9]

Nitrogenase itself is a complex of enzymes usually consisting of a dinitrogenase and dinitrogenase reductase containing mainly iron, molybdenum and sulfide ions. Although variations on this theme abound in nature (including varying degrees of dependence on iron, molybdenum or vanadium as the coordinating atomic site for atmospheric nitrogen), the result of a complicated interaction of these proteins is the reaction below:

$$N_2 + 8H^+ + 8e^- + 16\,ATP \rightarrow 2NH_3 + H_2 + 16ADP + 16\,P_i$$

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[6] Ibid. pg. 580

[7] Jenkinson, D.S. "The impact of humans on the nitrogen cycle, with focus on temperate arable agriculture" Plant and Soil vol. 228 pg. 3 (2001)

[8] Madigan, et. al. "Brock Biology of Microorganisms: Tenth Edition" Prentice Hall, 2003 pg. 663

[9] Leigh 2002 pg. 5

As can be seen from the above equation, fixation is costly, with two molecules ATP required for each electron transferred to dinitrogen, and an apparently wasted molecule of dihydrogen produced for each N_2 reduced. The reasons for this are not entirely understood (in part because X-ray crystallographic techniques are problematic for nitrogenases) however for a review of potential explanations see Leigh 2004.

The origins of nitrogenase are unknown, but phylogenetic reconstruction and the presence of nitrogenase in diverse archaea as well as bacteria has led to the hypothesis that nitrogenase complexes were already evolved in the last common ancestor of the three domains of life, with the extant distribution of nitrogenases explained by gene loss.[10] A second hypothesis is that nitrogen fixation was evolved in methanogenic archaea and subsequently transferred into bacterial lineages in at least three separate events (representing three main families of nitrogenase complexes) along with other genes transferred laterally in the same direction.[11] Regardless of its origins, and despite the expense of the process and the need to scavenge trace metals, the success of nitrogenases has led to their wide distribution in microbial genomes, and has supported life on earth for over a billion years.

Today, nitrogen fixation through leguminous plants alone accounts for 25-35% of the worldwide human protein intake.[12]

NITRIFICATION-DENITRIFICATION

Transformations among inorganic N species take place mainly through two microbial pathways, broadly labeled as nitrification and denitrification. Both are energy yielding electron transfer processes that are generally regulated by the presence or absence of oxygen and availability of appropriate N substances and organic carbon. Nitrification is generally an aerobic process carried out by primarily autotrophic bacteria, resulting in the oxidation of NH_4 to NO_3. Once considered the sole province of denitrification, it is now recognized that NO and N_2O can be produced as nitrification by-products from NO_2 via incompletely known pathways.[13] A significant amount of NO and N_2O and trace N_2 can be produced during oxidation of ammonia by *Nitrosomonas* at low oxygen concentration.[14]

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[10] Raymond et al. "The Natural History of Nitrogen Fixation" Molecular Biology and Evolution, December 23, 2003

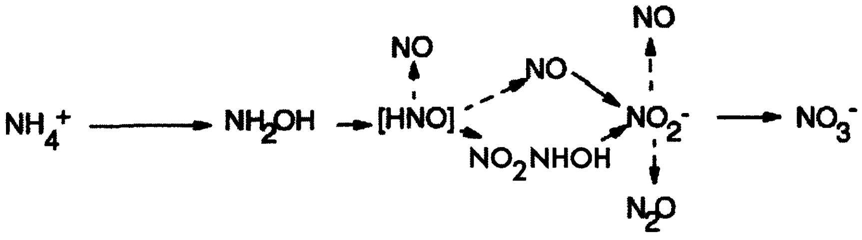
[11] Ibid.

[12] Finan 2002 pg. 339

[13] Parton, et. al. "Generalized model for N2 and N2O production from nitrification and denitrification" Global Biogeochemical Cycles, Vol. 10 No. 3 pgs. 401-412 September 1996 pg. 401

[14] Whittaker, Mark "Electron transfer during the oxidation of ammonia by the chemolithotrophic bacterium Nitrosomonas europaea" Biochimica et Biophysica Acta 1459 (2000) pgs 346-355 pg. 346

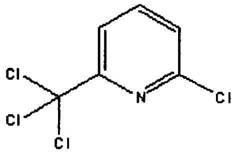
AMMONIA OXIDATION



Nitrosomonas and *Nitrobacter* species generally carry out the above oxidation of NH_4^+ to NO_2^- in two steps. Ammonium is first oxidized to hydroxylamine (NH_2OH) by ammonia monooxygenase (AMO). NH_2OH is subsequently oxidized to NO_2^- by hydroxylamine oxidoreductase (HAO) with either NO or Nitrohydroxyl-amine as intermediates.

$NH_4^+ + 2H+ +2e- +O_2 \rightarrow NH_2OH + H_2O$
$NH_2OH + H_2O \rightarrow NO_2^- + 5 H^+ + 4e-$

In the reaction catalyzed by AMO, one O from O_2 is inserted into NH_4^+ while the second O is reduced to H_2O. This reaction requires two additional electrons derived from the four *e* released by NH_2OH oxidation.[15] ATP synthase is driven by a proton gradient generated by oxidation of hydroxylamine.[16] AMO is membrane bound and consists of three polypeptides (most likely containing Cu), and has a remarkably nonspecific substrate range. It can catalyze the oxidation of C-H bonds to alcohols, C=C bonds to epoxides, and C≡C bonds to oxirenes and sulfides to sulfoxides. Substrates include alkyl and aryl hydrocarbons, halogenated hydrocarbons, and aromatics, among others.[17] Despite of the negative role of nitrification in croplands, nitrification is useful in treating sewage NH_4^+ and may have potential in the bioremediation of polluted soils and water through the nonspecific action of AMO.[18] Nitrification can be inhibited by nitrapyrin [2-choro-6-(trichloromethyl)-pyridine] (left) through a poorly understood mechanism, probably involving conversion to 6-chloropicolinic acid that binds to membrane proteins.[19] It is also readily inhibited by acetylene at low concentrations (x kpa).



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[15] Finan 2002 pg. 299
[16] Whittaker 2000 pg. 347
[17] Finan 2002 pg. 300
[18] Ibid. pg. 299
[19] Vannelli, Todd, and Hooper, Alan, "Oxidation of Nitrapyrin to 6-Chloropicolinic Acid by the Ammonia-Oxidizing Bacterium Nitrosomonas euroaea" Applied and Environmental Microbiology, July 1992, p. 2321-2325 pg. 2321

NITRATE REDUCTION

Denitrification is the primary process by which molecular nitrogen fixed biologically or chemically is reconstituted as N_2, and thereby removed from biological systems.[20] It is carried out by mainly heterotrophic facultative anaerobes that use NO_3^- as the terminal electron acceptor during a four stage reduction that completes with molecular N_2.[21] *Pseudomonas* and *Alcaligenes* species are perhaps of greatest significance in denitrification.[22] The most common *e-* donor is organic carbon, which most denitrifiers will oxidize preferentially with oxygen as an electron acceptor until supplies are limiting, at which point they will switch to the next best *e-* acceptor, usually nitrate. The O_2 threshold for denitrification varies among organisms,[23] spanning 90% of air saturation for *Thiosphaera pantotropha* to 53% for *Alcaligenes* sp. to practically completely anaerobic conditions for *Paracoccus denitrificans*.[24]

Nitrogen oxide reductases include NaR (nitrate reductase) NiR (nitrite reductase) NoR (nitric oxide reductase) and N_2OR (Nitrous oxide reductase). NO_2^-, NO and N_2O are all free obligatory intermediates in the complete reduction of NO_3^- to N_2.[25] They fulfill the criteria of kinetic competence; the possibility to feed the intermediates as precursors into the process and to detect them upon chemical or mutational blockage of the pathway, and biochemical and genetic evidence for the enzymes responsible for metabolizing these intermediates exists.[26]

Like nitrifiers, denitrifiers present opportunities for use in bioremediation strategies. The number of new isolates of denitrifiers that mineralize a wide spectrum of aromatic compounds under anaerobic conditions is steadily growing. The range of substrates utilized includes toluene, xylene, phenols, cresols, phthalate, cyclohexanol, benzoate, and other aromatic acids, alcohols, and aldehydes.[27]

N_2OR is inhibited by C_2H_2 at 5kPa, such that NO_3^- is stoichiometrically converted to N_2O (nitrification is also inhibited). Sulfide is also inhibiting to N_2OR and NoR.[28]

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[20] Martin 1998 pg. 176

[21] Parton 1996 pg. 401

[22] Knowles, Roger "Denitrification" Microbial Reviews, Mar. 1982 p 43-70 pg. 45

[23] Korom 1992 pg. 1658

[24] Korner, Heinz and Zumft, Walter "Expression of Denitrification Enzymes in Response to the Dissolved Oxygen Level and Respiratory Substrate in Continuous Culture of Psuedomonas stutzeri" Applied and Environmental Microbiology, July 1989 pg 1670-1676 pg.1670

[25] Knowles 1982 pg. 47

[26] Zumft, Walter "Cell Biology and Molecular Basis of Denitrification" Microbiology and Molecular Biology Reviews, Dec. 1997 p533-616 pg. 535

[27] Ibid. pg. 595

[28] Knowles 1982 pg. 51

FUNCTIONAL OVERLAP IN NITROGEN METABOLIZING COMMUNITIES

As microsensor and genetic techniques for assessing microbial processes improves, the boundaries between broad classes of bacteria and their environmental roles (ecotypes) become increasingly blurred. Newer evidence suggests that nitrification and denitrification are not as strictly aerobic or anaerobically regulated as was once believed.[29] *Nitrosomonas eutropha*, an obligately lithoautotrophic bacterium, is able to nitrify and denitrify simultaneously under anoxic conditions.[30] Using ^{15}N as a tracer Poth and Focht have demonstrated the production of N_2O from nitrite by *Nitrosomonas europaea.*[31]

Many microbes and flora can reduce nitrate to ammonium for use in biosynthetic pathways, if ammonium is not readily available. In anaerobic environments organisms that dissimilate nitrate to ammonium compete with denitrifiers for access to NO_3^-.[32] Dissimilatory nitrate reduction (DNRA), like reductive assimilation, generally conserves a system's N. Although data is scarce *Tiedje et al.* hypothesized that competition between DNRA and denitrification for NO_3^- supplies favors DNRA when NO_3^- is limiting, and denitrification when carbon (e- donor) supplies are limiting.[33] If nitrate is dissimilated to ammonia, it could end up volatilizing or escaping to the troposphere as NO during nitrification, in which case it will be transported off site but eventually redeposited by rain and cycled until reduced to N_2O or N_2. At least some of these dissimilatory reductions to NH_4^+ can yield small amounts of N_2O as a minor product.[34] N_2O has been increasingly studied because it is a greenhouse gas roughly 200 times as efficient at trapping heat as CO_2, and because it contributes to stratospheric ozone destruction.[35]

Anaerobic ammonia oxidation ("annamox") has been observed in a fluidized-bed reactor treating effluent from methanogenesis according to the reaction:

$$3\,NO_3^- + 5NH_4^+ \rightarrow 4N_2 + 9H_2O + 2H^+ \ (\Delta G^{o\prime} = -297 \text{ kJ/mol } NH_4^+)$$

However, the organisms catalyzing the reaction remain elusive.[36] Alternatively, an annamox reaction currently being used in wastewater treatment in the Netherlands uses a

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[29] Anderson, Iris Cofman "A Comparison of NO and N2O production by the autotrophic nitrifier Nitrosomonas europaea and the Heterotrophic Nitrifier Alcaligenes faecalis" Applied and Environmental Microbiology, Nov. 1993 p. 3525-3533 pg. 3525

[30] Schmidt, Ingo and Bock, Eberhard "Anaerobic ammonia oxidation with nitrogen dioxide by Nitrosomonas eutropha" Arch Microbiology 167:106-111 1997 pg. 106

[31] Zumft 1997 pg. 594

[32] Tesoriero 2000 pg. 1545

[33] Korom 1992 pg.1659

[34] Ibid.

[35] Delwiche, C.C. "Denitrification, Nitrification, and Atmospheric Nitrous Oxide" John Wiley & Sons 1981 pg. 20

[36] Ibid. pg. 595

stoichiometric amount of NO_2^-, according to the following equation (with hydrazine as a notable intermediate):[37]

$NH_4^+ + NO_2- \rightarrow N_2 + 2H_2O$

The main actors in this transformation are somewhat rare and slow growing planctomyces of the genera Brocadia and Kuenenia (fresh water), and Scalindua (marine).[38]

With the discovery of such alternative metabolisms comes an increasing awareness that nitrification and denitrification, once thought to occupy different physical zones according O_2 availability, probably coexist along with DNRA and annamox across a wider spectrum of the redoxcline, with individual species optimized for numerous niches along the substrate gradients.

REGULATION OF ENZYME ACTIVITY IN THE ENVIRONMENT

For many denitrifiers the presence of O_2 represses synthesis and activity of denitrifying enzymes, although the extent varies considerably.[39] The main exogenous signals that induce the synthesis of the denitrification systems are low oxygen tension and the presence of a respirable N oxide.[40] A high NO_3^- concentration has been found to inhibit NoR, causing accumulation of NO_2^- and a greater mole fraction of N_2O.[41] The later reductases in the denitrification sequence are somewhat more O_2 sensitive than the earlier ones.[42]

At high NO_3^- concentrations, the predominant gas produced is N_2O.[43] The reason is presumably that NO_3^- is a better electron acceptor than N_2O, so NO_3^- will be preferentially reduced whenever both are available. In highly anoxic environments where OC is not limiting, complete reduction of NO_3^- to N_2 or dissimilatory reduction to NH_4^+ with very little N_2O production is expected.[44] Bollmann et al. (1998) found that N_2O release by nitrification and denitrification increase with decreasing O_2 partial pressure, reaching a maximum under anoxic conditions when denitrification dominates. In their study the N_2O release by nitrification was dominant at higher O_2 partial pressure, reached a maximum at 0.1-0.5% O_2 and then decreased again. At lower partial pressures

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[37] Kuai Linping and Verstraete, Willy "Ammonium removal by the Oxygen Limited autotrophic nitrification-denitrification system" Applied and Environmental Microbiology, Nov. 1998 p 4500-4506 pg. 4500

[38] Wikipedia "Anammox" - http://en.wikipedia.org/wiki/Anammox

[39] Martin 1998 pg. 175

[40] Zumft pg. 583

[41] Knowles 1982 pg. 49

[42] Ibid. pg. 48

[43] Delwiche 1981 pg. 142

[44] Ibid. pg. 143

denitrification was the main source of gaseous N emissions with a higher N_2O mole fraction.[45]

The presence of NO_3^- has been found to stimulate the expression and induction of all reductases, while NO_2^-, NO and N_2O each stimulate synthesis of their own respective enzymes.[46] The conversion of NO to N_2O has a redox potential E_o'(pH 7) of +1,177 mV and a free energy $\Delta G^{o\prime}$, of –306.3kJ/mol. It is energetically comparable to the respiration of N_2O to N_2 [E_o' (pH 7) = 1,352 mV; $\Delta G^{o\prime}$=-339.5 kJ/mol] and both reactions are thermodynamically more favorable than the respiration of nitrate to nitrite.[47] Thermodynamic considerations alone however may not govern the amount of usable energy obtainable for the organism. For example NO reductase is not considered to be a proton pump. Growth yield studies show that the overall reduction of nitrite to N_2O is energy conserving.[48] Although the energetics are poorly understood, it seems likely that denitrifiers in the presence of adequate NO_3^- may prefer to loop the more favorable reduction sequence from NaR through NoR neglecting the final reductive step and resulting in a buildup of N_2O. Some researchers have attributed observed net N_2O production when NO_3^- and OC are not limiting to a lag in synthesis of N_2OR[49]

Nitric Oxide in excess is toxic in varying degrees to bacteria, fungi, microbial parasites, tumor cells and viruses, due to the formation of metal-nitrosyl complexes with heme, copper and iron-sulfur proteins.[50] NO metabolism is integral to denitrification, but the compound is toxic for denitrifiers as well.[51] The control of nitrite reduction and nitric oxide reduction is coordinated to ensure removal of toxic NO by NoR or alternatively to down regulate nitrite reduction. The steady state concentration of free NO during denitrification is maintained at a very low level, by tight coupling of reactions and by configuration of the NO reductase in the inner membrane and NO generation in the periplasm to form an effective barrier to NO penetration to the cytoplasm.[52] This efficient regulation and suppressed release of NO initially made it difficult to establish nitric oxide as an obligatory free intermediate.[53]

MOLE FRACTION OF GASEOUS N RELEASE

The regulation of NO, N_2O and N_2 release by nitrification and denitrification has been described by the 'hole in the pipe' model.[54] This concept has two dimensions analogous

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[45] Bollmann, Annette and Conrad, Ralf, "Influence of O2 availability on NO and N2O release by nitrification and denitrification in soils" Global Change Biology 1998 4 387-396 pg. 387

[46] Korner and Zumft 1989 pg. 1670

[47] Zumft 1997 pg. 565

[48] Ibid pg. 565

[49] Betlach, Michael and Tiedje, James "Kinetic Explanation for Accumulation of Nitrite, Nitric Oxide, and Nitrous Oxide During bacterial Denitrification" Applied and Environmental Microbiology, Dec. 1981, p 1074-1084 pg. 1074

[50] Schmidt and Bock 1997 pg. 110

[51] Zumft pg. 563

[52] Ibid pg. 565

[53] Ye, et al. "Denitrification: Production and Consumption of Nitric Oxide" Applied and Environmental Microbiology, Apr. 1994, p. 1053-1058 pg. 1053

[54] Bollmann and Conrad 1998 pg. 388

to nitrification and denitrification: the 'diameter of the pipe' relates to factors that regulate their rates, and the size of consecutive holes in the pipe relates to factors that regulate the ratio of the released gases. A third factor considers the diffusion of the gases away from the pipes.[55]

When concentration of nitrate ion is high compared with available organic substrate, N_2O is usually a larger fraction of the total denitrified gas.[56] In general the proportion of N_2 is smaller earlier in the denitrification process than later on.[57] NaR and NiR undergo derepression before N_2OR does, with the result that N_2O becomes the dominant product.[58] In the Aberjona river, high but variable BOD and constant flushing by storm events may serve to continually modulate the redoxcline, essentially resetting the denitrification pathways and favoring a high N_2O mole fraction. In small urban rivers shifting chemical gradients caused by hydrologic events, storm drain and effluent turbulence, and the influx of groundwater nitrate may act to refresh the sequence of reductase derepression, with an emphasis on conversion of more oxidized species.[59] This type of environment may in fact select for nitrifying and denitrifying bacteria at the sediment water interface suited to a wider fundamental niche for potential redox conditions.

Other factors influencing mole fraction include the availability and type of organic carbon compounds. Different organic compounds that support equal rates of denitrification may nevertheless give different mole fractions of N_2O in the products.[60] In general, as temperature and pH decrease, the N_2O mole fraction increases.[61] Some studies have shown surprisingly little temperature dependence of nitrification and denitrification in aquatic sediments, while others note a seasonal variability (probably due to changes in DOC and uptake of NO_3^-).[62]

NITROGEN TRANSPORT

In croplands fertilized by ammonia or urea-based compounds, or in soils where organic N pools are mineralized, oxidation of NH_3 by bacteria leads to the loss of available N primarily through leaching of nitrate, although other N species are soluble and are often important components of watershed fluxes. While NH_3, present primarily as ammonium (NH_4^+) in soils, remains bound to negatively charged clay particles exhibiting "cation exchange capacity," negatively charged NO_3^- is repelled and more readily leached into ground and surface waters.[63]

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[55] Ibid.
[56] Delwiche, 1981 pg. 8
[57] Ibid. pg. 144
[58] Knowles 1982 pg. 48
[59] Ibid.
[60] Ibid.
[61] Delwiche 1981 pg. 144
[62] Knowles 1982 pg. 49
[63] Finan 2002 pg. 299

Once NO_3^- is leached from soils several fates are possible, including uptake by plants, assimilatory reduction into microbial biomass, dissimilatory nitrate reduction to ammonia, denitrification, and export to receiving waters.[64]

Riparian zones have been described as "hot spots" of denitrification activity. As NO_3^- loaded groundwater flows through carbon rich, anaerobic sediments, high rates of denitrification can be supported.[65] Sites of nitrification and denitrification can be heterogeneously distributed in three dimensions in and around streams, with N supplied as various species in groundwater flowing into sediments and in surface water flowing over biofilms at the sediment water interface.[66] It has been established that high rates of hyporheic exchange can support extraordinary rates of nitrification and denitrification; in one large plains river close to half the annual nitrate input was removed by denitrification.[67]

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[64] Korom 1992 pg.1658

[65] McClain et al. "Biogeochemical Hot Spots and Hot Moments at the Interface of Terrestrial and Aquatic Ecosystems" Ecosystems (2003) 6:301-312

[66] Nishio et al. "Estimates of denitrification and Nitrification in Coastal and Estuarine Sediments" Applied and Environmental Microbiology Feb, 1983 p. 444-450 pg. 447

[67] Sjodin, et al. "Denitrification as a component of the nitrogen budget for a large plains river" Biogeochemistry 39:327-342 1997 pg. 327

CHAPTER II
ANTHROPOGENIC NITROGEN: HISTORY, TRENDS, AND CONSEQUENCES

HISTORY

In 1840 prodigious chemist Justus von Liebig, renowned among other things for his law of the minimum (that plant growth is limited by the nutrient present in the least adequate amount), proclaimed the principle objective of agriculture to be the production of digestible nitrogen.[68] Before von Liebig's time, long before Winogradsky isolated nitrifying bacteria (1889), before Hellriegel and Wilfarth demonstrated the nature of symbiotic nitrogen fixation (1888) (suggested by the work of Boussingault in 1838), before even Scheele and Rutherford (independently in 1772) and later Lavoisier (1770s) described "nitrogen," (so named by Chaptal in 1790), farmers since the dawn of the agricultural revolution had collectively and empirically evolved a regime dedicated to the delivery of limited nitrogen supplies in food crops: fertilization, fallow and crop rotation.[69]

It is therefore not surprising that when in 1804 the German explorer Alexander von Humboldt brought a sample of pacific guano to Europe, it was immediately prized as a valuable fertilizer and so launched a century of Peruvian guano and Chilean nitrate mining enterprise in the Americas.[70] Importation of guano into Britain began around 1820, and eventually peaked at 300,000 tons per annum.[71] Aware of their interest in this sphere, the United States (with imports peaking at 175,000 tons) promulgated the Guano Islands Act of 1856:

"Whenever any citizen of the United States discovers a deposit of guano on any island, rock, or key, not within the lawful jurisdiction of any other government, and not occupied by the citizens of any other government, and takes peaceable possession thereof, and

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[68] Smil, 2001, pg. 155

[69] Ibid. pg. 3-15

[70] Leigh, G.J., "The Worlds Greatest Fix, A History of Nitrogen and Agriculture", Oxford University Press, 2004 pg. 80

[71] Ibid. pg. 81

occupies the same, such island, rock, or key may, at the discretion of the President, be considered as appertaining to the United States."[72]

The acquisition of several pacific islands (Christmas and Midway for example) ensued.[73] Of course, in addition to inorganic nitrogen in fertilizer, the importance of nitrates in particular is paramount in explosives manufacture, and for this reason "Instructions for the Manufacture of Saltpetre" from organic waste piles was a relevant military publication in the blockaded south during the Civil War.[74] Meanwhile, conflicting claims over guano and nitrate trading and territory rights (and the substantial sums of money involved) escalated into a full-blown war in 1879 between an ultimately victorious Chile and an allied Peru and Bolivia.[75]

Considerations of wartime nitrogen necessity provoked the US to pass laws as late as 1933 reserving the right, in case of national emergency, to:

"...take possession of all or any part of the property [ ] for the purpose of manufacturing explosives or for other war purposes; but, if this right is exercised by the Government, it shall pay the reasonable and fair damages that may be suffered by any party whose contract for the purchase of electric power or fixed nitrogen or fertilizer ingredients is violated, after the amount of the damages has been fixed by the United States Court of Federal Claims in proceedings instituted and conducted for that purpose under rules prescribed by the court.[76]

By far the most important nitrogen-related historical development, and arguably the most important invention of the 20th century, is the discovery by German chemist Fritz Haber in 1909 of a process for fixing atmospheric nitrogen. Using an osmium catalyst, at a temperature and pressure of about 550°C and 18Mpa, Haber demonstrated the viability of synthetic ammonia production from its elements.[77] Under the direction of Carl Bosch of the BASF corporation, and using a cheaper iron catalyst, Haber's laboratory experiment was scaled up to an industrial process that, while continually improving, differs remarkably little from the 1909 patent today.

In 1911, 11 tons of ammonia were synthesized at the BASF corporation's Ludwigshafen compound using the Haber-Bosch Process, and by 1913 the world's first nitrogen fixing industrial plant was opened at Oppau.[78] The advent of World War I and the allied blockade of Chilean nitrates precipitated the creation of the first "military industrial complex," as the Second Reich turned to BASF to greatly expand ammonia synthesis and

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[72] US Code TITLE 48, CHAPTER 8, § 1411

[73] Leigh, 2004, pg. 81

[74] Leconte, J "Instructions for the Manufacture of Saltpetre" Charles P. Pelham, State Printer, Columbia S.C. 1862

[75] Ibid. pg. 85

[76] US Code TITLE 16 CHAPTER 12A § 831s

[77] Smil, 2001, pg. 80

[78] Ibid. pg. 102

oxidation to $NaNO_3$ for munitions to support (and ultimately prolong) the war effort. After the war the plants were reconfigured for fertilizer manufacture, and globally production remained stable until the second World War, at which point the need for explosives again led to a major increase in synthetic nitrogen production. Between 1940 and 1950 the number of ammonia plants worldwide had doubled. After the war production was again shifted back to fertilizers and markets were sought to match the huge gains in capacity, which soared to a peak of 141 million tons in 1989.[79] By 1996, the total worldwide annual commercial value of synthetic nitrogen products had reached U.S. $50 billion.[80]

TRENDS

Throughout the 20th century, synthetic nitrogen production has been a strategic and economic necessity for nation states, for its critical role in both destroying and sustaining human life. Today more than 60 countries produce nitrogen, although since the 1970's the pressures of global markets have resulted in a shift in new construction to natural gas-rich countries, because the feedstock can be up to 90% of the production cost.[81] However, since around 80% of fertilizer is consumed in the country where it is produced, the distribution of capacity is shifting generally towards developing countries (55% of global production), with China and India now producing over one-third of the world's synthetic nitrogen.[82]

Although the efficacy of fertilizers in agriculture yields was recognized earlier, the widespread and systematic use of fertilizers took off only in the 1950's because of the confluence of three favorable factors. The first is the overcapacity in the wake of WW II mentioned above, and the second is the demand driven by population expansion. The third factor that wedded the first two was the highly productive agricultural approach combining fertilizers, hybrid grain varieties and chemical pest control developed in the 1950's by the Rockefeller foundation and propagated worldwide as "the green revolution." During this period, the burgeoning world population (which grew from 2.5 to 6.5 billion) was supported by a spectacular increase in global agricultural productivity, accomplished with an actual (slight) decline in the area of cropped land (figure x). This revolution was fueled by fixed nitrogen - and by extension the fossil fuels used in Haber-Bosch and fuels for mechanization, overhead and transportation - supplied to crops specifically bred for high yields under fertilization.

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[79] Maxwell, Gary R. "Synthetic Nitrogen Products, A Practical Guide to the Products and Processes", Kluwer Academic/Plenum Publishers, 2004, pg. 25

[80] Ibid. pg. 15

[81] Ibid. pg. 16

[82] Ibid.

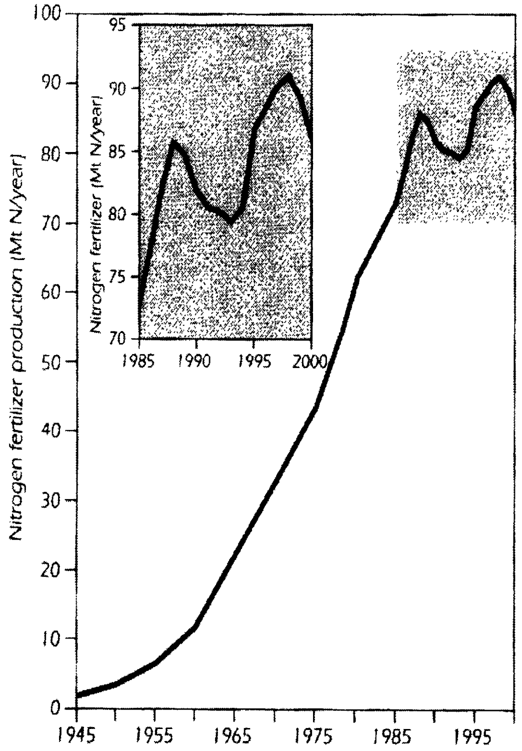
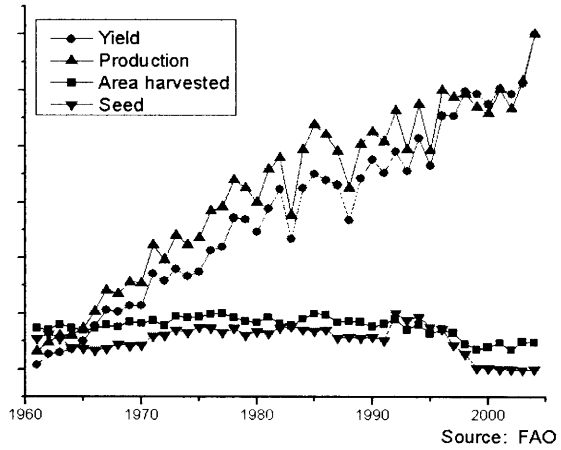


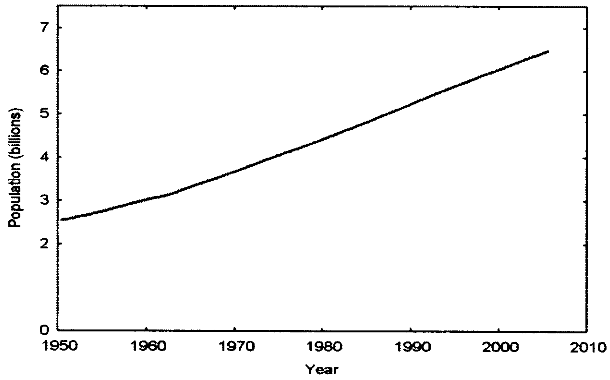
Figure 4 Global Production of NH3 based fertilizers, 1945-2000, Smil 2001

Total world production of coarse grain, 1961-2004



Source: FAO

Figure 3.1 and 3.2



Modern agriculture has consumed a growing amount of modern energy supplies, with a 110% increase in indirect energy use in the US agricultural sector since 1965, due largely to the methane feedstock required for nitrogen fixation.[83] However, direct energy use (farm machinery, irrigation equipment, transportation) has remained nearly constant, reflecting the overall mechanization of agriculture and the increasing efficiency of production methods. In terms of both direct and indirect energy consumption per unit of agricultural output, U.S. agriculture has increased the energy efficiency of production by 27% since 1965.[84] Food production in its entirety accounts for about 17% (62,200PJ) of global energy consumption, while fertilizers account for 1% (3660PJ).[85] Significant gains have been made in improving the energy efficiency of industrial nitrogen fixation, from about 120GJ ton^{-1} N at Oppau down to around 30 GJ ton^{-1} N in the best plants today

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[83] Schnepf, Randy "Energy Use in Agriculture: Background and Issues" CRS Report for Congress, November 19, 2004 pg. 8

[84] Ibid.

[85] Ramirez, C.A., Worrell, E. "Feeding fossil fuels to the soil, An analysis of energy embedded and technological learning in the fertilizer industry" Resources, Conservation and Recycling 46(2006) 75-93

(close to the stoichiometric limit of 20GJ ton^{-1} N).[86] However, with prices as low as $300 ton^{-1} NH_3 since the 1970s, the growth in demand (3.8% per annum) has outstripped gains in efficiency, resulting in a growing share of world energy demand.[87]

CONSEQUENCES

Since the 1970's the large-scale production of reactive nitrogen has been increasingly examined from the perspective of release to the environment and its potential ecological or human health consequences. Since then a number of concerns have been articulated, including nitrate toxicity at high concentrations in drinking water, acid rain and smog formation from atmospheric (usually combustion derived) nitrogen oxides, eutrophication of surface waters, hypoxia and coastal "dead zones," and the global warming potential of anthropogenic N_2O emissions.

Although application methods, timing, and differences between cropping schemes plays a large role in the fate of fertilizer N, an example from rice agriculture indicates that for every 100kg fertilizer applied to a hectare, 4.3kg remains as inorganic NH_4^+ in soils, 54.7kg are lost to denitrification and leaching, 19.1 kg are assimilated into harvested plant biomass, and 21.4kg are retained as organic N in soil and crop residue.[88] A large fraction of fertilizer exits the agricultural system and is leached into ground and surface waters, typically as nitrate (see chapter I, nitrogen transport).

Methemoglobinemia

Nitrate in water supplies can be toxic to human and animal health: when ingested at high levels gut microbes convert nitrate to nitrite, which then changes the structure of hemoglobin cells in the blood and renders them unable to carry oxygen (a condition known as methemoglobinemia or blue baby syndrome).[89] For this reason in the U.S. the MCL (maximum concentration level) standard for nitrate in drinking water is 10mg L^{-1}.[90]

Eutrophication and hypoxia

Nitrogen fertilizers provide substantial productive and economic gains at relatively low costs, but their pervasive use in agriculture and deposition from combustion sources has led to "N saturated conditions."[91] Under N saturation, nitrogen is no longer the limiting nutrient and hence further uptake by natural systems ceases, and excess nitrate leaches from soils and enters surface and groundwater supplies where it combines with dissolved reactive nitrogen from industrial effluent and urban wastewater. This load of excess nutrient eventually flows downstream from watersheds to major drainage basins and

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[86] Smil. 2001, pg. 202

[87] Ramirez 2006. pg 75

[88] Smil. 2001, pg. 186

[89] Martin, et. al. "Review: Denitrification in Temperate Climate Riparian Zones" Water, Air, and Soil Pollution 111:171-186 1999 pg. 173

[90] Korom, Scott F. "Natural Denitrification in the Saturated Zone: A Review" Water Resources Research, Vol. 28 No. 6 pgs 1657-1668 June 1992 pg. 1659

[91] Aber, J.D, Nadelhoffer, K. J, Steudler, P, Melillo, J. M "Nitrogen Saturation in Northern Forest Ecosystems" Bioscience; Jun 1989; 39, 6

ultimately to bays and coastal areas where it creates conditions of "eutrophication", or nutrient pollution, the largest overall source of impairment of U.S. rivers and streams.[92].

Eutrophication often results in increased primary productivity, and a decrease in species richness and diversity in aquatic systems.[93] Increased Nr shifts the payoff structures for various N assimilation strategies and thus alters the dynamics of competetive ecology. A commonly observed result is an overabundance of algal species (some of which are toxic) that lack predators and overwhelm the ecosystem, block incoming light, eventually die off and sink to sediments where they are decomposed by microbes that consume oxygen. The resulting lack of O_2 ("hypoxia" or "anoxia") in the water column leads to decrease in species diversity and an alteration of ecosystem structure in favor of tolerant species.[94] The phenomenon is popularly referred to as a "dead zone" because many aquatic communities (including ones that support commercial fisheries) can no longer flourish.[95] There are now major "dead zones" in 42 of 138 U.S. bays, the most infamous of which forms nearly every year in the Gulf of Mexico at the mouth of the Mississippi and Atchafalaya rivers, covering up to 20,000 km^2 and attributed to fertilizer application throughout the Midwest.[96]

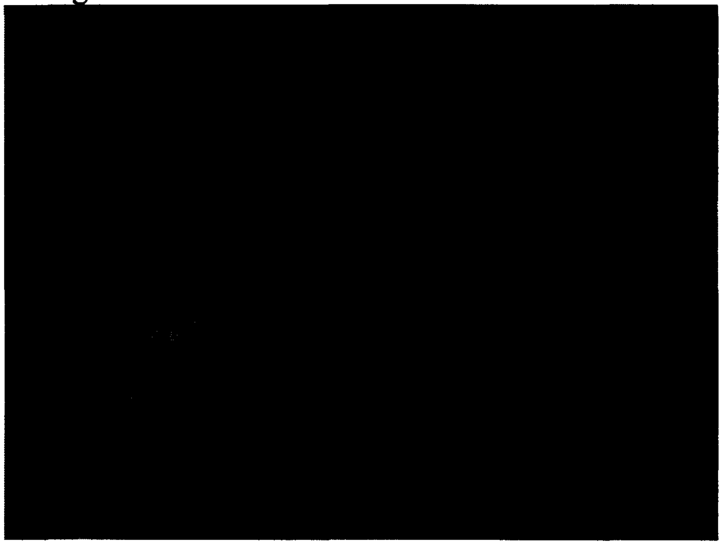

Figure 5 Satellite Image of "Dead Zone" hypoxia

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[92] Tesoriero, et. al "Mechanism and rate of denitrification in an agricultural watershed: Electron and mass balance along groundwater flow paths" Water Resources Research Vol 36 No 6 pgs 1545-1559, June 2000 pg. 1545

[93] Coles, J.F., Cuffney, T.F., McMahon, Gerard, and Beaulieu, K.M., 2004, The effects of urbanization on the biological, physical, and chemical characteristics of coastal New England streams: U.S. Geological Survey Professional Paper 1695

[94] Rabalais, N. N, Eugene Turner, R, Scavia Donald "Beyond Science into Policy: Gulf of Mexico Hypoxia and the Mississippi River" Plenary Address, American Institute of Biological Sciences annual meeting, March 2001

[95] Driscoll et. Al. "Nitrogen Pollution in the Northeastern United States: Sources, Effects, and Management Options" BioScience Vol. 53 No. 4 April 2003 (pg 365)

[96] Franz, Damon "Group's report links coastal 'dead zones' to farm policy" Greenwire 08/29/2001

http://serc.carleton.edu/images/microbelife/topics/General_Collection_deadzone_350.jpg

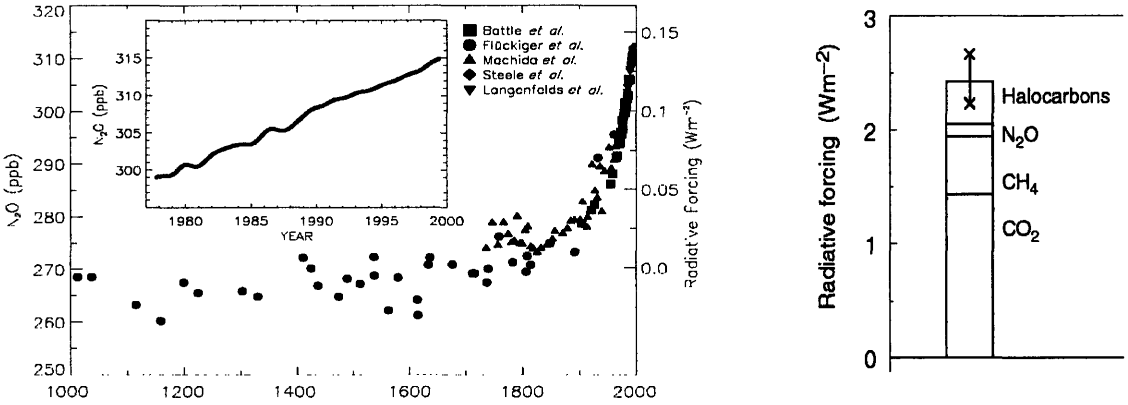

Figure 6 Nitrous Oxide Concentration in the Atmosphere

Nitrous oxide

Nitrous oxide is generally non reactive in the troposphere; however, as it migrates into the stratosphere it plays a significant role in terms of heat trapping potential (100-yr GWP = 296)[97] as a "greenhouse gas," and can deplete stratospheric ozone upon photochemical degradation to NO.

Atmospheric nitrous oxide concentration has increased from 280ppbv during the preindustrial period to 330 ppbv today, and is estimated to be responsible for about 5% of total "greenhouse effect."[98] Although present at much lower concentrations than CO_2 or CH_4, it traps heat at a much higher efficiency (by a factor of 200 and 10 respectively).[99] Thus much attention has been paid to the role of N_2O in global climate change and as a source of ozone-destroying NO in the stratosphere.[100] The sources for N_2O are not well quantified, but a global emission of 16.4 Tg N yr^{-1} is inferred from the sink strength (1510 Tg N in the atmosphere divided by a lifetime of 114 years) plus the rate of increase in atmospheric pools.[101]

As discussed in Chapter I, non-limiting concentrations of NO_3^- and organic carbon may favor N_2O production, and eutrophication generally tends to lead to an accumulation of

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[97] IPCC, 2001: Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change [Houghton et al.] Cambridge University Press, 2001, pg. 244

[98] Kumar, Upendra et. al. "Role of nitrification inhibitors on nitrous oxide emissions in a fertilized alluvial clay loam under different moisture regimes." Current Science Vol. 79. No. 2, July 200 pg. 224

[99] TAR 2001, pg. 244

[100] Zumft 1997 pg. 534

[101] TAR 2001, pg. 250

both. It is currently unknown as to whether N_2O production under anthropogenic N loading is strictly proportional or whether perturbations of the natural N cycle alters the mole fraction of denitrification products. There is evidence of faster than linear feedback of N_2O production from soils in response to N addition.[102] If this observation holds generally, then the chain of relationships linking industrial N-fixation, the modern agricultural N regime, the organization of livestock, and the waste infrastructure of population centers may not only accelerate N_2O production through increased throughput, but actually bias microbial transformation pathways towards an increased N_2O mole fraction in the denitrificaton. This is of concern in light of the substantial increase in fertilizer applications projected in developing countries, and considering that while many feasible strategies exist to reduce CO_2 emissions, the same cannot be said for N_2O.[103] Characterization and quantification of the nitrification/ denitrification regime in polluted urban watersheds is therefore critical both to more accurately model global emissions budgets and understand potential avenues of N_2O emission mitigation.

Urban Stream Syndrome

While around 80 million tons[104]of industrially fixed nitrogen fertilizer are applied annually to agricultural fields, the fate of this nitrogen is not concluded by an estimation of plant uptake, immobilization, field nitrification, denitrification and leaching fluxes. Nitrate leaching and human consumption of agricultural products ultimately concentrate N into surface waters, primarily near urban centers which are in turn usually near coastal zones. Around half of the world's population, 3 billion people, live within 100km of the coast in increasingly dense urban settlements.[105] At excretion rates of approximately 3.3kg N per year per capita, human populations alone concentrate 10Mtons of nitrogen in coastal areas.[106] Wastewater treatment schemes increasingly reflect the need to handle high nitrogen loads to reduce Biological Oxygen Demand of effluents. As with other eutrified systems, urban streams exhibit significantly increased benthic algal biomass, increased rates of detrituts decomposition, and increased abundances of macroinvertebrate consumers.[107]

In addition to wasterwater loading, rising NO_3^- concentrations in groundwater, the draining of wetlands, narrowing urban riparian zones and increasing impervious surfaces are common attributes of the "urban stream syndrome," whereby yields from urban watersheds are disproportionally increased through land conversions, current and legacy pollutants, turf fertilizer, atmospheric deposition and decreased natural sinks due to storm drainage networks.[108][109] Land conversion from natural to urban and suburban uses

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[102] Ibid, pg. 251

[103] Ibid.

[104] "Global Estimates of Gaseous Emissions of NH_3, NO and N_2O from Agricultural Land" Food and Agriculture Organization, Chapter 1, pg. 1

[105] Paerl et al.

[106] Bowen

[107] Smith, V.H. "Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems" Environmental Pollution 100 (1999) 179-196 pg. 184

[108] Wakida, F.T., and Lerner, D.N. "Nitrate leaching from construction sites to groundwater in the Nottingham, UK, urban area" Water Science and Technology, Vol 45 No 9 pp 243-248, 2002

releases organic N stored in soil pools (by far the largest pool of fixed N in terrestrial systems at 2-7 tons N ha^{-1} in the top meter of soil).[110][111] Industrial operations that handle N in some way may legally (via NPDES permit) or illegally release reactive nitrogen to the environment, and may have done so in the past to an unknown extent. In 1999 49.2 million households purchased lawn and garden fertilizers.[112] Approximately 50% of New England suburban households apply lawn fertilizers at an average rate of 0.86 kg N ha^{-1} per year, and certain land uses such as golf courses may apply fertilizers at agricultural rates of more than 20 kg N ha^{-1} per year.[113] Depending on proximity to industrial and urban centers, atmospheric deposition of reactive nitrogen can range from negligible amounts to nearly 20 kg N ha^{-1} per year. The ability of urban catchments to retain and denitrify increased N loads is typically compromised by the effect of drainage systems that collect runoff from impervious surfaces and inject N loads directly into rivers and streams, bypassing groundwater flow and "hot spots" of denitrification in riparian zones, which are themselves reduced by artificial channel banks and flood control structures. The confluence of these factors has lead to a steady increase in nitrate concentrations in major urban river basins of the world.[114]

NOx

NOx, shorthand for various species of nitrogen oxides, is a direct precursor of ground-level ozone and photochemical smog. It is also, after SOx, the second largest contributor to acid precipitation.[115] Ozone and smog contribute to acute respiratory illness, especially in urban centers where sources are concentrated and spikes in ambient concentration can be induced by stagnant weather conditions. Acid precipitation can negatively affect plant and animal health and ecosystem function, notably in the forests and lakes of the northern U.S. and Canada. It also contributes to the premature weathering of stone buildings and sculptures.

In most pristine and especially upland catchments, atmospheric deposition is a major source of N.[116] However, even in some heavily eutrophic catchments, such as the

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[109] Walsh et al. "The urban stream syndrome: current knowledge and the search for a cure" J. N. Am. Bethnol. Soc, 2005, 24(3):706-723

[110] Legg and Messeinger

[111] Wakida 2002, pg. 243

[112] Robbins, Paul and Sharp, Julie "Producing and Consuming Chemicals: The Moral Economy of the American Lawn" Economic Geography, Oct 2003; 79, 4 pg. 427

[113] White, L. "The Contribution of Lawn Fertilizer to the Nitrogen Loading of Cape Cod Embayments" Masters Thesis, University of Rhode Island, 2003

[114] Mosier, et al. "Policy Implications of human-accelerated nitrogen cycling" Biogeochemistry 57/58: 477-516, 2002

[115] Moomaw, W. R. "Energy, Industry and Nitrogen: Strategies for Decreasing Reactive Nitrogen Emissions" Ambio Vol. 31 No. 2, March 2002 pg. 184

[116] Li, X, Ambrose, R. B., Araujo, R, "Modeling Mineral Nitrogen Export from a Forest Terrestrial Ecosystem to Streams" Transactions of the American Society of Agricultural Engineers, Vol 47 (3): pg 733

Chesapeake Bay, atmospheric inputs of NOx can account for as much as 40% of nitrogen inputs.[117]

Prior to the industrial revolution the main global source of nitrogen oxides was the 7.7 M tons produced annually from lightning strikes.[118] Today anthropogenic inputs of nitrogen oxides from the burning of biomass and combustion of fossil fuels contribute approximately 30 M tons N yr^{-1} to the atmosphere.[119] In transportation, industry and energy production fuel N and molecular N from combustion air are oxidized into NO (approximately 2:1 depending on fuel N content), and subsequently react with ozone to produce NO_2.[120] At the high temperatures and pressures commonly found in internal combustion engines, dinitrogen and oxygen react directly to produce nitric oxide ($N_2+O_2 \rightarrow 2NO$), while organically bound nitrogen in fuel can be oxidized by pyrolysis according to the following schematic reaction:[121]

$$X\text{-}CH_2NH_2 + 3O_2 \rightarrow CO_2 + 2H_2O + NO_2 + X$$

Although there is no organic nitrogen in natural gas, it can be as much as 2% of petroleum fuels and coal.[122] While coal power plants can be fitted with scrubbing technology to remove NOx, it is particularly difficult to reduce emissions from the many small scale mobile sources in the transportation sector, which produce over half (55%) of all NOx emissions in the U.S.[123] Growth in this sector has tended to offset the effects of tail pipe regulations, and exhaust NH_3 and N_2O have actually increased as by-products of 3-way catalytic removal of NOx.[124]

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[117] Moomaw 2002 pg. 185

[118] FAO Chap. 1 pg. 3

[119] FAO "Global Estimates of Gaseous Emissions of NH3, NO and N2O from Agricultural Land" Chap. 1 pg. 3

[120] Erisman et al. "The European perspective on nitrogen emission and deposition" Environment International 29 (2003) pg. 312

[121] Moomaw 2002 pg. 184

[122] Ibid.

[123] Ibid. pg. 186

[124] Erisman 2003, pg. 323

CHAPTER III
POLITICAL RESPONSES TO NITROGEN POLLUTION ISSUES AND ANALYSIS OF RISK

GEOPOLITICAL RESPONSES TO NITROGEN POLLUTION

A clear relationship has been established between increases in urban land uses and nitrogen loads (see Chapter IV and discussion of the "urban stream syndrome" in Chapter II). Increased urbanization correlates with a number of water quality parameters, including nitrogen concentrations in streams, and is attributable to a variety of factors.[125] In the United States urban areas are expanding at rate of 1.4% per annum. Perhaps more significantly for global N fluxes, urbanization in developing countries with large rural populations is increasing at a much faster rate: 3.6% in China and 2.5% in India.[126] Global nitrogen export in rivers draining urban watersheds will most likely increase in the decades to come due to population growth and urban expansion.

Globally several agreements, mainly between European states, have been concluded to address international issues of nitrogen pollution. The early focus of these treaties was on trans-boundary (primarily atmospheric) pollutants, but by the end of the 20th century there was a recognized need for multi-pollutant initiatives addressing a range of consequences in both the atmosphere and terrestrial and aquatic environments. Major agreements are briefly summarized in the following paragraphs.

The EU Nitrates Directive is perhaps the most progressive treaty dealing with nitrogen pollution in that it addresses the vectors of N loading from a watershed perspective and identifies agricultural as a primary source. Compliance with the EU Nitrates Directives

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[125] Coles, James F., Cuffney, Thomas F., McMahon, Gerard, and Beaulieu, Karen M. "The Effects of Urbanization on the Biological, Physical, and Chemical Characteristics of Coastal New England Streams" Professional Paper 1695 U.S. Department of Interior, U.S. Geological Survey 2004

[126] The World Bank Group "World Development Indicators" 3.10 Urbanization, 2006

commenced for member states in 1991, whereby water quality is monitored annually and reported every four years, nitrate vulnerable zones (NVZs) are identified, codes of good practice in agriculture are adopted, and action programs are implemented in NVZs.[127] "Good practice" refers to specific guidelines on crop rotations, cover crops, irrigation and buffer zones to reduce nitrate leaching from agriculture.[128]

The earliest U.N. convention to address nitrogen pollution is the Convention on Long Range Trans-boundary Air Pollution (CLRTAP), signed in 1979 by 50 signatory countries as a direct outgrowth of scientific evidence in the 1960's linking sulphur emissions in continental Europe to the acidification of Scandanavian lakes.[129] Under the Gothenburg Protocol (1999) of the CLRTAP signed by 29 European nations, together with the U.S. and Canada, a multi-pollutant reduction strategy (including NOx) was stipulated to abate the effects of acidification, eutrophication and the effects of tropospheric ozone on human and ecological health.[130] Under the agreement each nation estimates its own critical loads, with an expected outcome of a 50% reduction in nitrogen oxides in the period 1990-2010 for Europe (excluding Russia). The U.S. and Canada have no defined emission reduction targets under this protocol.[131]

The U.N. Framework Convention on Climate Change (FCCC), initiated in response to concerns about the potential affects of global climate change, was ratified by 189 countries and entered into force in 1994, with more powerful, legally binding actions mandated via the 1997 Kyoto protocol (which the U.S. has not ratified as of 2006). The FCCC alone deals with N_2O emissions, and therein solely as a greenhouse gas. Despite the well-known effect whereby N_2O photochemically decomposes to NO and catalyzes stratospheric ozone depletion, N_2O is not featured in the Montreal Protocol on Substances that Deplete the Ozone Layer.[132]

Despite the human health and ecological costs of N pollution, both developing countries (especially China and India) and the United States have for the most part opted out of international agreements to limit atmospheric N emissions, presumably in the context of of perceived detrimental impacts of CO_2 reduction on their primarily hydrocarbon-based economies.

REGULATORY FRAMEWORKS FOR NITROGEN POLLUTION IN THE UNITED STATES

In the United States a comprehensive response to the effects of anthropogenic perturbation of the nitrogen cycle remains elusive, despite growing awareness and concern about this issue. However, most isolated problems arising from reactive nitrogen

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[127] Monteny GJ, "The EU Nitrates Directive: a European approach to combat water pollution from agriculture" ScientificWorldJournal. 2001 Dec 12;1 Suppl 2:927-35

[128] Ibid. pg 927

[129] United Nations Economic Commision for Europe, Convention on Long Range Trans-boundary Air Pollution website http://www.unece.org/env/lrtap/lrtap_h1.htm

[130] Erisman 2003, pg. 311

[131] Ibid. pg. 312

[132] Moomaw 2002, pg. 186

in the environment are currently addressed through some regulatory mechanism at the state or federal level.

Since the cities of Chicago and Cincinnati passed the first air pollution statutes in 1881, county governments had been involved in regulating smoke and soot from furnaces and locomotives.[133] The Federal government became involved with water pollution control with the passage of the Water Pollution Control Act of 1948, and with air pollution control in 1955 with the passage of the Air Pollution Control Act. Subsequent relevant legislation includes the Clean Air Act (CAA) (1963), the Water Quality Act (1965), Air Quality Act (1967), and the creation of the Environmental Protection Agency (EPA) on December 2, 1970.[134] The EPA was charged with the responsibility of setting National Ambient Air Quality Standards (NAAQS) and Maximum Concentration Levels (MCLs) and given the authority to develop emission standards for mobile and stationary sources.[135] The NAAQS standard for NOx is 0.053ppm (100 $\mu g\ m^{-3}$), while the MCL for nitrate and un-ionized ammonia is 10 $mg\ L^{-1}$ and 0.07-2.1 $mg\ L^{-1}$ respectively (the ammonia MCL depends varies with pH and temperature).

PERFORMANCE OF NITROGEN MANAGEMENT FRAMEWORKS

Despite redoubled regulatory oversight, nitrate concentrations in rivers globally have doubled since preindustrial times,[136] U.S. rivers increased 3 to 10-fold, and total national emissions of NOx increased 233 percent between 1940 and 1998 - although more slowly (by 19%) between 1970 and 1997 and with an actual slight decline in 1998.[137,138] Surface water data from 344 stations in the USGS National Stream Quality Accounting Network (NASQAN) from 1980 to 1989 showed no change in nitrate concentrations in 86% of stations, a downward trend in 8% and an upward trend in 6%.[139]

In the case of surface water N it is unclear whether this apparent plateau reflects changes in the anthropogenic N input regime, or merely mirrors earlier conditions and N fluxes largely independent of anthropogenic perturbations. If the former, a slowing of N loading may reflect the delayed formal recognition on the part of regulating agencies that 90% of total nitrogen discharge originates from non-point sources.[140] However, as discussed in Chapter II, reductions in emissions and effluents take place against a backdrop of growth in sources due to expansion of the population, agriculture and the

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[133] EPA, NATIONAL AIR POLLUTANT EMISSION TRENDS: 1900-1998 (March 2000) EPA 454/R-00-002 pg. 3-1

[134] Ibid.

[135] Ibid.

[136] Green et al. "Pre-Industrial and contemporary fluxes of nitrogen through rivers: a global assessment based on typology" Biogeochemistry 68:71-105, 2004 pg. 71

[137] Ibid. pg. 3-3

[138] Mosier, et al. "Policy Implications of human-accelerated nitrogen cycling" Biogeochemistry 57/58: 477-516, 2002 pg. 480

[139] Melillo, Jerry M, and Cowling, Ellis, B. "Reactive Nitrogen and Public Policies for Environmental Protection" Ambio Vol. 31 No. 2, March 2002, pg. 153

[140] Ibid.

economy, making appraisals of the efficacy of nitrogen policies difficult. Before attempting to evaluate serious, large scale attempts at mitigating nitrogen pollution in both the U.S. and Europe, this paper will briefly examine the issue of political will in the U.S. to effect N reduction strategies in contrast to available information that suggests European enforcement of N directives is broadly supported.

SECTOR ANALYSIS OF NITROGEN REGULATION

The responses to nitrogen pollution in the U.S. are deeply embedded in the political and economic reality of modern industrial agriculture, energy production, and automobiles.

Farmers in the United States (and Europe) are among the most productive in the world; they rightly view the application of fertilizer as a cheap, effective, and fundamental tool in their operations. In the U.S., agribusiness retains powerful lobbying forces (American Farm Bureau Federation, the National Corn Growers Association, the National Milk Producers Federation, the Association of Consulting Foresters of America, Deere & Co, etc.) to curry the favor of government representatives and secure protective policies and farm subsidies on the order of U.S. $15 billion per year.[141] Any move in the opposite direction, for example taxing nitrogen fertilizers to pay for remediation of N pollution, as is frequently suggested in the academic literature,[142,143,144] would instantly meet with tenacious opposition from agribusiness and the government representatives they influence, regardless of the economic and environmental sense of 'internalizing the external effects of N pollution.' Not only would it amount to a tax on farmers, the 'salt of the earth,' but it would easily be called "a tax on people" generally because it would affect food prices. For N loads due to fertilizers, the "polluter pays" approach is effectively off the table in the U.S.

In the automotive sector, the Arab oil embargo of 1973-74 precipitated the "Energy Policy Conservation Act," of 1975, Title V of which, "Improving Automotive Efficiency," established "Corporate Average Fuel Economy" (CAFE) standards for passenger cars and light trucks, with the goal of doubling new car fuel economy by model year 1985. Nitrogen oxide emission at the tailpipe is directly related to average miles per gallon, and today the CAFE standard for passenger car fleets is 27.5 mpg, as set by the National Highway Traffic Safety Administration (NHTSA) by reason of what Congress mandated as a "feasible" level.[145] Two major weaknesses of this arrangement are the relatively low penalty for non-compliance, and the notorious exemption of the increasingly popular greater than 8,500lb class Sports Utility Vehicle category. Asian

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[141] Environmental Working Group Farm Subsidy Database, November 2004, http://www.ewg.org

[142] Gömann, Horst, Kreins, Peter, Kunkel, Ralf, Wendland, Frank "Model based impact analysis of policy options aiming at reducing diffuse pollution by agriculture-a case study for the river Ems and sub-catchment of the Rhine" Environmental Modelling & Software 20(2005) 261-271 pg. 268

[143] Moomaw 2002, pg. 188, in the context of a general fossil fuel tax

[144] Wendland et al. "Impact of nitrogen reduction measures on the nitrogen loads of the river Ems and Rhine (Germany)" Physics and Chemistry of the Earth 30 (2005) 527-541

[145] NHTSA website http://www.nhtsa.dot.gov/cars/rules/cafe/overview.htm

manufactures have never been out of compliance with CAFE, while other major manufacturers routinely pay annual fines of U.S. $1-20 million, in an industry where manufacturers net profits ranging from the low billions to over U.S. $10 billion per year.[146] From a fuel economy point of view, drastic NOx emissions reductions are a dead issue.

However, to fulfill the 1990 Clean Air Act standard of 0.4g NOx mile^{-1} the EPA in 2004 and again in 2007 tightened regulations of tailpipe emissions of NOx and hydrocarbons, which the automotive industry meets by way of catalytic converters.[147] These three way converters (simultaneously performing the three reactions $2NOx \rightarrow O_2 + N_2$, $2CO + O_2 \rightarrow 2CO_2$, and $C_xH_y + n\ O_2 \rightarrow xCO_2 + mH_2O$) reduce combined NOx+HC emissions from 12 gram BHP-hour^{-1} to 3 gram BHP-hour^{-1} or less, with a further drop to 2 gram BHP-hour^{-1} by 2007.[148] Emissions regulations and catalytic converters have succeeded in keeping vehicular NOx emissions at 1970s levels despite a 280% growth in the fleet from 1969 to 2003 (from 73 to 204 million vehicles).[149]

Stationary sources of NOx have proven more difficult to abate than vehicles, due to the "grandfather" loophole in the Clean Air Act. In the U.S., older electric power plants are permitted to continue polluting at levels allowed prior to the promulgation of the latest regulations, on the assumption that they will eventually be phased out. In reality, the economic incentive is to maintain older power plants as long as possible to avoid the high pollution control costs of new plants.[150] Of the 886 coal power plants in America, half were built before 1975.[151]

Across the three sectors that generate the greatest N loads to U.S. watersheds, a familiar pattern of recalcitrance has emerged. Leveraging their particular economic or political endowments, the parties involved have responded to government regulation of nitrogen pollution by various strategies of preemption (agribusiness), non-compliance and token fines (automotive manufacturers), exploiting "grandfather" loopholes (energy industry) and extensive lobbying to preserve the status quo. This resistance is perhaps best exemplified in the ongoing controversy over the implementation of Total Maximum Daily Loads (TMDLs) for nitrogen species in surface waters.

CHALLENGES FACING AN INTEGRATED POLICY APPROACH TO NITROGEN POLLUTION

CASE STUDY: THE TOTAL MAXIMUM DAILY LOAD PROGRAM

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[146] Ibid.

[147] Moomaw, 2002, pg. 186

[148] Wikipedia, Purpose and function of Catalytic Converters, http://en.wikipedia.org/wiki/Catalytic_converter (BHP refers to "brake horse power," a measure of engine power apart from losses in the drive train)

[149] U.S. Census Bureau, Historical Household Statistics http://www.census.gov/hhes/www/income/histinc/h05.html, Federal Highway Administration, 1969 Nationwide Personal Transportation Survey, http://www.fhwa.dot.gov/ohim/1969/back.htm

[150] Moomaw, 2002, pg. 187

[151] Ibid.

Many experts have proposed a "cap and trade" policy for aquatic nitrogen pollutants, analogous to the successful market based approach taken with SOx in the EPA's Acid Rain Program and with NOx in the 1998 "NOx Sip Call".[152] This approach is designed to create an economic incentive for pollution reduction by encouraging action by those who can achieve reduction easily and cost-effectively and the sale of "credits" to those polluters who find it more efficient to purchase them than to reduce effluents.[153] While this market-based approach has been endorsed by the American Farm Bureau Federation, critics note that unlike air pollution trading, there is no total cap on watershed nitrogen budgets. Without a cap set significantly lower than current N loads, trading would merely serve to reallocate among sources.[154] The requisite "cap" aspect of the program is what the Clean Water Act designated the EPA to accomplish via the TMDL program. This initiative, however, has stagnated in the face of opposition on several levels.

As discussed earlier, the legal frameworks currently in place to deal with nitrogen pollution in the U.S. are fragmented across agencies and jurisdictions, are often unclear in their objectives, and in many cases rely on voluntary compliance. While the Federal Clean Water Act (CWA) of 1972 empowered the EPA to regulate 'point sources' and issue National Pollutant Discharge Elimination Systems (NPDES) permits to effluent dischargers, the monitoring and reporting of end-of-pipe discharges was in fact left to the discharger.[155] The EPA's authority to regulate non-point sources, while fairly explicit in the CWA, has been challenged repeatedly in court as recently as 2002.[156] Non point source pollution is both difficult and expensive to monitor and attribute, since runoff fluxes are highly dependant on a complex mixture of hydrologic, land use and climatic factors (see Chapter IV). Under section 303(d) of the CWA states are mandated to identify impaired waterways and establish Total Maximum Daily Limits (TMDLs) for nutrients such as nitrate. Since 1972 this has proceeded at a glacial pace, has included only point sources and has failed to result in reduced nutrient loads.

The EPA was propelled into action by citizen lawsuits in the 1980s to provide guidance for the TMDL program, and since then has faced constant political pressure from industry, state governments and environmental groups alike.[157] The former argue that the economic burden of compliance is too high, while the latter criticize the agency for betraying the goals of the CWA and failing to achieve adequate water quality (with states potentially arguing either position). Under the TMDL program states were responsible for designating impaired water bodies, developing TMDLs and implementing them, while the EPA had no framework in place to evaluate the legitimacy of the 303(d) designations and TMDLs, or enforce the implementation. An EPA initiative to reinforce the non-point source regulatory and enforcement aspect of section 303(d) by issuing an

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[152] USEPA website http://www.epa.gov/airmarkets/trading/basics/index.html

[153] Franz, Damon "EPA endorses pollution credit trading" Greenwire 01/14/2003

[154] Ibid.

[155] USEPA website http://www.epa.gov/owow/tmdl/policy.html

[156] Ibid.

[157] "Assessing the TMDL Approach to Water Quality Management" Committee to Assess the Scientific Basis of the Total Maximum Daily Load Approach to Water Pollution Reduction, Water Science and Technology Board, National Research Council, 2001 pg. 1

updated TMDL rule was suspended in October of 2000 in an unprecedented move by Congress, as agri-industry, point source dischargers, states and environmental groups alike objected to a spectrum of proclaimed deficiencies in the EPA's Announcement of Proposed Rulemaking (ANPRM).[158] Of the 34,000 comments entered into the record, 90% of them were critical of the TMDL rule.[159]

The political defeat of the TMDL rule was ultimately accomplished by an unwitting coalition of opposing interests. Agribusiness could read the writing on the wall: enforcement of TMDLs would inevitably require them to be held responsible for the millions of tons of fertilizer leaching from agricultural fields. EPA had already calculated that 70% of impaired river miles and half of impaired lake acreage was due to agricultural runoff.[160] Agribusiness spared no expense in damning the political torpedoes.

After years of bearing all responsibility for N loads, point source dischargers currently holding NPDES permits ostensibly might gain from a more equitable attribution of sources that held non-point agribusiness contributors accountable. Ultimately, however, permit holders begrudged a perceived extension of EPA authority and certain procedural changes to the permitting rules outlined in the ANPRM, and were clearly threatened by a cap on effluence that theoretically diminished in annual timesteps. Given that most point source dischargers of nitrogen are waste treatment plants, the enforcement of TMDLs would situate them uncomfortably between the lowering cap, and an obligation to treat the wastes of growing urban and suburban populations. Technical solutions to reducing N in wastewater treatment exist, but at an expense that thousands of publicly owned treatment works (POTWs) are disinclined to shoulder.[161]

Funding was the Achilles heel of the proposed TMDL rule, which had no provision for who would pay to assess and monitor 40,000 303(d) listed waterways, develop TMDLs, and implement abatement plans.[162] At a conservative estimate of $100,000 per TMDL, developing plans alone would cost U.S. $4 billion and implementation costs were speculated to be in the hundreds of billions.[163] Congress had no intention of allocating federal monies of that magnitude for the TMDL program, and states are generally not inclined to pursue unfunded mandates, especially in the face of strong resistance from both POTWs and the agri-industry lobby, which could bring considerably more pressure to bear at the state level.

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[158] USEPA website http://www.epa.gov/owow/tmdl/policy.html

[159] Ibid.

[160] Association of Metropolitan Sewerage Agencies (AMSA) TESTIMONY OF NORM LEBLANC, CHIEF, TECHNICAL SERVICES, HAMPTON ROADS SANITATION DISTRICT, VIRGINIA BEACH, VIRGINIA March 23, 2000, http://www.senate.gov/comm/environment_and_public_works/general/107th/leb_0323.htm

[161] Ibid.

[162] Ibid.

[163] AMSA, Leblanc 2000

Environmental groups monitoring the ad hoc TMDL process found much to protest in foot-dragging timetables, arbitrary designations of impairment and selection of criteria pollutants, and backlogs of unworkable implementation plans. Environmental groups such as the Sierra Club publicly decried state TMDL efforts as fraudulent betrayals of the public trust because the process was susceptible at the state level to "11th hour" back room deals with industry to relieve the economic burden of pollution reduction.[164]

Industry lobbies had ensured that Congress was alerted to the controversy surrounding TMDLs well in advance of the EPA's ANPRM. By march of 2000, the General Accounting Office (GAO) had issued a report highlighting a pervasive lack of data at the state level for setting ambient water quality standards to determine impaired waters and develop TMDLs.[165] The data collection requirements were onerous in extent and expense. Next the National Academy of Sciences got involved, after a Congressional request to validate the science of the TMDL program. A National Research Council committee was hastily assembled and four months later produced a report finding fault with the TMDL program on a number of procedural and methodological points ranging from model typology to calculation of uncertainty and error budgets.[166]

Rather than incorporating the suggestions of the NRC and others to fortify the proposed rule and move ahead, the EPA, in the midst of a sea change in political administrations and facing litigation in the DC circuit court, fully capitulated to political opposition in 2002.[167] In what reads as a rather bizarre formal withdrawal of the proposed rule, the EPA renounced its former logic, which had been clearly articulated in terms of its CWA mandate, in favor of the agribusiness argument for devolved authority to states. The EPA cited opposition on all sides, without addressing the effectively *countervailing* criticisms levied by environmental groups and the NRC on one hand, and agribusiness, dischargers the GAO and states on the other hand.[168] In a de facto victory for agribusiness, the EPA announced that the TMDL program would continue as before, with states free to choose their own level of commitment to slowly working through 303(d) lists to plan and implement what are in most cases toothless caps on N discharge.[169] Regarding the future direction of the TMDLs program, the EPA would not commit to any further rulemaking,[170] and as of 2006 TMDLs remain what they have been all along: a haphazard, dilatory, and somewhat fanciful exercise.

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[164] Benjamin, Charles "TMDL process a Fraud" Letter to Dennis Grams at EPA 1999 http://kansas.sierraclub.org/Planet/nl-99-0809-articles.htm#tmdl

[165] NRC 2001, pg 2.

[166] Ibid. pg 2-8

[167] USEPA website http://www.epa.gov/owow/tmdl/policy.html

[168] Ibid.

[169] Ibid.

[170] 40 CFR Part 9, "Withdrawal of Revisions to the Water Quality Planning and Management Regulation and Revisions to the National Pollutant Discharge Elimination System Program in Support of Revisions to the Water Quality Planning and Management Regulation; Final Rule" Federal Register, Vol. 68, No. 53, Wednesday, March 19, 2003

MAINTENANCE OF THE STATUS QUO

The history of EPA efforts to regulate nutrient pollution under the authority of the CWA is thus one of systematic obstruction by entrenched agribusiness interests, abetted by the occasional legal morass arising from their arch-rivals the environmental idealists and tossed by the winds of political change at the White House. Following the TMDL rule withdrawal, in another archetypical encounter in 2003 the EPA issued the Concentrated Animal Feedlot Operation (CAFO) rule aimed at reducing the substantial nutrient runoff from large animal feeding operations – and was promptly sued by both environmental and livestock groups for failing to adequately satisfy their (opposing) interests.[171] Analogous and parallel attempts by the U.S. Department of Agriculture (1998) to institute nutrient pollution control policies were similarly defeated by agribusiness lobbies arguing, with what must have been flagrantly transparent motives, that the legislation 'replicated' existing (ineffectual) EPA programs and interfered with its jurisdiction.[172]

The prevailing weak federal framework for capping nutrient loads to waterways has forced states to assume the burden for regulating non-point sources, in the absence of clear objectives and in the face of political pressure of agribusiness. In response to Chesapeake Bay fish kills numbering in the hundreds of thousands, Maryland issued the Water Quality Improvement Act of 1998. Attacked as 'anti-agriculture,' the law required farmers to carefully calibrate the amount of manure and other fertilizers they spread on farmland. Soon afterwards a bill was introduced that would suspend enforcement of the law and allow farmers to deny inspectors access to their properties – making compliance in essence voluntary.[173]

EXAMPLES OF LARGE SCALE N INPUT REDUCTION

Although many similarities exist, there is a significant departure between US and European approaches to air and water pollution management in that the U.S. employs a more fragmented approach driven by a legal code focused almost exclusively on human health standards, whereas the EU has adopted a "multiple-pollutant/multiple effects" mentality under a more integrated regulatory framework that more evenly weights both human health and ecosystem function criteria.[174] However, it is not clear that nitrogen management schemes of the past few decades have had any measurable impact on riverine nitrogen export in either the U.S. or Europe.

As discussed above, the political and regulatory climate in the U.S. is not currently sympathetic to the implementation of systematic reductions in anthropogenic N inputs to the environment. In Europe however, having largely eliminated point sources of N

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[171] Franz, Damon "EPA officials defend embattled CAFO rule" Greenwire 06/30/2003

[172] Breen, Tim "Lugar cool, White House cold to Harkin Farm pollution bill" E & E Daily 04/27/1998

[173] Huslin, Anita "Md. Official Urges Changes in Runoff Law; Panel Asked to Eliminate Penalties for Farmers" Washington Post, March 08, 2003

[174] Melillo 2002, pg. 155

through tertiary treatment in the 1970s, several nations subsequently embarked upon extensive controls on non point source loading.[175] The following examples represent a few examples of large watershed attempts at N controls.

North Carolina in the United States has aggressively pursued nutrient reductions to the coastal waters inside of the outer banks, because they are poorly flushed, prone to hypoxia, and are important fish habitat. In the Nuese watershed of the Albemarle-Pamlico sound, a decadal study found no significant change in N loading from 1994 to 2003 after correcting for climate induced changes in flow.[176] During this time the population of the watershed increased by 16%, impervious surface area doubled, use of synthetic fertilizers decreased by 20%, and swine populations in CAFOs increased 285%.[177] The management actions taken included nutrient reductions achieved by waste water treatment plants, and an agreement with cropland agriculturalists to apply 40% less fertilizer.[178] The State of Maryland set similar targets for the Chesapeake Bay watershed by 2000, with efforts including the reduction of both point and nonpoint sources and wetland and riparian zone restoration schemes. The 40% reduction goal for phosphorous was nearly met, but nitrogen was unaffected.[179] Because several changes with potential effects on nitrogen fluxes occurred during the intervention period, it is difficult to judge the relative efficacy of these nutrient management schemes.

One of Europe's most comprehensive measures to reverse the trend of eutrophication was enacted through the 1987 National Action Plan on the Aquatic Environment in Denmark, (subsequently joined by all nations with effluvia in the Danish straits), whereby first municipal wastewater loads were reduced through tertiary treatment measures, and subsequently an action plan for sustainable agricultural production was implemented in 1991, followed by a phase including both fertilizer reductions, wetland restoration, and buffer strips.[180] Despite these efforts and a significant reduction in point source loading of 20,000 tons yr^{-1}, a 2006 report found that total nitrogen loading to the Danish straits (~50,000tons yr^{-1}) was decreased by only 2 tenths of a percent.[181]

A large scale, uncontrolled experiment in fertilizer reductions occurred in Eastern Europe after the collapse of the Soviet Union in 1989. A 70% decline in fertilizer application coincided with, and explained 42% of an approximately 50% decline in gross agricultural output in Central and Eastern Europe.[182,183] Poland, Hungary, the then Czechoslovakia,

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[175] Grimvall et al. "Time scales of nutrient losses from land to sea – a European perspective" Ecological Engineering 14 (2000) 363-371 pg 365

[176] Burkholder, et al. "Comprehensive trend analysis of nutrients and related variables in a large eutrophic estuary: A decadal study of anthropogenic and climatic influences." Limnology and Oceanography, 51(1, part 2) 2006, 463-487 pg. 476

[177] Ibid. pg. 467

[178] Ibid.

[179] Rabalais, Nancy "Nitrogen in Aquatic Systems" Ambio, Vol 31 No. 2, March 2002

[180] Carstensen et al. "Coastal eutrophication and trend reversal: A Danish case study" Limnology and Oceanography 51(1, part 2) 2006, 398-408 pg 398

[181] Ibid. pg 401

[182] Macours, Karen and Swinnen, Johan F.M., "Causes of output decline in economic transition:

Albania, Bulgaria, Estonia, Latvia and Romania decreased fertilizer consumption from approximately 9 to 3 million tons per annum between 1987 and 1998.[184] Despite this drastic reduction in N fertilizer input across a range of watersheds, there has been no overall trend in nitrogen export in eastern European rivers or loading to the Baltic sea in the 15 years since then.[185]

N SATURATION AND ITS DISCONTENTS

Faced with the above examples, the most common explanation given for a lack of observed decrease in riverine nitrogen export from large watersheds in response to reductions in diffuse N loading is the "inertia" and time lag for saturated N systems, due to long water transit times in groundwater, and possibly a large buildup of organic N pools and persistent N yields due to mineralization.[186,187] The latter explanation of a buildup in organic N pools and subsequent mineralization seems unlikely, since most of the N loading in question is agricultural, and cropping tends to diminish rather than augment soil N pools, even under fertilization.[188,189,190,191,192,193] In fact, a decline in soil N due to tillage may represent the bulk of N yields in agricultural watersheds. While the above explanation is plausible, quantification of the nature or extent of the proposed time lag has not been forthcoming in the literature. Presumably we will have to wait and see.

An alternative and parsimonious explanation of the above dataset is that tinkering with anthropogenic N inputs to disturbed watersheds is ineffectual because the activity itself is the dominant mechanism of N release. N fluxes may be dominated by soil N, as this vast reservoir of organic N is increasingly tapped via agriculture, urbanization and population growth. While increased fertilizer use in the period 1950-2000 correlates with increased concentrations of nitrate in groundwater and rivers, so do correlations exist for fertilizer,

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the case of Central and Eastern European agriculture." Policy Research Group Working Paper No. 11 June, 1997

[183] Stalnacke, P et al. "Changes in nutrient levels in some Eastern European rivers in response to large-scale changes in agriculture" Water Science and Technology Vol 49 No 3 2004 pg 29-36 pg. 30

[184] Ibid.

[185] Grimvall et al. 2000, pg 371

[186] Stalnacke 2004 pg. 34

[187] Rabalais 2002, pg. 110

[188] Richter et al. "Legacies of agriculture and forest regrowth in the nitrogen of old-field soils" Forest Ecology and Management 138 (2000) 233-248 pg. 241

[189] Legg & Meisinger "Soil N Budgets" Nitrogen in Agricultural Soils, Agronomy Monograph no. 22 1982 pg. 516

[190] Bol et al. "The natural abundance of ^{13}C, ^{15}N, ^{34}S and ^{14}C in archived (1923-2000) plant and soil samples from the Askov long-term experiments on animal manure and fertilizer" Rapid Communications in Mass Spectrometry 19:3216-3226 2005 pg. 3216

[191] Reeves, D.W. "The role of soil organic matter in maintaining soil quality in continuous cropping systems" Soil & Tillage Research 43 (1997) 131-167 pg. 135-142

[192] Lerman, et al. "Coupling of the Perturbed C-N-P Cycles in Industrial Time" Aquatic Geochemistry 10:3-32, 2004 pg. 15-19

N yields, cultivated land and population density as well as for the number of automobiles and television programs. Correlation establishes the existence of a network of relationships with causal linkages, but the mechanism and direction of causation is determined through reasoning, hypothesis, and demonstration. The prevailing hypothesis assumes that industrial N fixation is the driving force behind increasing N loads. However, if the primary source of nitrogen to rivers under intensive land uses is the flushing of soil N, then there is little reason to expect river export to respond to what may amount to a relatively small change in input due to reduced fertilizer application, when the underlying land use regime remains unchanged. This could explain the relative insensitivity of the above watersheds to what appear to be substantial changes in the anthropogenic N regime.

The test of this alternative hypothesis merely requires the quantification of mobilized soil N pools in comparison to other N sources in large, disturbed watersheds. To date, the only comprehensive watershed scale budgets for N that account for soil fluxes have been constructed in forested watersheds. Interestingly, examples of perturbations in these watersheds have demonstrated that fertilizer N is largely retained, while land use conversion from forest to other types of land cover result in large nitrate fluxes.[194,195,196,197]

This hypothesis, at least in part, was suggested by Krug and Winstanley in 2002, in light of what they perceived as an misguided shift in conceptual models for N cycling, specifically in terms of the most prominent example of perturbation: the Mississippi and Atchafalaya River Basin (MARB).[198] Under the "new" conceptual model, work on the MARB by Rabalais, McIsaac, Goolsby and others from the early nineties onward highlighted the tripling in nitrogen flux since the 1950's and the growth in the areal extent of hypoxia in the Gulf of Mexico, and linked them to the growth in fertilizer inputs in the Midwest.[199,200,201] In contrast, the "older" and now (according to Krug and

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[194] Li et al. "Modelling Mineral Nitrogen Export from a Forest Terrestrial Ecosystem to Streams" Transactions of the ASAE, 47(3):727-739 pg. 727

[195] McDowell et al. "Effects of Chronic Nitrogen Amendments on Production of Dissolved Organic Carbon and Nitrogen in Forest Soils" Water, Air, and Soil Pollution 105:175-182, 1998 pg. 175

[196] Murty, et al. "Does conversion of forest to agricultural land change soil carbon and nitrogen? A review of the literature" Global Change Biology 8,105-123 2002 pg. 109

[197] Likens et al. "Effects of Forest Cutting and Herbicide Treatment on Nutrient Budgets in the Hubbard Brook Watershed-Ecosystem" Ecological Monographs, Vol. 40, No. 1 Winter 1970, pg 23-47 pg. 23

[198] Krug, E.C., Winstanley, D. "The need for comprehensive and consistent treatment of the nitrogen cycle in nitrogen cycling and mass balance studies: I. Terrestrial nitrogen cycle" The Science of the Total Environment 293 (2002) 1-29 pg. 4

[199] Goolsby et al. "Nitrogen Flux and Sources in the Mississippi River Basin"

[200] McIsaac et al. "Relating Net Nitrogen Input in the Mississippi River Basin to Nitrate Flux in the Lower Mississippi River: A Comparison of Approaches" Journal of Environmental Quality 31:1610-1622 (2002)

[201] Rabalais et al. "Gulf of Mexico Hypoxia, A.K.A. 'The Dead Zone'" Annual Review of Ecological Systems 33:235-63 2002

Winstanley) more obscured lineage of scientific thought recognized that human activities and especially agriculture mined soil N and resulted in a net transfer of N from terrestrial to aquatic systems.[202,203]

A major criticism of existing N Budgets for the MARB, which estimated that 74% of the nitrate load was agricultural in origin, is that they assumed steady state soil N conditions (i.e. net mineralization in balance with net immobilization).[204] A review of the published data by Panno et al. in 2006 resulted in a revised estimate for the MARB of 14% of the N load originating from sewage and manure, 5% from atmospheric deposition, 30% from synthetic fertilizers, and 51% from soil OM.[205] However, even this estimate is subject to scrutiny. Isotopic evidence ($\delta^{18}O$ vs. $\delta^{15}N$) not only suggested that *the relatively well quantified* sewage input was a much smaller fraction than predicted, it showed that values from both tile drains and river samples could have been consistent with either the author's estimation of 51% SOM and 30% fertilizer with a denitrification fractionation shift of 0-55%, *or any smaller fertilizer:SOM ratio and raised range of denitrification.*[206]

The highest $\delta^{18}O$ and $\delta^{15}N$ fraction in a river sample reported by Panno et. al was approximately %13 and 15% respectively, representing the 55% denitrification scenario assuming 30% synthetic NO_3^- fertilizer and 51% SOM. However, an equally plausible relationship for that isotope signature could be made at any point up to a SOM fraction of 100%, with 40 to 60% denitrification shifting the $\delta^{18}O$ and $\delta^{15}N$ fractions to observed values, depending on the starting SOM isotope signature (a range of values exists in the literature, but the actual distribution for the MARB has not been quantified). This illustrates the inherent and well-known limitations involved in using isotopic signatures to determine the sources of N draining watersheds, and reinforces the need for actual measurements of N fluxes.[207]

More so than for any other nitrogen issue, work by Mitsch, Rabalais and others had by the late nineties begun to emphasize the need to move "Beyond Science into Policy," raising the profile of the "Dead Zone" in the public eye and prompting both an NRC report and a White House Committee on Environment and Natural Resources (CENR) assessment.[208,209,210] The CENR integrated assessment and action plan, though criticized

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[202] Krug and Winstanley 2002, pg 4

[203] Lerman 2004, pg. 15

[204] McIsaac 2002 pg. 1614

[205] Panno et al. "Isotopic evidence of nitrate sources & denitrification" Journal of Environmental Quality, Vol. 35, March-April 2006 pg. 501

[206] Ibid.

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

[208] National Research Council 2000. Clean Coastal Waters: Understanding and reducing the effects of nutrient pollution. National Academy Press, Washington D.C.

[209] Rabalais et al. "Beyond Science into Policy: Gulf of Mexico Hypoxia and the Mississippi River" Plenary Address, March 2001 American Institute of Biological Sciences

by researchers funded by agribusiness (including Krug and Winstanley), was accepted by a broad segment of the research and regulatory communities, and included commitments to reducing the 5-year running average of areal extent of Gulf hypoxia to less than 5000 km^2 by 2015. According to model predictions, a 30% reduction in nitrogen loading would be necessary to achieve that goal.[211] This in turn would be accomplished by agricultural best management practices (BMPs), riparian buffer strips, and storm and wastewater nutrient removal.[212] In response to criticisms raised, the lead researchers involved asserted that the "science base was solid because the integrated assessment synthesized high-quality, peer-reviewed monitoring and research results in a policy-relevant manner; responded to public comment; and provided predictions that were tempered with an appropriate measure of uncertainty."[213]

Despite these assurances, one cannot help but wonder whether the action plan will succeed. Will the riparian zones in Illinois and Ohio be superior to Danish buffer strips? Will a 30% decrease in nitrogen loading affect the MARB where a 70% reduction in fertilizer application failed to register in Eastern European rivers? If the revised estimates of Panno et al. are correct (and they may well underestimate SOM contributions), then a reduction of N loads by 30% could only affect the N yield of the MARB by about 10%, which seems hardly likely to result in a decrease in the areal extent of the "dead zone" by a factor of 4. If soil organic N sources dominate riverine fluxes in perturbed watersheds, then attempts to curb synthetic nitrogen inputs will merely hack at the branches of eutrophication while leaving the root intact.

BALANCING THE RISKS OF NITROGEN

The need to measure N fluxes and fully quantify the N budget of the MARB and other perturbed basins is critical for a number of reasons. First, it is important for researchers to correctly interpret observations in terms of the underlying dynamics of N cycling in watersheds, and to understand the relative magnitudes of N fluxes under a range of natural conditions and human land uses. Second, a conceptual model grounded in reality is indispensable when developing plans to modify N fluxes for environmental reasons. Corollary to this point is the fact that environmental problems abound, political and economic resources to address them are limited, and by virtue of public trust scientific understanding is fundamental to identifying issues and informing efforts to efficiently allocate resources to problems. Flawed science that makes its way into the realm of policy and subsequently violates the public trust is inevitably costly for both science and the public.

Despite this danger, the fixation on threats to human health as opposed to ecological degradation in the U.S. (and perhaps its relation to research funding) has led many

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[210] Mitsch et al. "Reducing Nitrogen Loading to the Gulf of Mexico from the Mississippi River Basin: Strategies to Counter a Persistant Ecological Problem" American Institute of Biological Sciences 2001

[211] Rabalais 2001

[212] Ibid.

[213] Ibid.

researchers to cite the threatening human health aspects of nitrogen pollution without providing adequate context or proportionality. The justification of research by way of amplifying threats is of course not only repugnant and unnecessary: it also makes for perfunctory and formulaic journal articles. For example, introductions in the literature abound with cookie cutter descriptions of blue baby syndrome (see Chapter II and the sources cited). Typically the details of the danger are mentioned, but no epidemiology is discussed. In the health related cases, quantification is perhaps avoided because an embarrassingly few people are affected by N-induced illness in relation to the amount of discussion generated by the literature. Nitrates have been frequently implicated in stomach and related cancers due to the endogenous reduction of nitrate to carcinogenic N-nitroso compounds.[214] However, the relevance of this pathway fits awkwardly with the strong negative correlation between upwardly trending of nitrate in ground and surface water and declining mortality due to stomach cancers.[215] Of course, the complex interaction between a wide variety of risk and protective factors and improvements in diagnosis and treatment makes direct comparisons with cancer mortality problematic. However, a study on stomach cancer mortality in 24 countries found an inverse correlation for nitrates in the UK and France and no significant correlation elsewhere.[216] Illustrating the influence of protective factors, the proposed reason for inverse correlation in UK and France was increased consumption of vegetables high in dietary nitrate, which implied higher consumption of fruits (known to protect against stomach cancer).[217]

Correlations have been found between cases of Non Hodgkins Lymphoma and elevated nitrate levels (greater than or equal to 4mg/L) in drinking water supply (an odds ratio of 1.1-3.6) in a study in Nebraska.[218] A similar study in Iowa found bladder and ovarian cancer risk was 2.83 and 1.84 times higher respectively when municipal water nitrate concentrations exceeded 2.46 mg/L. This study however contraindicated a relationship between increasing nitrate concentrations in drinking water and Non Hodgkins Lymphoma, and it also found a negative correlation for uterine and rectal cancer.[219] In general the cancer risk factor for high levels of nitrate in drinking water is lower than that for average exposure to pesticides, coffee, and beer (in ascending order of risk).[220]

Nitrate is found in vegetables, especially beetroot, spinach, lettuce and carrots (more than a 1000mg $NO_3^- \, kg^{-1}$), and endogenous production in the human body is on the order of

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[214] Townshend, et al. "Human health effects of a changing global nitrogen cycle" Frontiers of the Ecological Environment 1(5):240-246 2003

[215] Leigh 2004 pg. 213

[216] Joossens, JV et al. "Dietary Salt, Nitrate and Stomach Cancer Mortality in 24 Countries" International Journal of Epidemiology, Vol 25, No. 3 pg 494 1996

[217] Ibid.

[218] Ward, Mary H.; Mark, Steven D.; Cantor, Kenneth P.; Weisenburger, Dennis D.; Correa-Villasenor, Adolfo; Zahm, Shelia Hoar Drinking Water Nitrate and the Risk of Non-Hodgkin's Lymphoma.
Epidemiology. 7(5):465-471, September 1996.

[219] Weyer et al. "Municipal Drinking Water Nitrate Level and Cancer Risk in Older Women: The Iowa Women's Health Study." Epidemiology. 12(3):327-338, May 2001.

[220] Leigh 2004, pg 216 citing Lomborg (2001)

30-70mg daily.[221] An adult person drinking twice the MCL for nitrates intakes approximately 80mg of nitrate in a day, which is of the same magnitude as normal intake, especially if salad is a part of the diet. In 1995 the USGS estimated that more than 8,200 wells in the US (mostly private groundwater wells in rural agricultural areas) contain nitrate in excess of 10 mg L^{-1}.[222] However, many millions of people in the US are routinely exposed to salads (I myself take care to avoid them). According to the U.S. Department of Health and Human Services "The first reported case of fatal acquired methemoglobinemia in an infant due to ingestion of nitrate-contaminated well water occurred in 1945. Since then, about 2,000 similar cases of acquired methemoglobinemia in young infants have been reported worldwide; about 10% of such cases result in fatality. The most recently reported U.S. case of infant mortality due to this source was in 1987."[223] In other words, the average person is far more likely to get struck by lightning twice than die of methemoglobinemia.

The last reported U.K. fatality in 1950 had been drinking water in excess of 200 mg L^{-1} NO_3^-.[224] It is frequently reported that the incidence in Eastern Europe is much higher than elsewhere (albeit fewer than 1 per 100,000) and of course cases could be underreported.[225] While nitrates in drinking water resulting from anthropogenic Nr are justifiably a concern, obviously extremely so for those affected, from the point of view of managing a society this concern should be in proportion to the larger context of both the hazards and benefits derived from reactive N production, notably the fact that 40% of people alive today owe their existence to nutrition derived from synthetic N fertilizers.[226]

Cost benefit analysis is useful tool in improving human-environment interactions, if for no other reason than from the standpoint of quantifying risk and prudently 'picking ones battles.' Addressing nitrates in groundwater and river export is probably not the most efficient use of resources, despite economic losses associated with damaged fisheries and the non-commercial costs of altered ecosystem function. In the larger context of global environmental problems, and with the possible exception of future N_2O emissions affecting climate change, nitrogen pollution poses relatively minor concerns. Nitrogen is, after all, an essential nutrient and not a toxic metal or carcinogenic organic compound. In any case, the prospect for winning this particular battle is bleak.

Technically, there is not and will never be a substitute for reactive N in biological systems, and the growth of the human population and the food resource base required to sustain it will undoubtedly require substantial N inputs from the Haber-Bosch process in the future. Over the past century human settlements have grown substantially, to the

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[221] Leigh 2004 215

[222] US Geological Survey. 1995. Nutrients in groundwater and surface water of the United States: an analysis of data through 1992. Reston, VA: US Geological Survey.

[223] U.S. Dept. of Health and Human Services, ASTDR Case Studies in Environmental Medicine: Course SS3054, 2001

[224] Leigh 2004, pg 212

[225] Leigh 2004 212

[226] Smil 2001, pg.

point of utilizing 45% of the earth's terrestrial primary productivity in one form or another.[227] This trend is ultimately what drives the cascading fluxes of N that amplify naturally occurring phenomena such as eutrophication and hypoxia. Although treatment of point sources, smokestacks and tailpipes is technically feasible, without addressing the underlying demographic nature of diffuse N loading there can be no progress towards a balanced nitrogen cycle.

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[227] Leigh, 2004 pg. 191

CHAPTER IV

URBAN INTENSITY, LEGACY POLLUTION, AND INORGANIC AND ORGANIC N YIELDS: A CASE STUDY OF THE ABERJONA WATERSHED

ABSTRACT

To understand the role of land use in nitrogen yields in an urban watershed, flux and speciation was measured in sub basins of the Aberjona river, a heavily polluted urban watershed north of Boston. At 2.9mg/L, concentrations of TOTN are more than twice the median for 48 NAWQA U.S. urban watershed indicator sites (Campo 2003). While previous studies (Coles et al. 2004) have compared watersheds along an urbanization gradient, this study found that total nitrogen yield in sub-basins within a single watershed was correlated (r^2=.79) to percentage intense urban land use (as defined by USGS land use categories). However, the complex consequences of anthropogenic mediation of nitrogen cycling must be quantified to disentangle the effects of current and past land uses in a watershed. The presence of legacy N sources is suspected in a highly industrialized basin of the Aberjona, based on a localized, point source-like input of organic nitrogen (this study) and ammonia (Cutrofello 2005) to the Halls Brook Holding Area. Nitrogen transformations *in-situ* play a major role in regulating the flux of all species. An experimental setup was employed preserving the influence of infauna, hydrodynamics, and the structure of sediments and biofilms on transformation processes. While TOTN export from the watershed is 282kg d^{-1}, incubation experiments suggest that as much as 94kg d^{-1} of NH_4^+ and 48kg d^{-1} DIN is removed while as much as 100kg d^{-1} of NO_3^- is supplied by *in-situ* processes. While nitrification is clearly implicated, decreases in TOTN show that these rates represent an aggregation of simultaneous processes of coupled nitrification-denitrification, immobilization, mineralization and other transformation pathways. Measurements along the river corroborated the experimental rates of consumption and production of ionic species, with the nitrogen load progressively shifting from predominantly org N and NH_4^+ in the upper reaches of the Aberjona river to mainly NO_3^- at the outlet to the Upper Mystic Lake. This study underscores both the importance of organic nitrogen loading (~34% of TOTN) and transformations between nitrogen compartments in a watershed featuring industrial, commercial, and sub-urban land uses.

BACKGROUND

Eutrophication and its links to anthropogenic perturbations of the N cycle (Vitousek 1997, 2002, Kinzig and Socolow 1994, Matson 2002, Bouwman 2002, 2005, Paerl 2006) has motivated research programs covering a range from microbially mediated processes in sediments and groundwater (Groffman et al. 1998, Burket and Stoner 2002, Knowles 1982, Zumft 1997, Joelsson and Kylimar 2002, Tesoriero et al 2000), and watershed scale processes in forested (Li et al 2004, Lewis et al 1999, Fisk et al 2002, Lewis 2002, Aber et al 1989), agricultural (Nolan et al 2002) and more recently urban watersheds (Walsh et al. 2005, Bowen and Valiela 2001, Groffman et al. 2005, Coles et al. 2004, Smith 1999). Increased N loads associated with rising population densities in coastal regions and more intensive fertilizer usage in agricultural systems has been linked to alterations in ecosystem composition (Herbert 1999, Smith et al 1999, Burkholder et al 2006, Bowen and Valiela 2001, Walsh et al 2005, Coles et al. 2004). Concern about hypoxia in the near shore of major river outlets (Mallin et al 2006, Rabalais et al 2002, McIsaac et al 2002, Mitsch et al 2001) has driven N budget and modeling efforts to inform decision makers in developing policy measures to reduce N loading in watersheds (Moore et al 2004, Gomann et al 2004, Carstensen et al 2006, Erisman et al. 2001, 2002, Mosier et al 2002, Melillo and Cowling 2002, Schroder et al 2004, Arheimer et al 2003, Lory and Scharf 2003).

Despite these efforts, much uncertainty persists as to the magnitude of anthropogenic perturbations, and the physical and biochemical processes that mediate loading and export of nitrogen from watersheds across a spectrum of land uses and human activities.

This may be due in part to sparse measurements of nitrogen fluxes at the sub basin, watershed and global level in comparison to the inherent spatial and temporal variability of natural processes that mediate them (fixation, mineralization, nitrification, denitrification, uptake and immobilization, DnrA, etc.). Despite the advances made with isotopic analysis techniques, considerable difficulty remains in separating the effects of multiple co-varying natural processes on nitrogen pools *in-situ* with available methods (Panno et al 2006, Mayer et al 2002). One aspect of this difficulty arises because of a reliance on sediment incubation methods that tend to ignore the highly relevant structure of natural sediments and biofilms (Herbert 1999) and the physical and chemical heterogeneity present due to the hydrodynamics of surface flow (Marion 2006), sub-surface flow (McClain et al 2002, Hill et al 2000), infauna (Herbert 1999), or other factors (for example diurnal or seasonal temperature and radiation variation), especially in terms of the oxygen and carbon availability that drives microbial processes. For a review of the limitations and assumptions built into available N transformation methods, see Henriksen and Kemp (1988). There is yet no good way to verify the extent to which rates of N transformation in slurried or cored sediments incubated in a lab reflect the equilibrium of their new situation or that of the aquatic system they are meant to represent. Even if this problem were overcome, the natural distribution of "hot spots" (McClain et al. 2003, Hill et al 2000) in aquifers and riparian sediments are difficult and costly to evaluate with sufficient resolution at the watershed scale.

In addition to the intrinsic complexity of nitrogen cycling, past and present human activities have resulted in inputs of nitrogen to the environment that vary greatly geographically and historically, as well as in chemical composition (from fertilizers and explosives to organic wastes and atmospheric NOx from combustion). Historical "legacy pollutants" (Walsh et. al 2005) can be present in unknown quantities and locations, and are potentially confused with contemporary non-point source N, leading leading to uncertainty as to whether nitrogen yields from a watershed reflect current or historical trends in nitrogen cycling.

Historical and ongoing conversion of natural land, from forests and grasslands to pasture, agricultural fields, or urban or sub-urban types of land uses can affect the nitrogen yields of watersheds in several important ways. First, alteration of the biome will directly affect the natural type and quantity of nitrogen cycling. Second, human activities circulate nitrogen via import, export and deposition of N fixed elsewhere in sometimes non-obvious spatial patterns. Third, the creation of impervious surfaces and drainage networks directly alters surface and groundwater flow and redox regimes and the magnitude and timescale of N transport and transformation processes. Finally, disturbance of soil in cultivation and construction can release massive quantities of nitrogen stored in soils (Krug and Winstanley 2002, McCarty and Meisinger, Murty 2002, USDA tech note 12, Richter 2000, Wakida and Lerner 2002). Soil organic nitrogen ranges in the thousands of kilograms per hectare in most watersheds (Legg & Meisinger 1982), and typically represents the largest pool of potentially reactive nitrogen, and relatively small changes in soil N storage can result in substantial fluxes.

The above factors interact simultaneously, so when a molecule of nitrate runs the gauntlet of microbial and plant processes in soils, subsurface and surface flows to emerge at the outlet of a river, it is impossible to know, even with radioisotope techniques (Panno et al. 2006, Mayer et al 2002), whether it came from the atmosphere via nitrogenase or Haber-Bosch, whether it was fixed this year or centuries ago, what other forms it existed as (NH_4^+, NO_2, NO, N_2O, organic N), how many times it cycled through plant, animal, or microbial systems before being exported, what portion of its contemporaries remain in the watershed and what portion has been transported out by bulk river flow, denitrification or harvesting, and finally the extent to which human modifications of the environment, from pavements and drainage culverts to tillage, excavation or reforestation, have contributed to its fate of being in the river at precisely the moment the sample is taken.

Given the confluence of so many factors and a lack of resources to quantify all of them, the construction of mass-balanced nitrogen budgets for watersheds have been limited to a few well-researched forested watersheds (Likens 1970), receiving controlled perturbations in the form of clear cutting or fertilizer inputs. Mass balance for agricultural, urban, or especially large scale integrated watersheds such as the Mississipi Atchafalaya river basin (MARB) have been achieved only by ignoring one or more N transformation processes (McIsaac 2002) or relying on rates of N transformation extrapolated far beyond the circumstances of their derivation, or both.

While this study was unable to resolve the difficulties inherent in creating an N budget for a highly perturbed watershed, the measurements taken show an integrated set of processes acting upon the major dissolved inorganic nitrogen ions, nitrate and ammonium, as well as organic nitrogen, correlated in general along an urban gradient but in the context of nonpoint and highly localized N inputs from both historical industrial practices and past and current land uses.

Study Site

The Aberjona river (lat long) drains 60 km^2 of watershed north of boston and includes the merged Industriplex 128 and Wells G&H superfund sites (see figure x). For this reason it has been extensively (and often redundantly) studied by state and federal agencies and generations of researchers at area universities. Among other pollutants, the river is 303(d) listed as impaired for high non-ionized ammonia concentrations. About 68% of the watersheds land use is characterized as urban by the USGS (Campo 2003), but the extent of industrial and commercial land uses is unevenly distributed among sub watershed basins, with little intensive land usage around the Horn Pond sub basin and a cluster of industry surrounding Rt. 128. Features of potential interest to the nitrogen cycle include a golf course in the Horn Pond sub-basin, two golf courses and extensive residential developments in the Stoneham sub basin, wetlands between Rt. 128 and Montvale Avenue, and the presence of decaying hide piles at the Industriplex 128 superfund site from historical glue and tannery waste disposal. For more in depth characterization of the Aberjona river basin, we refer to the literature (Durant 1990, Spliethoff 1996, Aurilio 1994, Ahmann 1997, Hemond 1995, Campo 2003, Coles 2004, Wick 1997, USEPA 2005).

METHODS

To investigate the sources and patterns of nutrient loads and transformations in the watershed, nitrogen flux and speciation in the Aberjona river was quantified at six sampling sites draining sub basins of interest at bi-weekly to monthly intervals throughout 2003. Standard water quality parameters (DO, T, conductivity, pH) were measured with a hydrolab and stage was recorded at staff gages to obtain discharge using stage discharge relationships (Cutrofello 2005). Samples were taken approximately 15cm below the waterline midstream, in thrice-rinsed 60ml bottles, (filtered and unfiltered) and frozen for storage before measurement (a few days to over a month). Nitrate was measured by ion chromatography with an error of +/- 0.1mg/L, ammonium was measured by the phenolhypochlorite method using a spectrophotometer at either with an error of +/-15% (Cutrofello 2005), and total nitrogen was measured by persulfate digestion, oxidizing NH_4^+ and organic N to nitrate with subsequent measurement by ion chromatography. Although the persulfate digest compared reasonably well with a similar persulfate digest method (using cadmium reduction for nitrate anaylsis) at Orono's soil laboratory at the University of Maine (r^2=.89, n=10), the recovery efficiency of the MIT TOTN method was judged to be 74% upon comparison with a combustion method using a CHN analyzer at MIT (r^2=.99, n=23). Previous studies have reported a consistent underrecovery of organic N with persulfate digestion compared to other oxidation methods (Cornell 1999), while Bronk et al. (2000) and Sharp et al. (2002) have reported varied efficiencies in either direction in comparing methods, albeit with general lineal agreement. In this study, the correction of persulfate oxidation measurements based on subsequent comparison with a combustion method is considered appropriate based on full recovery of sulfanilamide and NH_4^+ standards with the CHN analyzer and lower observed recovery using persulfate oxidation. After correction for a 74% recovery efficiency, the standard deviation error in TOTN measurements was +/- 1.5mg/L.

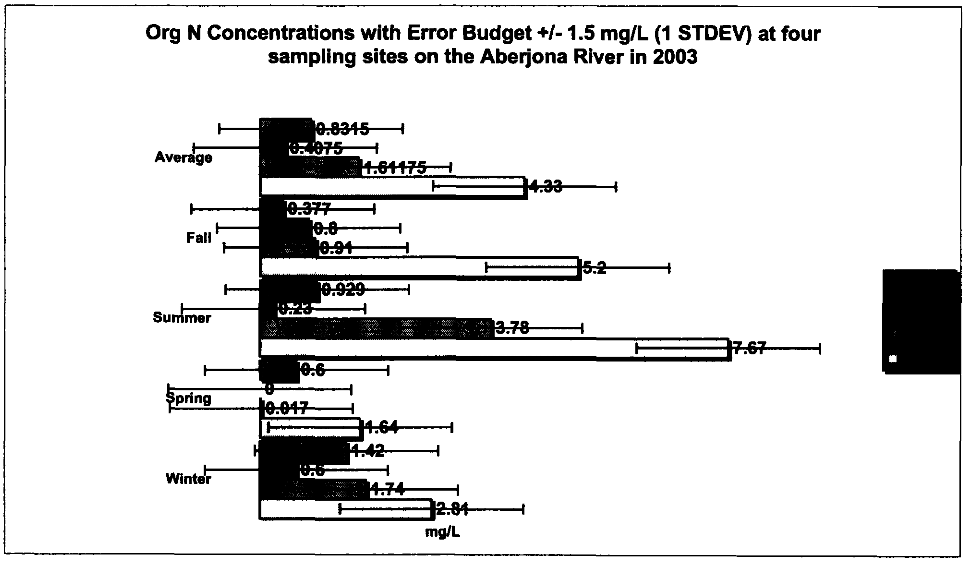
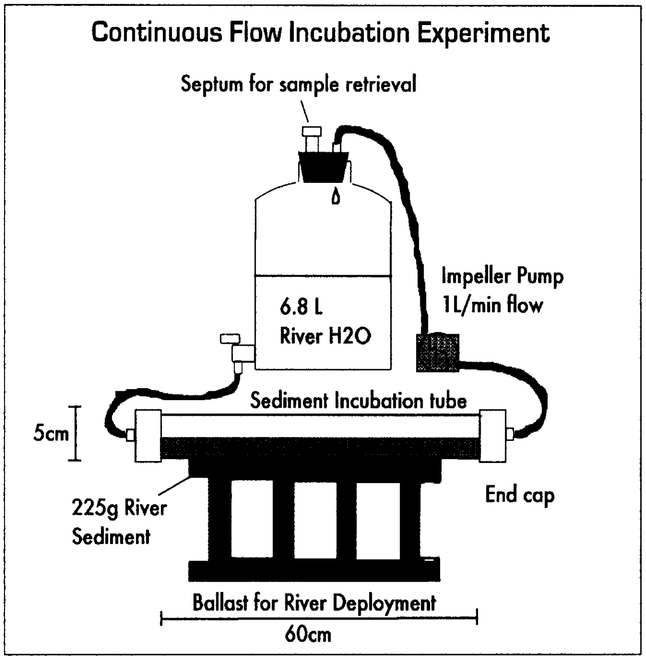


Figure 7

Organic N was calculated as the difference between TOTN and nitrate plus ammonium, with an error budget dominated by the +/- 1.5mg/L for TOTN. This error as a percentage of the mean concentration varied from site to site seasonally, with high uncertainty (above 100% of the mean) during low spring, summer and fall concentratinos at the USGS gage site and throughout the year at the Wedge Pond site. Organic N concentrations were consistently high at the Rt. 128 and Montvale Ave. sampling sites, with error as a percentage of the mean ranging from 20 to 53% and 39 to 93% respectively. For annual and seasonal average concentrations and fluxes in the watershed, see table 1.

To address problems of slurry and coring methods associated with a disturbance of the structure of sediments, biofilms and flow regimes, river sediment processes were evaluated with continuous flow incubation experiments using sediment that had equilibrated with river biota in-situ over a period of weeks to months. The incubation chambers were 60cm long, 5cm diameter PVC tubes loaded with 225g of river sediment (.0296m^2 surface area) and placed in line with the streamflow. By visual inspection, the sediment tubes were colonized by a robust biofilm within 2 weeks, which was assumed to be representative of the river sediment biofilm. After equilibration, the chambers were capped at each end, and immediately transported to the lab (~45 minutes) to run the experiment. During the experiment the chambers were maintained at the river temperature by immersion in a temperature controlled bath, with 6.8L of river water circulated through the chambers by impeller pumps at 1L min^{-1}. Nitrogen species were measured as described above, and organic matter in the sediments was measureby loss on ignition at 450°C. With respect to each other tubes displayed a high degree of similitude in terms of nitrogen transformations under no treatment over 6 hours (r^2=93 for NH_4^+ r^2=83 for NO_3^-) (Figure 9). The degree of similitude between the hydrodynamic conditions simulated in this experiment and the tubes *in-situ* is not known.



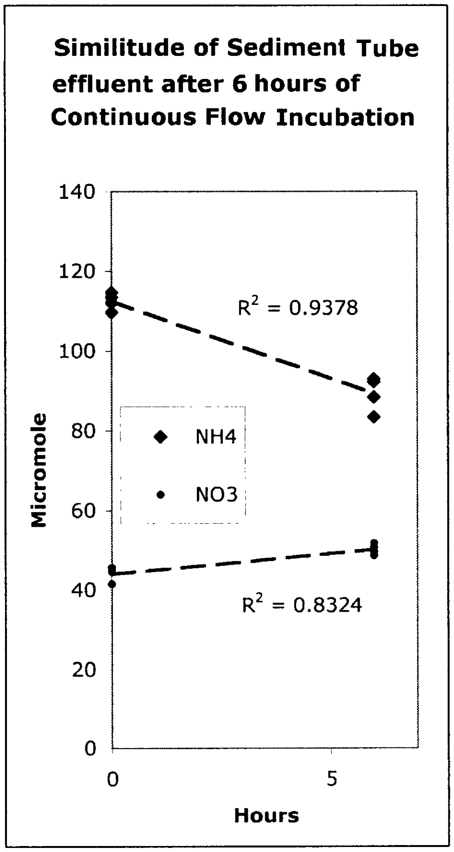


Figure 9

Although the problem of uniform movement of Acetylene into incubated soils has been widely reported (Martin et al. 1998), the general inferences gained from the method are still considered useful. We therefore performed several incubation experiments with inhibitors and controls. The incubation experiments applied differential metabolic inhibition with nitrapyrin (.25mg/L) and acetylene (5Kpa) to calculate the differences in N species concentration over time attributable to nitrification and denitrification. While general effects of inhibition were observed compared to no treatment, the two treatments were not significantly different from each other, indicating either the relative importance of nitrification, or incomplete inhibition of N_2O reductase by acetylene. In some experiments concentrations of N species, especially NH_4^+, fluctuated too widely to derive well-correlated rates of transformation. A lack of steady state NH_4^+ concentration in continuous flow incubations was reported by Binnerup et al. (1992), who suggested that the causes were variable excretion by burrowing invertebrates (bioturbation) and slow response to sediment mineralization. In this experiment faunal excretion may have been exacerbated in response to the treatments, and transport of inhibitors and newly mineralized NH_4^+ throughout the sediment may be poor. Incubated sediments, especially those in which the structure of the sediment has been preserved, may exhibit chemical transport characteristics that reflect unknown proportions of diffusion and advection through a non-homogenous media possibly containing faunal channels.

RESULTS

We concluded that comparison of differentially inhibited sediment tubes was not well suited to calculating *in-situ* transformation rates. The results of such a comparison would for example tend to show a net increase in NH_4^+ and decrease in NO_3^- resulting from the isolated effects of nitrification, which is not a valid outcome of that biochemical reaction. This may have been due to ineffective inhibition postulated above, a lack of sufficient similitude between tubes for direct comparison, or the general invalidity of assumptions about the important processes involved. We concluded that while the experimental setup is appropriate for modeling river processes under preserved biotic and hydrodynamic conditions, a labeled isotope approach would be necessary to determine the N fluxes of major metabolic pathways.

In light of experiments verifying an acceptable degree of similitude between tubes, and the general agreement between tube processes and river mass balance, data from the controls (untreated continuous flow incubations) was used to calculate aggregate sediment and biofilm processes. The transformation rates in figure x represent the areal mass transformation rates of N species based on 7 experiments equilibrated at the Rt. 128 sampling site, and is of interest in explaining the general fate and transport of N through the watershed. For NH_4^+ the aggregated processes include additions due to mineralization, DNRA, or transport from sediments, and removal due to immobilization, nitrification or transport into sediment. For NO_3^- the main contributions are from nitrification and sediment flux, with removal due to denitrification, DNRA or immobilization.

The difference in both species (DIN) after incubation revealed a net loss of nitrogen that included the combined effects of mineralization, immobilization, and denitrification (due to the nature of the experimental setup, any effects of lateral inflow are excluded). Many studies have reported a substrate concentration dependance on denitrification rates; in this study DIN removal was well correlated with NO_3^- concentrations (r^2=.97).

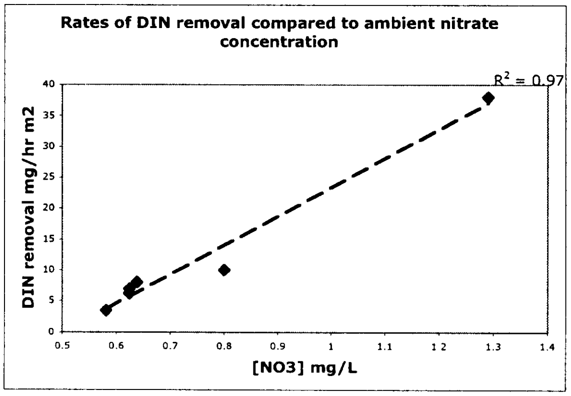


Figure 10

Aggregate areal rates of in-situ transformation were determined from continuous flow sediment incubations equilibrated at the Rt. 128 sampling site (table 2). As a first order approximation of in-situ transformations for the watershed, these rates were extrapolated to the entire river sediment bed (~110,000m^2), recognizing that this provisional approach should be reinforced by further experiments at additional sites along the river to capture spatial and temporal variations discussed in the introduction. Nevertheless, these rates provide a starting point for discussing experimentally derived in-situ transformations in comparison with observations of N speciation throughout the watershed.

Table 1

			Average Concentrations [mg/L]				
Source	**Year**	**Site**	**TOTN**	**NO3**	**NH4**	**Org N**	**%OrgN**
NAQWA	1999	USSG	2.85	1.39	0.97	0.48	19
MIT/TUFTS	2003	USGS	2.99	1.48	0.66	1.02	34
		Montvale Ave	5.00	1.63	1.73	2.62	52
		Rt 128	8.35	1.11	2.87	4.61	55

			Average Flux [g/sec]				
Source	**Year**	**Site**	**TOTN**	**NO3**	**NH4**	**Org N**	**Flow m3/sec**
NAQWA	1999	USSG	2.7	1.3	0.9	0.5	0.95
MIT/TUFTS	2003	USGS	3.9	1.9	0.9	1.3	1.29
		Montvale Ave	3.0	1.0	1.0	1.6	0.60
		Rt 128	1.9	0.3	0.7	1.0	0.23

Note: Averages are not exactly additive because the number of data points for each N species varies

Table 2

Average Daily N export from the Aberjona	**kg/day**
Nitrate	149
Ammonium	79
Organic N	86
TOTAL N	**282**

Average Daily N Tranformation in situ

	Processes	**kg/day**	**mg/m2 hr**
NH4 change	mineralization-nitrification	-100	-38
NO3 change	nitrification-(denitrification+immobolization)	94	36
DIN change	mineralization-(denitrification+immobilization)	-48	-18

The 2003 average annual concentration of total nitrogen at the USGS gage site in this study (2.9 mg/L) was only slightly higher than the median concentration reported by Campo et al for 1999 (2.7mg/L). This concentration remains the highest reported annual average for any New England stream that the authors are aware of, and more than twice the median concentration of 48 urbanized NAWQA indicator sites across the nation (Campo 1999).

The watershed as a whole yielded 15.9 kg of total nitrogen per hectare in 2003; however, factoring in the estimated in-situ riverine consumption of 48 tons yr^{-1}, and assuming it to be largely denitrification, the actual watershed yield upland to streams would have been

19 kg ha^{-1} yr^{-1} without an in-stream sink for nitrogen. This supports the hypothesis that in addition to riparian zones, river sediment processes can mitigate nitrogen loading.

The total nitrogen yield was distributed among sampling sites draining four subwatershed basins in a sequence corresponding (r^2=.79) to dominant land use type, with relatively small contributions from forested and residential areas around Horn Pond (4 kg ha^{-1} yr^{-1}) and high annual yield (30 kg ha^{-1} yr^{-1}) in the heavily industrialized region around Rt. 128 (figure 11). This confirms that the results of a comparative analysis across watersheds by Coles et al. (2004), where a number of water quality parameters (including TKN concentration) were correlated (r^2=.59-.79) to urban land use intensity, also holds true within watersheds along an urbanization gradient.

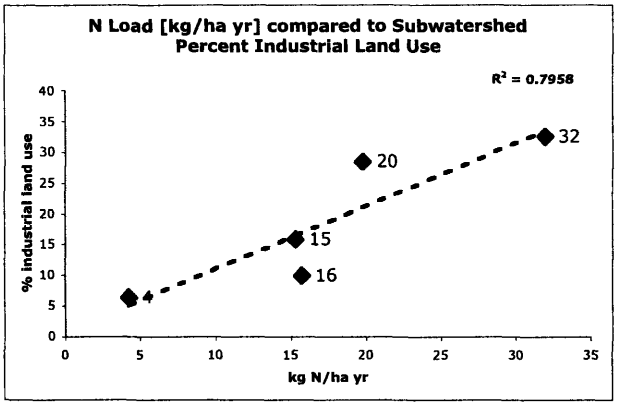
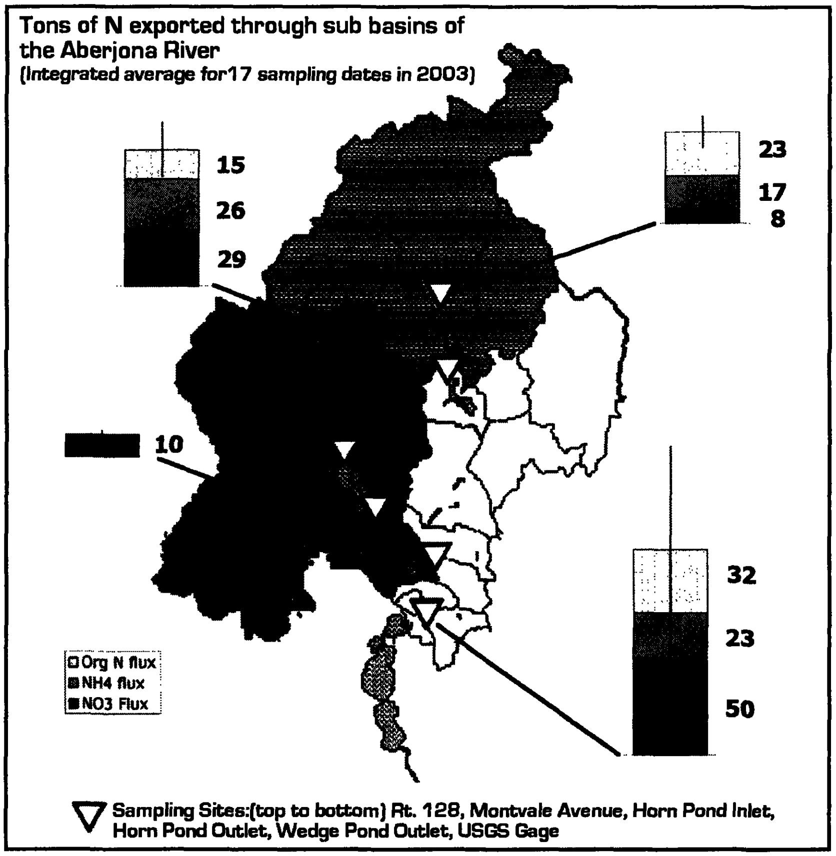


Figure11



Sampling Sites:(top to bottom) Rt. 128, Montvale Avenue, Horn Pond Inlet, Horn Pond Outlet, Wedge Pond Outlet, USGS Gage

Figure 12

Bracketing measurements indicate that a point source-like flux of nitrogen dominated by organic nitrogen (23 tons yr^{-1}) and ammonium (17 tons yr^{-1}), with comparatively little nitrate (8 tons yr^{-1}), emanates from the Halls Brook Holding Area (HBHA) north of Rt. 128. This signature of N speciation is unique to this sampling site, and is especially interesting given that this sub basin exhibits twice the yield of the watershed as a whole (32 kg ha^{-1} yr^{-1} compared to 16 kg ha^{-1} yr^{-1}).

Between Rt. 128 and Montvale Ave. the river exhibits a slight increase of NH_4^+ flux and a large increase in NO_3^-, with a large decrease in org N. This decrease in org N may be due to mineralization, or due to settling of particulate N in the near stagnant water of the Wells G&H wetlands. Throughout the rest of the watershed the N load is increasingly dominated by nitrate, with only slight increases in ammonium and org N after Montvale Ave. This pattern is consistent with in-situ nitrification and uptake, possibly at an accelerated rate in the intervening wetlands. Extrapolated results of sediment incubations indicate that as much as 100kg/day of NH_4^+ is removed and 94 kg day^{-1} of NO_3^- is added by in situ processes, with a net decrease in DIN of 48 kg day^{-1}. This corresponds well with the observation of increasing nitrate flux as the river flows downstream; however, the effects of individual processes (nitrification, denitrification, lateral inflow, macrophyte uptake and microbial immobilization, as well as mineralization of org N) could not be separated and are therefore combined into net transformation rates of nitrogen species. In general, the trend of N transformation leading to higher nitrate yields has significant implications for the chemistry of Upper Mystic lake, where nitrate contributes to oxidation potential of the hypolimnion and interacts with the mobilization of metal species (Senn 2002).

Table 3

Estimated N Budget for the Aberjona River Watershed (6400 ha) based on 2003 dataset

Import	**Source/Derivation for Estimation**	**Tons/year**	**kg/ha yr**
Atmospheric Deposition wet/dry	Valiela et al 2002	**70**	**11**
Turf Fertilizer	White 2003	**10**	**2**
Fixation	Legg & Meisinger 1982	**128**	**20**
Sewage Leakage/Overflow	assuming 15% percent leakage	**36**	**6**
	TOTAL	**244**	**38**
Standing Stock		**Tons**	
Legacy Pollutant	This study	**10,000**	
Non-human Biota Nitrogen		**unknown**	
Soil Nitrogen	Legg & Meisinger 1982 (top meter of soil only)	**44,800**	
In situ transformations			
Mineralization of org N stocks		**unknown**	
Immobilization of inorganic N		**unknown**	
Plant uptake		**unknown**	
Export		**Tons/year**	**kg/ha yr**
Riverine N flux	This study	**103**	**16**
Riverine Denitrification	This study	**17**	**3**
Riparian and Soil Denitrification		**unknown**	
Volatilization		**unknown**	

DISCUSSION

A mass balance of nitrogen for the Aberjona river (Table 3) is an important tool for understanding the relationship between human activities and the cycling of this important nutrient. However, many gaps remain in quantifying source and sink terms for the watershed. Sources of mobile N to the Aberjona river watershed include wet and dry atmospheric deposition (estimated by Valiela et al to be ~11 kg ha^{-1} yr^{-1} for the northeast), N fixation and mineralization of previously fixed organic N in soil pools, legacy pollutants, animal and human wastes, and inorganic N in lawn fertilizers. Few of these terms have been quantified rigorously, and the following discussion is intended to identify areas of future research to fill in the gaps in urban watershed N budgets.

The application of lawn fertilizers in suburbia has received considerable attention from the perspective of watershed N load analysis. In a survey of three Massachusetts towns however, White (2003) found that the reported rates of application have been somewhat exaggerated in the literature, and proposed instead an average nitrogen load of 0.86 kg N yr^{-1} for the 50% of surveyed households using fertilizers. Based on this information, and including the turf of three golf courses, we estimated an annual N input of 10 tons to the Aberjona watershed.

Data on the leakage of sewage systems in this watershed is lacking, although combined sewage overflow and illegal connections have been reported (Cutrofello 2005). In the absence of information, we made what we hope was a conservative estimate of 15% leakage from the sewage N flux of approximately 60,000 people.

While the source of nitrogen to HBHA has not been conclusively demonstrated, this meromictic lake is known to receive groundwater input from the Industriplex 128 Superfund site, which contains four capped waste piles with a total volume of 216,000m^3 across 5 hectares (USEPA 2005). The piles are known to contain residue from leather tanning and glue production industries, and one parsimonious explanation of the influx of organic nitrogen and ammonia to HBHA is that it originates in decaying organic matter undergoing mineralization. The composition of collagen (the main constituent of hides and glue) is approximately 50% carbon and 20% nitrogen as aminated polypeptides. If the piles were estimated to contain only 30% decaying hide and glue residue, then a "back of the envelope" calculation (0.30 * 216000m^3 * .89 tons collagen m^{-3} * 0.20 N:collagen) suggests the potential source of nitrogen would still be over 10,000 tons.

The lack of nitrate in the water samples draining HBHA could indicate that little nitrification occurs under reducing conditions, or that it is strongly coupled with denitrification. The extent of denitrification occurring within the groundwater plume and highly reducing HBHA sediments (Cutrofello 2005) is unknown, but if the above hypothesis is representative of the situation, then at current export rates the piles could continue to be a significant source of nitrogen to the watershed for well over 300 years.

CONCLUSIONS

The presence of both organic nitrogen and ammonia in HBHA may implicate an organic based legacy pollutant at the Industriplex 128 superfund site. However, the large quantity of organic nitrogen in the watershed generally indicates an important flux from soil nitrogen pools. Although organic N has been known to be a major fraction of nitrogen export from forested watersheds (Perakis and Hedin 2001), most studies of perturbed watersheds have focused on the inorganic species that are directly implicated in eutrophication. However, organic N can play a significant role in eutrophication via mineralization and through direct uptake (Schimel and Bennett 2004), and should be included in N budgets. In this study, organic nitrogen loads were found to comprise on average 34% of the nitrogen flux in the Aberjona. This is a considerable fraction considering that the watershed is the possibly the most N polluted in the Northeast and among the most eutrophic in the U.S. (Coles 2004). The standard model that predicts increasing nitrogen loads from urbanization tends to assume that the increase occurs by way of inorganic N species; however that does not adequately explain the large flux of organic N in the Aberjona of approximately 5 kg ha^{-1} yr^{-1}. By comparison, export of organic N from a watershed at Hubbard Brook Experimental Forest from 1951 to 2000 was 0.98 kg ha^{-1} yr^{-1}, or 30% of TOT N (Li 2004). Evidence of significant org N loss in at least one reach between Rt. 128 and Montvale Avenue indicates the potential for organic N to undergo transformations in situ, and contrains the role of a perhaps unique legacy organic N source to around a third of riverine organic N export.

From the incomplete nitrogen budget estimated above, it can be seen that by far the largest pool of nitrogen exists in soils. It is therefore of critical importance to quantify the fluxes to and from this pool, especially in the context of disturbances from the built environment that can convert soil N to more mobile and labile forms. In general, digging in the soil, whether for construction, drainage or utility installation, exposes it to both precipitation and oxygen without any plant cover, and tends to result in significant net nitrification of soil N (Wakida 2002). This mechanism, in combination with the lowering of water tables and diminished biotic activity generally, explains the widely reported fact that urban soils contain less nitrogen (and organic matter) than natural soils (Groffman 2002). When lands are converted to urban uses, the large reservoir of nitrogen in the soils tends to be converted to nitrate and exported from the watershed, primarily via groundwater to surface water. What has received almost no attention however, is the fact that this process occurs along a continuum in space and time, and while some older urban areas may have reached a steady state, many watersheds undergoing an expansion in urban and suburban land uses will necessarily represent a transient case, even perhaps decades after the disturbance, given travel times along groundwater flow paths. Without quantifying the transient state of soil N fluxes, it is impossible to know whether and to what extent the N regime of a watershed hinges upon the usual suspects of deposition, fertilizer application, or sewage inputs.

Although further work is necessary to identify and quantify the sources, fluxes and transformations of nitrogen loading the Rt. 128 sub basin of the Aberjona, the picture presented by flux measurements underscores the importance of considering legacy pollutants both in urban N budgets, and in constructing relationships between land use and nitrogen yield. The correlation between current industrial land use and N yield in this study may only be valid inasmuch as current industrial land use is a proxy for historical industrial land use that had a specific bias towards nitrogen pollution.

The correlation of nitrogen yields with urban intensity may reflect increased N inputs from contemporary industrial processes, but may also reflect the delayed effects of historical industries (for example tanning and explosives manufactures in the Aberjona), land use conversions and alterations in the hydrologic regime by impervious surfaces and municipal drainage systems. The extent to which these processes contribute to N yield in the watershed remains unknown. In using intensive land use categories as a generalizable indicator of nitrogen pollution, it is possible to overlook activities with a specific nitrogen bias, such as fertilizer usage at golf courses or legacy nitrogen pollutants, as well as ecological systems such as wetlands and riparian zones which may be a net sink for nitrogen. A transient state of increased flux from soil nitrogen pools due to urban and suburban expansion remains a critical and under studied aspect of nitrogen regimes in densely settled watersheds, and future mass balance efforts should attempt to quantify the effects of land use conversions on nitrogen yields.

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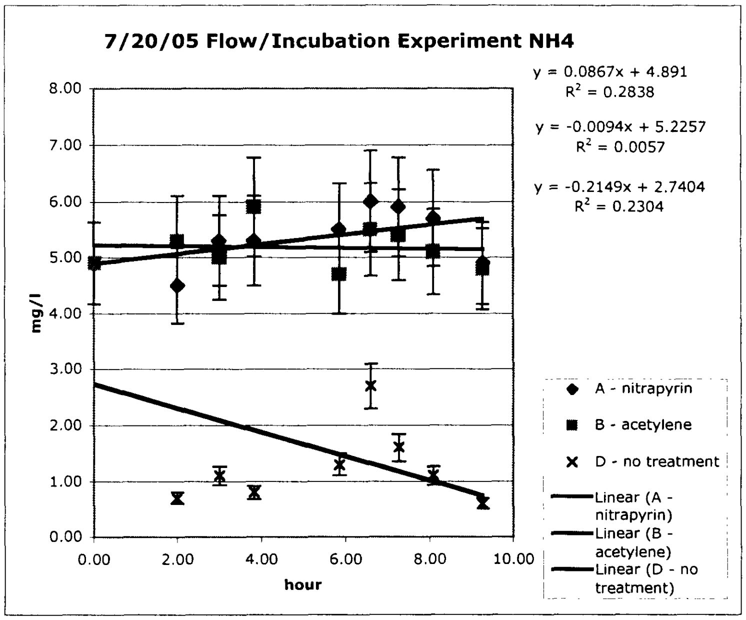
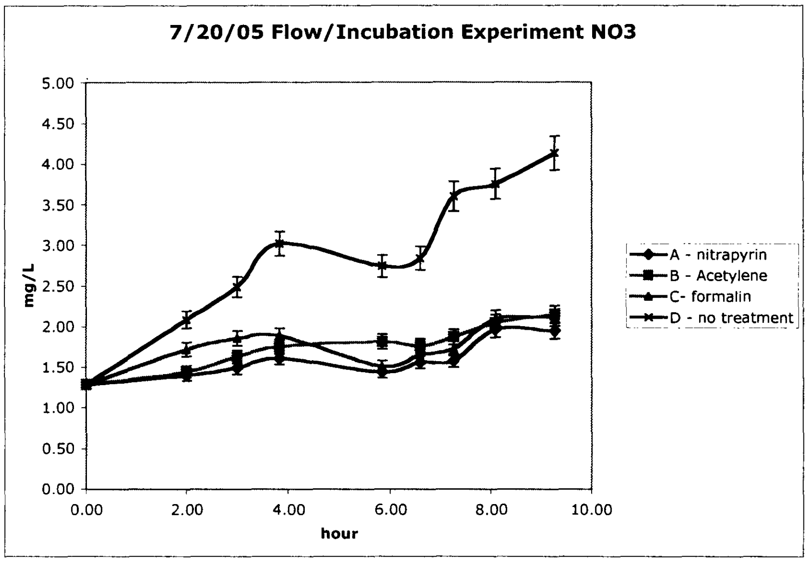
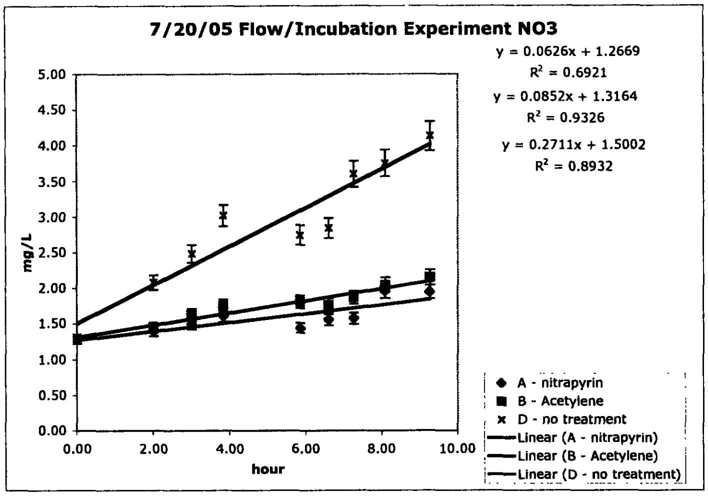
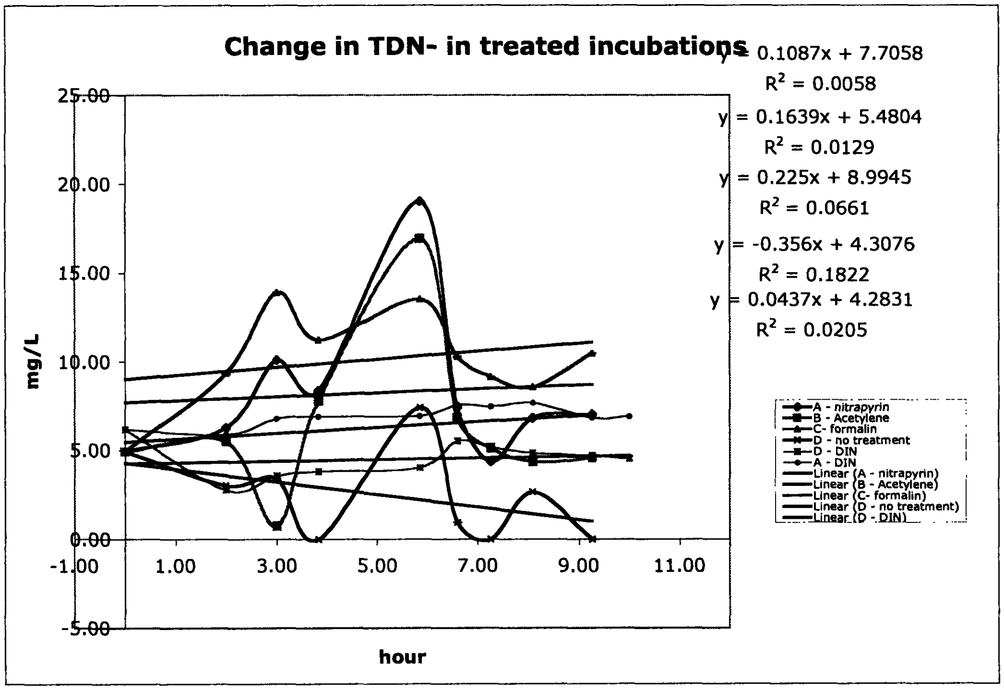
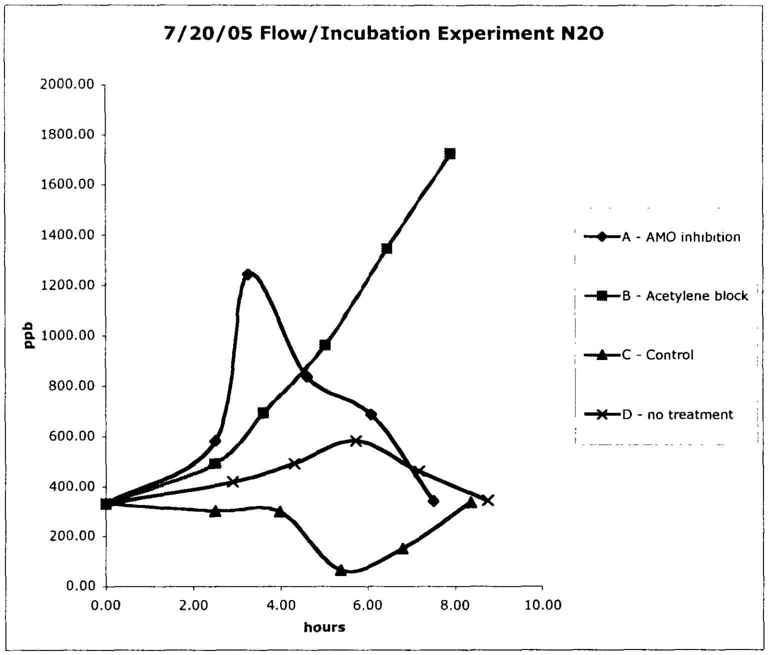
APPENDIX

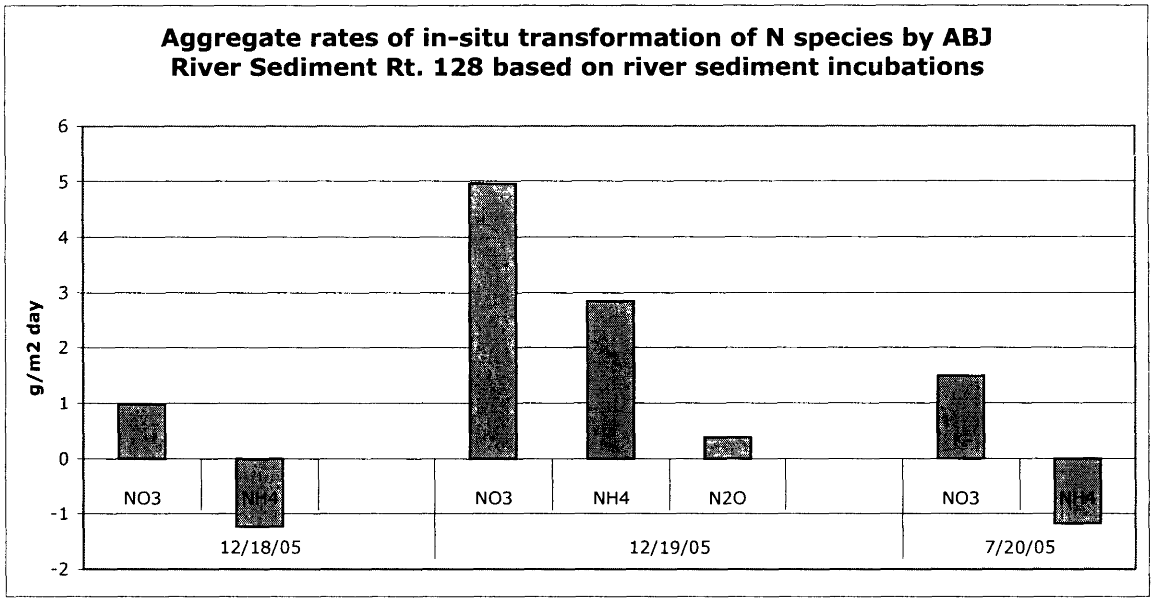

7/20/05 Flow/Incubation Experiment NH4
y = 0.0867x + 4.891
R² = 0.2838
y = -0.0094x + 5.2257
R² = 0.0057
y = -0.2149x + 2.7404
R² = 0.2304
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
0.00
mg/l
0.00
2.00
4.00
6.00
8.00
10.00
hour
◆ A - nitrapyrin
■ B - acetylene
X D - no treatment
Linear (A - nitrapyrin)
Linear (B - acetylene)
Linear (D - no treatment)

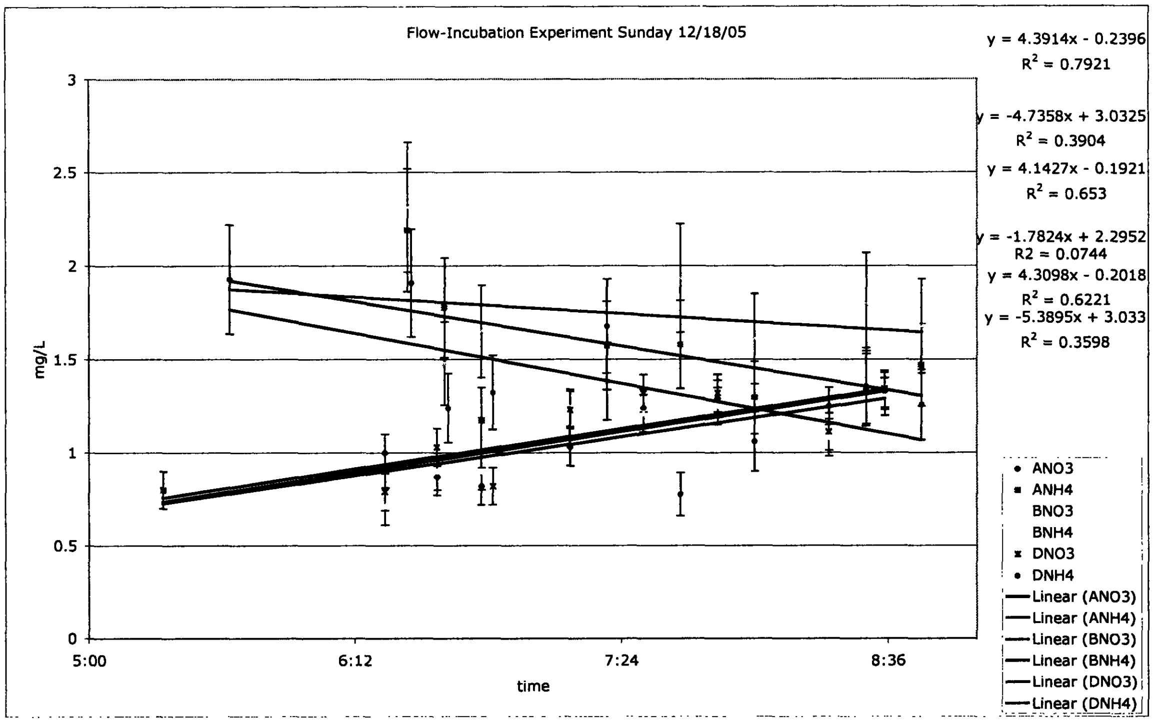

7/20/05 Flow/Incubation Experiment NO3
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
mg/L
0.00
2.00
4.00
6.00
8.00
10.00
hour
A - nitrapyrin
B - Acetylene
C- formalin
D - no treatment

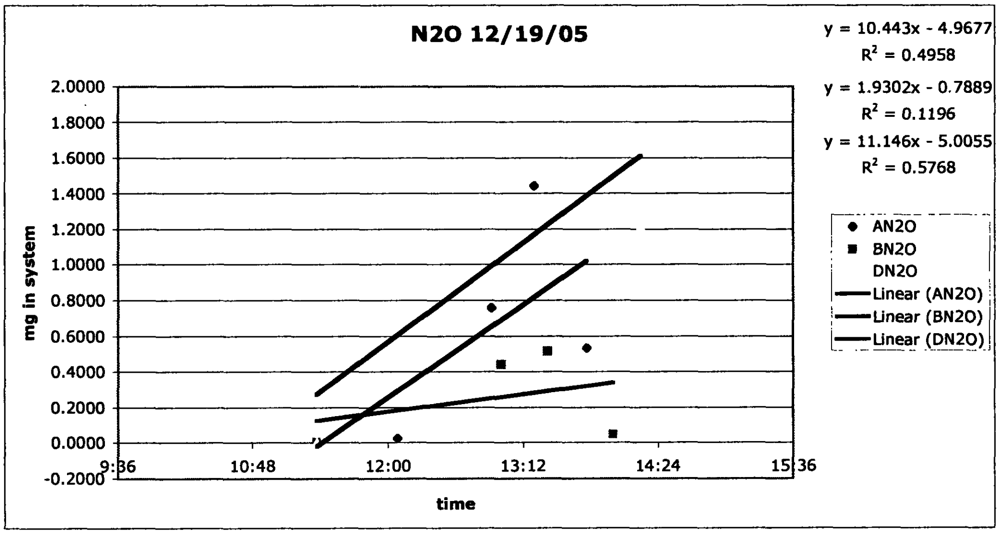

7/20/05 Flow/Incubation Experiment NO3
y = 0.0626x + 1.2669
R² = 0.6921
y = 0.0852x + 1.3164
R² = 0.9326
y = 0.2711x + 1.5002
R² = 0.8932
mg/L
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0.00
2.00
4.00
6.00
8.00
10.00
hour
◆ A - nitrapyrin
■ B - Acetylene
× D - no treatment
Linear (A - nitrapyrin)
Linear (B - Acetylene)
Linear (D - no treatment)

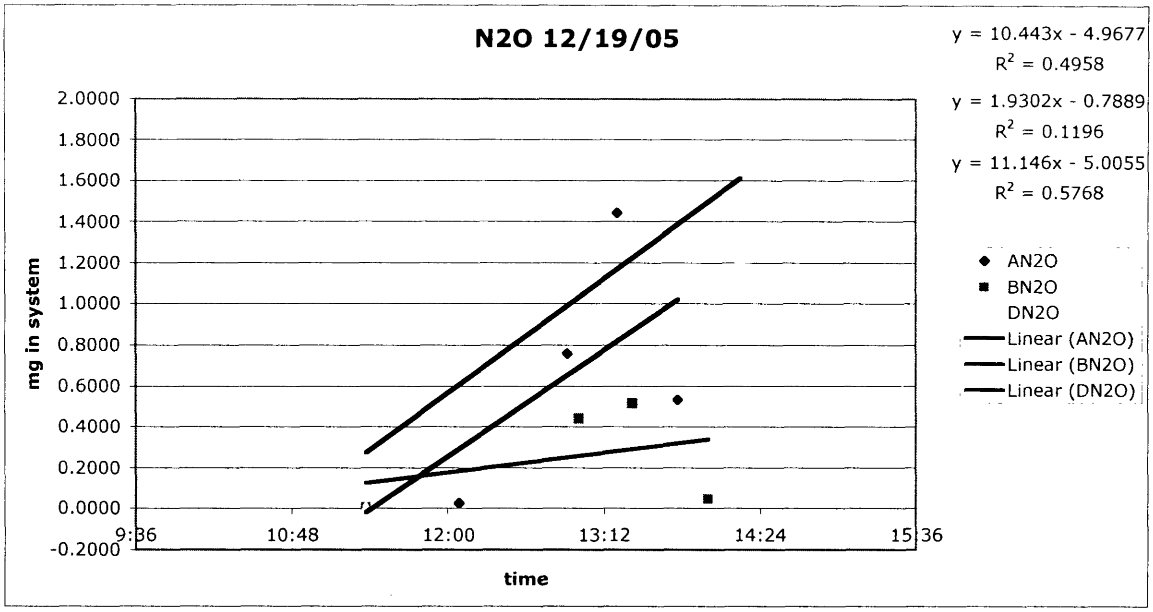

Change in TDN- in treated incubations
y = 0.1087x + 7.7058
R² = 0.0058
y = 0.1639x + 5.4804
R² = 0.0129
y = 0.225x + 8.9945
R² = 0.0661
y = -0.356x + 4.3076
R² = 0.1822
y = 0.0437x + 4.2831
R² = 0.0205
mg/L
25.00
20.00
15.00
10.00
5.00
0.00
-5.00
-1.00
1.00
3.00
5.00
7.00
9.00
11.00
hour
A - nitrapyrin
B - Acetylene
C- formalin
D - no treatment
D - DIN
A - DIN
Linear (A - nitrapyrin)
Linear (B - Acetylene)
Linear (C- formalin)
Linear (D - no treatment)
Linear (D - DIN)

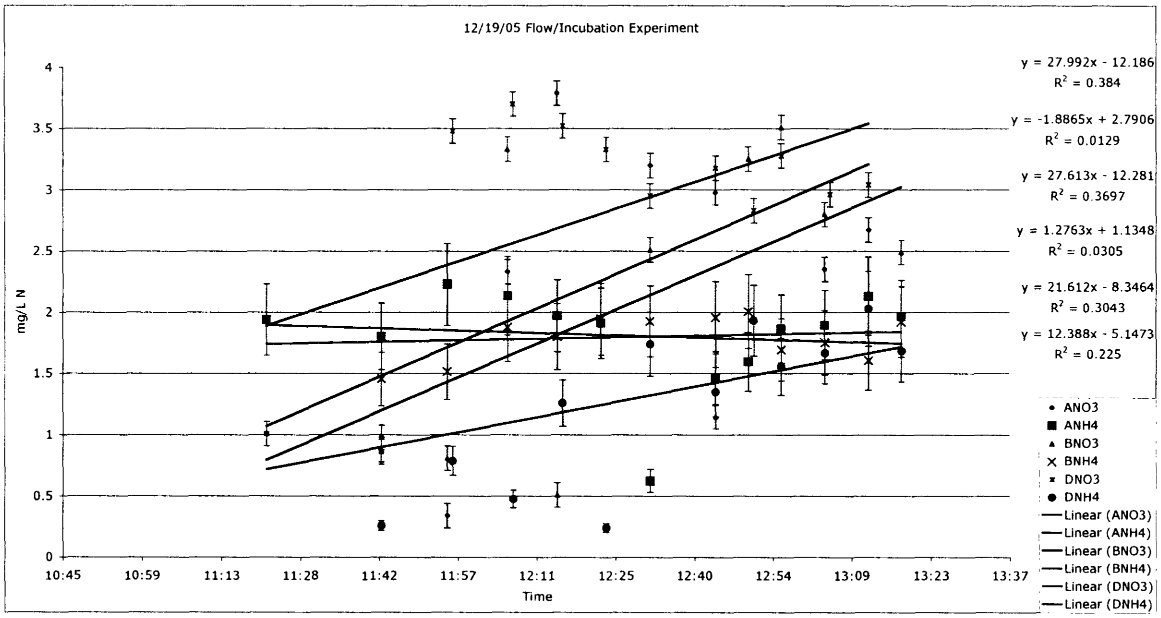

7/20/05 Flow/Incubation Experiment N2O

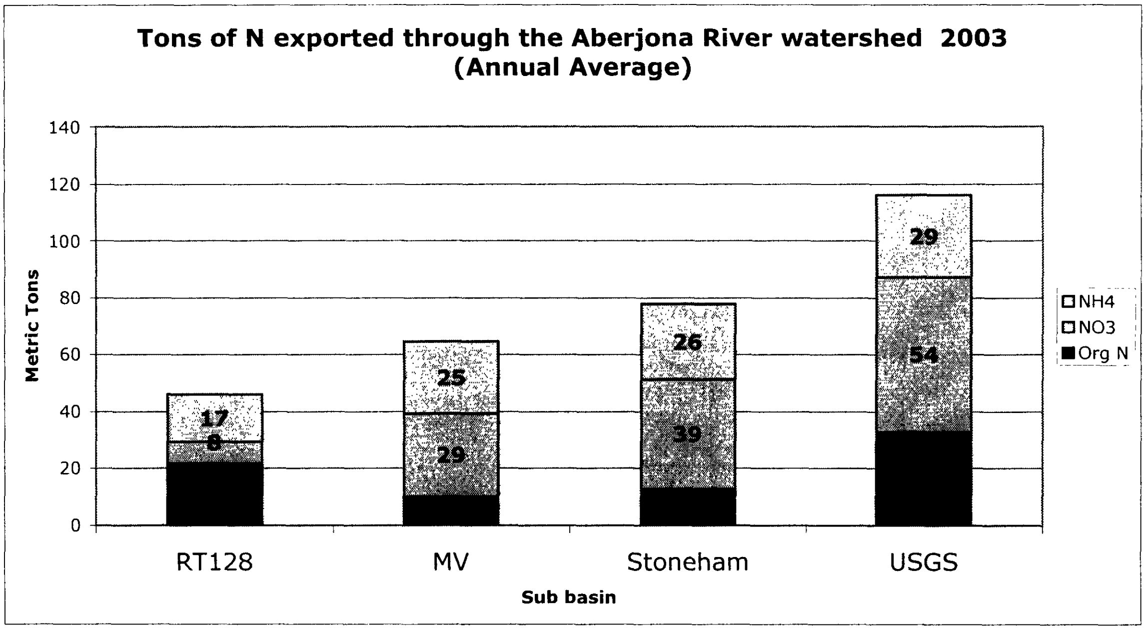

Aggregate rates of in-situ transformation of N species by ABJ River Sediment Rt. 128 based on river sediment incubations

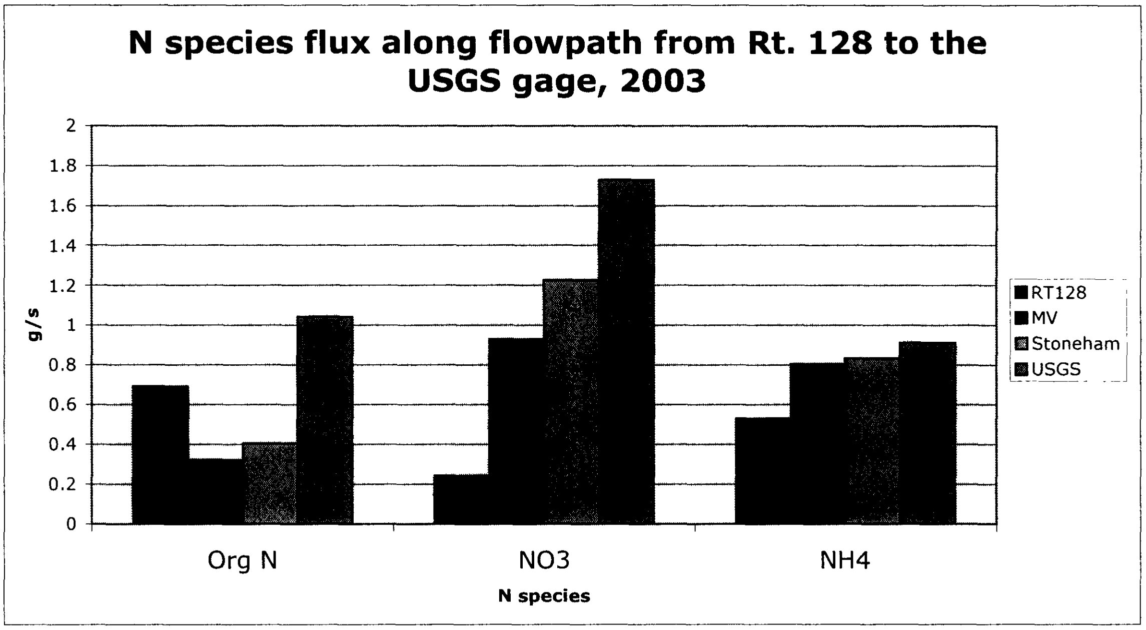

Flow-Incubation Experiment Sunday 12/18/05
y = 4.3914x - 0.2396
R² = 0.7921
y = -4.7358x + 3.0325
R² = 0.3904
y = 4.1427x - 0.1921
R² = 0.653
y = -1.7824x + 2.2952
R2 = 0.0744
y = 4.3098x - 0.2018
R² = 0.6221
y = -5.3895x + 3.033
R² = 0.3598
3
2.5
2
1.5
1
0.5
0
mg/L
5:00
6:12
7:24
8:36
time
ANO3
ANH4
BNO3
BNH4
DNO3
DNH4
Linear (ANO3)
Linear (ANH4)
Linear (BNO3)
Linear (BNH4)
Linear (DNO3)
Linear (DNH4)

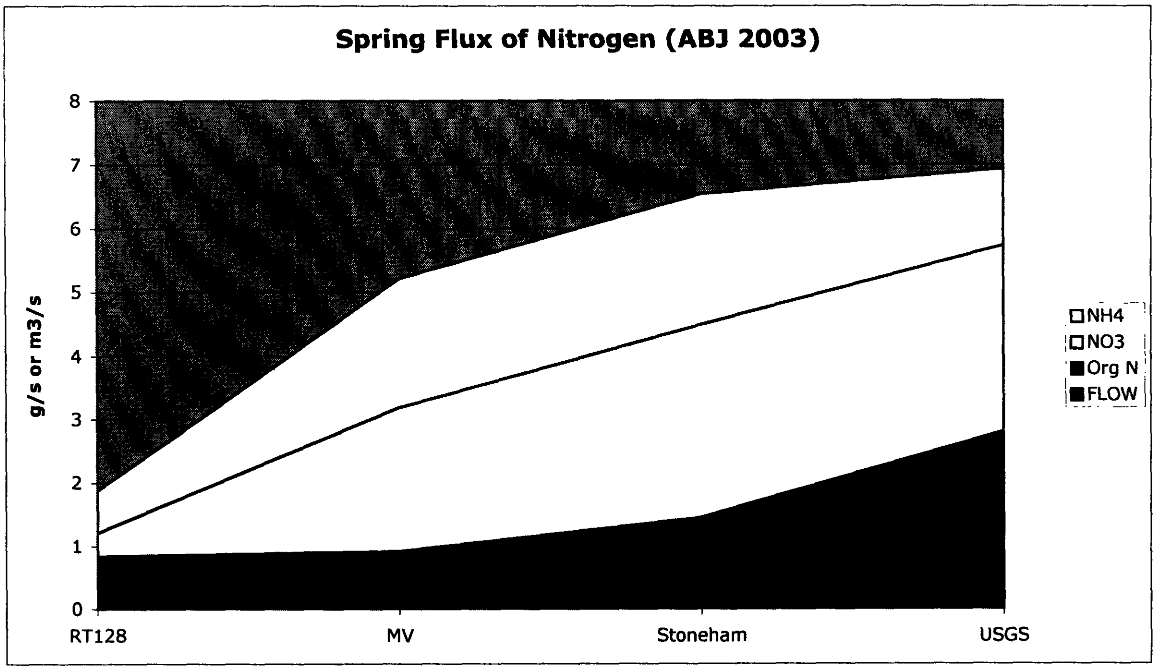

N2O 12/19/05
y = 10.443x - 4.9677
R² = 0.4958
y = 1.9302x - 0.7889
R² = 0.1196
y = 11.146x - 5.0055
R² = 0.5768
2.0000
1.8000
1.6000
1.4000
1.2000
1.0000
0.8000
0.6000
0.4000
0.2000
0.0000
-0.2000
mg in system
9:36
10:48
12:00
13:12
14:24
15:36
time
AN2O
BN2O
DN2O
Linear (AN2O)
Linear (BN2O)
Linear (DN2O)


N2O 12/19/05
y = 10.443x - 4.9677
R² = 0.4958
y = 1.9302x - 0.7889
R² = 0.1196
y = 11.146x - 5.0055
R² = 0.5768
2.0000
1.8000
1.6000
1.4000
1.2000
1.0000
0.8000
0.6000
0.4000
0.2000
0.0000
-0.2000
mg in system
9:36
10:48
12:00
13:12
14:24
15:36
time
AN2O
BN2O
DN2O
Linear (AN2O)
Linear (BN2O)
Linear (DN2O)

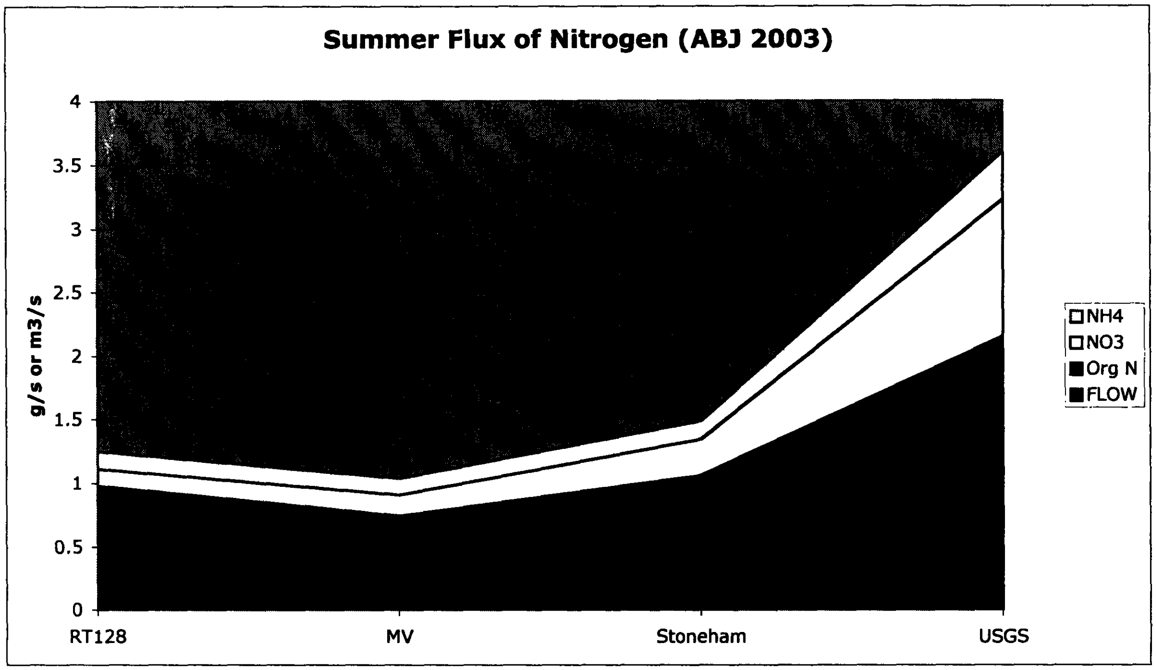

12/19/05 Flow/Incubation Experiment
y = 27.992x - 12.186
R² = 0.384
y = -1.8865x + 2.7906
R² = 0.0129
y = 27.613x - 12.281
R² = 0.3697
y = 1.2763x + 1.1348
R² = 0.0305
y = 21.612x - 8.3464
R² = 0.3043
y = 12.388x - 5.1473
R² = 0.225
4
3.5
3
2.5
2
1.5
1
0.5
0
mg/L N
10:45
10:59
11:13
11:28
11:42
11:57
12:11
12:25
12:40
12:54
13:09
13:23
13:37
Time
ANO3
ANH4
BNO3
BNH4
DNO3
DNH4
Linear (ANO3)
Linear (ANH4)
Linear (BNO3)
Linear (BNH4)
Linear (DNO3)
Linear (DNH4)


Tons of N exported through the Aberjona River watershed 2003 (Annual Average)

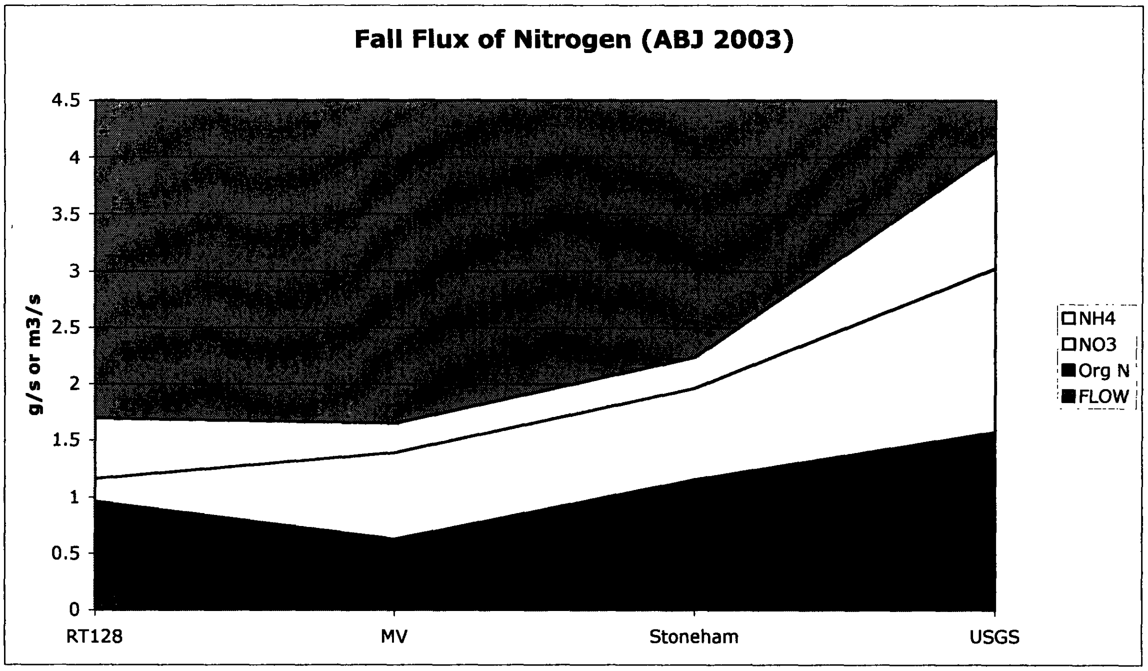

N species flux along flowpath from Rt. 128 to the USGS gage, 2003

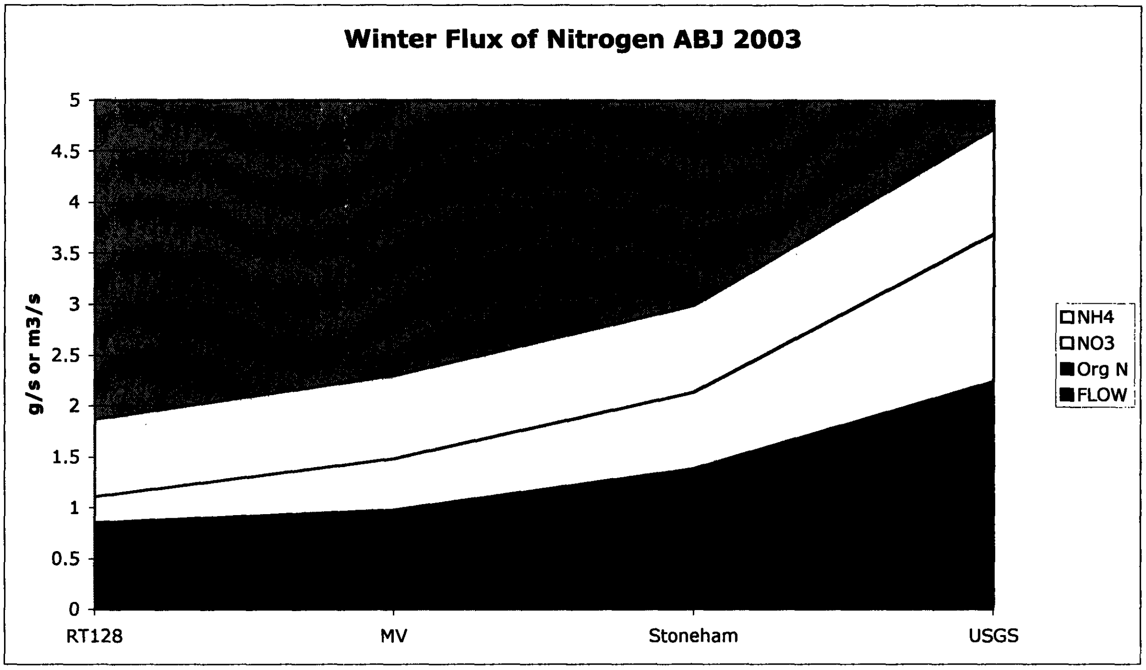


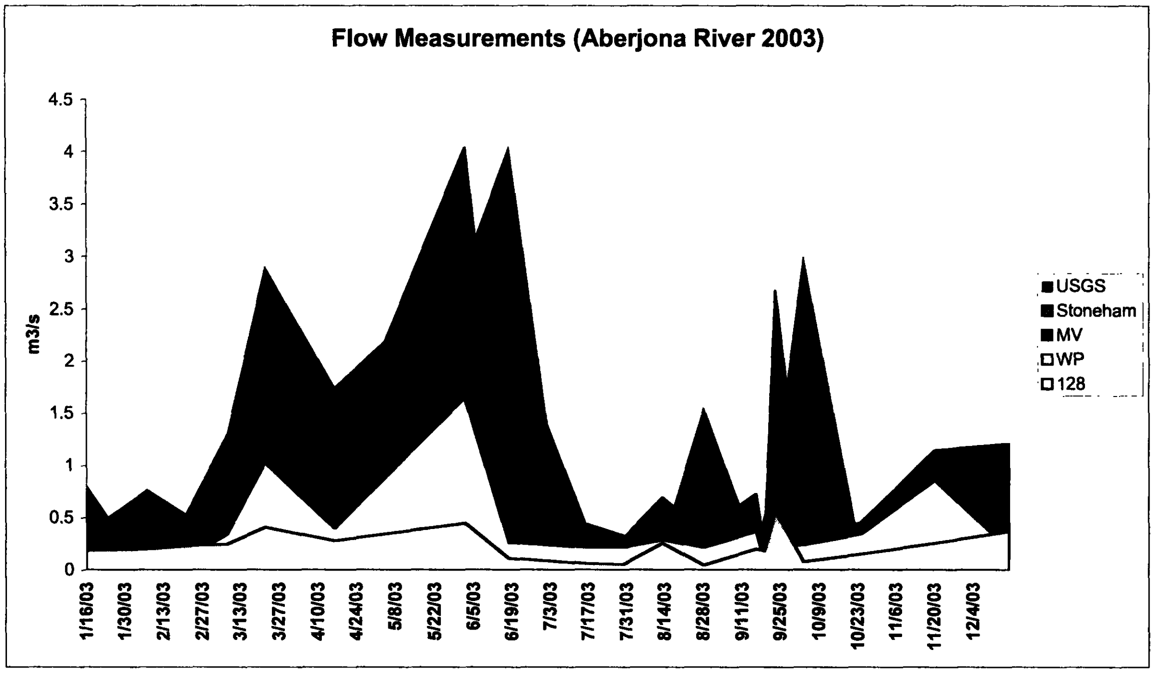
Spring Flux of Nitrogen (ABJ 2003)

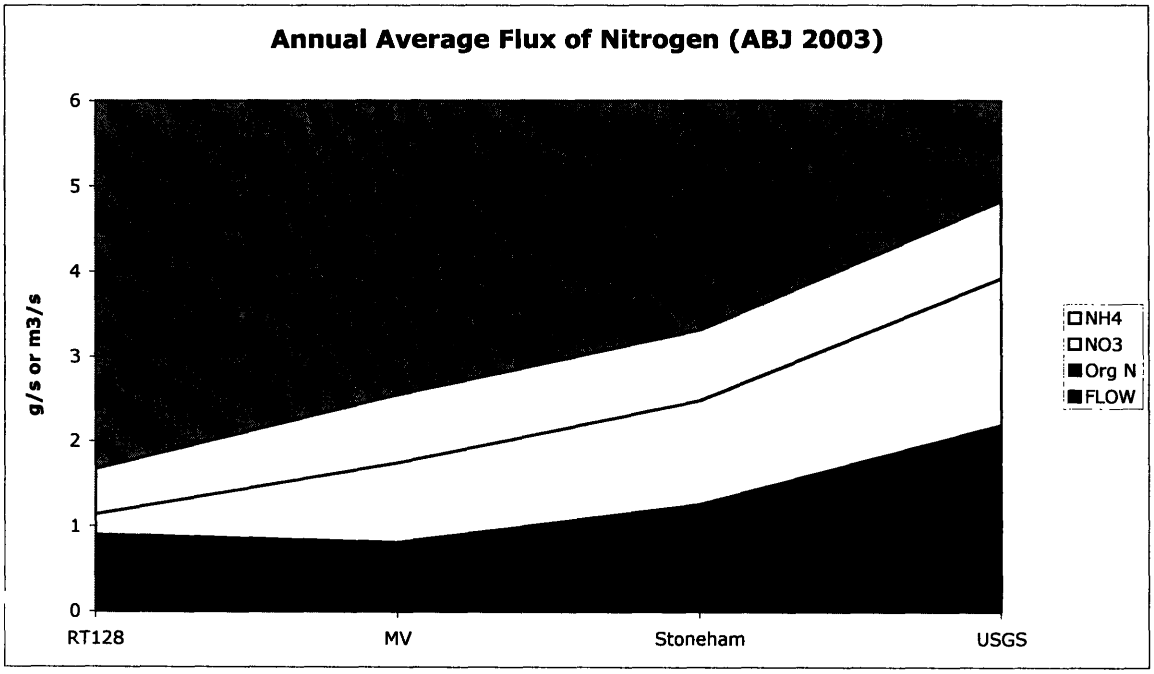


Summer Flux of Nitrogen (ABJ 2003)


Fall Flux of Nitrogen (ABJ 2003)
g/s or m3/s
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
RT128
MV
Stoneham
USGS
□NH4
□NO3
■Org N
■FLOW


Winter Flux of Nitrogen ABJ 2003
g/s or m3/s
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
RT128
MV
Stoneham
USGS
□NH4
□NO3
■Org N
■FLOW


Flow Measurements (Aberjona River 2003)
m3/s
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
1/16/03
1/30/03
2/13/03
2/27/03
3/13/03
3/27/03
4/10/03
4/24/03
5/8/03
5/22/03
6/5/03
6/19/03
7/3/03
7/17/03
7/31/03
8/14/03
8/28/03
9/11/03
9/25/03
10/9/03
10/23/03
11/6/03
11/20/03
12/4/03
■ USGS
■ Stoneham
■ MV
☐ WP
☐ 128


Annual Average Flux of Nitrogen (ABJ 2003)
g/s or m3/s
6
5
4
3
2
1
0
RT128
MV
Stoneham
USGS
☐ NH4
☐ NO3
■ Org N
■ FLOW

Site	Date	NO3	NH4	TOT N	OrgN	%orgN
128	1/17/07	0.95	3.74	10.52	5.84	0.55
128	1/25/07	1.16	3.70	11.04	6.18	0.56
128	2/8/07	0.95	3.14	7.78	3.69	0.47
128	2/22/07	0.92	3.22	2.07	0.00	0.00
128	3/9/07	1.01	4.05			
128	3/23/07	1.26	3.37	5.68	1.04	0.18
128	4/17/07	1.33	0.62	5.97	4.02	0.67
128	6/3/07					
128	6/19/07	1.18	0.75	12.97	11.04	0.85
128	7/3/07	1.03		7.02	5.99	0.85
128	7/17/07	0.71	2.30			
128	7/31/07	1.24	1.12	8.21	5.85	0.71
128	8/14/07	1.01	1.95	7.77	4.82	0.62
128	8/29/07	1.66	2.99	9.71	5.06	0.52
128	9/17/07	0.88	3.48	21.33	16.97	0.80
128	9/20/07	0.74	2.52			
128	9/24/07	0.99	1.11	2.57	0.47	0.18
128	10/4/07	1.47	5.76	10.82	3.59	0.33
128	10/25/07	1.62	5.22	8.97	2.13	0.24
128	11/21/07	1.65	3.68	6.50	1.17	0.18
128	12/18/07	0.54	1.92	3.03	0.57	0.19
128	2/5/08	0.43	8.04	-2.98	-11.45	3.85
128	3/6/08	0.90	4.52	-1.91	-7.33	3.85
128	4/10/08	3.96	2.71	-2.34	-9.02	3.85
128	4/24/08	2.13	2.38	-1.59	-6.10	3.85
128	5/18/08	1.10	2.95	-1.43	-5.48	3.85
128	6/23/08	1.70	4.29	-2.10	-8.09	3.85
128	8/6/08		3.04	-1.07	-4.11	3.85
HPin	1/25/07	1.84	0.06	3.94	2.04	0.52
HPin	2/8/07	1.35	0.16	2.92	1.41	0.48
HPin	2/22/07	1.25	0.09	1.64	0.29	0.18
HPin	3/9/07	1.42	0.02	-0.51	-1.96	3.85
HPin	3/23/07	3.13	0.09	0.84	-2.37	-2.81
Hpin	4/17/07	1.14	0.01	1.19	0.04	0.04
HPin	6/3/07			0.00	0.00	
HPin	6/19/07	0.58	0.01	2.03	1.44	0.71
HPin	7/3/07	1.01		1.23	0.22	0.18
HPin	7/17/07	1.02	0.01	-0.36	-1.39	3.85

HPin	7/31/07	0.64	0.12	0.78	0.01	0.01
HPin	8/14/07	0.63	0.07	0.21	-0.49	-2.40
HPin	8/29/07	1.33	0.03	1.53	0.17	0.11
HPin	10/4/07	1.47	0.06	1.19	-0.34	-0.29
HPin	11/21/07	1.17	0.07	1.12	-0.12	-0.10
HPin	2/5/08	0.91	0.35	-0.44	-1.70	3.85
HPin	3/6/08	1.27	0.09	-0.48	-1.85	3.85
HPin	4/10/08	1.87	0.04	-0.67	-2.58	3.85
HPin	4/24/08	1.08	0.08	-0.41	-1.58	3.85
HPin	5/18/08	0.74	0.06	-0.28	-1.09	3.85
HPin	6/23/08	1.26	0.05	-0.46	-1.78	3.85
HPin	8/6/08		0.03	-0.01	-0.04	3.85
Hpout	1/17/07	0.79	0.11	2.16	1.26	0.58
HPout	1/25/07	0.65	0.09	2.19	1.45	0.66
HPout	2/8/07	1.13	0.13	1.67	0.41	0.24
HPout	2/22/07	1.15	0.07	1.53	0.32	0.21
HPout	3/9/07	1.13	0.06	-0.42	-1.61	3.85
HPout	3/23/07	1.85	0.07	1.15	-0.77	-0.67
Hpout	4/17/07	0.93	0.01	1.12	0.18	0.16
HPout	6/3/07			0.00	0.00	
HPout	6/19/07	0.43	0.01	1.21	0.77	0.64
HPout	7/3/07	0.45		0.63	0.17	0.28
HPout	7/17/07	0.44	0.01	-0.16	-0.60	3.85
HPout	7/31/07	0.26	0.08	0.17	-0.17	-1.02
HPout	8/14/07	0.32	0.02	-0.28	-0.61	2.20
HPout	8/29/07	0.32	0.02	0.27	-0.07	-0.26
HPout	9/17/07	0.26	0.04	2.10	1.80	0.86
HPout	9/20/07	0.19	0.18	-0.13	-0.51	3.85
HPout	11/21/07	0.26	0.16	0.49	0.07	0.15
HPout	12/18/07	0.56	0.16	0.70	-0.02	-0.02
HPout	2/5/08	1.01	0.06	-0.38	-1.45	3.85
HPout	3/6/08	1.08	0.02	-0.39	-1.48	3.85
HPout	4/10/08	1.78	0.07	-0.65	-2.51	3.85
HPout	4/24/08	1.28	0.01	-0.45	-1.74	3.85
HPout	5/18/08	0.62	0.02	-0.23	-0.87	3.85
HPout	8/6/08		0.01	0.00	-0.01	3.85
MLD	7/3/07	0.85		1.61	0.76	0.47
MLD	7/17/07	1.18	0.10	-0.45	-1.73	3.85
MLD	7/31/07		0.34	2.04	1.69	0.83
MLD	8/14/07	0.90	0.03	0.30	-0.63	-2.10
MLD	8/29/07	0.64		1.92	1.27	0.66
MLD	9/17/07	0.42	0.03	5.01	4.55	0.91

MLD	9/20/07	0.63	0.04	-0.23	-0.90	3.85
MLD	10/4/07	0.93	0.19	1.72	0.61	0.35
MLD	10/25/07		0.24	1.51	1.27	0.84
MLD	11/21/07	1.34	0.31	1.39	-0.26	-0.19
MLD	12/18/07	1.50	0.44	1.56	-0.39	-0.25
MLD	2/5/08	1.60	0.47	-0.73	-2.80	3.85
MLD	3/6/08	1.08	0.57	-0.58	-2.23	3.85
MLD	4/10/08	4.55	0.48	-1.77	-6.80	3.85
MLD	4/24/08	3.92	0.27	-1.47	-5.66	3.85
MLD	5/18/08	0.43	0.20	-0.22	-0.86	3.85
MLD	6/23/08	1.09	0.19	-0.45	-1.73	3.85
MLD	8/6/08		0.01	0.00	-0.02	3.85
MV	1/17/07	1.35	2.83	7.92	3.74	0.47
MV	1/25/07	2.30	3.25	8.34	2.78	0.33
MV	2/8/07	1.19	2.40	7.16	3.57	0.50
MV	2/22/07	0.79	2.95	2.56		0.00
MV	3/9/07	1.16	2.65			
MV	3/23/07	2.90	2.83	4.94		0.00
MV	4/17/07	2.20	0.64	4.02	1.18	0.29
MV	6/3/07			0.00	0.00	
MV	6/19/07	1.13	0.42	7.85	6.30	0.80
MV	7/3/07	0.41		2.77	2.37	0.85
MV	7/17/07	1.26	0.48			
MV	7/31/07	1.27		4.73	3.46	0.73
MV	8/14/07	0.99	1.06	3.28	1.23	0.37
MV	8/29/07	3.18	0.38	4.57	1.01	0.22
MV	9/17/07	1.25	0.75	9.60	7.60	0.79
MV	9/20/07	1.31	1.38			
MV	9/24/07	1.69	0.28	1.20		0.00
MV	10/4/07	3.54	2.36	5.16		0.00
MV	10/25/07	2.16	2.73	3.92		0.00
MV	11/21/07	1.69	2.47	4.31	0.15	0.03
MV	12/18/07	0.83	1.27	2.72	0.62	0.23
MV	2/5/08	1.05	3.82	-1.71		0.00
MV	2/5/08	1.05	3.82	-1.71		0.00
MV	3/6/08	1.51	3.24	-1.67	-6.41	3.85
MV	4/10/08	2.78	1.71	-1.58	-6.07	3.85
MV	4/24/08	3.05	0.69	-1.31	-5.05	3.85
MV	5/18/08	0.55	1.43	-0.70	-2.68	3.85
MV	6/23/08	3.10	2.08	-1.82	-6.99	3.85
MV	8/6/08		0.52	-0.18	-0.71	3.85
NFB	10/25/07	1.70	0.46	2.03	-0.13	-0.07

SC	11/21/07	1.69	3.63	5.93	0.61	0.10
SC	12/18/07	0.79	1.54	2.14	-0.19	-0.09
SC	2/5/08	0.81	4.92	-2.01	-7.74	3.85
SC	3/6/08	1.20	3.85	-1.77	-6.82	3.85
SC	4/10/08	2.15	2.19	-1.52	-5.86	3.85
SC	4/24/08	2.48	0.98	-1.21	-4.67	3.85
SC	5/18/08	0.70	2.03	-0.96	-3.68	3.85
SC	6/23/08	1.98	3.74	-2.01	-7.73	3.85
SC	8/6/08		0.80	-0.28	-1.08	3.85
SWS	7/29/08		0.23	-0.08	-0.32	3.85
SWS	8/6/08		0.19	-0.07	-0.26	3.85
USGS	1/17/07	1.29	1.42	3.83	1.13	0.30
USGS	1/25/07	1.93	1.62	5.89	2.34	0.40
USGS	2/8/07	1.47	1.38	7.32	4.47	0.61
USGS	2/22/07	1.16	1.58	3.18	0.44	0.14
USGS	3/9/07	1.35	1.21			
USGS	3/23/07	1.93	0.99	3.14	0.22	0.07
USGS	4/17/07	1.38	0.17	2.50	0.94	0.38
USGS	4/17/07	1.38	0.17	2.50	0.94	0.38
USGS	6/3/07					
USGS	6/19/07	1.18	0.45	3.68	2.05	0.56
USGS	7/3/07	1.21		2.41	1.20	0.50
USGS	7/17/07	1.38	0.26			
USGS	7/31/07	1.51	0.35	1.64	0.00	
USGS	8/14/07	0.83	0.26	0.77	0.00	
USGS	8/29/07	2.51	0.26	2.38	0.00	
USGS	9/17/07	0.60	0.16	4.04	3.29	0.81
USGS	9/20/07	1.35	0.46			
USGS	9/24/07	0.78	0.38	3.10	1.95	0.63
USGS	10/4/07	2.84	0.24	2.42	0.00	
USGS	10/25/07	2.47	0.87	2.84	0.00	
USGS	11/21/07	1.81	0.87	4.06	1.38	0.34
USGS	12/18/07	0.81	0.54	1.21	0.00	
USGS	12/18/07	1.41	0.45	1.38	0.00	
USGS	12/18/07	1.46	0.46	1.44	0.00	
USGS	2/5/08	1.13	1.14		-2.26	
USGS	3/6/08	1.27	1.21		-2.49	
USGS	3/13/08	1.79	1.19		-2.98	
USGS	3/13/08	0.87	1.18		-2.05	
USGS	4/1/08	0.92	0.34		-1.27	
USGS	4/10/08	4.27	0.45	-1.66	-6.37	3.85
USGS	4/24/08	1.26	0.32	-0.55	-2.13	3.85

USGS	5/18/08	0.55	0.39	-0.33	-1.27	3.85
USGS	6/23/08	2.70	0.57	-1.15	-4.42	3.85
USGS	7/9/08	2.92	0.37	-1.16	-4.44	3.85
USGS	7/9/08	2.66	0.39	-1.07	-4.13	3.85
USGS	7/29/08		0.15	-0.05	-0.20	3.85
USGS	8/6/08		0.11	-0.04	-0.14	3.85
USGS	9/9/08		0.28	-0.10	-0.38	3.85
USGS	9/9/08		0.30	-0.11	-0.41	3.85
USGS	9/9/08		0.24	-0.08	-0.33	3.85
USGS	9/9/08		0.20	-0.07	-0.27	3.85
WP	1/17/07	0.70	0.12	2.35	1.53	0.65
WP	1/25/07	0.64	0.11	1.96	1.21	0.62
WP	2/8/07	1.15	0.15	3.04	1.74	0.57
WP	2/22/07	1.13	0.11	1.79	0.55	0.31
WP	3/9/07	0.89	0.07	-0.34	-1.29	3.85
WP	3/23/07	1.68	0.08	1.01	-0.76	-0.75
WP	4/17/07	1.27	0.01	1.10	-0.18	-0.16
WP	6/3/07			0.00	0.00	
WP	6/19/07	0.68	0.01	1.12	0.43	0.38
WP	7/3/07	0.56		0.57	0.01	0.02
WP	7/17/07	0.22	0.03	-0.09	-0.34	3.85
WP	7/31/07	0.16	0.09	0.29	0.05	0.16
WP	8/14/07	0.27	0.02	-0.04	-0.32	7.84
WP	8/29/07	0.14	0.18	0.68	0.37	0.54
WP	9/17/07	0.12	0.05	2.32	2.16	0.93
WP	9/20/07	0.10	0.07	-0.06	-0.22	3.85
WP	10/4/07	0.14	0.06	0.60	0.41	0.67
WP	10/25/07	0.27		0.72	0.45	0.62
WP	11/21/07	0.51	0.12	0.65	0.03	0.04
WP	12/18/07	0.63	0.15	0.57	-0.21	-0.37
WP	2/5/08	1.09	0.18	-0.45	-1.71	3.85
WP	3/6/08	0.98	0.01	-0.35	-1.34	3.85
WP	4/1/08	0.82	0.03	-0.30	-1.14	3.85
WP	4/10/08	2.74	0.06	-0.99	-3.79	3.85
WP	4/24/08	1.19	0.04	-0.43	-1.67	3.85
WP	5/18/08	0.35	0.02	-0.13	-0.49	3.85
WP	6/23/08	0.33	0.09	-0.15	-0.56	3.85
WP	7/29/08		0.02	-0.01	-0.02	3.85
WP	8/6/08		0.01	0.00	-0.02	3.85