Appendix A:
Nitrogen Deposition from the Atmosphere to the Earth's Surface

Review of Nr wet deposition

Substantial progress has been made in monitoring Nr wet deposition as is summarized in information provided by the National Atmospheric Deposition Program/ National Trends Network (NADP) established in 1979. This network monitors precipitation composition at over 250 sites in the U.S. and its territories (http://nadp.sws. uiuc.edu). Precipitation at each station is collected weekly according to well established and uniform procedures and sent to the Central Analytical Laboratory for analysis of acidity, NO_3^-, NH_4^+, chloride, as well as the base cations calcium, magnesium, potassium and sodium. For greater temporal resolution, the Atmospheric Integrated Research Monitoring Network AIRMON, composed of seven sites, was formed in 1992 as part of the NADP program to study wet deposition composition and trends using samples collected daily. The same species are measured as in NADP. By interpolating among sites, NADP is able to estimate the wet deposition of NH_4^+ (reduced N), and NO_3^- (oxidized N) for the 48 contiguous states (Table A-1 and Figure A-1).
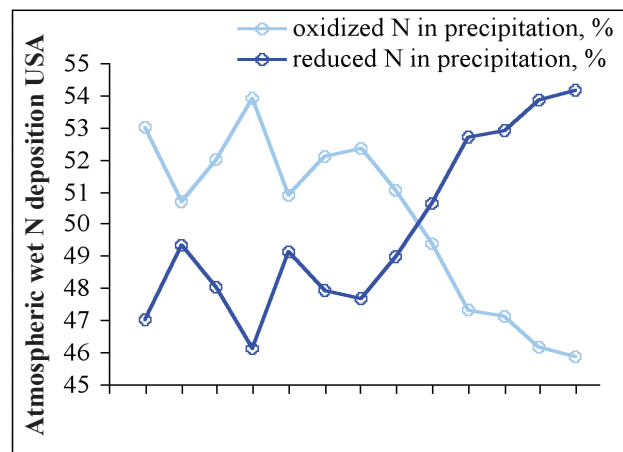

Figure A-1: Percent contribution of oxidized (NO_3^-) and reduced (NH_4^+) nitrogen wet deposition from 1994 to 2006.

As emissions of NO_x have decreased, the relative importance of NH_x has increased (data from National Atmospheric Deposition Program, 2010).

Table A-1: Annual wet deposition of reduced (NH_4^+), oxidized (NO_3^-), and total N to the 48 contiguous states

NADP/NTN deposition estimates			
	reduced N in precipitation, kg/ha/yr	oxidized N in precipitation, kg/ha/yr	total wet N deposition, kg/ha/yr
1994	1.49	1.68	3.17
1995	1.63	1.67	3.30
1996	1.66	1.80	3.45
1997	1.49	1.74	3.24
1998	1.72	1.78	3.49
1999	1.46	1.58	3.04
2000	1.48	1.62	3.10
2001	1.50	1.57	3.07
2002	1.59	1.55	3.14
2003	1.72	1.55	3.27
2004	1.70	1.52	3.22
2005	1.65	1.41	3.06
2006	1.65	1.40	3.05

Source: NADP/National Trends Network (NTN) http://nadp.sws.uiuc.edu

Although individual regions vary, the NADP data for the entire 48 states indicate an apparent decrease in NO_3^- wet deposition, but not in NH_4^+ deposition (Table A-1 and Figure A-2). Ammonium wet deposition shows a weak increase, although the correlation coefficient is small. As NO_x controls have become more effective, the role of reduced N appears to have grown in relative importance. The nitrate data appear to show a statistically significant trend and quantifying the response of deposition to a change in emissions would be useful to both the scientific and policy communities. A notable reduction in power plant NO_x emissions occurred as the result of the NO_x State Implementation Plan (SIP) call (McClenny et al., 2002; Gilliland et al., 2008; Bloomer et al., 2009). EPA should pursue a rigorous analysis of the emissions and deposition data, including identifying monitors and methods that are consistent from the beginning to the end of the record, as indicated in Recommendation 8.

How is Nr deposition related to emissions?

The relationship between emissions of Nr and observed deposition is critical for understanding the efficacy of abatement strategies as well as for partitioning local and large-scale effects of emissions. Only a few studies covering several individual sites have sufficient monitoring consistency and duration to determine rigorously long-term trends in NO_3^- and NH_4^+ and their relationship to emissions, and here we consider several
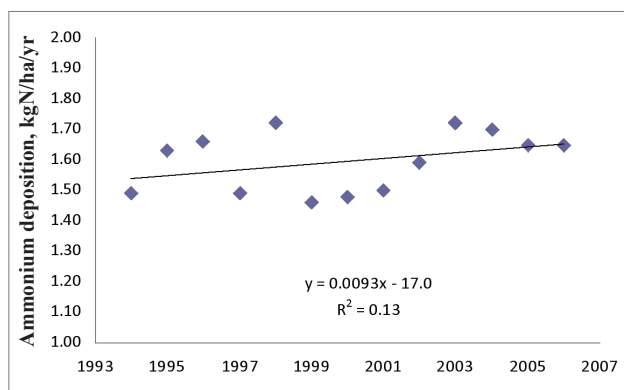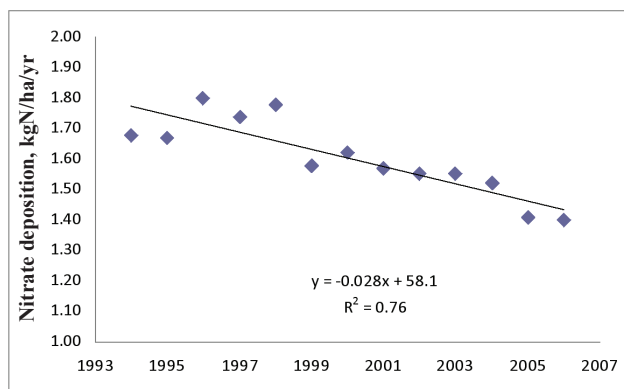
Figure A-2: Trend in reported wet deposition of NH_4^+ and NO_3^- for the 48 contiguous states

Note the sampling methods and locations have not been tested for temporal or spatial bias (data from National Atmospheric Deposition Program, 2010).

examples (Kelly et al., 2002; Butler et al., 2005; Likens et al., 2005). These sites tend to be in the eastern U.S. where monitoring is more concentrated and has a longer history and where upwind sources and downwind receptors are relatively well known. Examination of these studies reveals that concentrations of gaseous and particulate N species in the atmosphere, as well as the Nr content of precipitation over the eastern U.S., shows significant decreases. Correlation with regional emissions is stronger than with local emissions, in keeping with the secondary nature of the major compounds – NO_3^- and NH_4^+. Decreases in NH_4^+ concentration and wet deposition are attributed to decreases in SO_4^{2-} concentrations, meaning that more of the reduced Nr remains in the gas phase. For the period 1965 to 2000, NO_3^- levels in bulk deposition correlate well with reported NO_x emissions. For shorter and earlier time periods the correlation is weaker, and the authors attribute this to changes in the EPA's methods of measuring and reporting emissions; they find evidence of continued errors in emissions from vehicles. Decreases in deposition will probably not be linearly proportional to decreases in emissions; for example a 50% reduction in NO_x emissions is likely to produce a reduction of about 35% in concentration and deposition of nitrate.

The relationship between chemically reduced N emissions and deposition is more complex. The maps of ammonium deposition (Figure A-3) show that maxima occur near or downwind of major agricultural centers where emissions should be high. The full extent of the deposition record (see http://nadp.sws.uiuc.edu) shows the large intensification of NH_4^+ wet deposition in selected areas. The southeastern U.S., particularly North Carolina, has seen a long-term rise (Aneja et al., 2001; Aneja et al., 2003; Stephen and Aneja, 2008). The increase in deposition coincides with the increase in livestock production, but a swine population moratorium appears to have helped abate emissions (Stephen and Aneja, 2008).
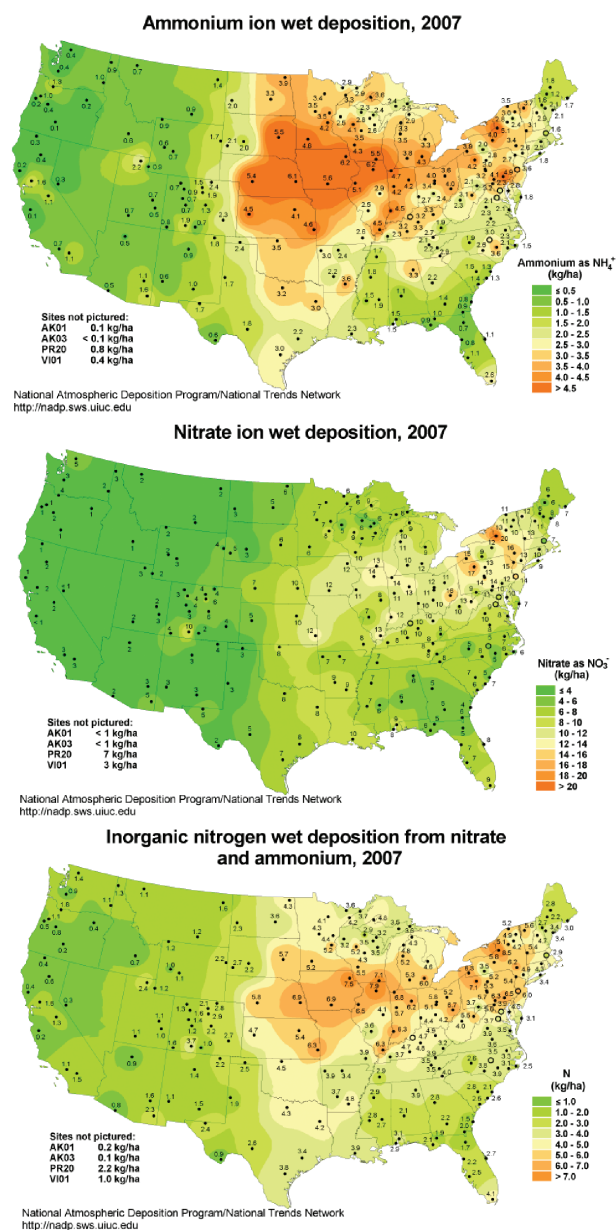

Figure A-3: Annual NH_4^+, NO_3^-, and total inorganic N deposition for the year 2007 showing spatial patterns of deposition

Source: National Atmospheric Deposition Program, 2010.

Concentrations of aerosol NH_4^+ have decreased in many parts of the country, and this may appear to contradict the trend in wet deposition, but a decrease in condensed phase NH_4^+ will be accompanied by an increase in vapor phase NH_3 if SO_4^{2-} and NO_3^- concentrations decrease; see http://vista.cira.colostate.edu/improve/. This potentially misleading information highlights the need for measurements of speciated NH_x (Sutton et al., 2003).

Review of dry deposition observations for the eastern United States

Monitoring dry deposition presents a greater challenge than monitoring wet deposition. The Clean Air Standards and Trends Network (CASTNET) and Atmospheric and Integrated Research Monitoring Network (AIRMON) were established to monitor chemical and meteorological variables to infer dry deposition in order to study the processes leading from emissions to atmospheric concentrations and through deposition to ecosystem effects. AIRMON dry deposition monitoring was discontinued in 2003. See www.epa.gov/castnet/, www.arl.noaa.gov/research/programs/airmon.html, and http://nadp.sws.uiuc.edu.

Recent reviews (Sickles and Shadwick, 2007a,b) analyze the seasonal and regional behavior of concentration and deposition of a variety of primary and secondary pollutants including Nr and investigated trends from 1990 to 2004 for the U.S. east of the Mississippi River. The investigators evaluated observations from more than 50 sites in the eastern states and concluded that for 2000-2004, the mean annual total measured N deposition for this area was 7.75 kg N per hectare per

Table A-2: Deposition of N to the eastern United States in units of kg N/ha/yr

	Annual deposition kg N/ha/yr
Dry NH_4^+	0.41
Wet NH_4^+	2.54
Dry HNO_3 + NO_3^-	1.88
Wet NO_3^-	2.92
Total measured N Dep.	7.75
Est. dry other NO_y	0.94
Est. dry NH_3	1.90
Est. total NO_y	5.74
Est. total NH_3 + NH_4^+	4.85
Est. Grand Total	10.59

Data are from the U.S. CASTNET program for the period of 2000-2004. Monitored species for 34 sites east of the Mississippi include vapor-phase HNO_3, particulate NO_3^-, and NH_4^+; unmonitored are other oxidized species such as NO_x and PAN and gas-phase reduced N species most notably NH_3 (Sickles and Shadwick, 2007a). For an explanation of how deposition of unmeasured species was estimated see text.

year (expressed as kg N/ha/yr); see Table A-2. This value includes vapor phase HNO_3, particulate NO_3^-, and NH_4^+; it does not include deposition of other oxidized species such as NO_x and PAN, nor gas-phase reduced N species, most notably NH_3. The measured deposition rates peak in spring and summer, but unaccounted for ammonia deposition is probably a substantial fraction of the total, and the true annual cycle remains uncertain.

Estimated total N deposition to the eastern United States

CASTNET monitors HNO_3 and NO_3^-, but not other members of the NO_y family – notably NO_x. Dennis (U.S. EPA, 2007d) estimated that the unmeasured NO_y species account for about 50% of the dry deposition of nitrates. Half of 1.88 (see Table A-2) is 0.94 kg N /ha/yr. Ammonia is also unmeasured by CASTNET, and model estimates (Mathur and Dennis, 2003) of NH_3 indicate that dry deposition should account for 75% of wet NH_4^+ deposition; 75% of 2.54 is 1.9 kg N /ha/yr. Adding these two values to the total from Table A-2 yields a reasonable estimate, within about ±50% absolute accuracy, of total deposition of about 10.6 kg N /ha/yr for the eastern U.S.

Characteristics of N deposition to the eastern United States

Analysis of production of N_2 and N_2O via gas phase reaction is provided in Appendix E. Warmer temperatures are conducive to release of NH_3 from soils and manure as well as from atmospheric particles, thus ammonia concentrations are typically highest in summer. Diffusion of gases is faster than diffusion of particles, and dry deposition of vapor-phase Nr is faster as well; for example the mean CASTNET reported HNO_3 deposition velocity is 1.24 cm/s while that for particulate NO_3^- is 0.10 cm/s. In 2003 and 2004 substantial reductions in emissions from electricity-generating units (power plants) were implemented under the NO_x State Implementation Plan (SIP) call. Many of these power plants are located along the Ohio River generally upwind of the measurement area. Significant reductions (p = 0.05) were found between the 1990-1994 and 2000-2004 periods (Sickles and Shadwick, 2007a).

Uncertainty in measured deposition

Analysis of uncertainties in the deposition of Nr is challenging. The coefficient of variation for total regional N deposition for 2000-2004 is 23%, representing a minimal value of uncertainty. Concentrations of some of the NO_y species are monitored, as is the wet deposition of major oxidized and reduced N species, but concentrations of ammonia and other Nr species are not monitored. The network for monitoring dry deposition is sparse and has not been evaluated for spatial bias. The monitors are located in flat areas with uniform surfaces – advective deposition into, for example, the edges of forests are estimated to contribute substantially to the uncertainty (Hicks, 2006). Other sources of error include the model

used to convert weekly average concentrations and micrometeorological measurements into depositions. Precision can be determined from collocated sites and is estimated at 5% for nitrate and 15% for ammonium in precipitation (Nilles et al., 1994). The uncertainty in estimated dry deposition arises primarily from uncertainty in deposition velocities (Hicks et al., 1991; Brook et al., 1997) and can be as high as 40% for HNO_3. Total uncertainty for deposition of Nr based on measurements is at least 25% and may be as high as 50%.

Deposition estimates from numerical models

The EPA Community Multiscale Air Quality model (CMAQ) was run for North America at 36 km resolution (R. Dennis et al., personal communication, January 2008). Simulation of Nr deposition is hampered by the lack of emissions information (especially for NH_3), by the need to parameterize planetary boundary layer (PBL) dynamics and deep convection, as well as by simplified multiphase chemistry. This run of CMAQ did not account for NO_x emissions from marine vessels, and these amount to about 4% of the total NO_x emissions in 2000. Calculated nitrogen deposition for the 48 contiguous states (Table A-3) was broadly consistent with direct measurements (Table A-2). CMAQ NO_x emissions were 5.84 Tg N for the year 2002; of that, 2.74 Tg N were deposited. This suggests that ~50% was exported – a number somewhat higher than has been reported in the literature; this discrepancy is discussed below.

Table A-3: Results from CMAQ* for total deposition in 2002 to the 48 contiguous states of oxidized and reduced N

	kg N/ha/yr	Tg N/yr
Oxidized N	3.51	2.74
Reduced N	2.66	2.07
Total N Deposition	6.17	4.81

The CMAQ results were adapted from Schwede et al., (2009) The Watershed Deposition Tool: A tool for incorporating atmospheric deposition in water-quality analyses, htttp://www.epa.gov/amad/EcoExposure/depositionMapping.html.

Ammonia emissions and ambient concentrations can be measured, but are not routinely monitored. For Nr, the CMAQ numerical simulation employed inverse modeling techniques – that is, NH_3 emissions were derived from observed NH_4^+ wet deposition (Gilliland et al., 2003; Mathur and Dennis, 2003; Gilliland et al., 2006). Model determinations of NH_3 therefore do not provide an independent source of information on NH_4^+ deposition.

The three-year CMAQ run gives an indication of the spatial pattern of deposition (Figures A-4). For NH_x, wet and dry are equally important, but for NO_y, dry deposition

accounts for about two-thirds of the total deposition, while wet deposition accounts for about one-third. While this does not hold for the eastern U.S. it is true for the U.S. as a whole; in arid southern California, for example, dry deposition of Nr dominates. Based on CMAQ, total NO_y deposition is 2.79 times the wet deposition and total NH_x deposition is 1.98 times the wet deposition. Using the data from Table A-1 for the average wet deposition for the period 2000- 2004, total deposition of oxidized N is 4.36 kg N /ha/yr (2.79 × 1.56 = 4.36). The total deposition for reduced N is 3.17 kg N /ha /yr (1.98 × 1.60). The grand total (wet and dry oxidized and reduced) is then about 7.5 kg N /ha /yr.

The model has highly simplified organic N deposition. Note that these values reflect emissions before the NO_x SIP-call, which resulted in substantial reductions in NO_x emissions from point sources over the eastern U.S.

For comparison purposes, a collection of chemical transport models (CTMs) (Dentener et al., 2006) yielded total (wet plus dry) deposition to the whole U.S. of about 3.9 Tg N /yr oxidized Nr and 3.0 Tg N /yr ammoniacal N for current emissions. The fate of NO_x is assumed to be primarily HNO_3 or aerosol NO_3^-; organic N species are generally not modeled in detail. Because this analysis includes Alaska, a better estimate for NO_x for the 48 contiguous states is 4.6 Tg N /yr. The variance among models was about 30% (one standard deviation) for deposition fluxes in regions dominated by anthropogenic emissions. Globally, the calculations from the ensemble of 23 CTMs estimated that 36-51% of all NO_y and NH_x emissions are deposited over the ocean. This load could be important to estuarine N loading estimates, as offshore N is carried inshore by currents or through advective processes.

Deposition estimates from mass balance

From estimated total emissions of Nr compounds and observed or simulated export, a reasonable estimate of rate of deposition can be obtained by mass balance – deposition equals emissions minus export. Although substantial uncertainty (about a factor of two) exists for the emissions of NH_3, NO_x release is reasonably well known. In general, advection in the boundary layer and lofting through convection followed by export at higher altitudes are the two main mechanisms that prevent removal of NO_y and NH_x by deposition to the surface of North America (Luke et al., 1992; Li et al., 2004).

Experimental observations have been conducted over the eastern U.S. for more than two decades (Galloway et al., 1984; Galloway and Whelpdale, 1987; Luke and Dickerson, 1987; Galloway et al., 1988). Most recent estimates (Dickerson et al., 1995; Li et al., 2004; Parrish et al., 2004b; Hudman et al., 2007), agree that annually 7-15% of the emitted NO_x is exported in the lower to mid-troposphere.

CTMs derived small export values – on the order of 30% of the total NO_x emitted into the lower atmosphere

TOTAL NITROGEN DEPOSITION (KG–N/HA)
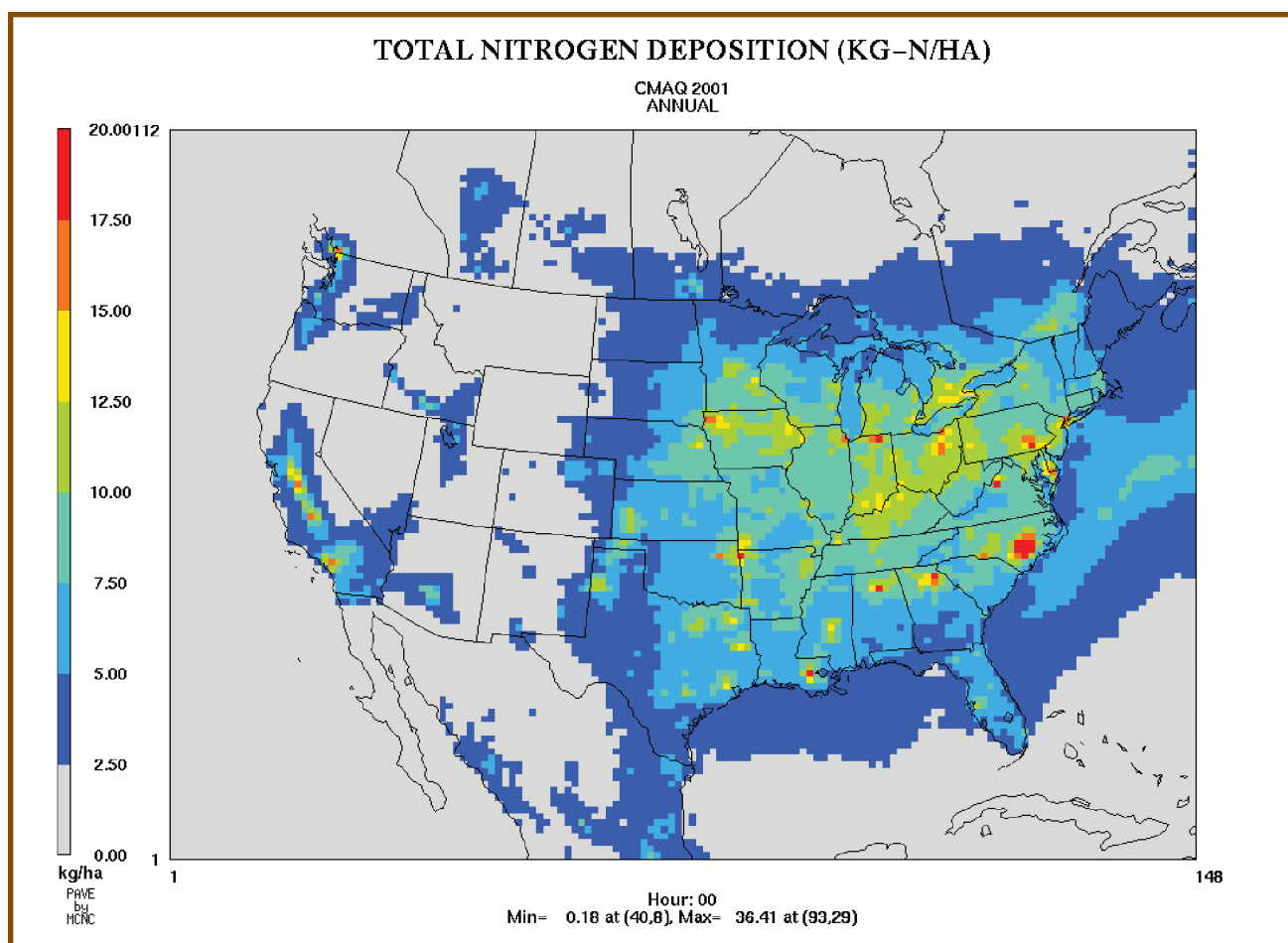
CMAQ 2001
ANNUAL

Figure A-4: CMAQ annual average (wet plus dry and oxidized plus reduced) nitrogen deposition (in kg-N/ha/yr) across the United States.

This is based on three years of differing meteorology – one dry, one wet, and one average precipitation year – across the Eastern United States

Source: U.S. Environmental Protection Agency, 2007f

(Penner et al., 1991; Kasibhatla et al., 1993; Holland et al., 1997; Horowitz et al., 1998; Liang et al., 1998; Galloway et al., 2004; Park et al., 2004; Holland et al., 2005; Doney et al., 2007). Reviewed publications using the mass balance approach have substantial uncertainty but indicate with some consistency that 25-35% of the NO_y emitted over the U.S. is exported.

Comparison of models and measurements of oxidized N deposition

Both ambient measurements and numerical models of NO_y have reached a level of development to allow reasonable estimates of deposition. For reduced nitrogen, neither ambient concentrations nor emissions are known well enough to constrain models. Recent model estimates of the U.S. N budget are reasonably uniform in finding that about 25-35% of total NO_x emissions are exported.

Results from CMAQ runs described above indicate that, of the NO_x emitted over the continental U.S., 50%

is deposited and 50% is exported. This is within the combined error bars of other studies, but well under the best estimate of 70% deposition. One possible source of this discrepancy is underestimation of deposition of organo-nitrogen compounds. The chemical mechanism used in CMAQ was highly simplified – only about 2-3% of the total Nr deposition can be attributed to organo-nitrogen compounds (R. Dennis personal communication, 2008). Ammonia from fossil fuel combustion, while important locally, is probably a small component of national Nr deposition.

Major sources of uncertainty in modeled and observed values include missing deposition terms and poorly constrained convective mass flux. As indicated above, convective mass flux (rapid vertical transport) is uncertain because most convective clouds are smaller than a grid box in a global model. There is evidence for nonlinearities in NO_2 deposition velocities with greater transfer from the atmosphere to the surface at higher concentrations (Horii et al., 2004; 2006).

Emissions from Canada and Mexico can have a substantive impact on atmospheric Nr over the U.S. near major sources, such as downwind of industrial Ontario and major cities of San Diego, CA, and Tijuana, Mexico (Wang et al., 2009). While Nr is imported into the U.S. from these border countries, there is also export. The emissions from Canada and Mexico are each 10-15% of those of the U.S. and the bulk of the Mexican population is distant from the U.S. We expect the overall impact of neighboring countries to add about 10% uncertainty to the estimated Nr budget for the 48 contiguous states.

Appendix B:
Sources and Cycling of Nr Input into Terrestrial Systems in the United States

Most of the new Nr introduced into terrestrial systems in the U.S. was used to produce food for human consumption and forage and feed for livestock and poultry (~17.7 Tg total with 9.7 Tg from synthetic fertilizer and ~8 Tg from biological N fixation; Table B-1). In addition to new Nr and Nr that was recycled from livestock and human excreta, crop production releases Nr that was stored in soil organic matter (see Section 2.3.2). The N in cereal crops is typically derived from added fertilizer (synthetic or manures) and from mineralization of soil organic matter (conversion of complex organic molecules to ammonium) in about equal amounts. As discussed in Section 2.2 and Section 5.3.4, crop production is not efficient in using Nr so only 30-70% (a global average of 40%) of all the N mobilized for crop production is harvested in the crop. The remainder is in crop residue (roots and above ground stover) stored in the soil, leached to aquatic systems as NO_3^-, volatilized to the atmosphere as NH_3 or NO_x or denitrified (see Section 4.8, Figure 18) to produce NO_x, N_2O and N_2. An additional ~1.1 Tg of synthetic fertilizer N is used to maintain turfgrass in the urban environment (see Section 2.2.5) and another 0.1-0.2 Tg N is used to enhance forest production.

Within the nitrogen cascade (Figure 1), the interactions between the agricultural and populated portions of the terrestrial system dictate the production and flow of Nr. Although occupying the largest area, forest and grassland portions of terrestrial ecosystems serve mainly to absorb atmospheric deposition and provide a source of forest products and forage for livestock production. Reactive nitrogen input into these systems is from biological N fixation in unmanaged lands, atmospheric deposition, and Nr from livestock manure that is deposited. The livestock that is grazing within grasslands (Table B-1) may lead to the N saturation of unmanaged forest and grassland ecosystems (Galloway et al., 2004; Bobbink et al., 2010).

This report uses the Nr input numbers from Table B-1 and food production numbers to estimate the flow of Nr through agricultural and populated parts of the terrestrial system (Table B-2). The FAO (20010b; www.fao.org/es/ess/top/country.html) lists the 20 largest agricultural commodities produced, imported, and exported in the U.S. in 2002. Of these commodities, corn (229 Tg), soybeans (75 Tg), wheat (44 Tg), and cow's milk (77 Tg) were produced in the greatest amount. Using commodity N content data derived from data used to calculate crop

Table B-1: Sources of reactive N into terrestrial systems in the United States in 2002 (from Table 1 data sources; in Tg N/yr).

Source	Environmental System				
	Agricultural	Vegetated		Populated	Total
		Forest	Grassland		
Atmospheric	1.3	1.4	1.9	0.4	6.9*
N fixation	7.7	–	6.4	–	14.1
Synthetic N	9.7	0.1	**	1.1	10.9
Animal manure##	1.2	–	3.8#	–	6.0#
Human sewage##	0.1	–	–	1.2	1.3

*The amount of atmospheric Nr deposition is based on area of each environmental system within the continental U.S. The total area does not sum to 100% because non-arable lands are not included in this table.

**Synthetic fertilizer N used for managed pasture fertilization is included in the agricultural land classification.

#Unrecoverable livestock manure deposited on grasslands, the unaccounted for ~1 Tg of Nr assumed to be lost through ammonia volatilization, leaching, or denitrification (U.S. EPA, 2007e).

##Note that livestock manure and human sewage used as fertilizer are recycled N components of the nitrogen cascade and not new Nr inputs.

residue N in the EPA inventory of U.S. greenhouse gas emissions and sinks (U.S. EPA, 2007e), an estimated 9 Tg of N was marketed in three crops, soybeans (4.4 Tg N; from U.S. EPA, 2007g), corn (3.2 Tg N), and wheat (0.9 Tg N). Whole milk contained ~ 0.5 Tg of N while other meat and egg produce contained ~1.4 Tg of N, totaling ~ 1.9 Tg N. Grain, fruits, nuts and vegetables contained ~9.3 Tg of N. If the total N input use efficiency is 40%, then ~23 Tg of N from all sources is required to produce 9.3 Tg of vegetative commodities. Table B-2 lists the estimated Nr input into agricultural systems (~ 20 Tg) and additional N input from crop residue that was returned to the field the previous year (4.4 Tg) and from mineralization of soil organic matter (4.7 Tg). All of this N input totals ~29 Tg of N that is actually involved in the production of the 9.3 Tg of crop commodity N. If one assumes that return of crop residue to the field is directly proportional to crop production, then 24.3 Tg of N was required to produce the 9.3 Tg of crop commodity N. These estimates indicate that ~38% of the total annual input of N that went into the agricultural crop production system was contained in the main crop commodities produced in the U.S. in 2002.

Of the 24.3 Tg N required to produce crop commodity N in 2002, approximately 2.5 Tg was used to grow feed used for milk, egg, and meat production. This estimate is made assuming that 4 units of N are required to produce a unit of milk, eggs, or meat (see Section 5.3.4). This estimate also assumes that one-third of N required for livestock production comes from commodities in the FAO top-20 list and the remaining two-thirds comes from alfalfa, silage, and grass over the course of a year (Oitjen and Beckett, 1996). Approximately 4.3 Tg of N in agricultural commodities (2.8 Tg in soybeans, corn, and wheat) were exported, while ~0.15 Tg N was imported in various food and drink commodities. The U.S. human populace consumed ~1.96 Tg of N in 2002 (292 million people, consuming 114.7 g protein/person/day, 0.16 g N/g protein, 365 days) (approximately 1.2 Tg from animal protein-N and 0.7 from vegetative protein).

These three consumption areas – internal consumption of vegetable N for livestock production, human consumption, and export – account for 77% of the commodities produced. The unaccounted for commodity N is likely partly in annual storage. Some smaller fraction of annual production is used for pet food and a small fraction is returned to the terrestrial environment because of spoilage and handling losses.

In forests and grasslands (vegetated system) N input in 2002 was ~3.5 Tg of anthropogenically introduced N, with the remaining ~10.1 Tg derived from BNF and livestock manure deposition. Of this anthropogenic N, ~21% was retained in soil and tree biomass, while the remainder was removed in tree harvest (~0.2 Tg, see Section 2.3.2.) or lost to other parts of the environment through NH_3 volatilization and NO_3^- leaching and runoff (Table B-2). Total N input into agricultural systems was ~20 Tg, with ~ 11 Tg being removed as products including the transfer of ~2 Tg N as food to the human population. Almost 40% of the N input into agricultural systems is lost through NH_3 volatilization, nitrification/denitrification, and NO_3^- runoff. The 4.2 Tg of Nr of Haber-Bosch N that is used for industrial feedstock is not included in this assessment. Of the input of ~3.3 Tg of N into the populated system ~80% is lost through human excreta processed in sewage treatment plants, denitrification in soils, and leaching and runoff of NO_3^- (Table B-2).

Table B-2 summarizes the input and flow of Nr in the main terrestrial systems within the continental U.S. Anthropogenic input of Nr into forests and grasslands totaled ~3.5 Tg in 2002, with an estimated 6.4 Tg of Nr being introduced through natural biological N fixation. Of this Nr ~ 0.7 Tg was stored in vegetation and soils (see Section 2.3.2) and ~2 Tg removed as livestock forage, while the remainder was lost to the atmosphere and aquatic systems, or removed as forest products and livestock forage. The largest anthropogenic Nr input (~20 Tg) was into agricultural production where ~11.2 Tg was removed as agricultural product, ~ 2 Tg transferred as

Table B-2: Nr input and flows (Tg N/yr) in the terrestrial portion of the Nitrogen Cascade (Figure 1) within the continental United States in 2002

Environmental System*	N Input to System	N Storage in System**	Agricultural & Forest Products	Transfers to Aquatic or Atmospheric	Transfers as a % of Input
Vegetated	13.6	0.7	2.2	10.7	79
Agricultural	19.6	0.8	11.2	7.6	39
Populated	3.3	0.1	0	3.2	97

*The Environmental Systems are those noted in the terrestrial portion of the N cascade shown in Figure 1. Data from Table B-1, derived from regrouping information from Table 1 data sources, are shown in Table B-2.

**Estimates are from section 2.3.2 of this report.

edible product to the "populated" portion of the terrestrial system, ~0.8 Tg was stored in agricultural lands, and ~7.6 Tg N was lost to the atmosphere and aquatic systems. New N input into the "populated" portion totaled ~3.3 Tg, which came from N transfer in food and use of fertilizer N in lawns, gardens and recreational areas. Within these areas an estimated 0.12 Tg was stored in urban forests.

Appendix C:
Water Quality Trading in the Illinois River Basin

For various reasons, wetland restoration has been proposed and the magnitude of needed restoration estimated. For the Wetland Reserve Program (WRP), the Farm Bill of 1990 set a goal of restoring approximately 1 million acres. A few years later, the NRC (1992) proposed a national goal of restoring 10 million acres of inland and coastal wetlands by 2010. The NRC went on to recommend that 400,000 miles of streams and rivers be restored by 2012 and that 1 million acres of lakes be restored by 2000, both of which would further the control of reactive nitrogen. While none of these goals has been or is likely to be met by the recommended date, they articulated a need for wetland restoration addressing the important relationship between wetlands and water quality.

Taking into account the economics of using wetlands to manage Nr adds yet another dimension to site selection. Based on the results of the Water Environment Research Foundation's study (Hey et al., 2005a,b), the Kinship Foundation sponsored a study (Scott et al., in preparation) to define the market for producing and selling Nr (as NO_3^-) credits. For this analysis, a real potential market area was selected: the Illinois River watershed in Illinois – the tributaries draining Wisconsin, Indiana, and Michigan were excluded. The producers of nitrogen credits were identified as "nutrient farmers" and they became the "sellers" of N credits. The "buyers" of nitrogen credits were restricted to municipal and industrial wastewater treatment facilities, those facilities that hold an NPDES permit. This restriction, of course, resulted in a considerable understatement of the market size since the identified buyers emit less than 11% of the total aquatic N load (David and Gentry, 2000) that finds its way to the Mississippi River – air emission/deposition and agriculture account for the remaining 89%.

The watershed was divided into 19 sub-watersheds, spatially locating credit supply and demand. A linear programming model was developed and used to: (1) examine the potential extent and distribution of nitrogen credit demand and supply; (2) compare the average seasonal demand levels to the supply capacity of nutrient farms; and (3) evaluate the relative effects of seasonality. Market efficiency was imposed through the objective function: the least costly distribution of credit production to meet the given monthly demand. Thereby, sellers and buyers were identified and linked and the spatial characteristics of the market mapped by sub-watershed. At the same time, the equilibrium price of a credit, or the prevailing price at which buyers and sellers are willing to trade, was determined. The market, as represented by the model, determined where the most intensive wetland investment (i.e., wetland restoration) would be, the revenues returned to these investments, and the costs and savings to the buyers.

All 290 permitted buyers are geographically distributed as shown in Figure C-1. The mass loading of the buyers (2,423 tons/month) is reflected in Figure C-2. Eighty-nine percent of the demand comes from the northeastern corner of the Basin (Upper Fox, Des Plaines, and Chicago/Calumet sub-watersheds), the Chicago metropolitan area. As illustrated by Figure C-3, 41% of the wetland restoration area (using the criteria discussed above) was identified in the southwestern corner of the watershed (Lower Illinois, La Moine, Macoupin, Lower Sangamon, and Middle Illinois sub-watersheds), where the floodplain is almost entirely leveed. For the market study, the available load of Nr (NO_3^-) by season and sub-watershed was mapped as illustrated in Figure C-4. The N load was computed using water quality and flow data collected by the U.S. Geological Survey from 1987 to 1997. The wetland and wastewater cost functions are described in Hey et al., 2005; however, the wetland cost functions were modified for the market study to reflect the variability of land costs across the watershed (i.e., higher land values in urban Chicago and lower land values in rural Illinois). This variability is reflected in the spatial distribution marginal costs shown for the spring marginal costs depicted in Figure C-5. Wetland treatment costs vary by time of year because the level of microbial activity, which drives the denitrification process, varies with water temperature. Therefore, treating an equivalent load of Nr requires more wetland area in winter than in summer.

Three regulatory scenarios

Regulatory agencies may require that dischargers and nutrient farms be located in proximity to each other and could impose "penalties" when the two are not. Thus, for the sake of analysis, the Committee created three regulatory scenarios:

1. Unrestricted – buyers can purchase nitrogen credits from nutrient farmers anywhere in the watershed without regard to location. The result of this scenario is given in Figure C-6.

2. Restricted intra-watershed – the buyer must purchase all available credits within its own sub-watershed before buying in other sub-watersheds

3. Accrued 10% penalty – buyers pay an increasing "tax" on credits purchased in consecutive downstream watersheds

The three regulatory scenarios were analyzed for each of the four seasons. (D. Hey, Wetlands Research, Inc., Personal Communication.)
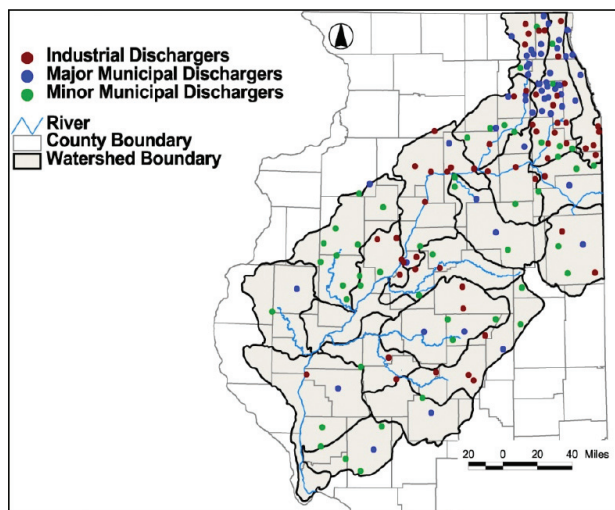
The "unrestricted" scenario is the least expensive because nutrient farms in this scenario are located downstate, where land is least expensive. In the other two scenarios, credits were purchased a little more evenly throughout the watershed. Still, most of the credits in the southern corner of the watershed were purchased. The

Figure C-1: Distribution of municipal discharge and industrial dischargers in the Illinois River Watershed

Municipal dischargers shown are those exceeding one million gallons per day. Symbols may represent more than one discharger at that location.

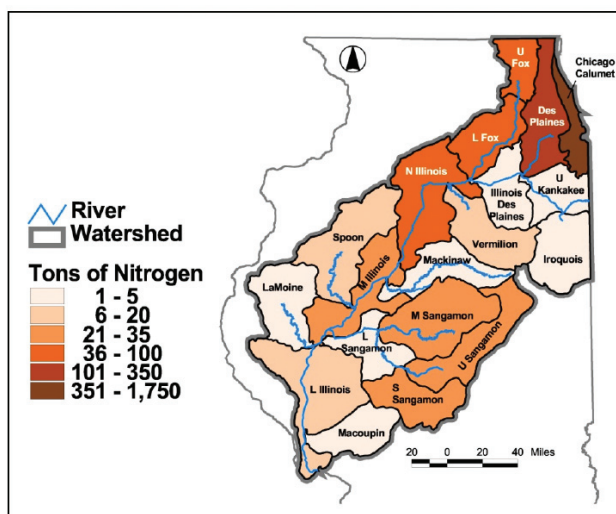Source: D. Hey, Wetlands Research, Inc., Personal Communication
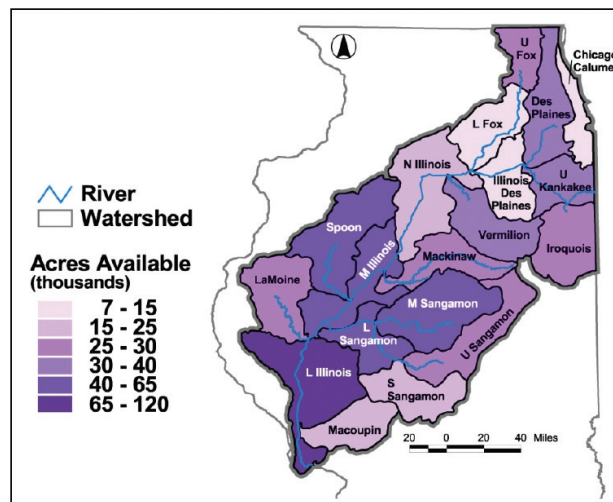
Figure C-3: Potential land availability in the 100-year flood zone for nutrient farming in each sub-watershed in the Illinois River watershed

Source: D. Hey, Wetlands Research, Inc., Personal Communication

Figure C-2: Distribution of total nitrogen emissions by sub-watershed

Source: D. Hey, Wetlands Research, Inc., Personal Communication

Figure C-4: Spring available total nitrogen load by sub-watershed

Source: D. Hey, Wetlands Research, Inc., Personal Communication

Figure C-5: Spring marginal cost (price) by watershed
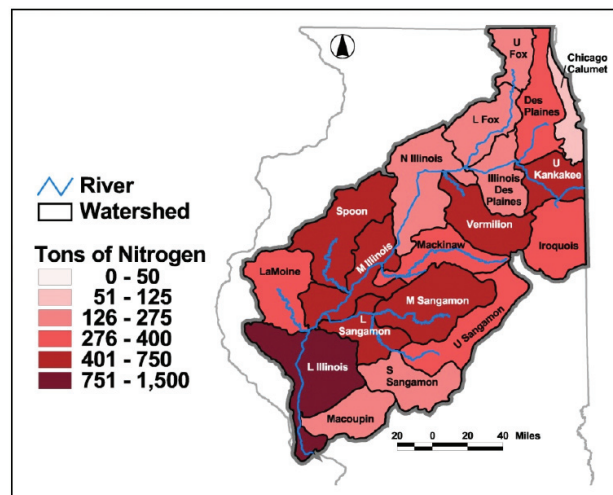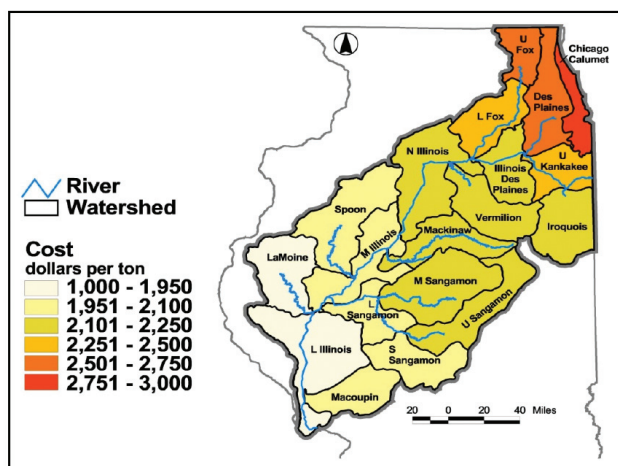
Source: D. Hey, Wetlands Research, Inc., Personal Communication

Figure C-6: Unrestricted spring credit sales (tons/month) by sub-watershed

Source: D. Hey, Wetlands Research, Inc., Personal Communication

"restricted intra-watershed" and "accrued 10% penalty" scenarios resulted in more credits being purchased. This resulted in the sale of N credits exceeding the mass of Nr emitted by wastewater treatment, which would benefit the overall control of reactive nitrogen. It also would increase the value of the market and the profits of the nutrient farmer. The downside of such regulatory controls is that they would drive up the effective price of nitrogen credits. If a buyer had to buy a 1.5 tons for every ton discharged because credits are not available in the tributary watershed, the effective price of a credit would be 1.5 times the price of the tributary sub-watershed. If prices rise too much, "concrete and steel" technologies may become competitive.

Considering all of the point source dischargers in the Illinois River watershed, between 29,000 and 36,000 tons TN/year could be removed through nutrient farming under the studied trading schemes (Table C-1). The range of removal is a function of the penalties imposed on the market by the regulatory agencies.
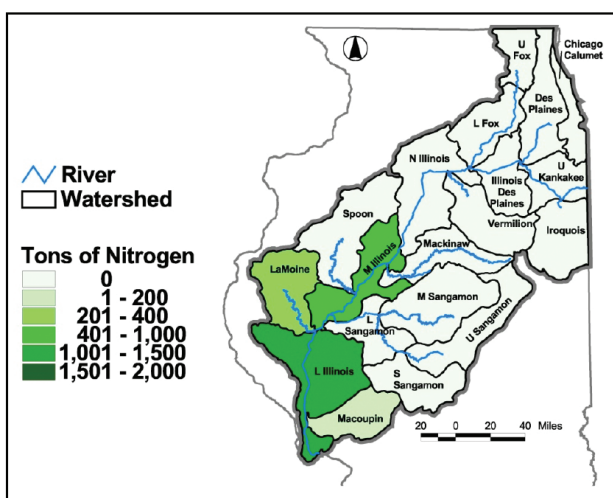
Accordingly, the market revenue would range from $70 million to $121 million/year. This is a sizeable market that could generate substantial profits, from $6 million to $38 million with the return on investment varying from 5 to 25%. If the savings are shared evenly between the seller and buyer, the nutrient farmer could earn between $200 and $300/acre/year net profit, which in many cases is greater than the profits from corn or soybean production. Further, these profits do not include any earnings from flood control or recreation, as suggested in a McKnight study report (Hey et al., 2004). With such profits, sufficient land should be available for nutrient farming.

This analysis indicates that appropriate lands are available and that wetlands can be effectively restored and efficiently used to control Nr. The market, structured as discussed above, could generate the capital to accomplish the needed large-scale wetland restoration while saving taxpayers the cost of upgrading their municipal wastewater treatment plant (TWI, 2007).

Table C-1: Nutrient farm market parameters under three trading scenarios

Parameter	Unrestricted	Restricted Intra-watershed	Accrued 10% Penalty
Total Credits Sold (tons)	29,078	29,078	35,781
Total Revenue [21]	$69,925,497	$99,571,889	$121,457,652
Total Cost to Produce Credits	$63,258,006	$66,193,924	$83,288,747
Profit	$6,667,491	$33,377,968	$38,168,905

Source: D. Hey, Wetlands Research, Inc., Personal Communication

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[21] Assumes all credits were sold at the cheapest cost within the Illinois River watershed.

Appendix D:
Management of Nr Measures Based on the Concept of Critical Loads

The European Union has undertaken broad measures, based on the critical-loads concept, to manage Nr. Tables D-1, D-2, and D-3 summarize several different environmental impacts currently used as indicators and identify whether there are current limit values set by the United Nations Economic Commission for Europe (UNECE) or European Union (EU). These tables identify the main links to the cascade of reactive nitrogen in the environment, the relevance and link to Nr of the effect/pollutant, and existing agreements in which the effect is currently addressed. In addition, some impacts are more relevant than others in relation to societal importance and the connection to the nitrogen cascade. The categorization on a scale of 1 (highest relevance) to 5 (unimportant) provides a first-level prioritization for future mitigation activity. The last column summarizes existing links to international regulations and conventions.

Where there is a limit and the relevance for the nitrogen cascade is high, then this might be the limiting factor for Nr production and its associated losses to the environment. Some limits might be more relevant in specific areas and less relevant in others. For example NO_2 concentrations relevant for human health are limited to 40 ppb in urban areas, limiting industry and traffic, but would probably not be an issue of concern in remote areas with low population densities. In these areas, however, loss of biodiversity might limit nitrogen deposition and therewith the sources in the region. The only way to determine the extent that critical thresholds are limiting is by overlaying them on different regions and determining, through the use of monitoring data or by modeling exercises, where and which sources contribute to exceeding the critical threshold. Then the best methods for putting caps on relevant sources can be identified. A pre-classification of regions might be useful, e.g., urban regions, remote regions, marine areas, etc. One aspect of this global view of nitrogen impacts and metrics that is evident is the mix of "classical-" and "service"-based categories, consistent with the need for an integrated approach to the management of nitrogen.

Table D-1: Summary of the effects of excess Nr on human health in relation to metrics, current international regulations and conventions, and the link to the nitrogen cascade

	Metrics	Regulated?	Link to Nr cascade	Relevance*	Regulatory or political convention
Respiratory disease in people caused by exposure to high concentrations of:					
Ozone	Sum of ozone over 35 ppb	YES	NO_x emissions	3	Convention on Long-range Transboundary Air Pollution Clean Air for Europe
Other photochemical oxidants	Org. NO_3, PAN concentration (atm)	NO	NO_x emissions	5	Convention on Long-range Transboundary Air Pollution et al.
Fine particulate aerosol	PM_{10}, $PM_{2.5}$ concentration (atm)	YES	NO_x, NH_3 em	1	Convention on Long-range Transboundary Air Pollution Clean Air for Europe
Direct toxicity of nitrite NO_2^-	NO_2^- concentration	YES	NO_x	2	World Health Organization Convention on Long-range Transboundary Air Pollution Clean Air for Europe
Nitrate contamination of drinking water	NO_3^- concentration (aq.)	YES	NO_3^- leaching	2	EU Essential Facilities Doctrine
Depletion of stratospheric ozone	NO_x, N_2O concentration/ flux (atm)	NO	NO_x, N_2O	3	Montreal Protocol
Increase allergenic pollen production, and several parasitic and infectious human		NO		5	None
Blooms of toxic algae and decreased swimability of in-shore water bodies	Chlorophyll a NO_3^- (&P) concentration (aq)	NO	Runoff, Nr deposition	1	Convention for the Protection of the Marine Environment of the North-East Atlantic Helsinki Commission Barcelona Convention

atm – atmospheric; aq – aqueous

*Relevance and link to nitrogen incorporates societal priority and N contribution: 1. highest relevance, 2. high relevance, 3. significant relevance, 4. some relevance, 5. unimportant.

Table D-2: Summary of the effects of excess Nr on ecosystems related to currently used metrics, the existence of European regulatory values, and the link to the nitrogen cascade.

	Metrics	Regulated?	Link to Nr cascade	Relevance*	Regulatory or political convention
Ozone damage to crops, forests, and natural ecosystems	AFstY (O_3 flux), AOT40**	YES	NO_x	2	Convention on Long-range Transboundary Air Pollution Clean Air for Europe
Acidification effects on terrestrial ecosystems, ground waters, and aquatic ecosystems	Critical loads	YES	Nr deposition	2	Convention on Long-range Transboundary Air Pollution Clean Air for Europe WFD
Eutrophication of freshwaters, lakes (incl. biodiversity)	Biological Oxygen Demand, NO_3^- conc (aq) Critical loads	YES NO	Runoff, Nr deposition	3	Water Framework Directive
Eutrophication of coastal ecosystems inducing hypoxia (incl. biodiversity)	BOD, NO_3^- conc (aq) Critical loads	BOD, NO_3^- conc (aq) Critical load	Runoff, Nr deposition	1	Convention for the Protection of the Marine Environment of the North-East Atlantic Helsinki Commission Barcelona Convention
Nitrogen saturation of soils (incl. effects on GHG balance)	Critical loads	YES	Nr deposition	1	Convention on Long-range Transboundary Air Pollution Clean Air for Europe
Biodiversity impacts on terrestrial ecosystems (incl. pests and diseases)	Critical loads, critical levels (NH_3, NO_x)	YES	Nr deposition	1	Convention on Long-range Transboundary Air Pollution Clean Air for Europe Convention on Biological Diversity

atm – atmospheric; aq – aqueous

*Relevance and link to nitrogen incorporates societal priority and N contribution: 1. highest relevance, 2. high relevance, 3. significant relevance, 4. some relevance, 5. unimportant.

**Accumulated ozone exposure over a threshold of 40 parts per billion

Table D-3: Summary of the effects of excess N on other societal values in relation to metrics and regulatory values in current international regulations and conventions and the link to the nitrogen cascade

	Metrics	Regulated?	Link to Nr cascade	Relevance*	Regulatory or political convention
Odor problems associated with animal agriculture	Acidity in precipitation., O_3, PM	YES	NO_x, NH_3	3	Convention on Long-range Transboundary Air Pollution
Effects on monuments and engineering materials	$PM_{2.5}$ conc (atm)	NO	NO_x, NH_3	4	
Global climate warming induced by excess nitrogen	N_2O, conc/flux (atm)	NO	NO_x, NH_3	1	United Nations Framework Convention on Climate Change
Regional climate cooling induced by aerosol)	$PM_{2.5}$ conc (atm)	NO	NO_x, NH_3	1	United Nations Framework Convention on Climate Change

atm – atmospheric; aq – aqueous

*Relevance and link to nitrogen incorporates societal priority and N contribution: 1. highest relevance, 2. high relevance, 3. significant relevance, 4. some relevance, 5. unimportant.
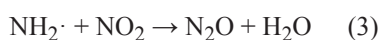
Appendix E:
Technical Annexes

Production of N_2 and N_2O via gas-phase reactions

Atmospheric conversion of NO_x and NH_x to less reactive N_2 or N_2O appears to play a minor role in the global N budget, but currently is not well quantified. The gas-phase reactions in the troposphere that convert NH_3 and NO_x to N_2 and N_2O, start with attack of NH_3 by OH:

$$NH_3 + OH\cdot \rightarrow NH_2\cdot + H_2O \quad (1)$$

Several potentially interesting fates await the NH_2 radical:

$$NH_2\cdot + O_3 \rightarrow NH, NHO, NO \quad (2)$$
$$NH_2\cdot + NO_2 \rightarrow N_2O + H_2O \quad (3)$$
$$NH_2\cdot + NO \rightarrow N_2 + H_2O \quad (4)$$

$$kO_3 = 1.9\text{x}10^{-13} \text{ cm}^3 \text{ s}^{-1}$$
$$kNO_2 = 1.8\text{x}10^{-11} \text{ cm}^3 \text{ s}^{-1}$$
$$kNO = 1.8\text{x}10^{-11} \text{ cm}^3 \text{ s}^{-1}$$

The first step, attack by OH, is slow. The rate constant for the Reaction 1 is 1.6×10^{-13} cm^3 s^{-1} and the lifetime of NH_3 for a typical concentration of 106 OH cm^{-3} is about 70 days. In most areas of the world where concentrations of NH_3 are high, concentrations of sulfates are also high, and NH_3 is removed by conversion to condensed phase ammonium sulfate or bisulfate on time scales much faster than 70 d. The mean lifetime of these aerosols with respect to wet deposition is about 10 d.

There are some areas of the world, notably California and South Asia, where NH_3 and NO_x are emitted in large quantities, but SO_2 is not, and there gas-phase conversion can take place. NH_3 is usually removed by wet or dry deposition. Reaction 2 is relatively slow and oxidation of ammonia is in general an unimportant source of NO_x. But Reactions 3 and 4 may be atmospherically noteworthy. As an upper limit to current N_2O production, we can assume that each of these regions covers an area of 10^6 km^2 and that they contain ammonia at a concentration of 10 g N m^{-3} in a layer 1,000 m deep. The annual production of N_2 and/or N_2O would then be on the order of 0.1 Tg N, a minor but nontrivial contribution to denitrification and about 1% of the anthropogenic N_2O production. If NH_3 rich air is lofted out of the boundary layer into the upper troposphere where deposition is impeded, it will have an atmospheric residence time on the order of months, and the probability of reaction to form N_2O or N_2 becomes greater. This possibility has not been investigated extensively. It is also possible than Europe and North America will continue to reduce S emissions without reducing NH_3 emissions and the atmospheric source of N_2O will grow in importance.

In the stratosphere, N_2O photolysis leads to loss of Nr via

$$N_2O + h\mu \rightarrow N_2 + O \quad (5)$$
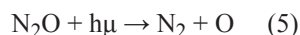
While reaction with an electronically excited oxygen atom O(1D) leads to production of NO via

$$N_2O + O(^1D) \rightarrow 2NO \quad (6)$$
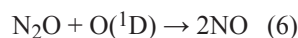
Photolysis (Reaction 5) dominates, but a large enough fraction of the N_2O reacts with O(^{1}D) that this is the main source of NO_x in the stratosphere. The fate of this oxidized nitrogen (NO_y) is transport back into the troposphere where it is removed by wet deposition. Downward transport of the odd N from the oxidation of N_2O is a minor (~1%) source of NO_y in the troposphere. Most of the N_2O released into the atmosphere is eventually converted to N_2 – the problem is that it destroys stratospheric ozone in the process.

In summary, our current understanding of the chemistry of atmospheric ammonia suggests that *in situ* conversion to N_2 and N_2O plays a minor (~1%) role in global N budgets, but if assumptions about kinetics or concentrations are in error, these mechanisms could become important.

SPARROW model for estimating watershed Nr

Estimates of Nr transfers in aquatic ecosystems are difficult to quantify at the national scale, given the need to extrapolate information from sparse monitoring data in specific watersheds to the geographic boundaries of the nation. One excellent tool for estimating Nr loads at regional scales is the spatially referenced regression on watershed attributes (SPARROW) modeling technique. The SPARROW model has been employed to quantify nutrient delivery from point and diffuse sources to streams, lakes, and watershed outlets at the national scale (Smith et al., 1997). The model infrastructure operates in a geographic framework, making use of spatial data to describe sources of pollutants (e.g., atmospheric deposition, croplands, fertilizers) and characteristics of the landscape that affect pollutant transport (e.g., climate, topography, vegetation, soils, geology, and water routing). Though empirical in nature, the SPARROW modeling approach uses mechanistic formulations (e.g., surface-water flow paths, first-order loss functions), imposes mass balance constraints, and provides a formal parameter estimation structure to statistically estimate sources and fate of nutrients in terrestrial and aquatic ecosystems. The spatial referencing of stream monitoring stations, nutrient sources, and the climatic and hydrogeologic properties of watersheds to stream networks explicitly separates

landscape and surface-water features in the model. This allows nutrient supply and attenuation to be tracked during water transport through streams and reservoirs, and accounts for nonlinear interactions between nutrient sources and watershed properties during transport. The model structure and supporting equations are described in detail elsewhere (Smith et al., 1997, Alexander et al., 2000, Alexander et al., 2008). Figure E-1 provides an estimate of contemporary Nr loading in surface waters of the U.S., representing long-term average hydrological conditions (over the past three decades). There are hot spots of high Nr yields to rivers associated with land use and watershed characteristics, and SPARROW allows considerations of the fate of these Nr inputs to streams and rivers as they flow downstream to coastal receiving waters (Alexander et al., 2008).
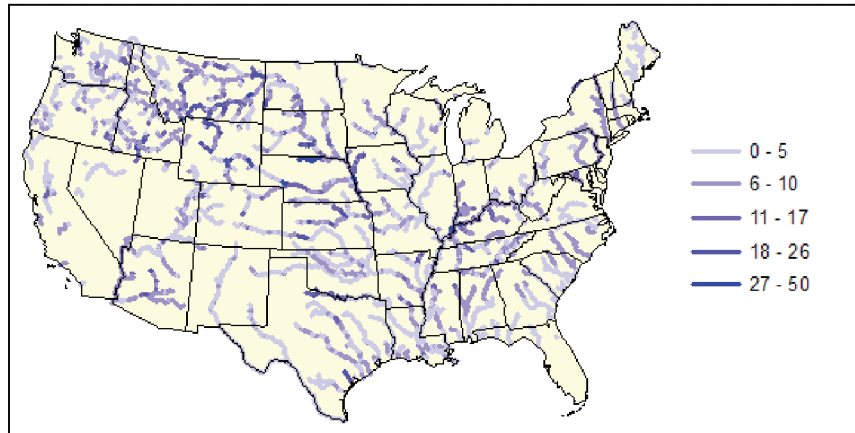

Figure E-1: Total Nr yields (kg/ha/yr) in large rivers of the U.S.

Data Source: Alexander et al., 2008

Appendix F:
Recent Major EPA Mobile Source Rules to Control NO$_X$

EPA informed the Committee that it is in the process of implementing a number of regulations to reduce NO$_X$ from a variety of mobile sources[22]. These include clean diesel regulations for trucks and buses and nonroad engines, as well as locomotives and smaller marine vessels. EPA first regulated NO$_X$ emissions from motor vehicles for the 1973 model year and since then has tightened these standards. EPA's efforts to control NO$_X$ emissions from nonroad vehicles, locomotives, and commercial marine vessels started in the 1990s. NO$_X$ reductions for each rule were calculated by EPA based on inventories available at the times of the rules.

1. Light Duty Tier 2 Rule – EPA's Tier 2 Vehicle and Gasoline Sulfur Program (65 FR 6698, February 10, 2000). This program requires new cars, sport utility vehicles (SUVs), pickup trucks, and vans to be 77 to 97% cleaner than 2003 models, while reducing sulfur levels in gasoline by 90%. EPA estimates that as newer, cleaner cars enter the national fleet, the new tailpipe standards will reduce emissions of nitrogen oxides from vehicles by 3 million tons, or about 74% in 2030. Prior to that, the EPA Tier 1 vehicle regulations, effective with the 1995 model year, also resulted in significant NO$_X$ reductions.

2. EPA's Clean Heavy Duty Truck and Bus Rule. When the Agency finalized the Heavy Duty Truck and Bus Diesel Rule (66 FR 5002, January 18, 2001) in 2001, trucks and buses accounted for about one-third of NO$_X$ emissions from mobile sources. In some urban areas, the contribution was even greater. With model year 2010, all new heavy duty trucks and buses will result in NO$_X$ emission levels that are 95% below the pre-rule levels. EPA projects a 2.6 million ton reduction of NO$_X$ emissions in 2030 when the current heavy-duty vehicle fleet is completely replaced with newer heavy-duty vehicles that comply with these emission standards.

3. Clean Air Nonroad Diesel – Tier 4 Rule (69 FR 38957, June 29, 2004). In 2004, EPA adopted a comprehensive national program to reduce emissions from future nonroad diesel engines by integrating engine and fuel controls as a system to gain the greatest emission reductions. EPA estimates that in 2030, this program will reduce annual emissions of NO$_X$ by about 740,000 tons.

4. Marine-Related NO$_X$ Reductions from 1999 to 2003. EPA completed three rulemakings with respect to the diesel marine sector that will reduce NO$_X$ emissions. These rules are now in effect and being phased-in. In 1999 (64 FR 73299, December 29, 1999), EPA promulgated NO$_X$ requirements for diesel engines used in commercial boats (large inland and near-shore boats) and commercial vessels (ocean-going vessels). EPA estimates that these reduced emissions from these vessels by about 30%. In 2002 (67 FR 68241, November 8, 2002), EPA promulgated rules reducing NO$_X$ emissions from diesel engines used in recreational marine vessels by 25%. In 2003 (68 FR 9746, February 28, 2003), EPA promulgated another rule further reducing NO$_X$ from diesel engines used in commercial vessels by about 20%. EPA projects that on a nationwide basis, these four programs will reduce marine-related NO$_X$ by more than 1 million tons in 2030.

5. Locomotive and Marine Diesel Rule (73 FR 25098, May 6, 2008). In March 2008, EPA adopted standards that will reduce NO$_X$ emissions from locomotives and marine diesel engines. The near-term emission standards for newly-built engines phased in starting in 2009. The long-term standards begin to take effect in 2015 for locomotives and in 2014 for marine diesel engines. EPA estimates NO$_X$ emissions reductions of 80% from engines meeting these standards. EPA projects that in 2030, about 420,000 tons of NO$_X$ will be reduced from the locomotive engines, and 375,000 tons of NO$_X$ will be reduced from commercial and recreational marine engines.

6. Non-road Spark-Ignition Engines (73 FR 59034, October 8, 2008). In 2002, EPA promulgated emissions standards for large spark-ignition engines. These took effect in 2004 for Tier 1 standards and in 2007 for Tier 2 standards. EPA promulgated emissions standards for small spark-ignition engines in 2008. EPA projects that, when fully implemented, the new standards will result in a 35% reduction in HC+NO$_X$ emissions from new engines' exhaust, reduce evaporative emissions by 45%, and that together these programs will reduce NO$_X$ by more than 585,000 tons in 2030.

7. EPA's Coordinated Strategy for Control of Emissions from Ocean-Going Vessels (www.epa.gov/otaq/ oceanvessels.htm). EPA's coordinated strategy to

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[22] The information in Appendix F was provided to the Integrated Nitrogen Committee by Mazrgaret Zawacki of the U.S. EPA Office of Transportation and Air Quality.

control emissions from ocean-going vessels consists of actions at the national and international levels. On December 22, 2009, EPA finalized emissions standards for ocean-going vessels which take effect in 2011. In addition to this rule the U.S. Government has also amended MARPOL Annex VI to designate U.S. coasts as an Emission Control Area (ECA) in which all vessels, regardless of flag, will be required to meet the most stringent engine and marine fuel sulfur requirements in Annex VI. New engine emission and fuel sulfur limits contained in the amendments to Annex VI are also applicable to all vessels regardless of flag and are implemented in the U.S. through the Act to Prevent Pollution from Ships (APPS). EPA projects that when fully implemented, the coordinated strategy will reduce NO_x emissions from ocean-going vessels by 80% and that in 2030, the coordinated strategy is expected to yield a reduction in NO_x of about 1.2 million tons.

8. EPA's Voluntary Clean Diesel Programs. EPA has created a number of programs designed to reduce emissions (including both PM and NO_x) from the diesel fleet. In conjunction with state and local governments, public interest groups, and industry partners, EPA has established a goal of reducing emissions from the over 11 million diesel engines in the existing fleet by 2014. Looking at these engines, EPA determined there were general sectors that provided the best opportunity to obtain significant reductions and created programs for Clean Agriculture, Clean Construction, Clean Ports, Clean School Bus, and SmartWay Transport.

9. Section 177 of the Clean Air Act allows states outside of California to adopt California emissions standards, once EPA has granted such a waiver. As a result, several northeastern states have adopted California standards. Maryland adopted its California LEV II NO_x standards as part of its Low Emission Vehicle Program (COMAR 26.11.34, effective December 17, 2007). These standards take effect with the 2011 model year. Maryland submitted that program to EPA as a SIP revision. Pennsylvania adopted California LEV II NO_x standards as part of its Clean Vehicles Program (codified at Pa. Code Chapters 121 and 126, effective December 9, 2006). Pennsylvania's program began with model year 2008 vehicles. Pennsylvania submitted this program as a SIP revision.

Appendix G:
Impacts of Reactive Nitrogen on Aquatic Systems

Nitrogen contamination of groundwater

In addition to environmental concerns about N-nutrient loading to freshwaters from a groundwater pathway, there are also potential human health impacts from elevated levels of N in groundwater, especially from NO_3. It has been long established that excess NO_3 in drinking water supplies can cause blue baby syndrome (methemoglobinemia) (Knobeloch and Proctor 2001; Ward et al. 2005, 2006), the indicator of which is MetHb. To protect public health from effects of NO_3 in drinking water, EPA has established a maximum contaminant level goal (MCLG) that considers a lifetime exposure plus a margin of safety. For NO_3 in drinking water, the MCLG is 10 mg/L. Nitrite-N also has an established MCLG of 1 mg/L, and the combined NO_3 and NO_2 MCLG set by EPA is 10 mg/L. These same values are used to regulate NO_3 and NO_2 as maximum contaminant levels (MCL), which are the highest levels of contaminants allowed in drinking water (40 CFR § 141.62).

The drinking water standard is commonly exceeded in streams and rivers of the U.S., particularly in the agricultural Midwestern U.S. For example, there were 13 episodes over a 25- year period of formal warnings by authorities to local citizens in Columbus, Ohio, about not drinking tap water because nitrate-nitrogen was higher than 10 mg-N/L (Mitsch et al., 2008). These episodes lasted from one to several weeks each. The pattern is generally for high concentrations of nitrate-nitrogen in Midwestern rivers from February through June or July. In one pattern, averaged over 7 years with weekly river sampling, nitrate-nitrogen in a central Ohio river peaked with an average of 7 mg-N/L in June after which concentrations decrease to 1-2 mg-N/L for the rest of the summer and fall. The year-to-year variability was high for that month as well (Mitsch et al. 2005) as these spring "high-nitrate" floods do not occur every year. The nitrate "pulses" generally are part of flood events after fertilizer has been applied to fields in the watershed.

Public policy by water supply agencies is to treat high concentrations of nitrate-nitrogen in drinking water supplies as a real public health threat. Recent studies have brought the concern of high nitrate-nitrogen in drinking water into dispute (Ward et al., 2005, 2006). While there is a definite link between excessive nitrate in drinking water and methemoglobinemia, there is also a need to better understand the interaction of the range of environmental factors (e.g., cofactors such as diarrhea and respiratory diseases reportedly increase MetHb levels) that promote methemoglobinemia. This will help identify the environmental conditions under which exposure to nitrate in drinking water poses a risk of methemoglobinemia.

According to the USGS (Barber, 2009) *Summary of Estimated Water Use in the U.S. in 2005,* total water withdrawals in the U.S., excluding thermoelectric power usage, were 210 billion gallons per day, of which 44,200 million gallons per day (MGD) were for public water supply. About two-thirds of that supply is provided by surface water, the rest is from wells and about 58% (25,600 MGD) of public water supply goes towards domestic use, including drinking water. Private wells (Figure G-1) that are not part of public water supply systems are estimated to provide an additional 3,830 MGD, providing domestic water for 42.9 million people (14% of the U.S. population in 2005).

Groundwater N in forested and low intensity (<10%) agriculture or urban land use areas is estimated to be fairly low, having 75th percentile concentrations of 0.5 and 1.1 mg/L in two USGS studies (Nolan and Hitt, 2002). They consequently concluded that a "reasonable" background concentration, as NO_3-N, would be 1.1 mg/L, which would include effects in more sensitive aquifers with nominal loading for urban or agricultural sources.

Nitrate can enter groundwater from a variety of sources, including all of those described in this report, but fertilizer and animal waste in rural, agricultural areas are especially prominent sources (Nolan and Ruddy, 1996). Other sources include septic systems, more important in densely-developed and unsewered urban areas, and atmospheric deposition. Vulnerability to elevated NO_3 levels is also variable, but an assessment and model by Nolan and Hitt (2006) predicted that "… areas with high N application, high water input, well-drained soils, fractured rocks or those with high effective porosity, and lack of attenuation processes…" are especially vulnerable ($r^2 = 0.801$).

As illustrated in Figure G-2, surveys confirm that NO_3 in groundwater is elevated in many areas of the U.S., well above the 1.1 mg/L background upper bound described above (Figure G-2). The background colors on the map in Figure G-2 are indicative of different types of aquifers. In a 1992-1995 survey (Nolan and Stoner, 2000), shallow groundwater underlying agricultural areas was found to be most severely impacted by elevated NO_3-N levels (median concentration of 3.4 mg/L). Urban shallow aquifers were less impacted (median concentration of 1.6 mg NO_3-N/L) and deeper, major

aquifers, in general, had a median NO_3-N concentration of 0.48 mg/L. However, NO_3-N concentrations did exceed the 10 mg/L MCL threshold set by EPA for drinking water in more than 15% of the groundwater samples in the survey from drinking water aquifers.

In the most recent survey of domestic well water quality (DeSimone et al., 2009), USGS found concentrations of NO_3-N greater than 10 mg/L in 4.4% of the wells sampled. Concentrations exceeding the nitrate MCL were most frequently encountered in certain basins of the Southwest and California, west-central glacial aquifers in the Upper Midwest, and coastal plain aquifers and Piedmont crystalline rock aquifers in central Appalachia. Lowest concentrations were found in the coastal plain aquifers of the Southeast. In general, higher NO_3-N concentrations were found near agricultural lands. In an additional analysis of shallow groundwater wells in agricultural areas, separate from the national survey, nearly 25% of the sampled wells exceeded the 10 mg/L MCl for NO_3-N. DeSimone et al. (2009) suggested that redox could be a defining factor in some cases, and perhaps was the reason for low NO_3-N concentrations in the Southeast in soils that promote denitrification, as well as higher NO_3-N levels in other areas where aquifers were better oxygenated.

Ammonia toxicity in freshwater systems

The EPA and states have long regulated ammonia (NH_3) in the environment, not because of its nutrient contribution to cultural eutrophication, but because of its toxicity to freshwater aquatic life (U.S. EPA, 1986). The un-ionized ammonia molecule has been identified as the primary toxic form, rather than the ammonium ion (NH_4^+), and research has further demonstrated the relationship between pH, temperature, and NH_3 partitioning from the total ammonia pool in freshwaters (U.S. EPA, 1999). Because of the relationship to temperature in particular, and the variable sensitivity of species and life stages of aquatic organisms, state water quality standards in application generally consider cold and warm water conditions, as well as acute and chronic exposures to life stages of sensitive organisms, plus a margin of safety to derive criteria.

While water quality criteria were initially set for concentrations of NH_3, as criteria development skills and understanding improved, it made sense to develop criteria for total ammonia concentration for specific water quality conditions, e.g., cold or warm (salmonids present or absent) with consideration of ambient pH factors as appropriate, for protection of the most sensitive species likely to be present (early life stages present or absent), plus a margin of safety. This was because of evidence that the NH_4^+ fraction may also be contributing to toxicity. Criteria could be presented as formulas in adopted state criteria to calculate total ammonia thresholds based on prevailing pH and temperature conditions and organisms present/absent, as appropriate.

Based on this research and analysis, EPA currently recommends adoption of ammonia criteria as criterion continuous concentration (CCC) and criterion maximum concentration (CMC) as described in Box G-1 (U.S. EPA, 1999).

EXPLANATION

Population (1995) supplied by domestic wells, in percent of total county population

- ≥ 80
- ≥ 60 and < 80
- ≥ 40 and < 60
- ≥ 20 and < 40
- < 20

In many parts of the United States, domestic wells supply drinking water for large percentages of the population. Nationwide, more than 43 million people rely on domestic wells. Data shown are from Solley and others (1998).
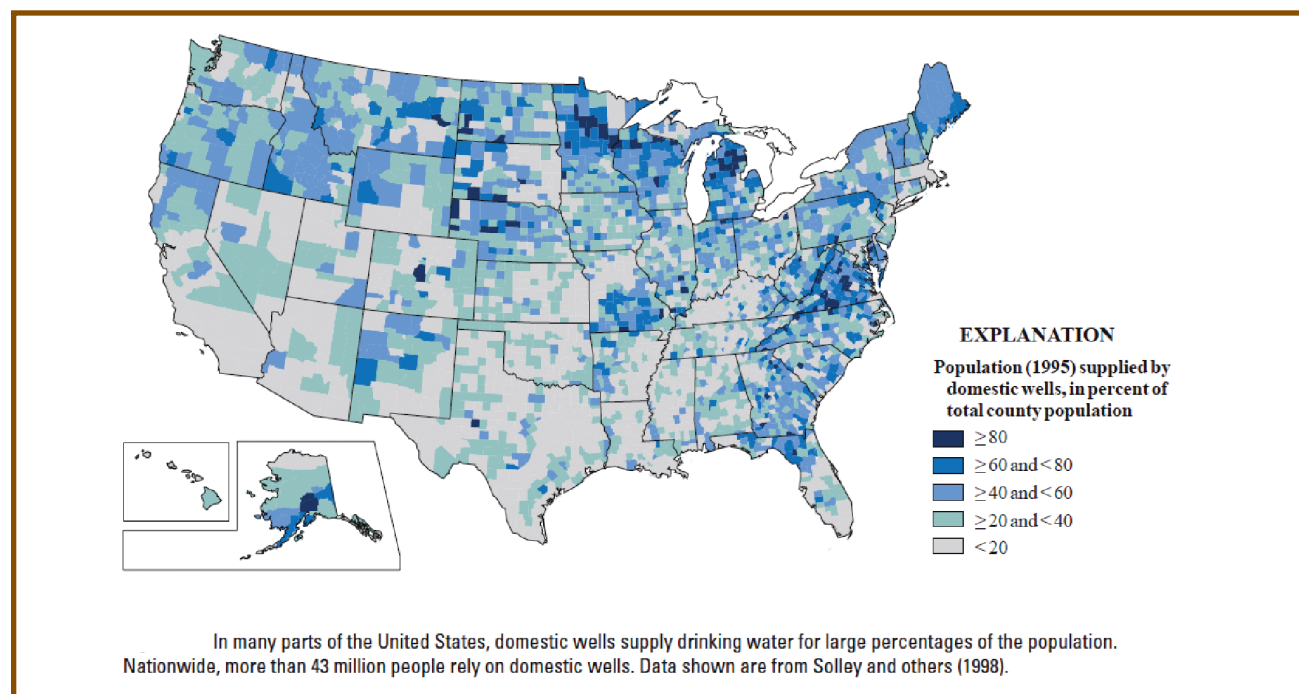
Figure G-1: U.S. Population (1995) supplied by domestic drinking water wells
Source: DeSimone et al., 2009.

EXPLANATION

Nitrate, in milligrams per liter as N

● >10   ● >1 and ≤10   ○ ≤1

Concentrations of nitrate were greater than the U.S. Environmental Protection Agency Maximum Contaminant Level of 10 milligrams per liter (mg/L) as N in 4.4 percent of the wells. Elevated concentrations of nitrate occurred throughout the United States, but least commonly in the Southeast. Concentrations greater than 1 mg/L as N, which is usually indicative of human activities in many areas (Nolan and Hitt, 2003), were found in about 40 percent of wells located throughout the sampled areas.
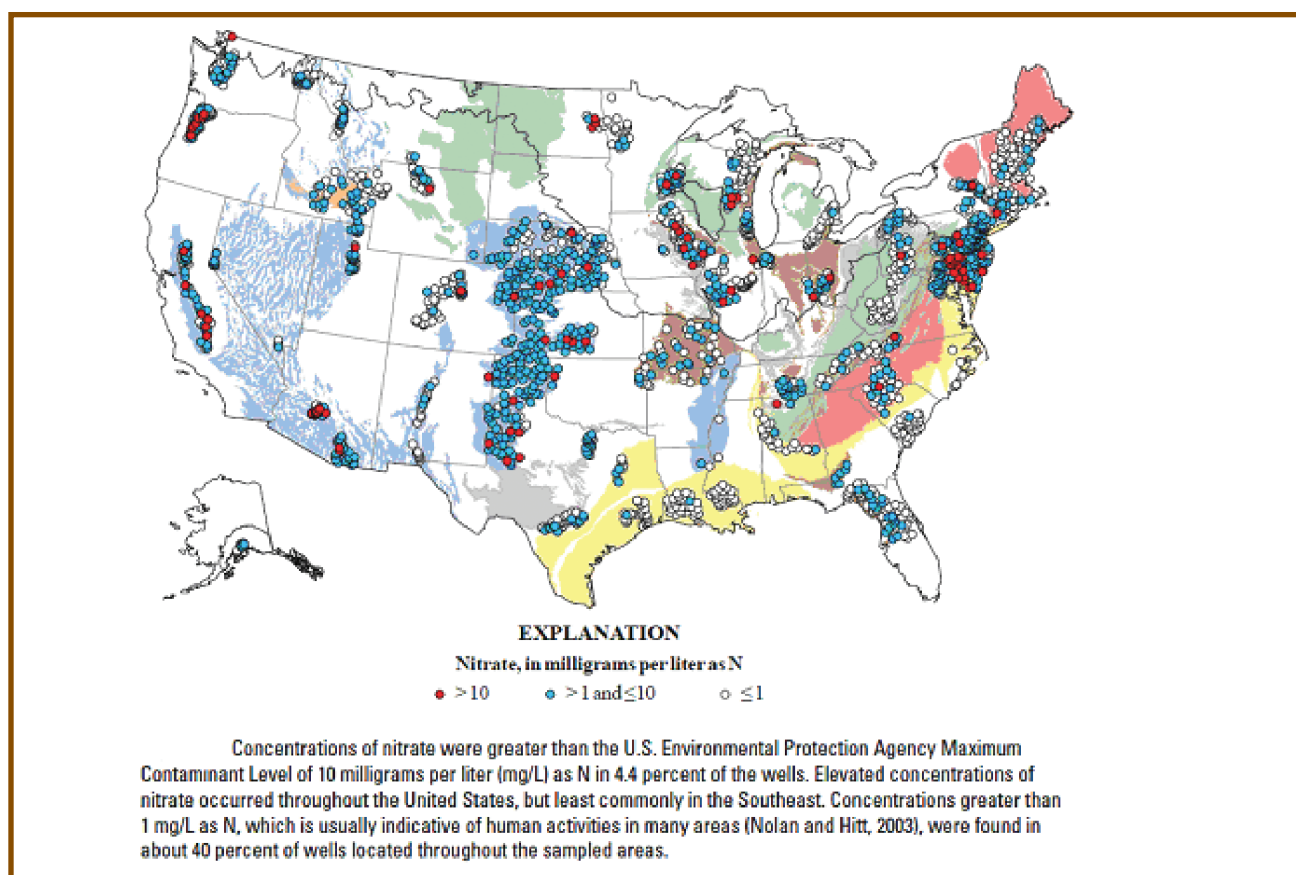
Figure G-2: Nitrate concentrations in U.S. domestic drinking water wells

(Background colors on the map are indicative of different aquifer types)
Source: DeSimone et al., 2009

Recent research on the sensitivity of freshwater unionid mussels (Family, Unionidae), and the rare and endangered status of several unionid species, has led the EPA to issue a draft update to the ammonia criteria guidance (U.S. EPA, 2009b) that would supersede the current 1999 guidance. Mussels have been found to be more sensitive to ammonia toxicity than the most sensitive species used to derive the 1999 criteria (Augspurger et al., 2003). Augspurger et al. (2003) found that the CMC with unionids considered would range from 1.75 to 2.50 mg total ammonia-N/L, 60% lower than the current method calculation of 5.62 mg total ammonia-N/L, for example. In the draft 2009 update, EPA proposed a two-tiered process for ammonia CMC and CCC development for waters with and without sensitive unionid species.

With this new sensitivity identified, ecosystem imbalances due to eutrophication and the presence and die off of invasive species may result in toxic levels of ammonia for mussels in freshwater systems, in addition to the conventional sewage and agricultural sources. For example, Cooper et al., (2005) suggested that die offs of invasive Asian clam (Corbicula fluminea), common in most southeastern U.S. waters, could produce enough

sediment pore water ammonia during decay to be lethal to sensitive unionid mussels. Further, combination of ammonia with other toxic substances may compound toxic effects, as found by Wang et al. (2007a,b) for ammonia and copper. Their research suggests that the 1999 criteria for total ammonia might not be protective of sensitive mussel species.

Impacts of Nr on freshwater ecosystems

Reactive nitrogen (Nr), including reduced (ammonium, organic N compounds) and oxidized (nitrate, nitrite) forms, play central roles in modulating and controlling (limiting) primary and secondary production and species composition in freshwater ecosystems. These include lakes, reservoirs, streams, rivers, and wetlands (Goldman, 1981; Paerl, 1982; Elser et al., 1990, 2007; Wetzel, 2001). While phosphorus has been considered the primary limiting nutrient in freshwater ecosystems (c.f. Schindler, 1971; Schindler et al., 2008), there are numerous examples where Nr plays either a primary or secondary (i.e., co-limiting) role as a limiting nutrient (Paerl, 1982; North et al., 2007; Wurtsbaugh et al., 1997; Lewis and Wurtsbaugh, 2008). In particular, oligotrophic, alpine, tropical and subtropical, and other lakes having small watersheds

Box G-1: The National Criterion for Ammonia in Fresh Water

The available data for ammonia, evaluated using the procedures described in the "Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses," indicate that, except possibly where an unusually sensitive species is important at a site, freshwater aquatic life should be protected if both of the following conditions are satisfied for the temperature (T) and pH of the waterbody:

1. The one-hour average concentration of total ammonia nitrogen (in mgN/L does not exceed, more than once every three years on the average, the CMC (acute criterion) calculated using the following equations. Where salmonid fish are present:

$$CMC = \frac{0.275}{1+10^{7.204-pH}} + \frac{39.0}{1+10^{pH-7.204}}$$

Or where salmonid fish are not present:

$$CMC = \frac{0.411}{1+10^{7.204-pH}} + \frac{58.4}{1+10^{pH-7.204}}$$

2A. The 30-day average concentration of total ammonia nitrogen (in mg N/L) does not   exceed, more than once every three years on the average, the CCC (chronic criterion) calculated using the following equations.

When fish early life stages are present:

$$CCC = \left(\frac{0.0577}{1+10^{7.688-pH}} + \frac{2.487}{1+10^{pH-7.688}} \right) \cdot MIN(2.85, \ 1.45 \cdot 10^{(0.28 \cdot 25 - T)})$$

When fish early life stages are absent:

$$CCC = \left(\frac{0.0577}{1+10^{7.688-pH}} + \frac{2.487}{1+10^{pH-7.688}} \right) \cdot 1.45 \cdot 10^{0.028 \cdot (25 - MAX(T,7))}$$

2B. In addition, the highest 4-day average within the 30-day period should not exceed 2.5 times the CCC.

Source: U.S. EPA, 1999.

relative to the lake surface/volume, and lakes experiencing incipient stages of eutrophication, tend to be N-limited (Wetzel, 2001; Lewis and Wurtsbaugh, 2008). N limitation was illustrated for Lake Tahoe (in California and Nevada) which was highly sensitive to N enrichment during its early stages of eutrophication (Goldman, 1981; 1988). As the lake accumulated anthropogenic N inputs from both land-based runoff and atmospheric deposition within the Tahoe Basin, it began exhibiting symptoms of accelerating eutrophication, including noticeable "greening" of its formerly transparent near-shore waters and excessive epiphytic growth and fouling on its rocky bottom. Continued excessive N loading in the 1960s through 1980s has led to accelerating rates of algal primary production and a tendency to shift to more P limited conditions due to excessive N, relative to P, loading (Goldman,1988). This greater than 30-year

progression to more eutrophic, and less desirable (from ecological, trophic and economic perspectives—i.e., tourism, water use) conditions has largely been spurred on by excessive N loading. Recent measures taken to reduce N inputs have been successful in reducing the lake's rate of eutrophication (Goldman, 2002). Similarly, Lake Erie, which has experienced P-driven nuisance algal blooms starting in the 1950s, is now facing excessive N loading. This is largely a result of P input restrictions, which have been enacted since the 1970's, accompanied by a lack of control on ever-increasing N loads. This shift in nutrient loading (increasing N:P) has led to a resurgence of toxic cyanobacterial blooms dominated by the non-N2 fixing genus *Microcystis,* an indicator of excessive N loading (North et al., 2007).

Numerous lakes, reservoirs, rivers, estuaries (e.g., the Gulf of Mexico), and fjords worldwide exhibit N and

P co-limitation, either simultaneously or in seasonally-shifting patterns (Dodds et al., 1989; Elser et al., 1990, 2007; Elmgren and Larsson, 2001; Forbes et al., 2008; Scott et al., 2008; Wetzel, 2001; North et al., 2007; Xu et al., 2010). For example, many reservoirs in Texas exhibit seasonal N limitation in the river-reservoir transition zone, regardless of their trophic status (Scott et al., 2009). Under these circumstances, N inputs tend to determine the spatial and temporal extent of summer nuisance algal blooms, a key symptom of degrading water quality (Dodds et al., 1989; Paerl, 2009; Xu et al., 2010). N inputs, including those from increasing levels of atmospheric deposition, impact nutrient stoichiometry, with cascading effects on nutrient limitation, productivity, and lake nutrient cycling characteristics (Elser et al., 2009). Therefore, the inputs of N play a critical role in the overall trophic response, trophic state, and water quality conditions of affected freshwater ecosystems.

In Florida lakes, algae are often limited by the availability of Nr (Kratzer and Brezonik, 1981). The most well-studied example is Lake Okeechobee, the largest lake in the Southeastern U.S., and a system that periodically displays large blooms of noxious blue-green algae. This lake has high availability of reactive P, and changes in the availability of Nr control the wax and wane of algae. In the 1980s and 1990s, blooms of algae were predominantly caused by cyanobacterial nitrogen (N2) fixer *Anabaena.* However, the most widespread recent bloom, which covered almost the entire lake surface in summer 2006, was caused by *Microcystis,* a non-N2- fixing cyanobacterium that depends on dissolved inorganic N (DIN: ammonium, nitrate, nitrite) and possibly organic N for its growth. This alga is the most common producer of toxins in Florida lakes, and it has the ability to "luxury consume" P from lake sediments and then rise through the water column, increasing its biomass to a level that largely is controlled by the amount of DIN. Because Lake Okeechobee's sediments contain massive quantities of reactive P (Havens et al., 2007), successful control of *Microcystis* blooms will require reduction in *both* P and N inputs to this lake.

In addition to the importance *total* N loads play in determining water quality status and trends, the supply rates and ratios of various Nr forms play an important role in structuring microalgal and macrophyte communities mediating freshwater primary production (Paerl, 1988; McCarthy et al., 2007, 2009; Lin et al., 2008). For example, the ratio of ammonium to oxidized N was related to the proportion of cyanobacteria composing the total phytoplankton community of Lake Okeechobee (McCarthy et al., 2009). Non-N_2-fixing cyanobacteria, such as Microcystis, are superior competitors for reduced N (Blomqvist et al., 1994), but even N_2-fixing cyanobacteria will preferentially assimilate ammonium if it is available (Ferber et al., 2004). Ammonium is the initial N form produced by

recycling processes (via invertebrate excretion and bacterial mineralization), but standing concentrations often remain very low because they are assimilated rapidly. Ammonium and other reduced N forms, such as dissolved free amino acids, are more available than oxidized N forms (nitrate and nitrite) to bacteria (Vallino et al., 1996) and cyanobacteria because less energy is required to incorporate reduced N into biomass than for oxidized forms (Syrett, 1981; Gardner et al., 2004; Flores and Herrero, 2005).

Lastly, it should be pointed out that both freshwater and marine systems do not respond to nutrient inputs in isolation. These systems are hydrologically and biogeochemically connected and coupled, functioning as a freshwater to marine *continuum* (Paerl, 2009). Nutrient limitation may shift along the continuum, and eutrophication and other symptoms of N and P over-enrichment, including harmful algal blooms, hypoxia, loss of biodiversity, and food web alterations impact water quality, habitat condition, use, and sustainability of downstream waters. Therefore, excessive N loading in upstream freshwater ecosystems, ranging from the headwaters of pristine alpine streams to lowland lakes, reservoirs, and rivers can adversely affect downstream estuarine and coastal marine waters (Conley et al., 2009; Paerl, 2009). Examples of such continuum-scale impacts include such prominent systems as Chesapeake Bay, Albemarle-Pamlico Sound, Florida Bay, Mississippi River plume (Gulf of Mexico), Baltic Sea, and Coastal North Sea (Elmgren and Larsson, 2001; Boesch et al., 2001; Paerl, 2009).

Impact of nitrogen on wetlands

In this section, the possible impact of reactive nitrogen on wetlands is discussed. In Chapter 5 considerable attention is devoted to the subject of wetlands serving as effective nitrogen sinks. There are about 110 million ha of wetlands in the U.S., with more than half of those in the state of Alaska (Mitsch et al., 2009). Of those wetlands, roughly 97% are inland (and mostly freshwater) and 3% are estuarine (and mostly saline). Of the total wetlands, approximately half (166 million acres or 55 million ha) are peatlands, which, by their nature as low-nutrient systems, are most susceptible to nitrogen loadings, either from the atmosphere or from rivers and streams. More than any other ecosystem, wetlands are central to the cycling of nitrogen because they have both aerobic and anaerobic conditions that allow for a wide variety of important nitrogen processes, not the least of which is denitrification.

Wetlands are similar to lakes and streams and any other ecosystem in that their productivity is limited by nutrient availability. But with wetlands the hydrology limits or enhances productivity as well (Mitsch and Gosselink, 2007). The addition of excessive nutrients to wetlands, while often done purposefully when the wetlands are so-called treatment wetlands (Kadlec and

Wallace, 2009), can cause vegetation shifts and decreases in plant diversity. Verhoeven et al. (2006) suggested 4.5 g-N m^{-2} yr^{-1} as critical loading rate of nitrogen, generally from atmospheric sources, for peat-dominated wetlands. Morris (1991) had suggested that bogs and fens generally had loading rates of 1 to 6 g-N m^{-2} yr^{-1} respectively. Thus Verhoeven et al. (2006) were suggesting that wetlands should not be loaded beyond what is currently occurring in fen peatlands. These limitations do not apply for most mineral soil wetlands, particularly those connected to streams and rivers. Most freshwater and tidal marshes have nitrogen loading rates closer to 60 g-N m^{-2} yr^{-1} and they maintain a reasonably high and sustainable productivity. Using a sustainable rate of nitrogen retention as a measure, Mitsch and Jørgensen (2004) suggest a range of nitrogen retention rate of 10-20 g-N m^{-2} yr^{-1} for wetlands to maintain their biodiversity while being nitrogen sinks at the same time. Overall, this is a fruitful direction for wetland research to determine the assimilative capacity of wetlands for nutrients, including nitrogen, while not surpassing a limit that will dramatically change the wetland's structure and function.

Impacts of Nr on coastal systems

Mitsch et al. (2001) suggest that streams and rivers themselves are not always as much affected by nutrient loading as are lakes, wetlands, coastal areas, and other lentic bodies of water. However, in most cases, these nutrient-enriched waterways flow to the sea, with eutrophication of coastal waters the unfortunate result. This problem now occurs regularly throughout the world (World Resources Institute, 2008), in locations such as the Gulf of Mexico (Rabalais et al., 1996), the Baltic Sea (Larson et al., 1985), and the Black Sea (Tolmazin, 1985).

During the past century, following large-scale use of synthetic N fertilizers in agriculture, rapid expansion of industrial and transportation-related fossil fuel combustion and coastal urbanization, humans have significantly altered the balance between "new" N inputs and N losses in the marine environment (Codispoti et al., 2001; Galloway and Cowling, 2002). During this time frame, terrestrial discharge and atmospheric N emissions have increased 10-fold (Howarth et al., 1996; Holland et al., 1999). This number keeps growing as human development continues to expand in coastal watersheds (Vitousek et al., 1997a,b).

Researchers have long recognized this growing imbalance, especially in estuarine and coastal waters where anthropogenically-derived N over-enrichment has fueled accelerated primary production, or "cultural" eutrophication (Vollenweider et al., 1992; Nixon, 1995). Eutrophication is a condition where nutrient-enhanced primary production exceeds the ability of higher ranked consumers and organic matter-degrading microbes to consume and process it. D'Elia (1987) characterized this condition as "too much of good thing" or over-fertilization of N-limited marine ecosystems with "new"

N, the bulk of it being anthropogenic (Howarth et al., 1996; Vitousek et al., 1997a,b; Galloway and Cowling, 2002). Symptoms of N-driven eutrophication vary: from subtle increases in plant production to changes in primary producer community composition; to rapidly accelerating algal growth, visible discoloration or blooms, losses in water clarity, increased consumption of oxygen, dissolved oxygen depletion (hypoxia), which is stressful to resident fauna and flora; to, in the case of total dissolved oxygen depletion (anoxia), elimination of habitats (Paerl, 1988, 1997; Diaz and Rosenberg, 1995; Rabalais and Turner, 2001). Other effects include submerged aquatic vegetation (SAV) losses, possible impacts on tidal wetland health, and disruption of estuarine food chain dynamics that may favor an imbalance towards lower trophic levels (e.g., jellyfish).

Anthropogenic or cultural eutrophication has been closely linked to population densities in coastal watersheds (Peierls et al., 1991; Nixon, 1995; Vitousek et al., 1997a,b). Primary sources of N enrichment include urban and agricultural land uses as well as wastewater treatment plants, many of which have not been designed to remove N. A significant, and in many instances increasing, proportion of "new" N input can also be attributed to remote sources residing in airsheds. Delivery routes can also be complex, especially when via subsurface aquifers outside the immediate watershed, which can confound source definition and create long delays in delivery and management response (Paerl, 1997; Jaworski et al., 1997; Galloway and Cowling, 2002; Paerl et al., 2002).

The availability of N controls primary production in much of the world's estuarine, near-shore coastal, and open-ocean waters (Dugdale, 1967; Ryther and Dunstan, 1971; Nixon, 1995; Paerl, 1997; Boesch et al., 2001). As previously discussed, nitrogen can also play a role as either a primary or secondary limiting nutrient in freshwater environments, especially large lakes (e.g., Lake Tahoe, Lake Superior). As such, the fertility of these waters is often closely controlled by N inputs, which are provided either internally by regeneration of pre-existing N and biologically-fixed atmospheric N2, or supplied externally (i.e. "new" N) as combined N sources delivered via surface runoff, sub-surface groundwater, or atmospheric deposition.

The extent to which accelerated N loading promotes eutrophication and its symptoms varies greatly among marine ecosystems. Receiving waters exhibit variable sensitivities to N and other nutrient [phosphorus (P), iron (Fe), and silica (Si)] loads that are controlled by their size, hydrologic properties (e.g., flushing rates and residence times), morphologies (depth, volume), vertical mixing characteristics, geographic and climatic regimes and conditions. In addition, the magnitude and distribution of N in relation to other nutrient loads can vary substantially. In waters receiving very high N loads relative to

requirements for sustaining primary and secondary production, other nutrient limitations may develop. This appears to be the case in coastal waters downstream of rivers draining agricultural regions that are enriched in N.

On the ecosystem level, estuarine and coastal waters exhibit individualistic responses to N loads over seasonal and longer (multi-annual, decadal) time scales. The degree to which these systems are exposed to freshwater discharge, tidal exchange, and vertical mixing is critical for determining how they respond to specific N loads (Vollenweider et al., 1992; Nixon, 1995; Cloern, 1999, 2001; Valdes-Weaver et al., 2006; Paerl et al., 2007). Another variable is the manner in which N loading takes place, which may range from acute pulsed events such as storms and associated flooding, to longer-term gradual (chronic) increases in N loading associated with more predictive seasonal, annual and inter-annual hydrologic cycles. There are striking contrasts in ecosystem response to N inputs that reflect a range in physical (hydrodynamic, optical) and climatic conditions (Cloern, 1999, 2001). Examples include contrasts between strong tidally-driven estuarine systems, such as Delaware Bay and San Francisco Bay, and non-tidal, lagoonal systems, such as North Carolina's Pamlico Sound and Texas's Luguna Madre, or semi enclosed coastal systems, such as Florida Bay and the Long Island Sound (Bricker et al., 1999; Valdes-Weaver et al., 2006; Paerl et al., 2007).

Externally-supplied N comes in various forms, including organic N and inorganic reduced (NH_3 and NH_4^+ ion) and oxidized (NO_3^-) N, all of which are potentially available to support new production and eutrophication. Laboratory experiments on phytoplankton isolates and bioassays with natural phytoplankton communities have indicated that these contrasting forms may be differentially and preferentially utilized, indicating that, depending on composition of the affected phytoplankton community, some forms are more reactive than others (Collos, 1989; Stolte et al., 1994; Riegman, 1998). Phytoplankton community composition can also be altered by varying proportions and supply rates of different forms of N (Dortch, 1990; Stolte et al., 1994; Harrington, 1999; Pinckney et al., 1999; Piehler et al., 2002). Monitoring and research on dissolved organic N inputs and their effects should be conducted in receiving streams, rivers, lakes, estuarine, and coastal waters, since there is evidence that these compounds can be utilized by phytoplankton, including harmful bloom species (Paerl, 1988; Antia et al., 1991; Carlsson and Granéli, 1998; Gilbert et al., 2006). In addition, specific N compounds may interact with light availability, hydrodynamics and other nutrients, most notably P, Si, Fe, and trace metals, to influence phytoplankton community growth rates and composition (Harrison and Turpin, 1982; Smith, 1990; Dortch and Whitledge, 1992).

Over the past 25 years, there has been a growing recognition of cultural eutrophication as a serious problem in coastal estuaries (NRC, 2000). Globally, Selman et al. (2008) have reported "Of the 415 areas around the world identified as experiencing some form of eutrophication, 169 are hypoxic and only 13 systems are classified as 'systems in recovery.'"Comprehensive surveys of U.S. estuaries have been conducted by the National Oceanic and Atmospheric Administration (NOAA) as part of the National Estuarine Eutrophication Assessments (NEEA) in 1999 and 2004 (Bricker et al., 1999, 2007). The most recent report, released in 2007 (Bricker et al., 2007) focused on nutrient enrichment and its manifestations in the estuarine environment and relies on participation and interviews of local experts to provide data for the assessment. Among the key findings for nearly 100 assessed U.S. estuaries were that eutrophication is a widespread problem, with the majority of assessed estuaries showing signs of eutrophication—65% of the assessed systems, representing 78% of assessed estuarine area, had moderate to high overall eutrophic conditions. The most common symptoms of eutrophication were high spatial coverage and frequency of elevated chlorophyll *a* (phytoplankton)—50% of the assessed estuaries, representing 72% of assessed area, had a high chlorophyll *a* rating.

Further field evaluations by EPA and state and university collaborators under the National Coastal Assessment (NCA) used probabilistic monitoring techniques. The NCA National Coastal Condition Reports (NCCR) (U.S. EPA, 2001a, 2004, 2006b) are more closely related to nutrient enrichment assessments, especially for manifestations of nutrient enrichment such as hypoxia, nuisance algal blooms, and general habitat degradation. The last comprehensive national NCCR was published in 2004 (U.S. EPA, 2004) with a more recent assessment focused on 28 National Estuary Program estuaries published in 2007 (U.S. EPA, 2006). The 2004 NCCR included an overall rating of "fair" for estuaries, including the Great Lakes, based on evaluation of more than 2,000 sites. The water quality index, which incorporates nutrient effects primarily as chlorophyll-*a* and dissolved oxygen impacts, was also rated "fair" nationally. Forty percent of the sites were rated "good" for overall water quality, while 11% were "poor" and 49% "fair."

Attainment of water quality management goals and standards for coastal systems

Estuarine systems, where bio-available Nr is more likely to be the limiting nutrient, are most often susceptible to Nr enrichment (Paerl, 1997; Boesch et al., 2001). Defining single-number criteria for nutrients or related indicators representative of undesirable levels of productivity (e.g., chlorophyll-*a*) is difficult, even using the ecoregional approach recommended by EPA. State managers more often use the formal TMDL process or collaborative estuarine management plans to set site- or estuary-specific N management targets to meet existing, related water quality criteria (e.g., dissolved O_2 or

chlorophyll *a*). Some of the more prominent efforts and targets for nitrogen control are summarized in Table G-1.

These targets all exceed nitrogen load reduction goals that the Committee has found to be readily achievable using existing technology and management authority (i.e., less than 25% from specific source categories). Some sources of nitrogen loading to the estuaries in Table G-1 pose greater management challenges and the expectation is that reductions in Nr loadings to estuaries would cumulatively be less than 25%. This suggests that efforts will be needed to enable even greater nitrogen load reductions in the future. Many of the management actions the Committee has proposed in this report would require substantive changes in national programs, regulatory authority, management technologies and societal demands to be accomplished. This is a nutrient management concern that state managers are well aware of as they develop TMDLs and management plans that range above attainment potential, not only for Nr but more frequently for other pollutants that are predominately nonpoint source and stormwater loaded (including atmospheric source contributions).

The Chesapeake Bay Program, for example, is a model for Nr and P management in many ways. Considerable resources were committed, and many BMPs were implemented. Yet despite regional efforts and commitments from all watershed states, and more funding than any other estuary program is likely to see, management targets have not been met, and recent data (2007) reveal the occurrence of a severe hypoxic episode. Concerns over the slow progress in restoring the Chesapeake Bay led to the issuance of an Executive Order on May 15, 2009, establishing a Federal Leadership Committee led by the EPA to develop and implement a plan to restore the Bay in collaboration with state agencies (*Federal Register* 74(93): 23097-23104). Similarly, the adoption of the Long Island Sound TMDL, which was driven by the presence of reactive nitrogen (see Box G-2), sets an implementation plan that could attain Connecticut and New York dissolved oxygen criteria, but only if "alternative technologies" such as mechanical aeration of the Sound or biological harvesting of nutrients, are used.

Table G-1: Estuaries with nitrogen management plans or TMDLs and percent nitrogen load reduction targets

Estuary	Nitrogen Load Reduction Target	TMDL or Plan
Casco Bay, Maine	45%	Plan
Chesapeake Bay	>40%	Plan
Northern Gulf of Mexico		
Mississippi Plume Region	45%	Plan
Long Island Sound	60% for CT & NY sources	TMDL
Neuse River Estuary, NC	30%	TMDL
Tampa Bay, FL	Maintain TN (total nitrogen) load at 1992-1994 levels	TMDL & Plan

Box G-2: Long Island Sound Total Maximum Daily Load: Focus on Reactive Nitrogen

A TMDL sets a goal for reducing the load of a specific pollutant that is causing impairment to a waterbody. In the case of Long Island Sound, the impairment constitutes low concentrations of dissolved O_2 that violate both Connecticut's and New York's water quality standards. Nitrogen has been identified as the pollutant that causes substandard levels of dissolved oxygen in Long Island Sound and, accordingly, Connecticut's and New York's environmental agencies have developed a TMDL that assigns nitrogen reductions from both point sources (the wasteload allocation or WLA) and nonpoint sources (the load allocation or LA) in their respective states to meet the established 58.5% reduction of anthropogenic sources.

The Long Island Sound TMDL is set at 23,966 tons of N/year, which represents a 23,834 ton/year reduction from the total baseline (anthropogenic + natural sources considered) of 47,788 tons/year from Connecticut and New York only. Most of that N load comes from point sources – POTWs (publicly owned treatment works) and CSOs (combined sewer overflows) – accounting for 38,899 tons/yr of the total N load from the two states, or 81% of the load. For that reason, the focus has been on managing point sources, although attainment of water quality standards will require more widespread reductions from atmospheric deposition, stormwater, and nonpoint sources, and from other watershed states north of Connecticut.

Connecticut and New York have some flexibility in the apportionment of those reductions between the WLA and the LA, but must have completed 40% of the required reductions by 2004, 75% by 2009, and 100% by 2014 when the final TMDL will be met. However, the TMDL is presently undergoing revision to incorporate findings from a new model of Long Island Sound, and to reflect changes in dissolved O_2 criteria in both states. The revised TMDL will likely require more aggressive reductions of nitrogen to meet dissolved O_2 criteria and may formalize targets for upstream state contributions and atmospheric deposition.

Appendix H:
Nr Saturation and Ecosystem Function

There are limits to how much plant growth can be increased by N fertilization. At some point, when the natural N deficiencies in an ecosystem are fully relieved, plant growth becomes limited by availability of other resources such as phosphorus, calcium, or water and the vegetation can no longer respond to further additions of Nr. In theory, when an ecosystem is fully Nr-saturated and its soils, plants, and microbes cannot use or retain any more, all new Nr deposits will be dispersed to streams, groundwater, and the atmosphere. Nr saturation has a number of damaging consequences for the health and functioning of ecosystems. These impacts first became apparent in Europe almost three decades ago when scientists observed significant increases in nitrate concentrations in some lakes and streams and also extensive yellowing and loss of needles in spruce and other conifer forests subjected to heavy Nr deposition. In soils, most notably forest soils because of their natural low pH, as NH_4^+ builds up it is converted to nitrate by bacterial action, a process that releases hydrogen ions and contributes to soil acidification. The buildup of NO_3^- enhances emissions of nitrous oxides from the soil and also encourages leaching of highly water-soluble NO_3^- into streams or groundwater. As negatively charged NO_3^- seeps away, positively charged alkaline minerals such as calcium, magnesium, and potassium are carried along. Thus, soil fertility is decreased by greatly accelerating the loss of calcium and other nutrients that are vital for plant growth. As calcium is depleted and the soil acidified, aluminum ions are mobilized, eventually reaching toxic concentrations that can damage tree roots or kill fish if the aluminum washes into streams (Vitousek et al., 1997a,b).

Forests, grasslands, and wetlands vary substantially in their capacity to retain added nitrogen. Interacting factors that are known to affect this capacity include soil texture, degree of chemical weathering of soil, fire history, rate at which plant material accumulates, and past human land use. However, we still lack a fundamental understanding of how and why N-retention processes vary among ecosystems, much less how they have changed and will change with time and climate change (Clark and Tilman, 2008).

An overarching impact of excess Nr on unmanaged terrestrial ecosystems is biodiversity loss. In North America, dramatic reductions in biodiversity have been created by fertilization of grasslands in Minnesota and California. In England, N fertilizers applied to experimental grasslands have led to similarly increased dominance by a few N-responsive grasses and loss of many other plant species. In formerly species-rich heathlands across Western Europe, Nr deposition has been blamed for great losses of biodiversity in recent decades, with shallow soils containing few alkaline minerals to buffer acidification (Vitousek et al., 1997a,b; Bobbink et al., 2010).

Losses of biodiversity driven by Nr deposition can in turn affect other ecological processes. Experiments in Minnesota grasslands showed that in ecosystems made species-poor by fertilization, plant productivity was much less stable in the face of a major drought. Even in non-drought years, the normal vagaries of climate produced much more year-to-year variation in the productivity of species-poor grassland plots than in more diverse plots (Vitousek et al., 1997a,b).