Lecture 25  Nutrients as Contaminants (Nitrate/Phosphate)

I. Nutrients as Contaminants--Nitrogen
   A. Nitrogen, either in its reduced inorganic form, NH$_3$ (ammonia, -3 oxidation state), NO$_3$ (nitrate, +5 oxidation state), or NO$_2$ (nitrite, +3 oxidation state), can be hazardous under certain circumstances. As with essential trace metals, the biosphere depends on these compounds, but too high concentrations in the wrong place at the wrong time result in ecological or human health hazards;
      1. The most important sources of anthropogenic nitrogen include fertilizer use (with subsequent generation, runoff and/or leaching of excess nitrate) and combustion processes that release nitrogen oxide species.
      2. The hazard of most concern regarding human health is methemoglobinemia in infants, the binding of nitrite to hemoglobin, effectively reducing the capacity to bind oxygen.
      3. The ecological hazards include potential toxicity to aquatic organisms and a causal factor in aquatic hypoxia, especially in the Gulf of Mexico.
   B. Note that nitrogen is a limiting nutrient supply in soil because it is mostly in an organic form, inaccessible to microorganisms and plants; nitrogen undergoes several biochemical pathways in soil that lead to bioavailable forms.

C. Nitrogen Cycle--As with the trace elements, the reduced and oxidized forms of nitrogen are all part of natural biogeochemical cycles; there are six major processes (see numbers on diagram below) or reactions that characterize the nitrogen cycle; (Above figure from Rechcigl, 1995, Soil Amendments & Environmental Quality, CRC Press)
1. Assimilation of inorganic N (mainly $\text{NH}_4^+$, which is in a pH dependent equilibrium with $\text{NH}_3$ and $\text{NO}_3^-$) by microorganisms and plants to form organic N such as amino acids (which become proteins) and nucleotide bases (which become “polymerized” into DNA, RNA);
   a. a.k.a. immobilization
   b. Metabolic pathway known as the glutamine synthase-synthetase pathway
2. Heterotrophic conversions, involving the transfer of organic N among organisms;
3. Mineralization (or ammonification)
   a. Degradation of organic matter containing N to $\text{NH}_4^+$ by bacteria and fungi;
   b. $\text{NH}_4^+$ and $\text{NH}_3$ are in equilibrium; at typical soil and solution pHs, most of the N will be present in the ionized form.
4. Nitrification
   a. Conversion of $\text{NH}_4^+$ to $\text{NO}_2^-$ and $\text{NO}_3^-$;
   b. Microbially mediated oxidation (by nitrifying bacteria);
   c. Energy derived from oxidation of ammonium ion or nitrite ion
   d. Two functional groups of microbes: oxidation of ammonium to nitrite and oxidation of nitrite to nitrate
5. Denitrification
   a. Microbial reduction of nitrate to nitrite and then to gaseous $\text{N}_2\text{O}$ and $\text{N}_2$
   b. Enzymes: nitrate reductase and nitrite reductase
   c. Reduction in absence of oxygen
   d. Loss of nitrate can occur by leaching
6. Biological Nitrogen Fixation
a. Direct absorption of atmospheric N\textsubscript{2} to form NH\textsubscript{4}\textsuperscript{+}

b. Nitrogenase enzyme; microbes are present as symbiotes in roots, for ex. of leguminous plants;

D. Atmospheric Transformations

1. Gaseous losses of N from soils occur primarily as nitrous oxide (N\textsubscript{2}O) and N\textsubscript{2}
   (remember that 78% of the atmosphere is composed of N\textsubscript{2});
   a. Volatilization of free NH\textsubscript{3} and chemical decomposition of NO\textsubscript{2} to form N\textsubscript{2}, NO
      (nitric oxide) plus NO\textsubscript{2} (nitrogen dioxide), and smaller quantities of N\textsubscript{2}O also
      contribute to gaseous losses of N to the atmosphere;

2. As the use of nitrogen fertilizers has increased, there has been concern that increasing
   N\textsubscript{2}O emissions could destroy ozone (O\textsubscript{3}) in the stratosphere;
   a. Actually, when N\textsubscript{2}O is emitted it can translocate to the stratosphere where it is
      photolytically transformed to NO, which is reactive in combining with O\textsubscript{3},
      causing its degradation to O\textsubscript{2}; this reaction was actually the first concern about
      ozone destruction due to anthropogenically emitted contaminants.

\[ \text{N}_2\text{O} \rightarrow \text{NO} \rightarrow \text{NO}_2 + \text{O}_2 \]

3. Thus, release of other NO\textsubscript{x} (i.e., various oxidized N species) compounds like NO and
   NO\textsubscript{2} should also be a threat, but these compounds are actually allayed from reaching
   the stratosphere by a variety of chemical reactions and sink processes;
   a. NO is also released from incomplete combustion processes, of which cars are
      major sources; this problem is discussed under with ozone in lecture 25.

4. Concerns about increasing worldwide fertilizer use and ozone destruction have been
   quieted somewhat by studies showing N\textsubscript{2}O releases from fertilizer use are generally
   small (Muchoveg, R. & Rechcigl, J. E., 1995, Nitrogen fertilizers; pp. 1-64 in
   Boca Raton, FL)
   a. It has been estimated that if 100 Tg (i.e., terra grams) of N fertilizers are used
      globally each year, no more than 3 Tg (i.e., 3\%) is released as N\textsubscript{2}O

E. Historical trends in nitrogen use correspond to increased incidence of nitrates at levels >3
   mg NO\textsubscript{3}-N/L in water (Historical trend graph from Williamson et al. 1998. \textit{Water
   Quality in the Central Columbia Plateau, 1992-1995}. USGS NAWQA Circular 1144;
   http://water.usgs.gov/lookup/get?circ1144)

1. Note that the natural background levels of nitrate are considered to be <3 mg NO\textsubscript{3}-N/L
2. The water solubility, practically nil sorption potential, and widespread increase in intensity of use of mineralized fertilizers have led to an increase in nitrate concentrations in water throughout the U.S., especially in agricultural areas;
   a. Excessive fertilization of soil (i.e., applying nitrogen in excess of plant needs) coupled with rapid infiltration (due to high hydraulic conductivity of soil, preferential flow, or very high rainfalls) leads to contamination of ground water supplies by nitrates;
   b. Being an anion, NO$_3^-$ is not adsorbed by the soil, and thus it is highly leachable;
   c. Nitrates can also translocate to surface waters through tile drainage systems that empty in streams and rivers;
   d. Also municipal sewage effluent has high nitrate loads;
      1. Another possible source are defective septic systems, especially in rural or suburban areas that are highly dependent on septic systems;
3. A National Water-Quality Assessment Program (NAWQA) study of the Columbia Basin and Palouse has shown numerous wells in parts of the Central Columbia Plateau exceed drinking water standards
   a. Franklin Co. has been especially singled out as having a high incidence of wells with nitrate levels above the public health standard;
   b. The nitrate standard has been set at 10 mg NO$_3^-$-N/L (the MCL; note that on a nitrate basis alone, the standard is 44.5 mg/L), which was deemed sufficient to protect infants (<6 months) from methemoglobinemia; the nitrite standard is 1 mg NO$_2^-$-N/L;
      1. The standard was formed about 45 years ago and is said to have no margin of safety (in other words it is based on a level that would not cause methemoglobinemia, but is not adjusted further by a safety factor)
      2. The USGS NAWQA study showed that 26% of sampled wells less than 300 feet had nitrate concentrations exceeding the MCL, but only 8% of wells deeper than 300 feet exceeded the MCL.

Percentage of WA State wells with nitrate concentrations exceeding the MCL (1985-1996) (Williams et al. ’98)

<table>
<thead>
<tr>
<th>County</th>
<th>Class A Public Supply Wells</th>
<th>Class B Public Supply Wells</th>
<th>Shallow Domestic Wells</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adams</td>
<td>3</td>
<td>25</td>
<td>--</td>
</tr>
<tr>
<td>Douglas</td>
<td>7</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Franklin</td>
<td>28</td>
<td>29</td>
<td>33</td>
</tr>
<tr>
<td>Grant</td>
<td>1</td>
<td>3</td>
<td>35</td>
</tr>
<tr>
<td>Whitman</td>
<td>7</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>Subunit</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Quincy-Pasco</td>
<td>9</td>
<td>15</td>
<td>35</td>
</tr>
<tr>
<td>North-Central</td>
<td>3</td>
<td>5</td>
<td>--</td>
</tr>
<tr>
<td>Palouse</td>
<td>7</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Entire Study Unit</td>
<td>6</td>
<td>12</td>
<td>--</td>
</tr>
</tbody>
</table>

Class A wells are public water systems with at least 15 hook-ups (average depth of 411 wells sampled was 270 feet); Class B wells (n=270) have less than 15 hook-ups; (the average depth of 270 wells sampled was 210 feet); Domestic wells (n=67) averaged 140 feet deep.
Nitrate concentrations in wells sampled in the USGS NAWQA study in the Columbia Plateau and Palouse of Washington State (Williams et al. 1998)

c. Concentrations of nitrate tend to be lower the deeper the well (Williams et al. 1998)
d. The higher amounts of nitrate in Franklin Co. can be explained by both land use practices (more N is used owing to the types of crops, for ex. potatoes) and the artificially high recharge rate due to intense irrigation practices.

Fertilizer nitrogen use in the Columbia Plateau and Palouse (Williams et al. 1998)

Recharge Rates for Sub-Units in the Columbia-Plateau and Palouse (Williams et al. 1998)

II. Health concerns about nitrogen as a contaminant--Methemoglobinemia

A. Excessive levels of nitrate in drinking water has the potential to cause methemoglobinemia, a condition of reduced oxygen carrying capacity when nitrite binds to hemoglobin, producing methemoglobin; methemoglobin’s capacity to bind O₂ is inhibited;

1. Only infants, usually under 6 months are susceptible to methemoglobinemia;
   methemoglobinemia essentially causes oxygen deprivation, and thus infants suffering from methemoglobinemia turn a bluish color; a popularized name for the syndrome is “Blue Baby” syndrome;

2. The questions to be asked about the potential of nitrates to cause methemoglobinemia is what is the potential for exposure, what is the probability that nitrates will cause
methemoglobinemia (i.e., what is the epidemiology), and are the standards for protection of public health adequate.

B. The National Academy of Sciences issued a report in 1995, *Nitrate & Nitrite in Drinking Water*, that addressed the issue of the adequacy of the nitrate standard in light of current information about dietary exposures and known risk factors for methemoglobinemia; the report also addressed the issue of whether nitrate exposure was associated with an increased risk of stomach cancer (through possible nitrosation reactions that form nitrosamine, which are known to be mutagens); a summary of the NAS report follows:

1. Hazard Identification
   a. Methemoglobinemia in adults is rare; most victims are infants who have been fed
      b. Formula mixed with nitrate-containing well water
   c. Food with high nitrate content
   d. Methemoglobinemia also associated with Infants who have diarrhea;
   e. Epidemiology is inadequate to support an association between high nitrate/nitrite exposure from drinking water and cancer
   f. Studies in humans are inadequate to support an association between nitrate/nitrite exposure and reproductive or developmental effects;

2. Dose-Response Assessment
   a. Toxic effects closely related to conversion of nitrate to nitrite by bacteria in the alimentary tract
      1. The effects depend on dose and type & number of bacteria;
         a. In the infant stomach, there is more conversion of nitrate to nitrite;
         b. The infant stomach is not as acid as the adult stomach; this comparative lack of acidity allows a proliferation of denitrifying bacteria, which metabolize nitrate to nitrite;
         c. The nitrite can be absorbed by the upper intestinal tract; it is nitrite that binds to the hemoglobin.
         d. Methemoglobinemia cases are rare, especially below a water concentration of 10 mg NO$_3$-N/L;
      2. Most cases of methemoglobinemia are associated with bacterial contamination of a well;
         a. Bacterial infection increases endogenous nitrate production, which has the potential for producing greater amounts of nitrite;
      3. Animals dosed with nitrate or nitrite alone have no increased incidence of cancer.

3. Exposure Assessment
   a. Most of the exposure occurs in the diet (solid food, not water)
      1. A previous NAS report had concluded that for 99% of the U.S. population, about 97% of exposure comes from food in the diet;
      2. Certain vegetables are very high in nitrates;
      3. Vegetarian diets have been shown to be very high in nitrates; total nitrate exposure exceeds that of population drinking water contaminated with nitrates;
         b. Endogenous nitrate production accounts for ~50% of total nitrate “load;”

4. Risk Characterization
a. The current standard is based on epidemiological studies published by Walton in 1951 (Survey of literature relating to infant methemoglobinemia due to nitrate contaminated water, American Journal of Public Health 41:986-996).

1. There is no safety factor in the current MCL; i.e., on a concentration basis, the NOEL is 10 mg NO$_3$-N/L;

b. While the absence of a safety factor might seem alarming, bear in mind that the MCL was set based on human epidemiological data (i.e., we know what concentrations may be associated with methemoglobinemia) and the incidence of methemoglobinemia is very rare; for example, Muchoveg and Rechcigl (1995) showed the following table of incidences:

<table>
<thead>
<tr>
<th>Country (Date)</th>
<th>Cases</th>
<th>NO$_3$ Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U. S. (1945)</td>
<td>2</td>
<td>388/619</td>
</tr>
<tr>
<td>U. S. (1980)</td>
<td>1</td>
<td>1200</td>
</tr>
<tr>
<td>U. S. (1982)</td>
<td>1</td>
<td>545</td>
</tr>
<tr>
<td>U. S. (1987)</td>
<td>1</td>
<td>665</td>
</tr>
<tr>
<td>U. K. (1951)</td>
<td>2</td>
<td>200</td>
</tr>
<tr>
<td>U. K. (1985)</td>
<td>14</td>
<td>&gt;100</td>
</tr>
<tr>
<td>Hungary (1985)</td>
<td>95 &amp; 1258</td>
<td>40-100 &amp; &gt;100</td>
</tr>
<tr>
<td>Denmark (1985)</td>
<td>1</td>
<td>200</td>
</tr>
</tbody>
</table>

5. Recent Developments
a. In the NAS report, they noted that bacterial infection could be a causal factor for methemoglobinemia;

b. In fact, during the 1980's a number of clinical studies were published indicating that methemoglobinemia might be more related to bacterial infection rather than nitrate consumption (evidence most recently reviewed by Avery, A. A. 1999. Infantile methemoglobinemia: Reexamining the role of drinking water nitrates. Environ. Health Perspectives 107:583-586)

1. It has been shown that nitrate and nitrite are produced endogenously.
2. Infection can increase the rate of endogenous nitrate/nitrite production.
3. Thus, infants having bacterial infection may be at greater risk of developing methemoglobinemia through increases in endogenous nitrate/nitrite production.
4. If this hypothesis holds water, than all the monitoring for nitrate to protect infant health may be dollars down the drain.
5. If this hypothesis is correct, then maybe we should be monitoring for bacterial contamination.

a. The WA Dept. of Health has stated its position that nitrate monitoring is predictive of bacterial contamination. However, studies monitoring nitrate and bacteria together show that the correlation may be poor.

b. For example, in a Canadian study, 34-four percent of wells had more than the maximum acceptable number of coliform bacteria, 14% contained nitrate-N concentrations above 10 ppm (10 mg/L), and 7% were contaminated with both bacteria and nitrate. See next graph. (Rudolph, D. L, D. A. J. Barry, and M. J. Goss. 1998. Contamination in Ontario farmstead domestic wells and its association with agriculture: 2. Results from multilevel monitoring well installations. J. Contaminant Hydrology 32:295-311)
1. Compared to a 1954 study, the percentage of wells with nitrate contamination (i.e., >10 ppm) was about the same but the percentage with bacterial contamination had increased. The only point source indicator correlate was the distance of the well to a feedlot or cattle exercise area (inverse correlation; more contamination, the closer the point source). Well construction type was also significantly correlated with contamination.

**III. Ecotoxicological Concerns-Nitrogen Species**

A. **Ammonia** is very toxic to aquatic organisms; (Moore, J. W., 1991, *Inorganic Contaminants of Surface Water*, Springer-Verlag, New York)
   1. 96-h LC50’s typically range from 0.1 - 0.5 mg/L;
   2. More tolerant species exhibit LC50’s of 1 - 3 mg/L
   3. Possible sources include cattle feedlot runoff; spillage from waste treatment lagoons
   4. Under resting conditions, the LC50 for ammonia toxicity to fish was 207 mg/L; but under stress of swimming, the LC50 was lowered to ~32 mg/L (Wicks, B. J., R. Joensen, Q. Tang, and D. G. Randall. 2002. Swimming and ammonia toxicity in salmonids: the effect of sub lethal ammonia exposure on the swimming performance of coho salmon and the acute toxicity of ammonia in swimming and resting rainbow trout. *Aquatic Toxicology* 59:55-69.)

B. **Nitrate**: acute and chronic toxicity has been tested using aquatic invertebrate neonates, (*Ceriodaphnia dubia* and *Daphnia magna*) and fish larvae (*fathead minnow, Pimephales promelas*) (Scott, G. and R. L. Crunkilton. 2000. Acute and chronic toxicity of nitrate to fathead minnows (*Pimephales promelas*), *Ceriodaphnia dubia*, and *Daphnia magna*. *Environ. Toxicol. Chem.* 19(12):2918-2922)

**Acute Toxicity of nitrate (expressed as NO$_3$-N mg/L) to neonate aquatic invertebrates and larval fish**

<table>
<thead>
<tr>
<th>Species</th>
<th>Test 1</th>
<th>Test 2</th>
<th>Test 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LC50 (95% CI)</td>
<td>LC50 (95% CI)</td>
<td>LC50 (95% CI)</td>
</tr>
<tr>
<td><em>Ceriodaphnia dubia</em></td>
<td>374 (300-448)</td>
<td>374 (300-499)</td>
<td></td>
</tr>
<tr>
<td><em>Daphnia magna</em></td>
<td>323 (198-469)</td>
<td>453 (299-659)</td>
<td>611 (455-820)</td>
</tr>
<tr>
<td><em>Pimephales promelas</em></td>
<td>1,010 (877-1,143)</td>
<td>1,607 (1,492-1,723)</td>
<td>1,406 (1,236-1,577)</td>
</tr>
</tbody>
</table>
Chronic Toxicity of Nitrate (expressed as mg/L NO₃-N) to aquatic invertebrates and fish

<table>
<thead>
<tr>
<th>Organism (endpoint)</th>
<th>NOEC</th>
<th>LOEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceriodaphnia dubia (no. neonates per female)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Test 1</td>
<td>7.1</td>
<td>14.1</td>
</tr>
<tr>
<td>Test 2</td>
<td>56.5</td>
<td>113</td>
</tr>
<tr>
<td>Test 3</td>
<td>7.1</td>
<td>14.1</td>
</tr>
<tr>
<td>Test 4</td>
<td>17.9</td>
<td>35.9</td>
</tr>
<tr>
<td>Test 5</td>
<td>17.9</td>
<td>35.9</td>
</tr>
<tr>
<td>Daphnia magna (no. neonates per female)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Test 1</td>
<td>358</td>
<td>717</td>
</tr>
<tr>
<td>Test 2</td>
<td>358</td>
<td>717</td>
</tr>
<tr>
<td>Pimephales promelas</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Larvae (&lt;24 h through 7 d posthatch), 7 days total exposure</td>
<td>358</td>
<td>717</td>
</tr>
<tr>
<td>Embryos &amp; larvae (through 7 d posthatch, 11 days exposure)</td>
<td>348</td>
<td>717</td>
</tr>
<tr>
<td>Breeding adults &amp; offspring (through 7 d posthatch, 18+ days total exposure)</td>
<td>--</td>
<td>&gt;1,434</td>
</tr>
</tbody>
</table>

C. Experiments with frogs exposed to up to 200 µg/L atrazine and 30 mg/L nitrate showed no significant effect on development rate, percent metamorphosis, time to metamorphosis, percent survival, mass at metamorphosis, or hematocrit. (Allran, J. W. and W. H. Karasov. 2000. Effects of atrazine and nitrate on northern leopard frog (Rana pipiens) larvae exposed in the laboratory from posthatch through metamorphosis. Environ. Toxicol. Chem. 19(11):2850-2855.)
1. Nitrate did slow the growth of larvae but the effect was not considered biologically relevant considering the natural variation of growth rate in the environment.

D. Tadpoles were exposed to concentrations of nitrate up to 1000 mg/L;
1. No effects on development were observed
2. However, ammonia and nitrite might be the toxic compounds of concern (for ex., Johansson, M., K. Rasanen, and J. Merila. 2001. Comparison of nitrate tolerance between different populations of the common frog, Rana temporaria. Aquatic Toxicology 54:1-14.)
Effect of sodium nitrate (top) and ammonium nitrate (bottom) on survival of common from (Rana temporaria) (from Johansson et al. 2001).

E. Aquatic Hypoxic Zones—the Gulf of Mexico Case (much of the information taken from Goolsby 2000, Nitrogen in the Mississippi Basin—Estimating Sources and Predicting Flux to the Gulf of Mexico; USGS Fact Sheet 135-00, December 2000)

1. Each year in the Gulf of Mexico, a hypoxic zone develops off the coast Louisiana and southeastern Texas (a.k.a., the Louisiana-Texas shelf of the Gulf of Mexico).
   a. Hypoxia generally occurs when the dissolved oxygen concentrations are less than 2 mg/L
   b. Hypoxia causes stress or death in bottom-dwelling organisms that can not leave the low oxygenated zone.

2. The midsummer extent of the hypoxic zone has at least doubled in area since it was first systematically mapped in 1985.
   a. The largest hypoxic zone occurred in the summer of 1999 @ 20,000 km², but in 2000, the zone shrunk to about 4,400 km² during a droughty year (one of the smallest sizes measured).
   b. The intensification in use of mineralized nitrogen fertilizer in the Corn Belt, has been hypothesized as a major cause of the increase in extent of the hypoxic zone.

3. The hypoxic zone arises annually because of the influx of warmer (relative to the Gulf) freshwater from the Mississippi River basin and the influx of organic matter (that will eventually cause the consumption of oxygen).
   a. The influx of warmer comparatively less dense freshwater causes stratification in the Gulf, where the water is cooler and more dense (i.e., it is saltwater).
   b. Nutrients from the MS River stimulate the production of algae in the Gulf surface.
      1. When the organic material from the algae and other organisms settles to the bottom, it is decomposed by bacteria that consume the available oxygen.
2. Stratification blocks the replenishment of oxygen from the surface, and hypoxia develops.
3. Hypoxia may persist until late fall when stratification breaks up because of reduced freshwater inputs, cooler temperatures, and mixing by storms.

Mississippi River Basin drainage and location of midsummer hypoxic zone. Note that the highest N fertilizer use is in the Midwestern states of Iowa, Illinois, Indiana (western part), and Minnesota (southern part)

Areal extent of Gulf of Mexico hypoxic zone.
Nitrate loading in tributary rivers has increased since the early 1900’s.

The flux of nitrate has also gone up since 1955, the beginning of the intensification of the use of mineralized fertilizers in the Corn Belt. However, note that the flux is tied to streamflow, which means that it is going to be much higher during wet years than during dry years. Because the increase in nitrogen fertilizer has actually stabilized in the Corn Belt since the 1980’s, any relation to the hypoxic zone is due to increase flux because of increases in streamflow (i.e., precipitation leading to runoff and increased subsurface drainage) than due to increased uses of N fertilizer.
Sources of nitrogen inputs to the Mississippi River Basin. Note the soil mineralization processes (of native and added nitrogen) contributes the most inputs, but fertilizer nitrogen increased to comparable levels by 1980.

IV. Future Projections for Nitrogen Use & Deposition
A. The modern increase in nitrogen fixation and mobilization by fertilization and combustion has raised concerns that increasing emissions and thus deposition of N oxides and NH$_4$-N will have adverse ecological and/or human health consequences.
   1. We’ve discussed some of the modern human health and ecological issues, but are we still on a trend of increased deposition?
1. In the above graph from Frink et al. (1999), note that the upward swing in world use tonnage in 1994 is probably due to the previous years (1993) occurrence of flooding over widespread areas of the U.S. Midwest. Thus, a lot of nitrogen was “washed” out of the soils and was thus added as extra fertilizer the following year.
   a. Perhaps more importantly, however, is that the rate in change of use has slowed significantly for both the U.S. and the World.
   b. The rate of change is very close to zero, discounting the 1994 rise in use in the U.S.

C. Is there any evidence that total nitrogen deposition (N from fertilizer use as well as from combustion processes) is increasing still?
   1. An analysis of available bulk deposition data from the northeastern U.S. and from other places in the world suggests that emissions are unlikely to increase further and probably have leveled off (Frink et al. 1999).

<table>
<thead>
<tr>
<th>Location</th>
<th>N, kg/ha</th>
<th>Years</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geneva, NY</td>
<td>7.4</td>
<td>1922-1928</td>
</tr>
<tr>
<td>Ithaca, NY</td>
<td>4.9</td>
<td>1918-1925</td>
</tr>
<tr>
<td>Mays Point, NY</td>
<td>6.4</td>
<td>1965-1979</td>
</tr>
<tr>
<td>Huntington Forest, NY</td>
<td>6.2</td>
<td>1980s</td>
</tr>
<tr>
<td>Hubbard Brook, NH</td>
<td>6.5</td>
<td>1972-1992</td>
</tr>
<tr>
<td>Flahult, Sweden</td>
<td>5.1</td>
<td>1909</td>
</tr>
<tr>
<td>Three Swedish stations</td>
<td>7.1</td>
<td>1996-1997</td>
</tr>
<tr>
<td>Rothamsted, U.K.</td>
<td>4.5</td>
<td>1888-1916</td>
</tr>
<tr>
<td>Rothamsted, U.K.</td>
<td>5.3</td>
<td>1955-1966</td>
</tr>
<tr>
<td>Woburn, U. K.</td>
<td>8.7</td>
<td>1987-1996</td>
</tr>
<tr>
<td>Groningen, Netherlands</td>
<td>6.7</td>
<td>1908-1910</td>
</tr>
<tr>
<td>Kollumerwaard, Netherlands</td>
<td>14.5</td>
<td>1994</td>
</tr>
</tbody>
</table>

2. If the 80 Tg (metric tons) of fertilizer N and 25 Tg NOx-N was converted into a global emission and dispersal (assuming 51 billion ha of earth surface), the deposition would only be on average 2.1 kg/ha (Frink et al. 1999)
   a. The fertilizer alone would cause a global deposition of only 1.6 kg/ha.
   b. Thus, the long-term prospects for increasing deposition of total nitrogen due to anthropogenic sources is for either falling or stable depositional fluxes.
   1. Given, that the efficiency of worldwide fertilizer use relative to crop production has rapidly improved, the percentage annual change in fertilizer use should continue to fall.

V. Nutrients as Contaminants--Phosphorus
   A. The phosphorus cycle is different from other biogeochemical cycles because there is no gaseous form, i.e., no flux to atmosphere;
   B. Phosphates, which are cationic, are very insoluble; only a small fraction occurs in solution (~0.1 - 1 ppm)
C. Most phosphorus is in inorganic form (minerals) or organically bound (30-50% of soil P in soil)

(From Rechcigl 1995)
D. Historical Trends in Use


1. Human intensification of the global phosphorus cycle (Smil 2000)

<table>
<thead>
<tr>
<th>Fluxes</th>
<th>Natural (Mt P/yr)</th>
<th>Preindustrial (1800) (Mt P/yr)</th>
<th>Recent (2000) (Mt P/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural fluxes intensified by human actions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Erosion</td>
<td>&gt;10</td>
<td>&gt;15</td>
<td>&gt;30</td>
</tr>
<tr>
<td>Wind</td>
<td>&lt;2</td>
<td>&lt;3</td>
<td>&gt;3</td>
</tr>
<tr>
<td>Water</td>
<td>&gt;8</td>
<td>&gt;12</td>
<td>&gt;27</td>
</tr>
<tr>
<td>River transport</td>
<td>&gt;7</td>
<td>&gt;9</td>
<td>&gt;22</td>
</tr>
<tr>
<td>Particulate P</td>
<td>&gt;6</td>
<td>&gt;8</td>
<td>&gt;20</td>
</tr>
<tr>
<td>Dissolved P</td>
<td>&gt;1</td>
<td>&lt;2</td>
<td>&gt;2</td>
</tr>
<tr>
<td>Biomass combustion</td>
<td>&lt;0.1</td>
<td>&lt;0.2</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>Anthropogenic fluxes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crop uptake</td>
<td>--</td>
<td>1</td>
<td>12</td>
</tr>
<tr>
<td>Animal wastes</td>
<td>--</td>
<td>&gt;1</td>
<td>&gt;15</td>
</tr>
<tr>
<td>Human wastes</td>
<td>--</td>
<td>0.5</td>
<td>3</td>
</tr>
<tr>
<td>Organic recycling</td>
<td>--</td>
<td>&lt;0.5</td>
<td>&gt;6</td>
</tr>
<tr>
<td>Inorganic fertilizers</td>
<td>--</td>
<td>--</td>
<td>15</td>
</tr>
</tbody>
</table>

E. Ecological Concerns:
1. Although an essential nutrient, when phosphates run off into aquatic systems (via sediment erosion), overloading of concentrations leads to algal blooms
   a. P may be a limiting factor in algal growth
b. Blooms lead to die-offs
   1. Bacterial decomposition of algal cells leads to oxygen depletion
   2. Eutrophication results

c. In the 1950’s and 1960’s, many detergents had phosphates added “to boost cleaning power”
   1. The most notable effect was the commencement of eutrophication of parts of Lake Erie
   2. Phosphates were banned and Lake Erie recovered