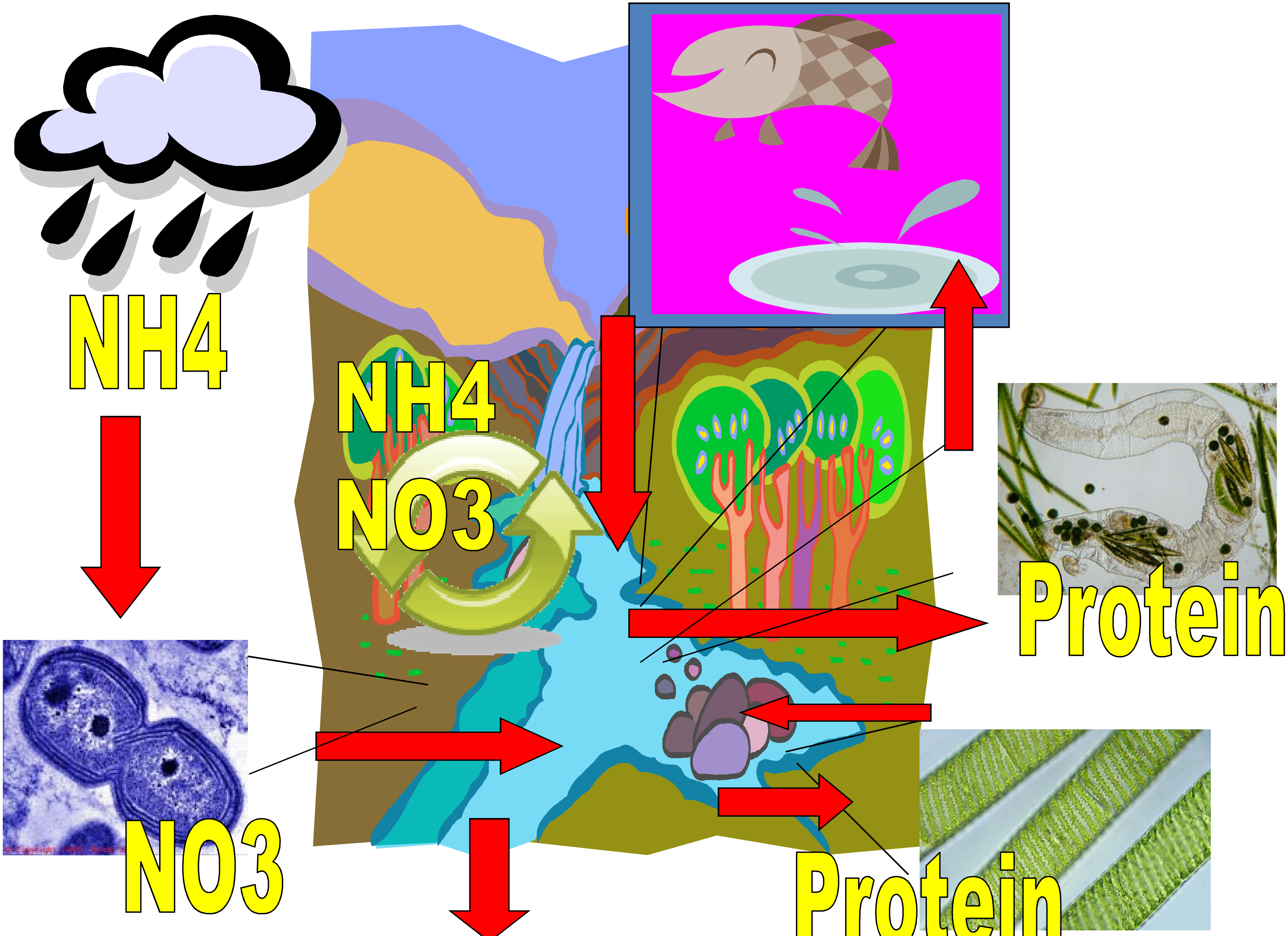
Cary Institute
of Ecosystem Studies

Nitrogen: Invisible, but Important!

Research & Education based on Ecosystem Ecology

Nitrogen K-W-L

KNOW	WANT TO KNOW	LEARNED

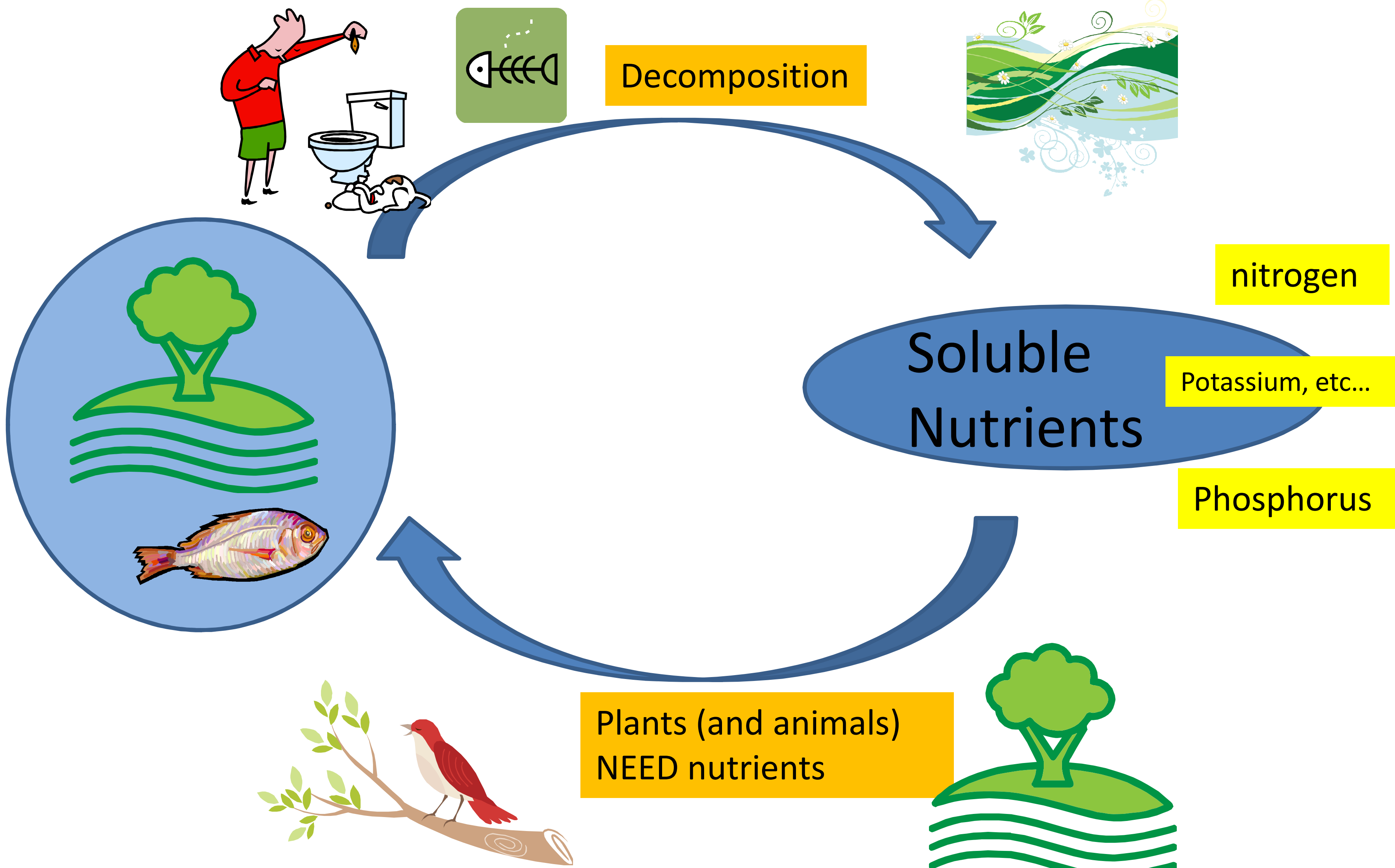

NH4
NH4
NO3
NO3
Protein
Protein

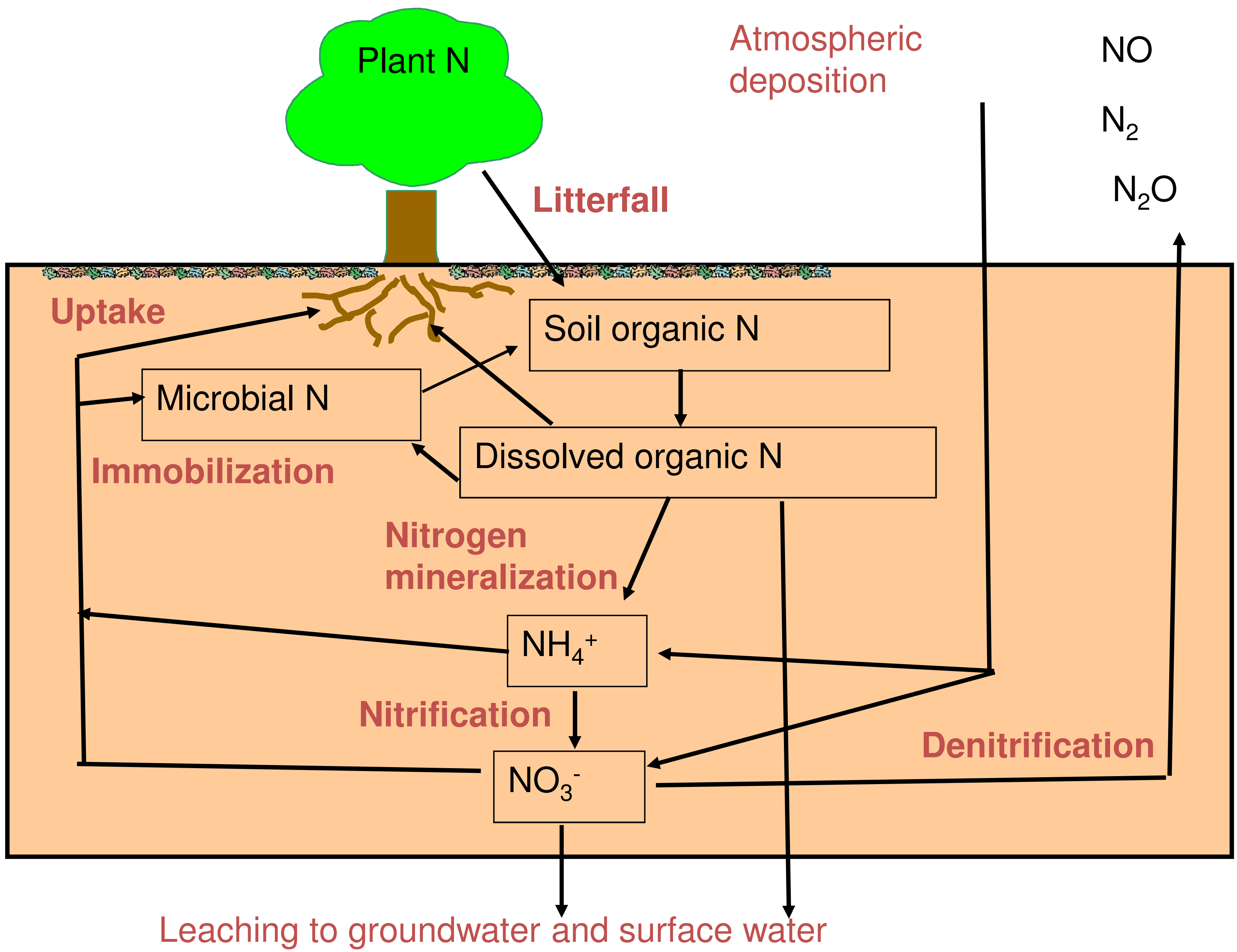
Why care about nitrogen?

We should care because it causes…

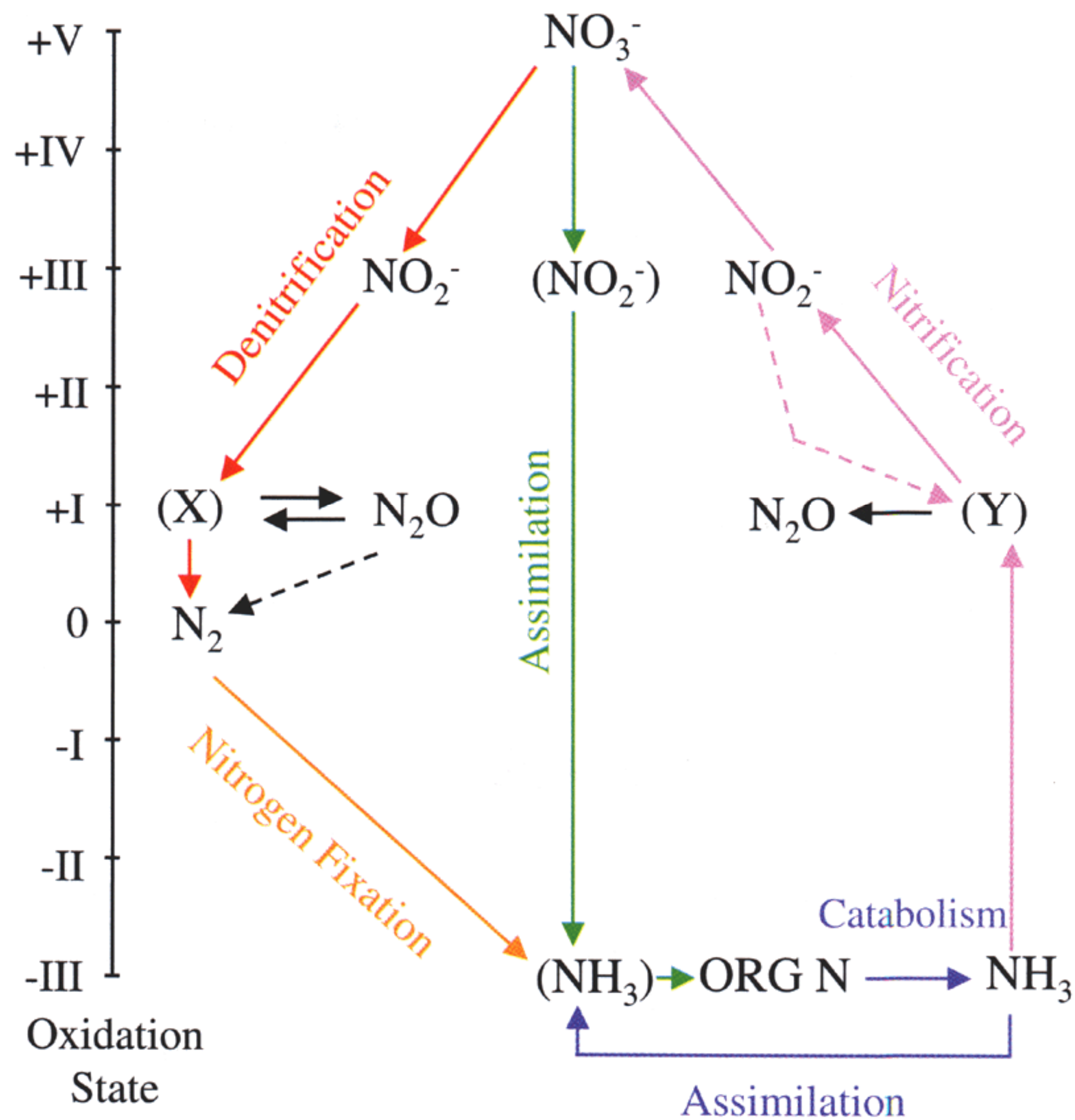
- Water pollution (eutrophication, dead zones)
- Acidic precipitation (rain, snow, fog)
- Climate change (nitrous oxide)
- Air pollution (nitric oxide=smog)
- Acidification of soils, reduction of biodiversity

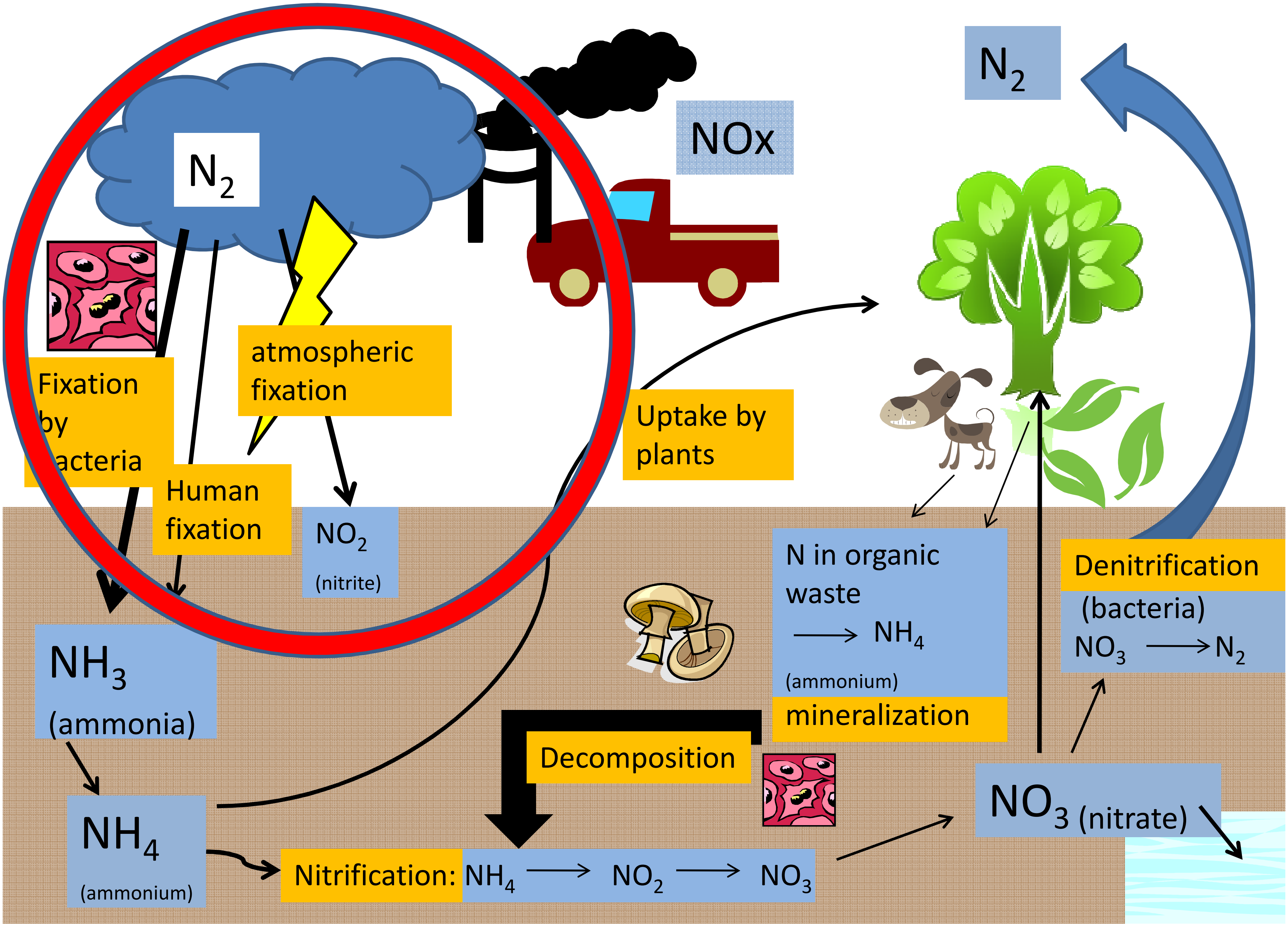
The basics…what IS a nutrient cycle?




Plant N
Atmospheric deposition
NO
N_2
N_2O
Litterfall
Uptake
Soil organic N
Microbial N
Dissolved organic N
Immobilization
Nitrogen mineralization
NH_4^+
Nitrification
Denitrification
NO_3^-
Leaching to groundwater and surface water

N TRANSFORMATIONS & REDOX





N_2
NOx
N_2
Fixation by bacteria
Human fixation
atmospheric fixation
NO_2 (nitrite)
Uptake by plants
N in organic waste → NH_4 (ammonium)
mineralization
Denitrification
(bacteria) NO_3 → N_2
NH_3 (ammonia)
NH_4 (ammonium)
Decomposition
NO_3 (nitrate)
Nitrification: NH_4 → NO_2 → NO_3

Part 1: Nitrogen Fixation

- The atmosphere is ~ 79% N gas
- BUT…it must be converted into ammonia (NH4) or nitrate (NO3) to be taken up by living things
- There is natural and human fixation of N2

    Natural: lightning, bacteria (root nodules, free-living in soil, cyanobacteria)

    Human: fertilizer manufacturing
- Humans have DOUBLED the amount of nitrogen available through the Haber-Bosch process (most fertilizer today is produced using methane as the H source)

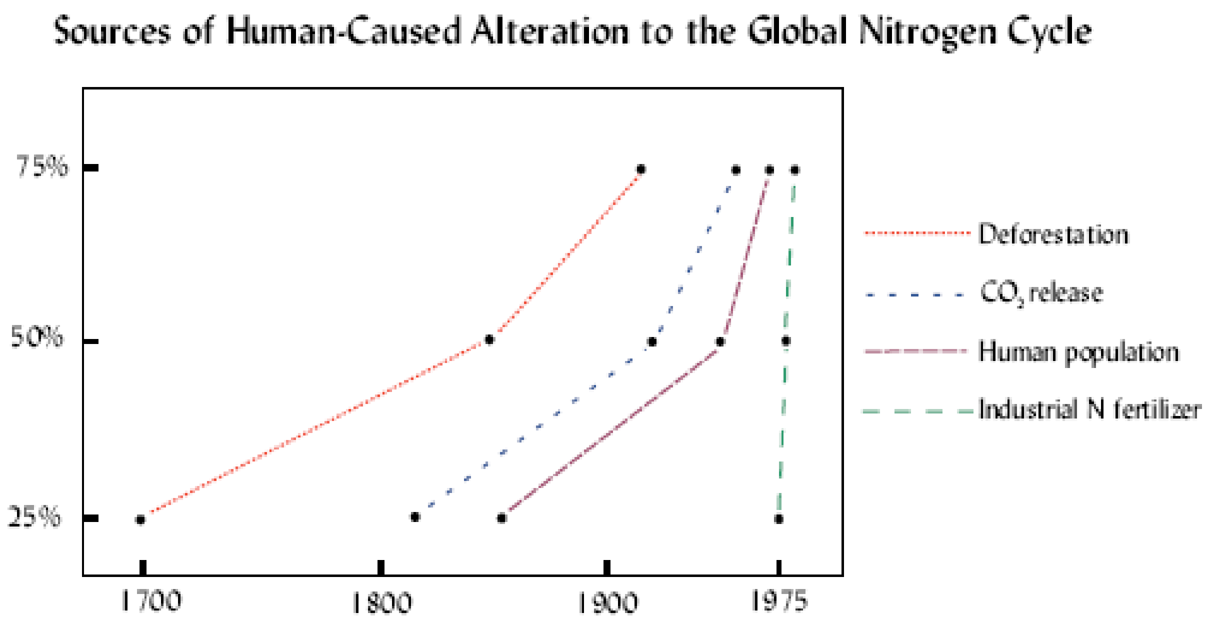
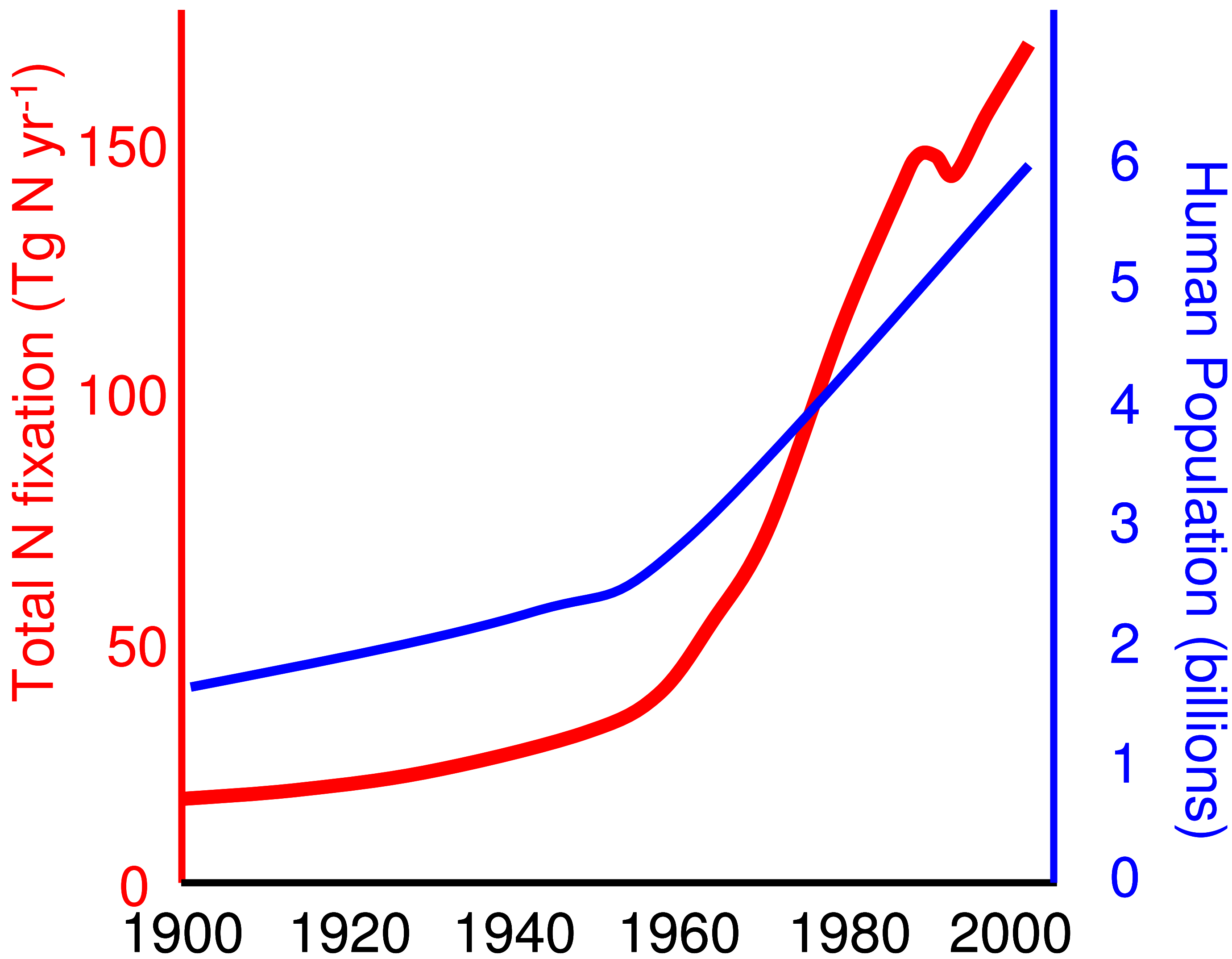


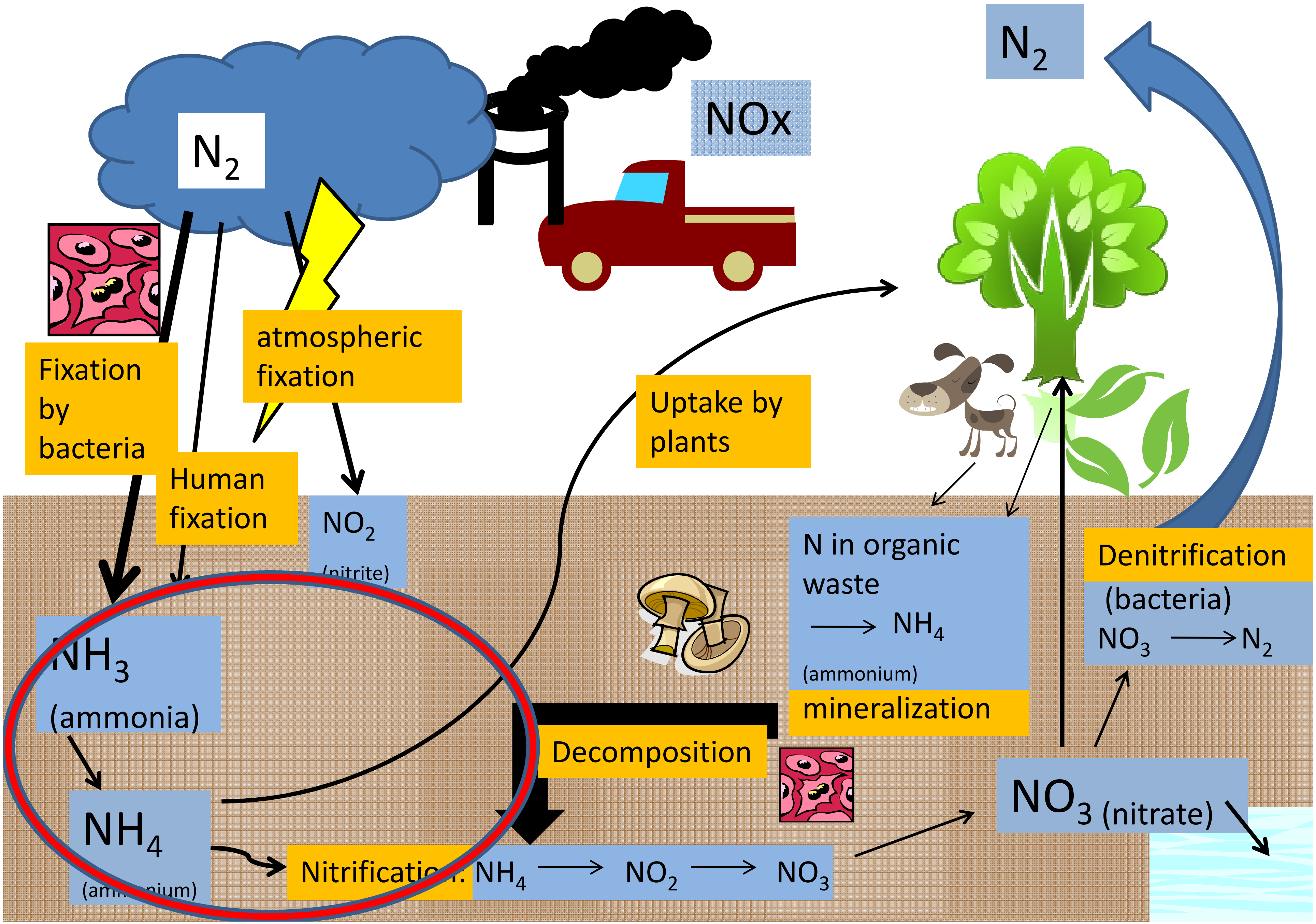
Figure 3-The pace of many human-caused global changes has increased starkly in modern history, but none so rapidly as industrial production of nitrogen fertilizer, which has grown exponentially since the 1940s. The chart shows the year which changes in human population growth, carbon dioxide release, deforestation, and fertilizer production had reached 25%, 50%, and 75% of the extent seen in the late 1980s. Revised from Kates et al. (1990).

People and Nitrogen



Where does all the extra N go?

- About 30% is transported as nitrate through waterways to the ocean (in the eastern US and Europe)
- The rest is removed through denitrification or stored in forests



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atmospheric fixation
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(nitrite)
Uptake by plants
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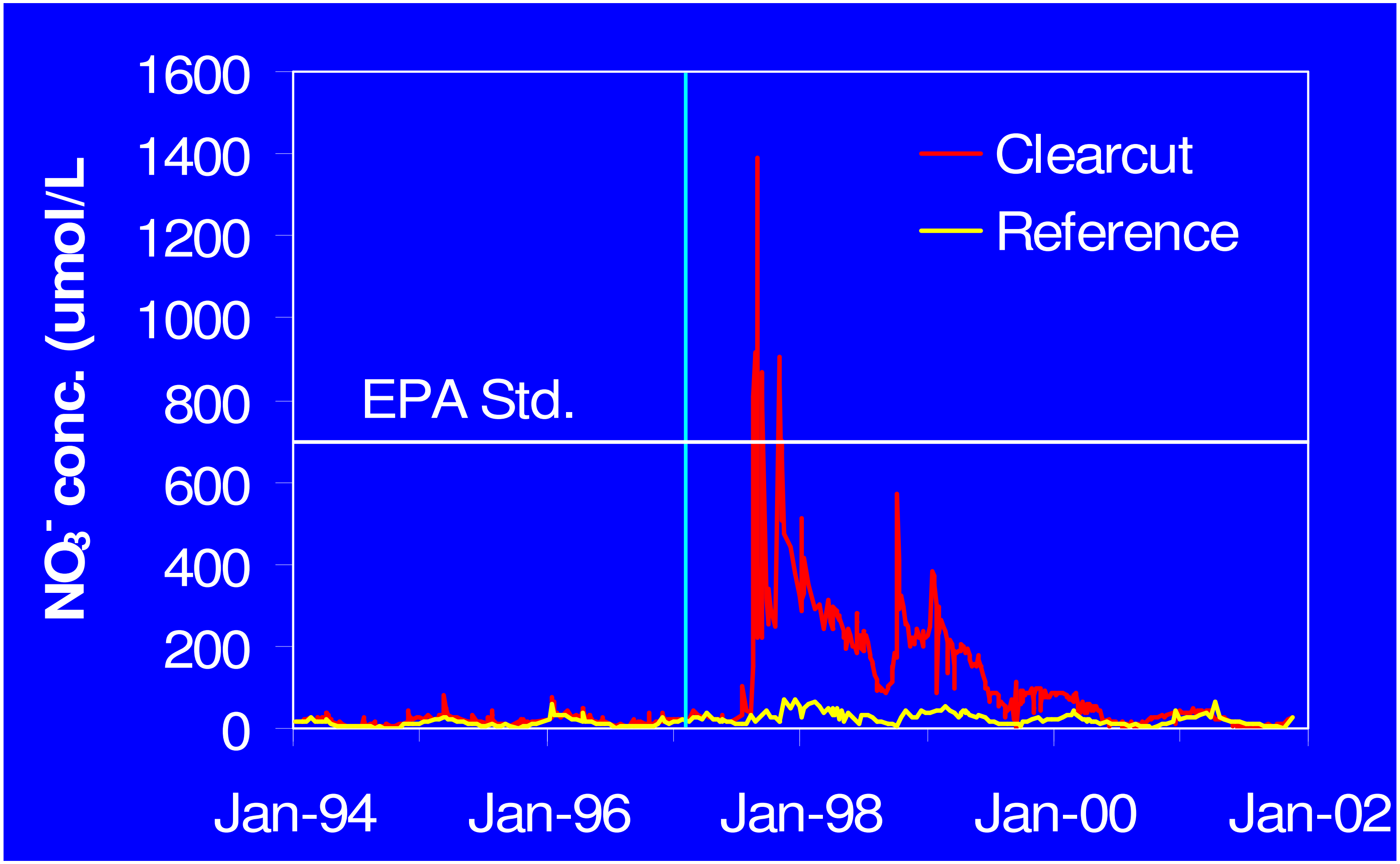
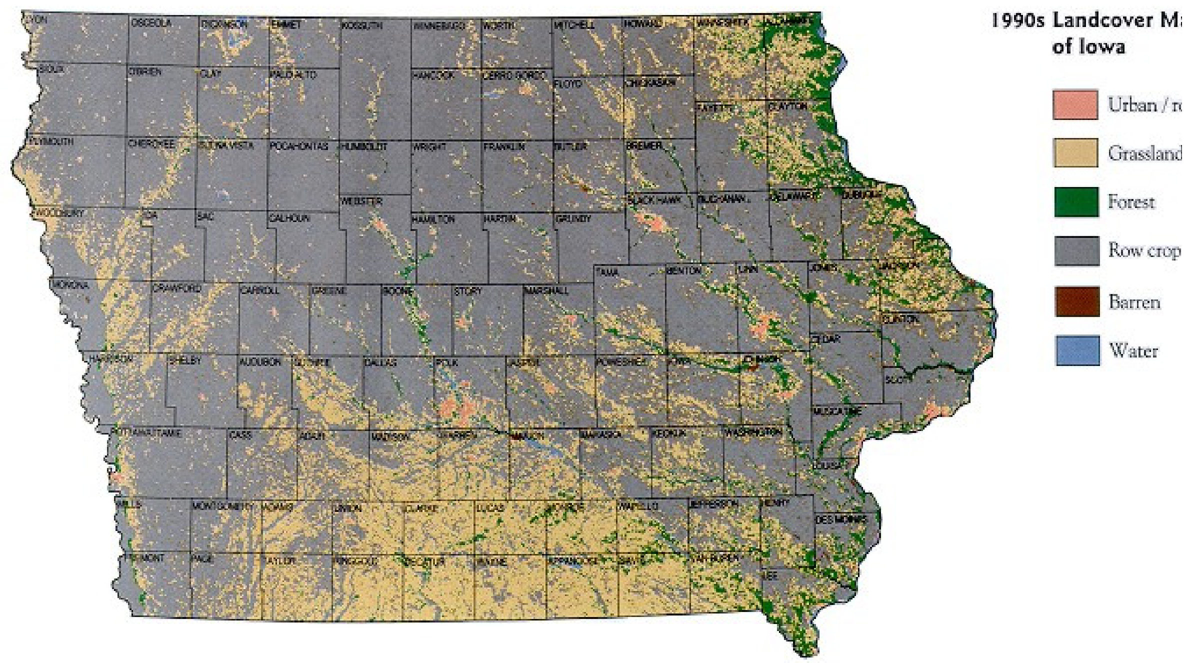
(ammonium)
mineralization
Denitrification
(bacteria)
$NO_3 \longrightarrow N_2$
NH_3
(ammonia)
NH_4
Decomposition
NO_3 (nitrate)
Nitrification: $NH_4 \longrightarrow NO_2 \longrightarrow NO_3$

How does a clearcut forest affect nitrogen levels?

1997 Clearcut – Wildcat Mountain, Frost Valley YMCA

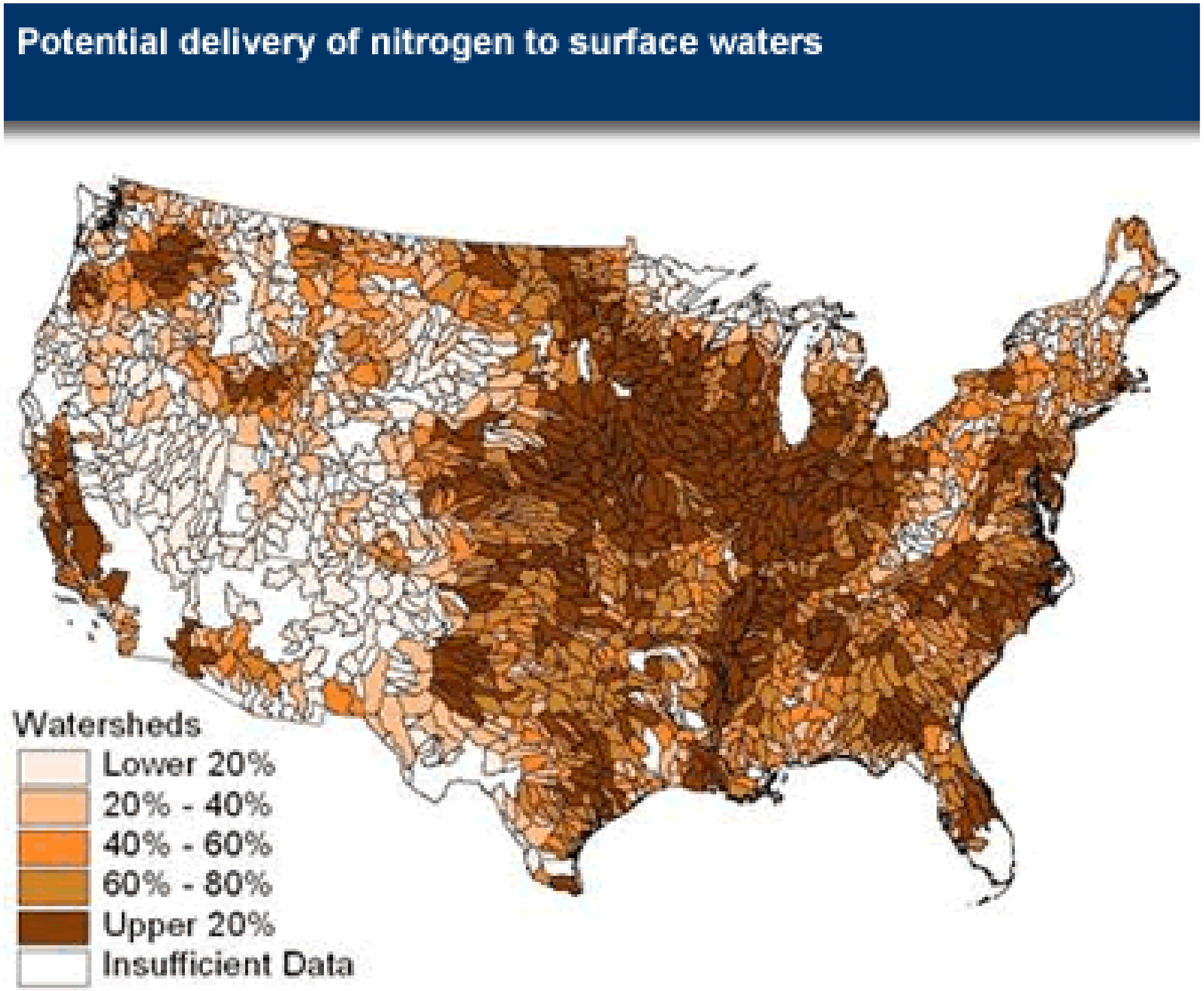
1997 Clearcut Results - Nitrate





Source: Compiled from Landsat Thematic Mapper satellite imagery, Iowa Dept. of Natural Resources.

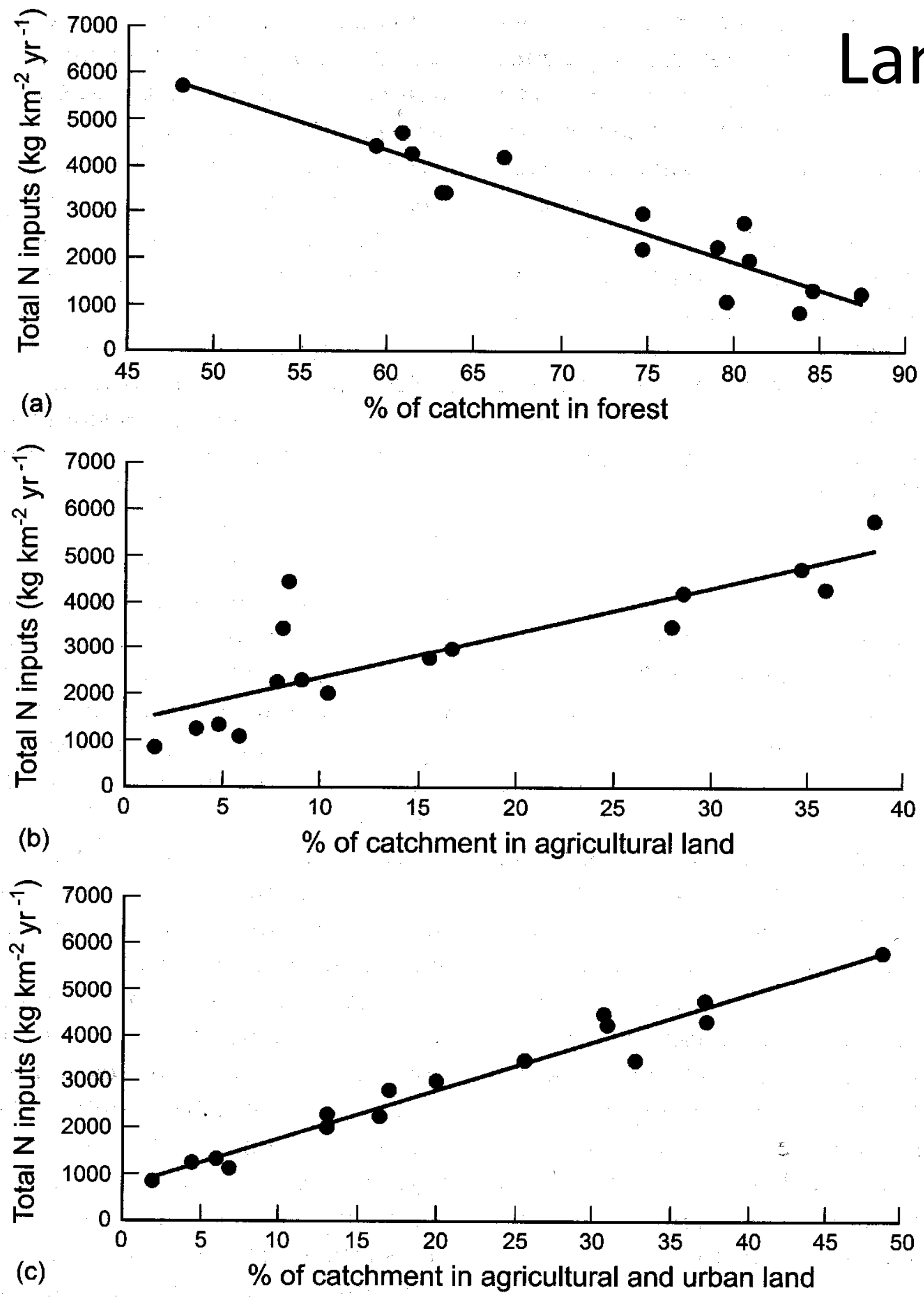
Fertilizer in the US



Note: The potential for cropland within a watershed to discharge nitrogen in surface water is determined by runoff factors (climate, distance from water, erosion) and nitrogen source factors (total inorganic and organic fertilizer applications), which are influenced by the economic choices farmers make.

Source: Economic Research Service, USDA. Nitrogen data from Association of American Plant Food Control Officials (1998) and Kellogg et al. (2000).

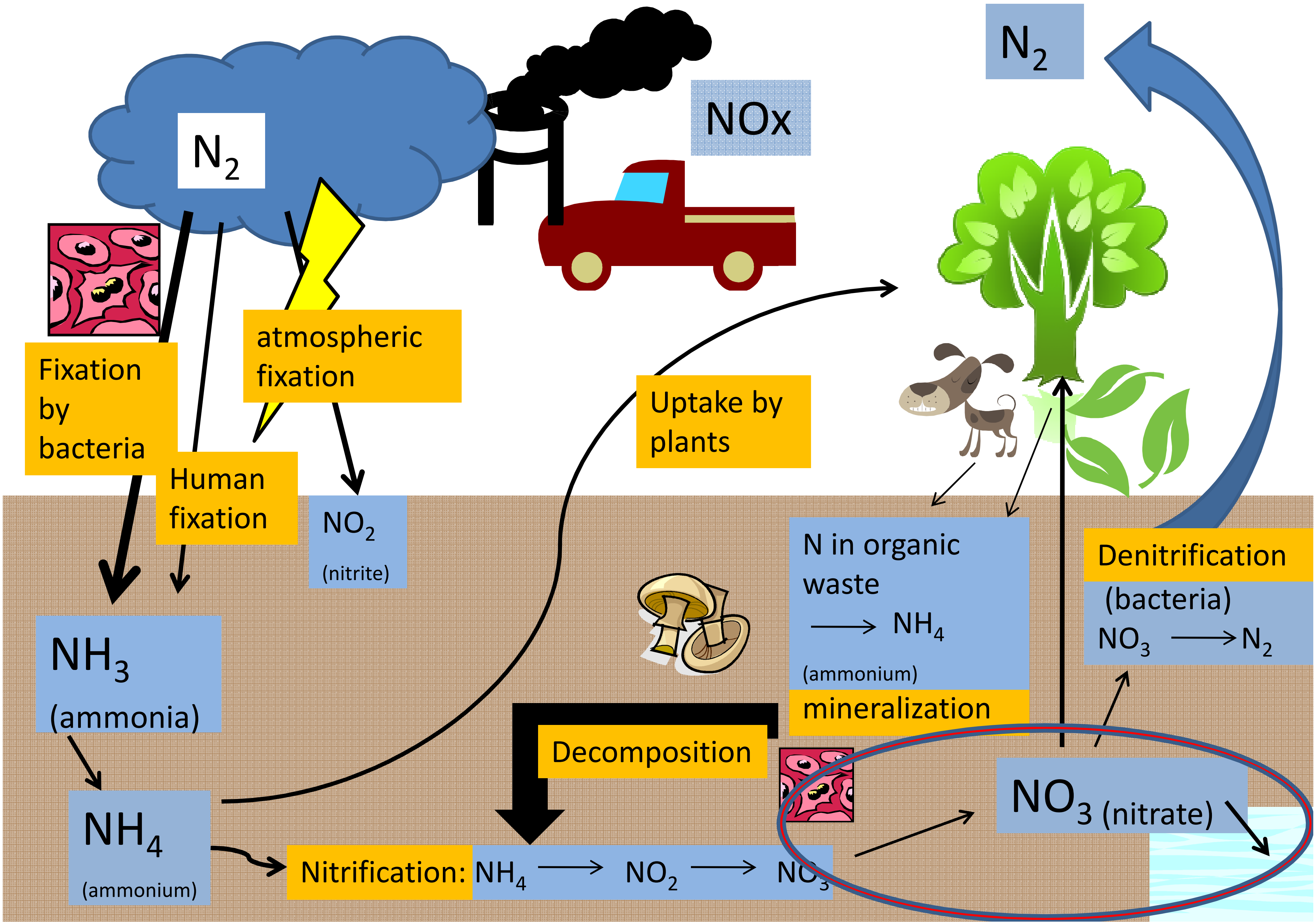
Land Use and N loading



More forests = less N

More ag lands = more N

More ag + urban = more N



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NO3 → N2
NH3
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NH4
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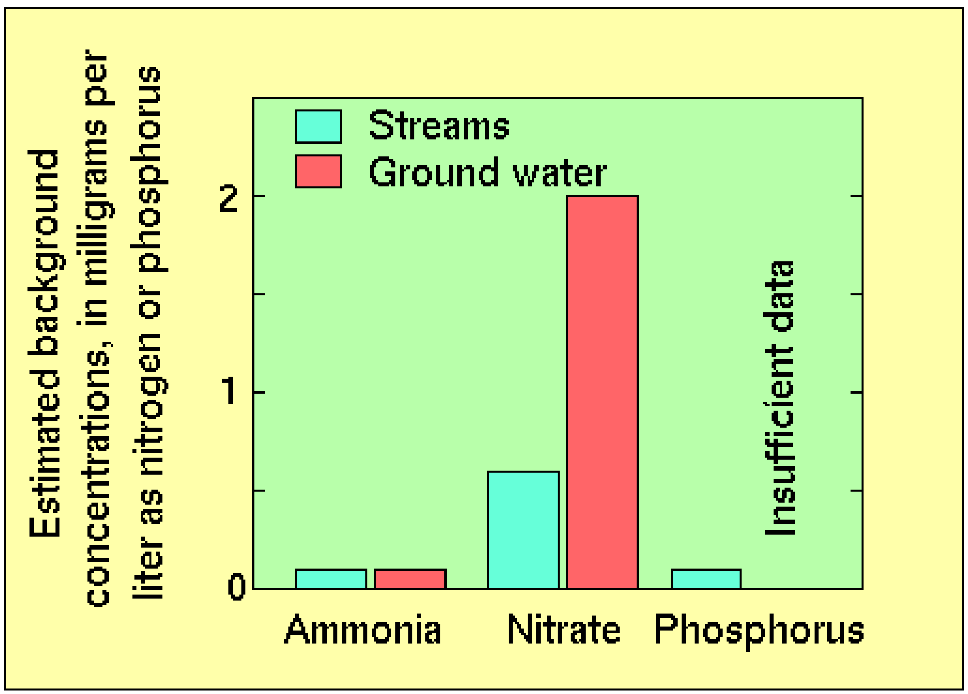
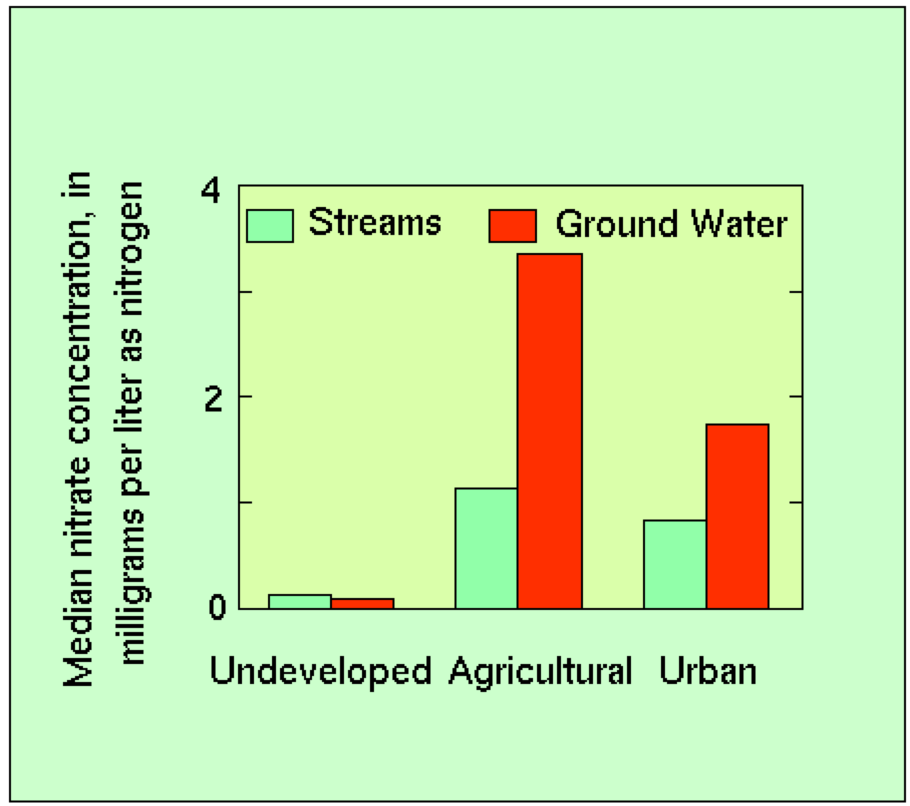
Nitrification: NH4 → NO2 → NO3
NO3 (nitrate)

Nitrate pollution of waterbodies

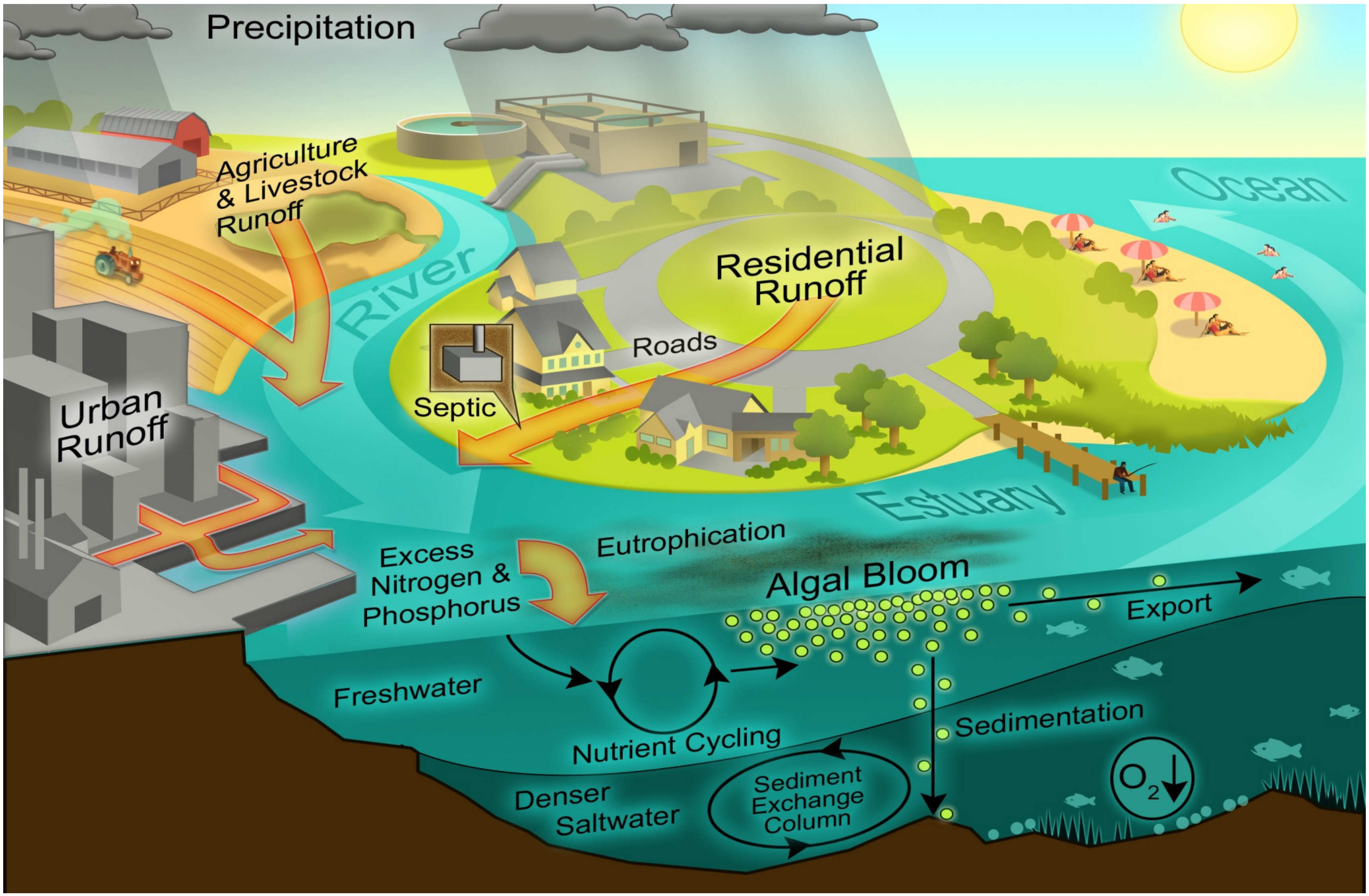
- NO_3^- pollution in groundwater is a serious problem in agricultural areas, including southern Michigan, and may one day threaten the sustainability of our agricultural systems
- Source: Mueller and Helsel (1996)





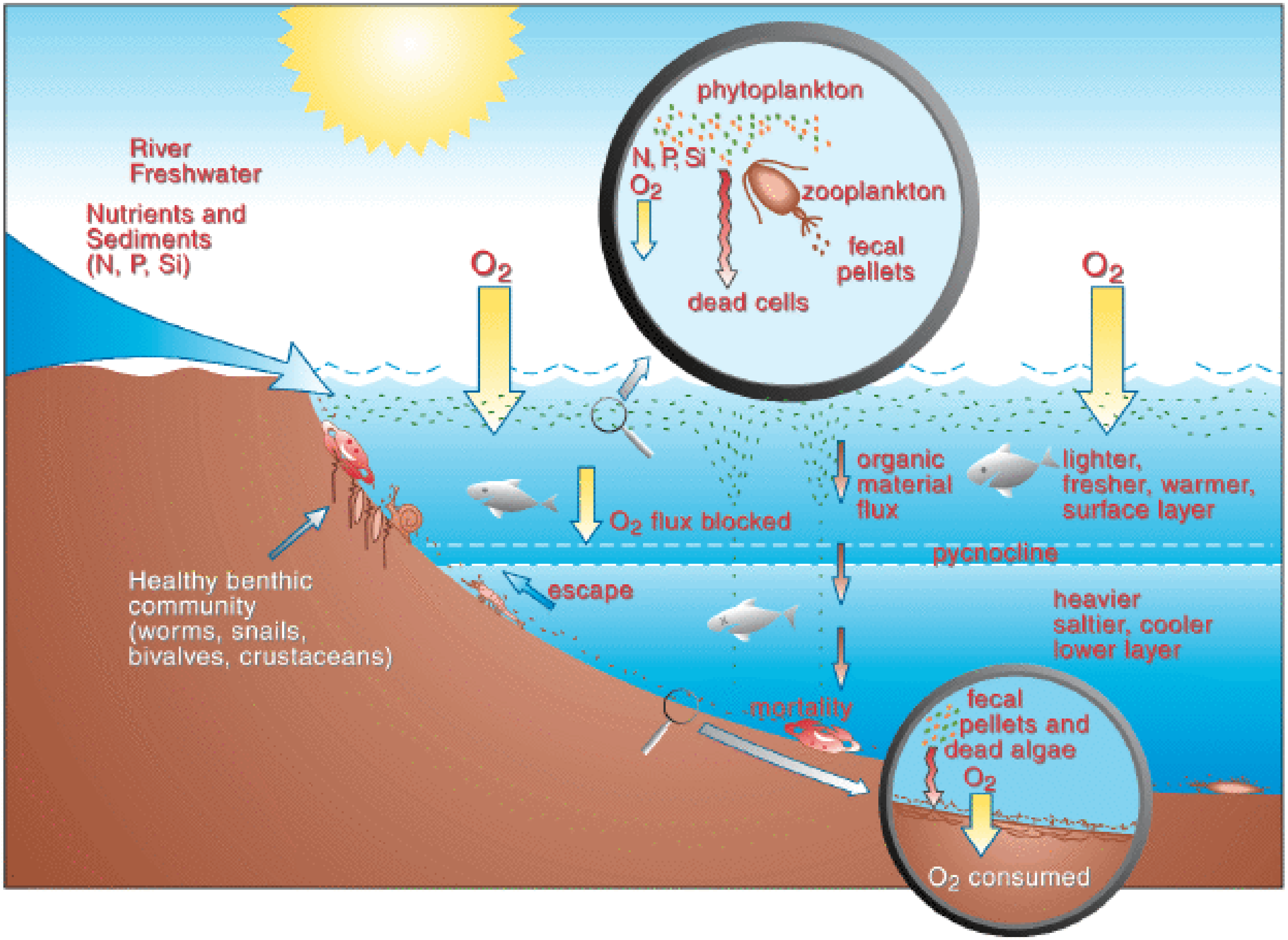
Excess N from humans

Eutrophication: excess nutrients stimulate plant growth (algal bloom); when these plants die, decomposers use up the available oxygen during decomposition

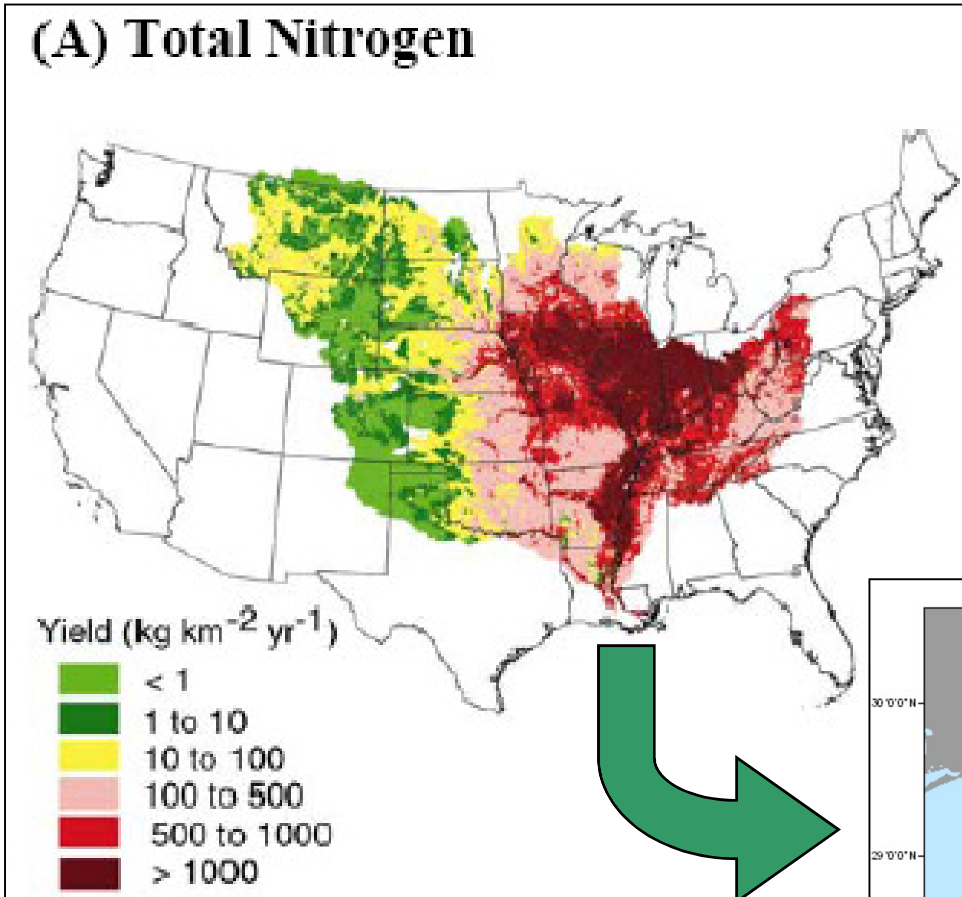


Precipitation
Agriculture & Livestock Runoff
River
Residential Runoff
Ocean
Roads
Septic
Urban Runoff
Estuary
Eutrophication
Excess Nitrogen & Phosphorus
Algal Bloom
Export
Freshwater
Nutrient Cycling
Sedimentation
Denser Saltwater
Sediment Exchange Column
O_2

Anatomy of Hypoxia



Excess N Loading



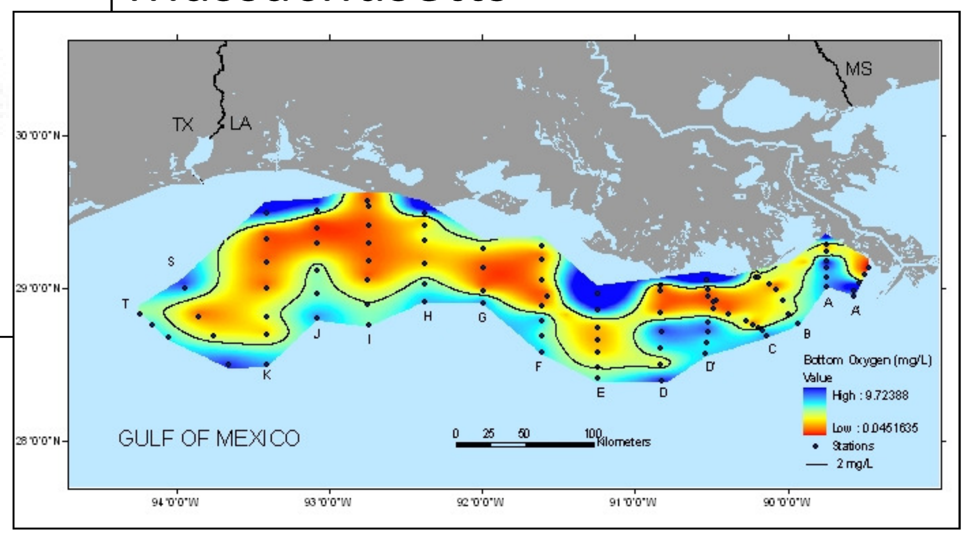
Alexander et al. 2008

"Dead Zones"

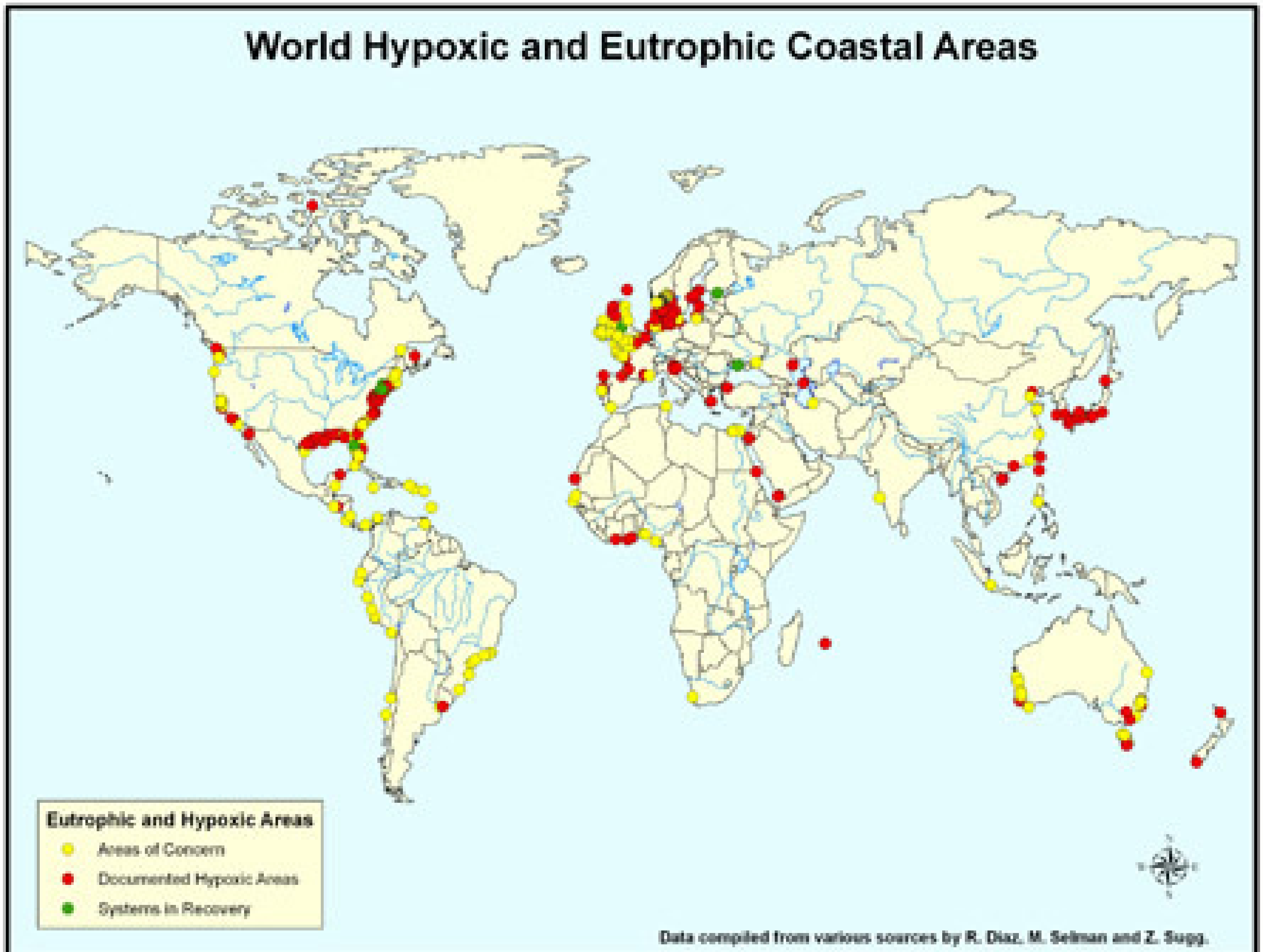
Impacts on commercial and recreational fisheries

Gulf of Mexico:

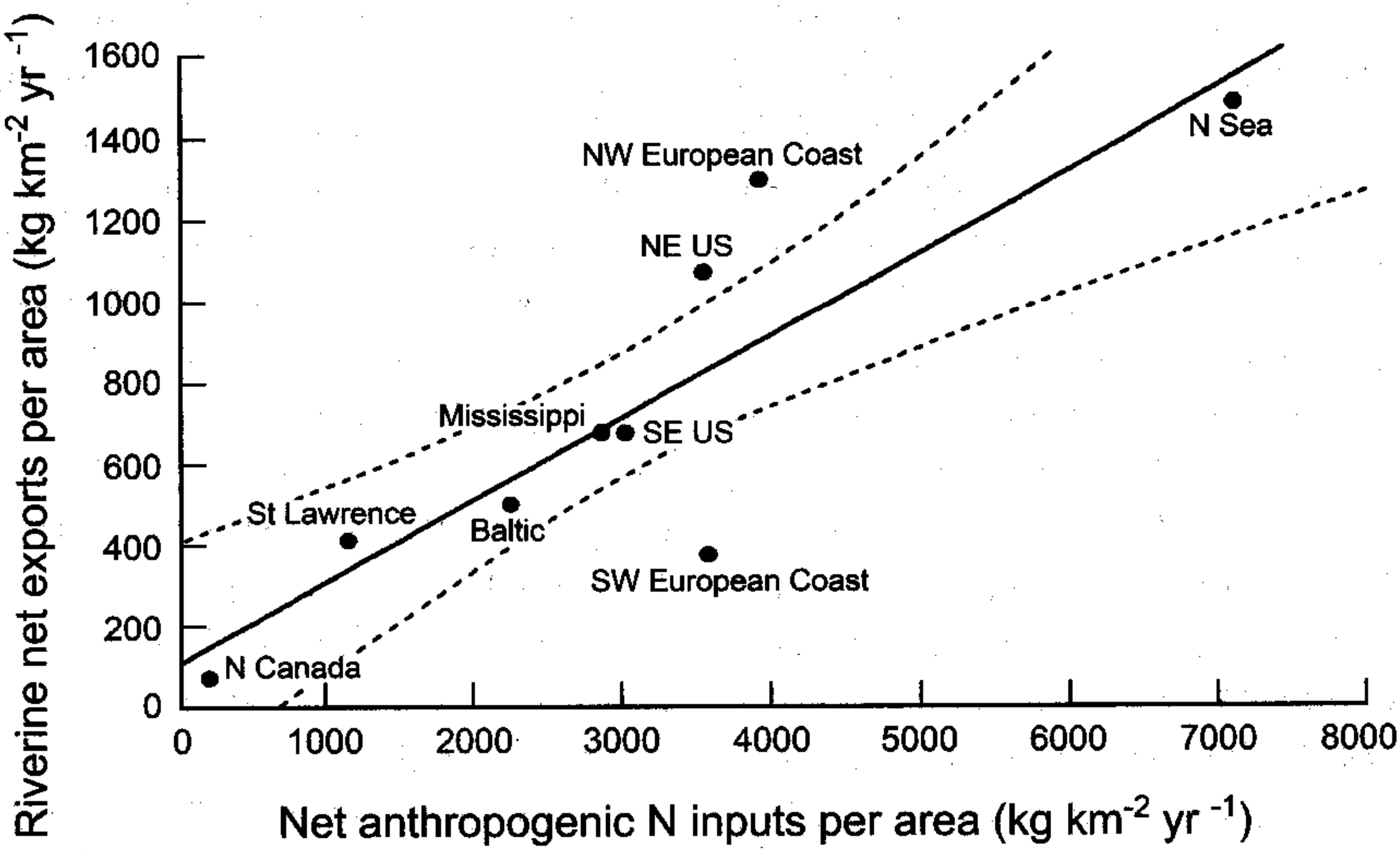
In 2007, area ~ size of Massachusetts



Rabalias et al. 2007: http://www.gulfhypoxia.net/shelfwide07/


World Hypoxic and Eutrophic Coastal Areas
Eutrophic and Hypoxic Areas
Areas of Concern
Documented Hypoxic Areas
Systems in Recovery
Data compiled from various sources by R. Diaz, M. Selman and Z. Sugg.

More human inputs = more river N



Nitrogen in the Hudson

Where does it come from?

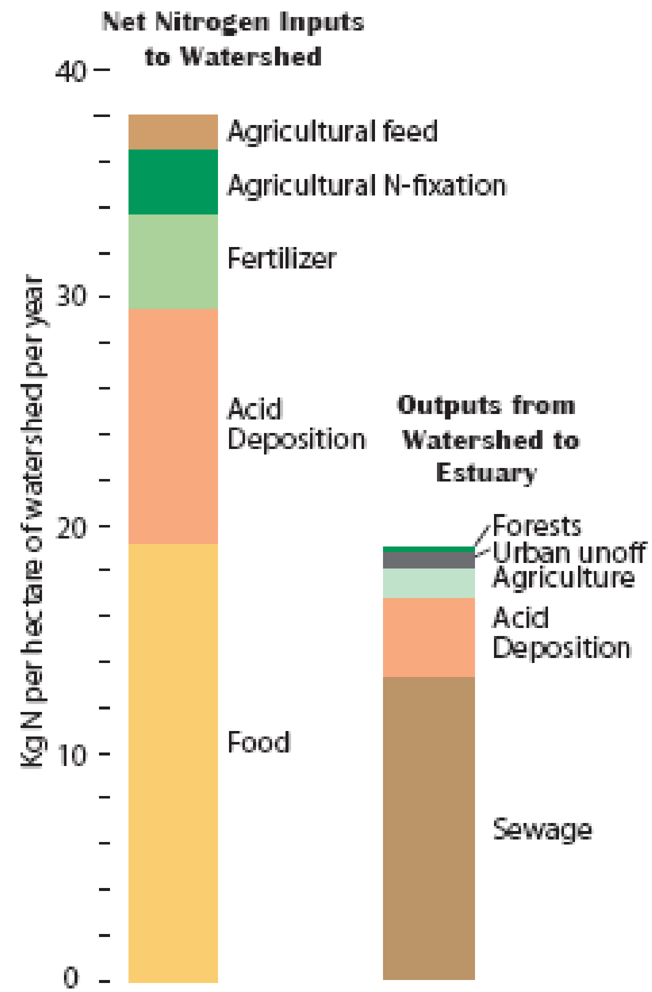
-human waste

-acid deposition

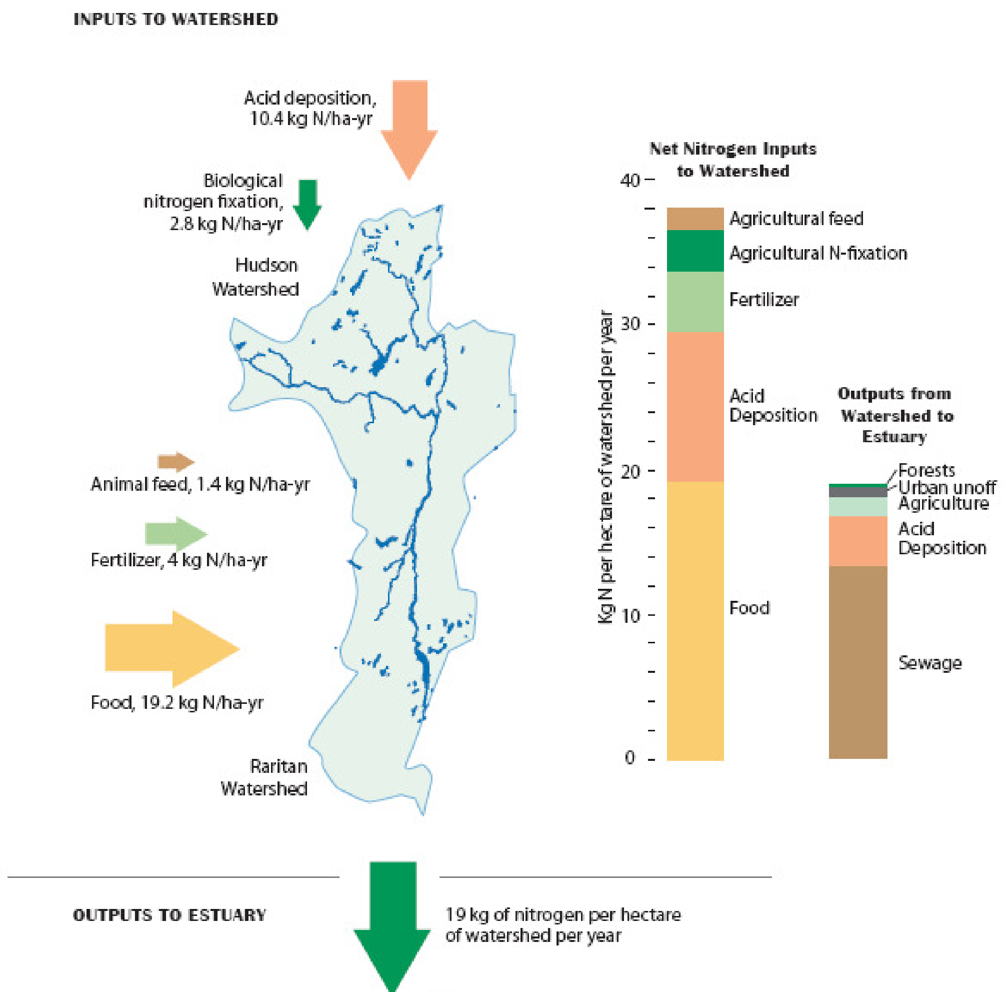
-fertilizer

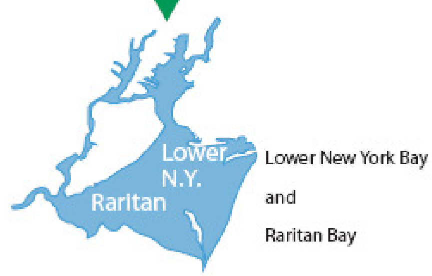
-agriculture: fixation and feed

Where does it go?



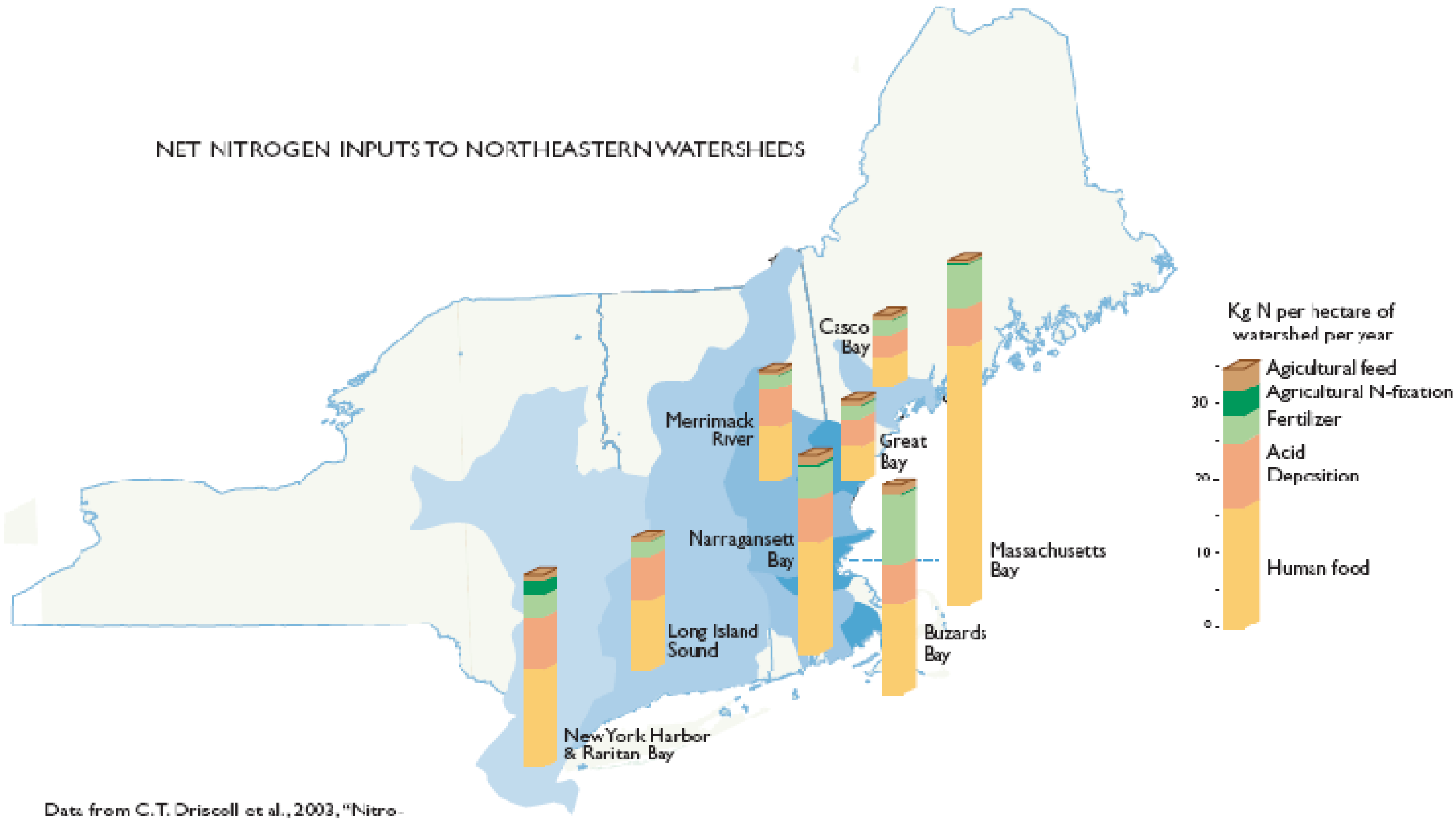
THE NITROGEN BALANCE OF THE HUDSON - WATERSHED





Data from C.T. Driscoll et al., 2003, "Nitrogen pollution in the northeastern United States: Sources, effects, and management options," Bioscience 53(4): 357-374. Pet foods and N-fixation in forests and wetlands are not included.

Nitrogen in local watersheds



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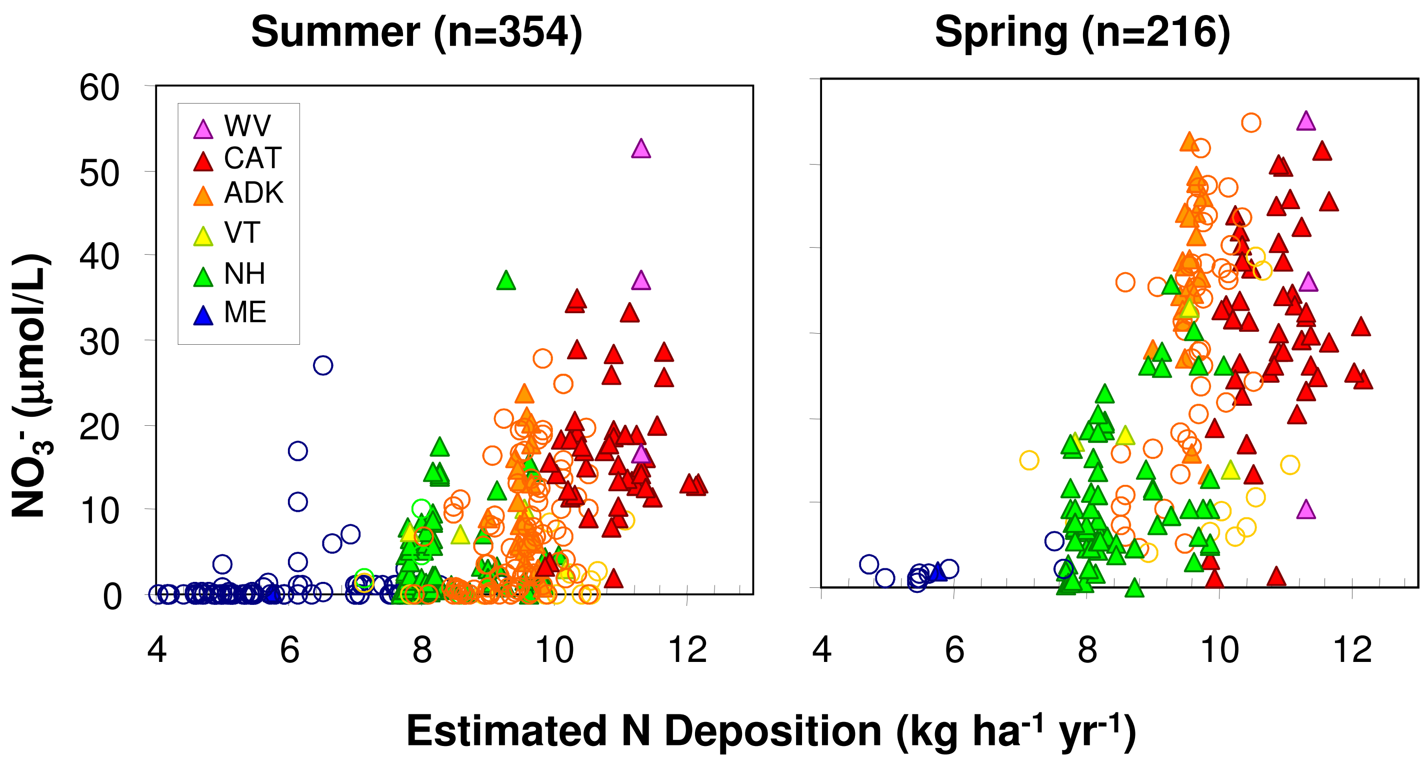
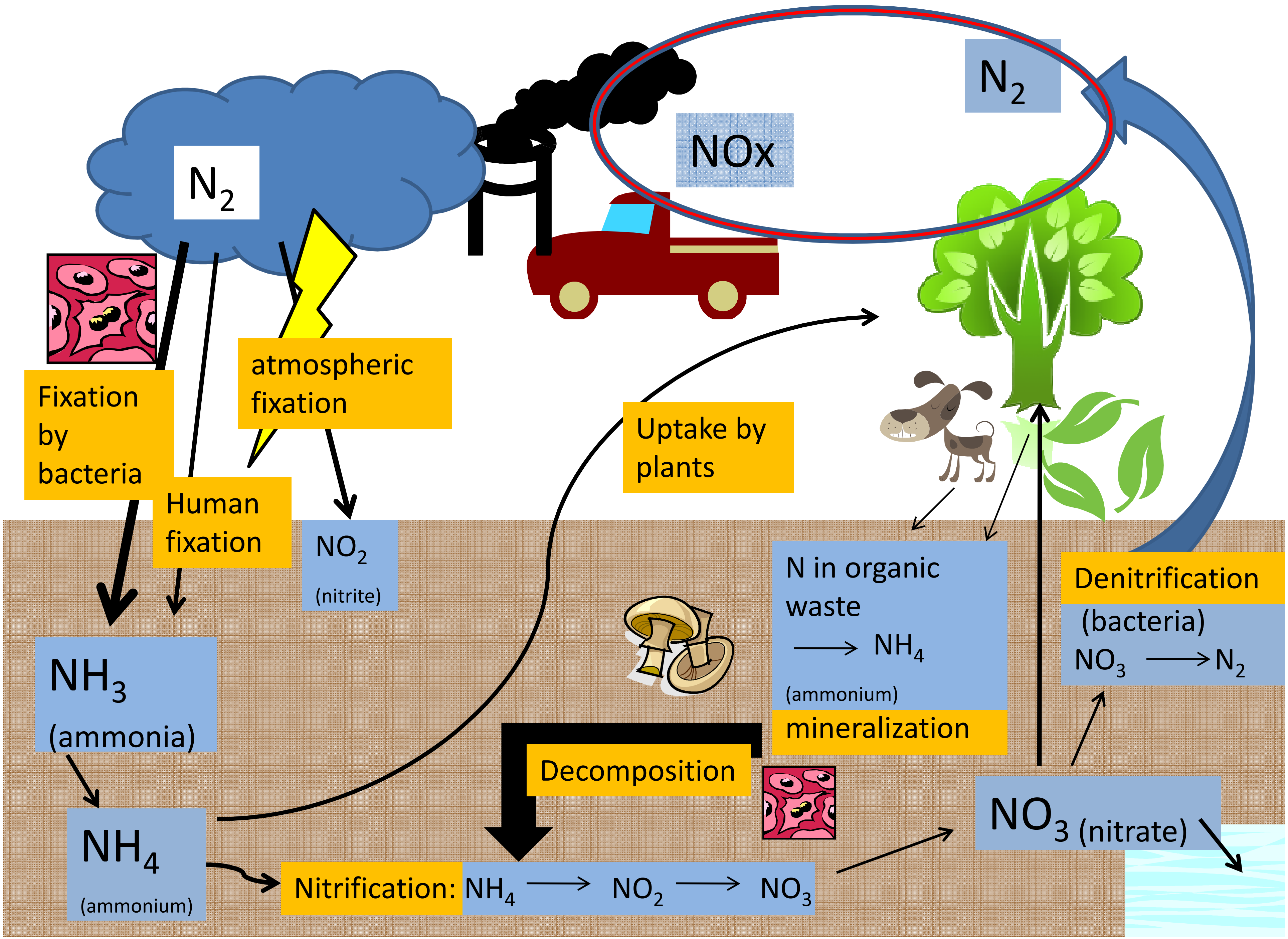
Surface Water Nitrate in Northeastern U.S.



From Aber et al *Bioscience* 2003



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Decomposition
Nitrification: NH4 → NO2 → NO3
NO3 (nitrate)

Nitrogen in the air

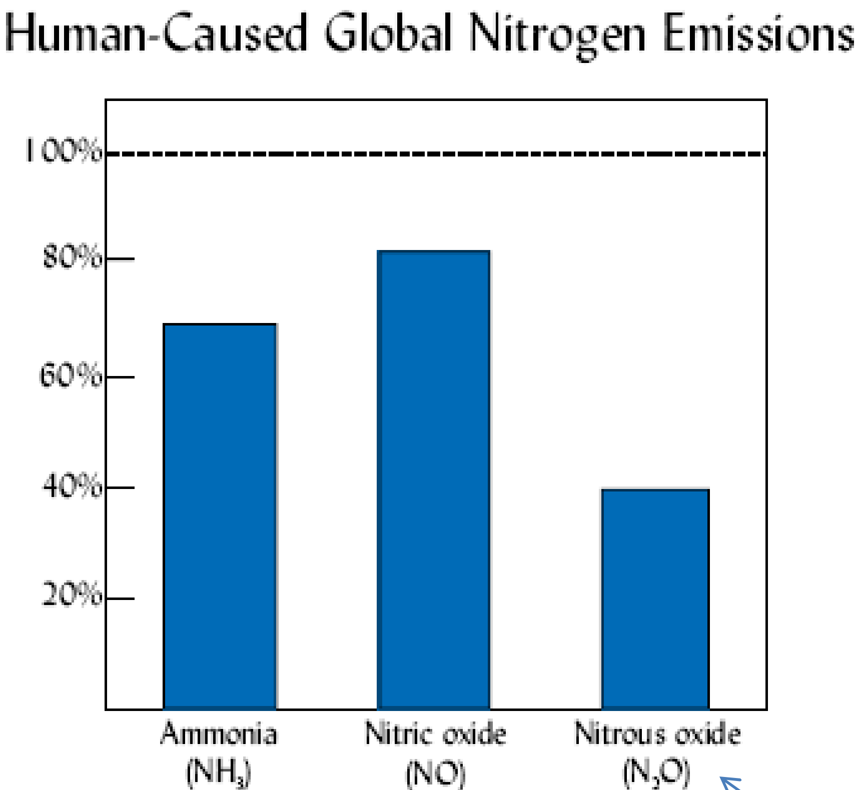


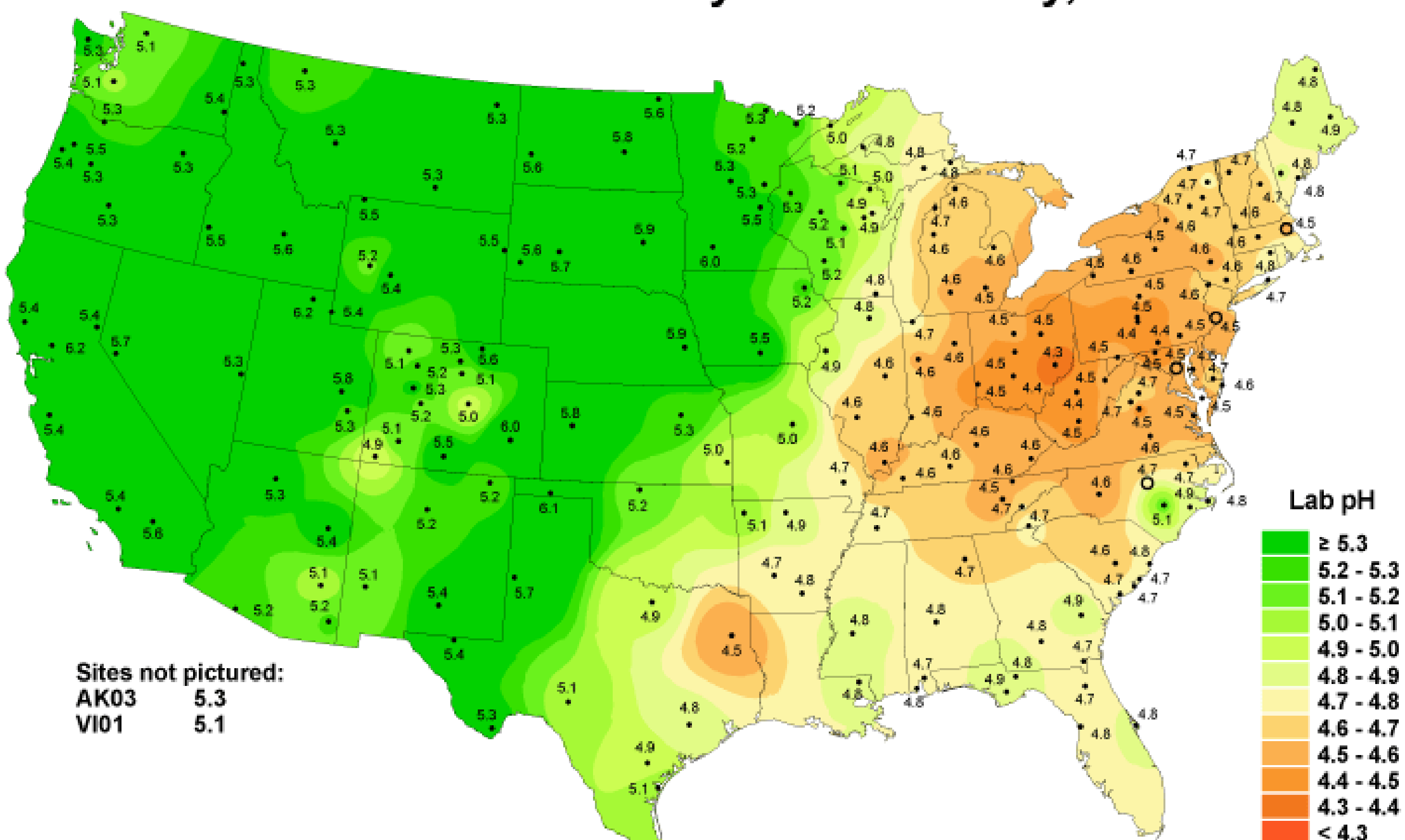
Figure 4-Human activities are responsible for a large proportion of the global emissions of nitrogen-containing trace gases, including 40% of the nitrous oxide, 80% or more of nitric oxide, and 70% of ammonia releases. The result is increasing atmospheric concentrations of the greenhouse gas nitrous oxide, of the nitrogen precursors of smog, and of biologically available nitrogen that falls from the atmosphere to fertilize ecosystems. Ammonia data are from Schlesinger and Hartley (1992), nitric oxide from Delmas et al. (in press), and nitrous oxide from Prather et al. (1995).

Greenhouse gas

Precursor to smog (ozone), acid rain

Acidic Deposition

Hydrogen ion concentration as pH from measurements made at the Central Analytical Laboratory, 2005



National Atmospheric Deposition Program/National Trends Network
http://nadp.sws.uiuc.edu

Increasing Greenhouse Gases

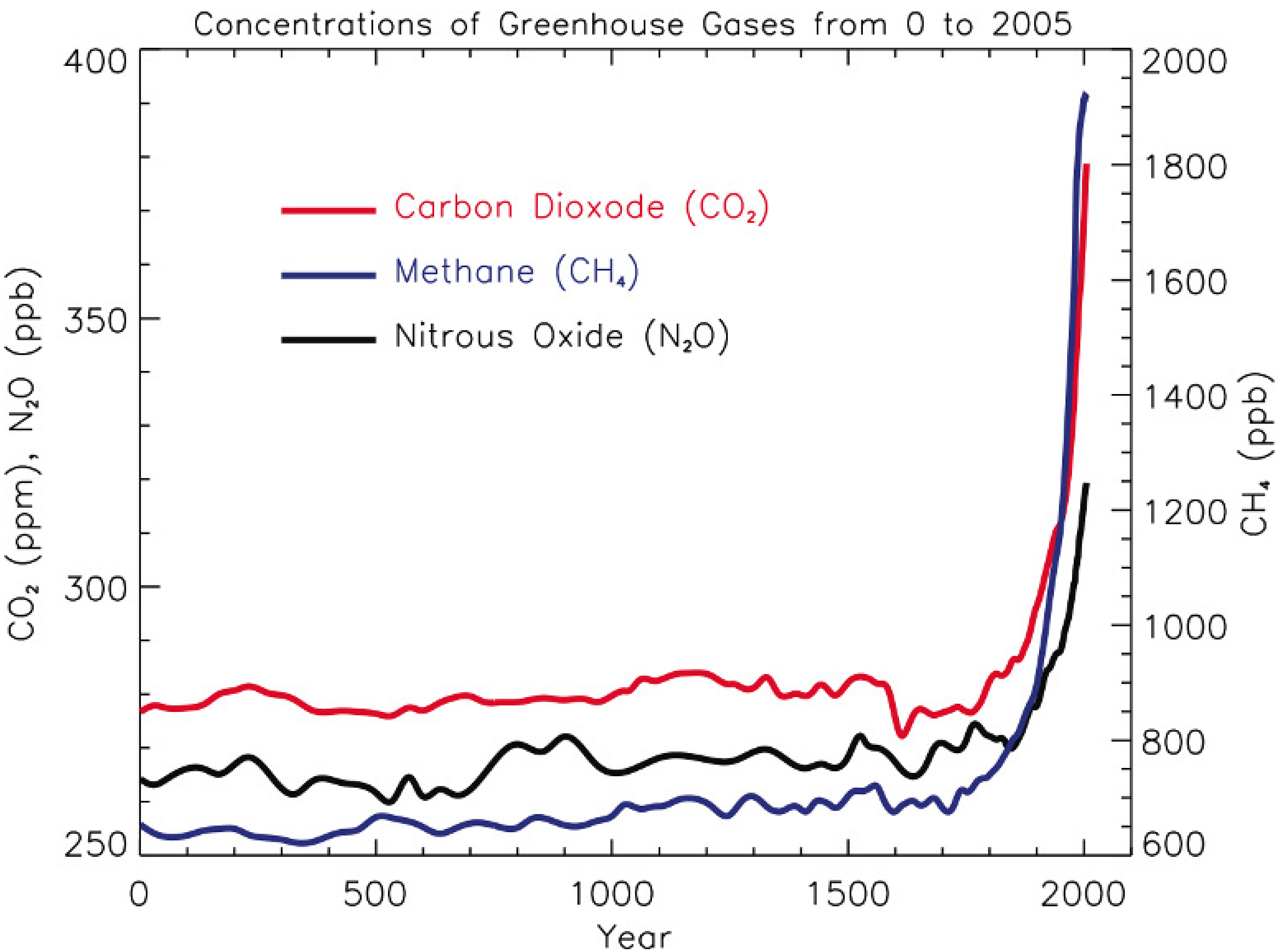


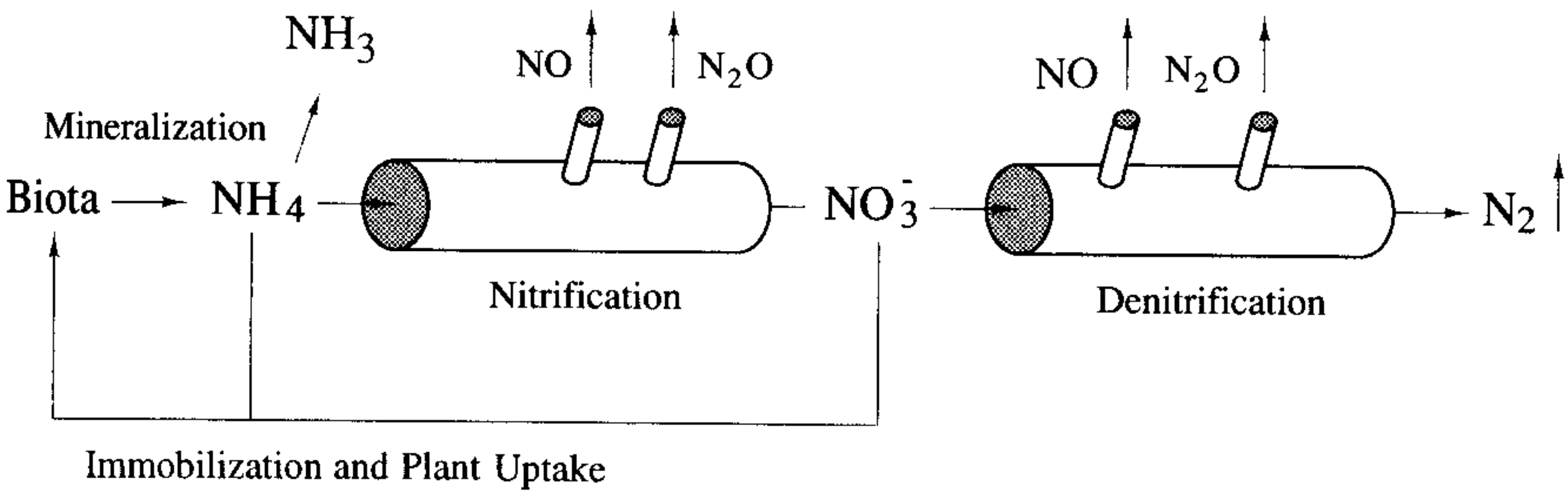
Table 16-1 Science: Major Greenhouse Gases from Human Activities

Greenhouse Gas	Human Sources	Average Time in the Troposphere	Relative Warming Potential (compared to CO_2)
Carbon dioxide (CO_2)	Fossil fuel burning, especially coal (70–75%), deforestation, and plant burning	100–120 years	1
Methane (CH_4)	Rice paddies, guts of cattle and termites, landfills, coal production, coal seams, and natural gas leaks from oil and gas production and pipelines	12–18 years	23
Nitrous oxide (N_2O)	Fossil fuel burning, fertilizers, livestock wastes, and nylon production	114–120 years	296
Chlorofluorocarbons (CFCs)*	Air conditioners, refrigerators, plastic foams	11–20 years (65–110 years in the stratosphere)	900–8,300
Hydrochloro-fluorocarbons (HCFCs)	Air conditioners, refrigerators, plastic foams	9–390	470–2,000
Hydrofluorocarbons (HFCs)	Air conditioners, refrigerators, plastic foams	15–390	130–12,700
Halons	Fire extinguishers	65	5,500
Carbon tetrachloride	Cleaning solvent	42	1,400

*CFC use is being phased out, but these compounds remain in the troposphere for 1–2 decades and then enter the stratosphere.

How does this happen? If denitrification means that NO3 – N2…

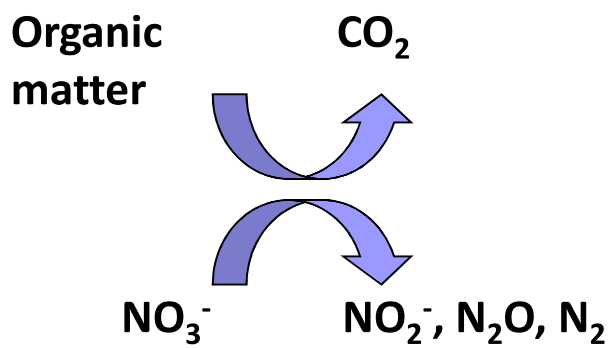
“Leaky pipe” analogy for N_2O production



- Recent studies have documented that other N transformations involving NO_3^- and NH_4^+, such as nitrification, can also produce N_2O
- This model (by M. Firestone) holds only generally and exceptions are well-known (Davidson et al. 2000)

Denitrification ($NO_3^- \Rightarrow N_2O \Rightarrow N_2$)

- A form of dissimilatory anaerobic respiration carried out by heterotrophic microorganisms that are facultatively anaerobic
- NO_3^- (nitrate) and NO_2^- (nitrite) serve as alternate electron acceptors; the reduction is coupled with the oxidation of organic matter by anaerobic respiration



Denitrification as a redox reaction

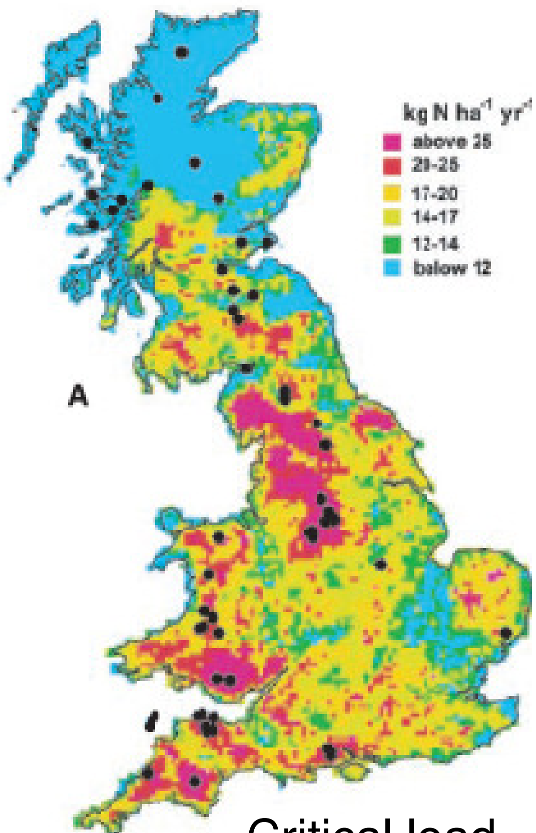
What are the consequences of all this extra nitrogen?

Consequences

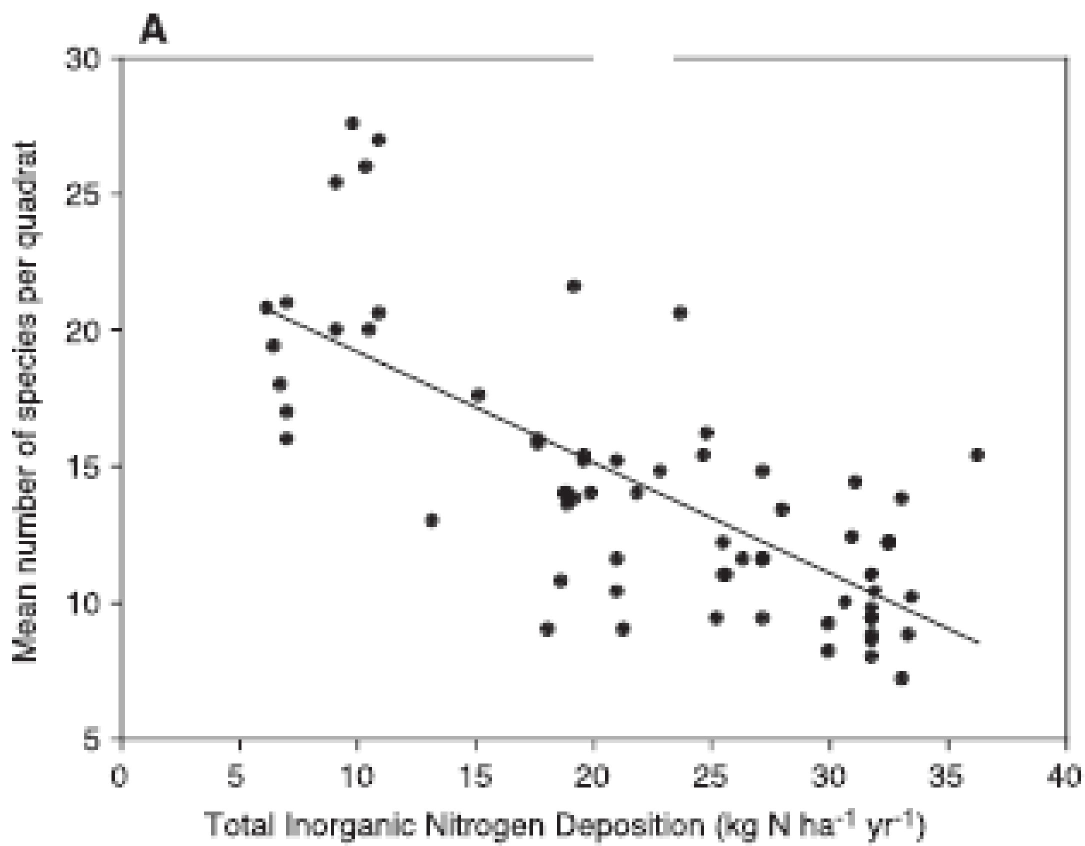
Grasslands

•In MN, N additions decreased plant diversity (Wedin and Tilman 1993)

•In the U.K., plant species richness in acid grasslands declines along a gradient of N deposition (Stevens et al. 2004)



Critical load = 10-20 kg N/ha/y



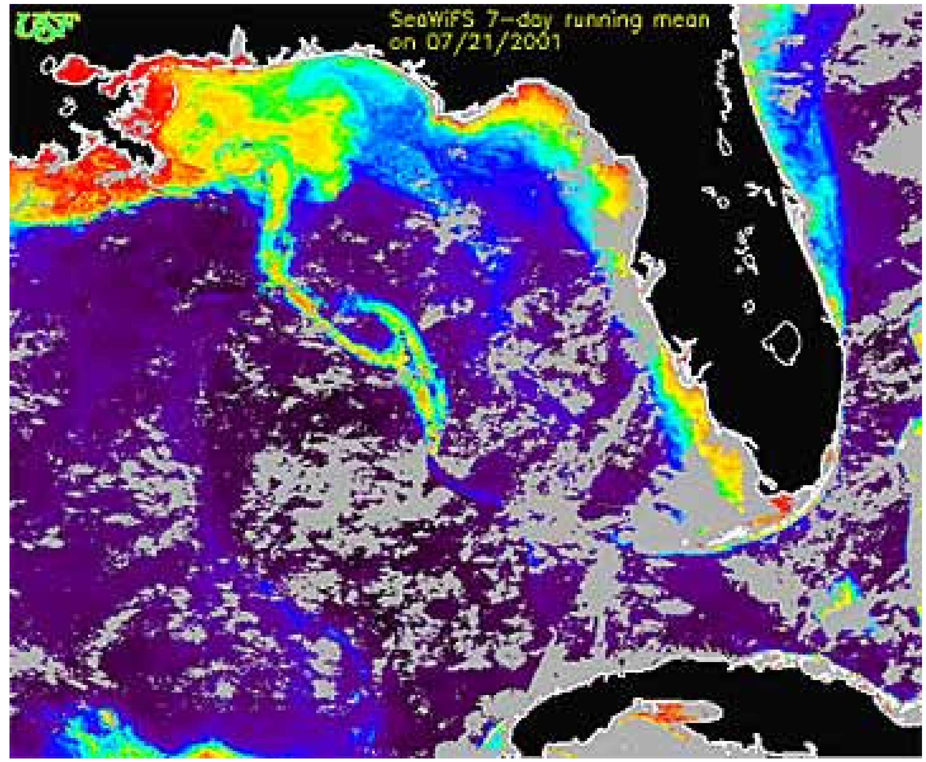
Wetlands: Nitrogen and Pitcher Plants

Experiments in New England bogs show that increasing nitrogen deposition reduces pitcher development and survivorship

Ellison and Gotelli (2002), Gotelli and Ellison (2002)

European data suggest this is probably true for other bog species also, but little data from eastern U.S.

Dead zones along coastlines



Phytoplankton Bloom -- Plume of the Mississippi

N Deposition Effects on Forest Communities

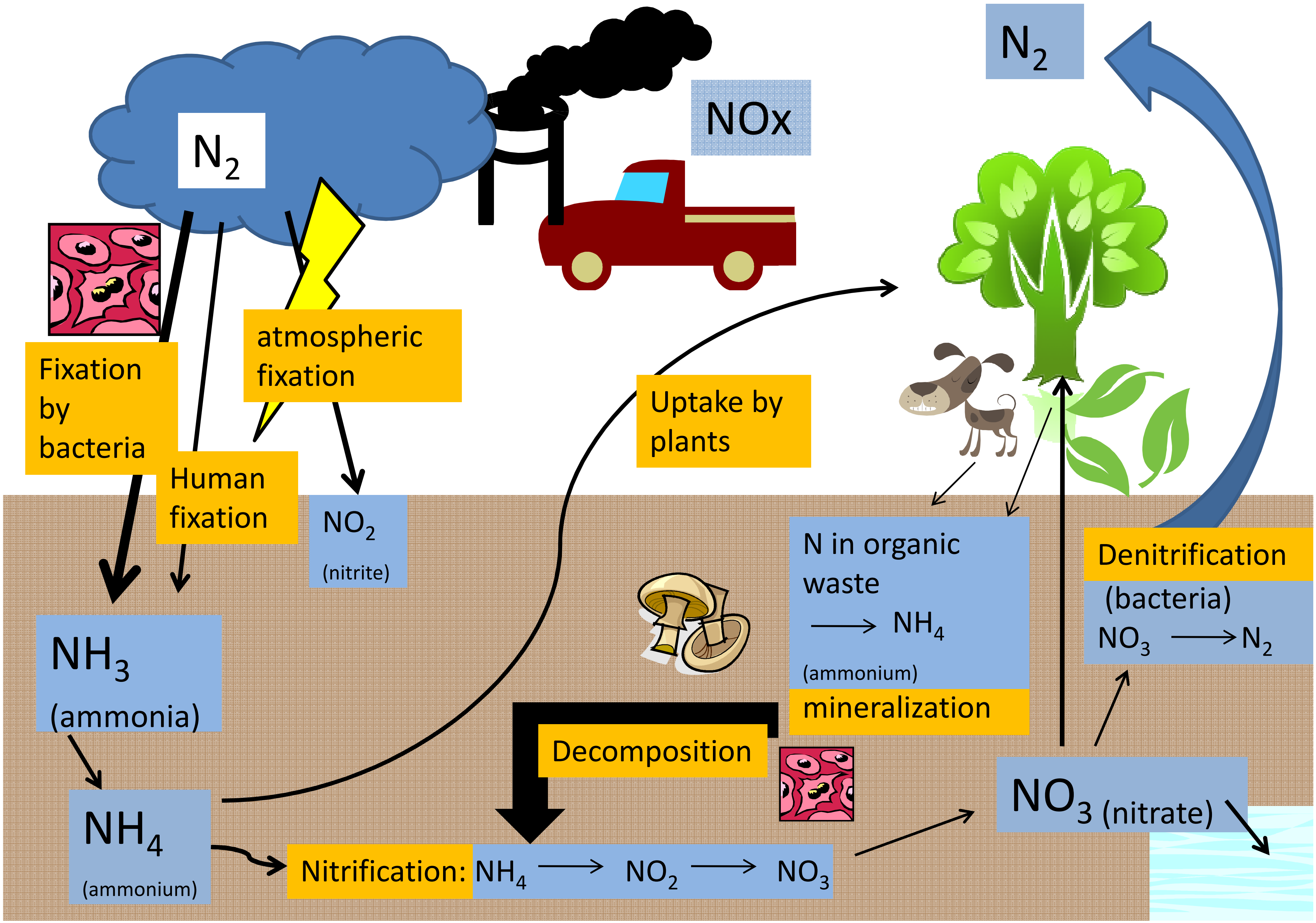
Scientists are studying…How will trees and forests respond over the long term?

- Acidification vs. N enrichment responses
- Effects on susceptibility to insects: e.g. gypsy moth, hemlock woolly adelgid, beech scale

- Effects on mycorrhizae
- Effects of changing N source: Organic N or NH_4^+ to NO_3^-?

Human perturbation of the global N cycle

- In the last few decades, the global production of fixed N has *doubled* due to anthropogenic sources, which are predominantly associated with food and energy production (Galloway et al. 1995, 2003):
  - Industrial N fixation for fertilizer production (~57% of the anthropogenic sources);
  - Cultivation of N-fixing crops such as legumes (~29%);
  - Combustion of fossil fuels (~14%); most of this is combustion of organic nitrogen in the fuel to yield nitric oxide, but includes some "fixation" of atmospheric N_2
- Our current global population is largely dependent on the industrial production of N fertilizer
  - "In one lifetime, humanity has developed a profound chemical dependence" (Smil 1997)



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NO_3 (nitrate)

Table 1. Sources of nitrogen in the Mississippi River Basin and measured nitrogen discharge to the Gulf of Mexico from the basin (Goolsby et al. 1999).

Source	**Nitrogen flux, 10^3 t/yr**
New nitrogen	
Fertilizer	6495
Legume nitrogen-fixation	4375
Atmospheric deposition	1411
Recycled nitrogen	
Feedlots/manure	1296
Mineralization from soil	6464
Atmospheric deposition: Wet ammonia	651
Point sources: Municipal	201
Point sources: Industrial	86
Urban nonpoint sources	?
Approximate total inputs	20,979
River discharge to Gulf of Mexico	1567

Table 7. Recommended approaches for the reduction of significant amounts of nitrogen loading to streams and rivers in the Mississippi River Basin and Gulf of Mexico.

Approach	Potential nitrogen reduction[1] (10^3 metric tons per yr)
Changing farm practices	
Nitrogen management: Reduction in "insurance" rates of nitrogen fertilizer application, proper distribution of manure, application of appropriate credits for previous crop legumes and manure, and application of improved soil nitrogen testing methods	900–1400
Alternative cropping systems: perennial crops substituted for 10% of the present corn–soybean area	500
Improved management of animal manure in livestock-producing areas	500
Minimum spacing of 15 m between farm drainage tiles	?
Creating and restoring wetlands and riparian buffers	
Create or restore 21,000–53,000 km² (5–13 million acres) of wetlands in the Mississippi River Basin (0.7% to 1.8% of the Basin)	300–800
Restore 78,000–200,000 km² (19–48 million acres) of riparian bottomland hardwood forest (2.7% to 6.6% of the Basin)	300–800
Reducing point sources	
Tertiary treatment of domestic wastewater	20
Flood control in the Mississippi	
River diversions in the delta	50–100

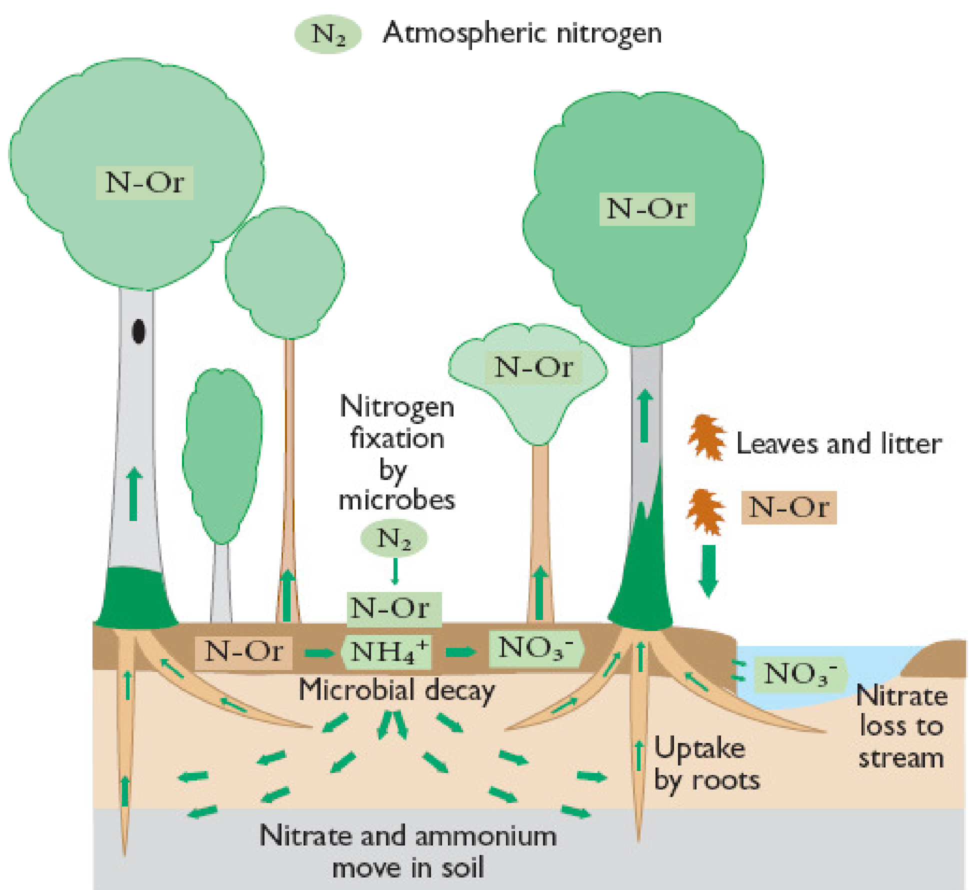
[1]Estimated on-site source reductions do not translate to equivalent reductions in Gulf of Mexico nitrogen loading, because only about 8% of nitrogen sources reach the lower Mississippi River (see Table 1).

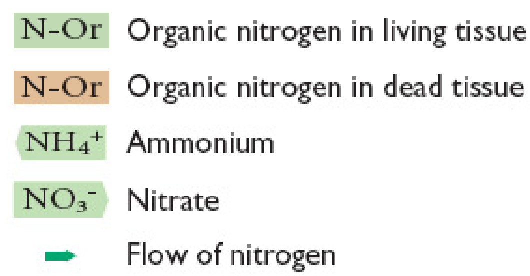
Your turn

Use the Nitrogen Cycle Computer Assignment & the handouts to answer the questions

Nitrogen Cycle

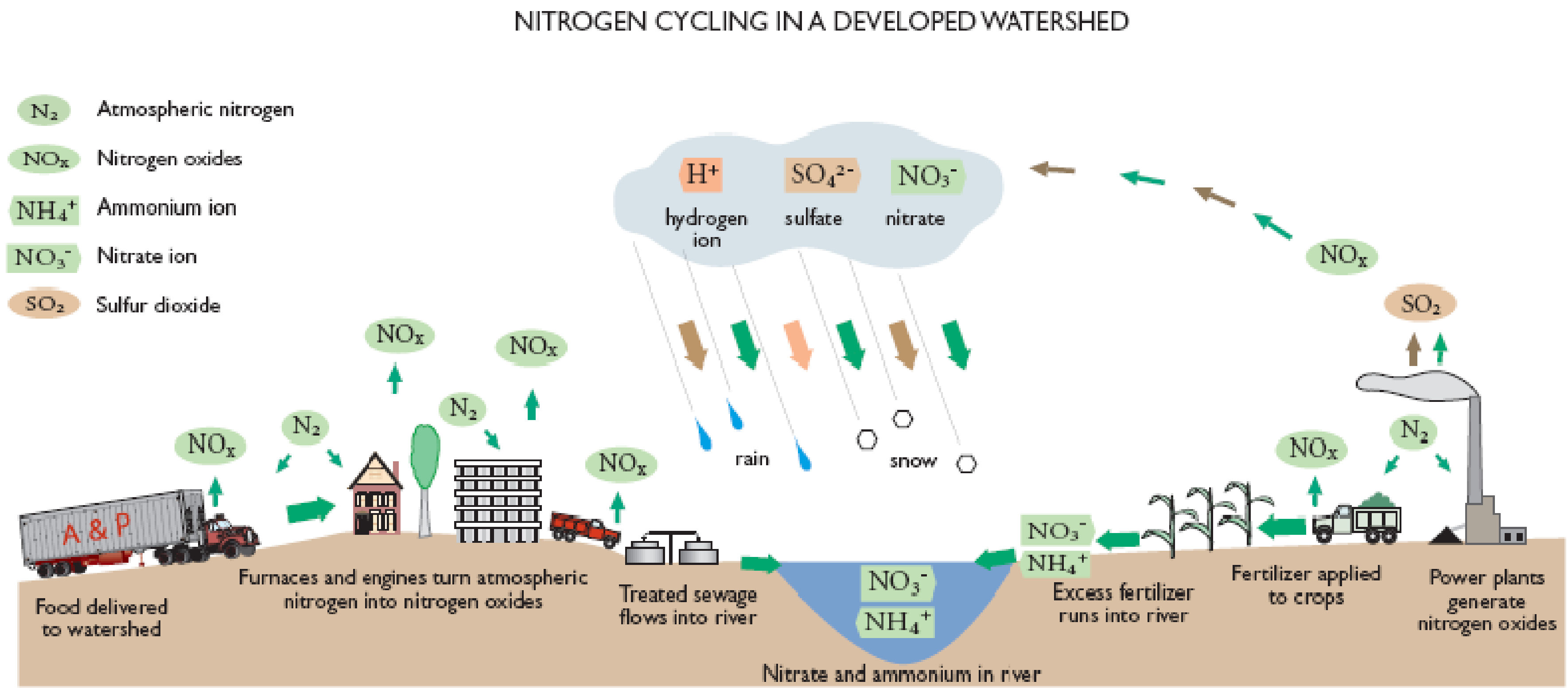
NITROGEN CYCLING IN AN UNDISTURBED FOREST





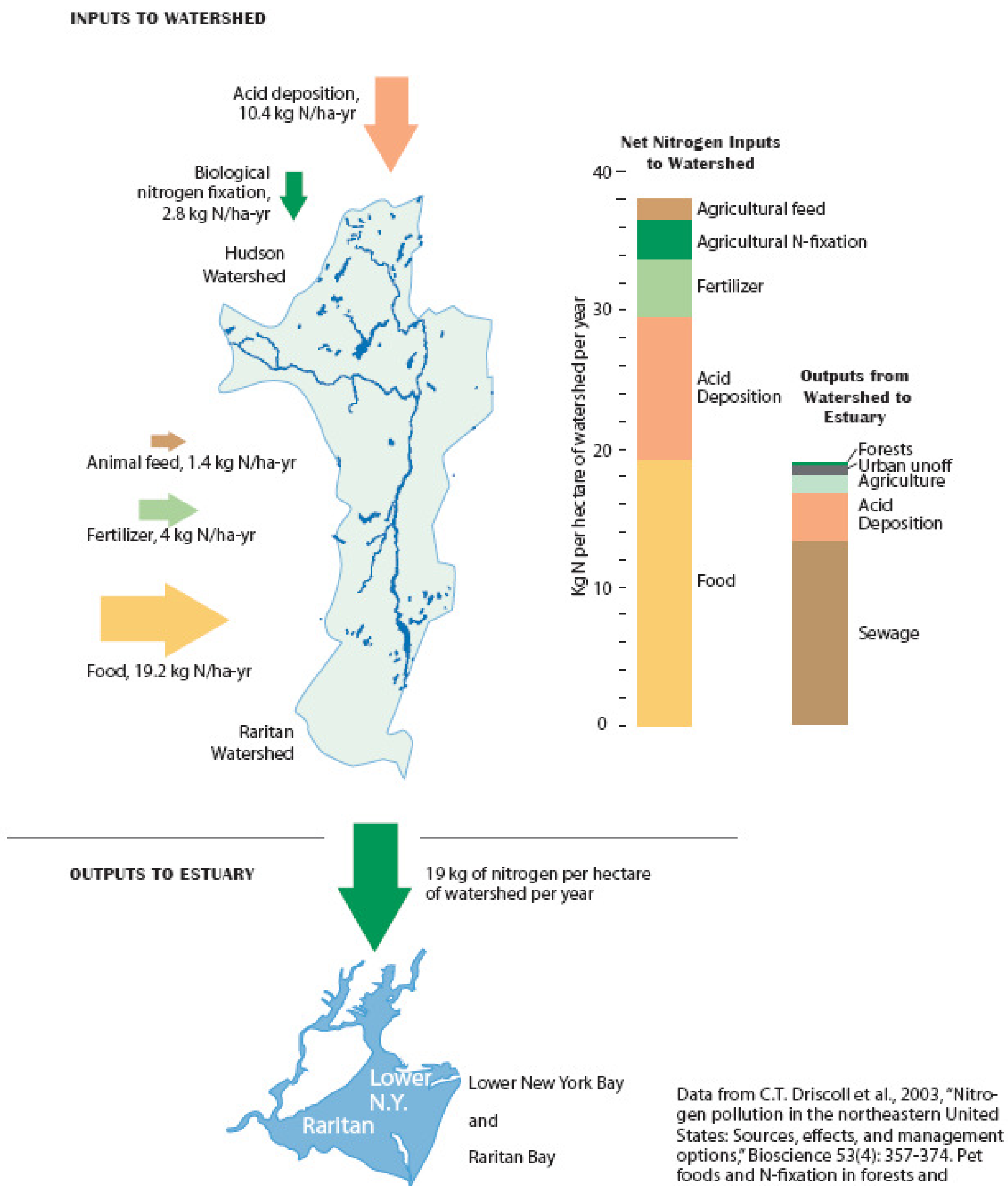
In an undisturbed forest most of the nitrogen cycles between living plants and dead organic mater in the soil. Plants take up nitrogen through their roots; microbes release the nitrogenfrom dead leaves and branches to the soil. Small amounts enter the cycle through nitrogen fixation, and even smaller amounts leave in stream water.

Nitrogen Cycle



Developed watershed import nitrogen in food and fertilizer. They also receive nitrogen from acid rain, which in turn gets its nitrogen from the nitrogen oxides produced by furnaces, boilers, and engines. About half the nitrogen a watershed receives is stored in the soil or in trees or exported as crops. The flows into rivers.

THE NITROGEN BALANCE OF THE HUDSON - WATERSHED



Data from C.T. Driscoll et al., 2003, "Nitrogen pollution in the northeastern United States: Sources, effects, and management options," Bioscience 53(4): 357-374. Pet foods and N-fixation in forests and wetlands are not included.

Forms of N

- "Reactive" or "combined" N refers to nitrate (NO_3^-), nitrite (NO_2^-), and ammonium (NH_4^+), in contrast to dinitrogen (N_2).
- N is not a significant component in minerals, and thus mineral weathering supplies little N
- Ammonia (NH_3) occurs largely as ionized ammonium (NH_4^+) in aqueous solutions at normal pH
- N reactions can be assimilatory (assimilation, N fixation), meant to build structures or dissimilatory (denitrification, nitrification) meant to create energy

N availability

- Nearly all plants and algae can assimilate either NO_3^- or NH_4^+, but most bacteria and fungi preferentially assimilate NH_4^+
- Nitrate reductase is required to assimilate NO_3^-
- Plants generally assimilate NH_4^+ preferentially over NO_3^- when both are abundant…
  - but NO_3^- is often more abundant because NH_4^+ is nitrified to NO_3^- in aerobic soils, and certain situations may favor NO_3^- uptake by plants even when both are available

Nitrification ($NH_4^+ \Longrightarrow N_2O \Longrightarrow NO_3^-$)

- Oxidation of ammonium to nitrate is a form of chemoautotrophic metabolism carried out by certain bacteria (e.g., the genera *Nitrosomonas* and *Nitrobacter*)
- Requires aerobic conditions. Inhibited by low pH.
- Nitrate is a relatively mobile ion in soils and groundwater
- Nitrite is an intermediary but does not usually accumulate, and would be toxic if it did
- Nitrification may be closely coupled to bacterial denitrification of the resultant NO_3^- in a closely situated anaerobic environment
  - Anaerobic vs. aerobic environments = closely linked

N fixation ($N_2 \Longrightarrow R\text{-}NH_2$)

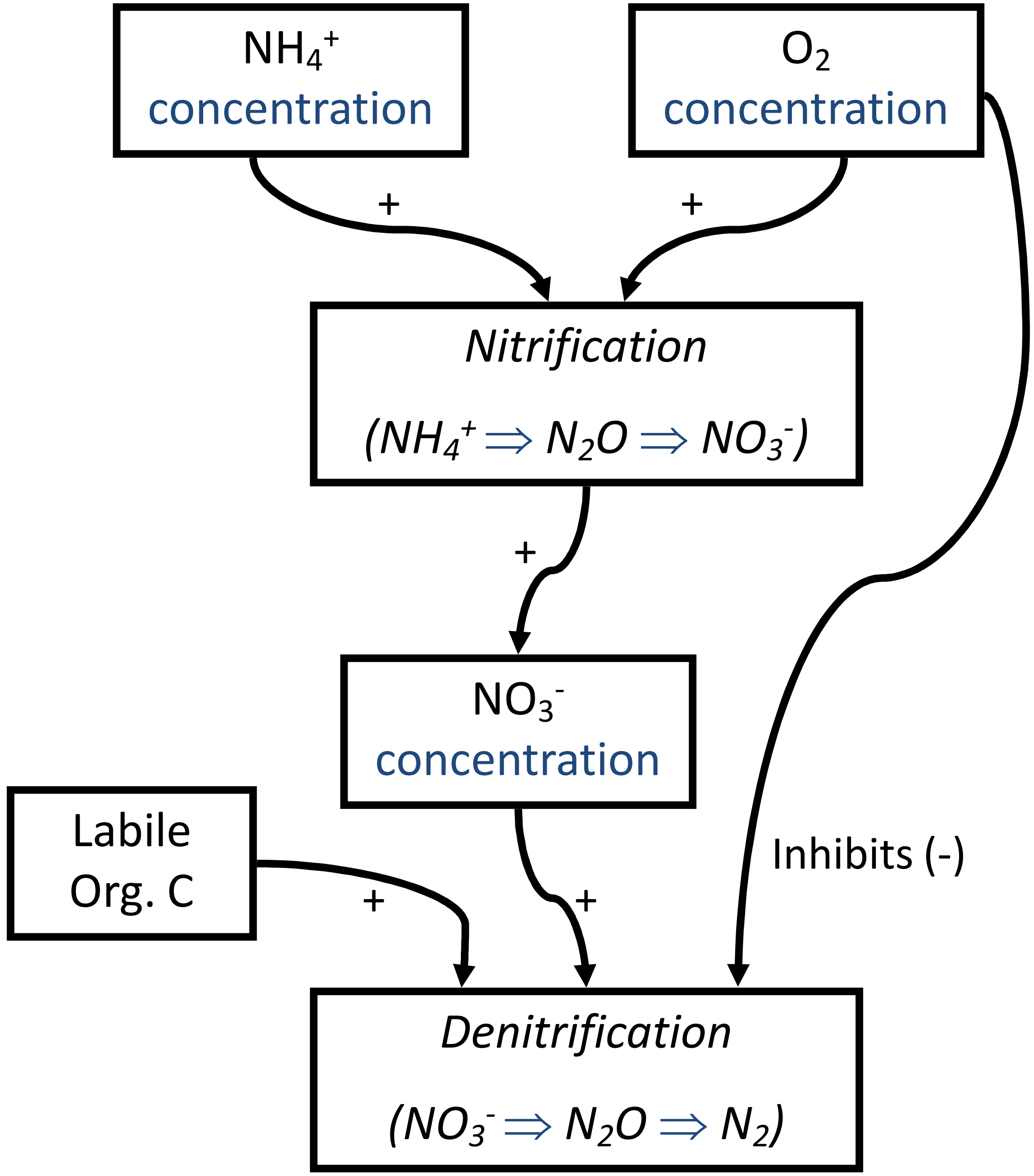
- Provides “fixed” or “combined” N for use by the biota
- Only prokaryotes can fix N but these are often closely associated with eucaryotes
  - Symbiotic associations with vascular plants and algae are important (e.g., legumes-*Rhizobium*, *Azolla-Anabaena*, *Alnus*-actinomycetes)
- Most N fixers live in aerobic environments (e.g., blue-green “algae” (cyanobacteria), *Rhizobium*, *Azotobacter*), but there are also anaerobic bacteria that fix N (e.g., *Clostridium*)
- Abiotic N fixation also occurs via lightning and combustion, but natural sources of abiotically fixed N are less important
- Synthetic fertilizer production is effectively N fixation accomplished with fossil-fuel energy

Importance of denitrification

- Denitrification results in the loss of available N from the ecosystem, and in many ecosystems the rate of denitrification appears to balance the rate of N fixation
- Denitrification removes much of the excess NO_3^- from pollution sources before it reaches downstream waters
  - Most N disappears somewhere along landscape flow paths
  - Hotspots of denitrification on landscapes (e.g., riparian strips between farmland and streams: Cirmo and McDonnell 1997)
- Nitrous oxide (N_2O) is produced in addition to N_2, and emission of N_2O to the atmosphere is an important GHG
  - N_2O is one of the key radiatively-active "greenhouse gases" whose atmospheric concentrations have been increasing
  - N_2O is also involved in the depletion of stratospheric ozone

Controls on nitrification and denitrification

- Denitrification requires the combination of anaerobic conditions, labile organic matter, and oxidized N
- High rates of denitrification are commonly found in sediments
- Often these processes are coupled in closely situated oxic/anoxic zones



Ultimate fate of anthropogenic N?

- The ultimate fate of anthropogenically added N is not well known
- For the eastern US and Europe, about 25% of the added N can be accounted for in riverine exports from terrestrial watersheds to the ocean, which have clearly increased in many regions (Howarth et al. 1996, Conley 1999).
- The atmosphere is an important route for N transport but it does not store a significant amount of reactive N
- The remaining 75% must either be stored in ecosystems or denitrified
  - Most storage would be as organic N in forest ecosystems; groundwater appears to be small sink
  - Denitrification, especially in wetlands and other aquatic ecosystems but also in soils, is presumably the most important sink for excess N