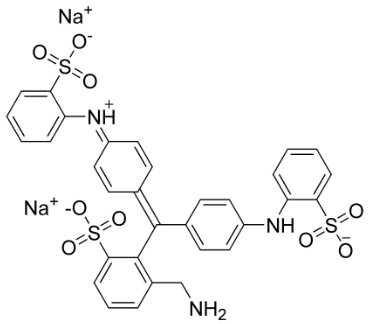

STROUD™
WATER RESEARCH CENTER
ADVANCING KNOWLEDGE AND STEWARDSHIP OF FRESH WATER SYSTEMS
THROUGH RESEARCH, EDUCATION, AND RESTORATION

Water Chemistry
Nitrogen and Phosphorous

Marc Peipoch, PhD



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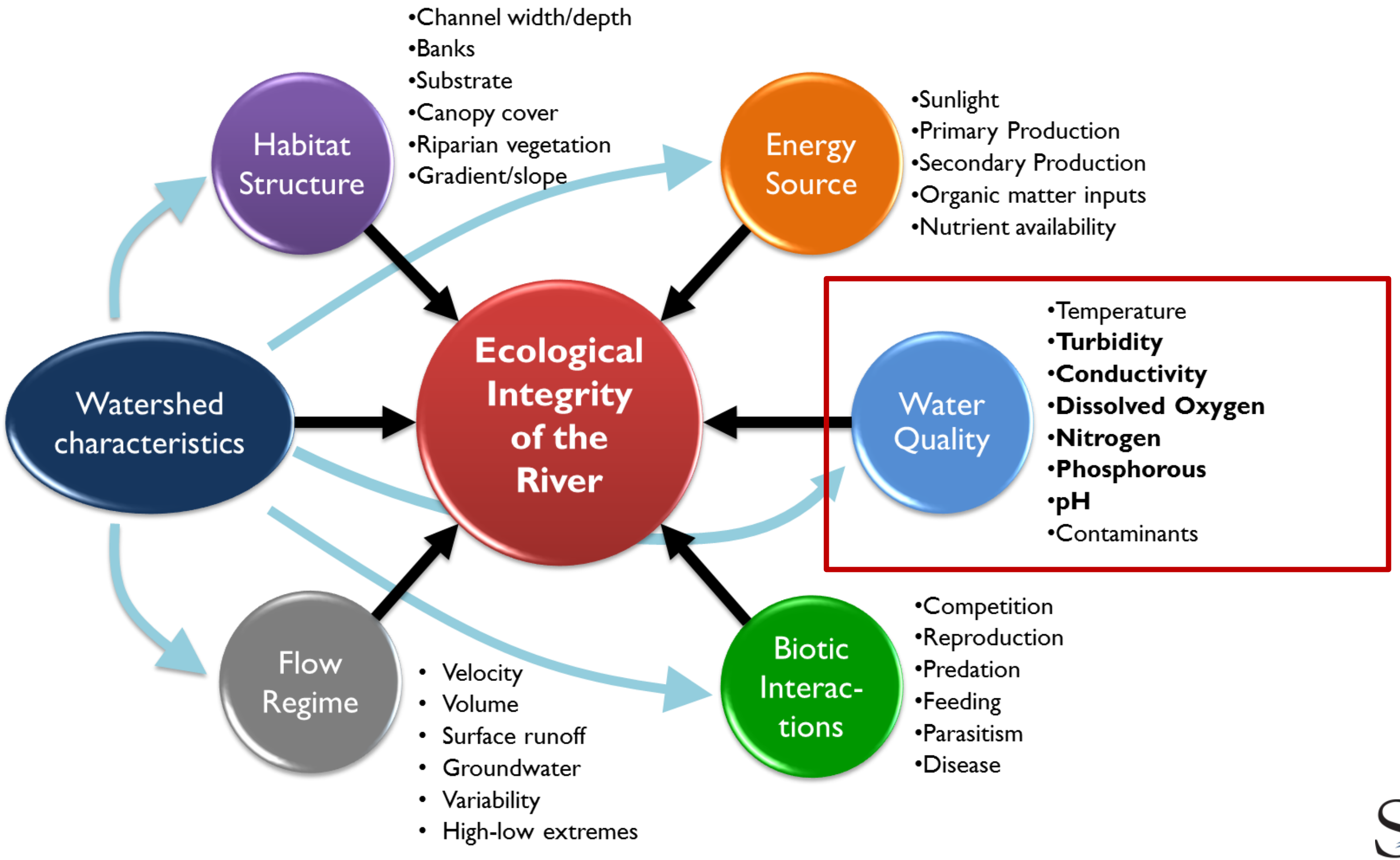
Factors affecting ecosystem integrity



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Outline

1. Introduction and Natural Conditions
    a. What's in the water?
    b. How do we measure it?
    c. Nitrogen and Phosphorous Cycles
2. Urban and Agricultural Impacts
    a. Sources and processes
    b. How do N and P get to the stream?
3. Effects and Efficacy of Remediation
    a. Riparian buffers/Farming practices
    b. Stormwater BMPs
    c. Are we cleaning our waters?

What’s in the water?

p.c: L. Kaplan

Dissolved vs. Particulate

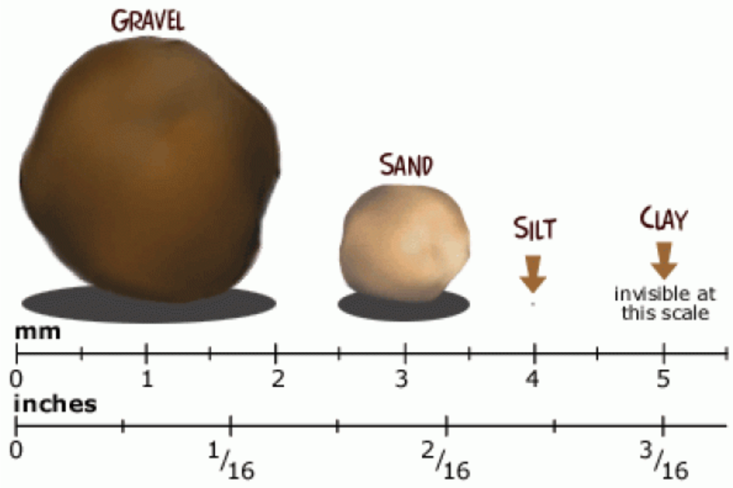
Particulate (suspended) material: > 0.45µm,

(~100 thinner than human hair)

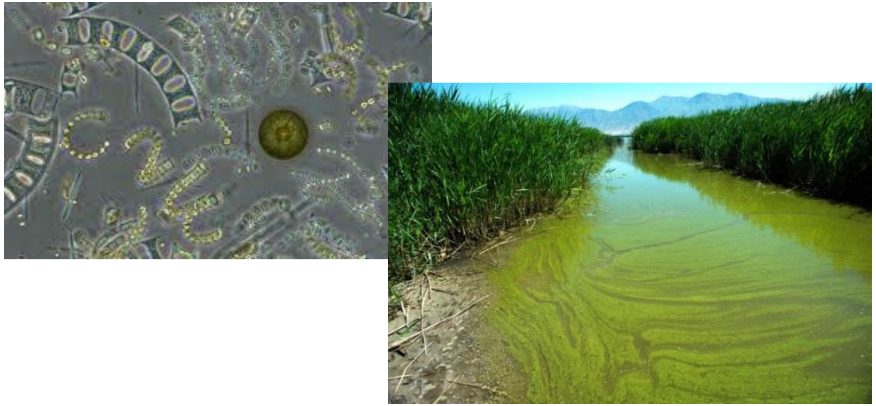
Total Suspended Solids = TSS

Major Particulate Constituents

Mineral



Organic



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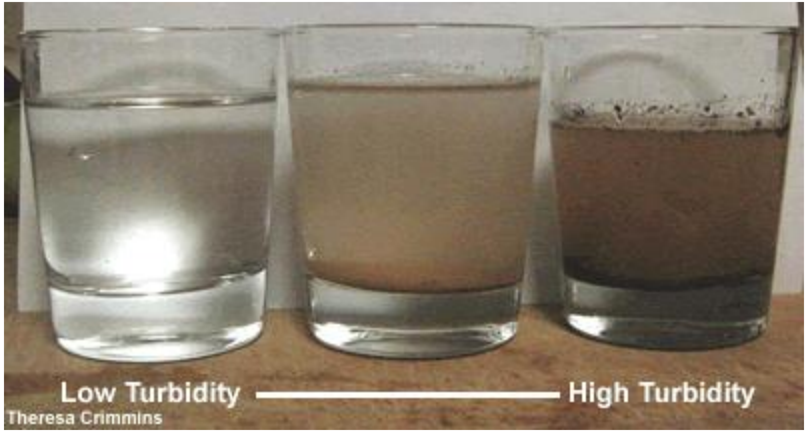
Major Particulate Constituents

Turbidity (NTU) = the degree to which light is scattered by particles suspended in water.

Depends on the presence of suspended particles

Turbidity ~ TSS



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Dissolved vs. Particulates

Dissolved vs. Particulates

Particulate (suspended) material: > 0.45μm, - human hair ~ 60μm

clay, silt, sand, algae, etc.
add up as Total Suspended Solids = TSS

Dissolved material: < 0.45 μm

Total Dissolved Solids = TDS

a. Dissolved salts

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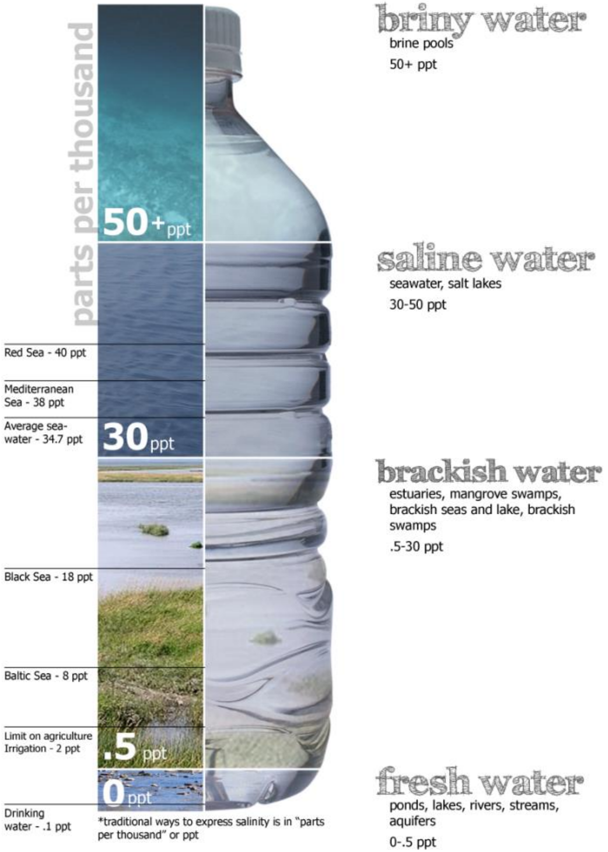
Major Dissolved Constituents

Freshwater is the least concentrated solution

Freshwater is in constant dilution

Freshwater is a unique salt mixture tied to underlying geology



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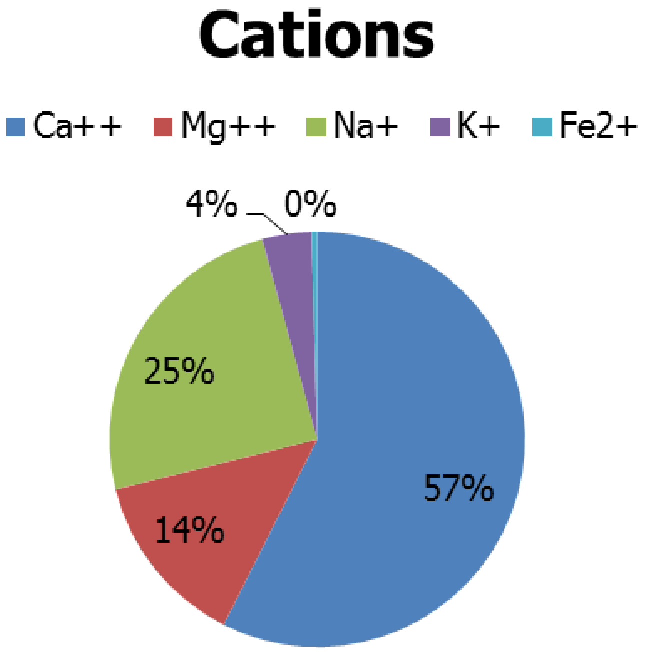
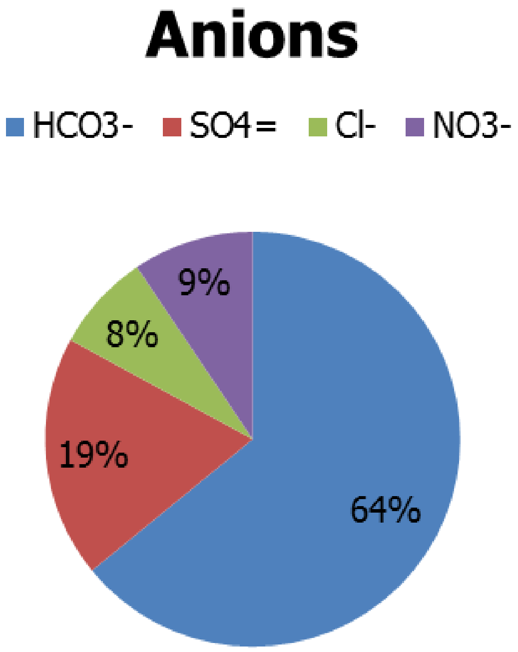
Major Dissolved Constituents





Average water chemistry in North America (Wetzel 1978)

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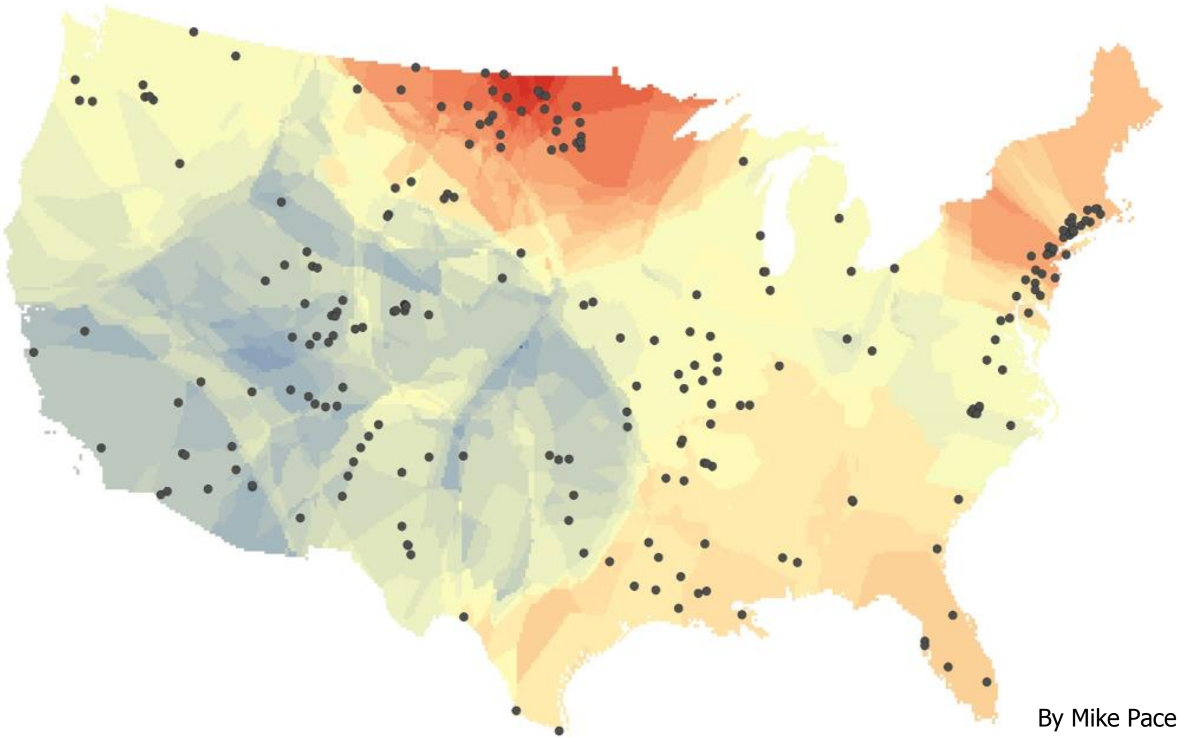
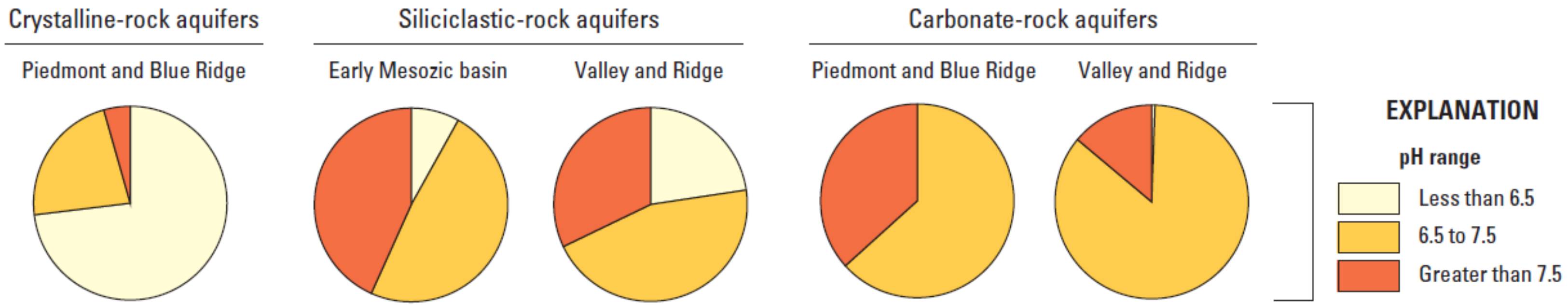
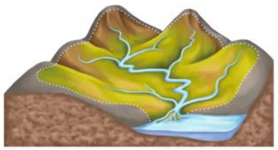
Major Dissolved Constituents

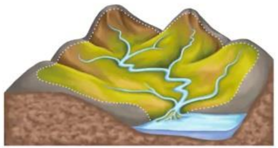


By Mike Pace

Dissolved Solutes > Hardness > Alkalinity > pH







Granite-based geology

- Low in $CaCO_3$
- Lower TDS
- Soft water and low Alkalinity
- Acidic pH

Limestone geology

- High in $CaCO_3$ or $MgCO_3$
- Higher TDS
- Hard water and high alkalinity
- Neutral pH

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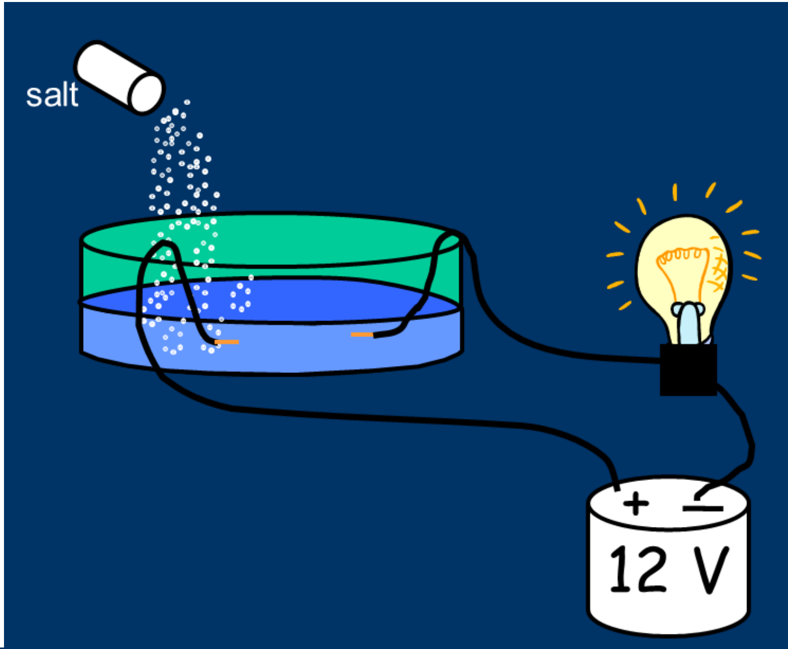
Major Dissolved Constituents

Conductivity (µS cm-1) = ability of water to conduct e^-

Depends on the presence of dissolved ions.

Conductivity ~ TDS ~ Hardness



Major Dissolved Constituents

Particulate (suspended) material: > 0.45µm, - human hair ~ 60µm

clay, silt, sand, algae, etc.
add up as Total Suspended Solids = TSS

Dissolved material: < 0.45 µm

Total Dissolved Solids = TDS

a. Dissolved salts
b. Nutrients

Major Dissolved Constituents

NITROGEN

- nitrate (NO_3^-)
- ammonium (NH_4^+)

PHOSPHOROUS

- phosphate (PO_4^{-3})

Major Dissolved Constituents

Particulate (suspended) material: > 0.45µm, - human hair ~ 60µm

clay, silt, sand, algae, etc.
add up as Total Suspended Solids = TSS

Dissolved material: < 0.45 µm

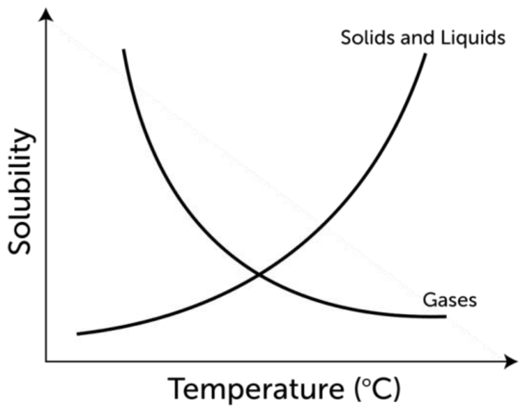
Total Dissolved Solids = TDS

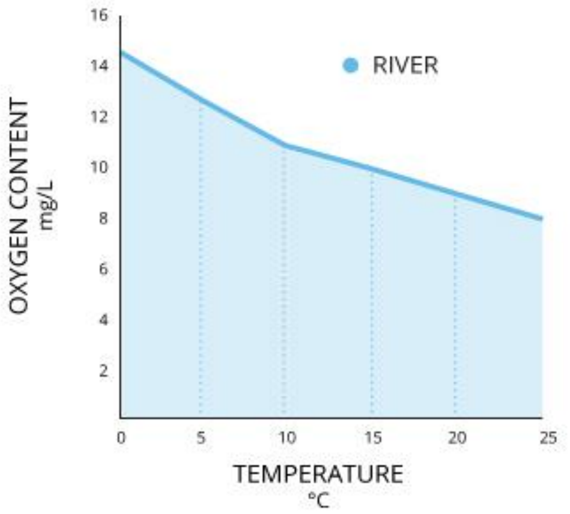
a. Dissolved salts
b. Nutrients
c. Dissolved gases

Dissolved Gases

Most ecologically relevant: dissolved O_2

- Seek for equilibrium with atmosphere
- More soluble with warm temperatures





Dissolved Gases

Most ecologically relevant: CO_2 and O_2

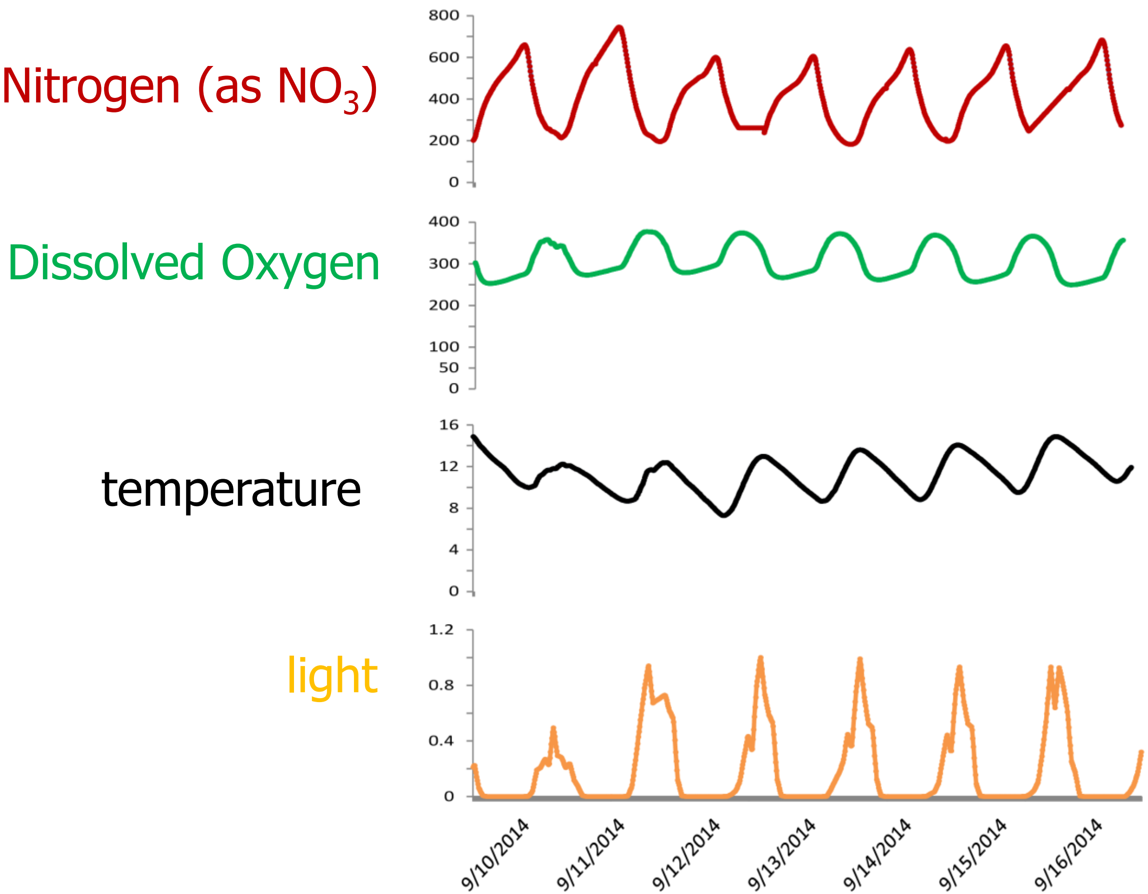
- Seek for equilibrium with atmosphere
- Their solubility varies with Temperature
- Biology consume and generate them

photosynthesis

$$\mathbf{CO_2 + H_2O \rightleftharpoons (CH_2O)_n + O_2}$$

respiration

Day-night variations in water chemistry



A typical week at the creek…

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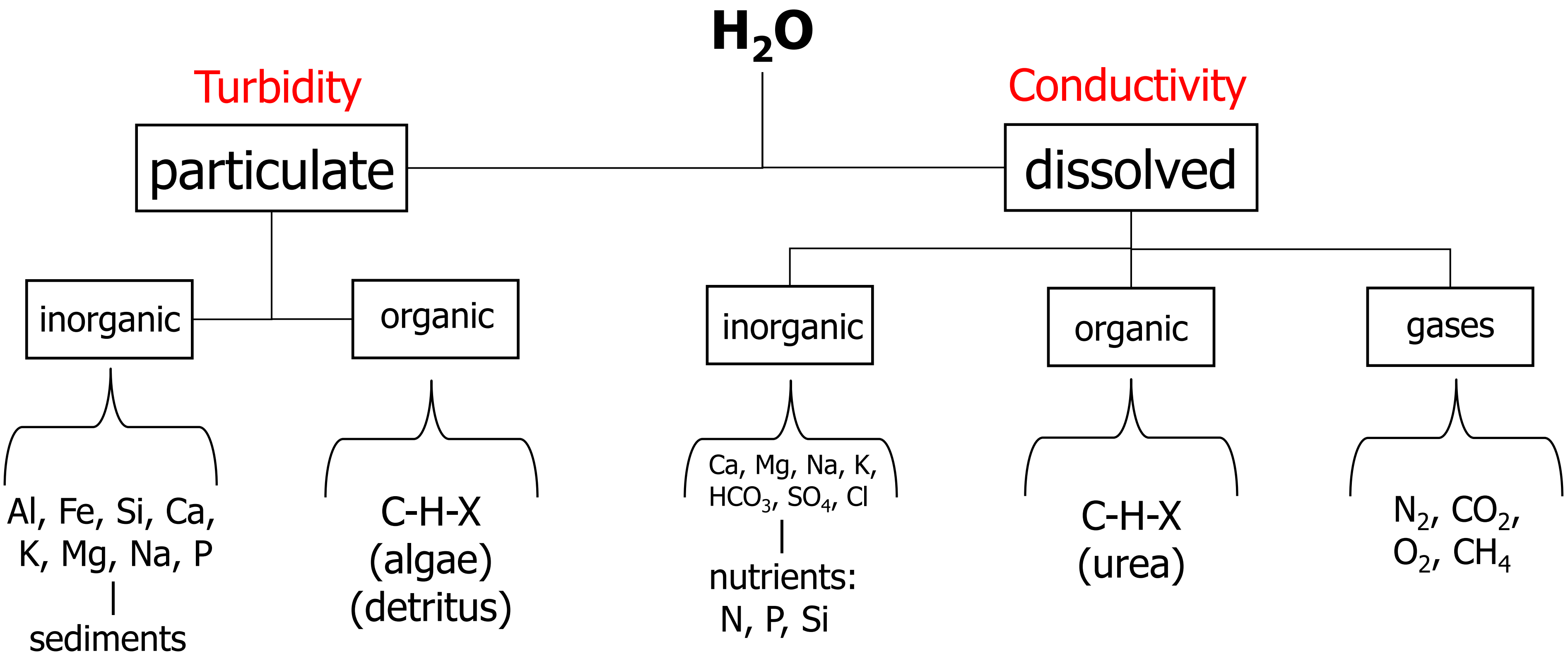
What's in the water?



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How do we measure it?

Concentration: amount of solute in a given volume of water, (mass/volume)

Example : mg of NO_3/L

Load: total mass transported per unit time.

concentration * discharge = mass/time

Example : 3 mg of NO_3/L * 1000 L/s = 3000mg NO3/s

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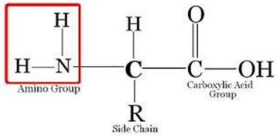
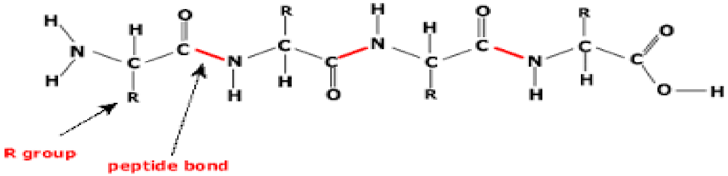
Nitrogen and Phosphorous

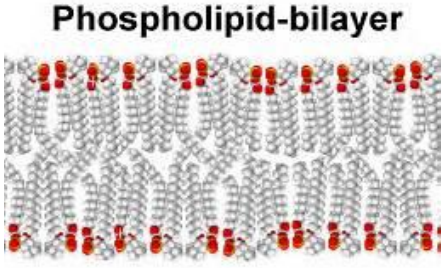
Nitrogen and Phosphorous

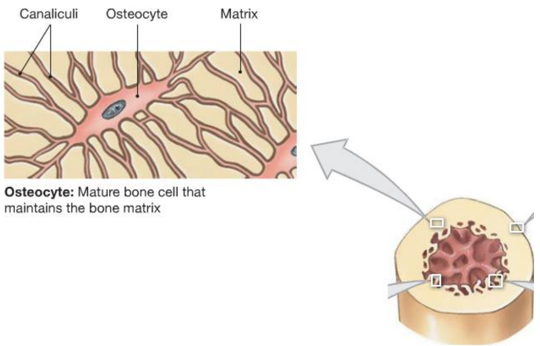
nitrogen (N) – needed for proteins, enzymes, nucleic acids





phosphorus (P) – ATP, membranes, apatite (bones)





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Global Nitrogen Reservoirs

Nitrogen Reservoir	Petatonnes nitrogen	Actively cycled
Atmosphere	3.9	No
Ocean		
inorganic	0.0069	Yes
Biomass	0.000052	Yes
Continental		
inorganic	0.0011	Slow
Biomass	0.00025	Yes

N is the 5th most abundant element in the universe

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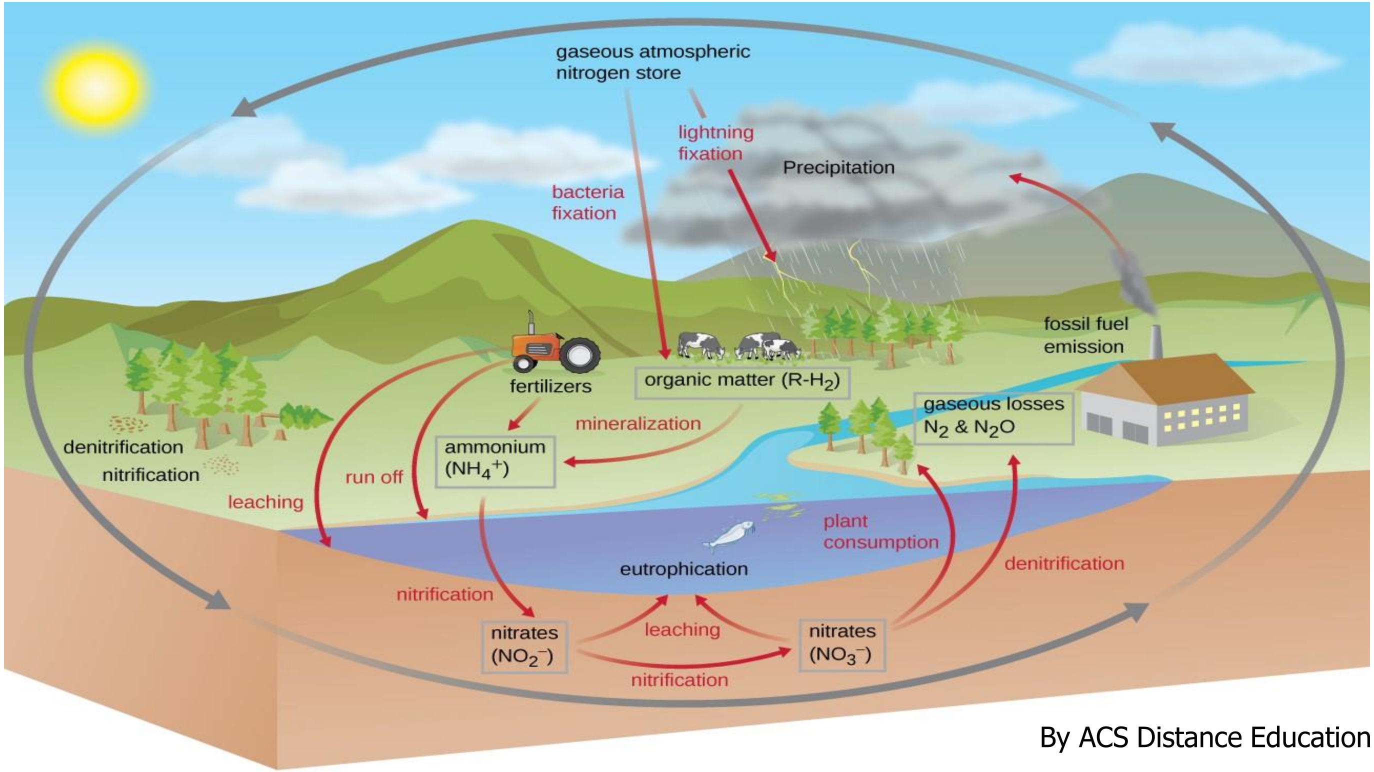
Global Nitrogen Cycle



By ACS Distance Education

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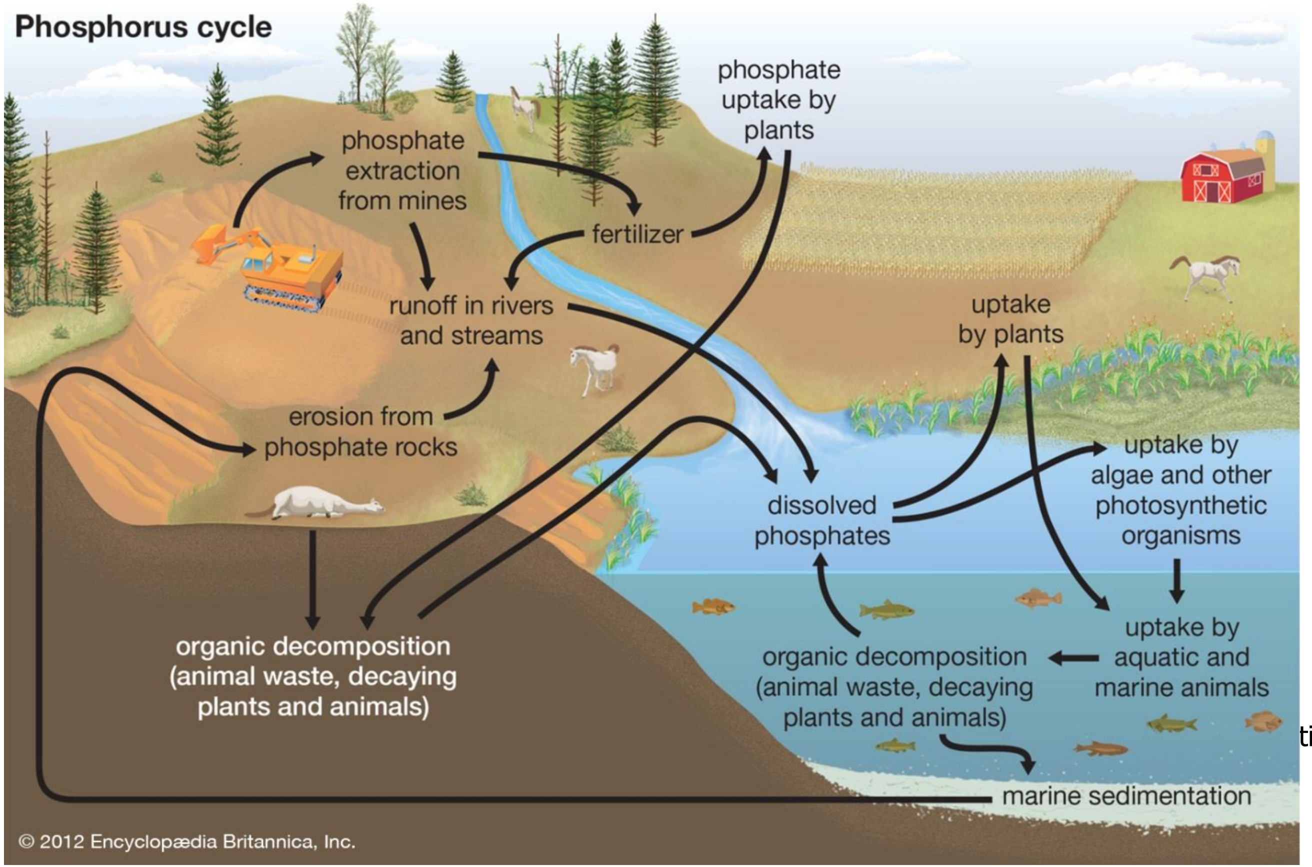
Phosphorous in the Biosphere

Phosphorous Reservoir	Gigatonnes Phosphorous	Actively cycled
Atmosphere	0.000001	No
Ocean		
Inorganic	0.3	Yes
Living biomass	1.2	Yes
Dead biomass	11.4	Slow
Continental		
Inorganic (mostly apatite)	108	Slow
Living biomass	0.4	Yes
Dead biomass	2.9	Yes

Global Phosphorous Cycle



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Nutrient forms

Total Nitrogen
Total Phosphorus

- particulate
  - inorganic
    - Sediment dust
  - organic

Other detritus

mineralization →

- dissolved
  - inorganic
    - NH_4 , NO_3
    - PO_4
    - ↓ Algae, plants
  - organic
    - Urea (N & P)
    - Aminoacids
    - P_xO_x
    - ↓ bacteria
  - gases
    - N_2, N_2O

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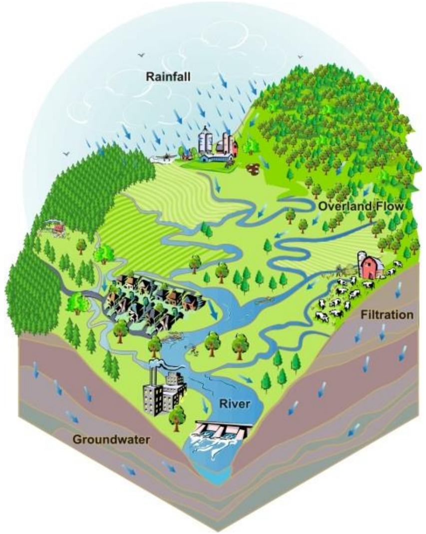
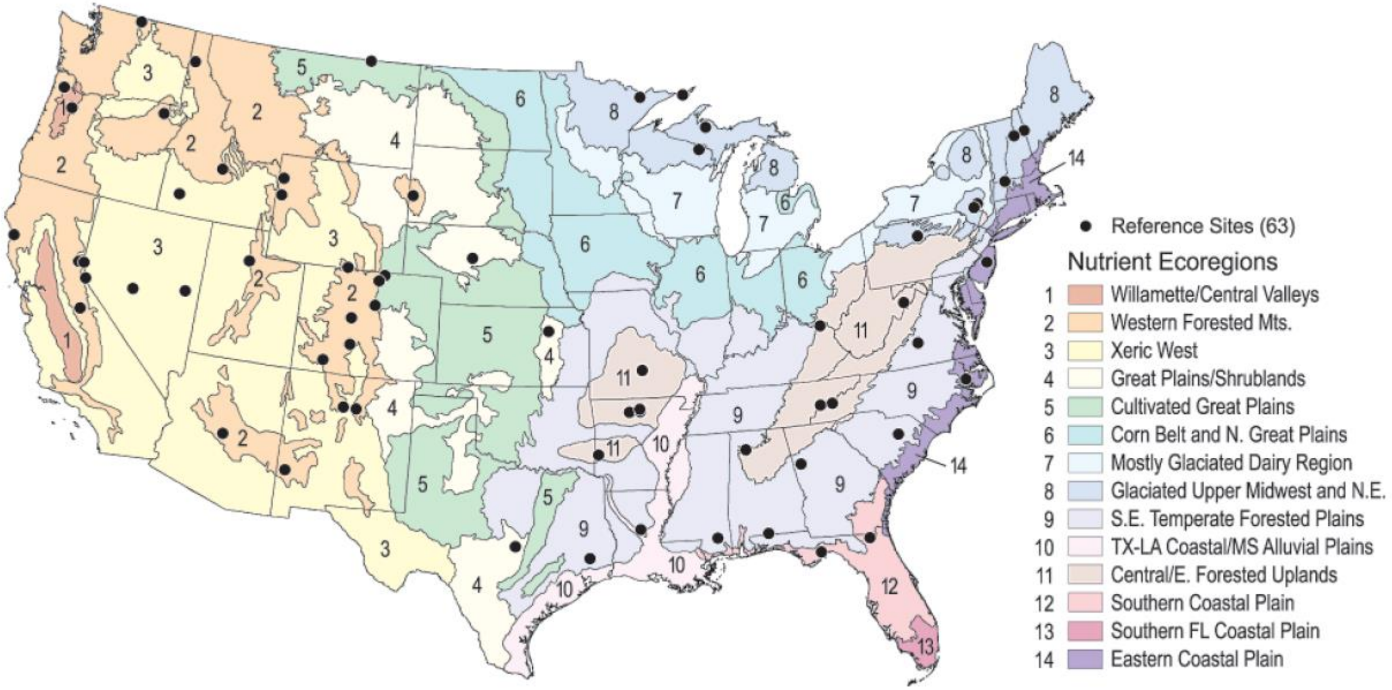


Urban and Agricultural Sources

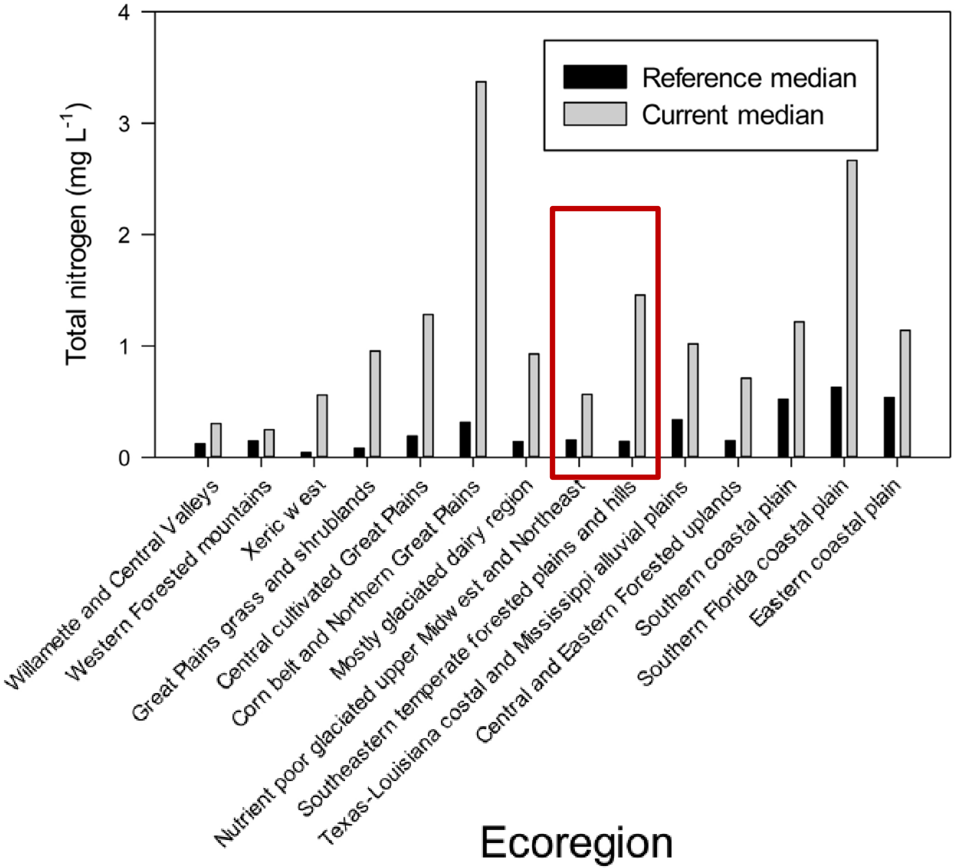
Reference Conditions



Smith et al. 2003

Reference Conditions

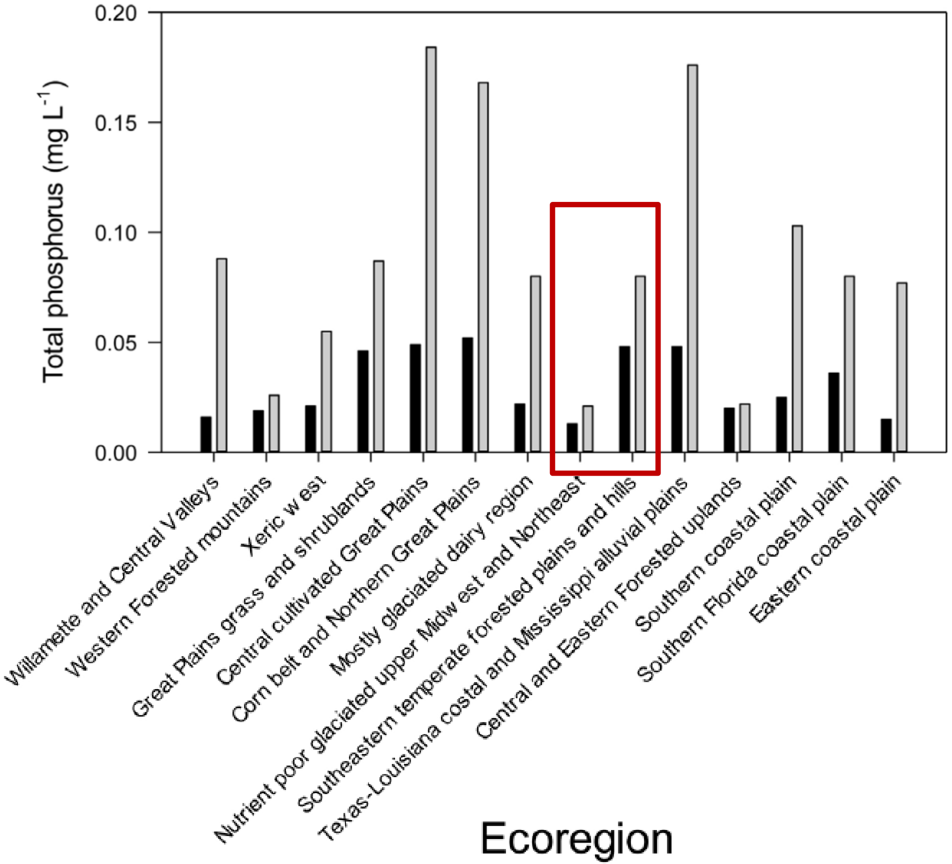
x5 times over reference values for Total N



Dodds and Smith 2016

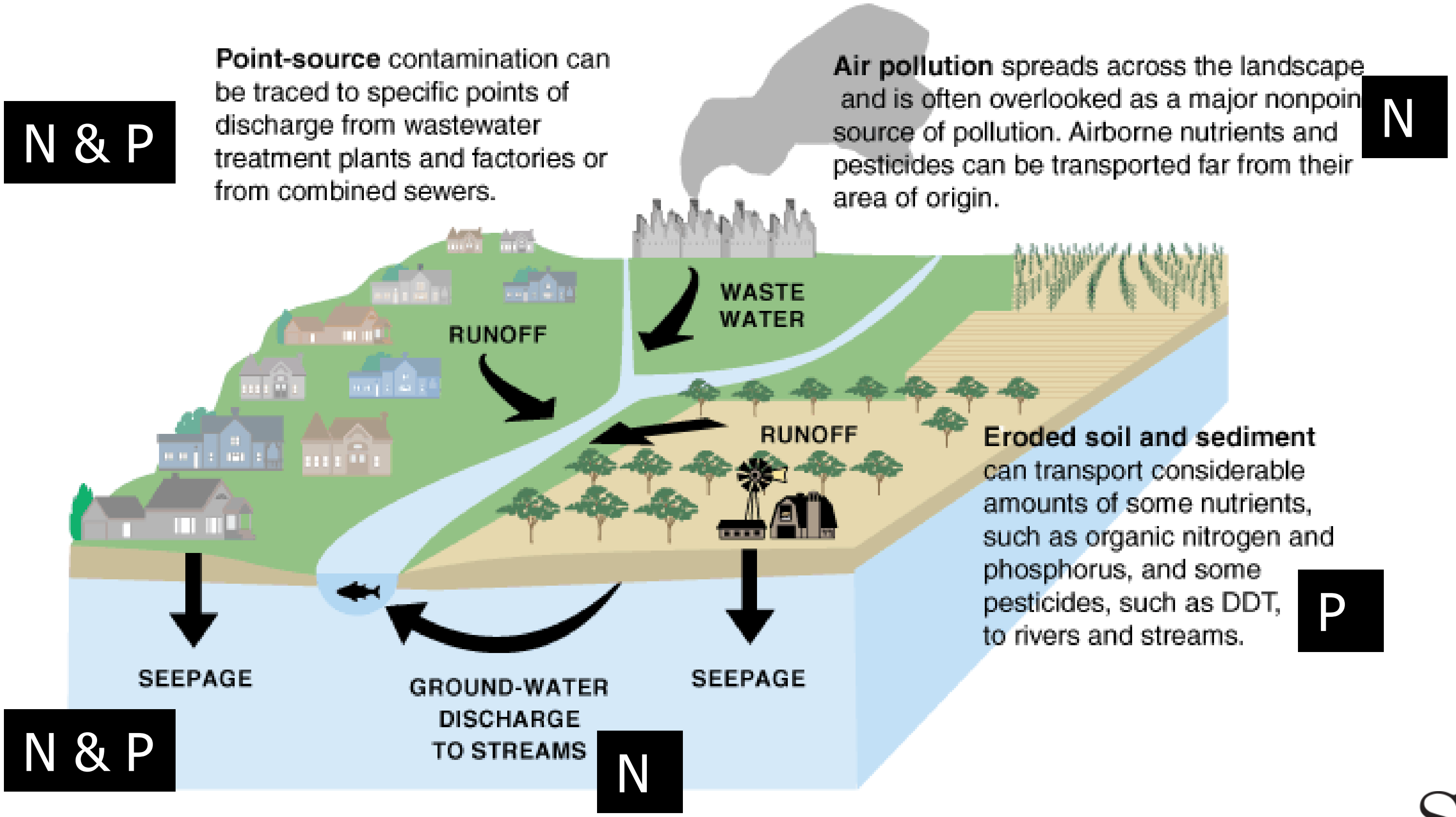
Reference Conditions

X0.5 times over reference values for Total P



Dodds and Smith 2016

How did we get here?



U.S. Geological Circular 1225--The Quality of Our Nation's Waters--Nutrients and Pesticides

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Agricultural Nutrient Sources

1. Fertilizers
   a. Synthetic

Nitrogen Fixation

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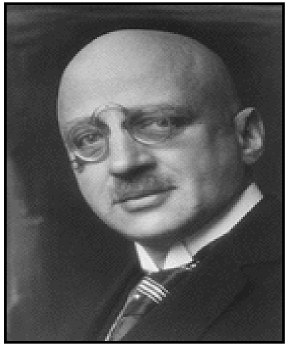
Human Influence on Nitrogen Fixation

7 14.0067

N

Nitrogen

Fritz Haber



nobelprize.org

Carl Bosch

Sci. and Soc. Pict. Lib.

Nitrogen Gas

$:N \equiv N:$

Haber-Bosch process

$$N_{2(g)} + 3H_2 \Longleftrightarrow 2NH_{3(g)} + \Delta H$$

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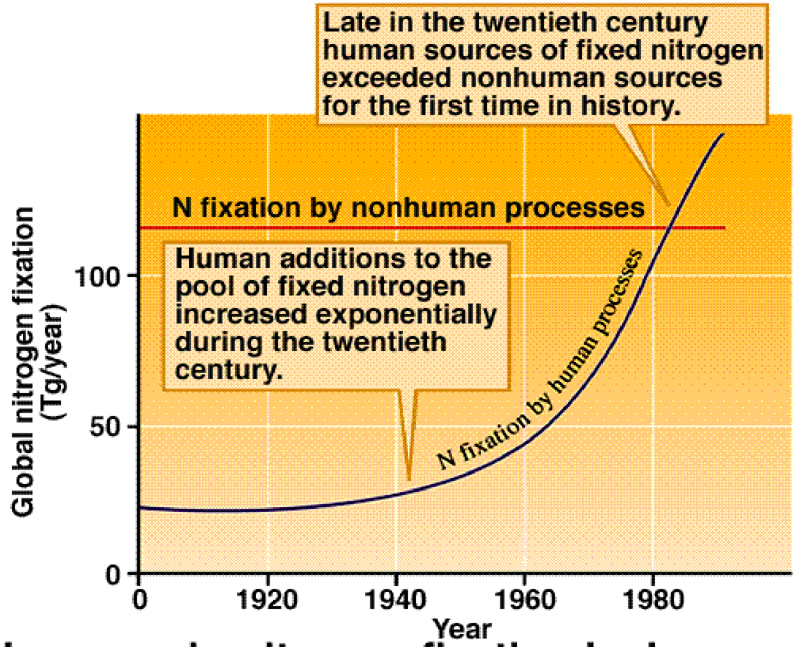
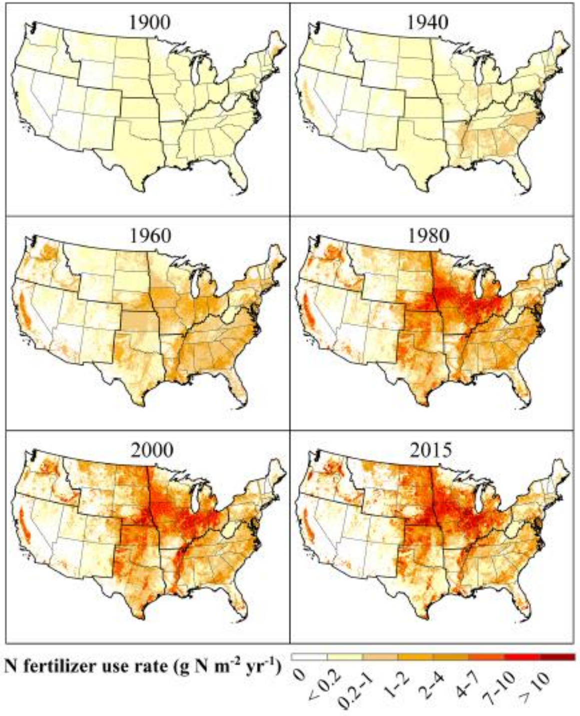
Human Influence on Nitrogen Fixation



Increase in nitrogen fixation by human processes during the twentieth century.



Cao et al. 2018

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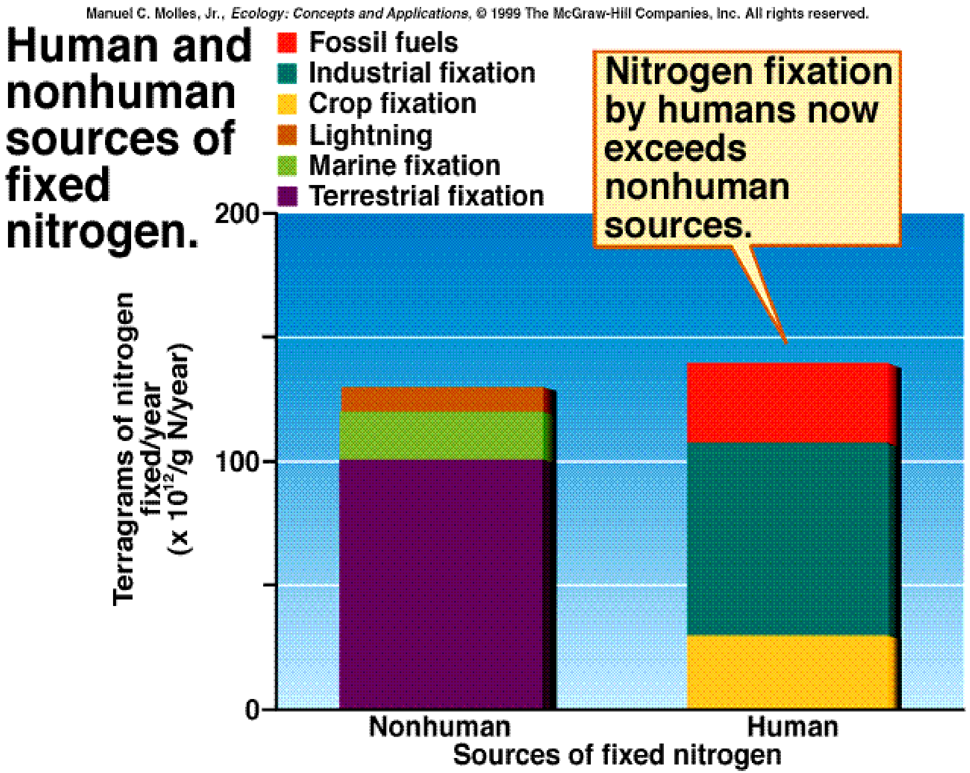
Human Influence on Nitrogen Fixation



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Agricultural Nutrient Sources

1. Fertilizers
    a. Synthetic
    b. Organics (manure)

Agricultural Nutrient Sources

Estimated nitrogen (N) and phosphorus (P) produced from animal manure in 2007 (EPA).

State	Estimated animal manure	Estimated animal manure	Estimated animal manure per farm land area (kg of N/km^2)	Estimated animal manure per farm land area (kg of P/km^2)
Delaware	20,080	5,994	9,729	2,880
North Carolina	215,818	80,115	6,201	2,302
Maryland	37,297	10,548	4,474	1,265
Pennsylvania	125,555	32,946	3,978	1,044
Georgia	158,802	48,575	3,810	1,165
Alabama	133,956	41,438	3,678	1,138
Vermont	15,934	3,047	3,201	612
Iowa	398,551	144,981	3,198	1,163
California	327,287	75,388	3,184	733
Arkansas	179,024	56,005	3,183	996
Virginia	102,834	30,895	3,137	943
Wisconsin	191,761	42,098	3,117	684

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Agricultural Nutrient Sources

1. Fertilizers
   a. Synthetic
   b. Organics (manure)
2. Livestock residues

Agricultural Nutrient Sources

The problem with Herbivores….

- Imbalanced diet
- Only assimilate 50%
- They eat constantly
- Excrete 50% of it which is more bioavailable than it was before

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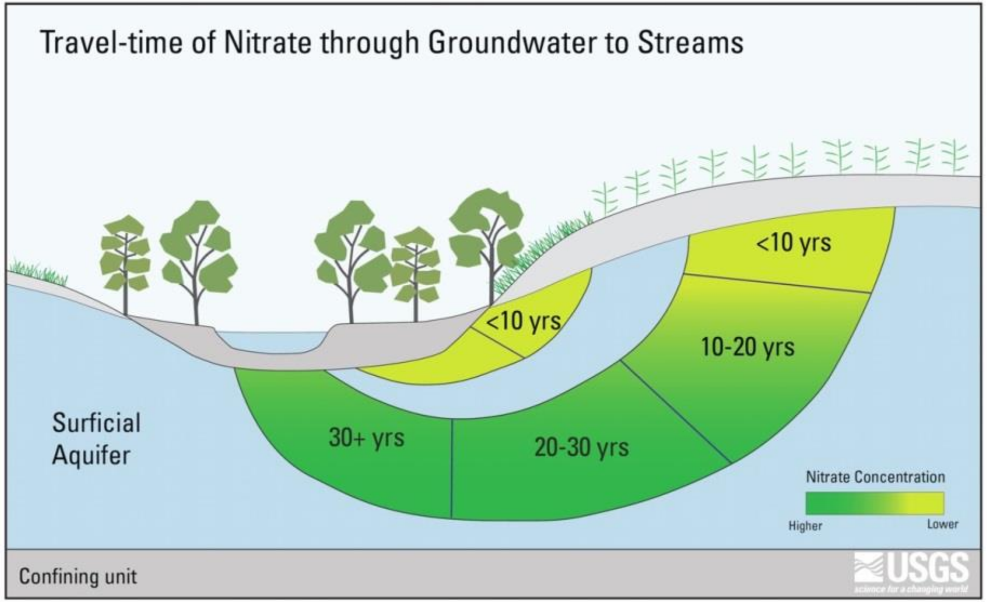
Agricultural Nutrient Sources

1. Fertilizers
    a. Synthetic
    b. Organics (manure)
2. Livestock residues
3. Groundwater contamination

Agricultural Nutrient Sources

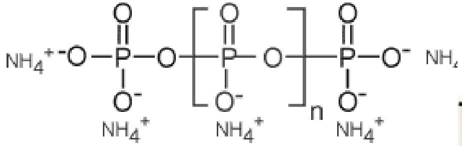
It can take a long time to clean a watershed

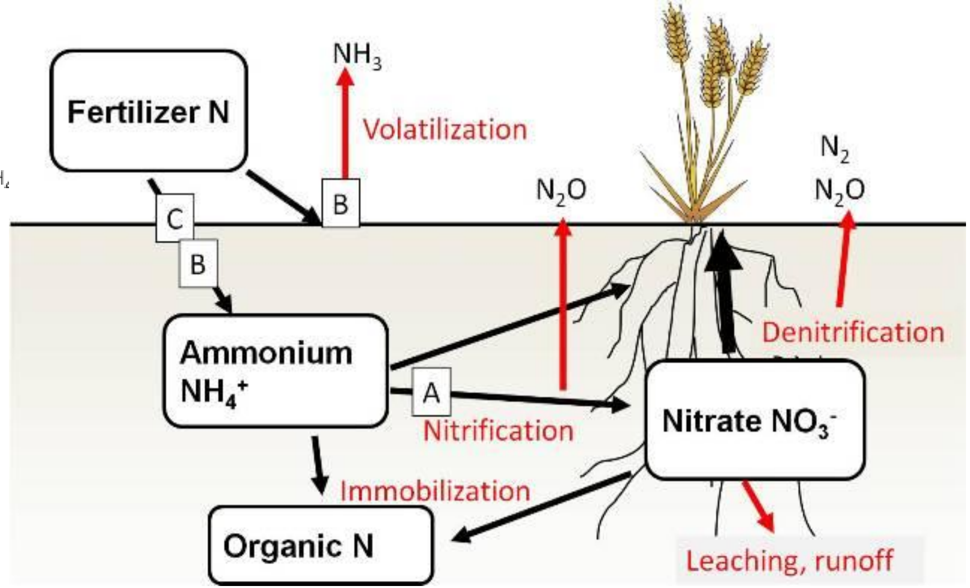


Why nitrate?

Agricultural Nutrient Sources

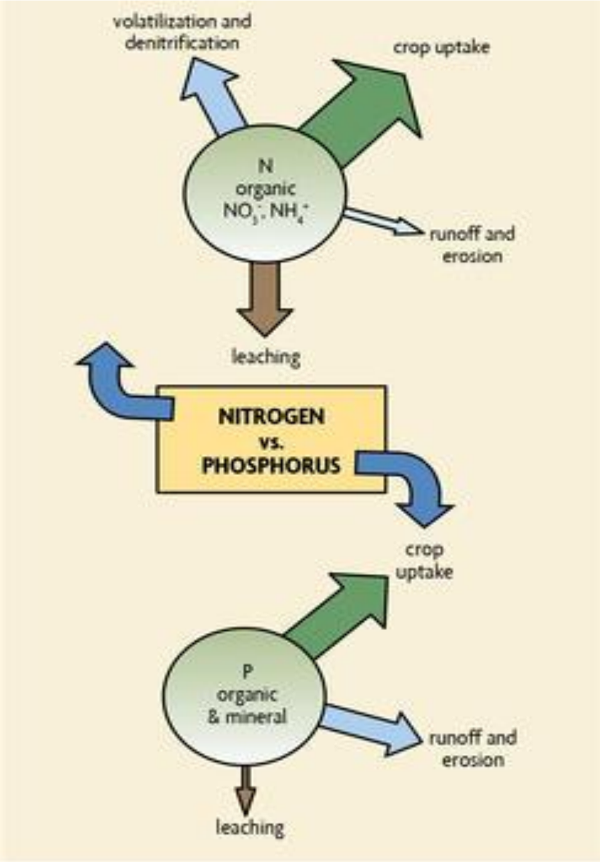
N as NH_4
P as PO_4





Agricultural Nutrient Sources

How does N and P end up in agricultural streams?



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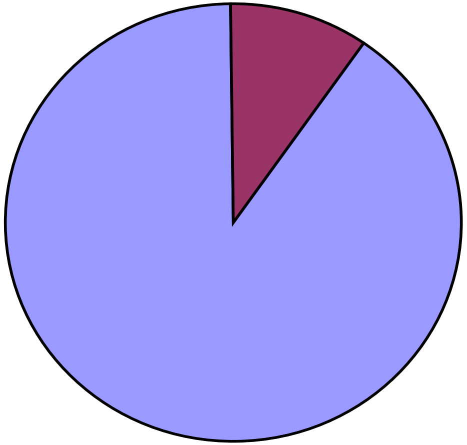
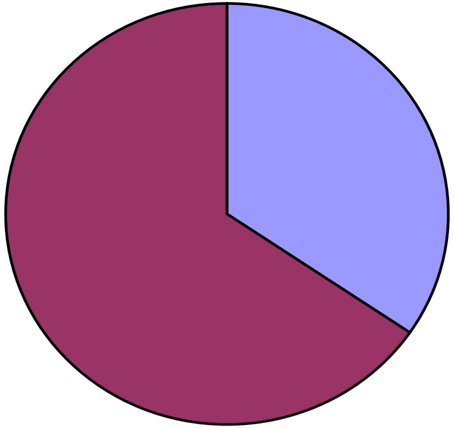
Agricultural Nutrient Sources

Most nitrogen enters via baseflow

Most phosphorus enters via stormflow



NITROGEN



PHOSPHORUS

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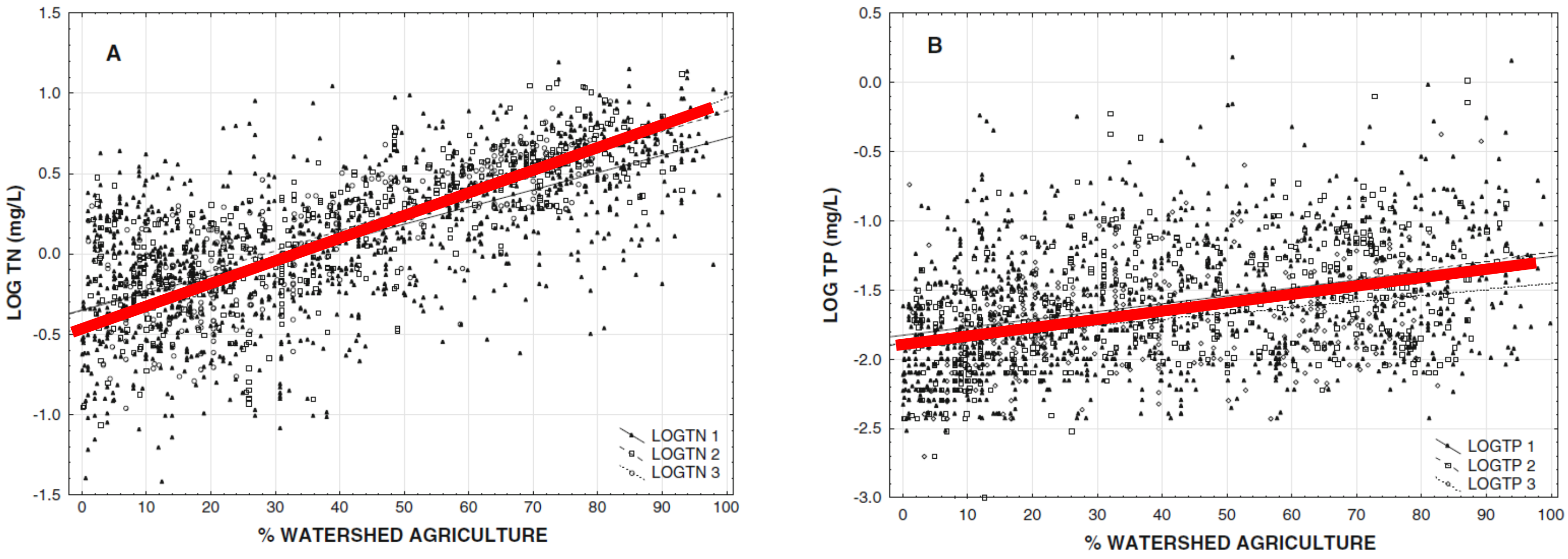
Agricultural Nutrient Sources



Maryland Biological Stream Survey (Morgan et al. 2012)
total nitrogen (TN) and total phosphorus (TP) of small-order

Differences between N and P in the watershed

Nitrogen

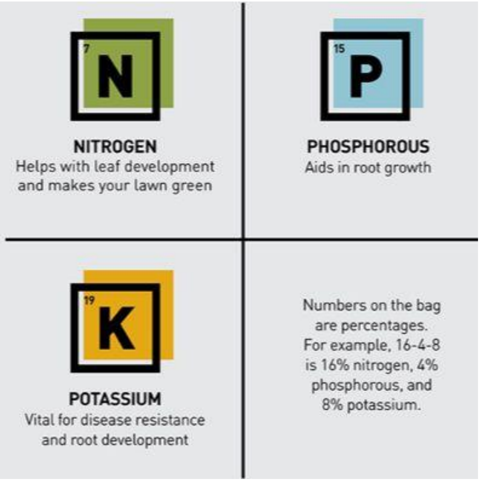
- Available from decomposing soil organic matter.

Phosphorus

- Available from organic matter and minerals.

Urban Sources

1. Lawn fertilizers



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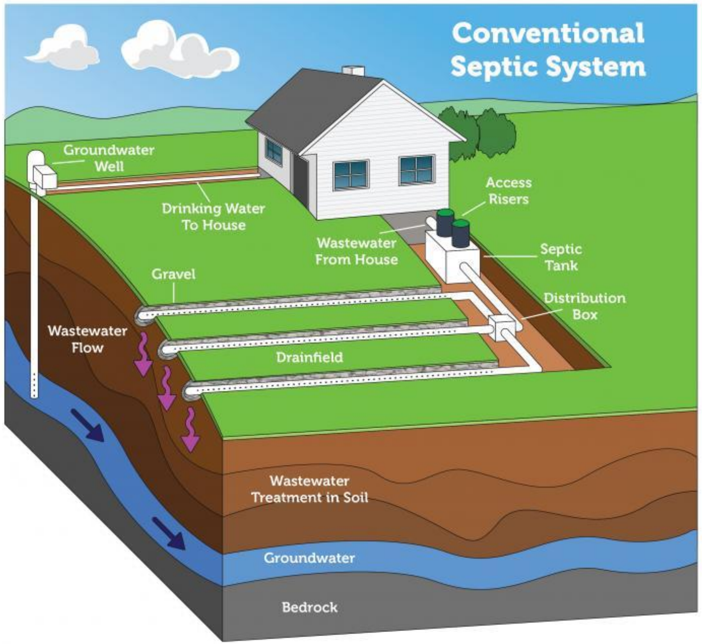
Urban Sources

1. Lawn fertilizers
2. Sewage (grey infrastructure)

Urban Sources

1. Lawn fertilizers
2. Sewage
3. Septic



Please note: Septic systems vary. Diagram is not to scale.

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Urban Sources

1. Lawn fertilizers
2. Sewage
3. Septic
4. Stormwater

Grey infrastructure

Green infrastructure

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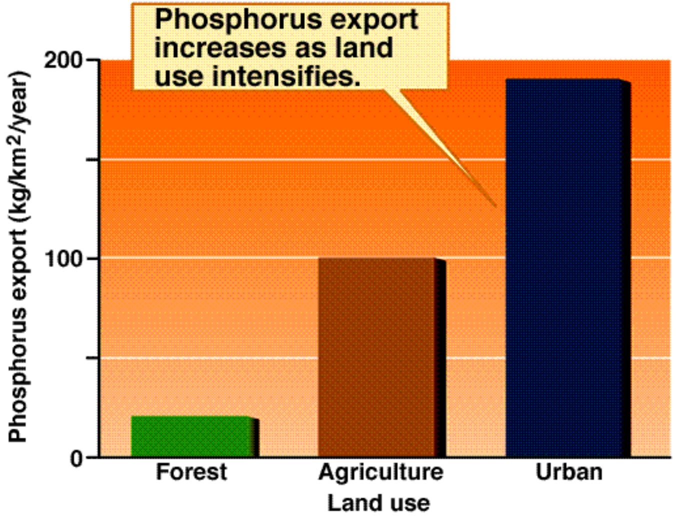
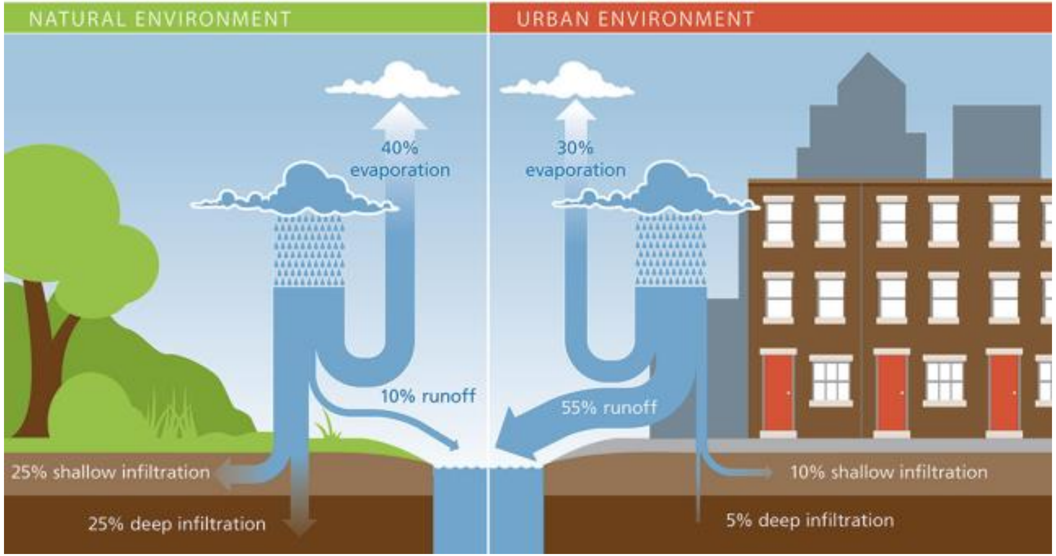
Urban Sources

1. Lawn fertilizers
2. Sewage
3. Septic
4. Stormwater
5. Industrial sources

Urban Sources

How does N and P end up in urban streams?





+ urban development → more P and at high-flows

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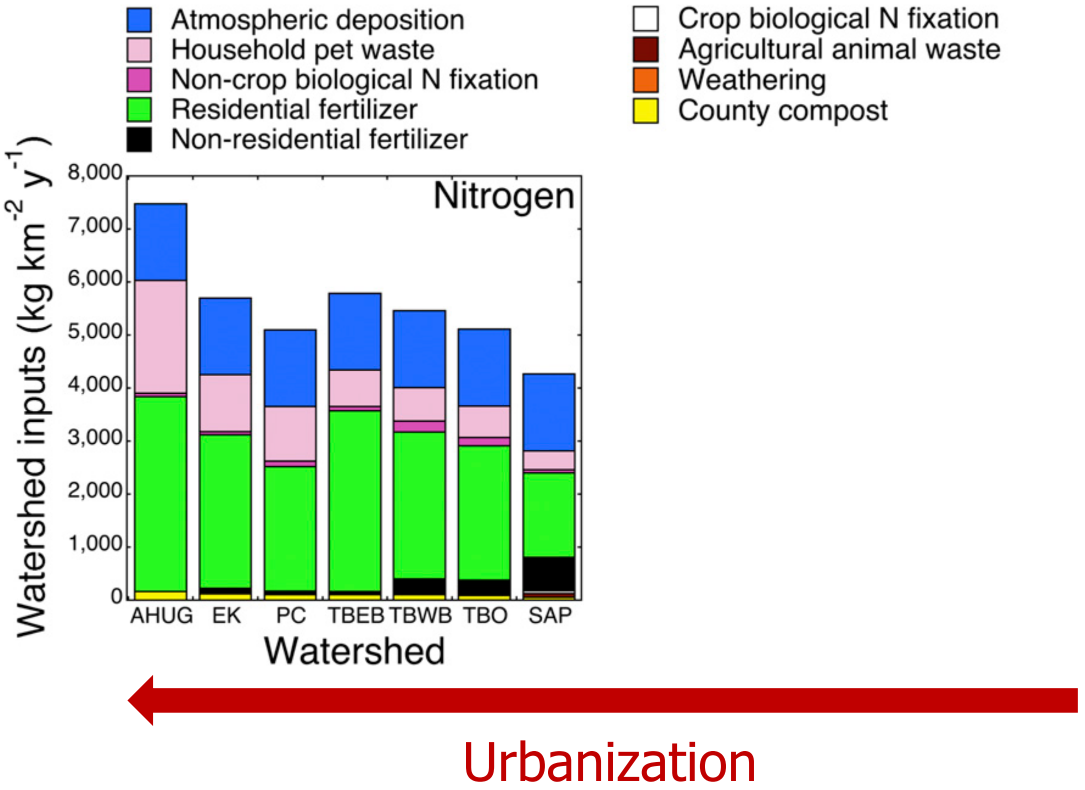
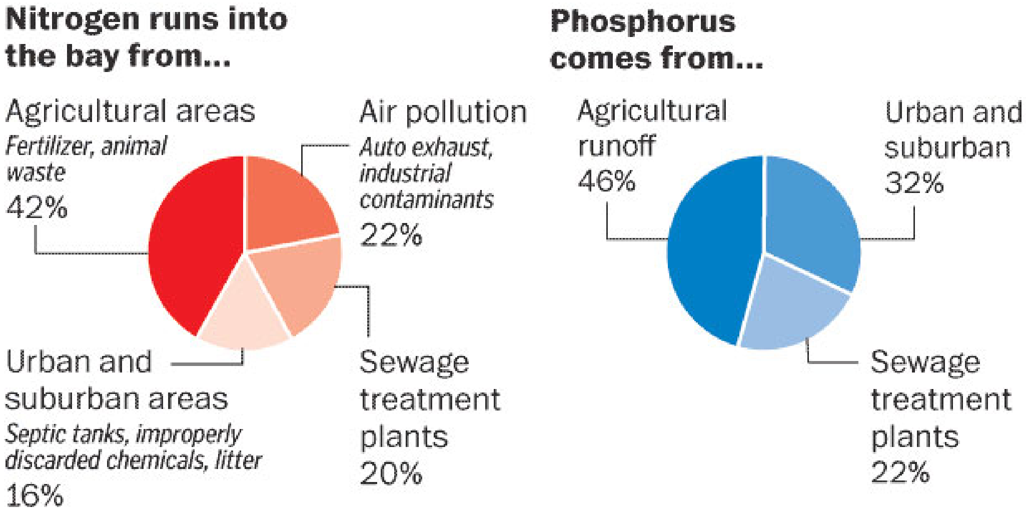
How does N and P end up in urban streams?



Hobbie et al. 2017

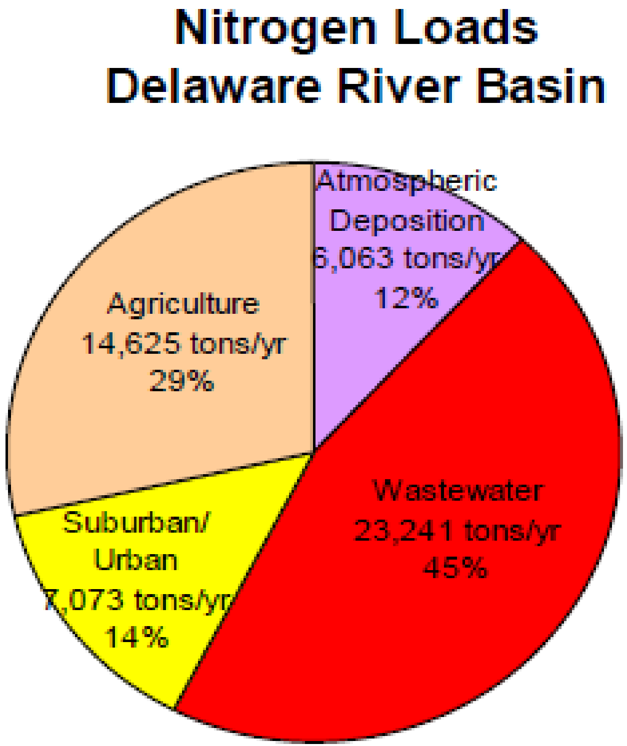
Agricultural and Urban Impacts on Watersheds

In the Chesapeake Bay Watershed



Agricultural and Urban Impacts on Watersheds

In the Delaware River Watershed



Kauffman 2018

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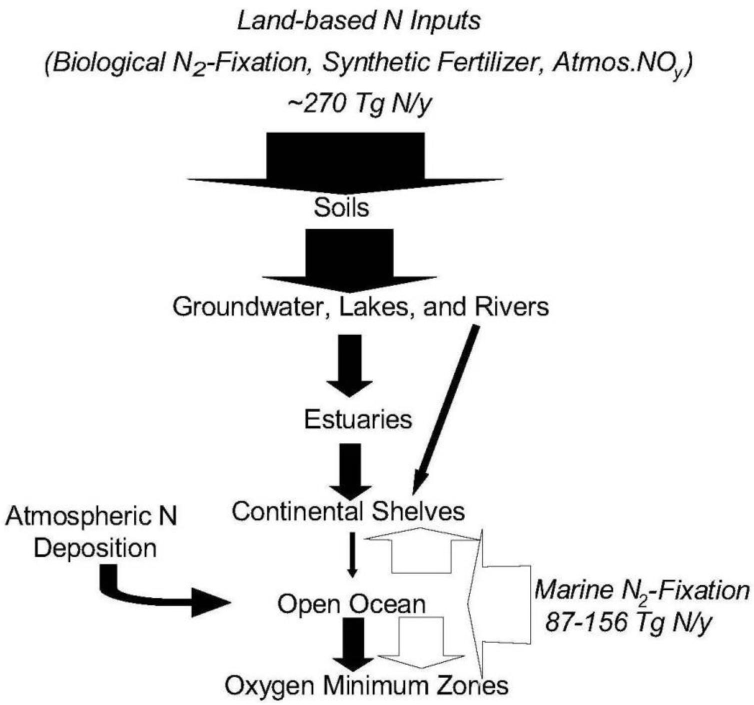
Agricultural and Urban Impacts on Watersheds

Consequences of increasing loads of nutrients in urban and agricultural watersheds…

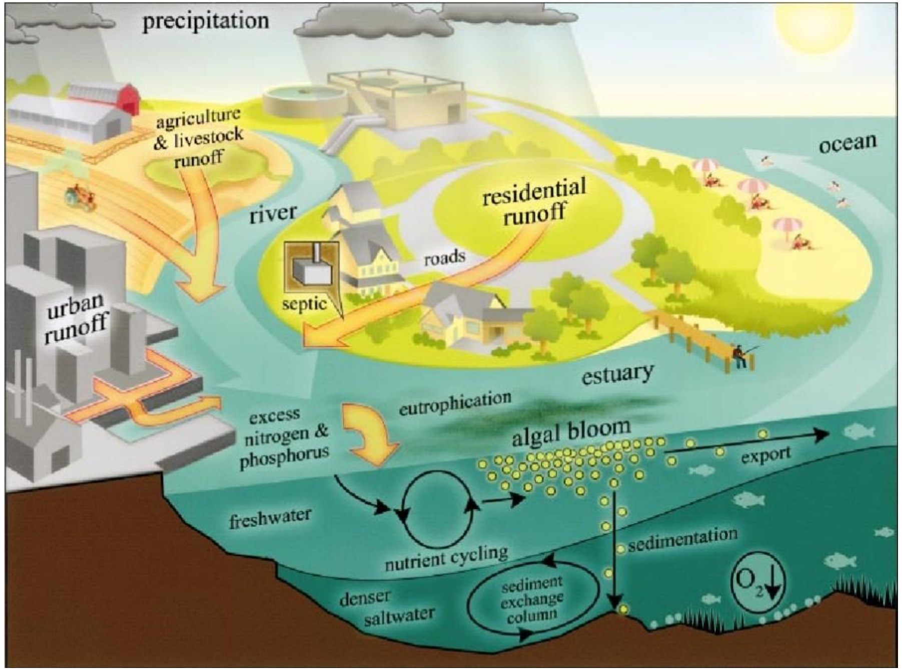
Freshwater Eutrophication



Vast majority of land-based N inputs disappear in terrestrial ecosystems (soils) and at the interface between terrestrial and aquatic environments (groundwater, lakes and rivers).

Seitzinger et al. (2006).

Eutrophication



Causes:

- Warm Temperatures
- High N or High P or High N&P
- Light

Consequences:

- Biomass growth
- Temporal Loss of biodiversity
- Anoxia
- Permanent Loss of biodiversity

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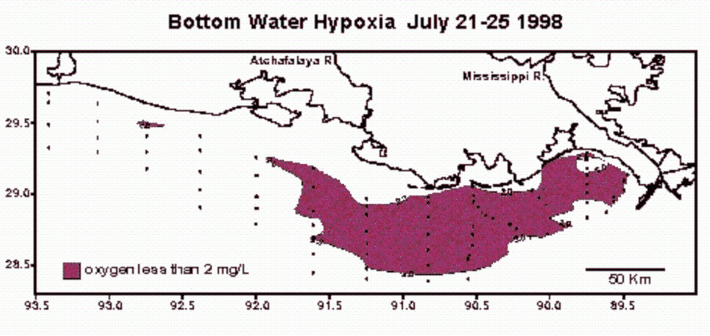
Marine Eutrophication

Anoxic zone in the Gulf of Mexico



Algal blooms in Great lakes

Algal blooms in the Bays

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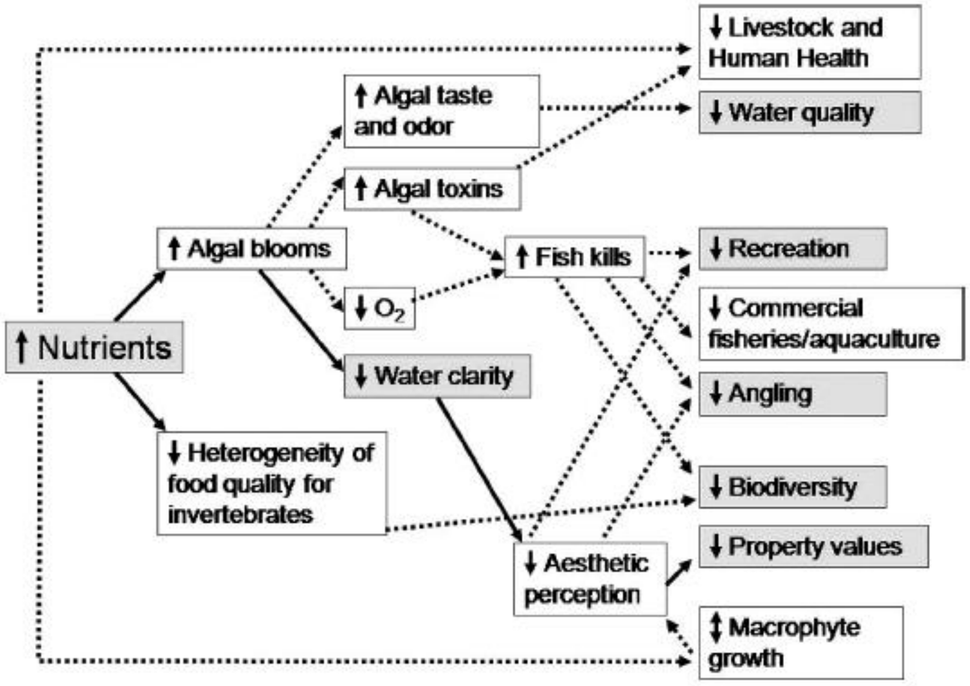
Eutrophication in Running Waters



Dodds et al. 2009

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Eutrophication in Running Waters

Nitrogen Enrichment	Phosphorus enrichment
Decline in species numbers	Decline in species numbers
Decline in rare species	Decline in numbers of rare species
Decline in mosses	Decline in mosses
Increase in *Lemna* sp	Increase in *Cladophora, Enteromorpha, Potamogeton pectinatus, Sparganium erectum, Apium nodiflorum and Lemna minor*

Dawson et al. 1999

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Stream Eutrophication

Effluents of sewage treatment facilities

Effluent input

Flow direction

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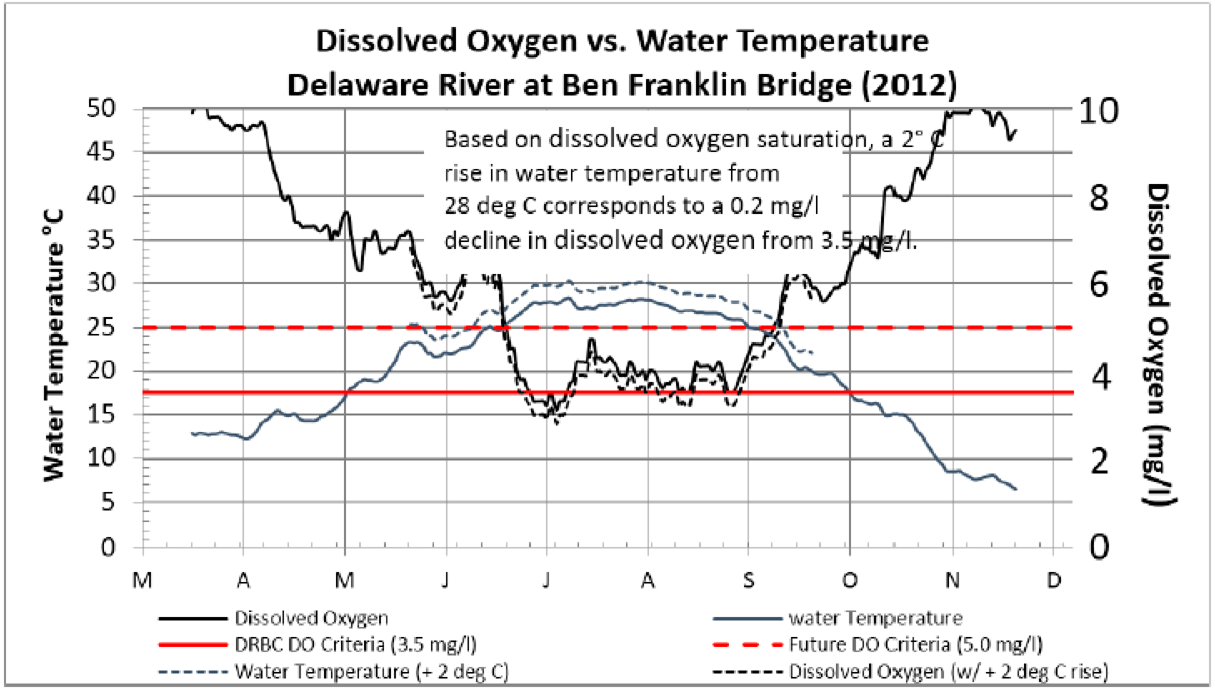
River Eutrophication



Kauffman 2018

Outline

1. Introduction and Natural Conditions
   a. What's in the water?
   b. How do we measure it?
   c. Nitrogen and Phosphorous Cycles
2. Urban and Agricultural Impacts
   a. Sources and processes
   b. How do N and P get to the stream?
3. Effects and Efficacy of Remediation
   a. Riparian buffers/Farming practices
   b. Stormwater BMPs
   c. Are we cleaning our waters?

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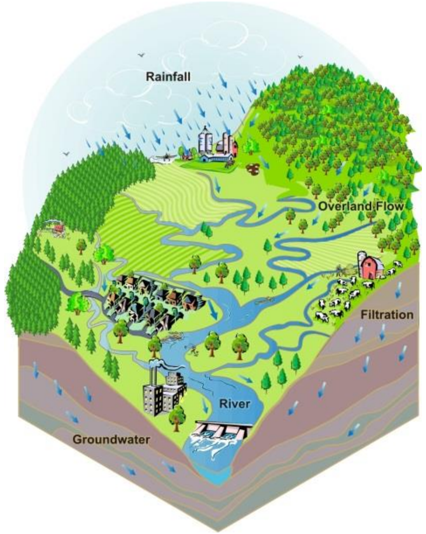

Riparian Buffers/Farming Practices

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Riparian Buffers

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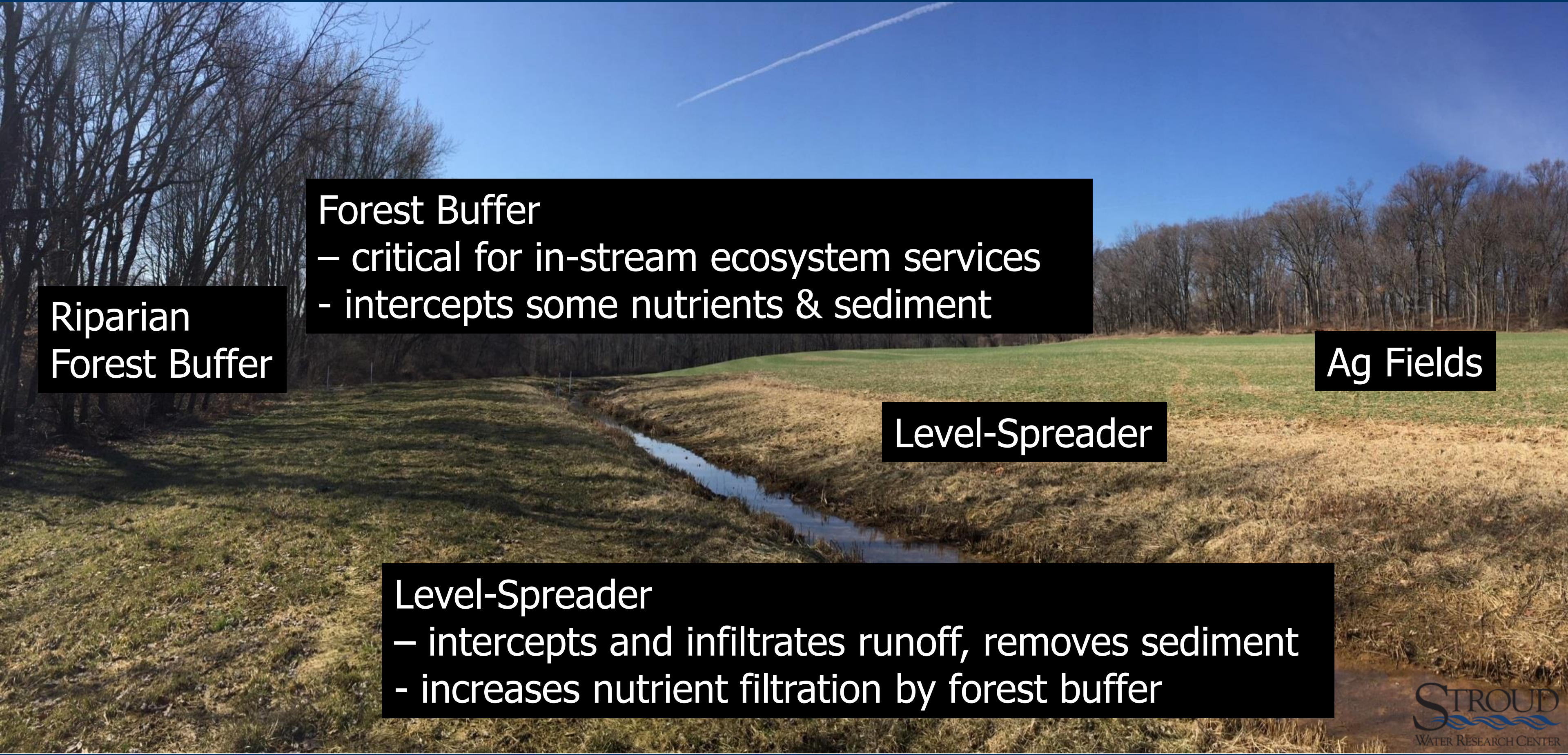
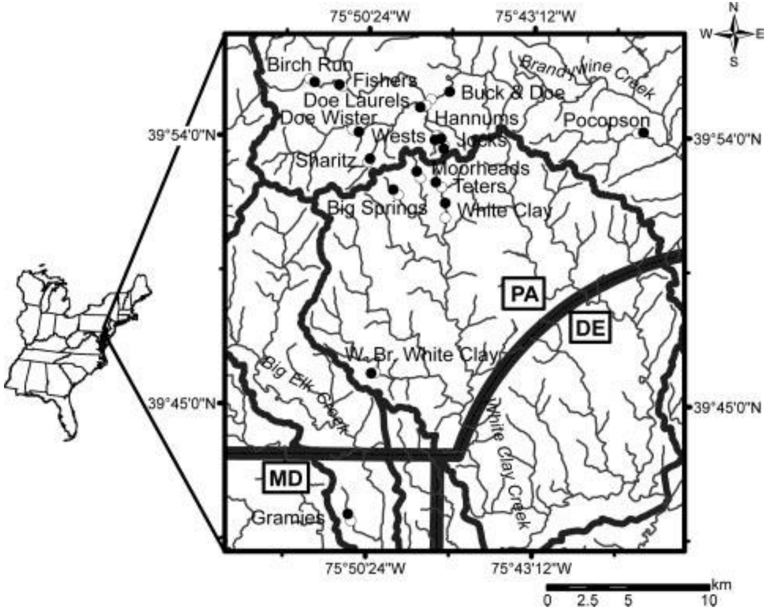
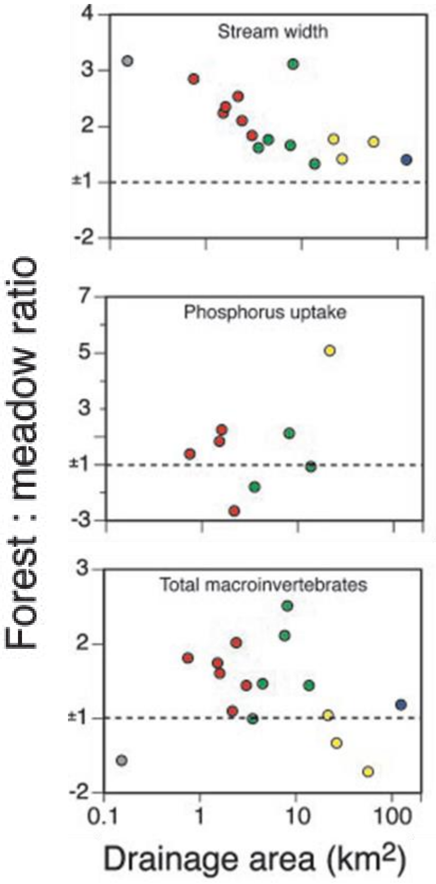
Riparian Buffers



Riparian Buffers

Ecosystem Services of Riparian Buffers





Sweeney et al. 2004

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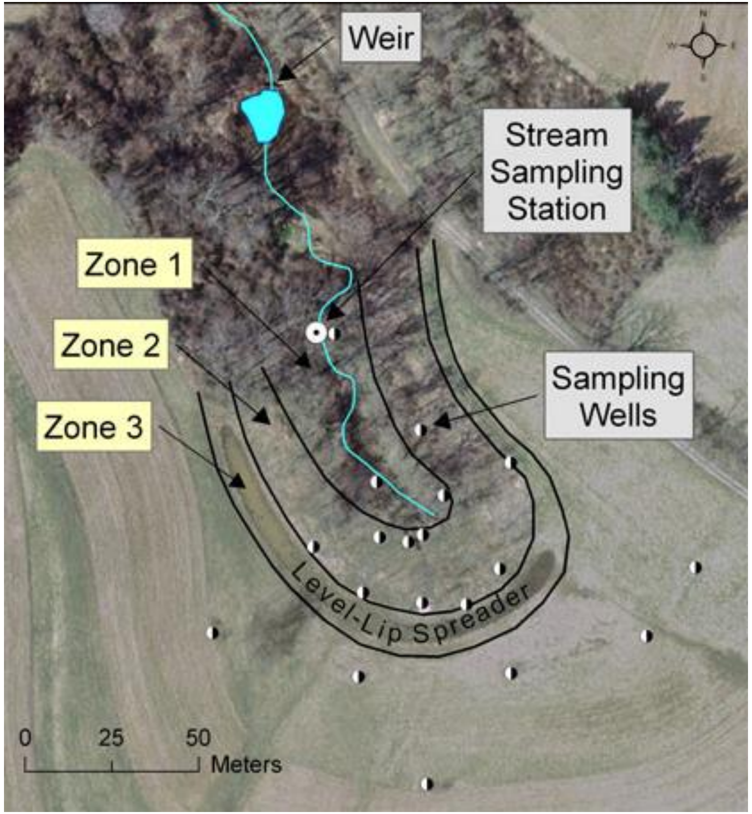
Riparian Buffers

Case study:
The Stroud Preserve

Riparian Buffers: The Stroud Preserve

Proof of Concept:

1) Demonstrate ability of riparian reforestation to improve water quality
2) Assess time needed to achieve full benefit of restoration



Riparian Buffers: The Stroud Preserve

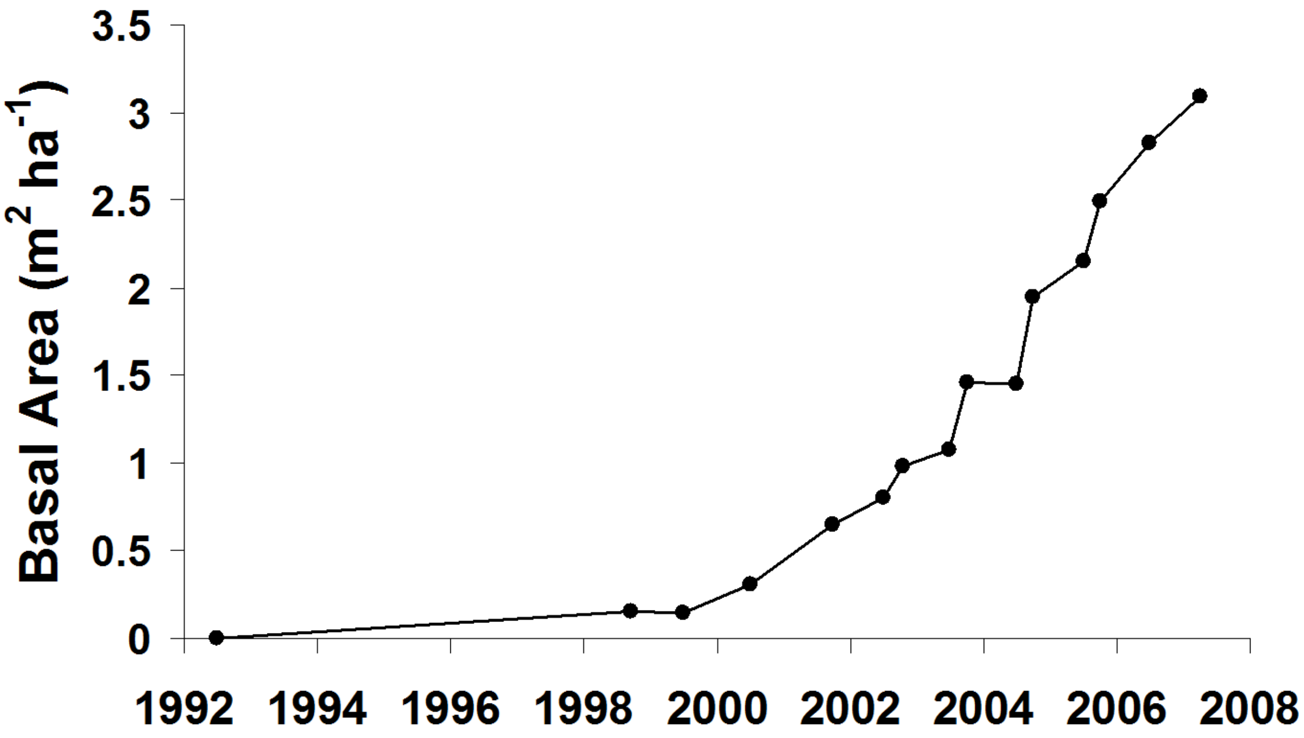
Trees planted in 1992

Level-lip spreader
1994

1999

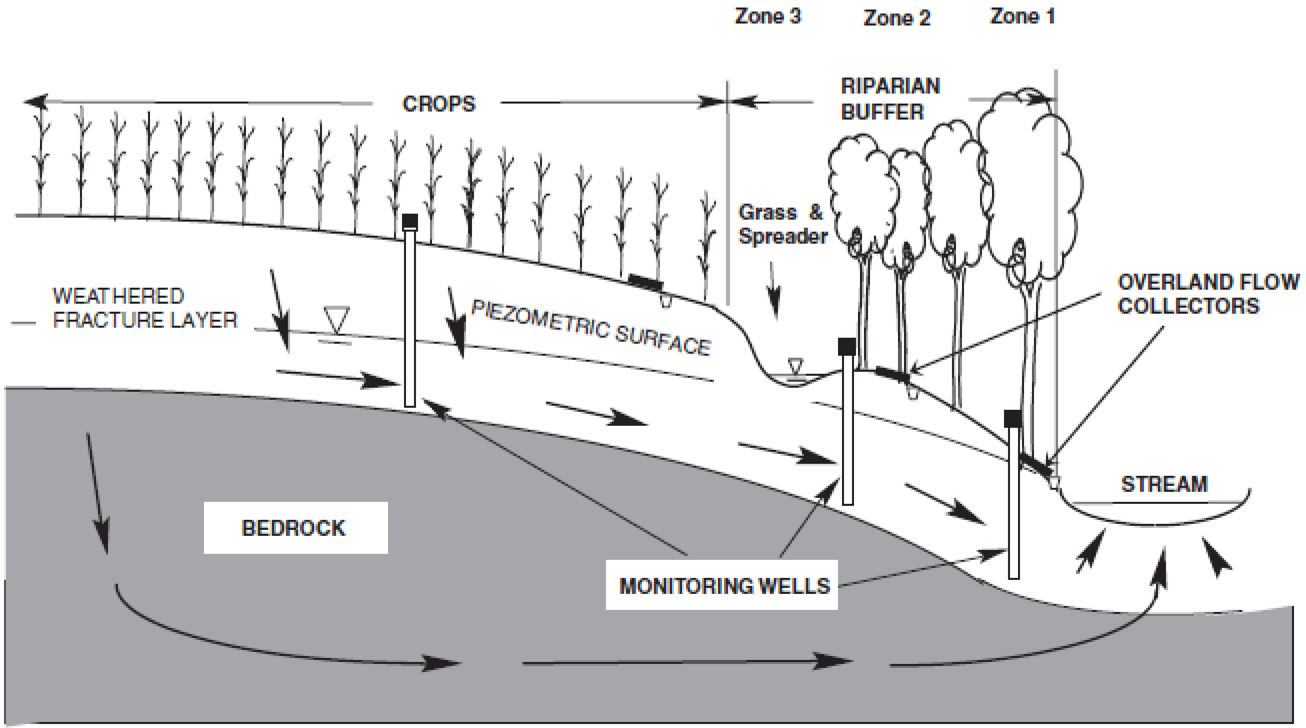
2006

Riparian Buffers: The Stroud Preserve



Newbold et al. 2012

Riparian Buffers: The Stroud Preserve



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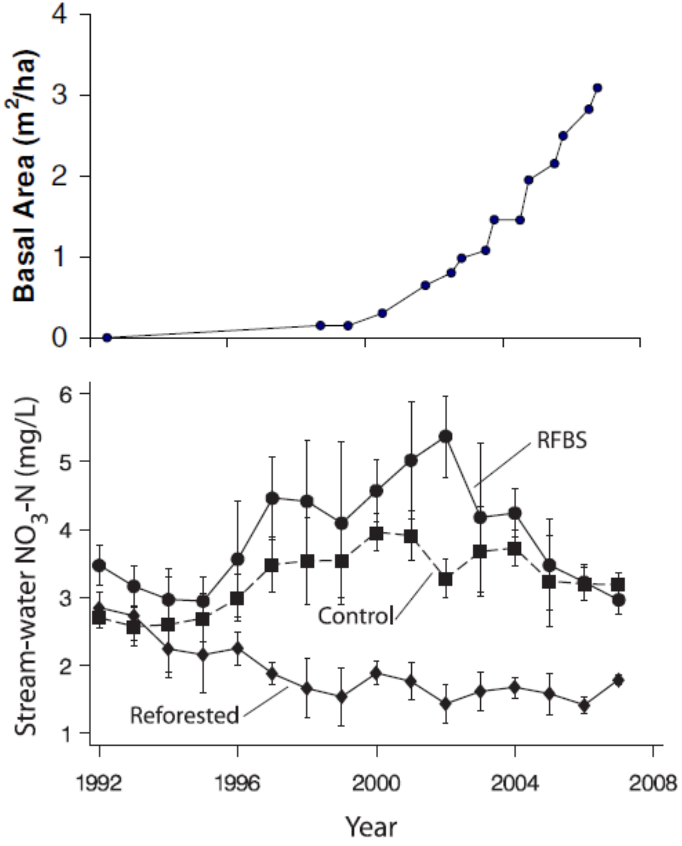
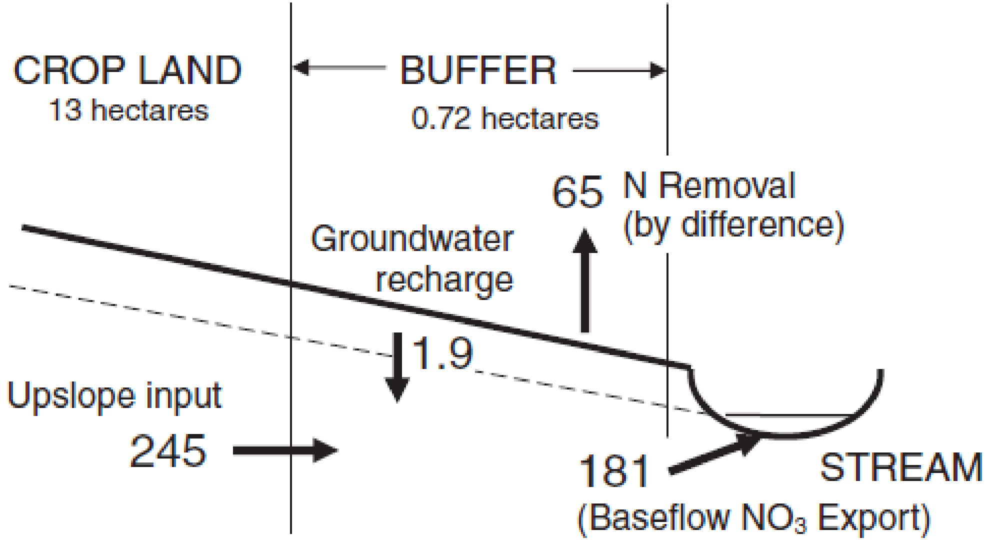
Riparian Buffers: The Stroud Preserve



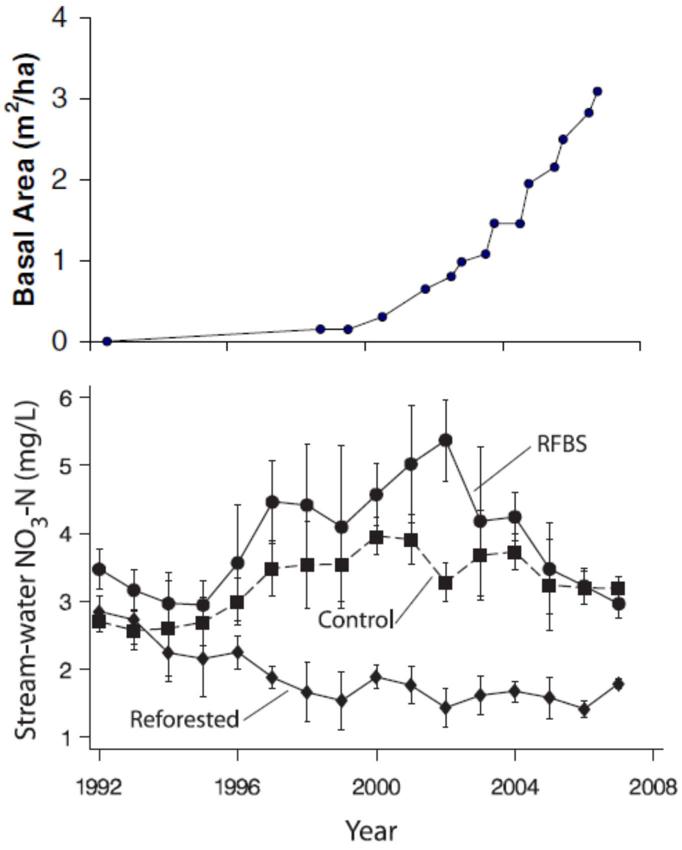
- N pollution decreasing as buffer grows
- N enters via baseflow (leaching)

Riparian Buffers: The Stroud Preserve



26% of upslope subsurface N inputs

Riparian Buffers: The Stroud Preserve



- N pollution decreasing as buffer grows
- N enters via baseflow (leaching)

- P pollution unaffected
- P enters via stormflow (runoff)
- But TSS was reduced by 43%, and particular P was 22% lower on average

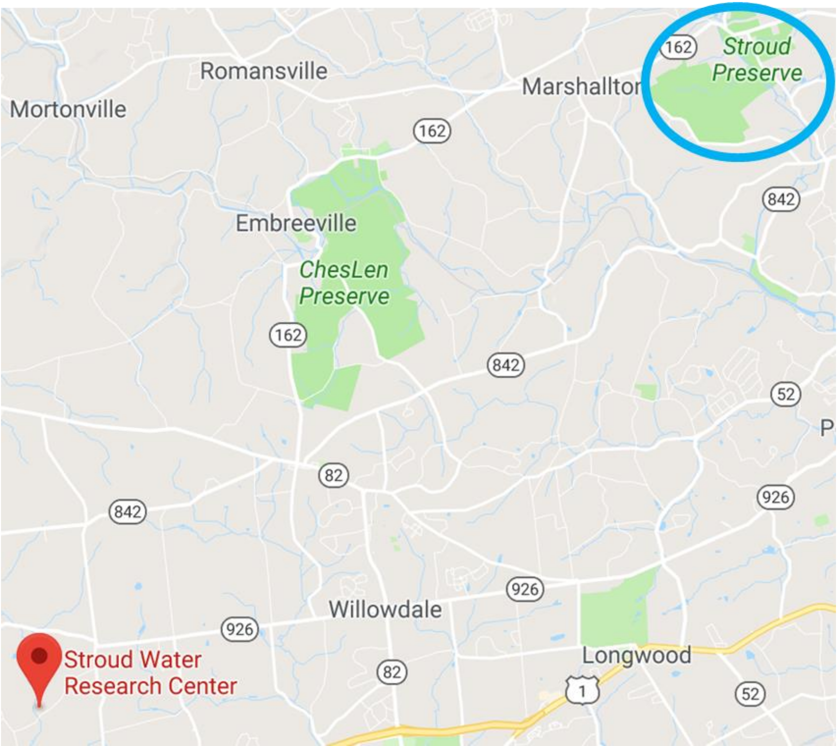
Riparian Buffers: The Stroud Preserve

- The riparian buffer removes ~26% of nitrate from subsurface flow.
- The riparian buffer removes ~40% of sediment from overland flow.
- The spreader removes ~26% of particulate phosphorus, but removal by buffer system is not significant.

The Stroud Preserve

The work continues: 2018-2023

Farming Practices: The Stroud Preserve



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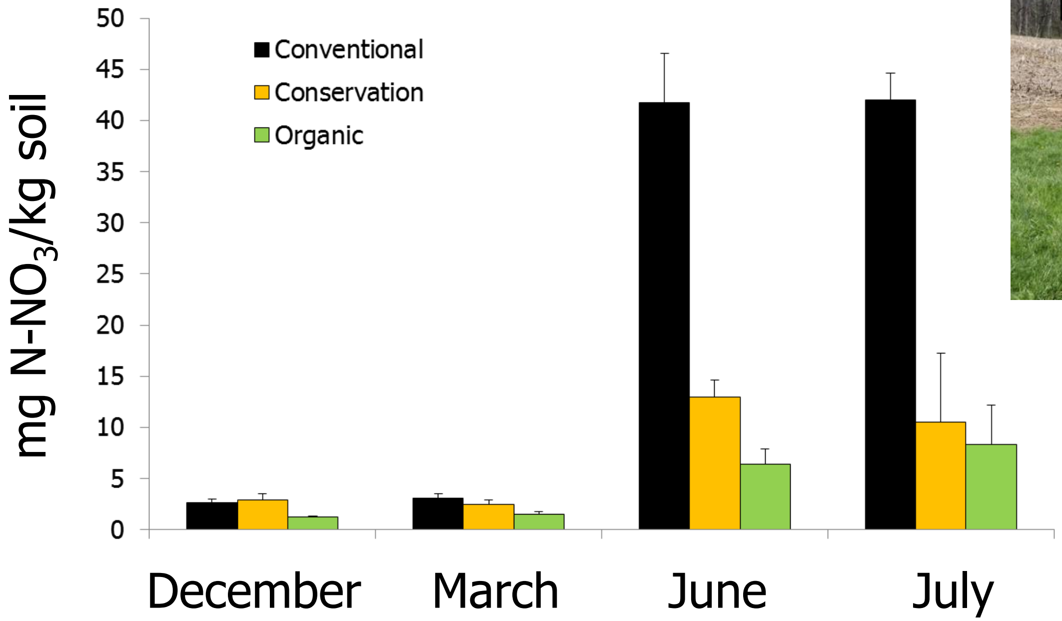
Farming Practices: The Stroud Preserve

Farming Systems	Cover Crop	Tilled	Fertilizer	Pesticides
Conventional	No	Yes	Synthetic	Synthetic
Conservation	Yes	No	Synthetic	Synthetic
Organic till	Yes	Yes	Manure/Compost	Non-synthetic
Organic no-till	Yes	No	Manure/Compost	Non-synthetic

Farming Practices: The Stroud Preserve

Farming practices and N storage



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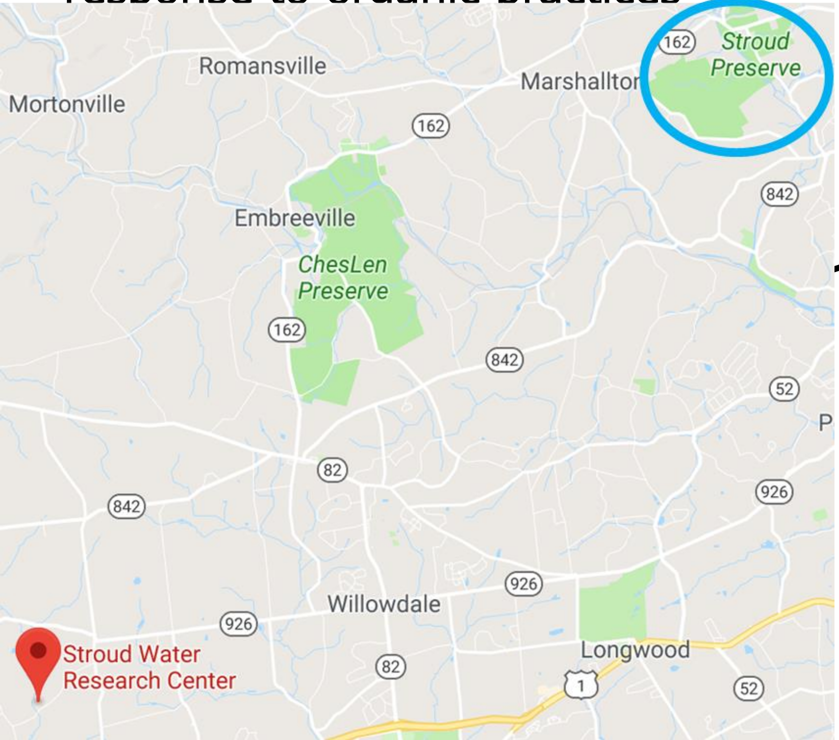
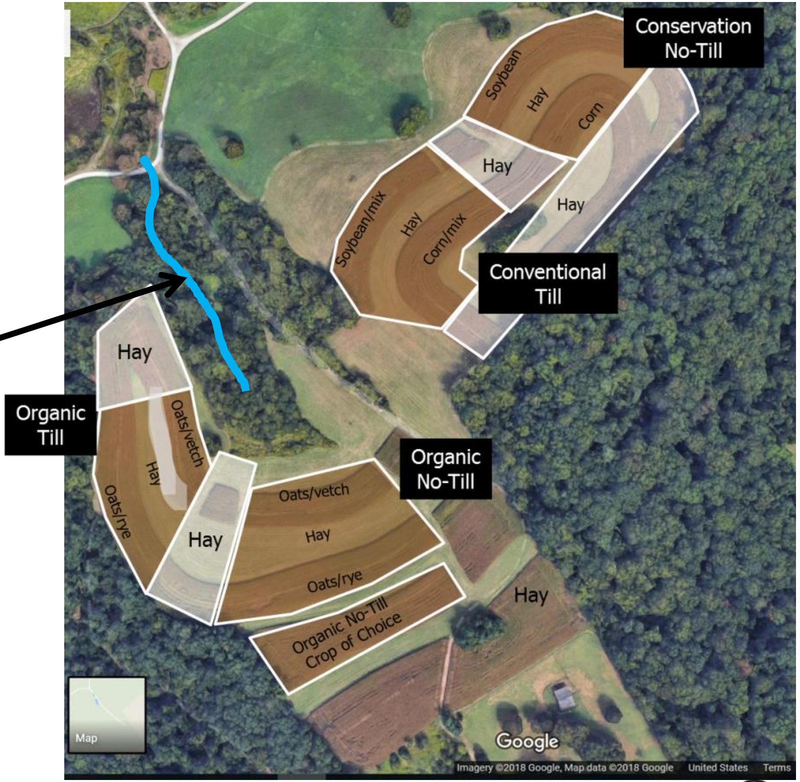
Farming Practices: The Stroud Preserve

Measure whole watershed stream response to organic practices





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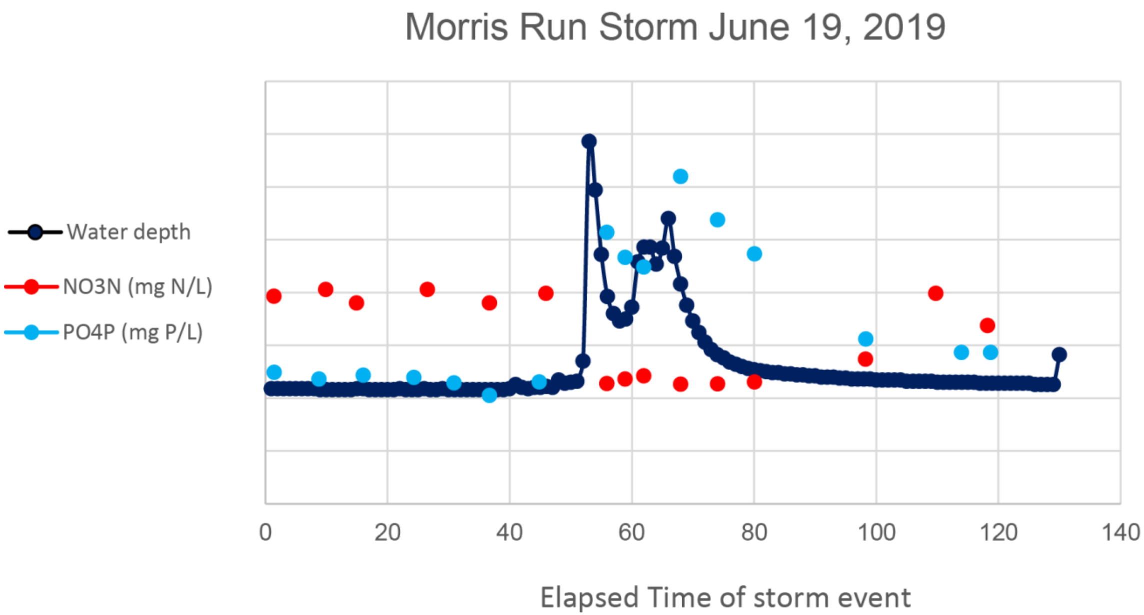
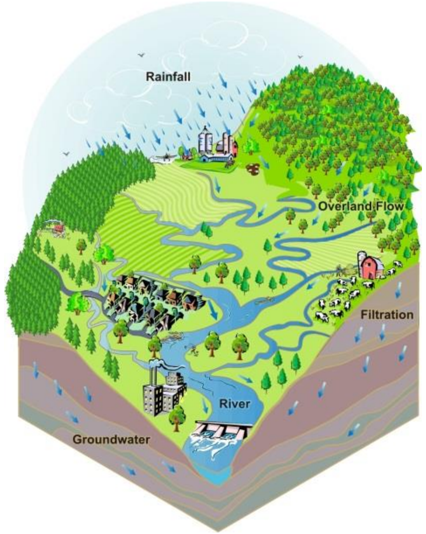
Farming Practices: The Stroud Preserve

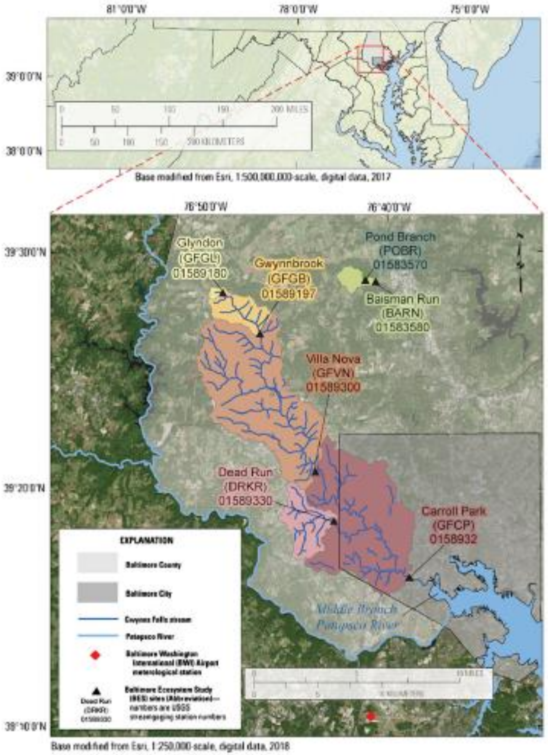
Morris Run, 27 years after tree planting

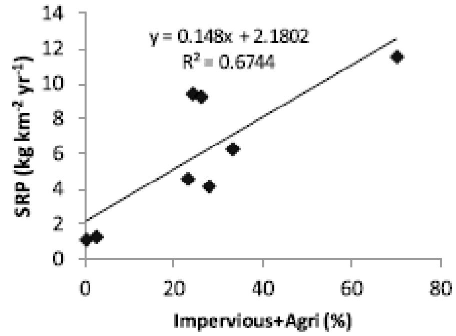


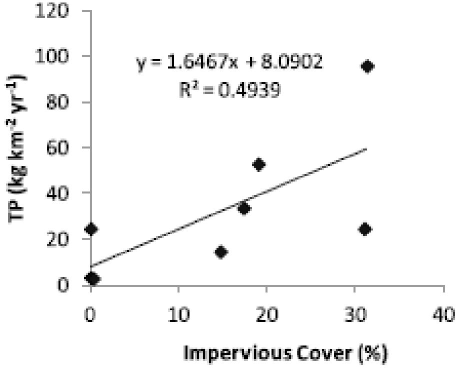


Stormwater infrastructure

Stormwater infrastructure



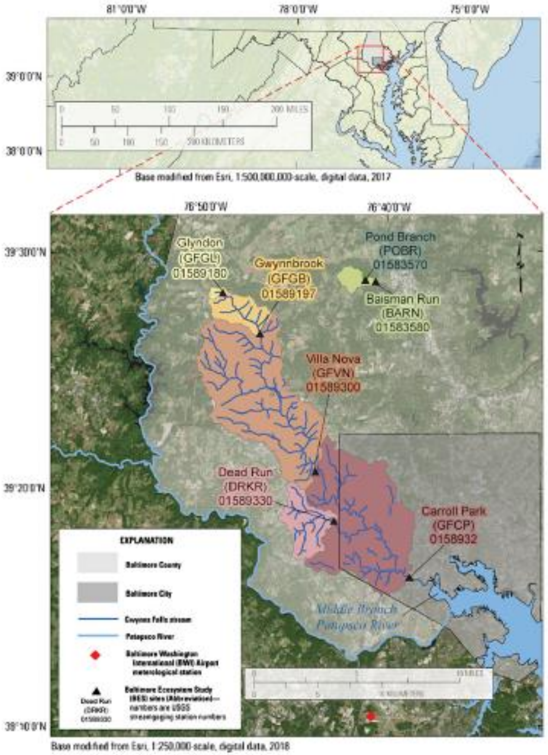


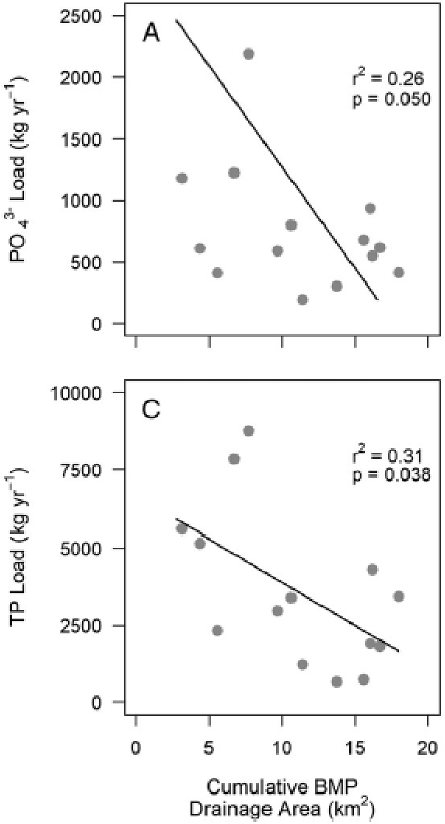


Urban and Ag practices increasing loads of PO4 and TP

Duan et al. 2012
Reisinger et al. 2019

Stormwater infrastructure





Grey and Green BMPs resulting in decreased loads of PO4 and TP

Duan et al. 2012
Reisinger et al. 2019

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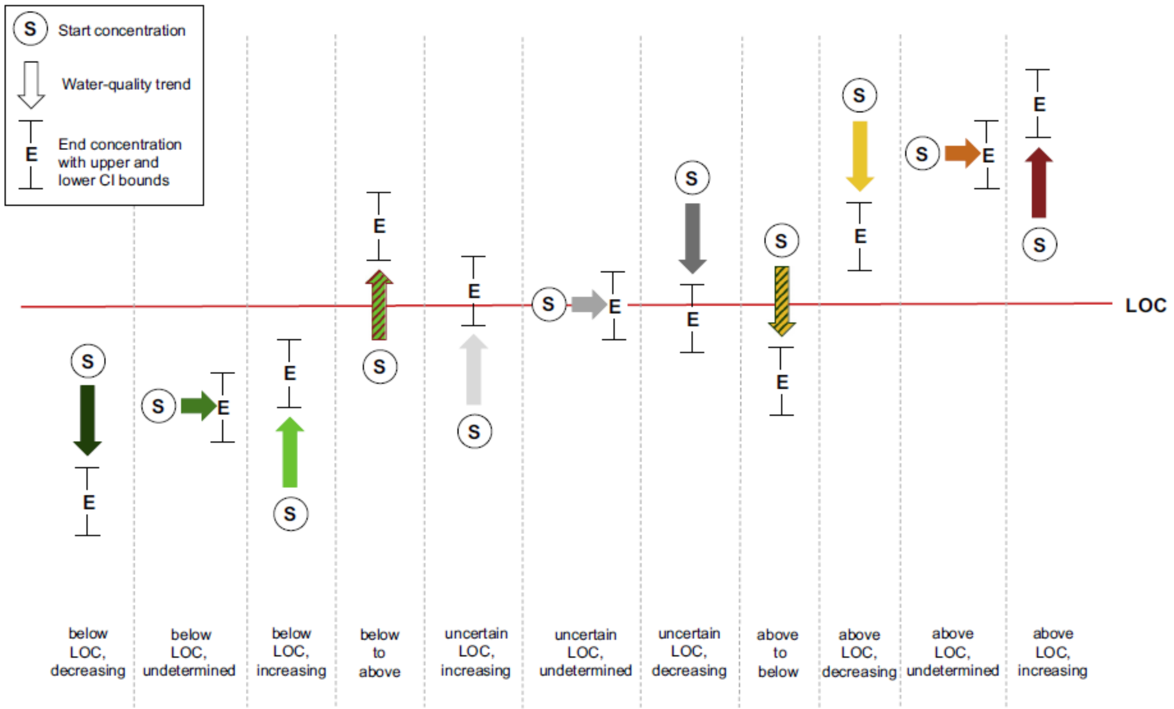
Are we improving water quality?

Water-quality trends for TDS at 762 sites in the conterminous US between 2002 and 2012.



US EPA National Primary drinking water Regulation

Shoda et al. 2018

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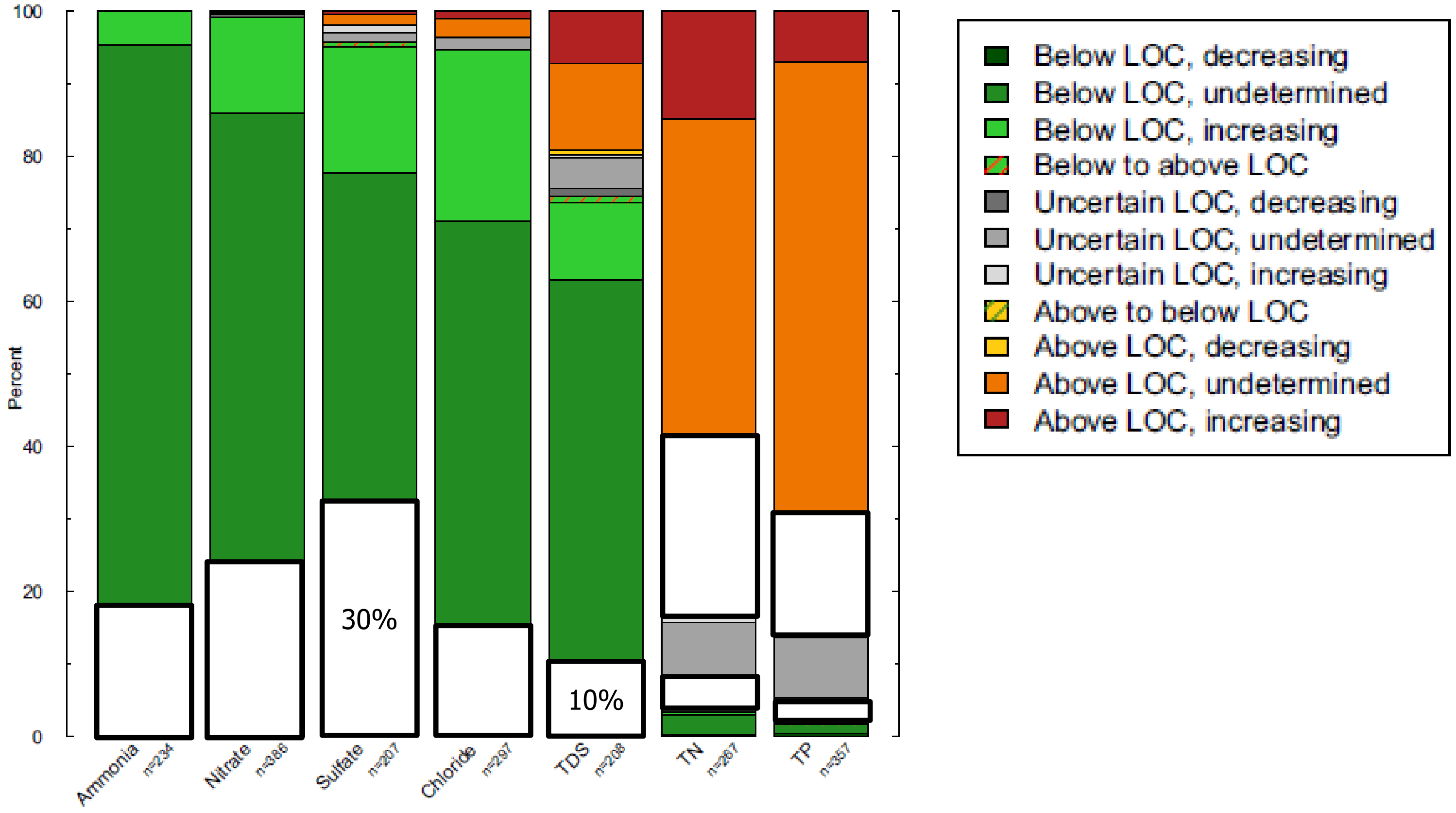
Are we improving water quality?



Shoda et al. 2018

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