Chemical Properties of Watersheds

Stream Ecology and the Chemical Template
Geologic Influence on Water Chemistry
Temperature, pH, Alkalinity, Acidity
Nitrogen, Phosphorus, Carbon Cycles

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Learning Objectives

- Multi-dimensional nature of stream water chemistry
- What is “water quality”?
- Influences/drivers of patterns of stream water chemistry
- How and why does water quality change over time?

What's in your water?

- How many people know where their drinking water comes from?
- Do you know what the water quality is of your drinking water?
  - Or how to find that information?

https://i0.wp.com/www.nationofchange.org/wp-content/uploads/2017/04/drinkingwater.jpg?resize=696%2C391

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What's in your water?

2016
Drinking Water Quality Report
Featuring data collected in 2015

PHILADELPHIA WATER
EST. 1801

This report is produced for you as a requirement of the Federal Safe Drinking Water Act. NOTE: Industrial and commercial customers, including hospitals, medical centers and health clinics, please forward this report to your Environmental Compliance Manager.

PWD's Public Water System Identification #PA1510001

http://www.phila.gov/water/wu/Water%20Quality%20Reports/2016waterquality.pdf

What's in your water?

WHAT DO WE LOOK FOR?

Public Drinking Water Systems monitor their treated drinking water for approximately 100 regulated contaminants. These regulatory parameters are defined within federal rules such as the Total Coliform Rule, Surface Water Treatment Rule, Disinfectants and Disinfection Byproducts Rules, Lead and Copper Rule and the Radionuclides Rule. We monitor for the regulated parameters listed below. Tables on pages 14-17 summarize monitoring results for parameters found at detectable levels. Please see a glossary of terms and abbreviations on page 13.

Inorganic Chemicals:

Antimony, Arsenic, Barium, Beryllium, Cadmium, Chromium, Cyanide Free, Fluoride, Mercury, Nickel, Selenium, Thallium

Synthetic Organic Chemicals:

Alachlor, Atrazine, Benzopyrene, Carbofuran, Chlordane, Dalapon, Di(ethylhexyl)adipate, Di(ethylhexyl)phthalate, Dibromochloropropane, Endothall, Ethylene Dibromide, Hexachlorocyclopentadiene, Lindane, Methoxychlor, Oxamyl, PCBs Total, Pentachlorophenol, Picloram, Simazine

Volatile Organic Chemicals:

Benzene, Carbon Tetrachloride, 1,2-Dichloroethane, o-Dichlorobenzene, p-Dichlorobenzene, 1,1-Dichloroethylene, cis-1,2-Dichloroethylene, trans-1,2-Dichloroethylene, Dichloromethane, 1,2-Dichloropropane, Ethylbenzene, Monochlorobenzene, Styrene, Tetrachloroethylene, Toluene, 1,2,4-Trichlorobenzene, 1,1,1-Trichloroethane, 1,1,2-Trichloroethane, Trichloroethylene, o-Xylene, m,p-Xylenes

Appealing to Your Senses

We also test for aluminum, chloride, color, iron, manganese, odor, pH, silver, sulfate, surfactants, total dissolved solids and zinc to ensure that your water meets all water quality taste and odor guidelines. This is so that your water looks, tastes and smells the way it should.

Temperature and Cloudiness

The temperature of the Schuylkill and Delaware Rivers varies seasonally from approximately 34 degrees to 82 degrees Fahrenheit. Philadelphia Water does not treat the water for temperature. Cloudiness in tap water most commonly happens in the winter, when the cold water from the water main is warmed up quickly in household plumbing. Cold water and water under pressure can hold more air than warmer water and water open to the atmosphere. When really cold winter water comes out of your tap, it's simultaneously warming up and being relieved of the pressure it was under inside the water main and your plumbing. The milky white color is actually just tiny air bubbles. If you allow the glass to sit undisturbed for a few minutes, you will see it clear up gradually.

What’s in your water?

LEAD AND COPPER - Tested at Customers’ Taps - Testing is done every 3 years. Most recent tests were done in 2014.						
	EPA's Action Level - for a representative sampling of customer homes	Ideal Goal (EPA's MCLG)	90% of PWD customers' homes were less than	Number of homes considered to have elevated levels	Violation	Source
Lead	90% of homes must test less than 15 ppb	0 ppb	5.0 ppb	7 out of 134	No	Corrosion of household plumbing; Erosion of natural deposits
Copper	90% of homes must test less than 1.3 ppm	1.3 ppm	0.31 ppm	0 out of 134	No	Corrosion of household plumbing; Erosion of natural deposits; Leaching from wood preservatives

SYNTHETIC ORGANIC CHEMICALS (SOC)						
Chemical	EPA's MCL	EPA's MCLG	Highest Result	Yearly Range	Violation	Source
Atrazine	3 ppb	3 ppb	0.18 ppb	0 - 0.18 ppb	No	Runoff from herbicide used on row crops

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What's in your water?

INORGANIC CHEMICALS (IOC) – PWD monitors for IOC more often than required by EPA.						
Chemical	Highest Level Allowed (EPA's MCL)	Ideal Goal (EPA's MCLG)	Highest Result	Range of Test Results for the Year	Violation	Source
Barium	2 ppm	2 ppm	0.062 ppm	0.025 - 0.062 ppm	No	Discharges of drilling wastes; Discharge from metal refineries; Erosion of natural deposits
Chromium	100 ppb	100 ppb	1 ppb	0 - 1 ppb	No	Discharge from steel and pulp mills; Erosion of natural deposits
Cyanide Free	200 ppb	200 ppb	13 ppb	0 - 13 ppb	No	Discharge from steel/ metal factories; Discharge from plastic and fertilizer factories
Fluoride	2 ppm*	2 ppm*	0.74ppm	0.70 - 0.74 ppm	No	Erosion of natural deposits; Water additive which promotes strong teeth; Discharge from fertilizer and aluminum factories
Nitrate	10 ppm	10 ppm	4.30 ppm	0.74 - 4.30 ppm	No	Runoff from fertilizer use; Leaching from septic tanks; Erosion of natural deposits

**EPA's MCL and MCLG is 4 ppm, but DEP has set this lower MCL and MCLG which takes precedence.*

What's in your water?

TOTAL ORGANIC CARBON (TOC) -Tested at Water Treatment Plants					
Treatment Technique Requirement	Baxter WTP One Year Range	Belmont WTP One Year Range	Queen Lane WTP One Year Range	Violation	Source
Percent of Removal Required	35 - 45%	25 - 45%	25 - 45%	n/a	Naturally present in the environment
Percent of Removal Achieved	16 - 66%	14 - 56%	35 - 73%	No	
Number of Quarters out of Compliance	0	0	0		

PWD achieved TOC removal requirements in all quarters of 2015 at all WTPs. Compliance is based on a running annual average computed quarterly.

TURBIDITY - A MEASURE OF CLARITY - Tested at Water Treatment Plants					
	Baxter WTP	Belmont WTP	Queen Lane WTP	Violation	Source
Treatment Technique Requirement: *95% of samples must be at or below 0.300 NTU*	100% below 0.300 NTU	100% below 0.300 NTU	100% below 0.300 NTU	n/a	Soil runoff, river sediment
Highest single value for the year	0.088 NTU	0.093 NTU	0.100 NTU	No	

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What's in your water?

TOTAL CHLORINE RESIDUAL - Continously Monitored at Water Treatment Plants.					
Sample Location	Minimum Disinfectant Residual Level Allowed	Lowest Level Detected	Yearly Range	Violation	Source
Baxter WTP	0.2 ppm	1.91 ppm	1.91 - 3.40 ppm	No	Water additive used to control microbes
Belmont WTP		1.54 ppm	1.54 - 3.01 ppm		
Queen Lane WTP		1.02 ppm	1.02 - 3.66 ppm		

RADIOLOGICAL CONTAMINANTS						
	EPA's MCL	EPA's MCLG	Highest Result	Yearly Range	Violation	Source
Alpha Emitters	15 pCi/L	0 pCi/L	0 pCi/L	0 - 0 pCi/L	No	Erosion of natural deposits
Beta Emitters	50 pCi/L*	0 pCi/L	17.5 pCi/L	0.84 - 17.5 pCi/L	No	Decay of natural and man-made deposits
Combined Radium 226 & 228	5 pCi/L	0 pCi/L	0 pCi/L	0 - 0.0 pCi/L	No	Erosion of natural deposits
Combined Uranium	30 µg/L	0 µg/L	0 µg/L	0 - 0 µg/L	No	Erosion of natural deposits

NOTE: The state allows us to monitor for some contaminants less than once per year because the concentration for these contaminants does not change frequently. Required monitoring was conducted in 2014 except for Beta Emitters which was conducted in 2011.

**The MCL for beta particles is 4 mrem/year. EPA considers 50 pCi/L to be the level of concern for beta particles.*

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What's in your water?

DISINFECTION BY-PRODUCTS					
	Highest Level Allowed (EPA's MCL) - One Year Average	Running Annual Average 2015*	System Wide Range of Results	Violation	Source
Total Trihalomethanes (TTHMs)	80 ppb	49 ppb	16 - 89 ppb	No	By-product of drinking water disinfection
Total Haloacetic Acids (THAAs)	60 ppb	44 ppb	16 - 96 ppb	No	By-product of drinking water disinfection

**Monitoring is conducted at 16 locations throughout the City of Philadelphia. This result is the highest locational running annual average in 2015.*

What's in your water?

BACTERIA IN TAP WATER- Tested throughout the Distribution System. Over 380 samples collected throughout the City every month.						
	Highest Level Allowed (EPA's MCL)	Ideal Goal (EPA's MCLG)	Highest Monthly % or Yearly Total of Positive Samples	Monthly Range (% or #)	Violation	Source
Total Coliform	5% of monthly samples are positive*	0	1.20%	0 - 1.20%	No	Naturally present in the environment
Fecal Coliform or E. coli		0	0	0	No	Human or animal fecal waste

**Every sample that is positive for total coliforms must also be analyzed for either fecal coliforms or E. coli. If a system has two consecutive total coliform positive samples, and one is also positive for E. coli, then the system has an acute MCL violation.*

CRYPTOSPORIDIUM (Tested at Source Water to Water Treatment Plants Prior to Treatment)				
Treatment Technique Requirement	Baxter WTP One Year Range	Belmont WTP One Year Range	Queen Lane WTP One Year Range	Source
Total Number of Samples Collected	18	18	18	Naturally present in the environment
Number of Cryptosporidium Detected	5	5	9	
	0.028 count/L	0.033 count/L	0.050 count/L	

Cryptosporidium is a microbial pathogen found in surface water throughout the United States. Although filtration removes Cryptosporidium, the most commonly-used filtration methods cannot guarantee 100 percent removal. Our monitoring indicates the presence of these organisms in our source water. Current test methods do not allow us to determine if the organisms are dead or if they are capable of causing disease. For more information, please see the section on Cryptosporidium and Giardia on page 9.

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And still finding more to measure and be concerned about….

Nation of Change HOME ISSUES

Home › Environment › Popular farm pesticide found in drinking water

Environment | Food and Health | Politics

Popular farm pesticide found in drinking water

Though the study was exclusive to Iowa, it could have far-reaching effects on the entire U.S.

By **Cassie Kelly** - April 9, 2017 | News Report 645 7 Comments

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After evidence of pesticides killing off pollinators surfaced in 2016, scientists went on a quest to see if pesticides were seeping into anything else. Now, in an unprecedented study, the U.S. Geological Survey and University of Iowa reported findings of neonicotinoids – a class of pesticide used to kill off insects – in treated drinking water, marking the first time these chemicals have ever been identified.

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Environmental Science & Technology LETTERS

ACS Editors' Choice

Letter

pubs.acs.org/journal/estlcu

Occurrence of Neonicotinoid Insecticides in Finished Drinking Water and Fate during Drinking Water Treatment

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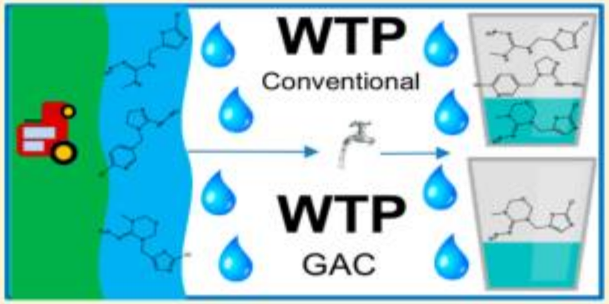
Supporting Information



ABSTRACT: Neonicotinoid insecticides are widespread in surface waters across the agriculturally intensive Midwestern United States. We report for the first time the presence of three neonicotinoids in finished drinking water and demonstrate their general persistence during conventional water treatment. Periodic tap water grab samples were collected at the University of Iowa over 7 weeks in 2016 (May–July) after maize/soy planting. Clothianidin, imidacloprid, and thiamethoxam were ubiquitously detected in finished water samples at concentrations ranging from 0.24 to 57.3 ng/L. Samples collected along the University of Iowa treatment train indicate no apparent removal of clothianidin or imidacloprid, with modest thiamethoxam removal (~50%). In contrast, the concentrations of all neonicotinoids were substantially lower in the Iowa City treatment facility finished water using granular activated carbon (GAC) filtration. Batch experiments investigated potential losses. Thiamethoxam losses are due to base-catalyzed hydrolysis under high-pH conditions during lime softening. GAC rapidly and nearly completely removed all three neonicotinoids. Clothianidin is susceptible to reaction with free chlorine and may undergo at least partial transformation during chlorination. Our work provides new insights into the persistence of neonicotinoids and their potential for transformation during water treatment and distribution, while also identifying GAC as a potentially effective management tool for decreasing neonicotinoid concentrations in finished drinking water.

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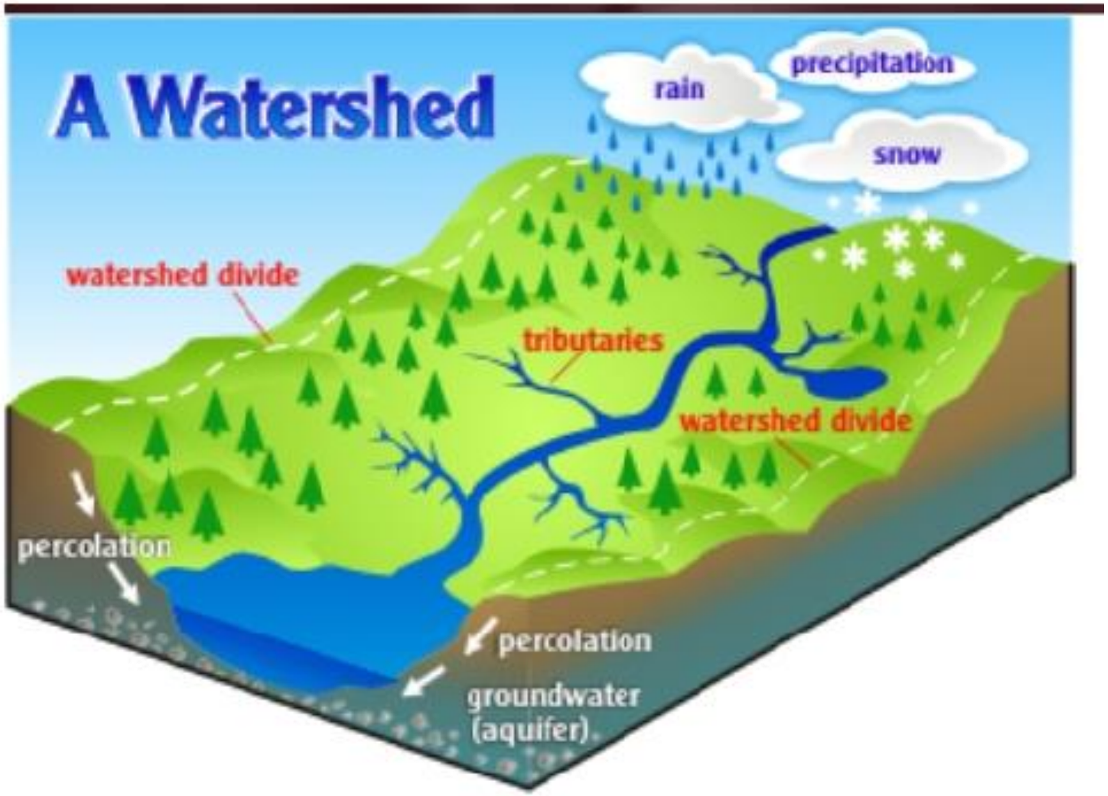
From drinking water to natural waters to stream and watershed ecology

- Drinking water is typically "processed" or treated in some way
- Surface waters in our watersheds even more chemical complexity AND they are dynamic
  - Changing with environmental conditions

Foundational Building Blocks

- Ecosystems…
  - Physical, chemical, and biological systems interacting, creating, transforming, decomposing, transferring materials and energy…



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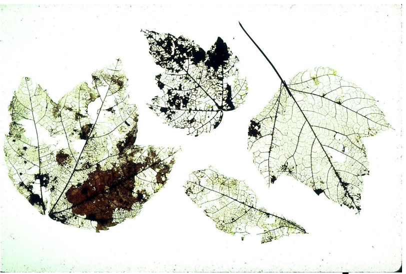
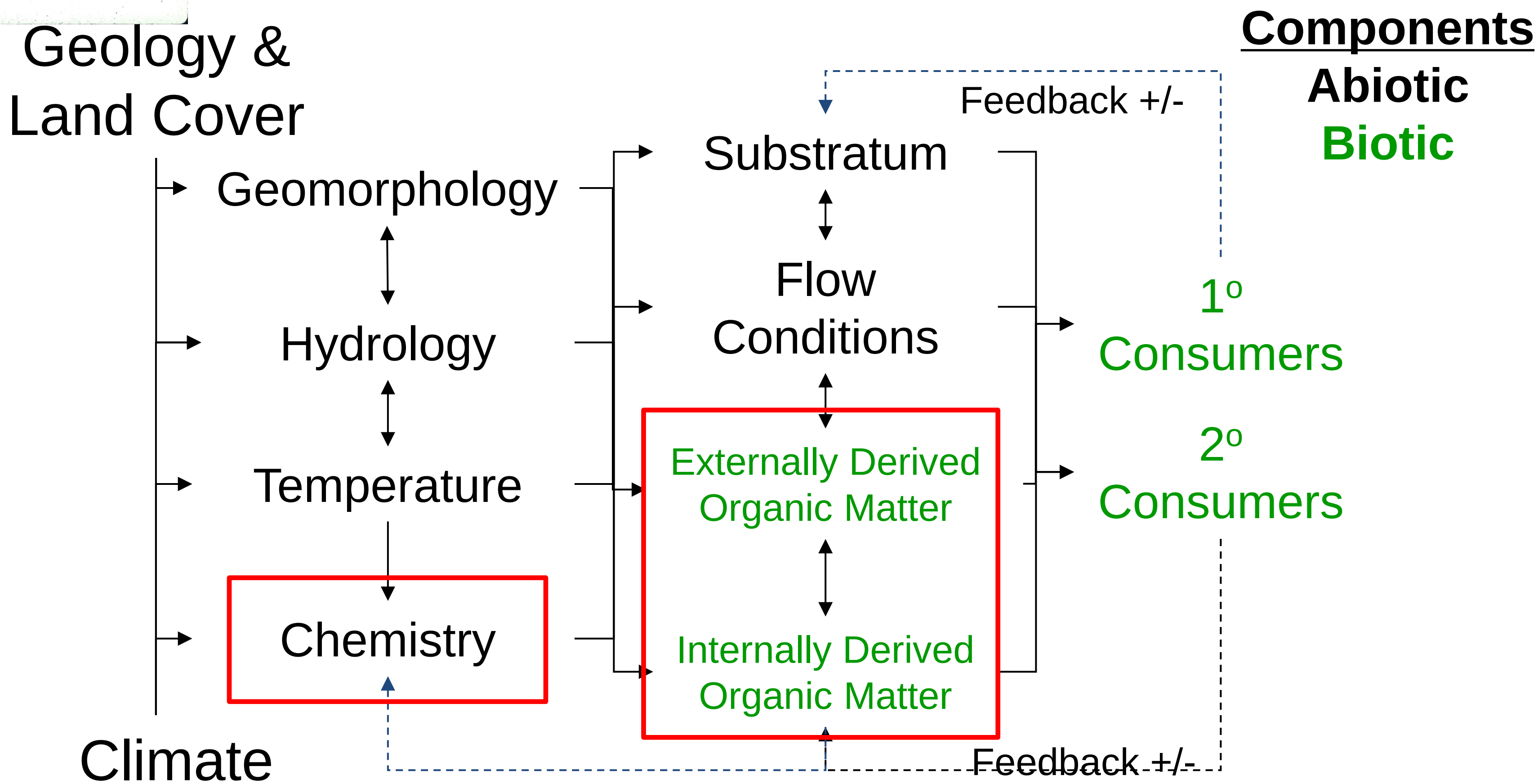
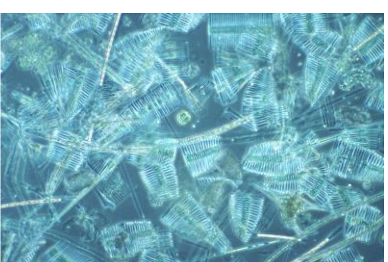
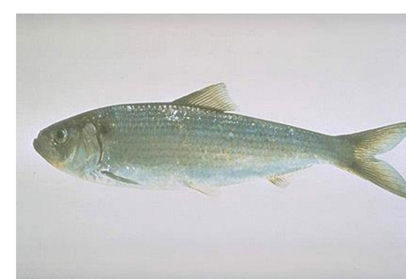
Stream Ecosystems









Chemical Composition of Freshwaters

- 100,000’s of potential compounds to consider
- Solids, liquids, gases
  - Particulate and dissolved material
- Abiotic, biotic (living or dead)
- Naturally occurring versus artificial

- Many “measurements” we make are estimates of a particular class of compounds or state of the aquatic system
  - These “bulk” measurements are influenced by water chemistry or influences water chemistry (or both)

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Chemical Composition of Freshwaters

- Particulate and dissolved material
- Natural
  - Nutrients, ions (minerals and salts), energy sources (natural organic matter), metals, dissolved gasses, radiological
- Artificial or human derived
  - Insecticides, fungicides, herbicides, pharmaceuticals, solvents, toxic organic compounds, oils, dissolved gasses, radiological, heavy metals, breakdown products from all of the above

What is Water Quality?

- “suitability of water for a particular use based on selected physical, chemical, and biological characteristics” (https://pubs.usgs.gov/fs/fs-027-01/)
  - NOTE: “USE” or designated “USE”; a reference to a particular expectation or condition

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Designated Uses

- Clean Water Act
  - Swimmable, fishable, drinkable
  - States need to designate uses of their waterways
- PA designated uses
  - Aquatic Life: CWF, WWF, MF, TSF
  - Water Supply: PWS, IWS, LWS, WWS, Irr
  - Recreation and Fish Consumption: B, F, WC, E
  - Special Protection: HQ, EV
  - Other: N.
- http://www.pacode.com/secure/data/025/chapter93/s93.3.html

PA Standards and Protected Waters

http://www.pacode.com/secure/data/025/chapter93/025_0093.pdf

WATER QUALITY CRITERIA

§ 93.6. General water quality criteria

(a) Water may not contain substances attributable to point or nonpoint source discharges in concentration or amounts sufficient to be inimical or harmful to the water uses to be protected or to human, animal, plant or aquatic life.

(b) In addition to other substances listed within or addressed by this chapter, specific substances to be controlled include, but are not limited to, floating materials, oil, grease, scum and substances that produce color, tastes, odors, turbidity or settle to form deposits.

Authority

The provisions of this § 93.6 amended under sections 5(b)(1) and 402 of The Clean Streams Law (35 P. S. §§ 691.5(b)(1) and 691.402); and section 1920-A of The Administrative Code of 1929 (71 P. S. § 510-20).

Source

The provisions of this § 93.6 amended March 10, 1989, effective March 11, 1989, 19 Pa.B. 968; amended November 17, 2000, effective November 18, 2000, 30 Pa.B. 6059; amended February 11, 2005, effective February 12, 2005, 35 Pa.B. 1197. Immediately preceding text appears at serial page (272025).

Notes of Decisions

Denial of an application for a mine drainage permit cannot be based solely on the ground that the watershed has been designated a conservation area, but must be reviewed on the basis of whether its proposed operation would discharge an effluent which would result in the degradation of the water quality of a stream in terms of its protected uses designated under this section. *Doraville Enterprises v. Commonwealth*, 73 Pa. D. & C.2d 635, 645, 646 (1975)

The water quality criteria do not preclude the allowance of a reasonable mixing zone if there is no significant effect on the ambient temperature of the stream outside the mixing zone. *Bartram v. Parrish*, 74 Pa. D. & C.2d 627, 649 (1974).

Cross References

TABLE 3

Parameter	*Symbol*	*Criteria*	*Critical Use**
Alkalinity	Alk	Minimum 20 mg/l as CaCO3, except where natural conditions are less. Where discharges are to waters with 20 mg/l or less alkalinity, the discharge should not further reduce the alkalinity of the receiving waters.	CWF, WWF, TSF, MF
Ammonia Nitrogen	Am	The maximum total ammonia nitrogen concentration (in mg/L) at all times shall be the numerical value given by: un-ionized ammonia nitrogen (NH_3-N) × ($\log^{-1}$[pK_T-pH] + 1), where: un-ionized ammonia nitrogen = 0.12 × f(T)/f(pH) $f(pH) = 1 + 10^{1.03(7.32-pH)}$ $f(T) = 1$, $T \geq 10°C$ $f(T) = \frac{1 + 10^{(9.73-pH)}}{1 + 10^{(pK_T-pH)}}$, $T < 10°C$ and $pK_T = 0.090 + \left[\frac{2730}{(T + 273.2)}\right]$, the dissociation constant for ammonia in water. The average total ammonia nitrogen concentration over any 30 consecutive days shall be less than or equal to the numerical value given by: un-ionized ammonia nitrogen (NH_3-N) × ($\log^{-1}$[pK_T-pH] + 1), where: un-ionized ammonia nitrogen = 0.025 × f(T)/f(pH) $f(pH) = 1$, $pH \geq 7.7$ $f(pH) = 10^{0.74(7.7-pH)}$, $pH < 7.7$ $f(T) = 1$, $T \geq 10°C$ $f(T) = \frac{1 + 10^{(9.73-pH)}}{1 + 10^{(pK_T-pH)}}$, $T < 10°C$ The pH and temperature used to derive the	CWF, WWF, TSF, MF

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Special Protection

HQ *High Quality Waters*

EV *Exceptional Value Waters*

Other

N *Navigation*—Use of the water for the commercial transfer and transport of persons, animals and goods.

Recreation and Fish Consumption

B *Boating*—Use of the water for power boating, sail boating, canoeing and rowing for recreational purposes when surface water flow or impoundment conditions allow.

F *Fishing*—Use of the water for the legal taking of fish. For recreation or consumption.

WC *Water Contact Sports*—Use of the water for swimming and related activities.

E *Esthetics*—Use of the water as an esthetic setting to recreational pursuits.

TABLE 1

Symbol	*Protected Use*
Aquatic Life	
CWF	*Cold Water Fishes*—Maintenance or propagation, or both, of fish species including the family Salmonidae and additional flora and fauna which are indigenous to a cold water habitat.
WWF	*Warm Water Fishes*—Maintenance and propagation of fish species and additional flora and fauna which are indigenous to a warm water habitat.
MF	*Migratory Fishes*—Passage, maintenance and propagation of anadromous and catadromous fishes and other fishes which move to or from flowing waters to complete their life cycle in other waters.
TSF	*Trout Stocking*—Maintenance of stocked trout from February 15 to July 31 and maintenance and propagation of fish species and additional flora and fauna which are indigenous to a warm water habitat.

Water Research Center

Water Supply

PWS	*Potable Water Supply*—Used by the public as defined by the Federal Safe Drinking Water Act, 42 U.S.C.A. § 300F, or by other water users that require a permit from the Department under the Pennsylvania Safe Drinking Water Act (35 P. S. §§ 721.1—721.18), or the act of June 24, 1939 (P. L. 842, No. 365) (32 P. S. §§ 631—641), after conventional treatment, for drinking, culinary and other domestic purposes, such as inclusion into foods, either directly or indirectly.
IWS	*Industrial Water Supply*—Use by industry for inclusion into nonfood products, processing and cooling.
LWS	*Livestock Water Supply*—Use by livestock and poultry for drinking and cleansing.
AWS	*Wildlife Water Supply*—Use for waterfowl habitat and for drinking and cleansing by wildlife.
IRS	*Irrigation*—Used to supplement precipitation for crop production, maintenance of golf courses and athletic fields and other commercial horticultural activities.

PA DEP designated use criteria for dissolved oxygen.

Designated Use	D.O. Criteria (mg/L) Daily Average	Minimum	Comments
Warm water fish (WWF)	5.0	4.0	
Cold water fish	6.0	5.0	
Trout stocking fishery	6.0	5.0	Feb 15 - Jul 31
	5.0	4.0	Aug 01 - Feb 14
High Quality CWF		7.0	Special Protection Waters
High Quality TSF	6.0	5.0	Special Protection Waters

Designated use criteria for basins containing the sites sampled and definitions of designated uses.

Stream	Designation Codes	Designated Uses
B4-Plum Run	WWF, MF	Warm Water Fishes, Migratory Fishes
B8-Taylor Run	TSF, MF	Trout Stocking Fishes, Migratory Fishes
B8-East Branch Brandywine	HQ-TSF, MF	High Quality, Trout Stocking Fishes, Migratory Fishes
B8-Valley Creek	CWF, MF	Cold Water Fishes, Migratory Fishes
B7-Indian Run	HQ-CWF	High Quality, Cold Water Fishes
B7-Culbertson Run	HQ-TSF, MF	High Quality, Trout Stocking Fishes, Migratory Fishes
B7-Shamona Creek	HQ-TSF, MF	High Quality, Trout Stocking Fishes, Migratory Fishes
B9-Beaver Creek	WWF, MF	Warm Water Fishes, Migratory Fishes
B-13 West Branch at Wawaset	WWF, MF	Warm Water Fishes, Migratory Fishes

KEY	
CWF	*Cold Water Fishes*—Maintenance or propagation, or both, of fish species including the family Salmonidae and additional flora and fauna which are indigenous to a cold water habitat.
WWF	*Warm Water Fishes*—Maintenance and propagation of fish species and additional flora and fauna which are indigenous to a warm water habitat.
MF	*Migratory Fishes*—Passage, maintenance and propagation of anadromous and catadromous fishes and other fishes which ascend to flowing waters to complete their life cycle.
TSF	*Trout Stocking*—Maintenance of stocked trout from February 15 to July 31 and maintenance and propagation of fish species and additional flora and fauna which are indigenous to a warm water habitat.
HQ	*High Quality Waters*—Surface waters having quality which exceeds levels necessary to support propagation of fish, shellfish, and wildlife and recreation in and on the water by satisfying § 93.4b(a).

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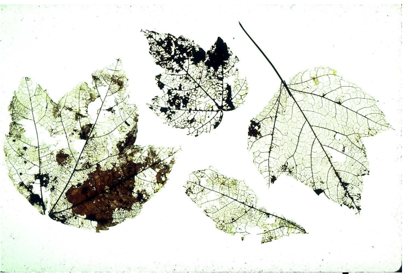
What is Water Quality? – Common Measurements

- Dissolved O_2 (previously mentioned)
- Water temperature (I know –not “chemical”, but highly relevant)
- pH
- Alkalinity
- Hardness
- Conductivity and/or total dissolved solids
- Nutrients
  - Phosphorus
  - Nitrogen
  - Major ions – calcium, magnesium, sulfate, potassium, etc…
- Organic matter/carbon
- Some metals



Stream Ecosystems

Components
Abiotic
Biotic

Geology & Land Cover

Geomorphology
Hydrology
Temperature
Chemistry

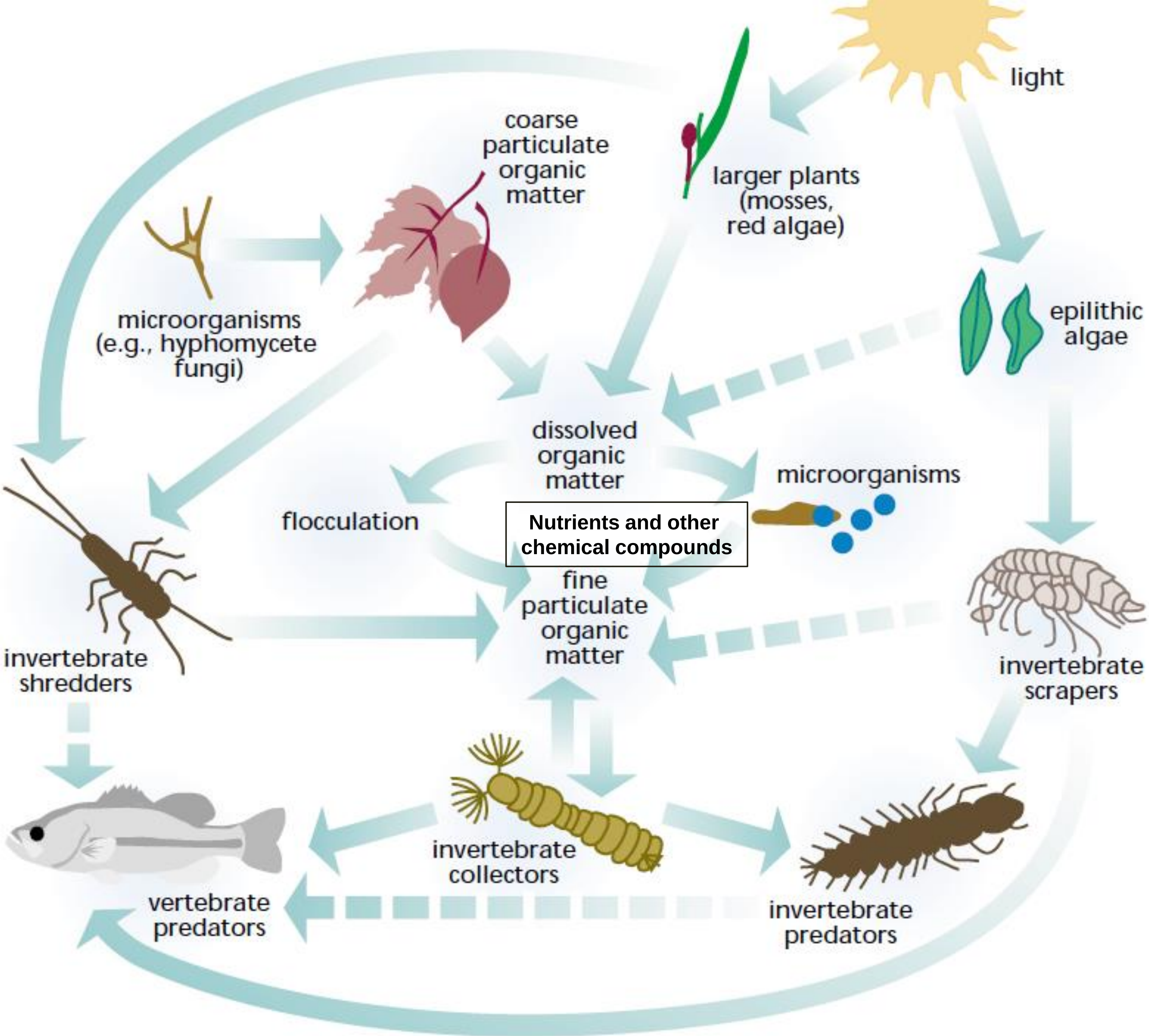
Climate

Feedback +/-

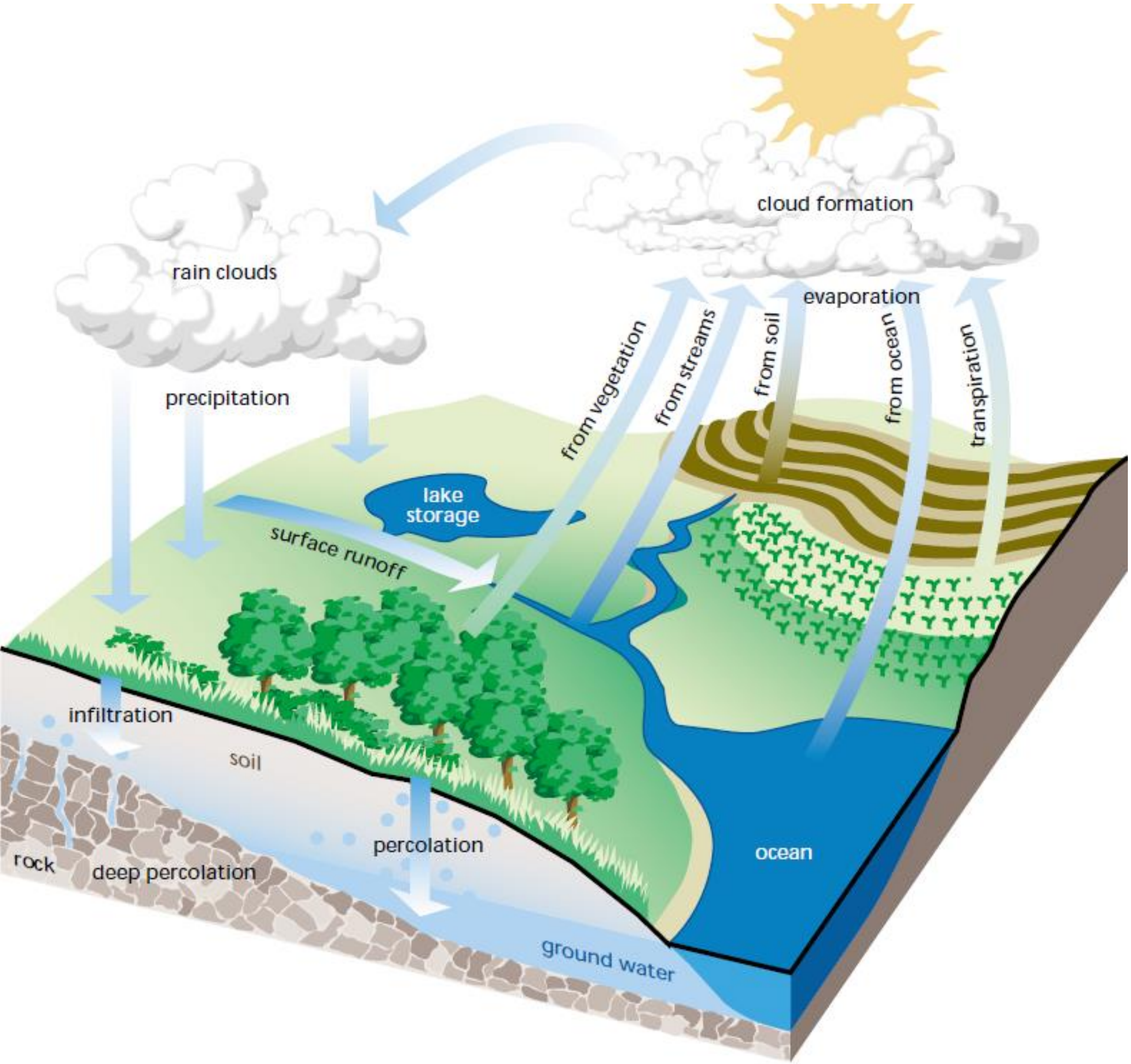
Substratum
Flow Conditions
Externally Derived Organic Matter
Internally Derived Organic Matter

Feedback +/-

1º Consumers
2º Consumers

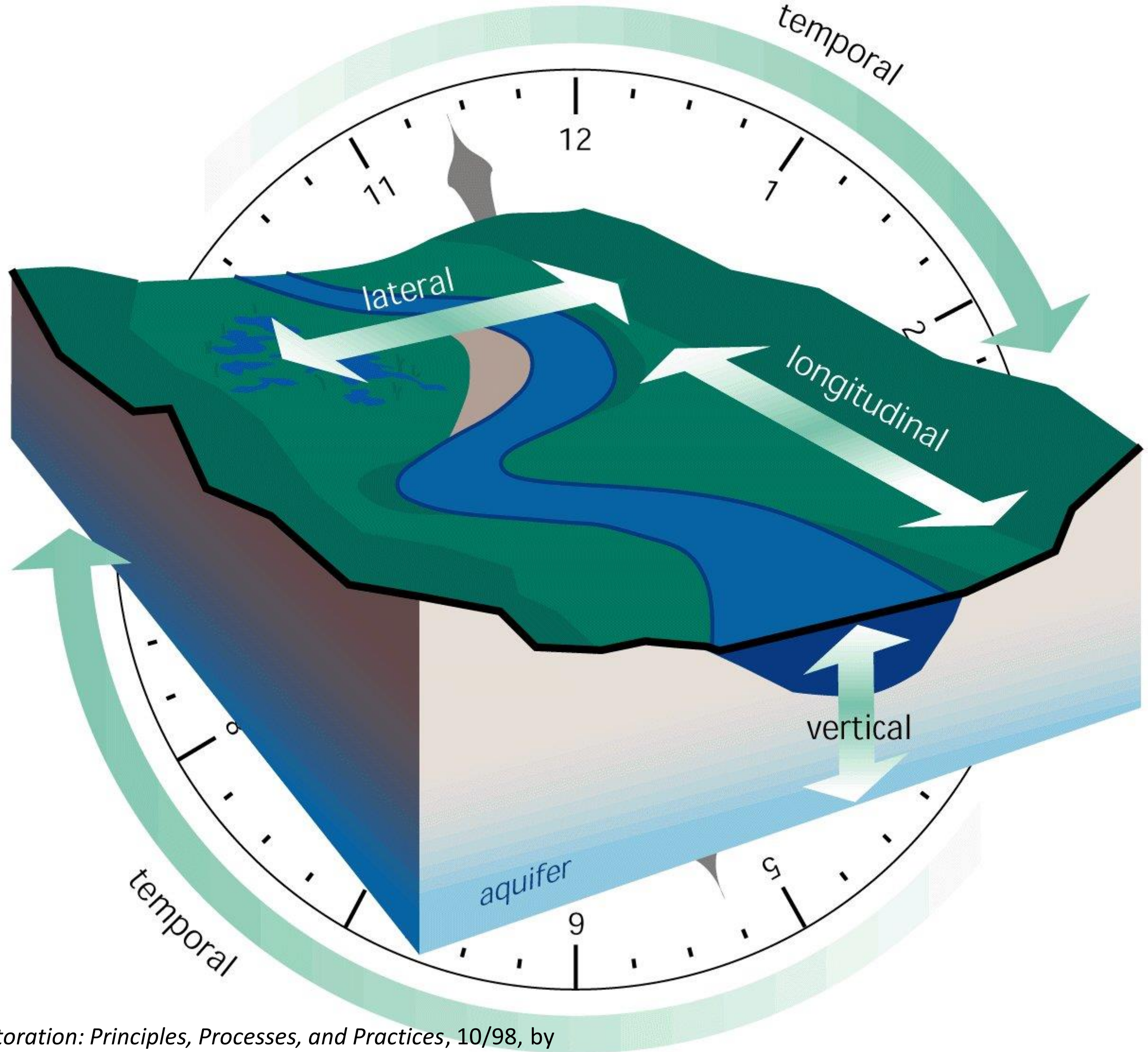


light
coarse particulate organic matter
larger plants (mosses, red algae)
microorganisms (e.g., hyphomycete fungi)
epilithic algae
dissolved organic matter
microorganisms
flocculation
Nutrients and other chemical compounds
fine particulate organic matter
invertebrate shredders
invertebrate scrapers
invertebrate collectors
vertebrate predators
invertebrate predators



Understanding the journey water takes to our streams, lakes, and wetlands is key to understanding water chemistry

Four Dimensional Nature of Rivers



Stream Corridor Restoration: Principles, Processes, and Practices, 10/98, by the Federal Interagency Stream Restoration Working Group (FISRWG).

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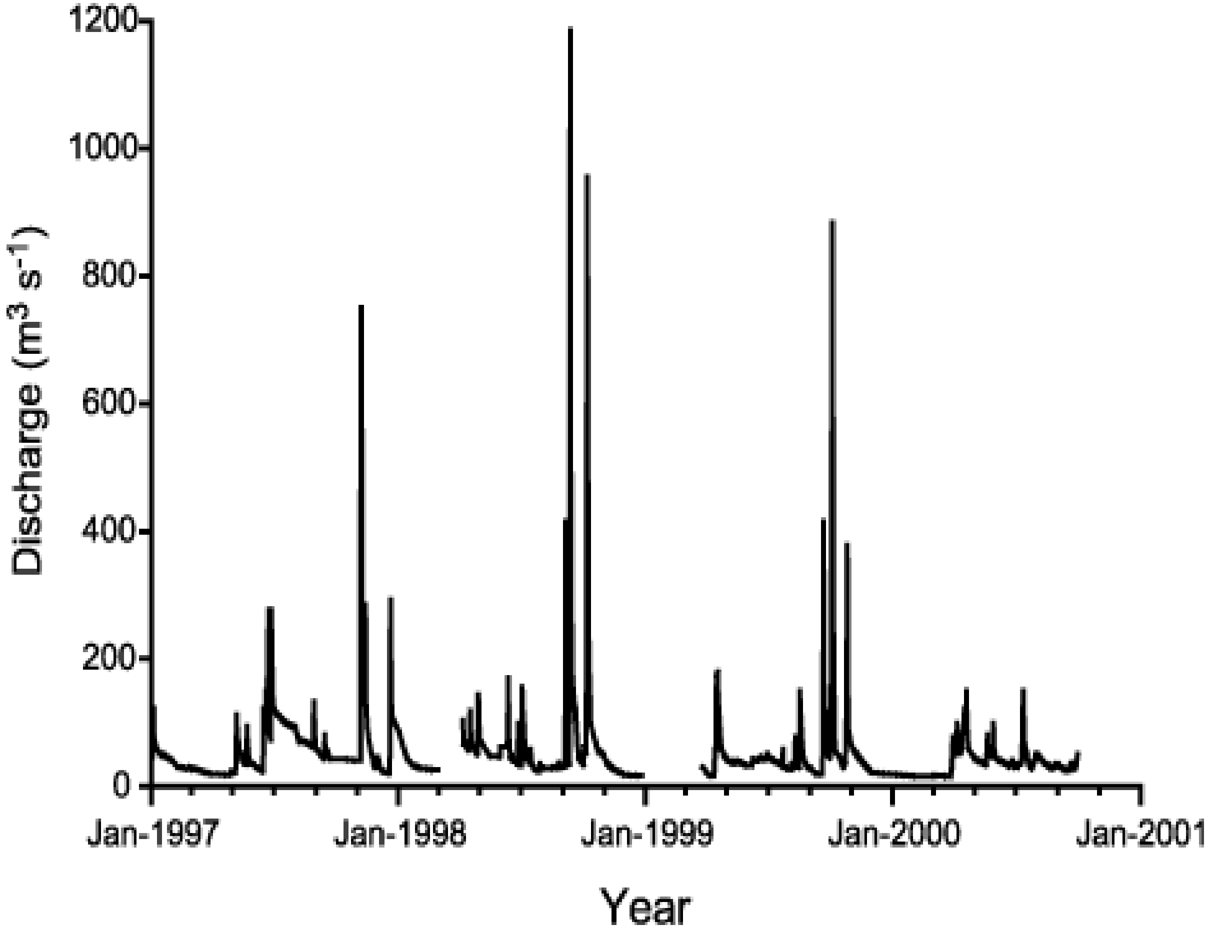
Environmental Heterogeneity

Heterogeneity = state of being diverse

- Variation in variables determining the habitat template



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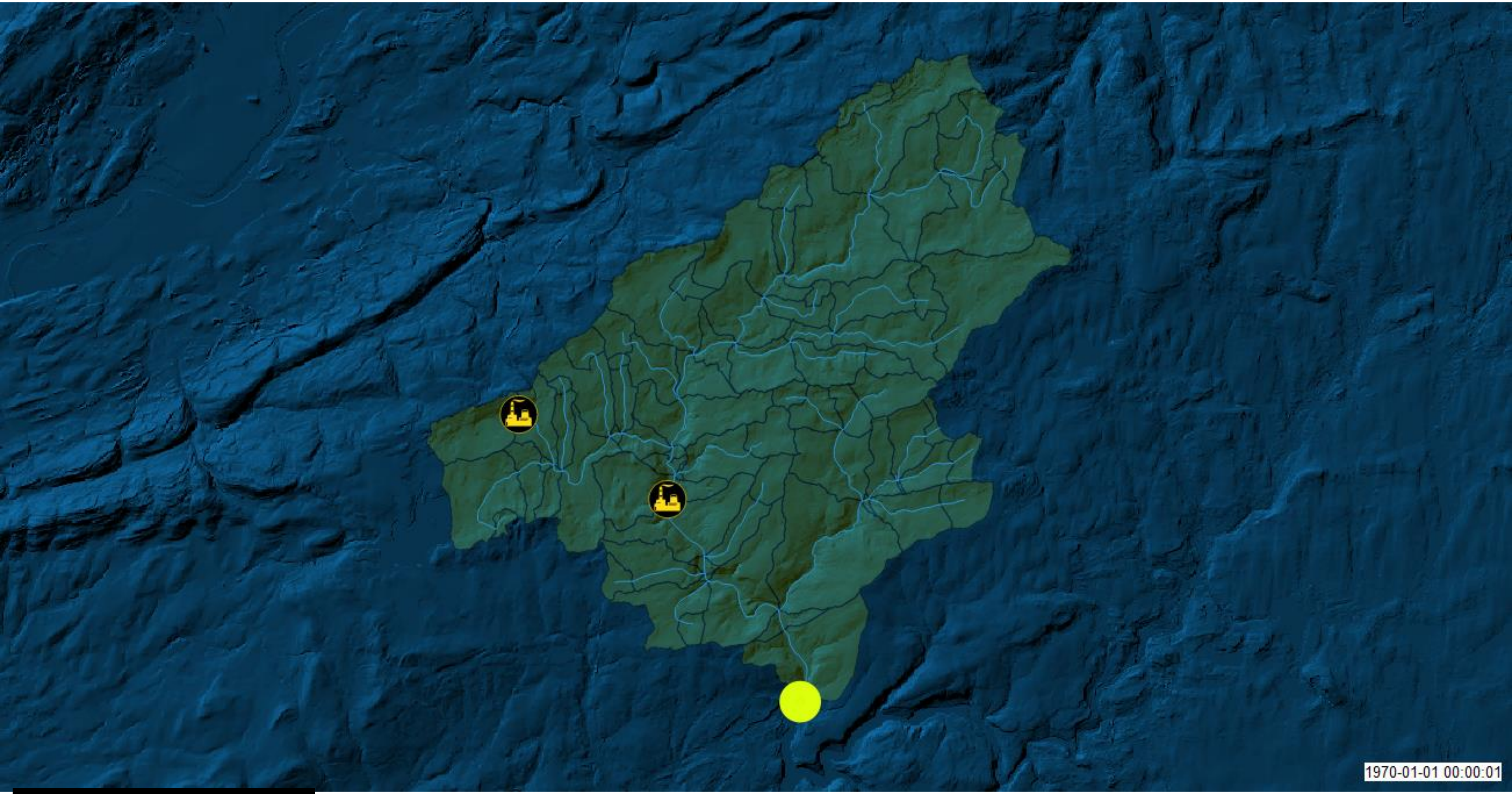
Stream Chemistry

FLOW PATHS, SPATIAL DIMENSIONs and FLOW DYNAMICS!



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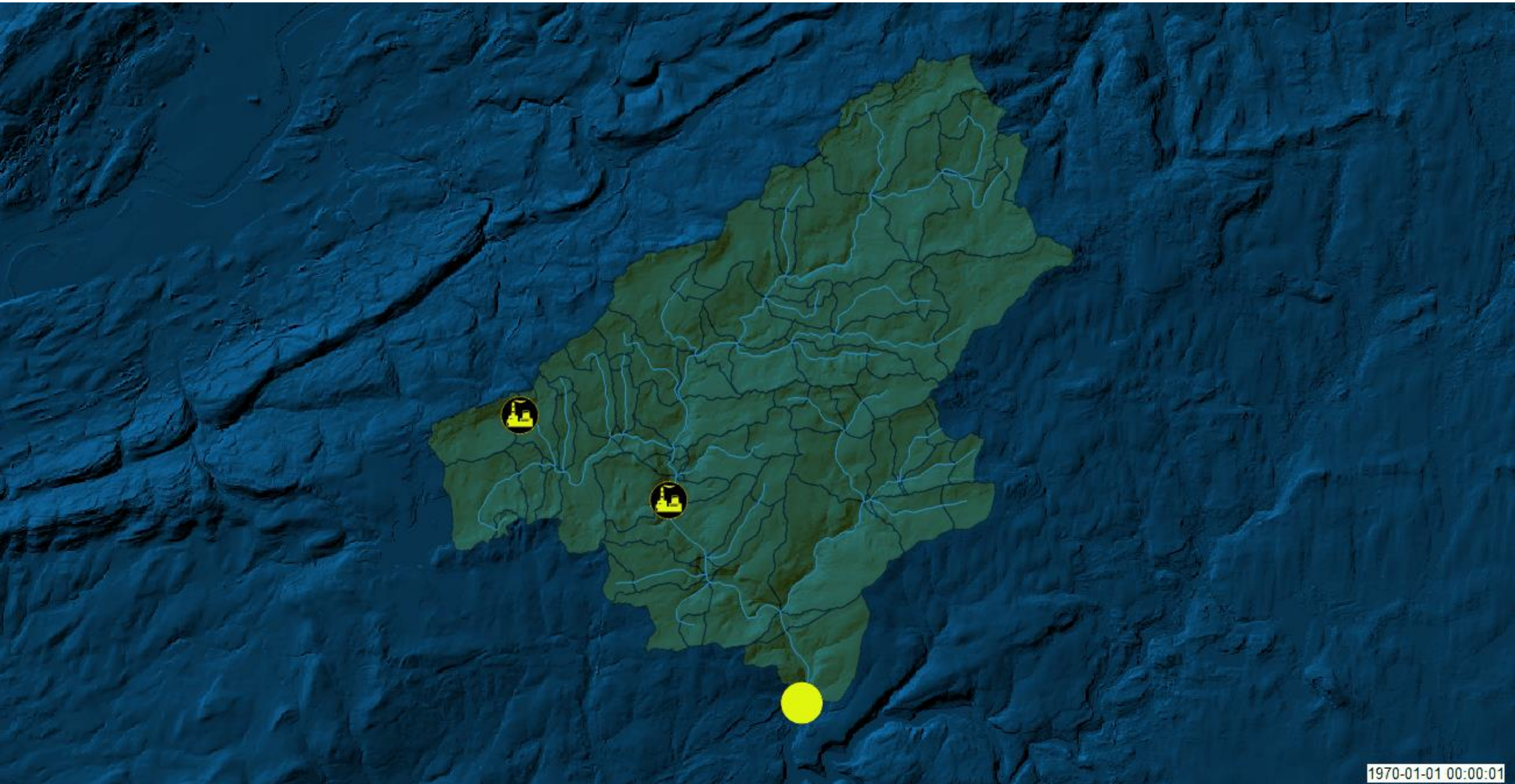

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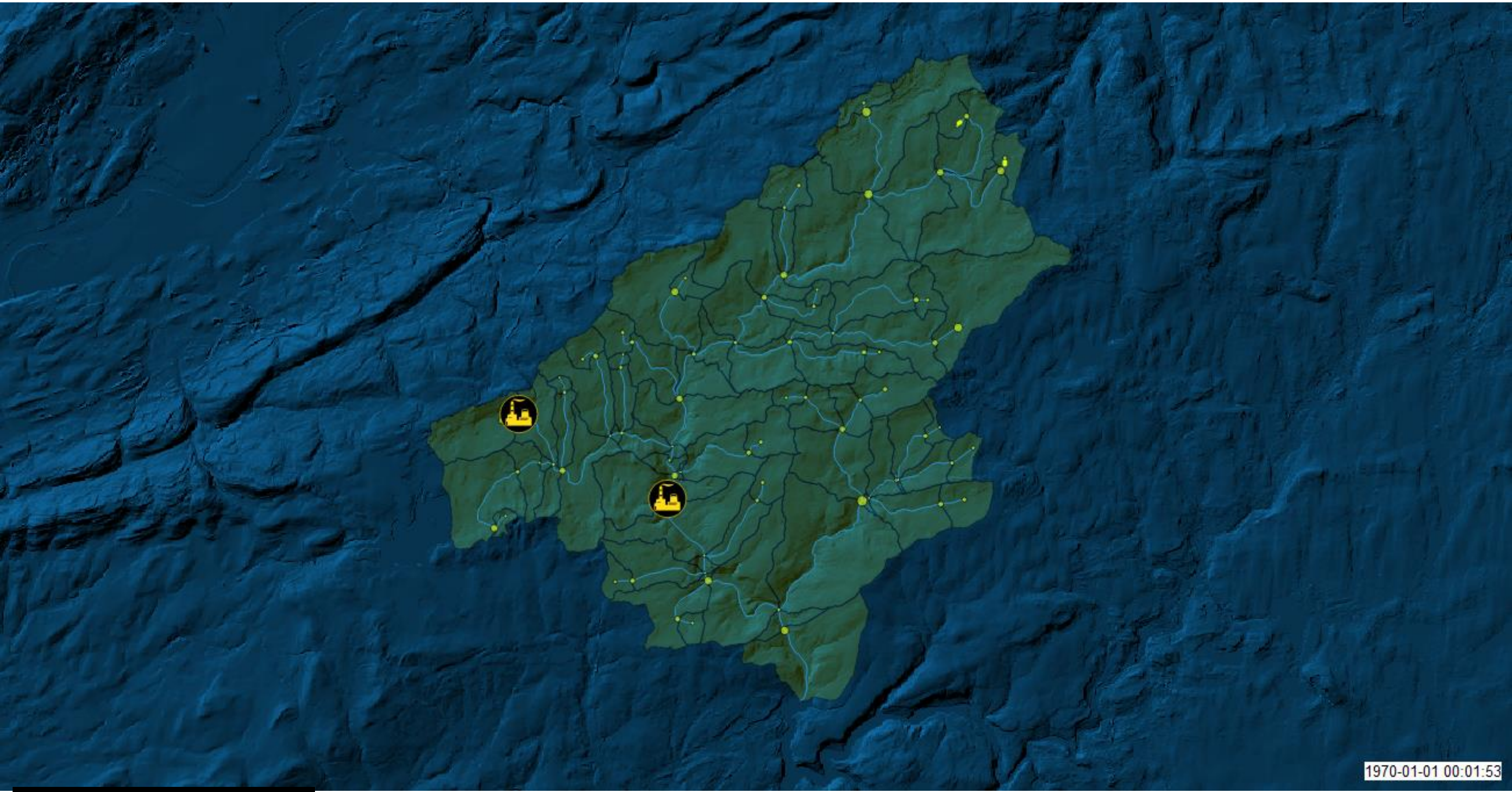

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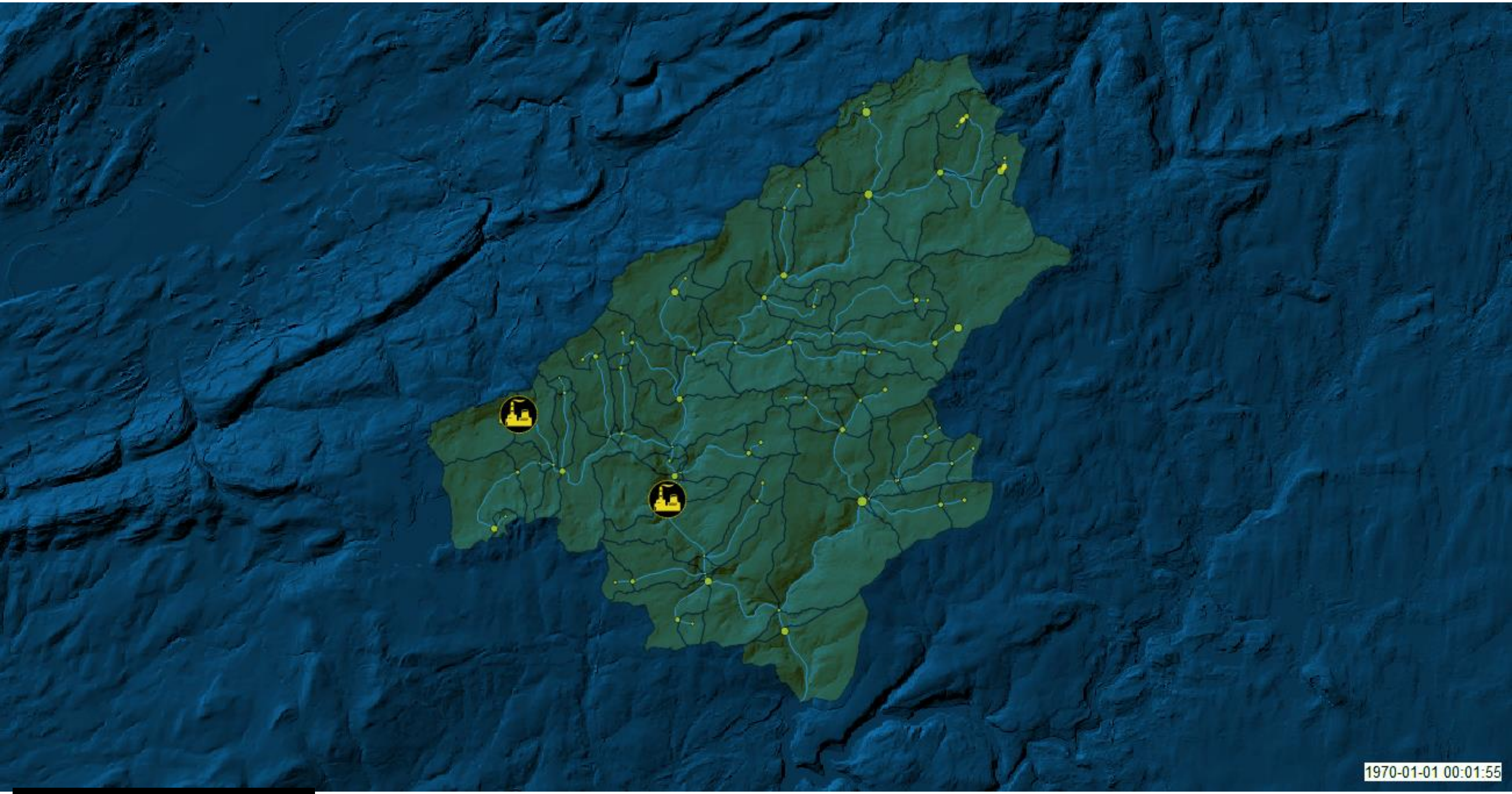

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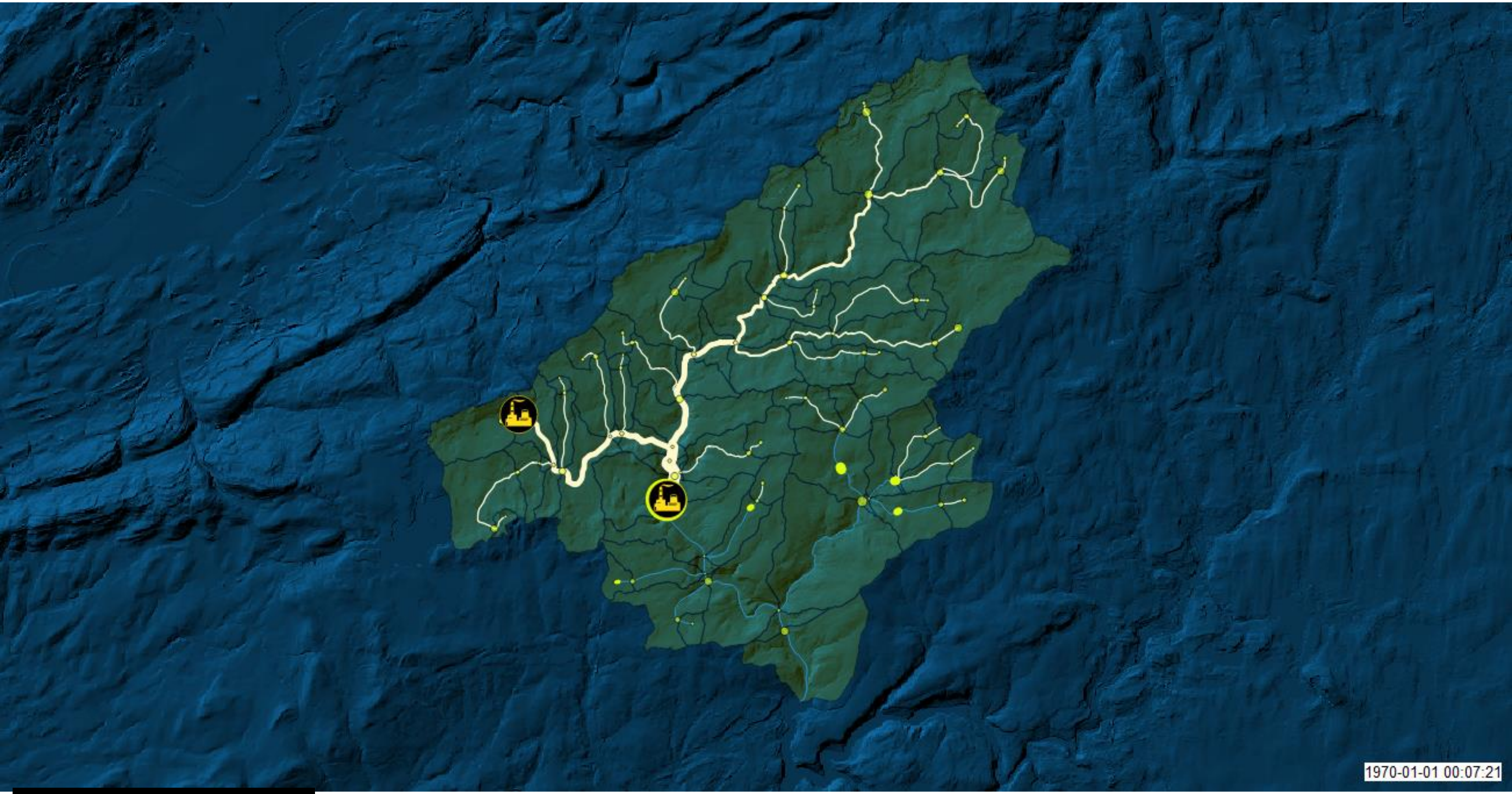

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B I O G E O I N F O R M A T I C S   G R O U P

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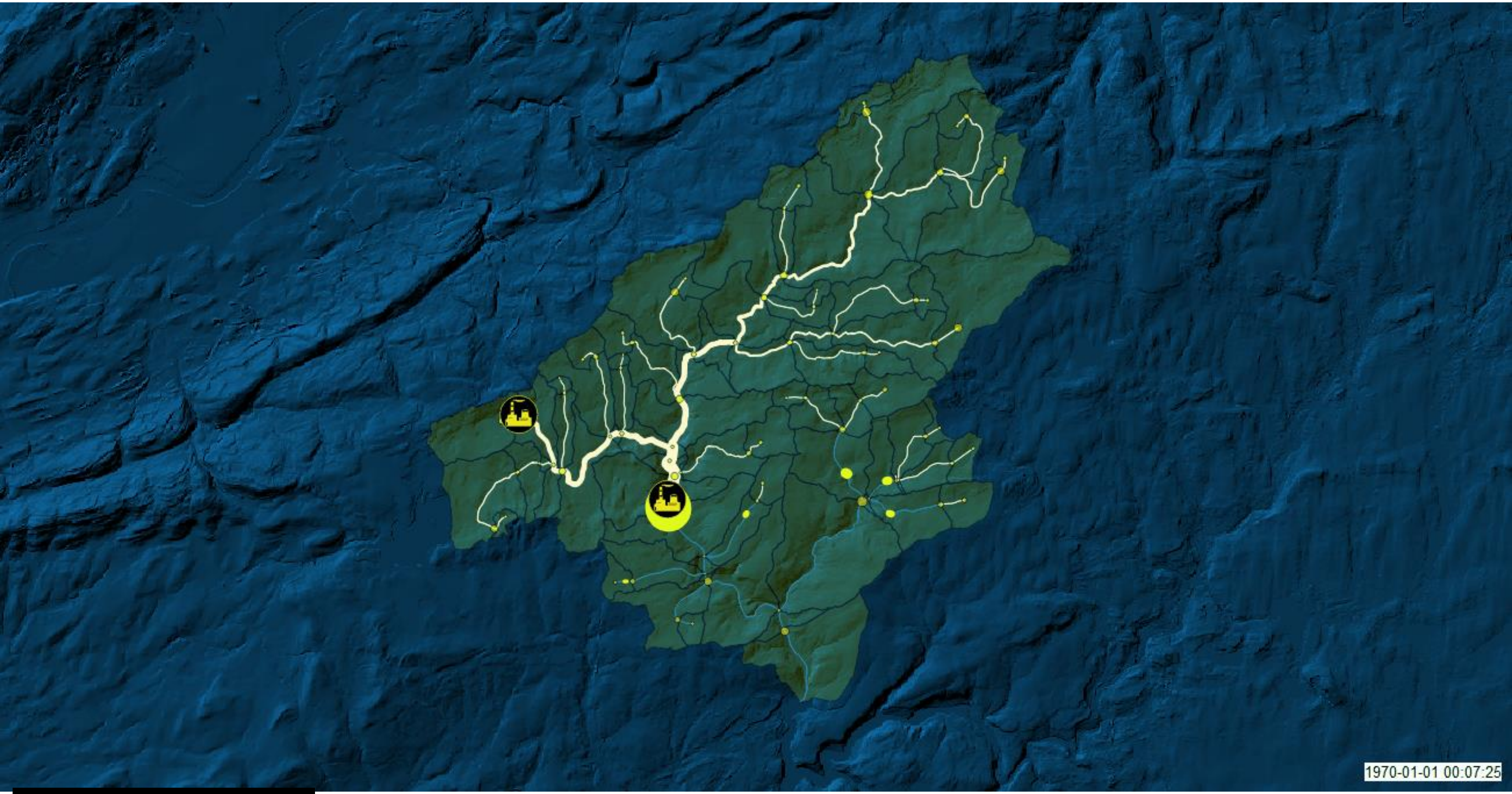
Stream Chemistry

FLOW PATHS, SPATIAL DIMENSIONs and FLOW DYNAMICS!



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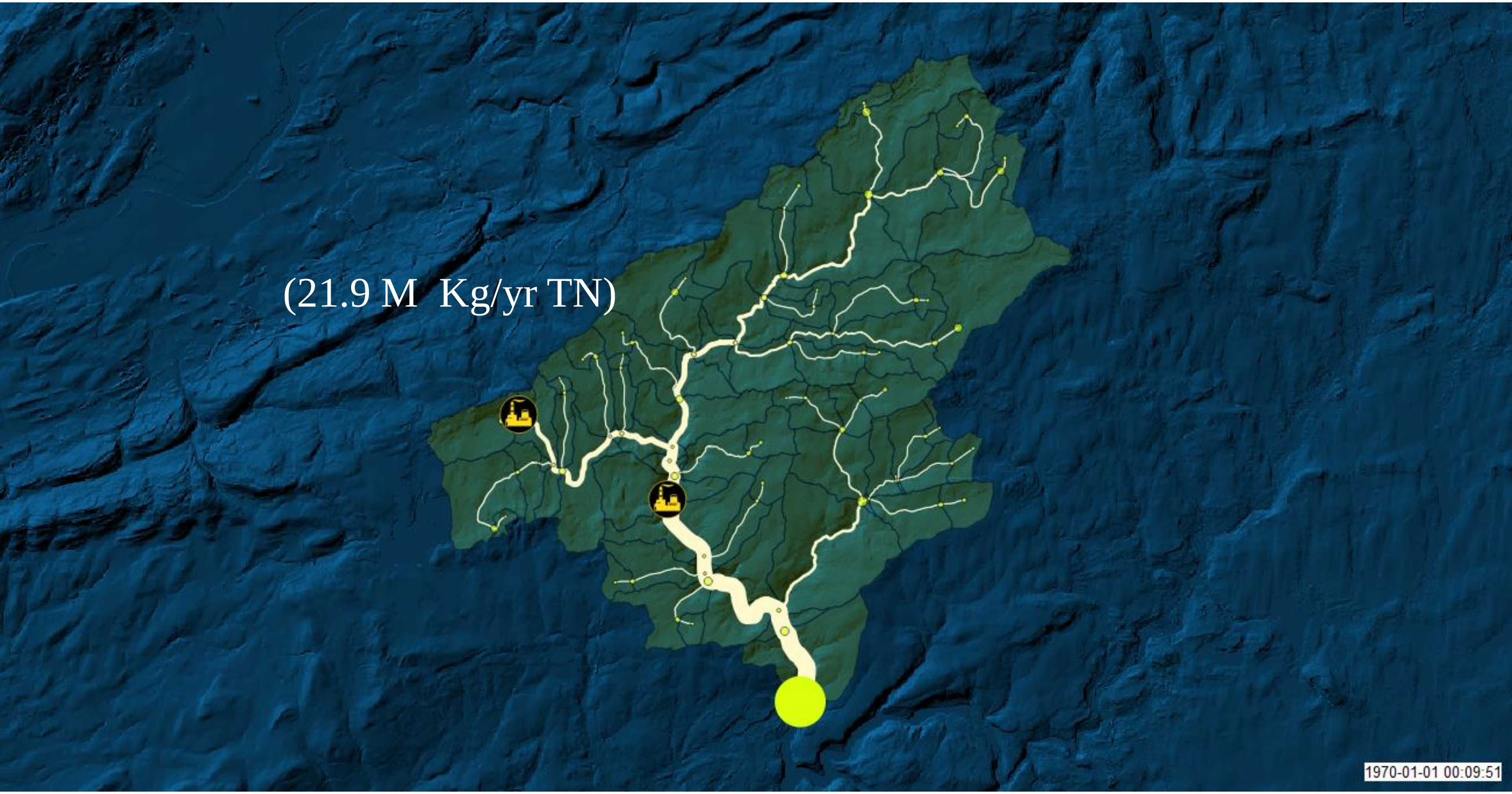

Stream Chemistry

Think about the TIME DIMENSION


SWRCCAM-04
09/07/11 02:17 PM

Flood Mediated Chemical Transport

State: Tennessee By: Tim McCabe Name: NRCSTN83010 Year: 1983
Flood water spills from Obion River in Central Tennessee.

http://photogallery.nrcs.usda.gov/Index.asp

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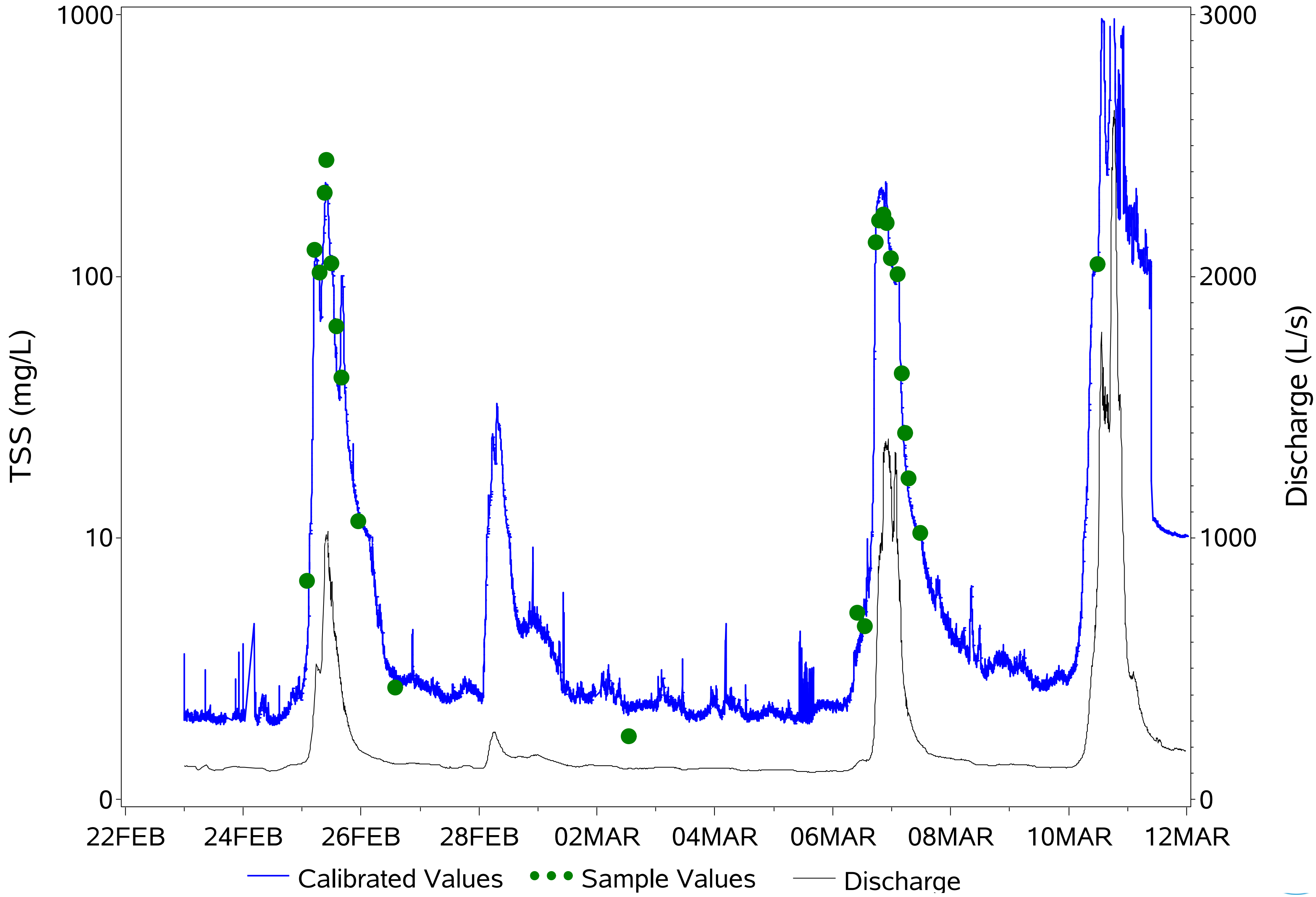
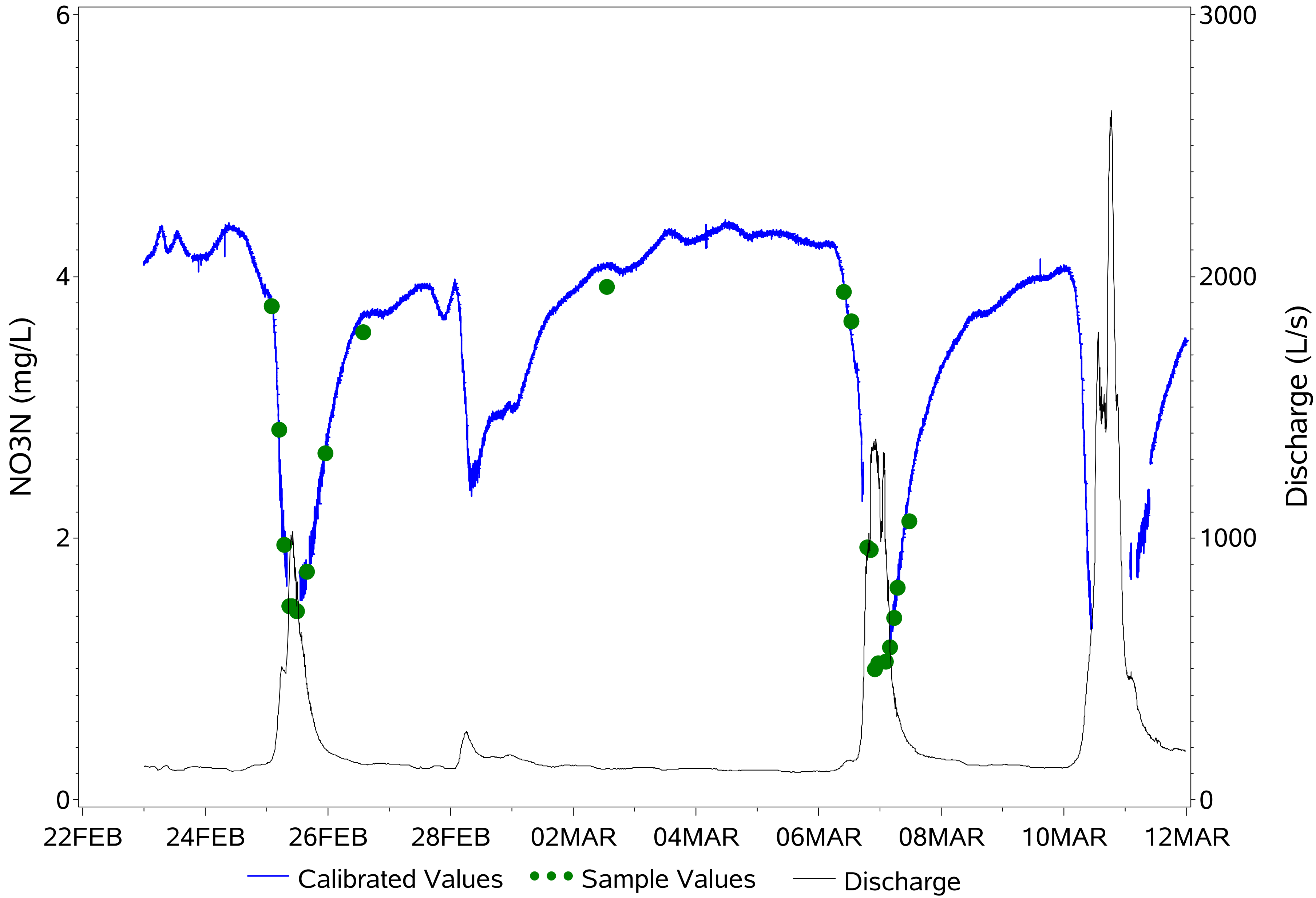
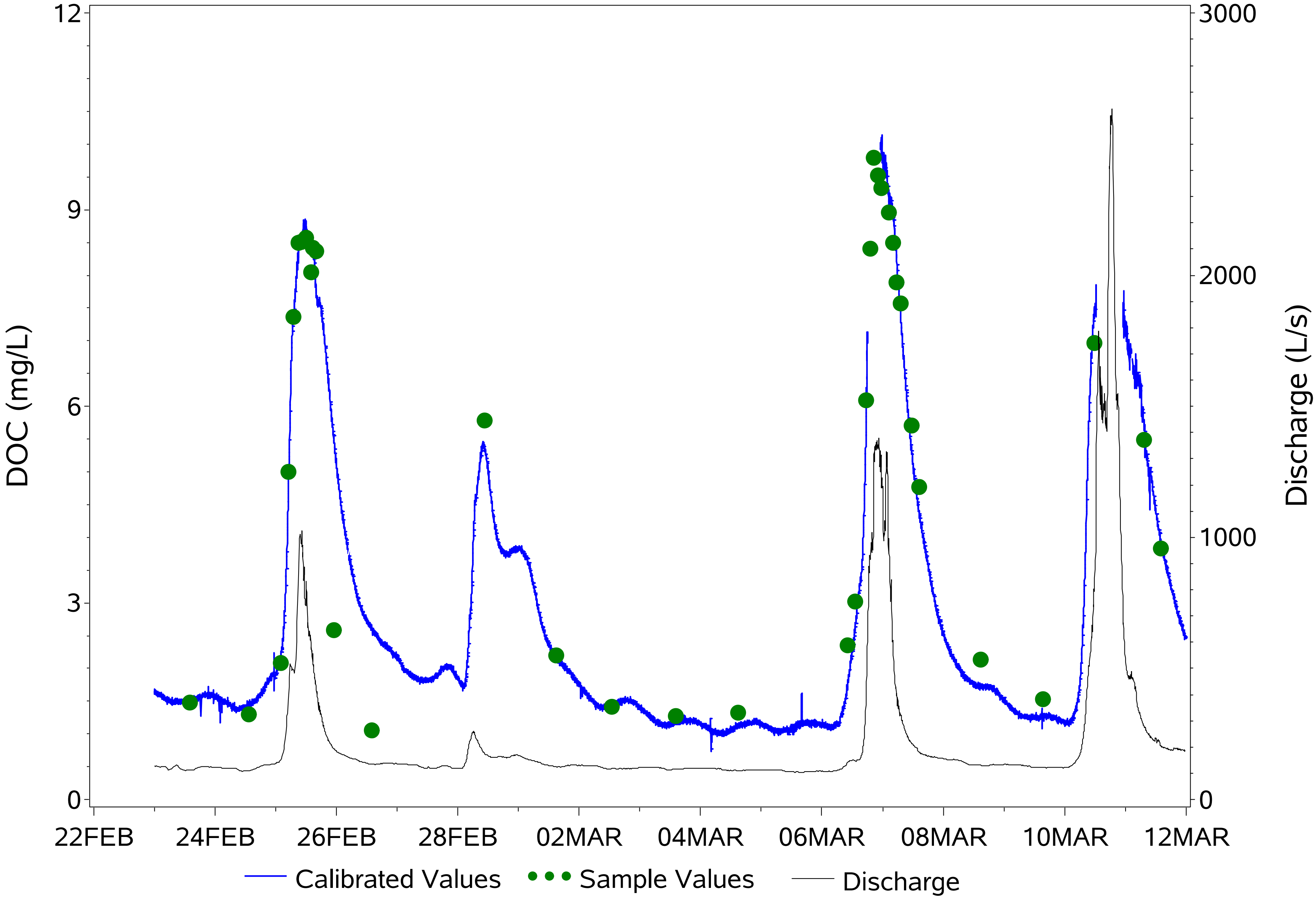
TSS w/ Drift-Correction & Local Calibration



Nitrate w/ Drift-Correction & Local Calibration



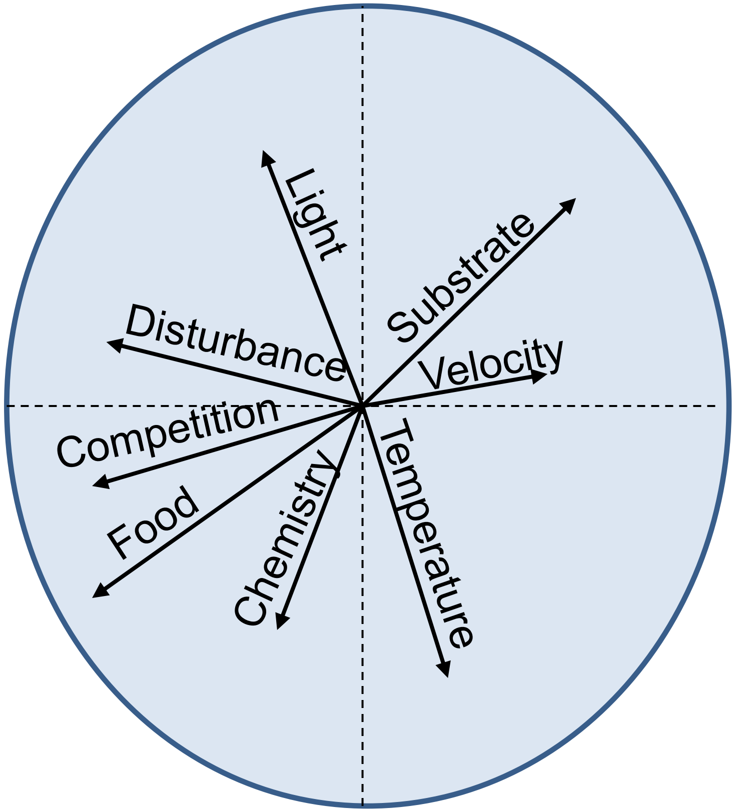
DOC w/ Drift-Correction & Local Calibration



Environmental Heterogeneity

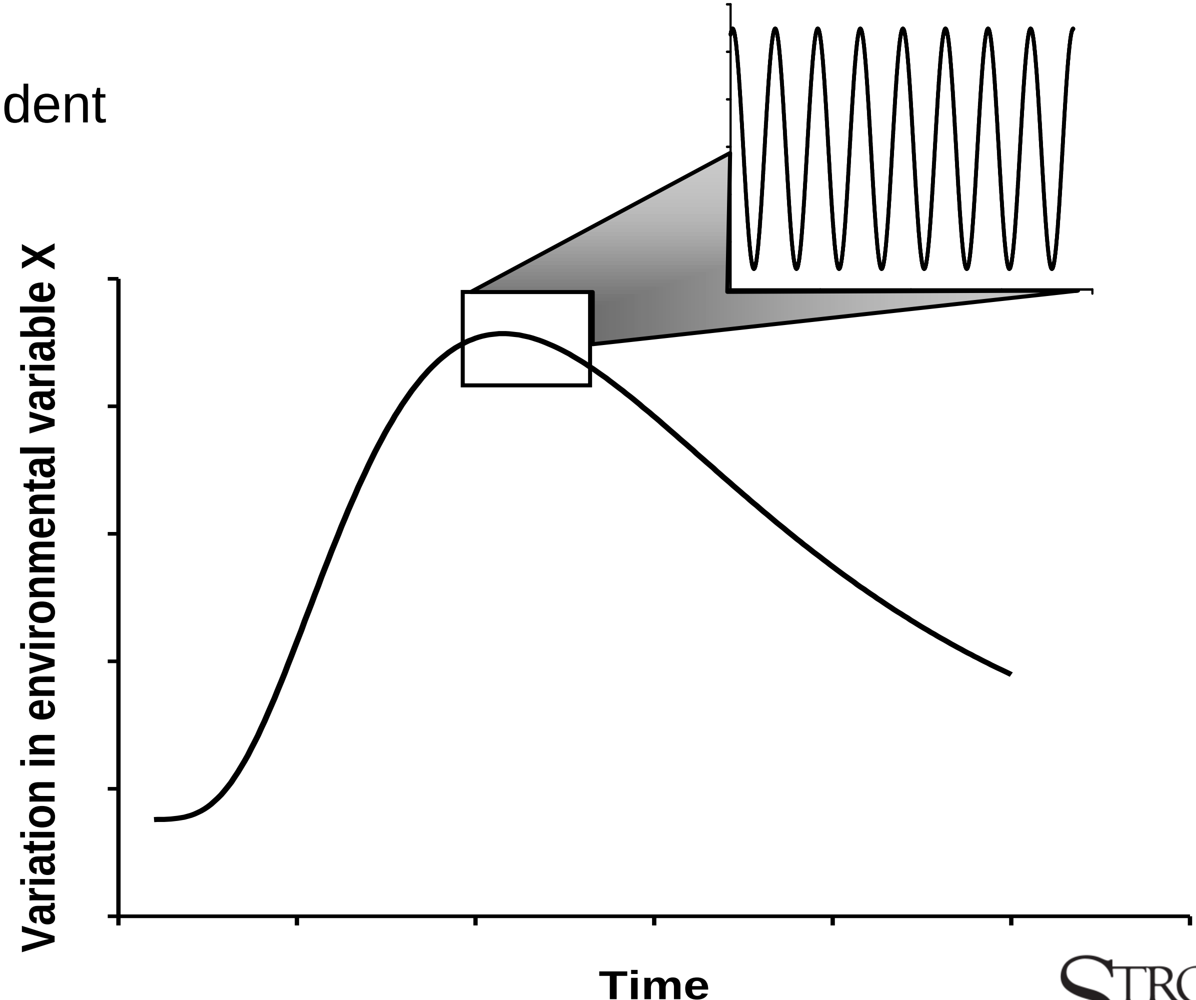
Heterogeneity = state of being diverse

- Multi-dimensional



Environmental Heterogeneity

- Scale dependent



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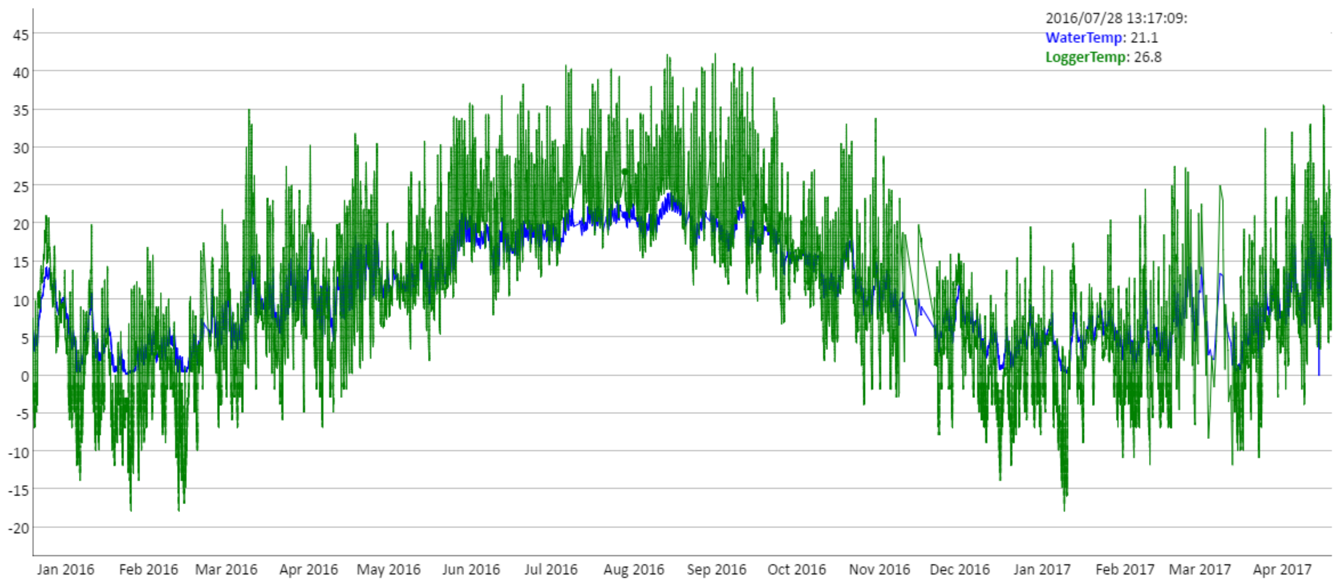

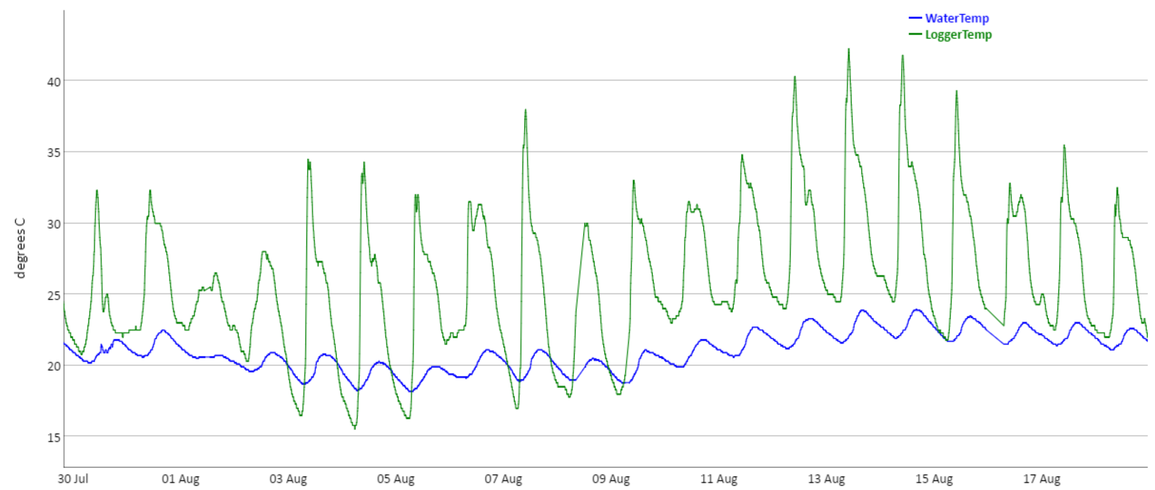

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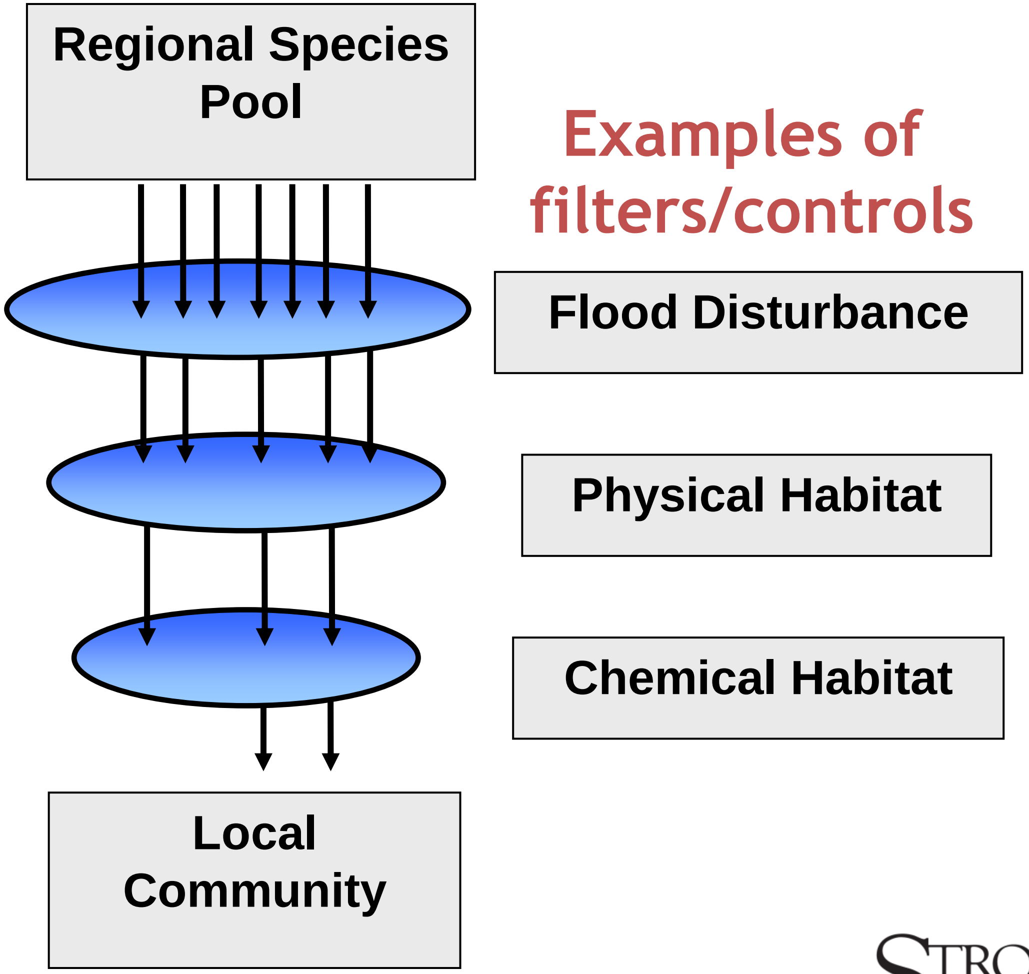
Multi-Dimensional Nature of Environmental Filters

- Hierarchical



Poff (1997)

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Example of hydro-geo-chemical-biological interactions (and e-filters)

- Changes in water chemistry can be mediated by
  - Biological interactions – BIOFILMS
  - Temperature and light
  - Inter-play between aerobic – anaerobic "habitats"/compartments
- BIOFILMS in most streams are on the stream bed!
  - Composed of microbes (bacteria, archaea, fungi, cyanobacteria, algae)
  - Invertebrates and some fish live in and on these biofilms
- What controls biofilm development/thickness?
  - How do biofilmsrespond to:
    - temperature, light, nutrients, hydrology (flooding and drought), current velocity, turbidity
    - Grazing by animals
    - Are they different on different sediment types? (sand/silt/clay versus gravel v boulders)

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Stream Chemistry

Think about biofilms and their dynamic responses to conditions

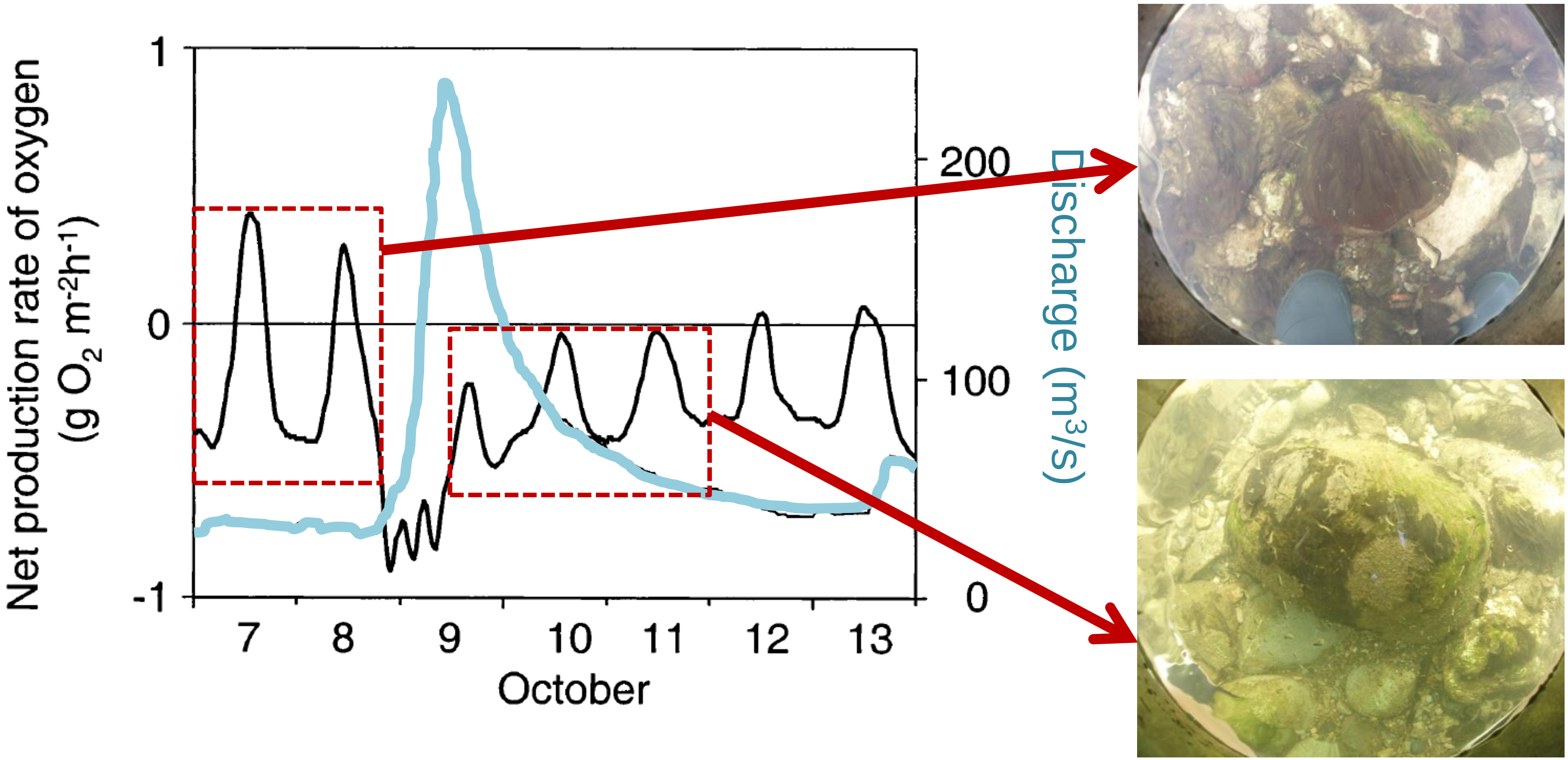

Fig. 2 Calculated net production rate of oxygen (bold line) and discharge (fine line) in River Thur between 7 and 14 October 1993.

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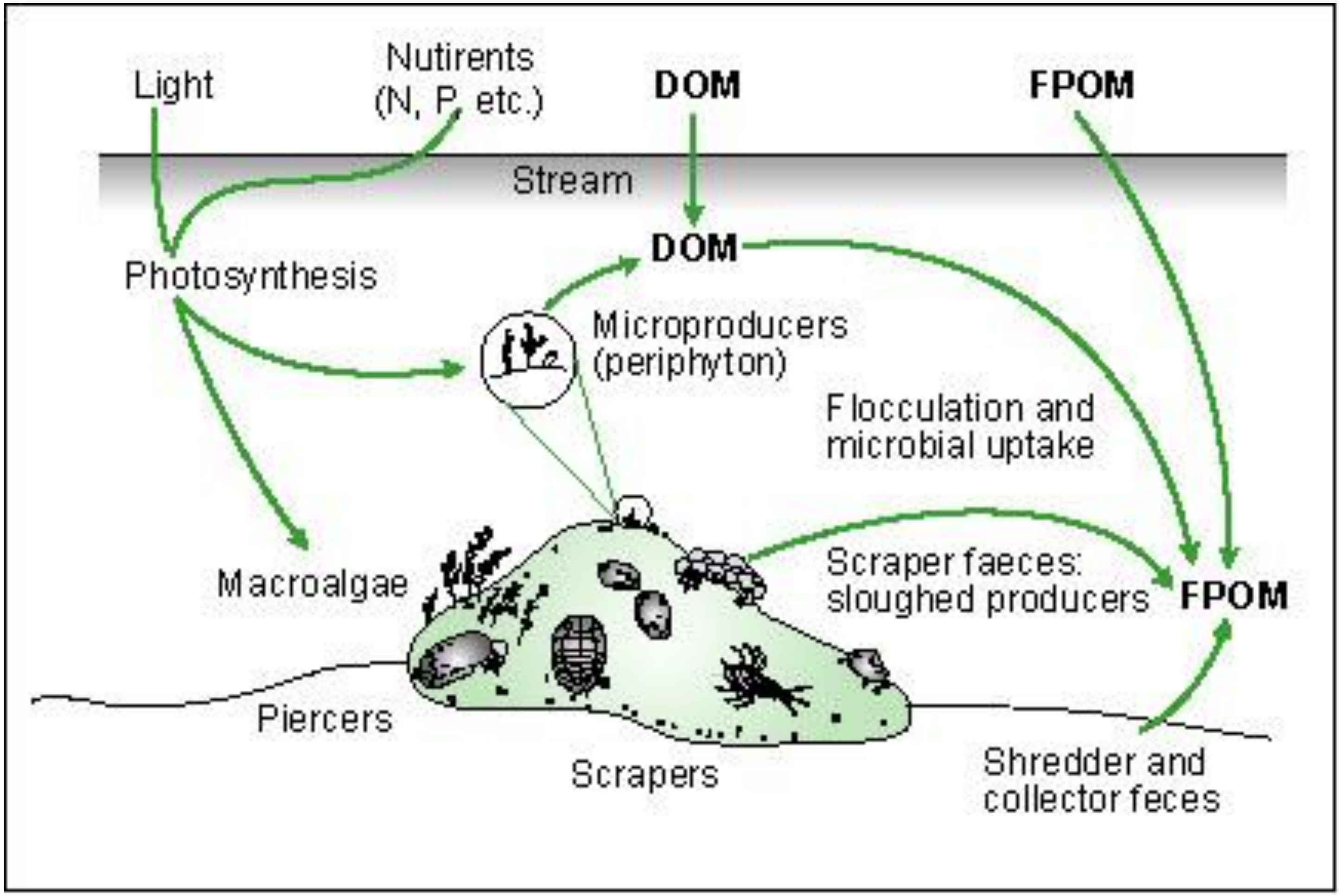
Biofilm Function and Dynamics



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Controls on Biofilm Growth in Rivers

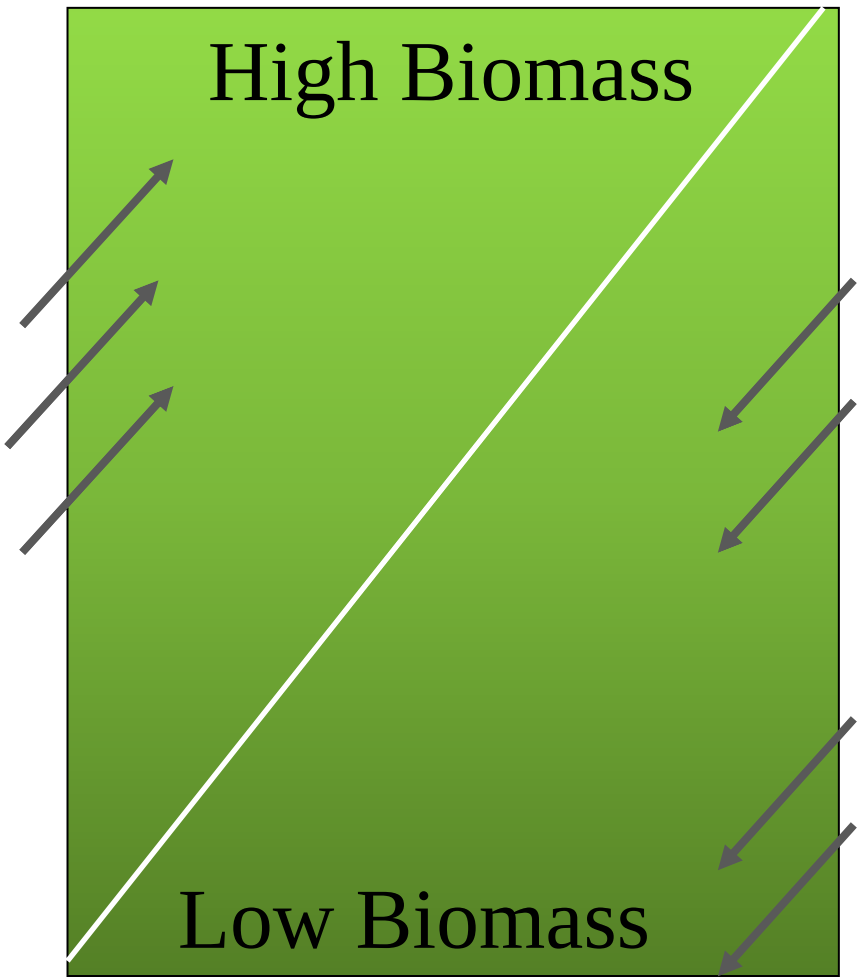
Biomass Gains

Resources

Nutrients

Light

Temperature



Biomass Loss

Disturbance

Scouring/sloughing

Substrate movement

Grazing

Invertebrates

fish

Modified from Biggs 1996

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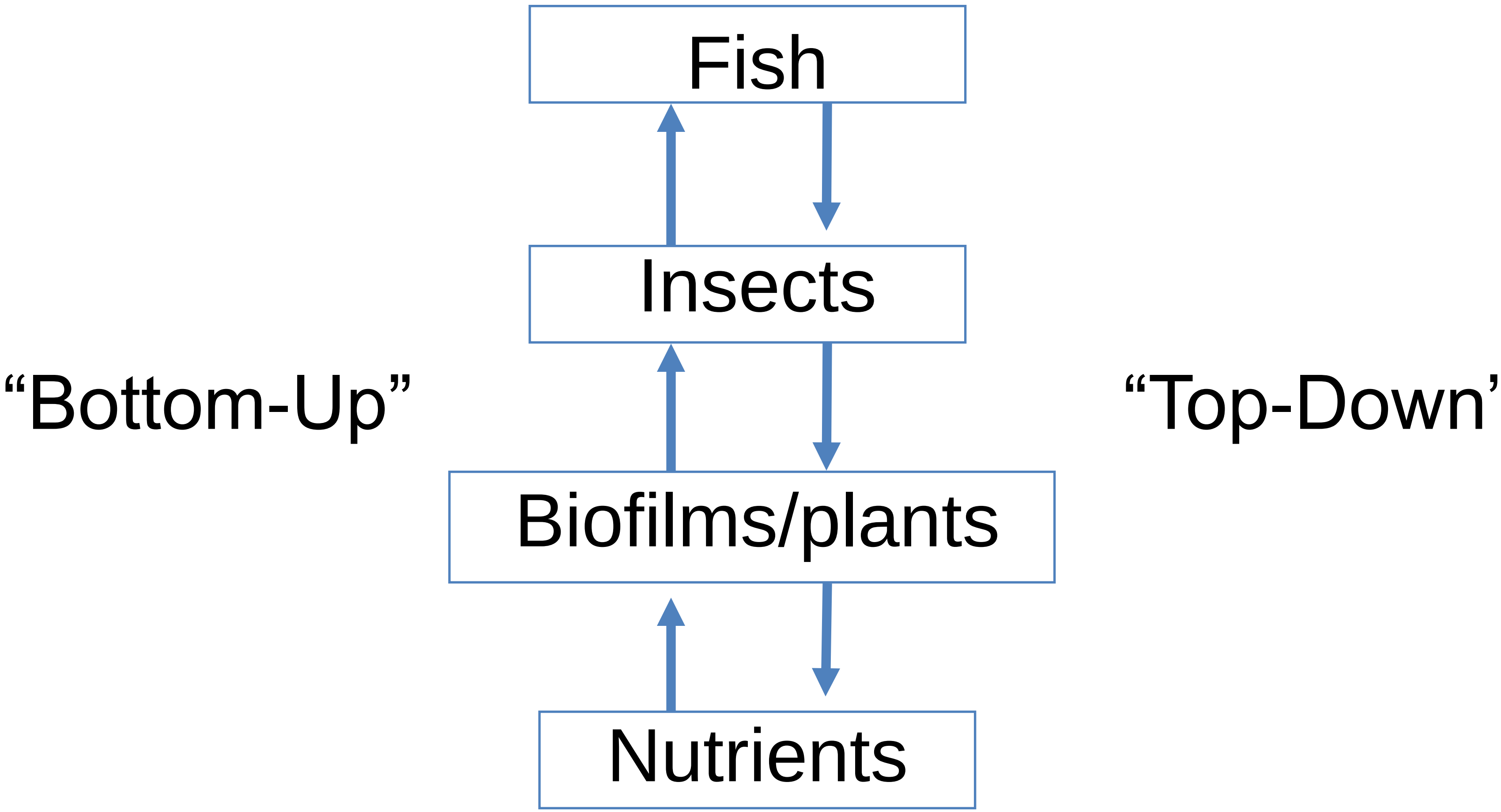
Ecosystem Responses to Changes in Resources



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How and Why Does WQ Change over Time?

- Natural processes
  - Seasonality
  - Daily conditions
  - Bottom up versus top down interactions
  - Geological time (landscape change)
  - Fluvial geomorphic change mediated by hydrologic disturbance (flood/drought)
    - Baseflow versus stormflow

How and Why Does WQ Change over Time?

- Human induced
  - Landscape alteration
    - Management/use/restoration
  - Pollution
    - Surface waters, groundwater, atmospheric
  - Climate changes
  - Water uses
    - Consumptive, non-consumptive

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BACKGROUND WATER CHEMISTRY

Learning objectives:

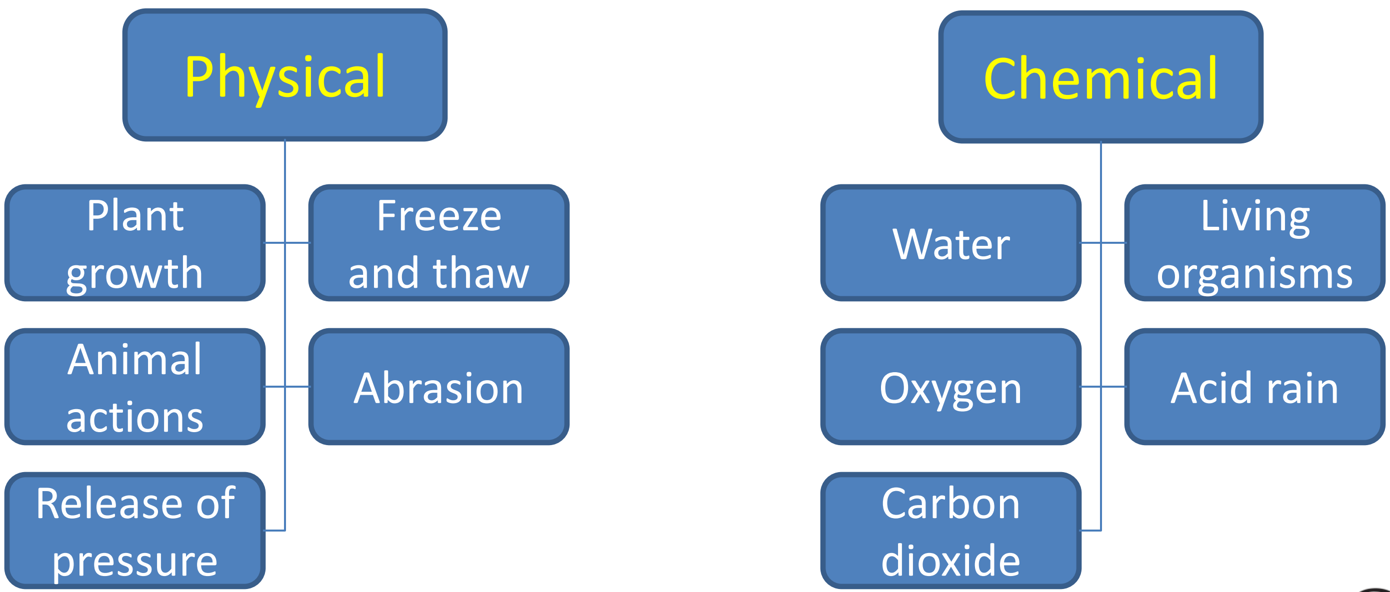
What is the relationship between geologic setting and stream water chemistry?

What is the Carbonate Buffering System

What controls the amount and dynamics of dissolved gases in stream water and why does it matter?

Geology sets the chemical foundation

- **Weathering** - *physical* and *chemical* breakdown of continental rock to small particles (>0.5 µm) and dissolved substances (<0.5 µm)



Geology sets the chemical foundation

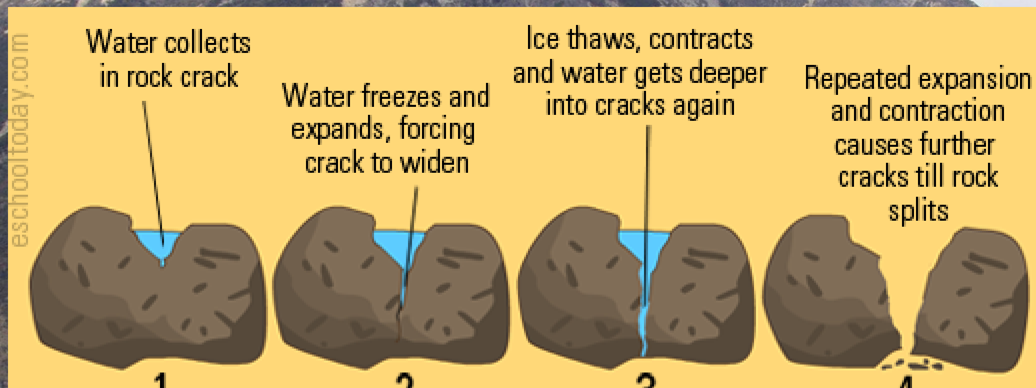


Image from: http://www.eschooltoday.com/rocks/what-is-physical-weathering-of-rocks.html

- **Physical weathering -** physical breakdown of rocks and minerals into smaller particles
  - Processes include: glacier scouring, frost heaves (freeze-thaw cycles), abrasion by wind- and water-borne particles, rain splatter and differential expansion/contraction of exposed rocks
  - Typically, physical weathering rates increase with mean elevation (Garrels and Mackenzie 1971)

Geology sets the chemical foundation

- Chemical weathering - dissolution of rock components, as minerals formed deep in the Earth are exposed to physicochemical conditions near the surface where they are no longer stable. These processes include:
  - Simple (congruent) dissolution
  - Carbonate weathering (typically of limestone)
  - Silicate weathering (with many mineral types involved)
  - Sulfide weathering (acid mine drainage)
- The dissolved composition of river water records the types of chemical weathering (both substrates and rates) that occur on in their drainage basins

http://www.absolutechinatours.com/UploadFiles/ImageBase/yeliu-geopark-disolution-rock.jpg

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Geology sets the chemical foundation

- Primary Dissolved Ions (other than nitrogen and phosphorus ions)

Major Cations	**Formula**
Calcium	Ca^{2+}
Magnesium	Mg^{2+}
Potassium	K^{+}
Sodium	Na^{+}
Major Anions	**Formula**
Bicarbonate/carbonate	HCO_3^{-}/CO_3^{2-}
Sulfate	SO_4^{2-}
Chloride	Cl^{-}
Silicate	$HSiO_3^{-}$

Stroud Water Research Center 50 Years Est. 1967

Table 1. Average composition, in parts per million, of igneous rocks and some types of sedimentary rocks

[After Horn and Adams (1966)]

Element	Igneous rocks	Sedimentary rocks: Resistates (sandstone)	Sedimentary rocks: Hydrolyzates (shale)	Sedimentary rocks: Precipitates (carbonates)
Si	285,000	359,000	260,000	34
Al	79,500	32,100	80,100	8,970
Fe	42,200	18,600	38,800	8,190
Ca	36,200	22,400	22,500	272,000
Na	28,100	3,870	4,850	393
K	25,700	13,200	24,900	2,390
Mg	17,600	8,100	16,400	45,300
Ti	4,830	1,950	4,440	377
P	1,100	539	733	281
Mn	937	392	575	842
F	715	220	560	112
Ba	595	193	250	30
S	410	945	1,850	4,550
Sr	368	28	290	617
C	320	13,800	15,300	113,500
Cl	305	15	170	305
Cr	198	120	423	7.1
Rb	166	197	243	46
Zr	160	204	142	18
V	149	20	101	13
Ce	130	55	45	11
Cu	97	15	45	4.4
Ni	94	2.6	29	13
Zn	80	16	130	16
Nd	56	24	18	8.0
La	48	19	28	9.4
N	46	...	600	...
Y	41	16	20	15
Li	32	15	46	5.2

…http://pubs.usgs.gov/wsp/wsp2254/pdf/wsp2254a.pdf

Hem, John D. USGS. 1995. Study and Interpretation of the Chemical Characteristics of Natural Waters (#USGS Water -Supply Paper 2254)

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Chemical – Geochemistry – geology as the foundation

- Chemical weathering
  - Carbonate weathering (typically of limestone) has the general form:

$CaCO_3(s) + CO_2 + H_2O \Leftrightarrow CaCO_3(s) + HCO^{3-} + H^+ \Leftrightarrow Ca^{2+} + 2HCO_3^-$

- one of the reactants is a pervasive gas (CO_2) and both products are highly soluble ions prone to export from soil by river systems to the ocean

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Carbonate Buffering System

- Why study carbonate buffer system (CBS)?
  - CBS controls pH of natural waters on short-term basis.
  - All chemical species in the CBS (e.g., CO_2) are involved in (and reflect) a variety of biological processes:
    - Photosynthesis/respiration
    - $CaCO_3$(s) formation and dissolution
  - CBS species also are involved in many physicochemical processes, including weathering, atmospheric cooling, ion complexation and transport of fossil fuel burning products.

Carbonate Buffering System

- CBS ion species as a function of pH:
  - Concentrations vary with **pH**, which is -log(H+).

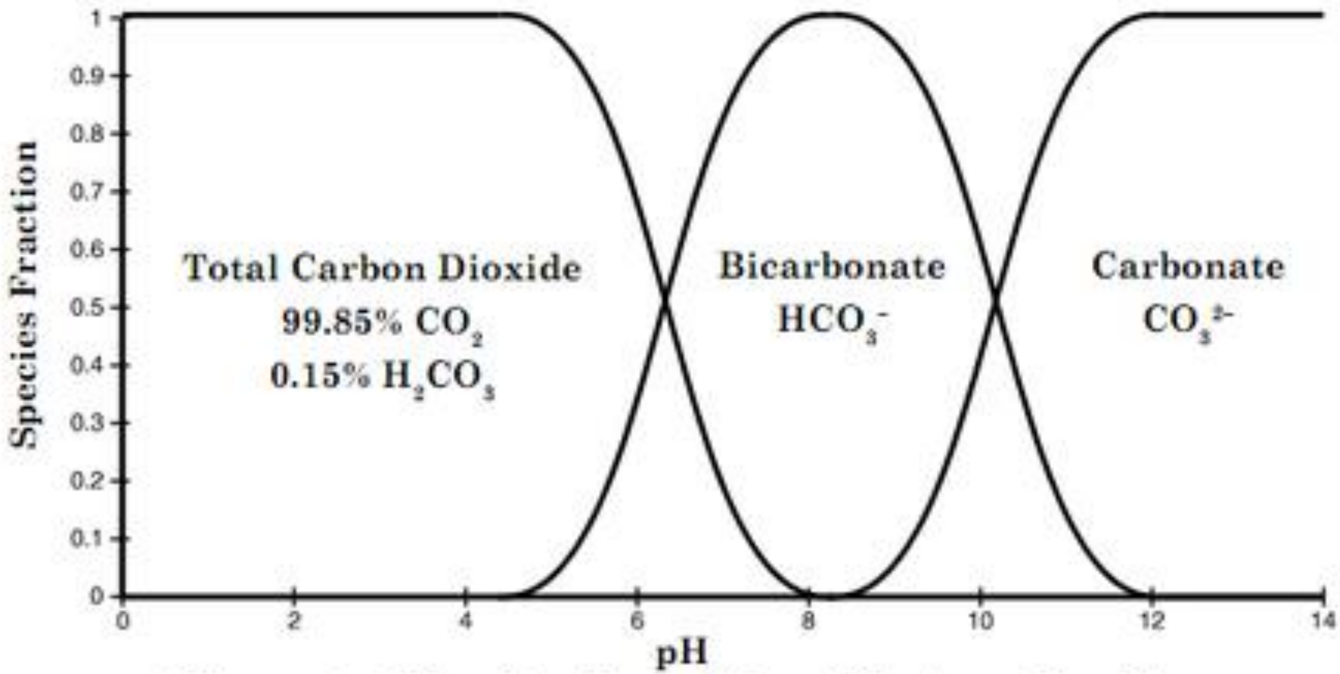
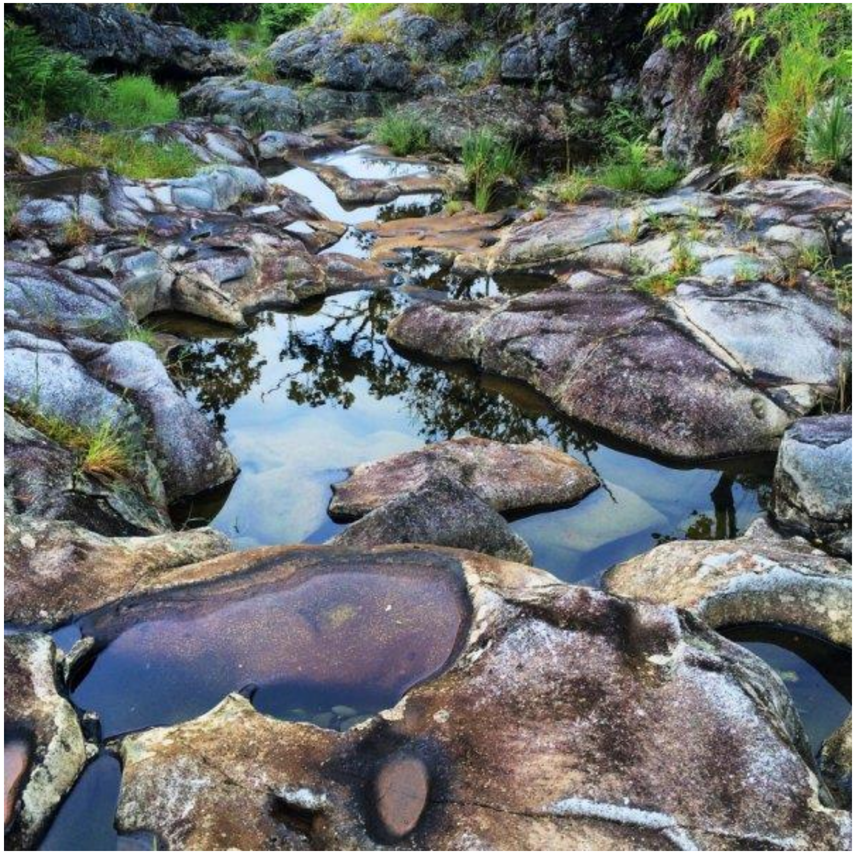


Figure 1 – Distribution of Total Carbon Dioxide, Bicarbonate, and Carbonate vs. pH

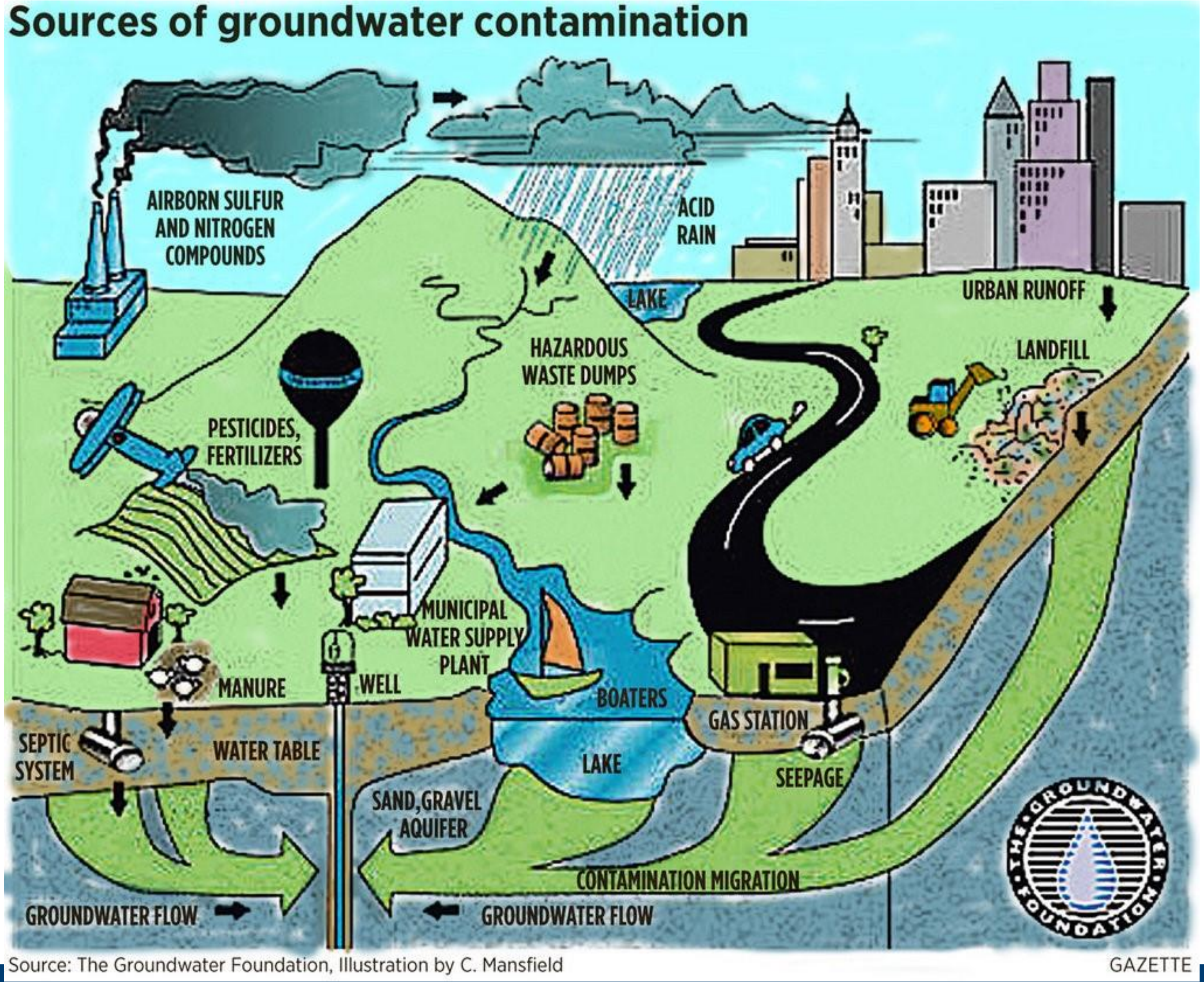
John A. Wojtowicz – Chapter 1.1

Stream baseflow ion chemistry set by watershed-scale geologic weathering

- Dissolved composition of river water records the types of chemical weathering (both substrates and rates) that occur on in their drainage basins



Surface land use can also have influences on baseflow stream chemistry



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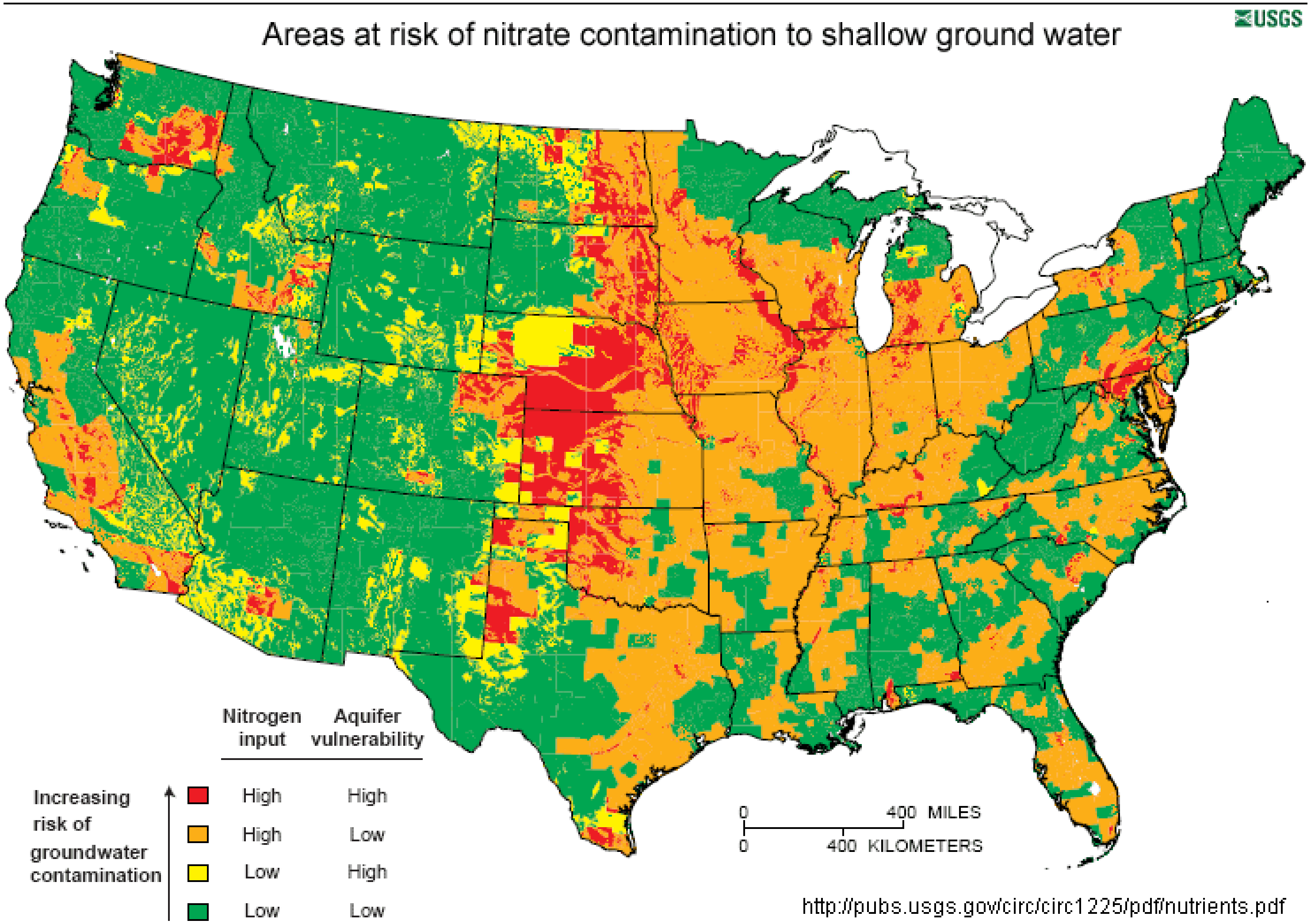

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During stormflow

- pH, acidity, and alkalinity of runoff reflects the chemical characteristics of precipitation and the land surface
- Dominant ion in most precipitation is bicarbonate (HCO_3^-)
  - Except in areas with significant ocean spray
- Bicarbonate ion produced by carbon dioxide reacting with water:
  - $H_2O + CO_2 = H^+ + HCO_3^-$
  - Reaction produces hydrogen ion (H^+), thus increasing acidity and lowering pH
- Due to CO_2 in the atmosphere, most rain is naturally slightly acidic (pH about 5.6)
  - Increased acidity in rainfall can be caused by inputs, particularly from burning fossil fuels.

Stormflow Water Quality

- Sediment
  - Compounds adsorbed to sediment
- Manure
- Nutrients
- Toxics
- Sewage
- Bacteria
- Etc…

Dissolved Gases

Why are dissolved gases important?

- Rates of change in concentrations of bioactive gases (e.g., O_2, CO, CO_2, H_2S, CH_4) can be directly related to rates of biological processes (if the gas exchange rate with the atmosphere is known)
- CO_2 influences the pH of natural waters and the chemical weathering rates of the continents
- Some gases set the reduction-oxidation conditions of water and sediments (e.g., O_2, H_2S, CH_4).

Dissolved Gases

Factors that affect gas solubility (i.e., Henry's Law Constant):

- Molecular weight (MW)→ directly related to the solubility of all inert gases.
- Temperature (T)→ inversely related
- Pressure (P) → directly related to the solubility of all inert gases.
- Salinity (S) → inversely related to solubility of all inert gases.

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Table 4. Mean composition of the atmosphere

[After Mirtov (1961)]

Gas	Percentage by volume	Partial pressure (atm)
N_2	78.1	0.781
O_2	20.9	.209
Ar	.93	.0093
H_2O	.1–2.8	.001–0.028
CO_2	.03	.0003
Ne	1.8×10^{-3}	1.8×10^{-5}
He	5.2×10^{-4}	5.2×10^{-6}
CH_4	1.5×10^{-4}	1.5×10^{-6}
Kr	1.1×10^{-4}	1.1×10^{-6}
CO	$(0.06-1)\times10^{-4}$	$(0.06-1)\times10^{-6}$
SO_2	1×10^{-4}	1×10^{-6}
N_2O	5×10^{-5}	5×10^{-7}
H_2	$\sim5\times10^{-5}$	$\sim5\times10^{-7}$
O_3	$(0.1-1.0)\times10^{-5}$	$(0.1-1.0)\times10^{-7}$
Xe	8.7×10^{-6}	8.7×10^{-8}
NO_2	$(0.05-2)\times10^{-6}$	$(0.05-2)\times10^{-8}$
Rn	6×10^{-18}	6×10^{-20}

The main reservoir of all gases, except CO_2 and H_2O, is in the atmosphere

- So, atmospheric concentrations primarily control corresponding dissolved concentrations

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Dissolved Oxygen

- **Dissolved Oxygen (mg/L or ppm)**
  - **Measurement:**
    - Measured in mg/L or ppm (1 mg/L = 1 ppm)
  - **Importance:**
    - Needed for respiration for all aquatic life
    - Can be altered by other physical/chemical parameters

PA State Standards for DO levels:

Dissolved Oxygen

The following specific dissolved oxygen criteria recognize the natural process of stratification in lakes, ponds and impoundments. These criteria apply to flowing freshwater and to the epilimnion of a naturally stratified lake, pond or impoundment. The hypolimnion in a naturally stratified lake, pond or impoundment is protected by the narrative water quality criteria in § 93.6 (relating to general water quality criteria). For nonstratified lakes, ponds or impoundments, the dissolved oxygen criteria apply throughout the lake, pond or impoundment to protect the critical uses.

Parameter	*Symbol*	*Criteria*	*Critical Use**
	DO_1	For flowing waters, 7-day average 6.0 mg/l; minimum 5.0 mg/l. For naturally reproducing salmonid early life stages, applied in accordance with subsection (b), 7-day average 9.0 mg/l; minimum 8.0 mg/l. For lakes, ponds and impoundments, minimum 5.0 mg/l.	CWF
	DO_2	7-day average 5.5 mg/l; minimum 5.0 mg/l.	WWF
	DO_3	For the period February 15 to July 31 of any year, 7-day average 6.0 mg/l; minimum 5.0 mg/l. For the remainder of the year, 7-day average 5.5 mg/l; minimum 5.0 mg/l.	TSF

Dissolved Oxygen

- **Dissolved oxygen (mg/L or ppm)**
  - **Inversely related to temperature:**
    - **As temp increases, DO decreases**
  - DO levels may **increase** due to
    - diffusion from the atmosphere,
    - plant metabolism/photosynthesis
    - turbulent mixing (riffles)
  - DO levels may **decrease** due to
    - warm temperatures
    - **an overload of decaying organic matter** (due to excess nutrients)
    - slow moving, deep water

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What is Water Quality? – Common Measurements

- Water temperature (I know –not “chemical”, but highly relevant)

- pH
- Alkalinity
- Hardness
- Conductivity and total dissolved solids
  - Major ions (chloride, Ca, Mg, K, Na, SO_4)
  - Contributes to conductivity/TDS
- Nutrients
  - Phosphorus
  - Nitrogen
  - Carbon
- Dissolved O_2 (already mentioned)

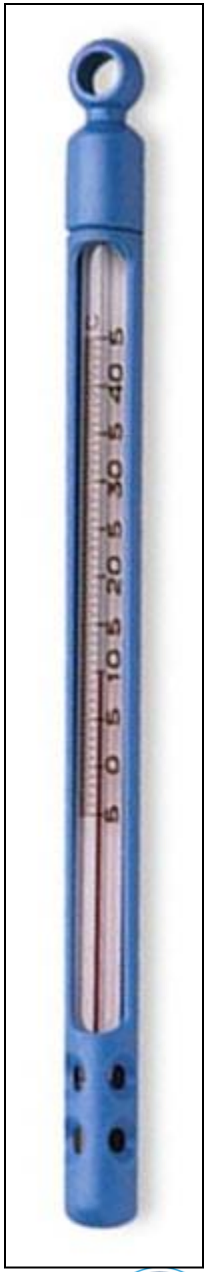
Temperature

Pa State Standards for Water Temperature (but recently revised):

- Depends on time of year

Temperature	Maximum temperatures in the receiving water body resulting from heated waste sources regulated under Chapters 92a, 96 and other sources where temperature limits are necessary to protect designated and existing uses.	See the following table.

SYMBOL: CRITICAL USE: PERIOD	*$TEMP_1$ CWF*	*$TEMP_2$ WWF TEMPERATURE °F*	*$TEMP_3$ TSF*
January 1-31	38	40	40
February 1-29	38	40	40
March 1-31	42	46	46
April 1-15	48	52	52
April 16-30	52	58	58
May 1-15	54	64	64
May 16-31	58	72	68
June 1-15	60	80	70
June 16-30	64	84	72
July 1-31	66	87	74
August 1-15	66	87	80
August 16-30	66	87	87
September 1-15	64	84	84
September 16-30	60	78	78
October 1-15	54	72	72
October 16-31	50	66	66
November 1-15	46	58	58
November 16-30	42	50	50
December 1-31	40	42	42



Importance:

- Temperature/dissolved oxygen relationship:

  The higher the temperature, the less oxygen the water can hold.
- Some species adapt to a narrow range of temperatures. Changes of only a few degrees can affect the life in a stream.
- Temperature **affects feeding, respiration, and aquatic metabolism**.

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Thermal Characteristics

- Factors affecting water temperature
  - Latitude, Altitude
  - Tree canopy
  - Reach volume to surface area
  - Groundwater accrual
  - Seasonality – meltwater from snow and ice
  - Diel – day/night
  - Turbidity
  - Impoundments (lakes, dams, ponds, etc…)
  - Point sources
  - Land use influences (impervious surface)

Why is water temperature so important?

- Temperature has effects on
  - Distribution of organisms
    - Eurythermal, Stenothermal
    - Algae – diatoms versus blue-green algae
    - Insects, Fish
  - Biological processes
    - Growth rates
    - Metabolic processes
  - Water chemistry
    - Concentrations of dissolved gasses
    - Reaction rates

Chemical – pH

- Measure of hydrogen ions (H^+)
- Measured on a 0-14 scale
- Pure water has equal amount of H^+ and OH^- ions and has a pH of 7
- **Importance:**
  - Aquatic organisms are sensitive to pH fluctuations
- Controls: geology, productivity of waters, bi-carbonate buffering system

***PA State Standards for pH:**

pH	From 6.0 to 9.0 inclusive.	CWF, WWF, TSF, MF

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Alkalinity

- Alkalinity or Alk (mg/L)
- Measure of the acid neutralizing capacity (buffering) capacity of a solution and defined as the sum of bases that are titratable with strong acid: **$[Alk] = [HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-] - [H^+]$**
  - Natural sources in water are: Carbonate (CO_3) and bicarbonate (HCO_3) ions
    - From Limestone ($CaCO_3$), Magnesium Carbonate ($MgCO_3$)
  - Importance: Higher alkalinity = better buffer against changes in pH; increased stability (fish kills example)

***Pa State Standards for Alkalinity:**

Parameter	*Symbol*	*Criteria*	*Critical Use**
Alkalinity	Alk	Minimum 20 mg/l as CaCO3, except where natural conditions are less. Where discharges are to waters with 20 mg/l or less alkalinity, the discharge should not further reduce the alkalinity of the receiving waters.	CWF, WWF, TSF, MF

Alkalinity

- Alkalinity (mg/L)
- Measure of the acid neutralizing capacity (buffering) capacity of a solution and defined as the sum of bases that are titratable with strong acid: $[Alk] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$
  - Nat ... ate (HC
    - ... gCO_3)
  - Imp ... ges in pH; inc

*Pa State

Water Alkalinity as $CaCO_3$	
0-10 mg/L	Very Low
11-50 mg/L	Low
51-150 mg/L	Moderate
151-300 mg/L	High
>300 mg/L	Very High

Parameter	*Symbol*	*Criteria*	*Critical Use**
Alkalinity	Alk	Minimum 20 mg/l as CaCO3, except where natural conditions are less. Where discharges are to waters with 20 mg/l or less alkalinity, the discharge should not further reduce the alkalinity of the receiving waters.	CWF, WWF, TSF, MF

Water Research Center

Hardness

- Concentration of calcium and magnesium ions in water
- Limestone=source of hardness
- Importance:
  - Plants and aq. life require Ca/Mg-cell walls, shells, bones. Mg for photosynthesis.
  - Fish repro limited in levels <15mg/L or >200mg/L
  - Long-term human consumption of 350 mg/L can be harmful.
  - Aquatic life toxicities to other pollutants can vary with Hardness (e.g., Chloride)

***No Pa State Standards for Hardness**

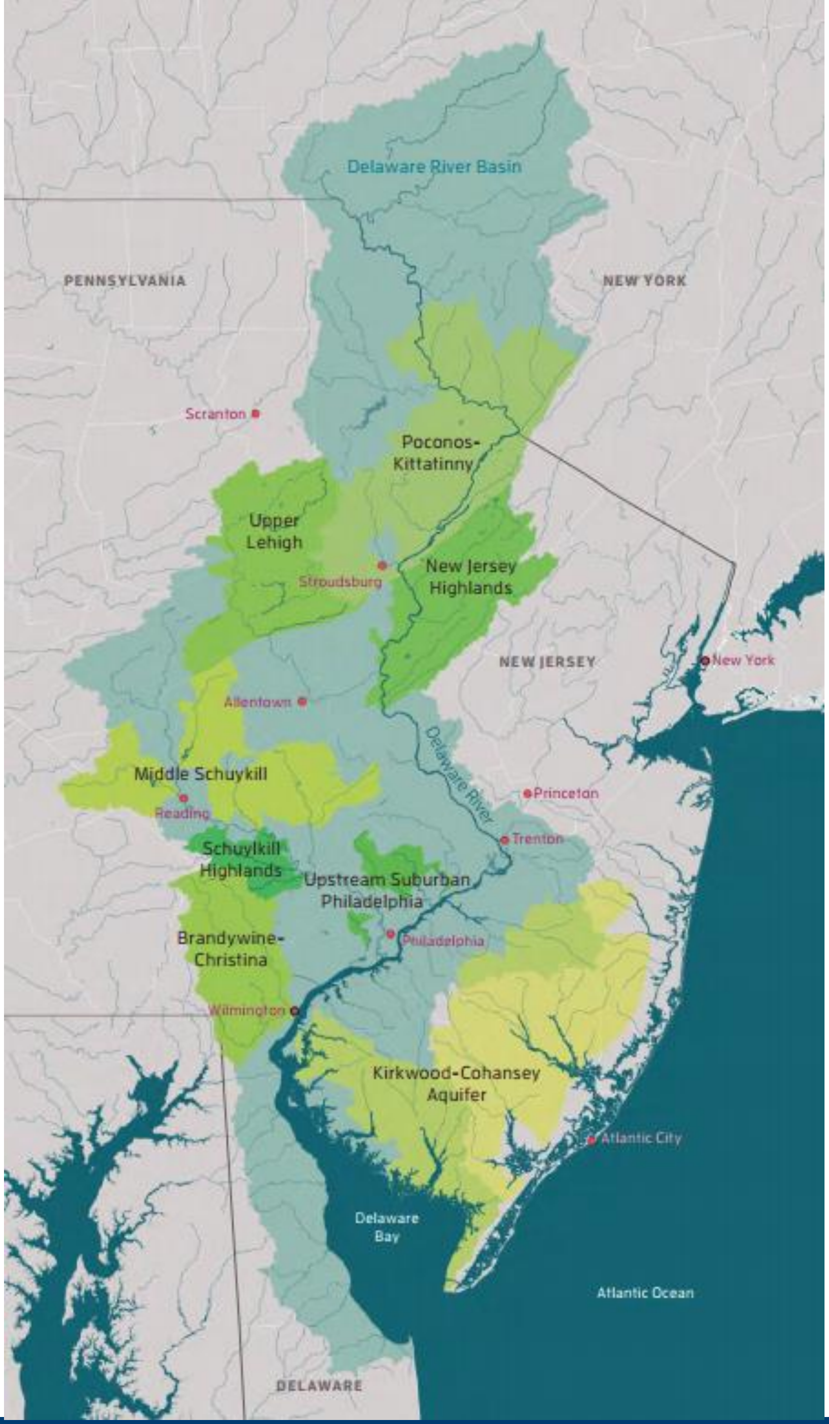
Water Hardness as $CaCO_3$	
0-20 mg/L	Soft
21-60 mg/L	Moderately soft
61-120 mg/L	Moderately hard

Hardness

- Concentration of calcium and magnesium ions in water
- Limestone=source of hardness
- Importance:
    - Plants and aq. life require Ca/Mg-cell walls, shells, bones. Mg for photosynthesis.
    - Fish repro limite
    - Long-term huma … harmful.
    - Aquatic life toxic … ith Hardness (e.g., Chloride)

***No Pa State Standard**

Water Hardness as $CaCO_3$	
0-20 mg/L	Soft
21-60 mg/L	Moderately soft
61-120 mg/L	Moderately hard
121-180 mg/L	Hard
>180 mg/L	Very Hard



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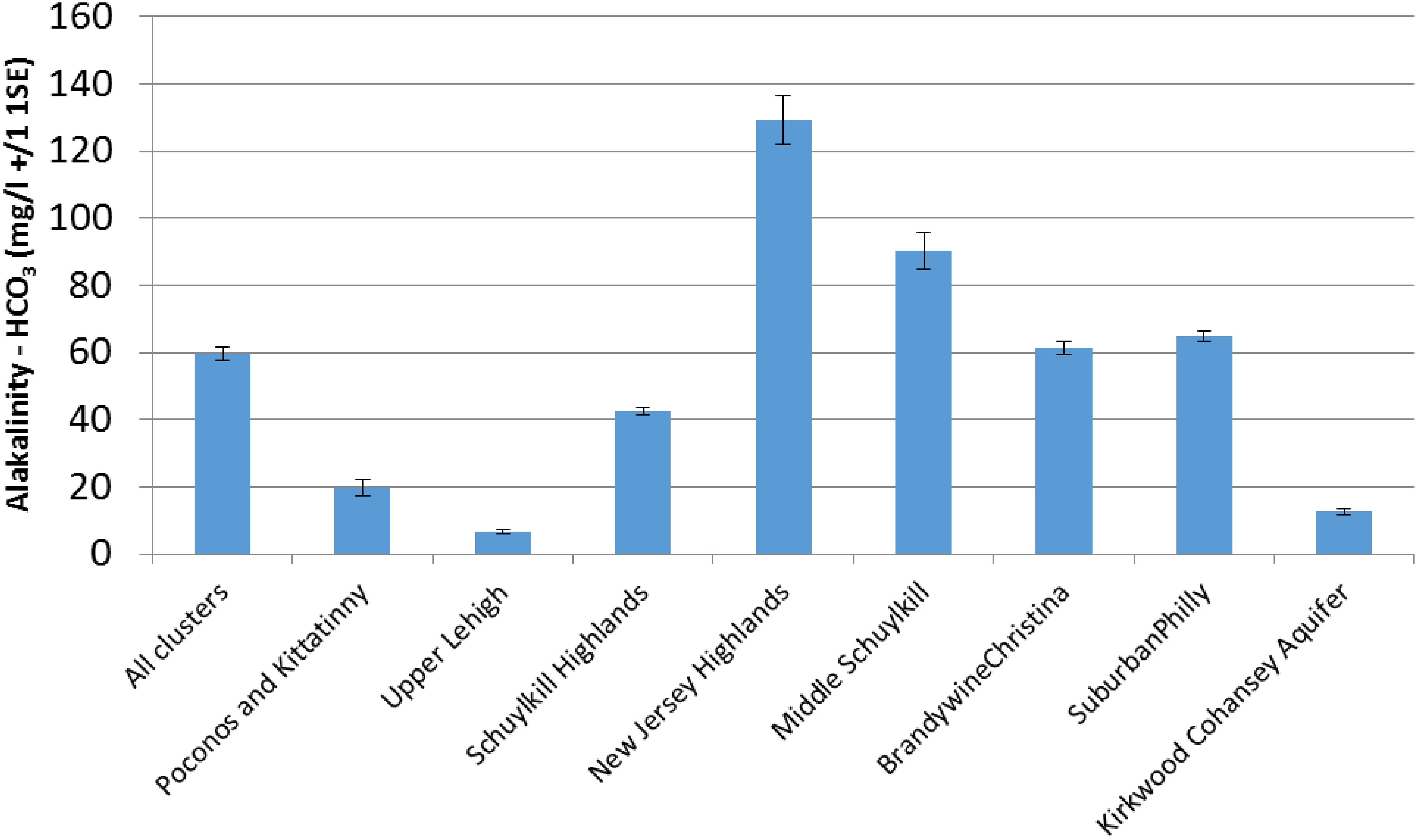
Alkalinity - carbonate



Data source: ANSD (M. Kurz) 2013-15 (ANSD + Cluster Partners)
Data are provisional (not final and subject to change)
n = 513; (75 PK; 53 UL; 62 SH; 54 NJH; 92 MS; 136 BC; 38 SP; 3 KCA)

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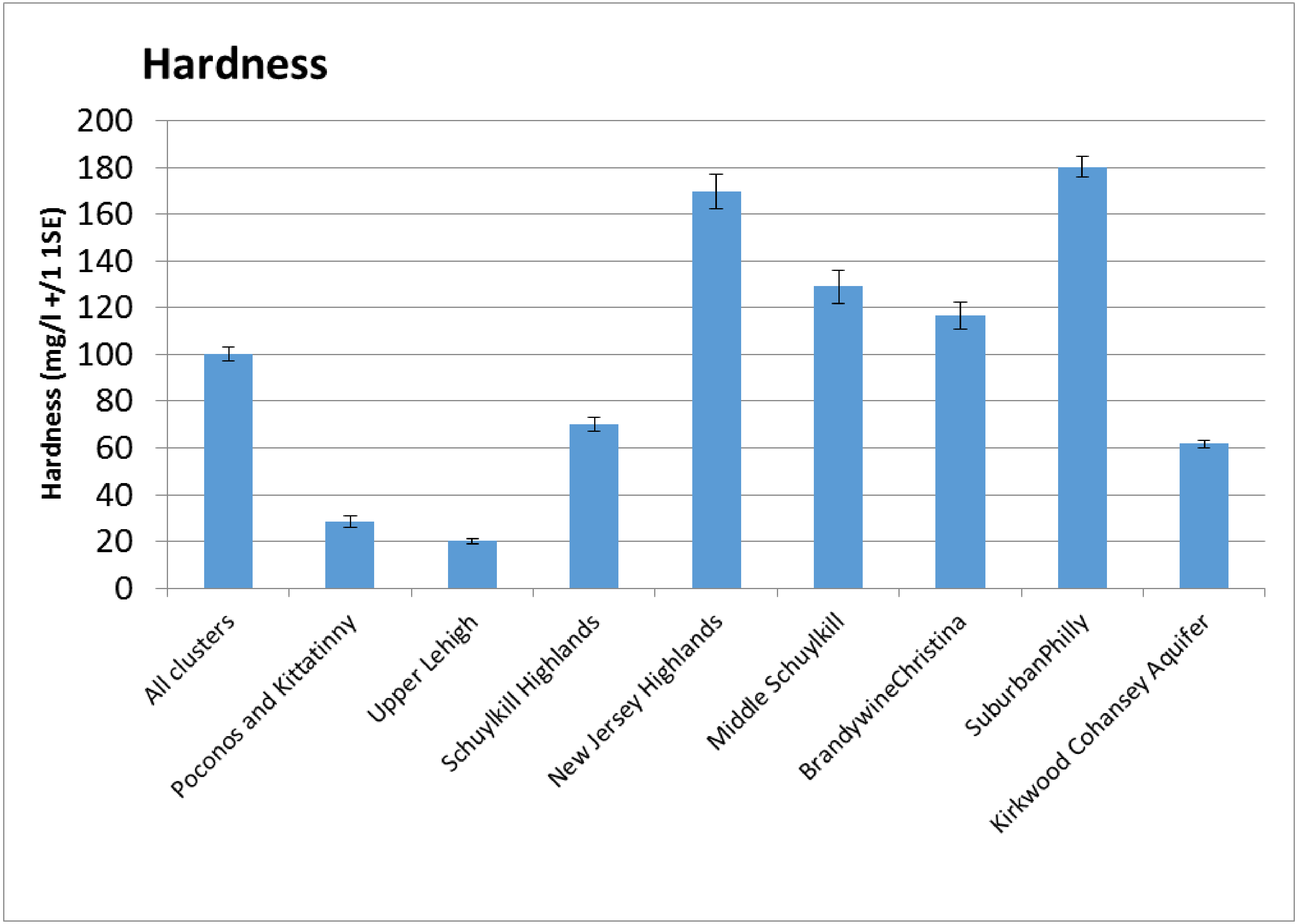

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n = 513; (75 PK; 53 UL; 62 SH; 54 NJH; 92 MS; 136 BC; 38 SP; 3 KCA)

Conductivity

- **Measures water's ability to pass an electrical current (AC voltage to nickel electrode)**
- Conductivity indicates the presence of ions in the water
- Data can determine concentration of solutions, detect contaminants, determine purity of water.
- Is affected primarily by geology of the area through which the water flows through
  - Water that flows through granite tends to have lower conductivity
  - Water that runs through limestone and clay has higher conductivity
- What else can affect conductivity levels?
  - **Mining operations** – release of iron, copper, cadmium
  - **Agriculture** – adds nutrient ions
  - **Sewage effluent** – chloride, nitrates, and phosphate
  - **Urban runoff** – auto fluids, salts, and chemical

Conductivity

Measurement for Specific Conductivity

- Temperature references at 25^oC or 20^oC typical

State Standards:

- No regulated level in Pennsylvania – but TDS for PWS's
- Pennsylvania generally ranges from 50 to 1500 µS/cm
- Find normal background levels/ Closely monitor any deviations

Parameter	*Symbol*	*Criteria*	*Critical Use**
Total Dissolved Solids	TDS	500 mg/l as a monthly average value; maximum 750 mg/l.	PWS

TABLE 1

Typical ranges of values for some water field measurements.

Type of waters:	Specific Conductance (µS/cm)	Eh (millivolts)	pH (pH units)
rain water	2 to 100	+400 to +600	4 - 7
freshwater lakes/streams	2 to 100	+300 to +500	6.5 - 8.5
ground water	50 to 50,000	-200 to +100	6 - 8.5
brines	up to 500,000	-300 to -600	near neutral
ocean water	~ 50,000	+300 to +500	7.8 - 8.4
landfill leachate	10,000	variable	near neutral
acid mine drainage	up to 500,000	+600 to +800	below 5
wetlands / bogs	50 to 50,000	+100 to -100	variable

From: Sanders, L.L., 1998, *A Manual of Field Hydrogeology*: Prentice-Hall, NJ, 381p.

TDS? – Total Dissolved Solids

- TDS is the combined total of solids dissolved in water
- Electrical Conductivity is the ability of something to conduct electricity (in this case, water's ability to conduct electricity).
- TDS is measured by weighing residue found in water after the water has evaporated.
  - TDS “meter” measures conductivity and then converts it to a TDS
  - Since different metals, minerals and salts will be more or less conductive than others, there are different conversion factors that can be used, e.g.,:
    - **TDS vs EC based on NaCl:** 0.47 to 0.50
      TDS vs EC based on KCl: 0.50 to 0.57
  - Most meters us NaCl = 0.5 (i.e., X uS/cm * 2 = TDS)

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Freshwater Science. 2014. 33(1):1–17.

Natural variation and current reference for specific conductivity and major ions in wadeable streams of the conterminous USA

Michael B. Griffith[1, 2]

[1]Office of Research and Development, National Center for Environmental Assessment, US Environmental Protection Agency, MS A-130, 26 W. Martin Luther King Drive, Cincinnati, Ohio 45268 USA

Abstract:
Variation in specific conductivity and major ions in streams must be understood to assess the effects of changes in ionic strength and salinity on stream biota. I compiled data for randomly selected sites from surveys conducted from 1985 to 2009 by the US Environmental Protection Agency (EPA). I followed EPA methods to estimate reference values for specific conductivity (60 ecoregions) and each major ion (34 ecoregions) as the 25th percentile of values in 1st- to 4th-order streams in Level III ecoregions with data from ≥25 sites (85 ecoregions). The 25th percentiles of specific conductivity were <200 µS/cm for most eastern and western montane ecoregions, except those dominated by limestone or calcareous till. Arid western ecoregions had higher specific conductivities. Ca^{2+} was generally the most abundant cation followed by Mg^{2+}, Na^{+}, and K^{+}. HCO_3^{-} was generally the most abundant anion followed by SO_4^{2-} and Cl^{-}. Ecoregions where SO_4^{2-} or Cl^{-} concentrations were greater than HCO_3^{-} concentration have been affected by acidic precipitation or are influenced by marine air masses, respectively, and have very low specific conductivities. Patterns of variation appear to be associated with 3 processes controlling total and relative concentrations of major ions in freshwaters. In many ecoregions, relative ionic concentrations reflect underlying geology, but in arid ecoregions, relative ionic concentrations show concentration by evaporation. Relative ionic concentrations in coastal ecoregions and those affected by acidic precipitation reflect the ionic content of precipitation. Verification of these factors awaits better quantification of the geological and climatic characteristics of each ecoregion.

Fres **Key words:** specific conductivity, calcium, magnesium, sodium, potassium, bicarbonate, sulfate, chloride, ecoregions, geographic variation, current reference, wadeable streams

FASTTRACKED

Effects of major ions on natural benthic communities: an experimental assessment of the US Environmental Protection Agency aquatic life benchmark for conductivity

William H. Clements[1, 2] **and Chris Kotalik**[1, 3]

[1]Department of Fish, Wildlife and Conservation Biology, Colorado State University, Fort Collins, Colorado 80523 USA

Abstract
Elevated concentrations of HCO_3^{-}, Cl^{-}, SO_4^{2-}, Mg^{2+}, Na^{+}, and Ca^{2+} in freshwater ecosystems are often associated with anthropogenic disturbances. The US Environmental Protection Agency developed a field-based specific conductance (SC) benchmark of 300 µS/cm for streams affected by mountain-top mining operations. The benchmark has been criticized because of the potential influence of confounding variables and difficulty in demonstrating a causal relationship between elevated SC and macroinvertebrate responses. We conducted 4 stream mesocosm experiments to quantify the effects of major ions on aquatic insect assemblages. We exposed insects from streams with low (60–72 µS/cm) and moderate (200–250 µS/cm) SC to major ions at values bracketing 300 µS/cm. We measured community metabolism, macroinvertebrate drift, community composition, and survival. Sixty-six taxa were exposed to $NaHCO_3$, $MgSO_4$, and NaCl in 4 mesocosm experiments, and 8 dominant families/subfamilies occurred in sufficient densities to develop SC-response relationships. Significant SC-response relationships occurred for each major ion tested. Drift increased and community metabolism decreased with increasing SC. Ephemeroptera were highly sensitive, whereas Trichoptera and Diptera were relatively tolerant. EC20 values (the SC that resulted in a 20% difference from controls) ranged from 151 to 3615 µS/cm and were >300 µS/cm for most endpoints. Mayfly drift, abundance of baetid and heptageniid mayflies, total mayfly abundance, and community metabolism were affected at SC levels near or <300 µS/cm. EC20 values were lower for $NaHCO_3$ and $MgSO_4$ than for NaCl, indicating greater toxicity of these 2 salts. Effects were greater on communities from the low- than the high-SC stream. Thus, accounting for context-dependent responses may be important when establishing contaminant benchmarks or thresholds. The 300-µS/cm benchmark is protective of aquatic insect communities in naturally low-conductivity streams.

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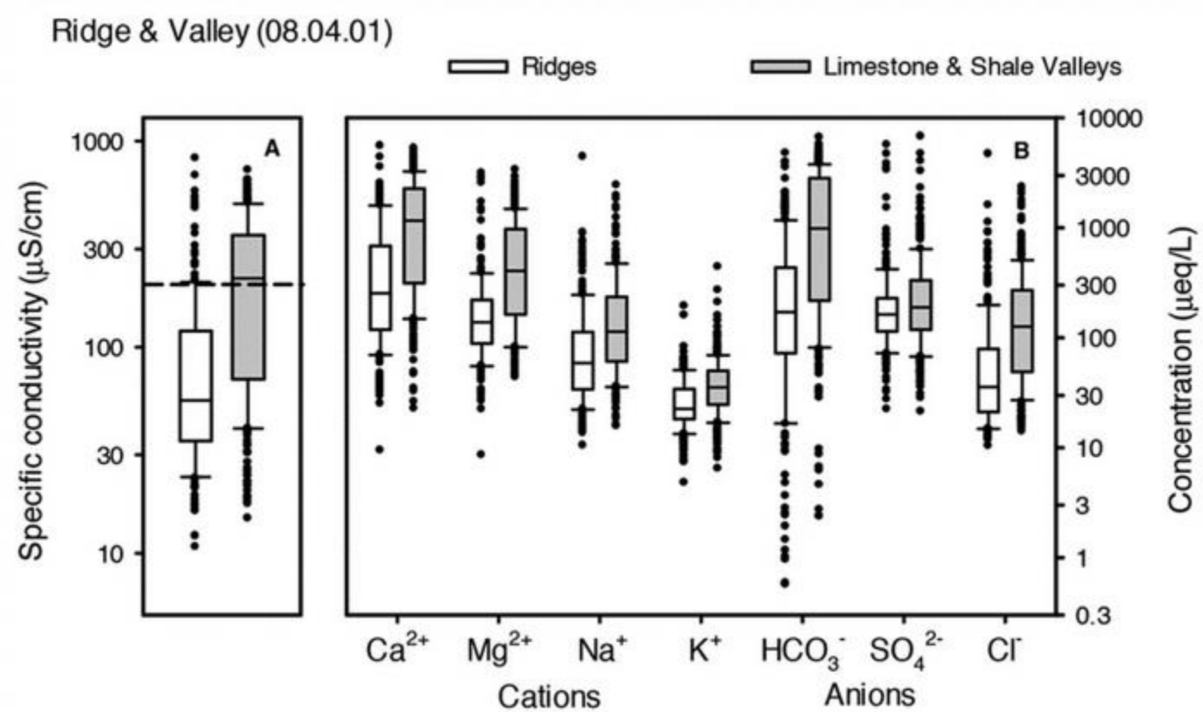

Figure 4. Box-and-whisker plots showing the 90th, 75th, 50th, 25th, and 10th percentiles of specific conductivity (A) and cation and anion concentrations (B). Dots indicate sites that exceeded the 90th and 10th percentiles in the Ridge (*n* = 222–225 depending on variable) and the Limestone and Shale Valleys (*n* = 286–295 depending on variable) subregions of the Ridge and Valley (08.04.01) ecoregion. The horizontal dashed line in panel A represents 200 µS/cm.

Natural variation and current reference for specific conductivity and major ions in wadeable streams of the conterminous USA
Michael B. Griffith
Freshwater Science 2014 33:1, 1-17

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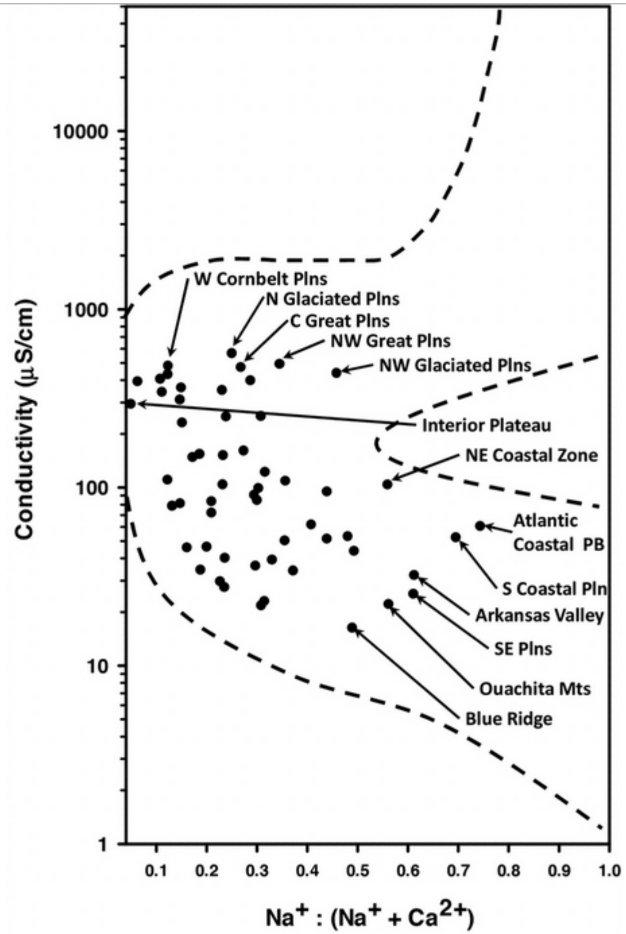

Figure 6. Plot of specific conductivity vs the ratio of Na^+:(Na^+ + Ca^{2+}) (25th percentiles) for each Level III ecoregion with sufficient data. Ecoregions that plot to the upper right (sites with characteristics of the evaporation–crystallization process) or lower right (sites with characteristics of atmospheric precipitation dominance) of the plot are labeled. The dashed lines approximate the outline surrounding the plotted surface waters in fig. 1 by Gibbs (1970). See Figs 2, 3 for abbreviations.

[Natural variation and current reference for specific conductivity and major ions in wadeable streams of the conterminous USA]
Michael B. Griffith
Freshwater Science 2014 33:1, 1-17

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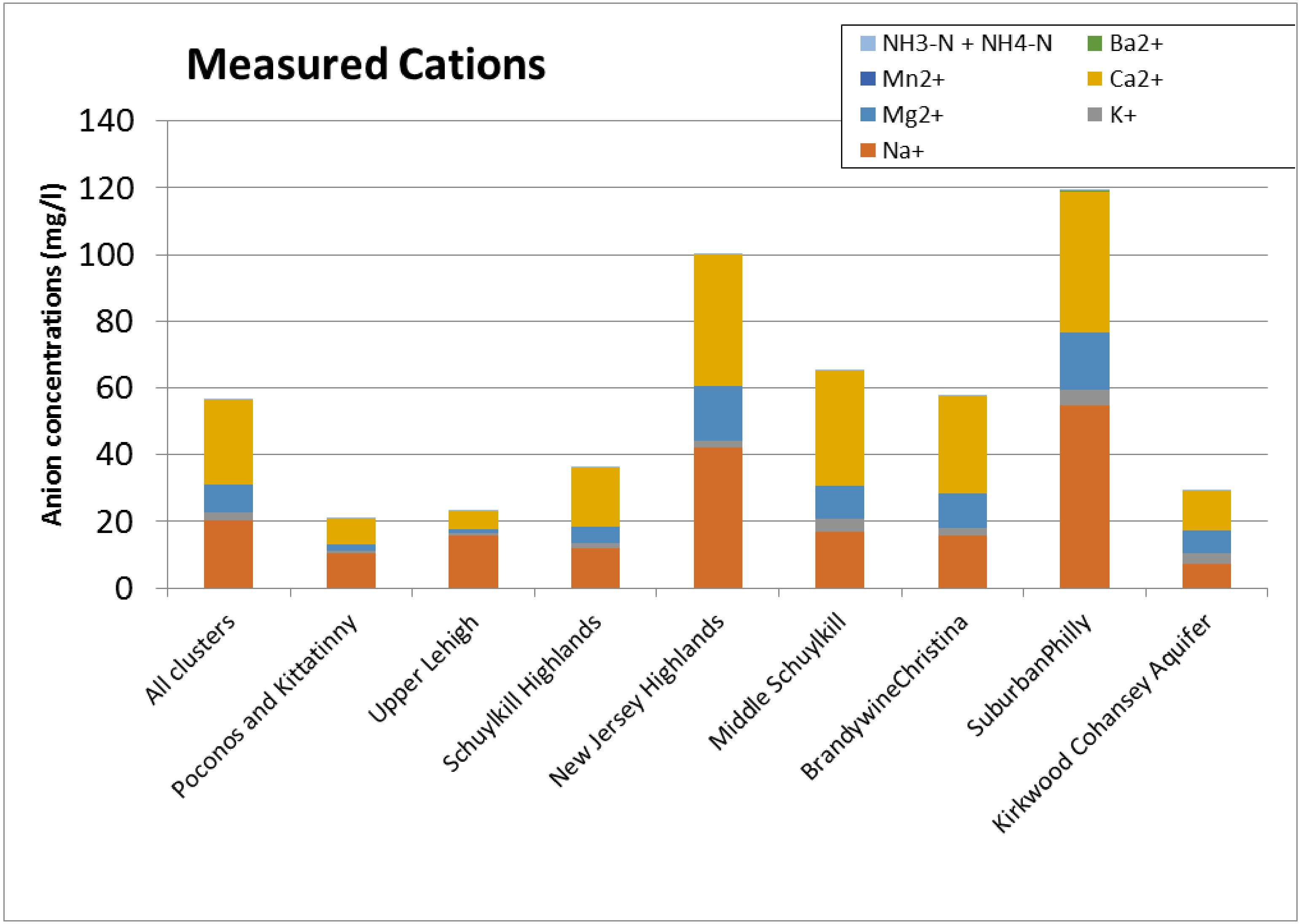

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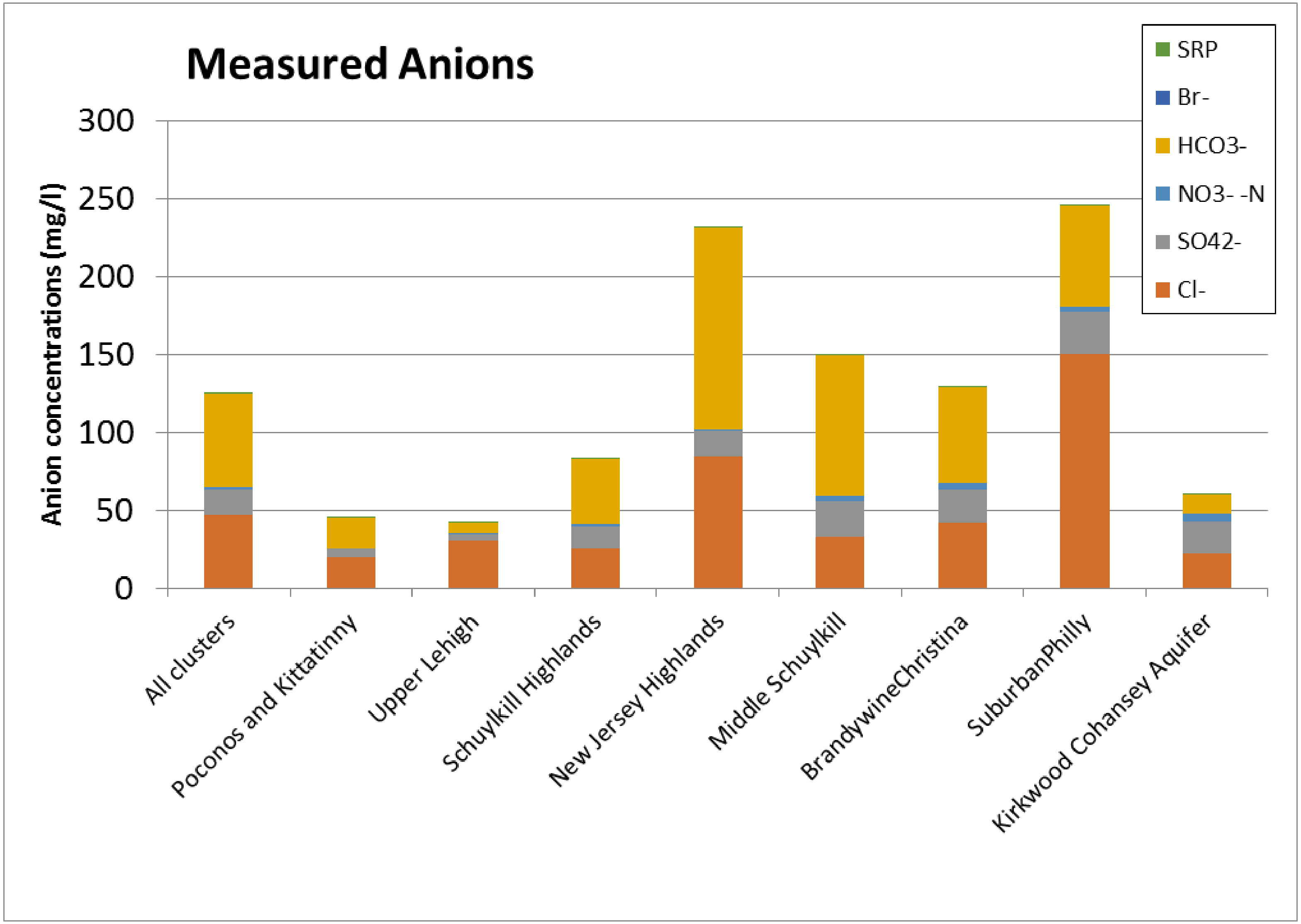

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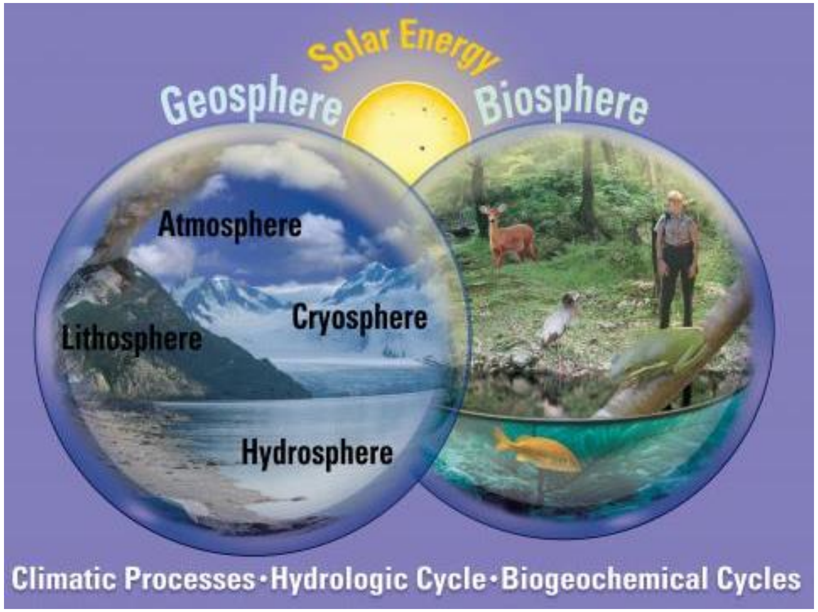
Intro to P, N, and C Cycling in Streams

- Agenda
  - Biogeochemistry introduction
  - Nutrient cycles – phosphorus and nitrogen
  - Carbon cycle and dynamics in streams
  - In-stream dynamics



https://www.fort.usgs.gov/sites/default/files/styles/large/public/slides/biogeochemical%20cycling.jpg?itok=o7pXsNQ2

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PHOSPHORUS, NITROGEN, AND CARBON CYCLES, DYNAMICS, AND TRANSFORMATIONS

Learning objectives:

Know your nitrogen, phosphorus and carbon cycles

Understand transformations of nutrients and energy in streams

Understand many of the factors that control and or drive the dynamics of changing concentrations in P, N, and C in streams

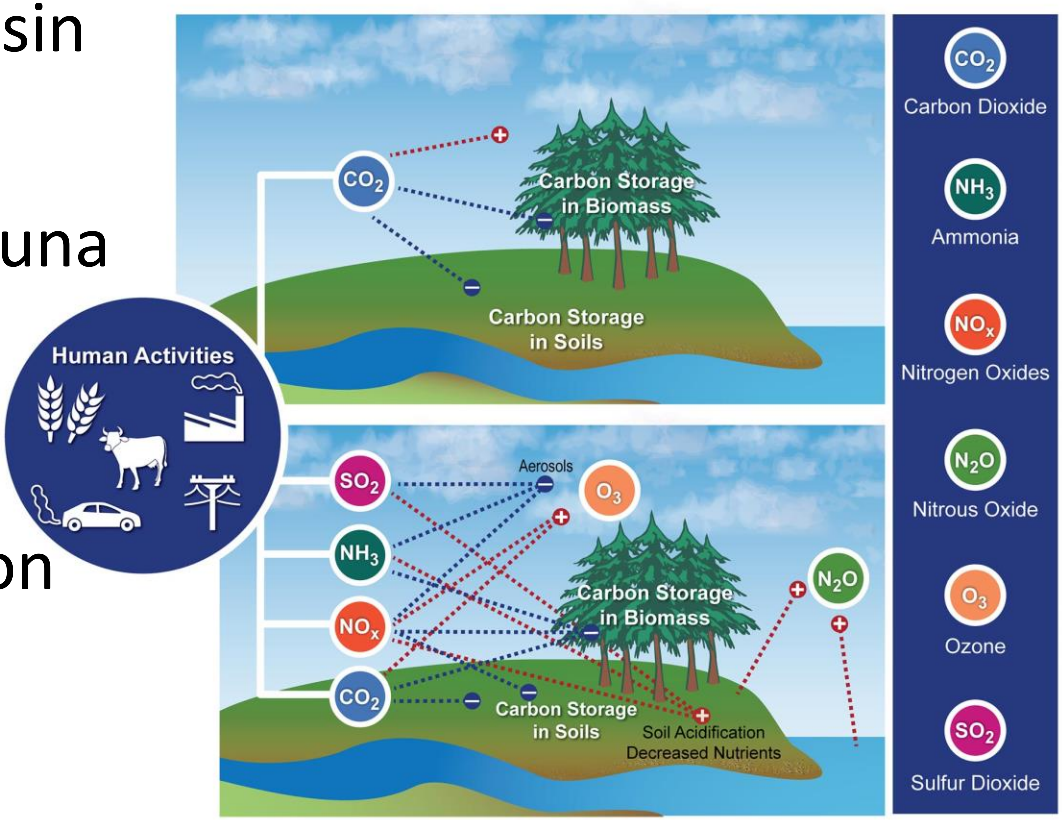
Biogeochemistry

- Biological & chemical transport and transformations to nutrients/energy in ecosystems
- Study of bioactive elements (C, N, P, H, O, S)
  - Sources? How they move through ecosystems?
- Energy flow
- Each element cycles between an organism and the non-living environment
- Bacteria and Archaea are integral to these cycles
- Presence/absence of O_2 very important

*Chemical and Physical Properties

- Vary from basin to basin
- Vary in time
- Influence flora and fauna
  - Growth
  - Reproduction
  - Species composition
  - Competition

Many Factors Combine to Affect Biogeochemical Cycles

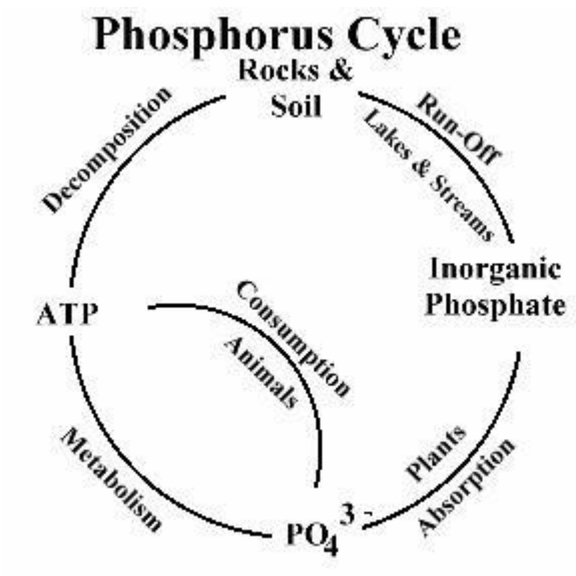


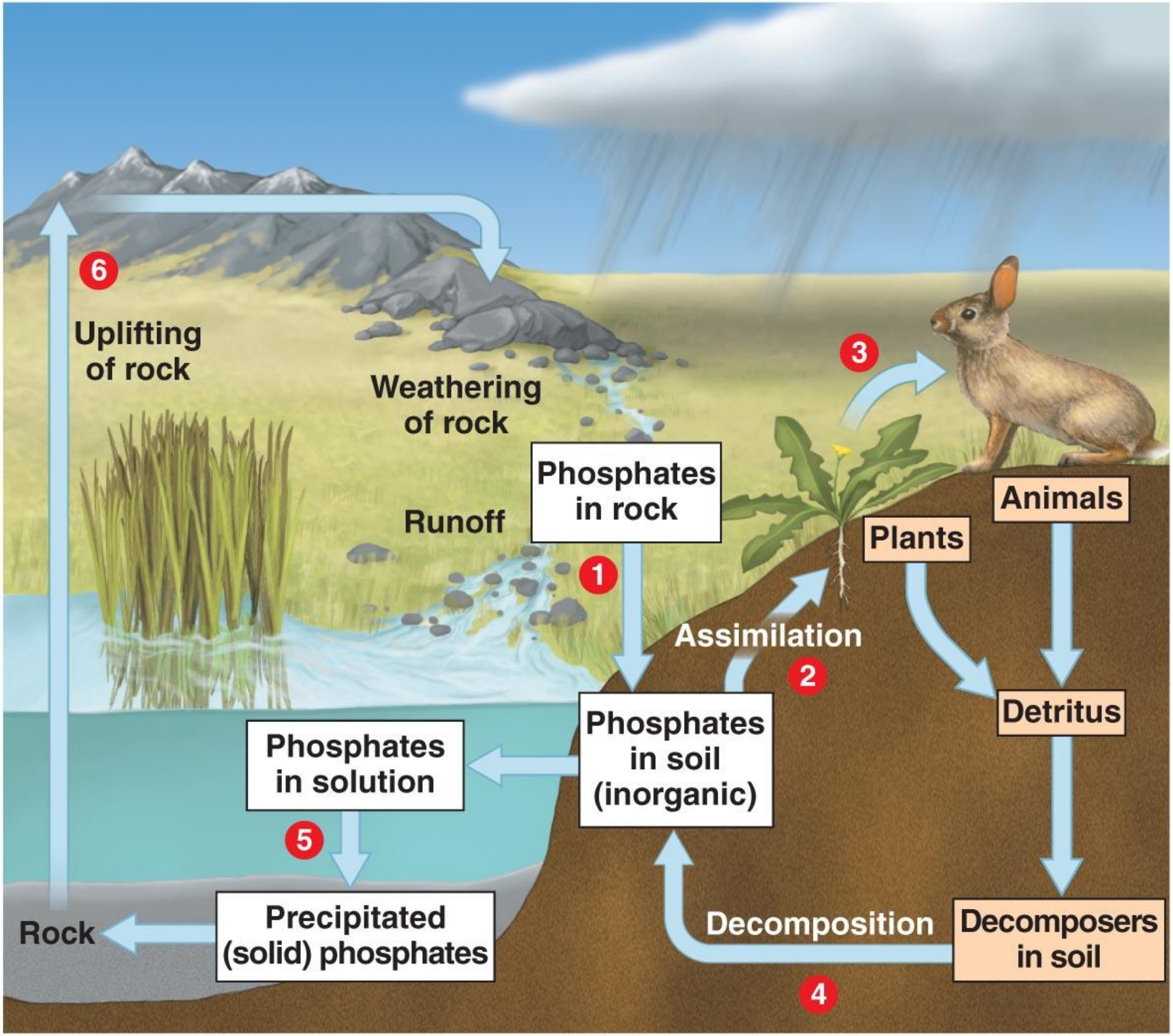
http://nca2014.globalchange.gov/report/sectors/biogeochemical-cycles

Phosphorus Cycle

- One of the most important chemicals in ecosystems
  - Important for plant growth
  - Low or limiting in many alpine and forested streams, northern bogs, freshwater marshes, southern deepwater swamps
  - High or excessive in agricultural watersheds
  - Phosphorus retention (i.e., keep it in place) is often a goal of stream and wetland restoration
- Energy transfer (ATP), phosphorylation

  (glucose-6-phosphate, 1st step in glycolysis)
- Nucleic acid synthesis
- Membrane integrity (phospholipids structure of membranes)





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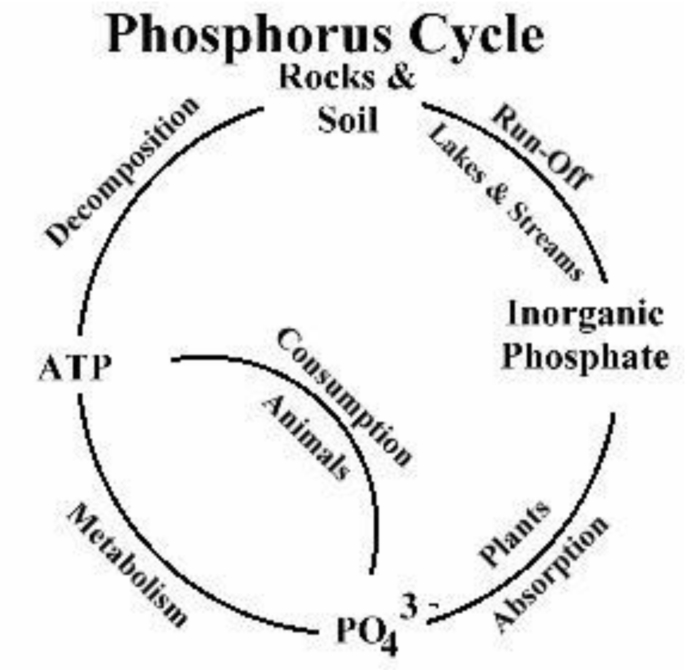
Natural Sources of Phosphorus

- Sedimentary cycle (N cycle is gaseous)
- 0.12% of the Earth's crust
- Sparingly soluble minerals such as apatite $Ca_5(PO_4)_3^+$
- Guano



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Forms of Phosphorus

- Soluble and insoluble complexes
- Organic and inorganic forms
- Aquatic P-cycle has **no significant gaseous component** and the cycle is limited to terrestrial and aquatic phases with the exception of atmospheric transport (e.g., dust)
- Greater than 90% of phosphorus in freshwater occurs as organic P, cellular constituents, and P adsorbed to inorganic particles and dead particulate organic matter.

Phosphates

- Phosphates are not toxic to people or animals unless they are present in very high levels
  - Digestive problems could occur from extremely high levels of phosphate
- In freshwater lakes and rivers, phosphorus is often found to be the growth-limiting nutrient, because it occurs in the least amount relative to the needs of plants
  - If excessive amounts of P and N are added, algae and aquatic plants can become prolific
  - When algae/plants die, bacteria decompose them, and use up oxygen
    - Eutrophication
    - Dissolved oxygen concentrations can drop too low for fish to breathe, leading to fish kills
    - The loss of oxygen in bottom waters can free phosphorus previously trapped in the sediments, further increasing the available phosphorus

Forms of Phosphorus

- Particulate or dissolved phase
- Particulate includes living and dead plankton, precipitates of phosphorus, phosphorus adsorbed to particulates, and amorphous phosphorus
- Dissolved phase includes inorganic phosphorus and organic phosphorus
  - P in natural waters usually found in inorganic form as orthophosphate (PO_4^{-3})
  - Biologically available portion of Ortho-P is termed soluble reactive P (SRP)

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Major Forms of Phosphorus

- Dissolved Inorganic Phosphorus (DIP) (also known as orthophosphate or PO_4^{-3})
- Dissolved Organic Phosphorus (DOP)
- Particulate Organic Phosphorus (POP)
- Particulate Inorganic Phosphorus (PIP)

Commonly Measured Forms of Phosphorus

- **Total phosphorus (TP)**
  - TP = dissolved inorganic P + particulate inorganic P + dissolved organic P + particulate organic P
    - a measure of all the forms of phosphorus, dissolved or particulate, that are found in a sample
  - Concentrations range from <20 μg/l to >200 μg/l **(ppb)**
- **Soluble reactive phosphorus** (SRP)
  - A measure of orthophosphate, the filterable (soluble, inorganic) fraction of phosphorus, the form directly taken up by plant cells
    - Biologically available portion of orthophosphate is termed soluble reactive phosphorus (SRP)

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Sources of P

- Precipitation and fallout
  - Concentrations variable
  - Lower than nitrogen
  - Generally range from 30-100 $\mu g/l$
  - Fallout as dust and fertilizers
- Groundwater
  - Concentrations generally low <20 $\mu g/l$
- Surface runoff
  - Soil related (metal complexation)
  - Often major source of input
  - Related to soil type, topography, vegetative cover, runoff quantity, land use, and pollution

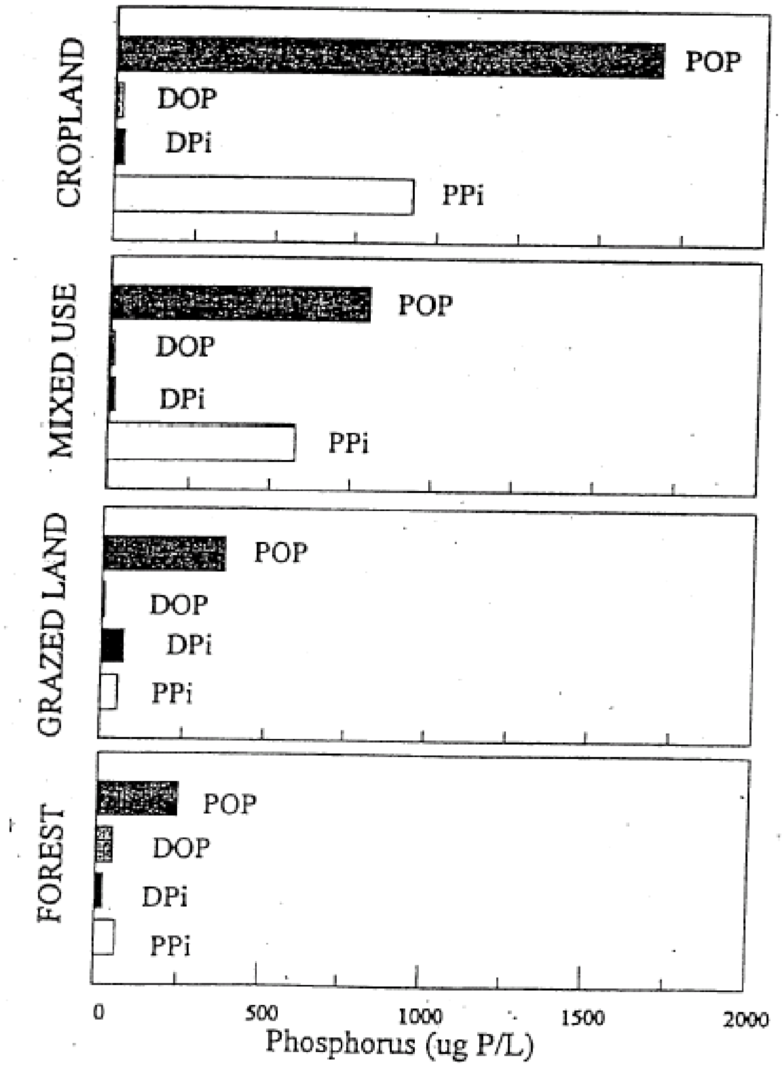

Figure 5. Comparisons of mean phosphorus concentrations in storm events from Rhode River watersheds. Abbreviations are as follows: POP, particulate organic P; DOP, dissolved organic P; DPi, dissolved phosphate; and PPi, particulate phosphate.

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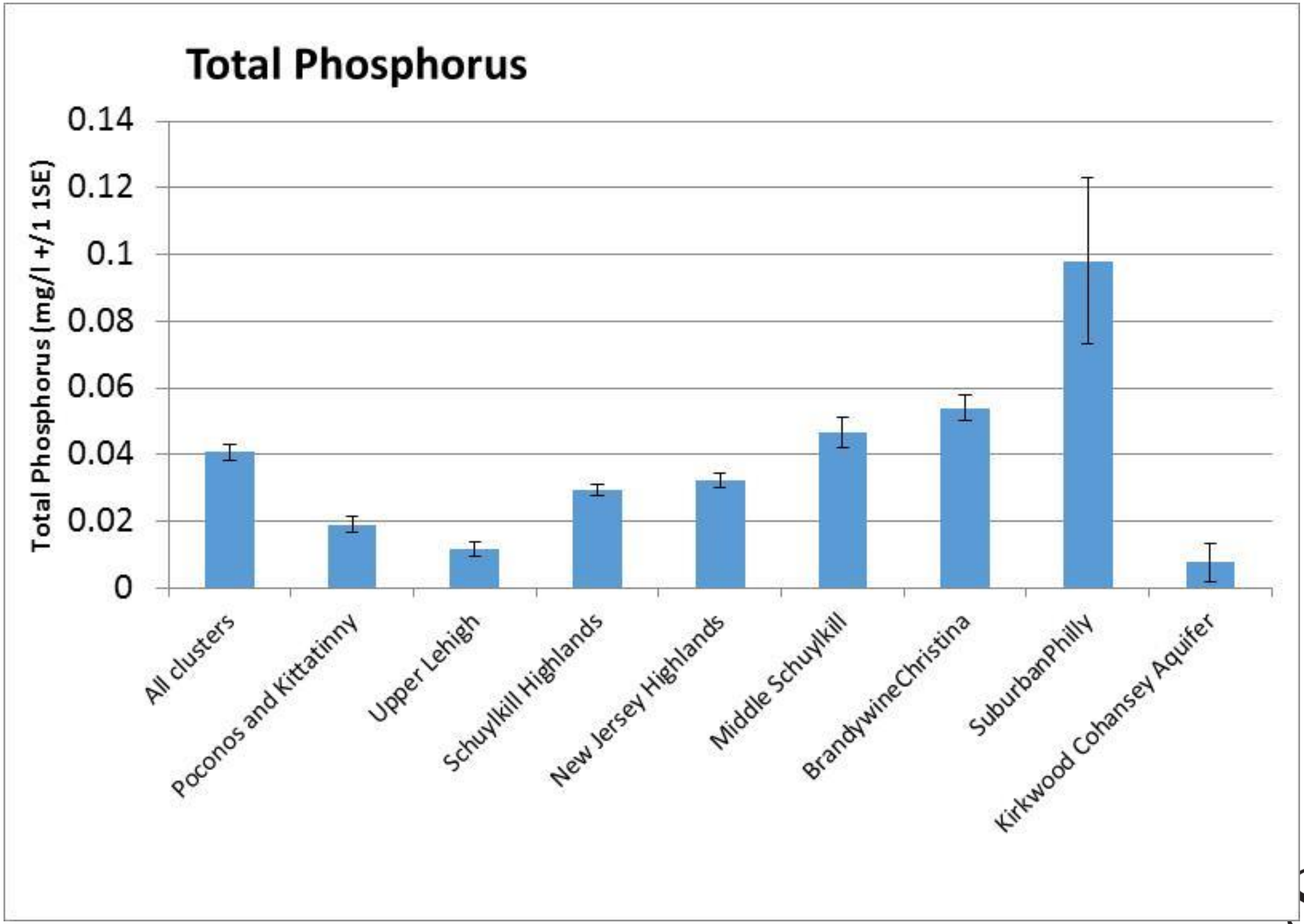
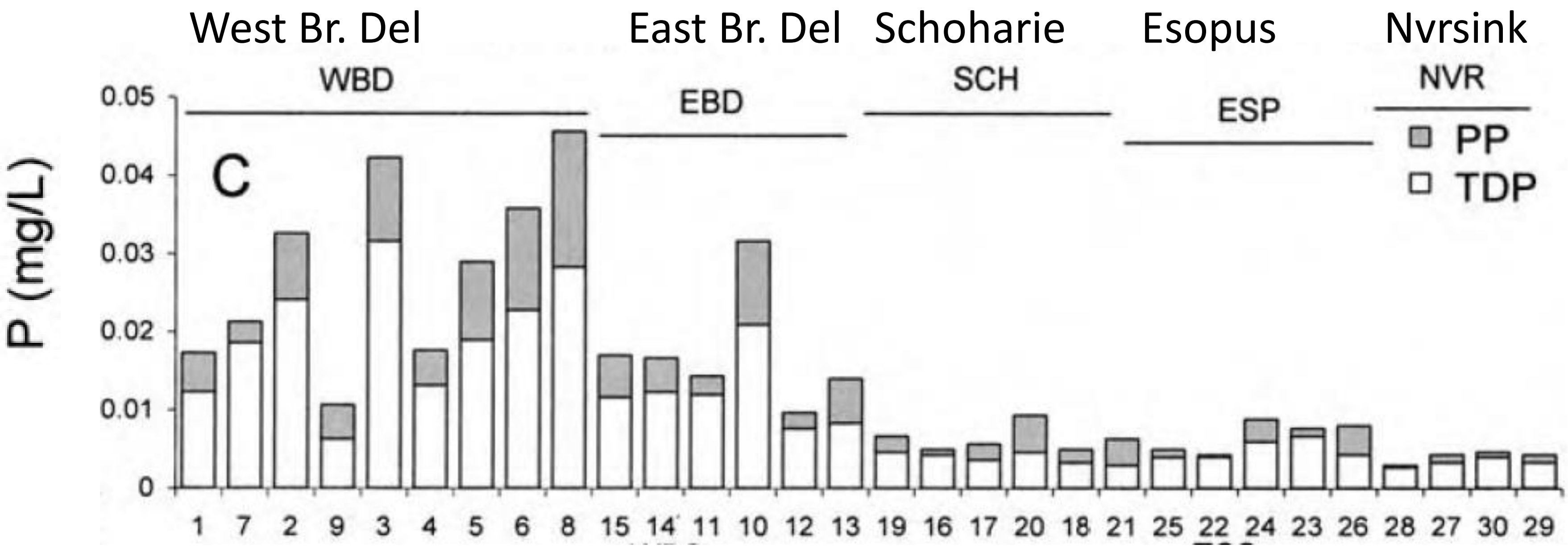
Total Phosphorus in DRWI Clusters



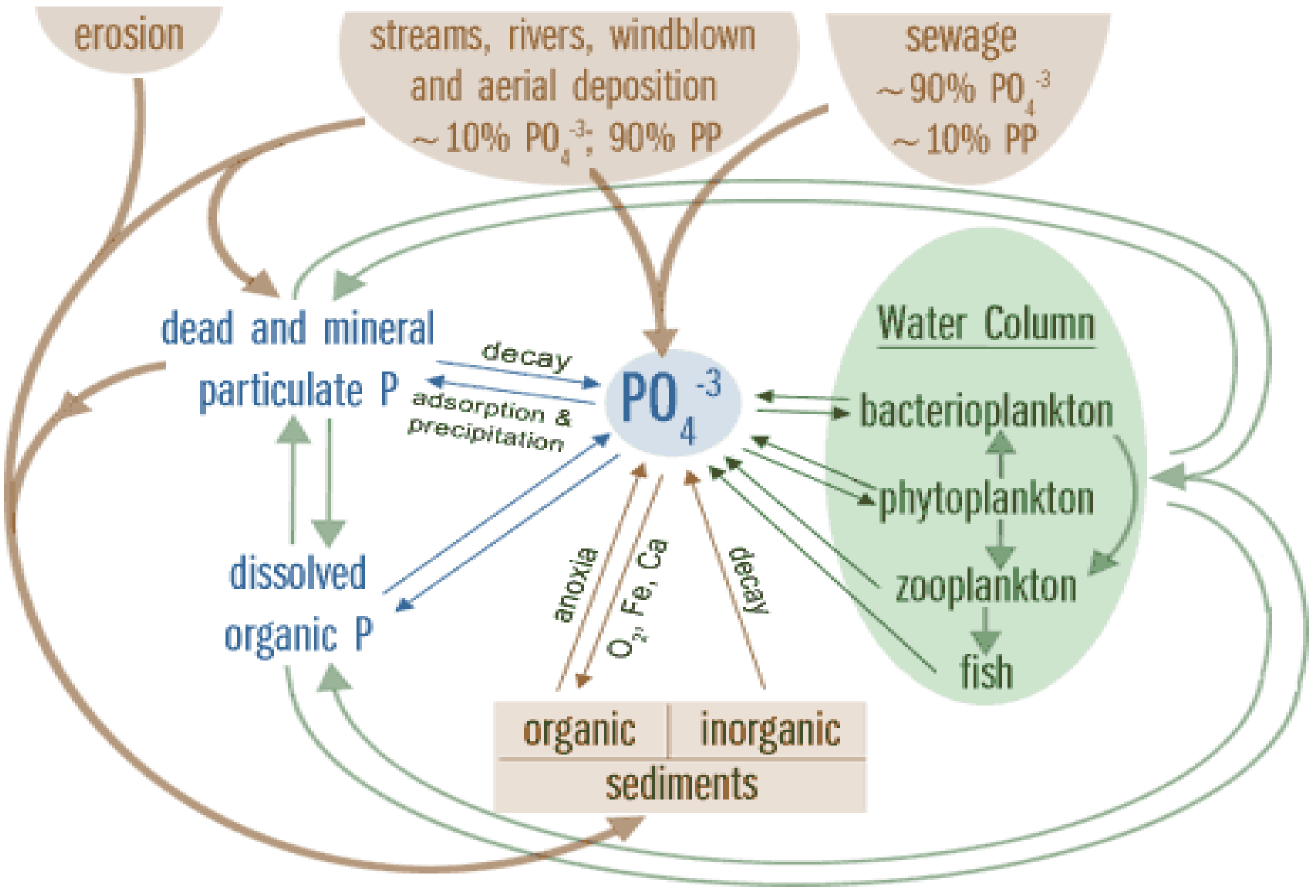
Phosphorus in the Catskills



Dow et al. 2006

Role of erosion of soils – creating sediment in freshwater systems

- Concentrations of phosphorus often increase near stream or lake bottom sediments because of the effects of reduced oxygen concentration on redox potential and subsequent release P from metal-PO_4 complexes that were bound with sediment and delivered to the water body

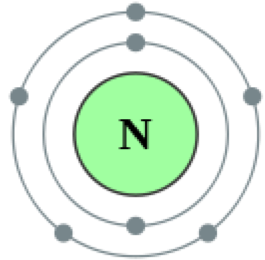


http://www.waterontheweb.org/under/streamecology/14_nutrientdynamics-draft.html

Transfer of P from Sediments to Water

- Mineral-water equilibria and anaerobic/aerobic conditions
- Turbulence
- Phosphorus-mobilizing bacteria
    - *Pseudomonas* and *Bacterium*
- Benthic algae
- Vascular macrophytes
    - Root uptake and/or leaching from dead plants
- Burrowing activity and migration of benthic invertebrates
    - Bioturbation - Small as related to other processes

Nitrogen



Elemental nitrogen is a colorless, odorless, tasteless, and mostly inert diatomic gas at standard conditions, constituting 78.09% by volume of Earth's atmosphere.
Atomic number: 7
Boiling point: -320.4° F (-195.8° C)
Atomic mass: 14.0067 ± 0.0001 u

- Essential element for living organisms
- Major constituent of proteins, nucleic acids, and other biomolecules
- Molecular nitrogen N_2 comprises 80% of the atmosphere, but it is relatively inert chemically and cannot be used by most forms of life.
- Most organisms obtain their nitrogen in some combined form such as NO_3^-, NH_4^+, or organic N
- Reduced nitrogen can be an energy source
- Oxidized nitrogen can be a terminal electron acceptor

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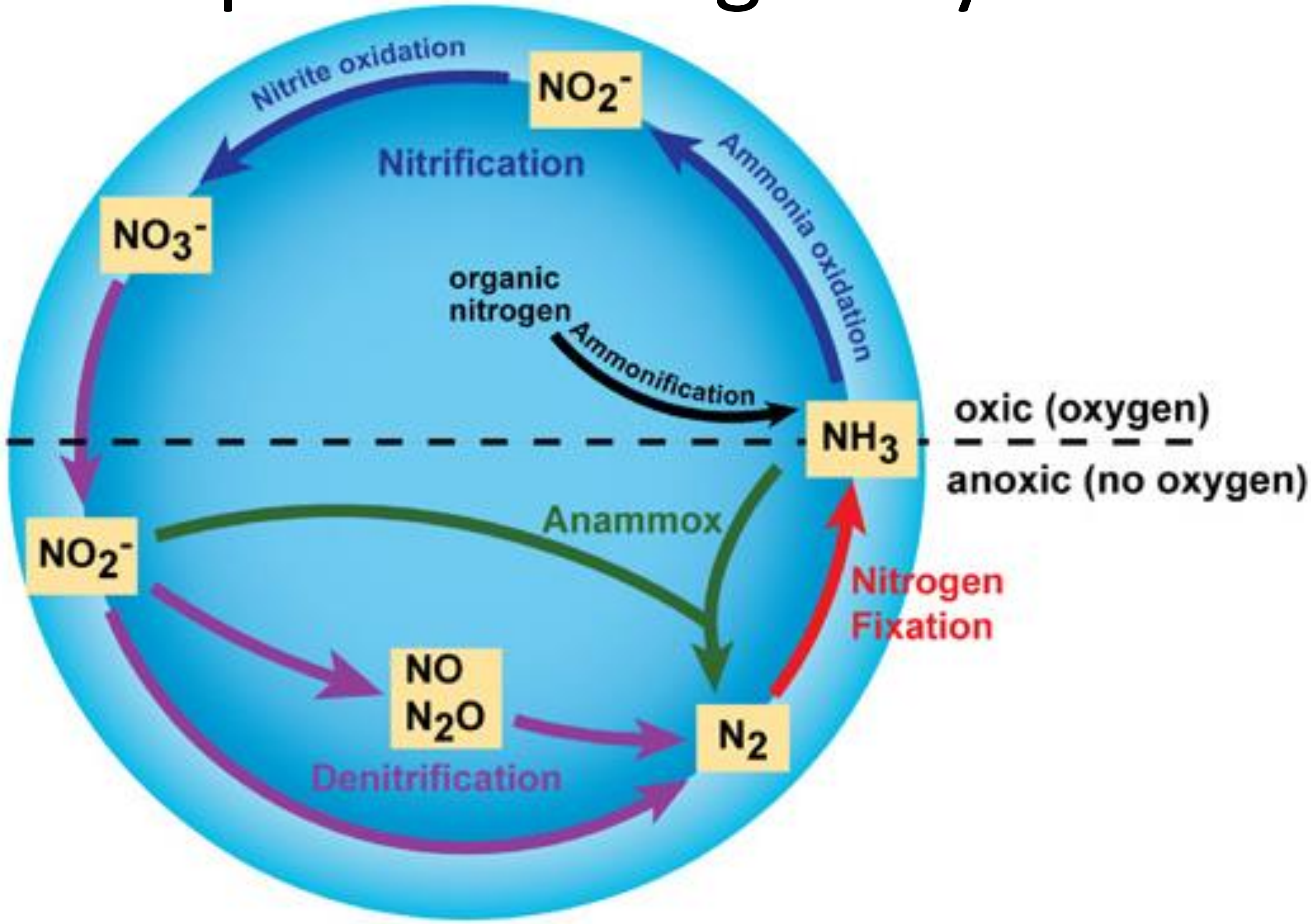
Major Forms of Nitrogen

- Nitrate (NO_3) and nitrite (NO_2)
- Ammonia (NH_3) and ammonium (NH_4)
- Dissolved and particulate organic nitrogen (DON, PON)
- Nitrogen gas (N_2 and N_2O)

Simplified Nitrogen Cycle



http://www.nature.com/scitable/content/ne0000/ne0000/ne0000/ne0000
/15673541/f1_bernhard.jpg

Nitrogen Transformations

- Often the most limiting nutrient in flooded soils
- Transformations are mediated by microbiological processes
- Presence of oxidized zone over anaerobic zone is critical for several pathways and the cycling of N in wetlands/streams/lakes

Natural Sources of Nitrogen

- Atmospheric N_2 as wet and dry deposition

- Igneous and Sedimentary Rock can contain small amounts of NH_4^+

Anthropogenic Sources of Nitrogen

- Fertilizers and manure (both ammonium and nitrate based)
- Human sewage (urea = ammonium)

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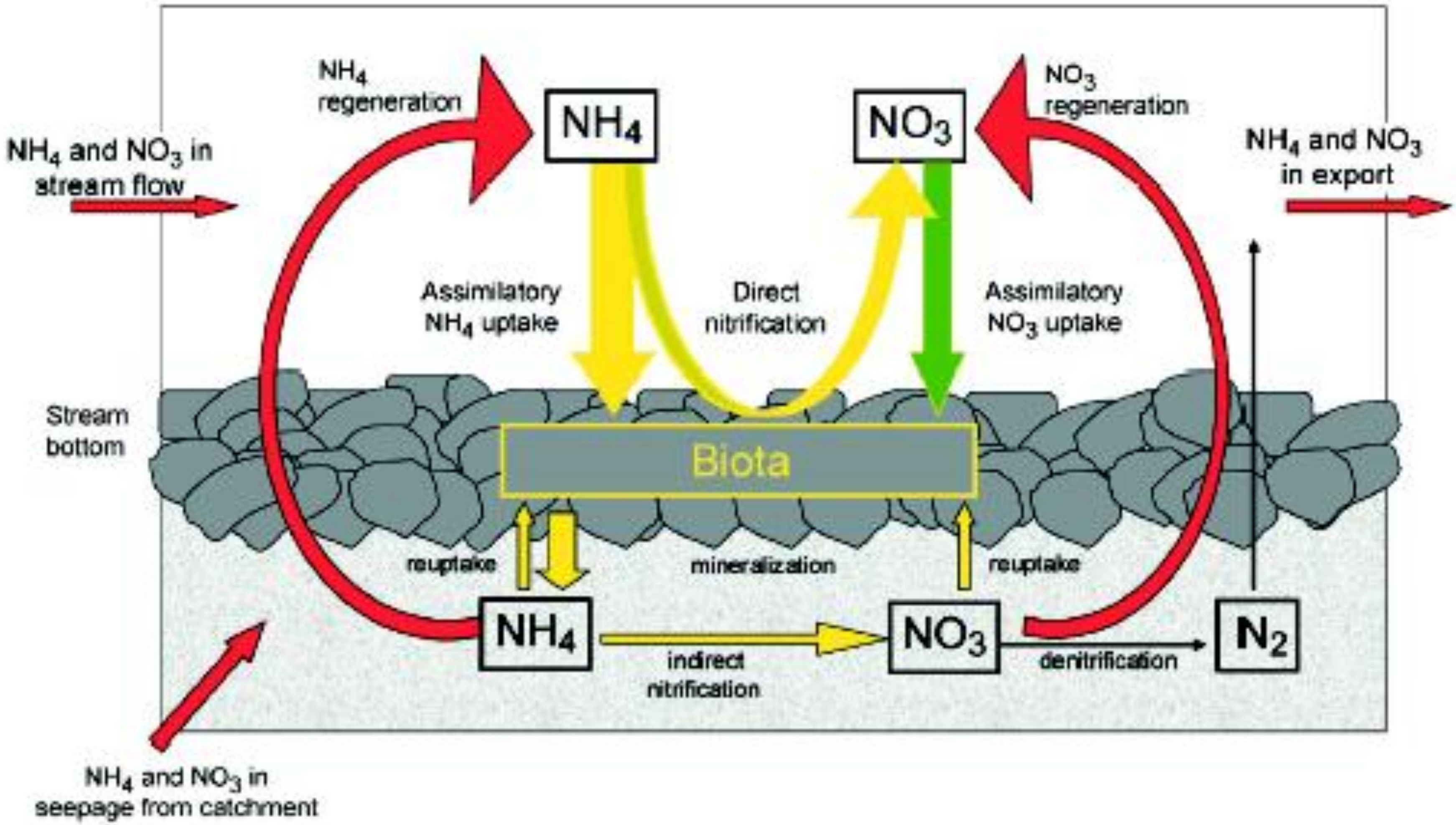
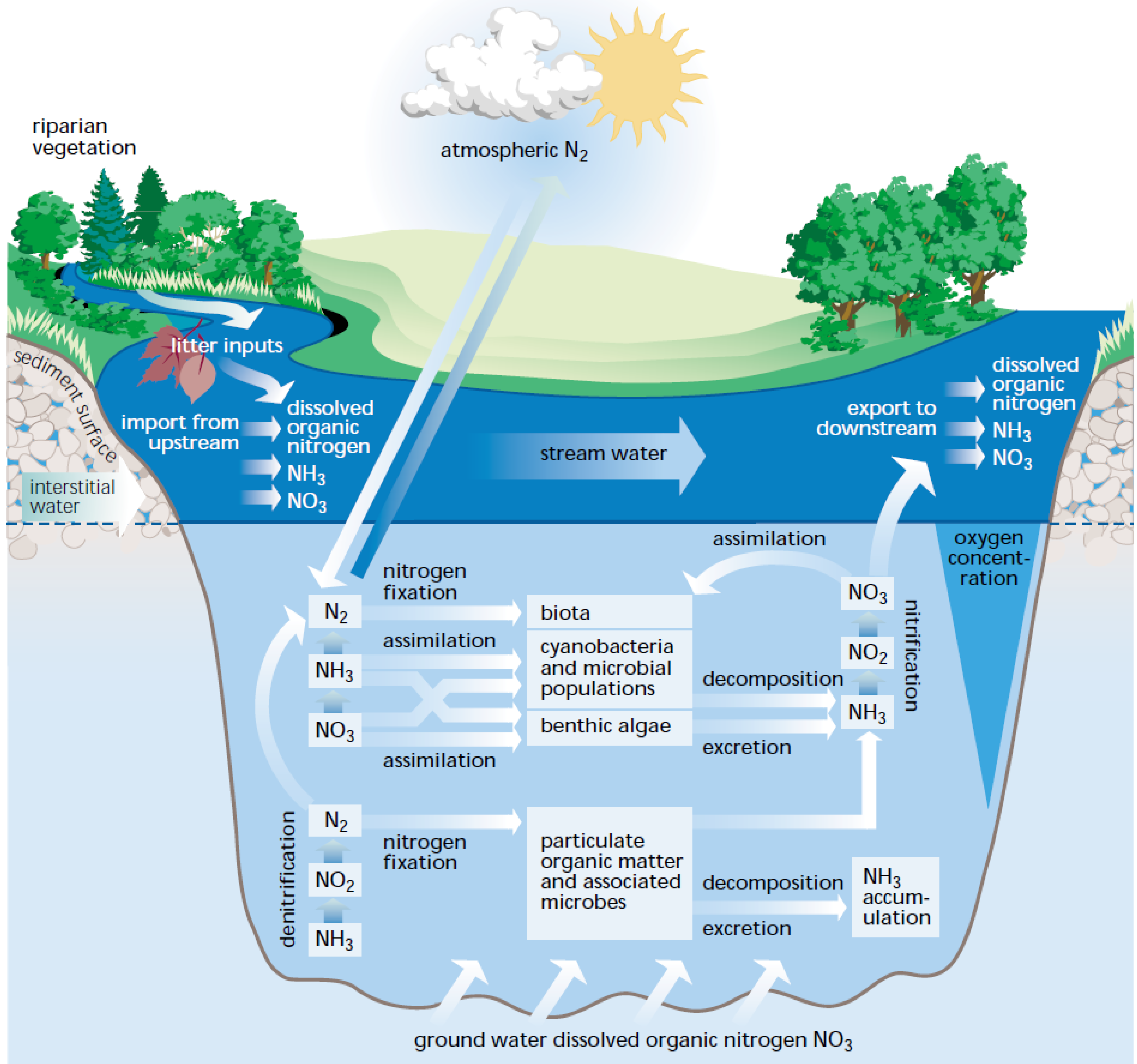
Nitrogen Cycling in Streams





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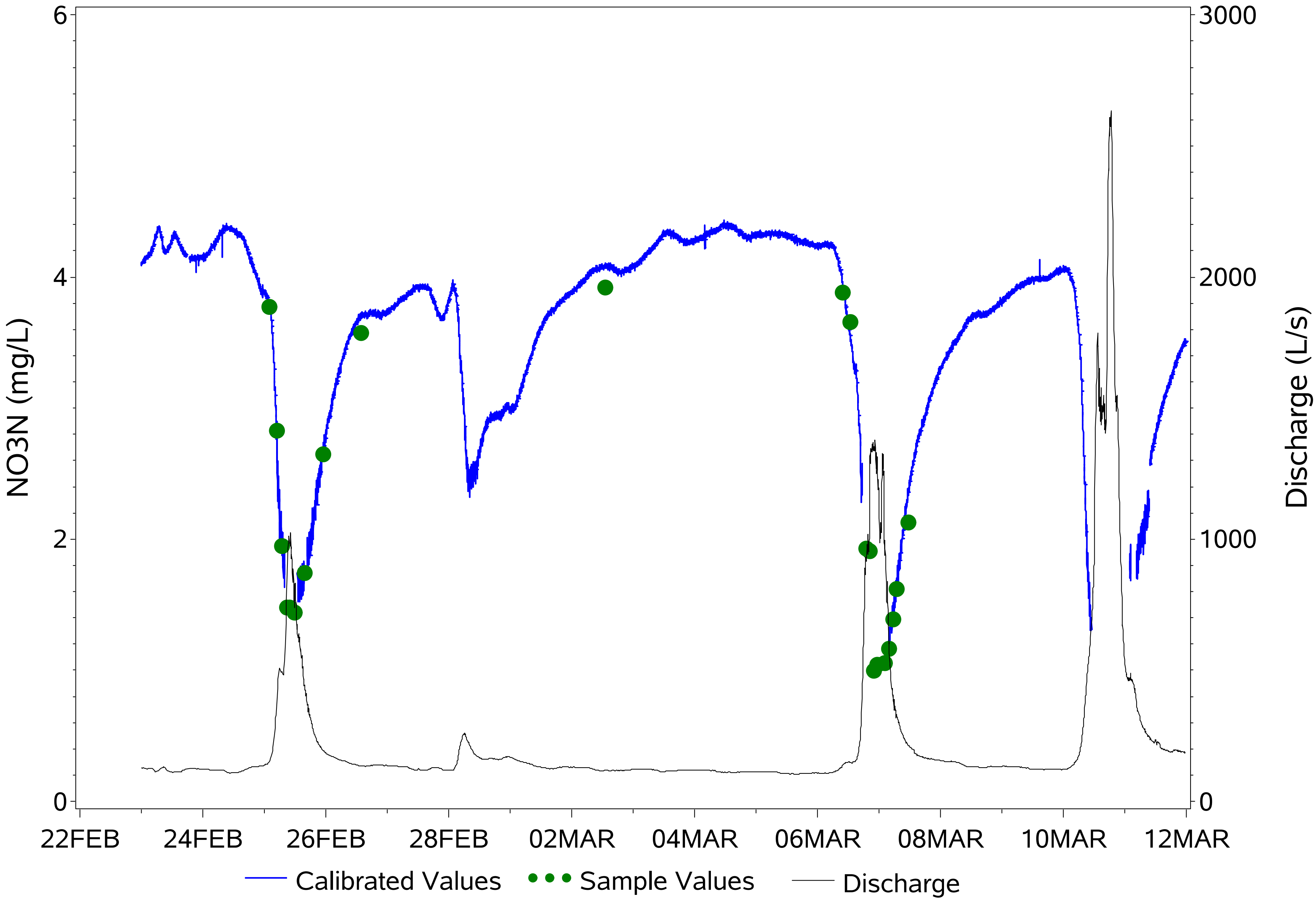
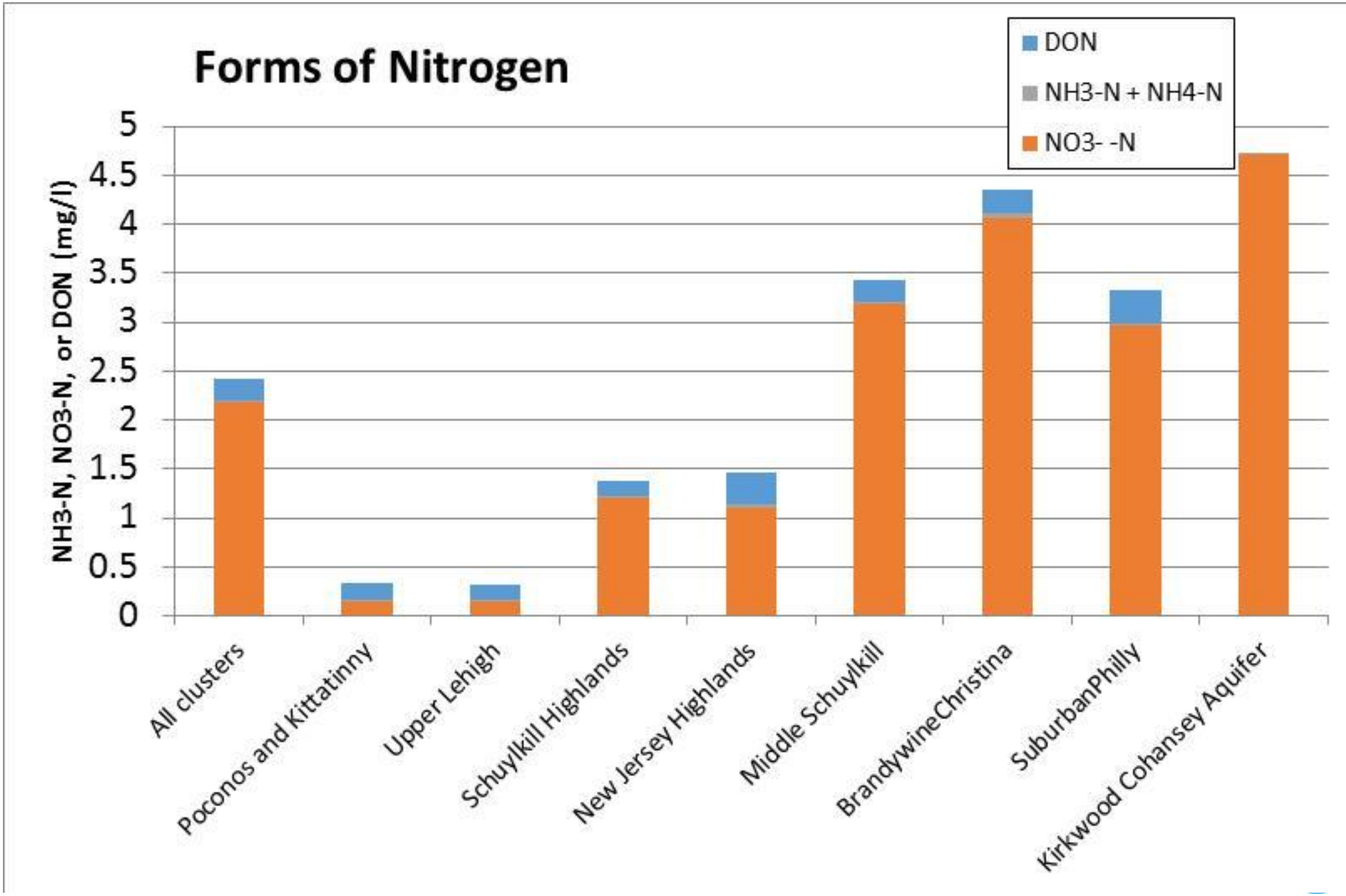
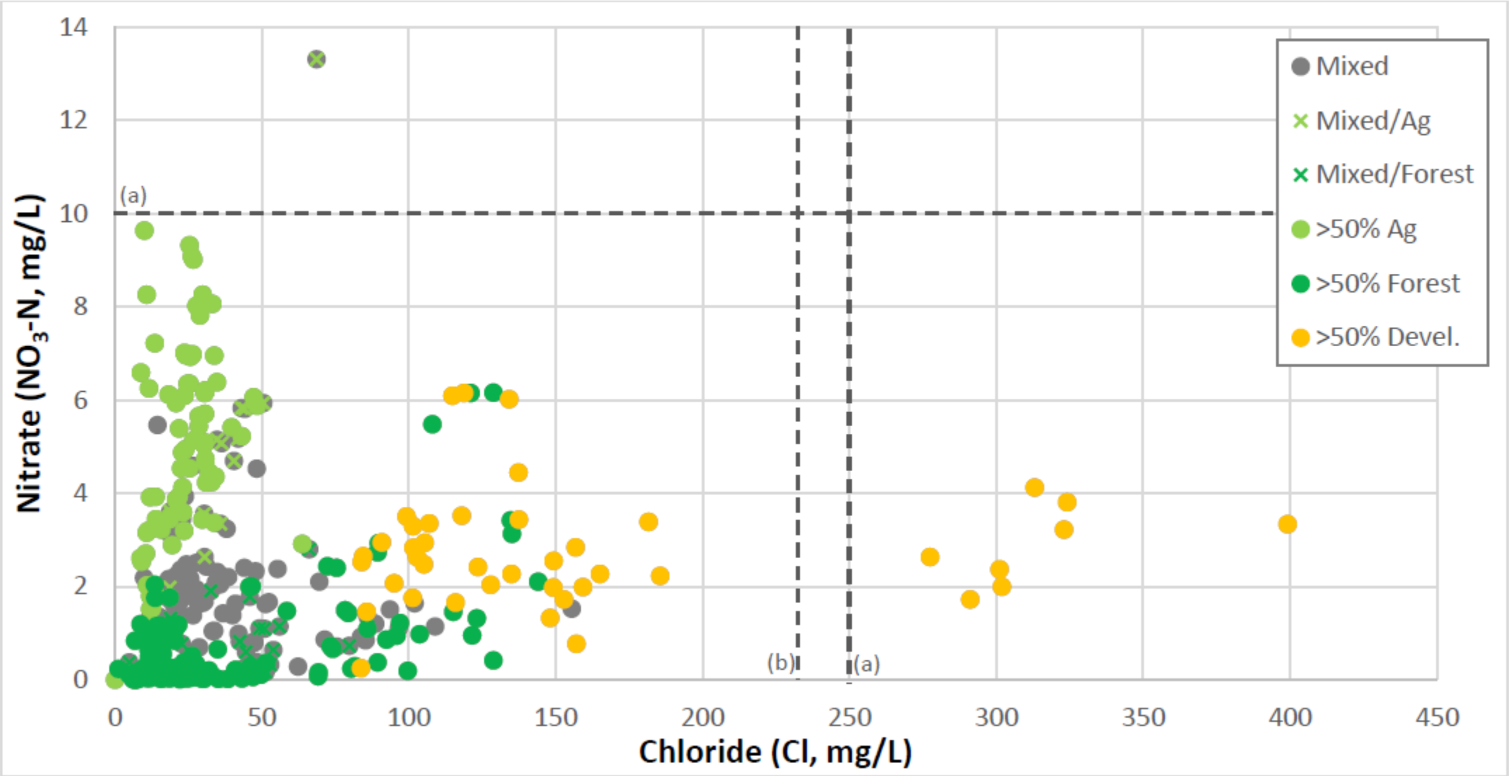
Nitrate w/ Drift-Correction & Local Calibration



Nitrogen in the DRWI Clusters





[a] PADEP Potable Water Supply Limit

[b] EPA Freshwater CCC (chronic) Aquatic Life Criteria Limit

- $[NO_3]$ relative to Cl differs depending on catchment land use
- Forested & developed catchments, $[NO_3]$increases with increasing Cl, suggesting $[NO_3]$ is controlled by hydrologic processes (surface runoff or groundwater inflow to streams)
- Agricultural catchments $[NO_3]$is uncorrelated to Cl, suggesting that $[NO_3]$ is controlled by non-hydrologic processes (e.g., fertilizers).

Data source: ANSD (M. Kurz) 2013-15 (ANSD + Cluster Partners)

n = 513; (75 PK; 53 UL; 62 SH; 54 NJH; 92 MS; 136 BC; 38 SP; 3 KCA)

Data are provisional (not final and subject to change)

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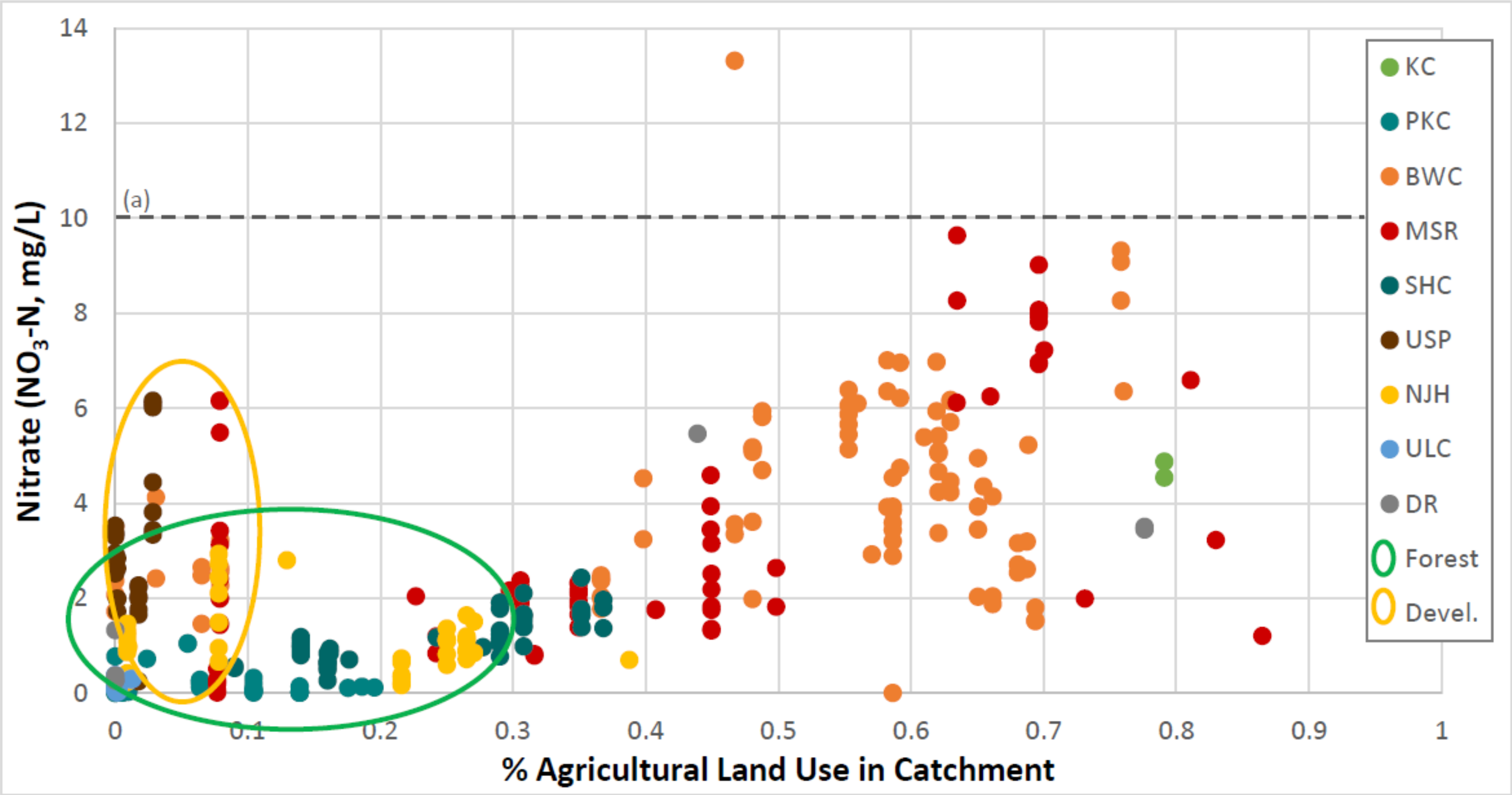

- Max [NO_3] correlated to percentage Ag land use in contributing catchments
  - Highest [NO_3] in catchments with > 60% Ag land
  - [NO_3] at high Ag land us is variable, why? Crop type, farming technique/intensity, BMPs, etc.?
- Catchments with lowest [NO_3] typically forested
  - Exceptions: catchments with high % developed land, where [NO_3] can also be moderately high.

Data source: ANSD (M. Kurz) 2013-15 (ANSD + Cluster Partners)

n = 513; (75 PK; 53 UL; 62 SH; 54 NJH; 92 MS; 136 BC; 38 SP; 3 KCA)

Data are provisional (not final and subject to change)

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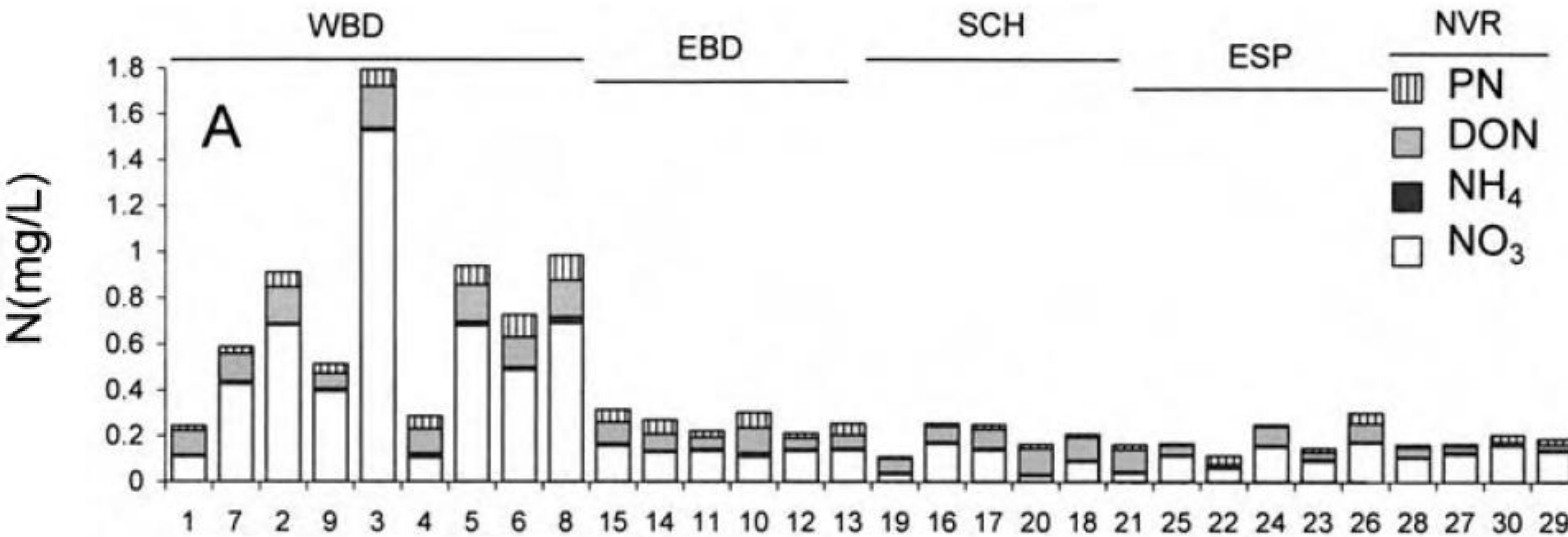
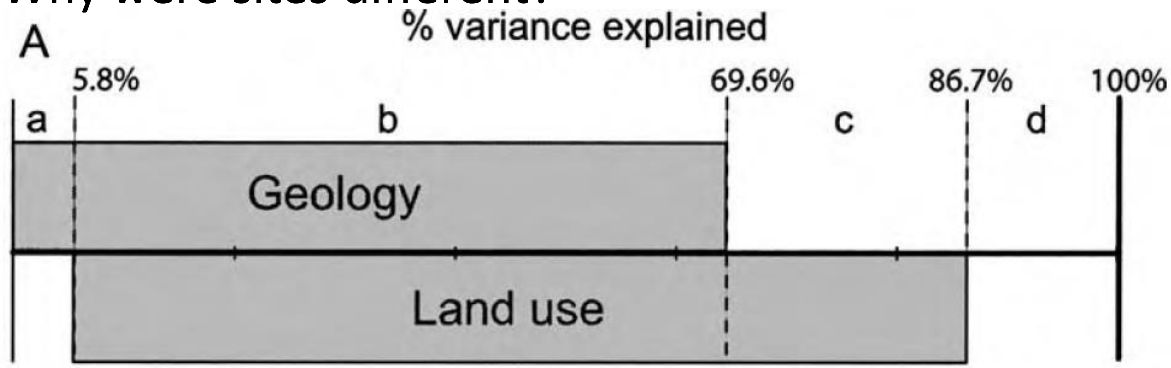
Nitrogen in the Catksills

West Br. Del East Br. Del Schoharie Esopus Nvrsink



Sites

Why were sites different?



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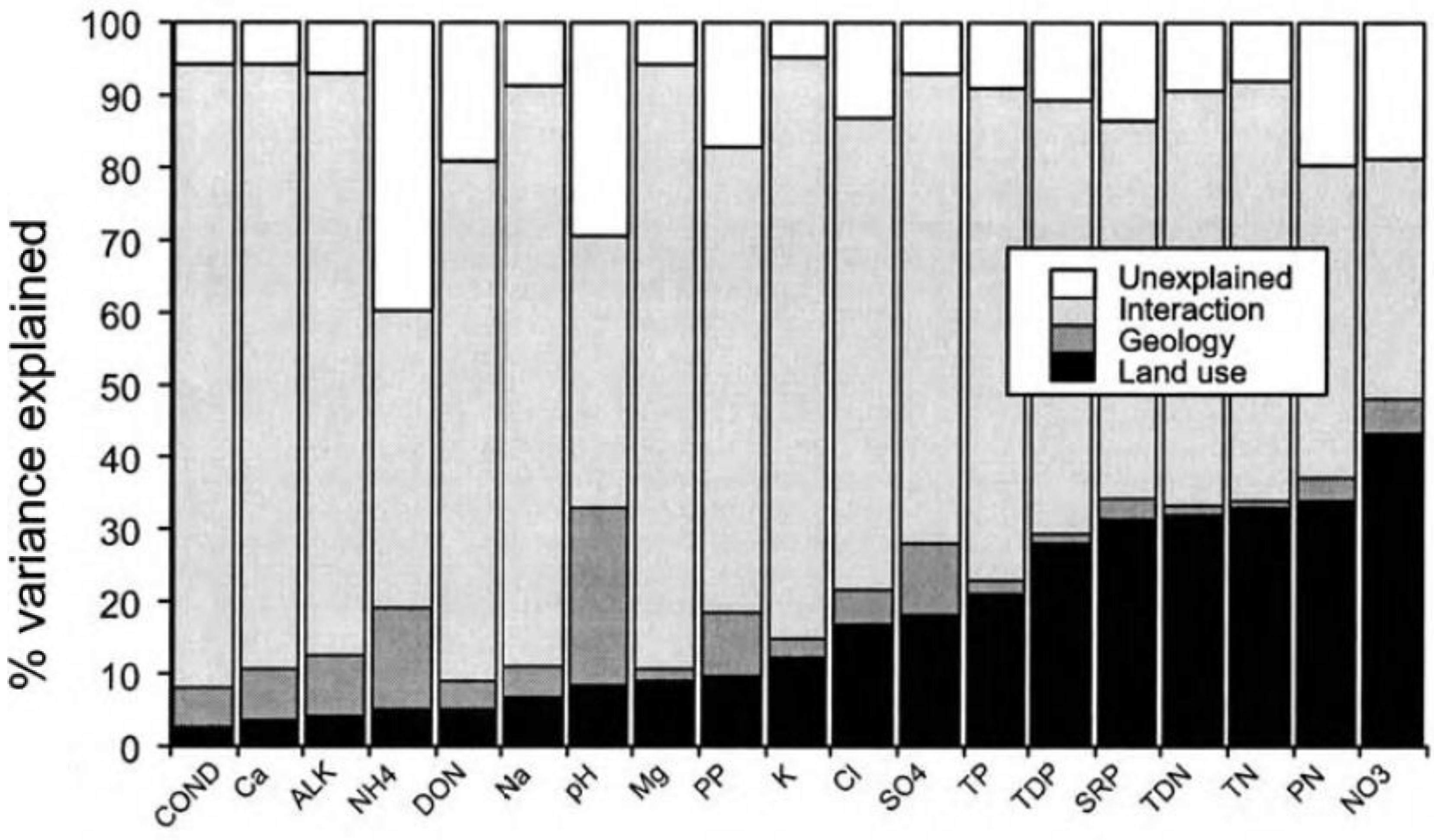
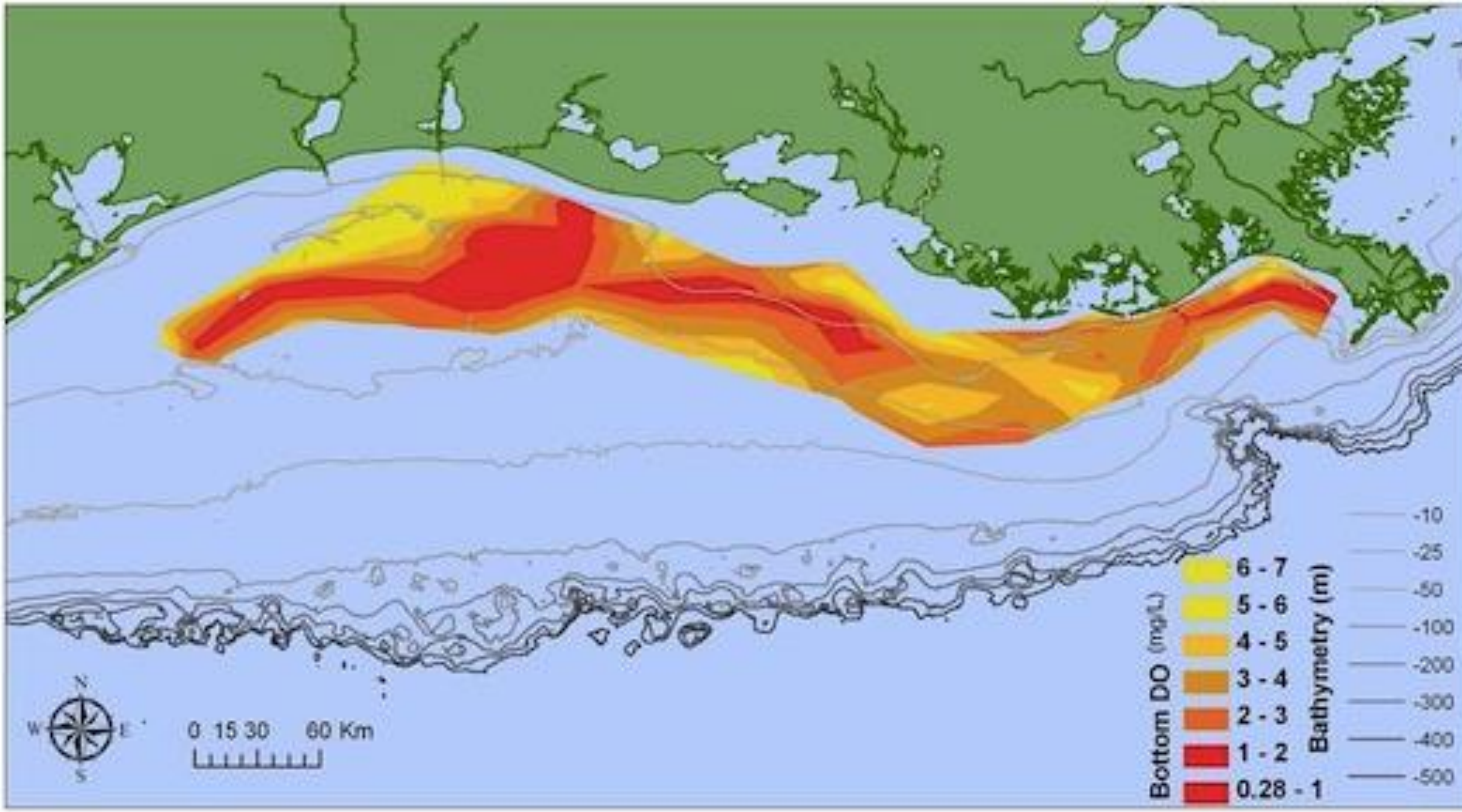


Dow et al. 2006

Gulf of Mexico Dead Zone in 2012



In 2012, the "dead zone" was much small, primarily due to the drought in the mid-west that resulted in small nutrient loadings to the Gulf of Mexico

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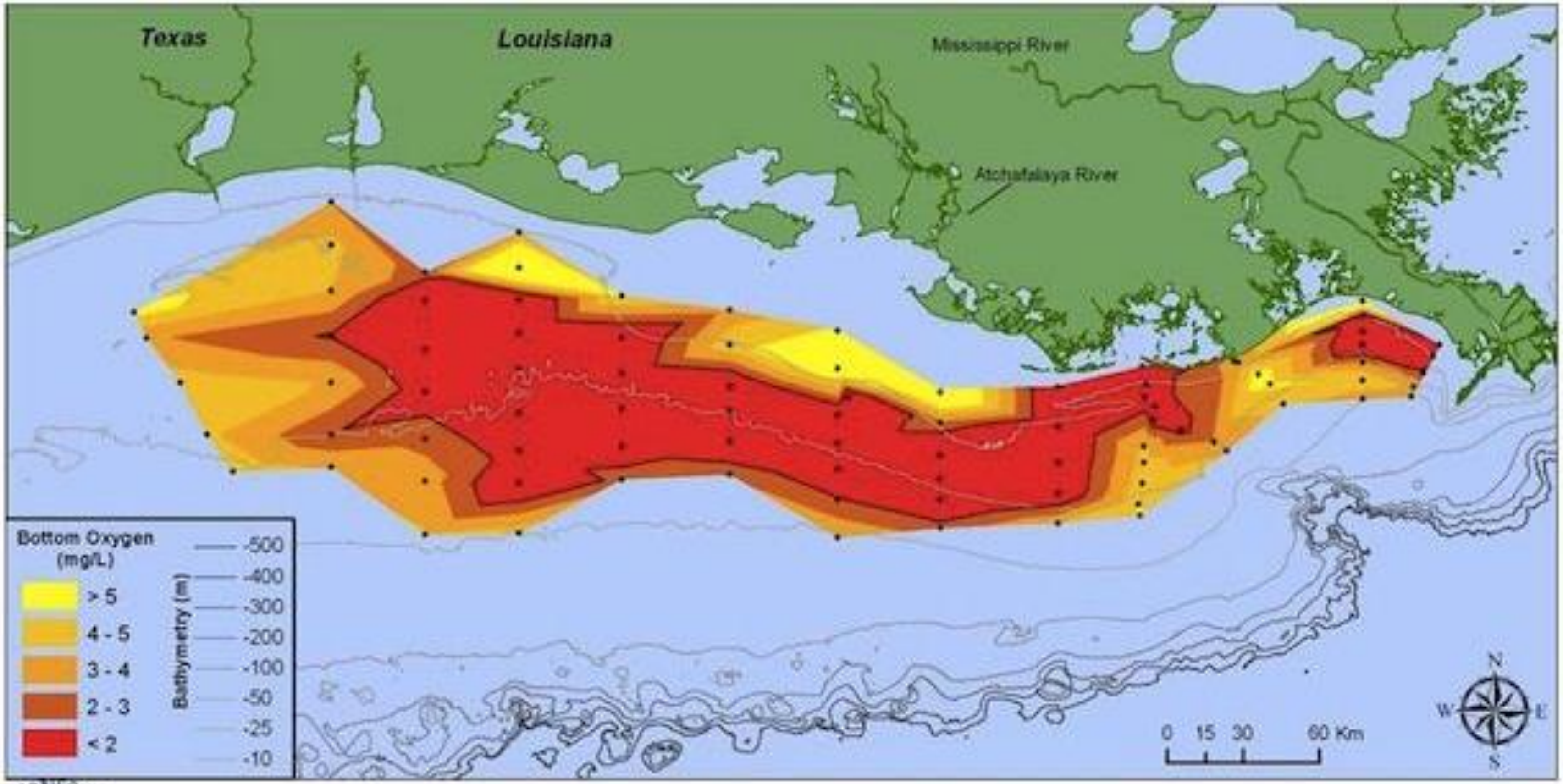
Gulf of Mexico Dead Zone in 2013



Data source: N.N. Rabalais, Louisiana Universities Marine Consortium, R.E. Turner, Louisiana State University
Funded by: NOAA, Center for Sponsored Coastal Ocean Research

Bottom-water dissolved oxygen across the Lousiana shelf from July 22-28, 2013.
This is the “dead zone” in the Gulf of Mexico off the Louisiana and Texas coast.

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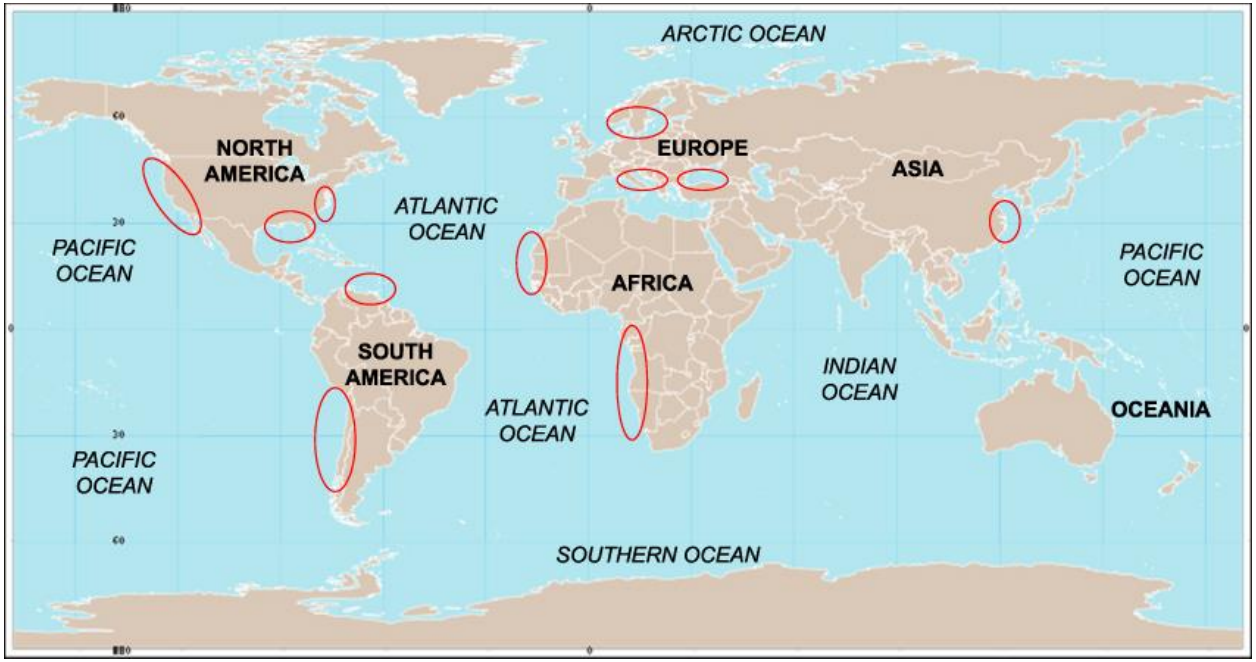
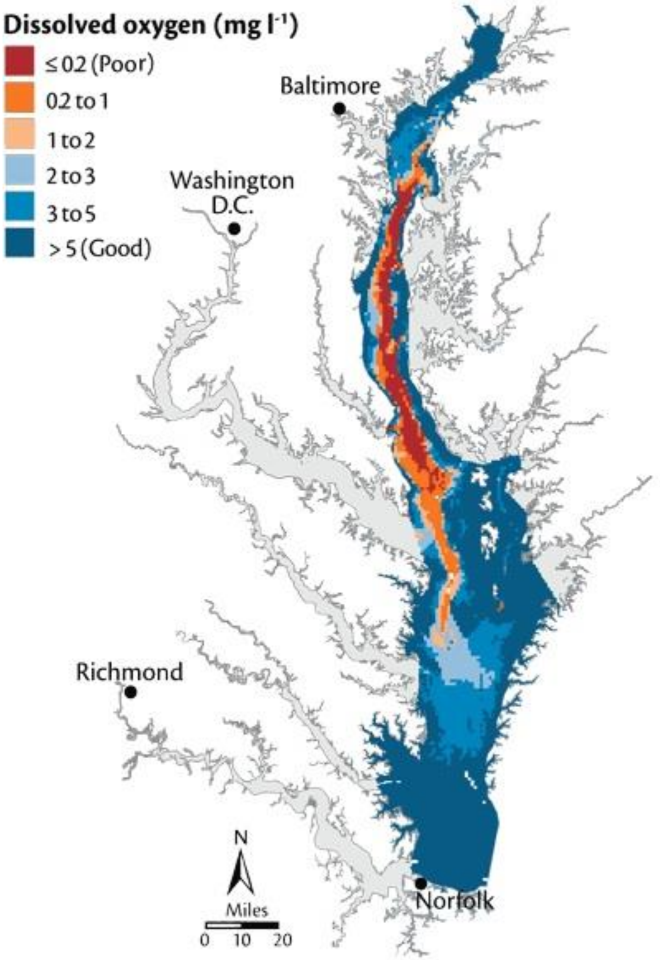
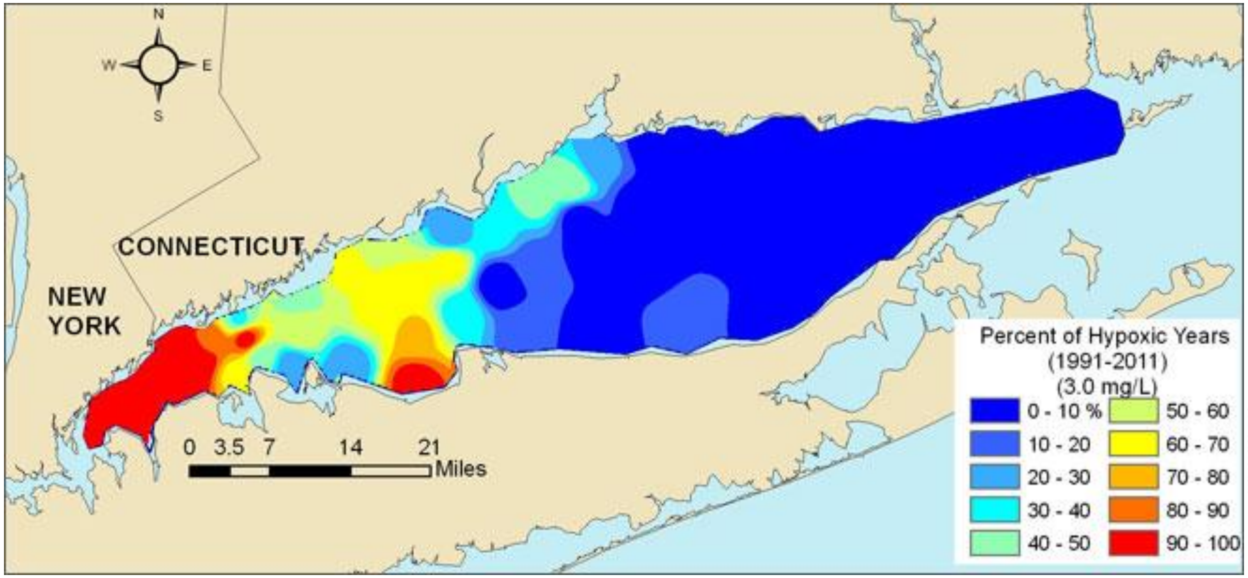




The highest measured amount of anoxia in Chesapeake Bay was in late August for 2009. Map shows minimum values of the late August cruise.



http://longislandsoundstudy.net/2010/07/frequency-of-hypoxia/
http://www.motherjones.com/tom-philpott/2013/08/gulf-of-mexico-dead-zone-growth
http://iopscience.iop.org/1748-9326/8/1/015025/article

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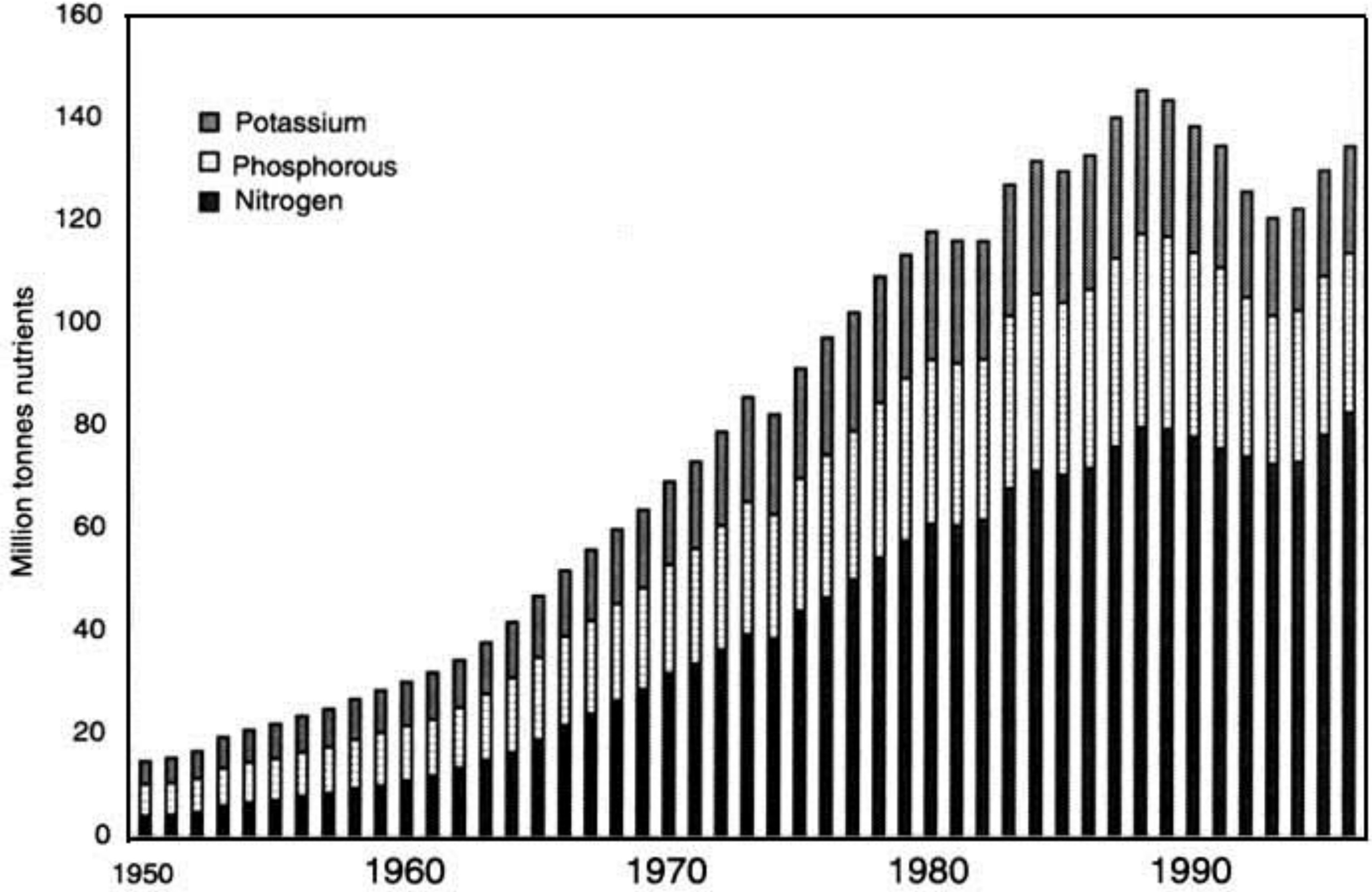

Figure 3. Global Fertilizer Consumption, 1950/51-1996/97
Source: International Fertilizer Industry Association

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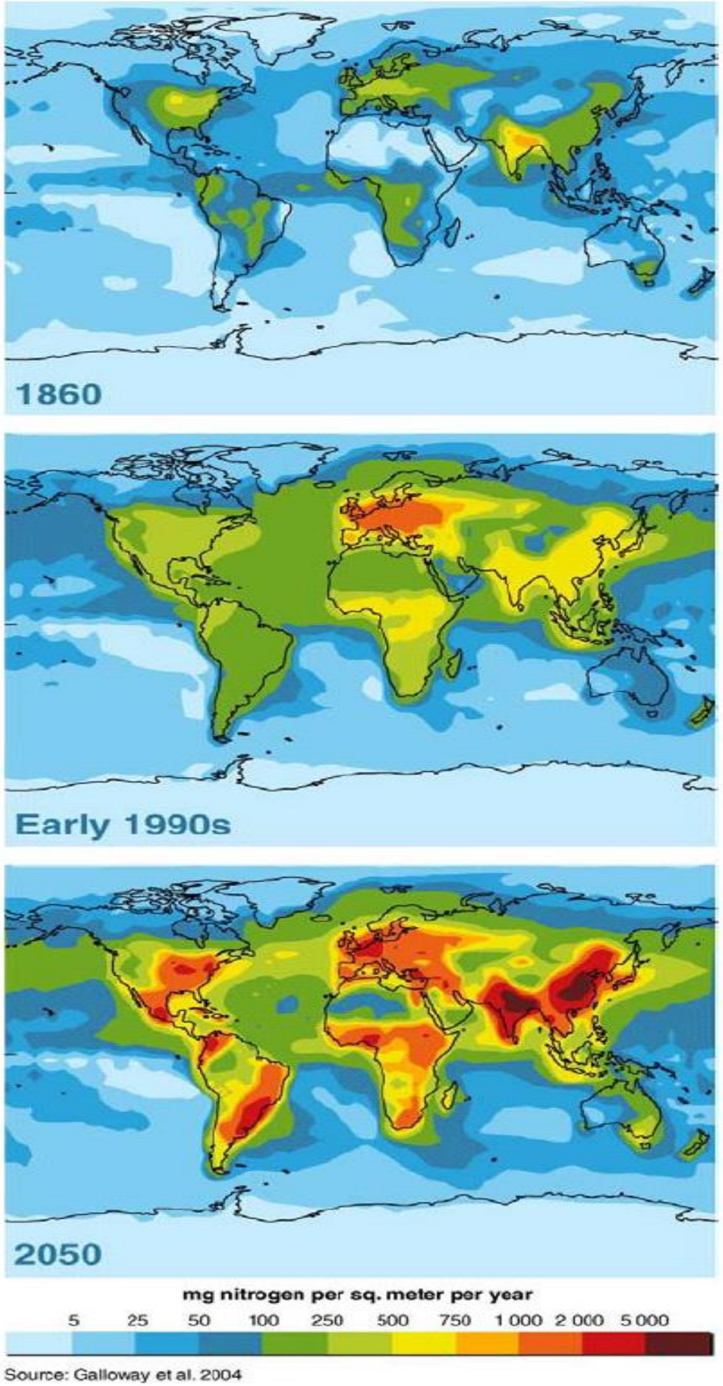

Estimated total reactive nitrogen deposition from the atmosphere (wet and dry) in 1860, early 1990s, and projected for 2050

Data from: Galloway, J.N., Dentener, F.J., Capone, D.G. et al. 2004. Nitrogen cycles: past, present, and future. Biogeochemistry. 70:153. doi:10.1007/s10533-004-0370-0

Image drawn by: Philippe Rekacewicz, Emmanuelle Bournay, UNEP/GRID-Arendal
http://www.grida.no/resources/6041

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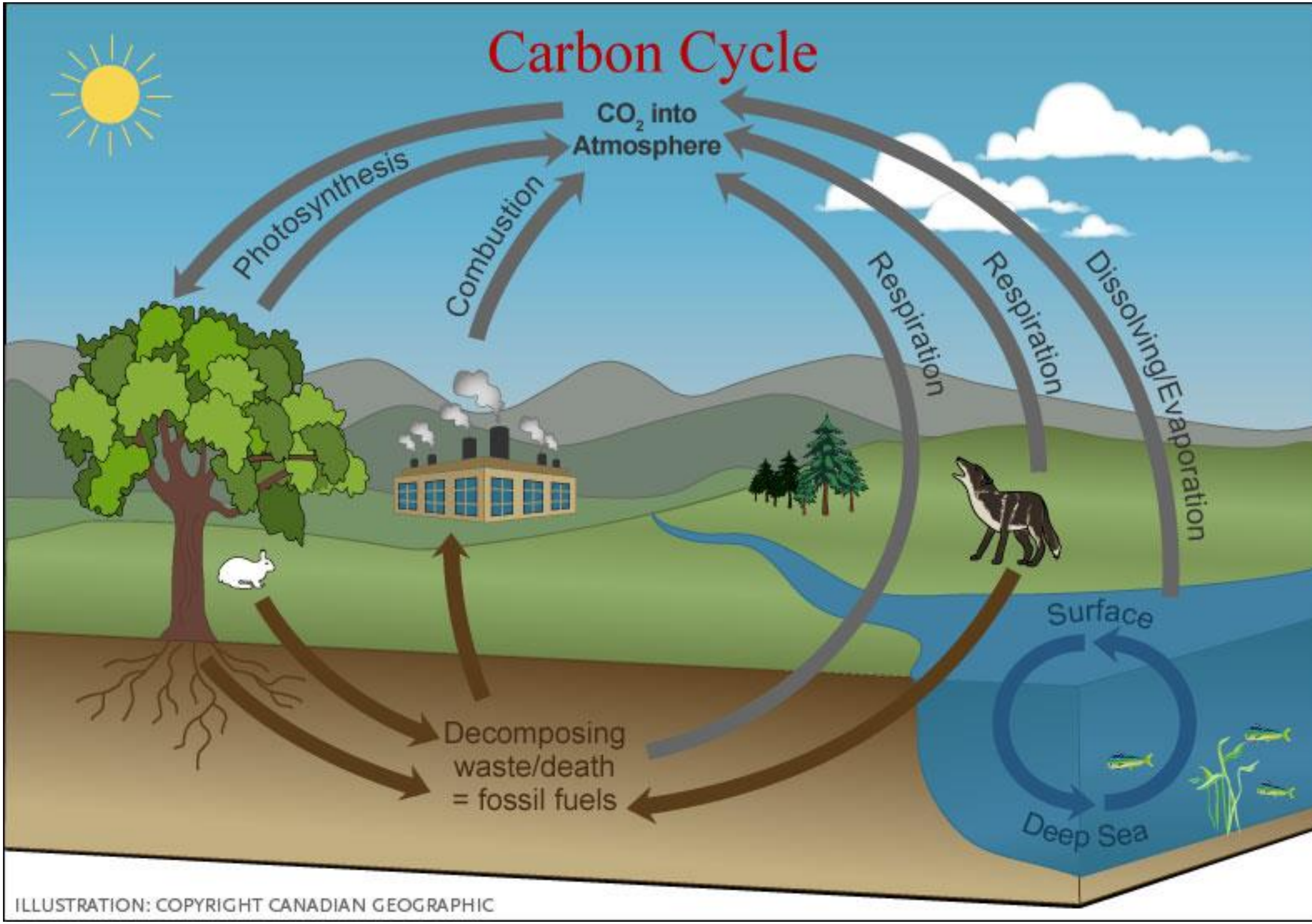

http://cahsbiology.weebly.com/uploads/1/3/5/0/13500838/1393932306.jpg

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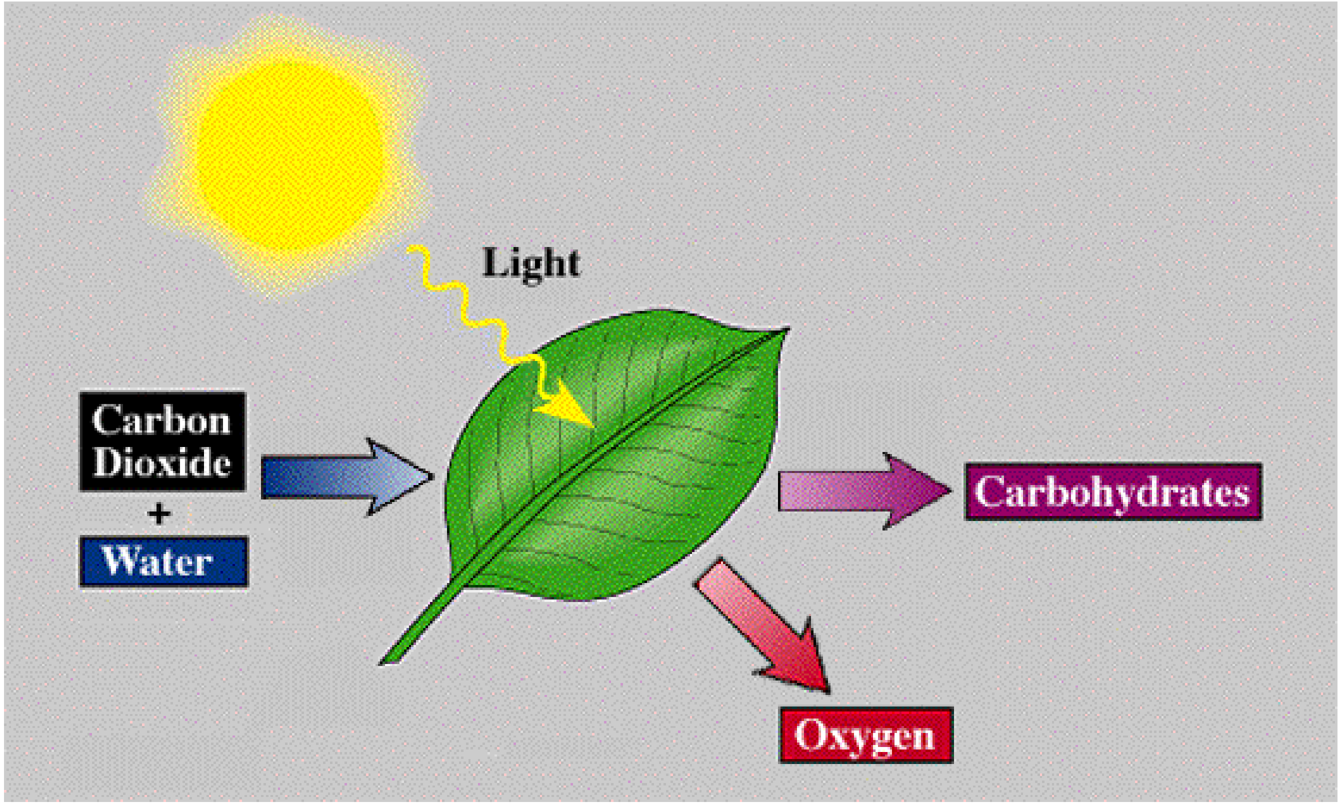
Important chemistry cycles – Carbon cycling

- Photosynthesis - Photosynthesis by ocean phytoplankton follow the **Redfield-Ketchum-Richards** (**RKR**) or simply **Redfield** Equation, as given in their (1963) paper:

  $$106\ CO_2 + 16\ HNO_3 + PO_4 + 122\ H_2O \rightarrow (CH_2O)_{106}(NH_3)_{16}PO_4 + 138\ O_2$$

- Classically simplified to $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$



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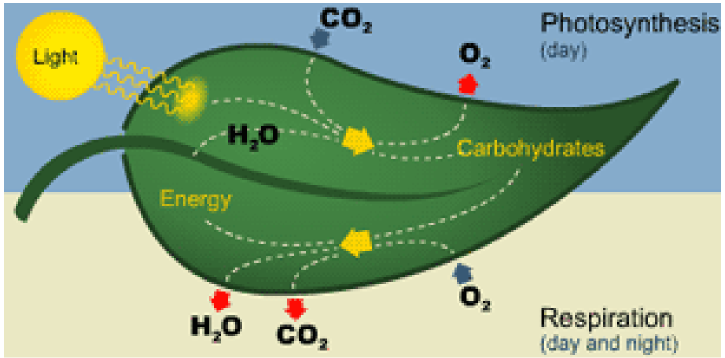
  - Classically simplified to $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$
- Respiration - Respiration (release of the sun's energy and mineralization of nutrients), follows the reverse:

  $(CH_2O)_{106}(NH_3)_{16}PO_4 + 138\ O_2 \Rightarrow 106\ CO_2 + 16\ HNO_3 + PO_4 + 122\ H_2O$

  - Classically simplified to
  - $C_6H_{12}O_6 + 6O_2 \rightarrow 6H_2O + 6CO_2 + \text{energy}$

(glucose + oxygen →water + carbon dioxide + energy)



http://www.mcqbiology.com/2012/11/mcq-on-plant-physiology-respiration.html#.V-qx-PkrLRY

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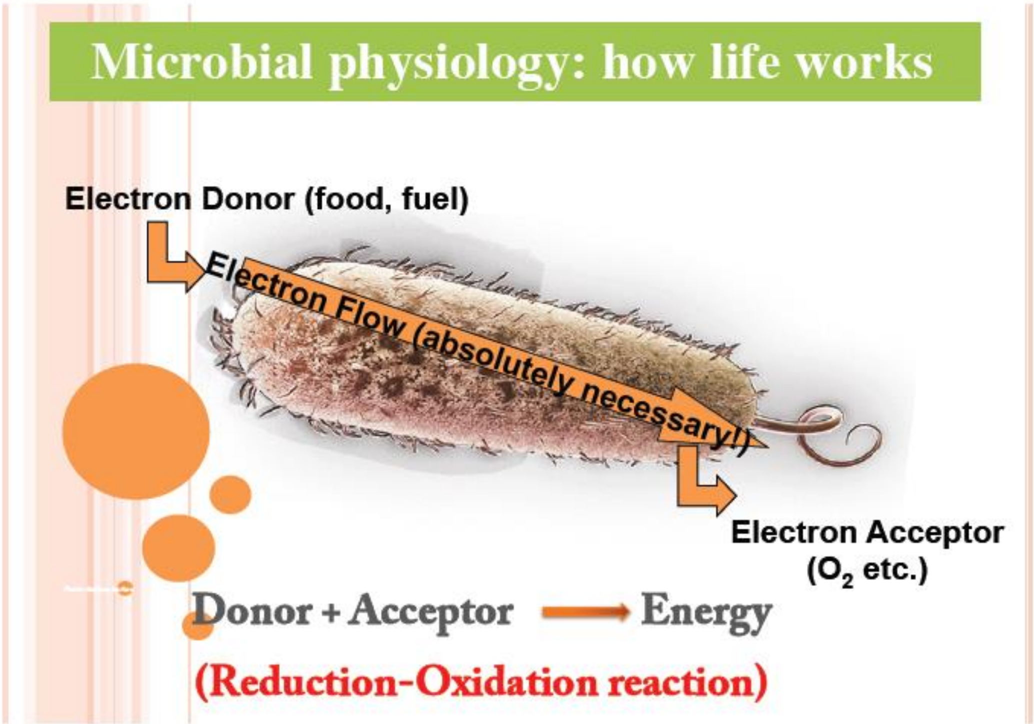
Carbon Cycle

- What Drives the Carbon Cycle?
  - Photosynthesis
  - Respiration
    - Not just all plants and people (animals) - **bacteria too**!



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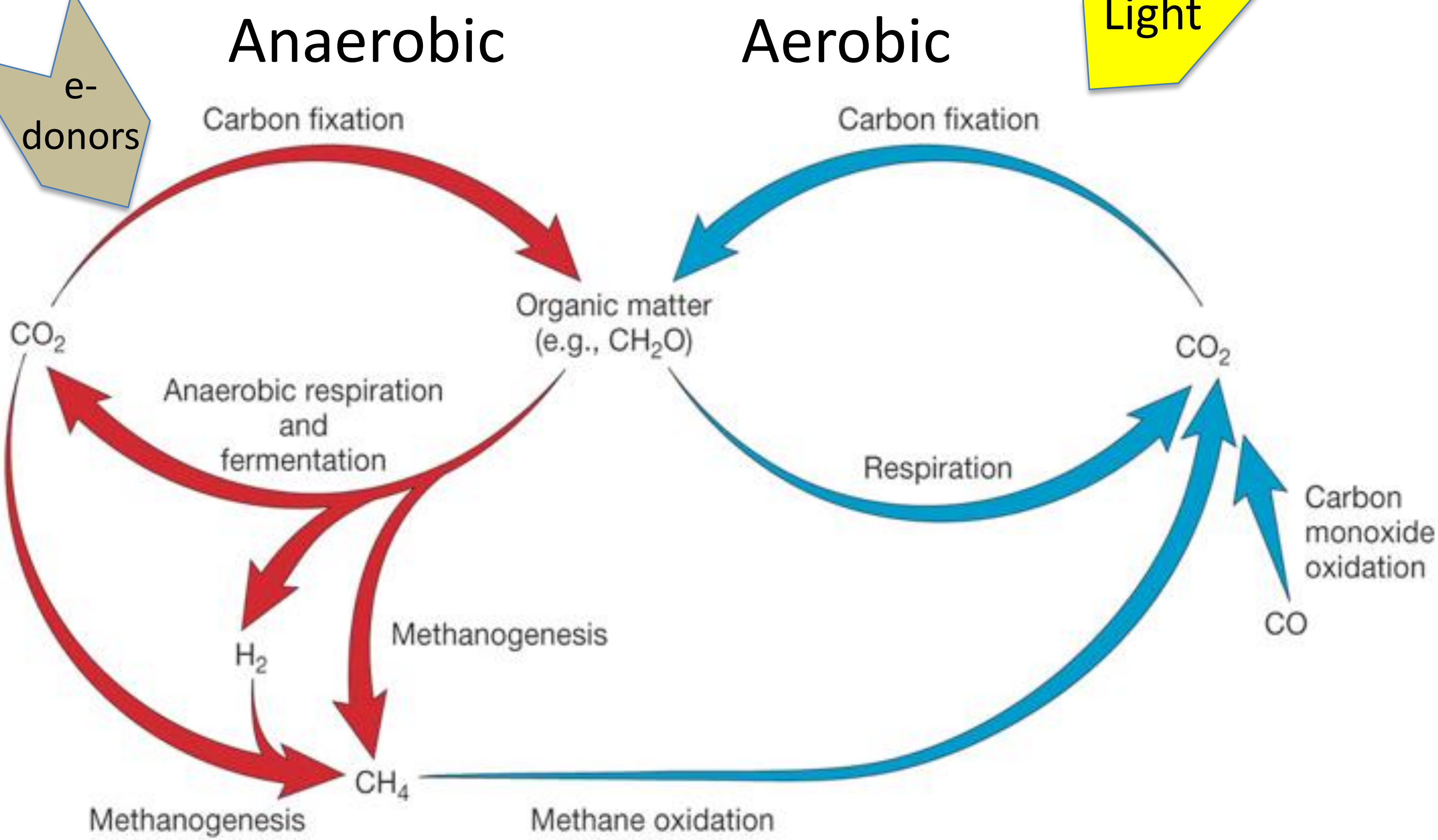
H_2S
S
Fe^{2+}
NO^{2-}

H_2
CO
NH_4
Hum_R

Carbon Cycle

e-
donors

Light



Graphic source: unknown

Carbon Cycle

- Organic Matter in Aquatic Ecosystems
  - Organic Matter = from living organisms, has carbon content and typically C-H bonds (couple of exceptions below)
    - Cellulose, tannin, lignin, proteins, lipids, sugars
    - Includes other elements bound to the OM molecule, e.g., N, P
  - Inorganic material
    - Traditionally viewed as being synthesized by the geological systems – not organic
    - But also result of respiratory processes
    - Also considered to be compounds without carbon – except for CO_2, H_2CO_3, HCO_3^-, CO_3^{2-}

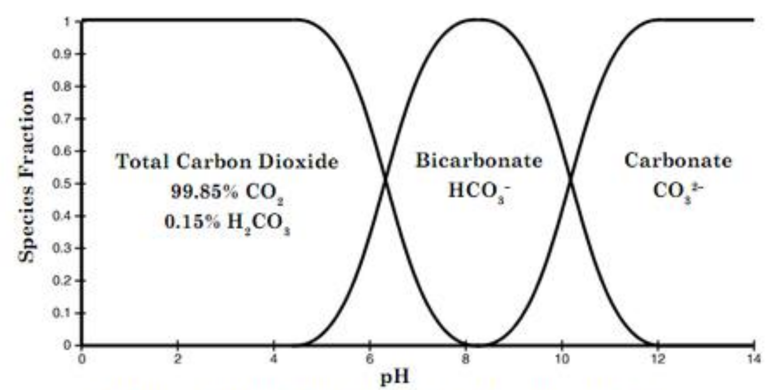


Figure 1 – Distribution of Total Carbon Dioxide, Bicarbonate, and Carbonate vs. pH

John A. Wojtowicz – Chapter 1.1

Carbon Cycle

- Functions of OM in Aquatic Ecosystems
  - Attenuates light (DOM, POM)
  - Influences animal behavior (DOM)
  - Complexes with metals, nutrients, and pollutants (DOM, POM)
  - Serves as a C and energy and nutrient source to heterotrophic microorganisms (DOM, POM)
  - Provides substrata for microbial attachment (POM)

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Carbon Cycle

Photo credit: D. Funk, Stroud Center

Sources of Organic Matter

Autochthonous: formed or originating in the place where it is found

Allochthonous: formed or originating outside the place where it is found

Carbon Cycle

- **OM versus OC**
  - **Organic matter** = complex mixture of molecules of diverse origin, but derived from living organisms and with C-H bonds (but includes other elements); can be living or dead
  - **Organic carbon** = is a common measure of the organic matter of a sampling; mass/concentration/amount of carbon present in the organic matter of interest; this excludes other elements bound to the organic molecule – e.g., nitrogen or phosphorus

Carbon Cycle

How We Define Organic Matter Compartments in Freshwaters

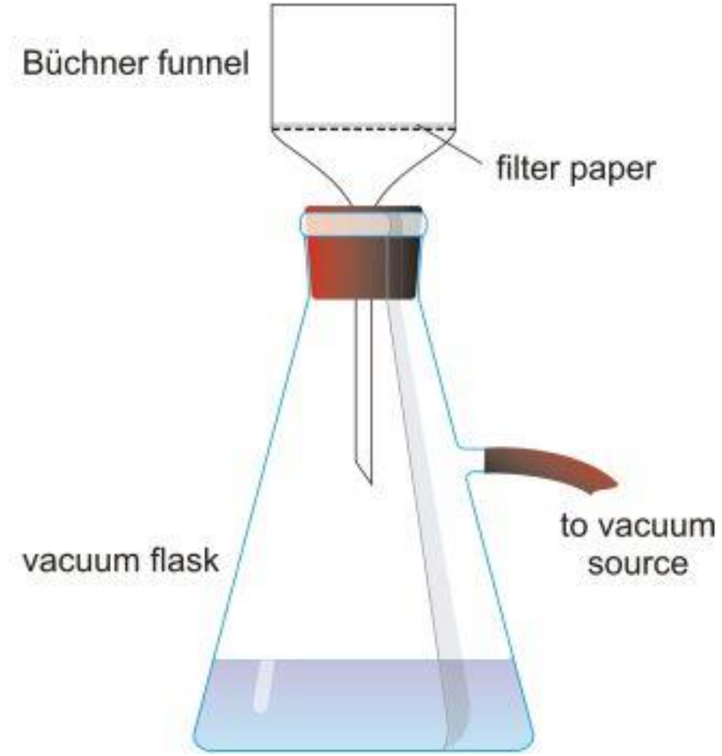
Particulate Organic Matter (POM) – Seston

Coarse (CPOM > 1 mm)

Fine (> 0.5 µm FPOM < 1mm)

Dissolved Organic Matter (DOM < 0.5 µm)

Terminology POC and DOC - beware



Carbon Cycle

Coarse Particulate Organic Matter (CPOM)

Also leaches organic molecules (e.g., lignin and tannin) that become DOM

Photo credit: C. Medved, Stroud Center

Carbon Cycle

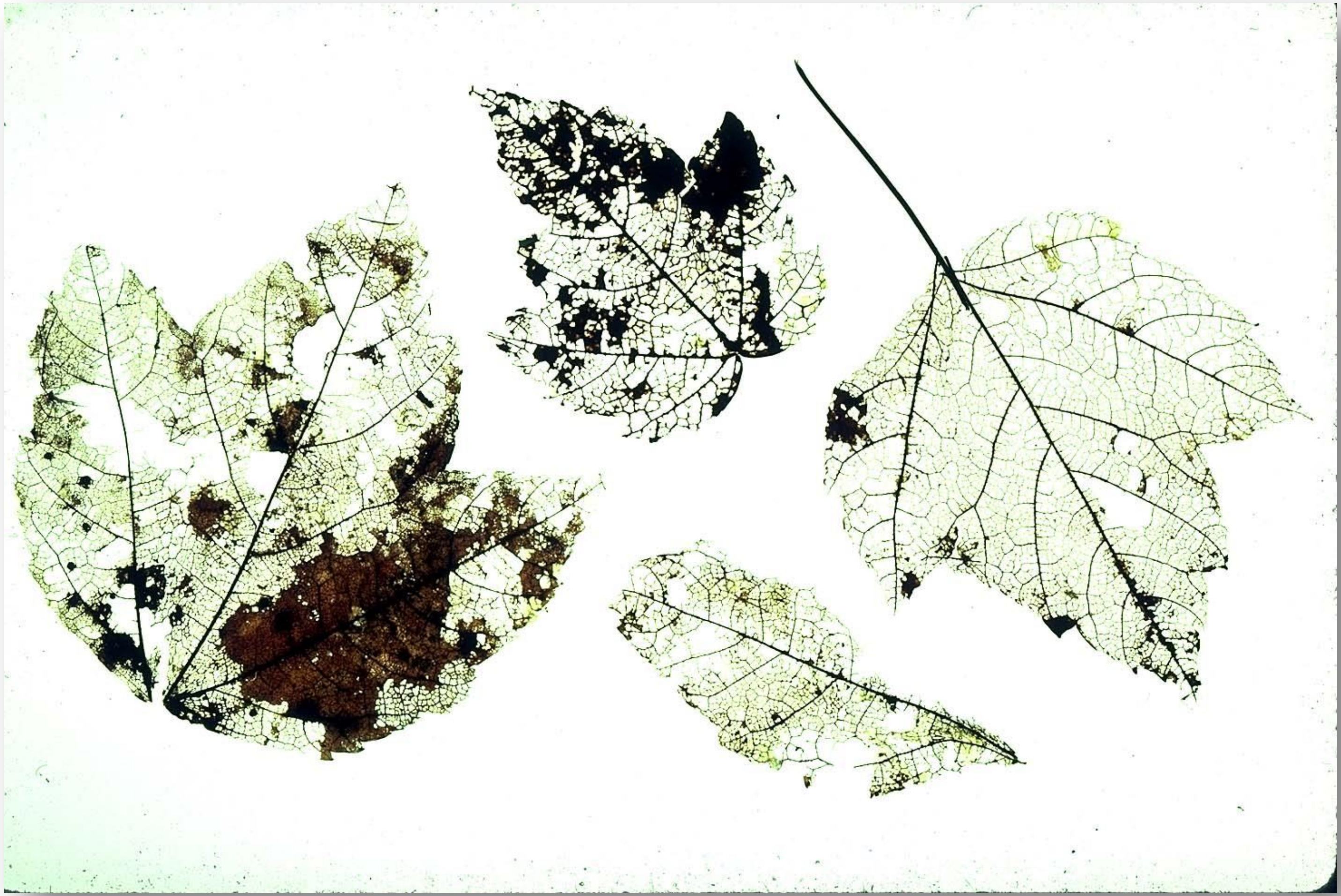


Photo credit: D. Funk, Stroud Center

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Carbon Cycle

Photo credit: Stroud Center

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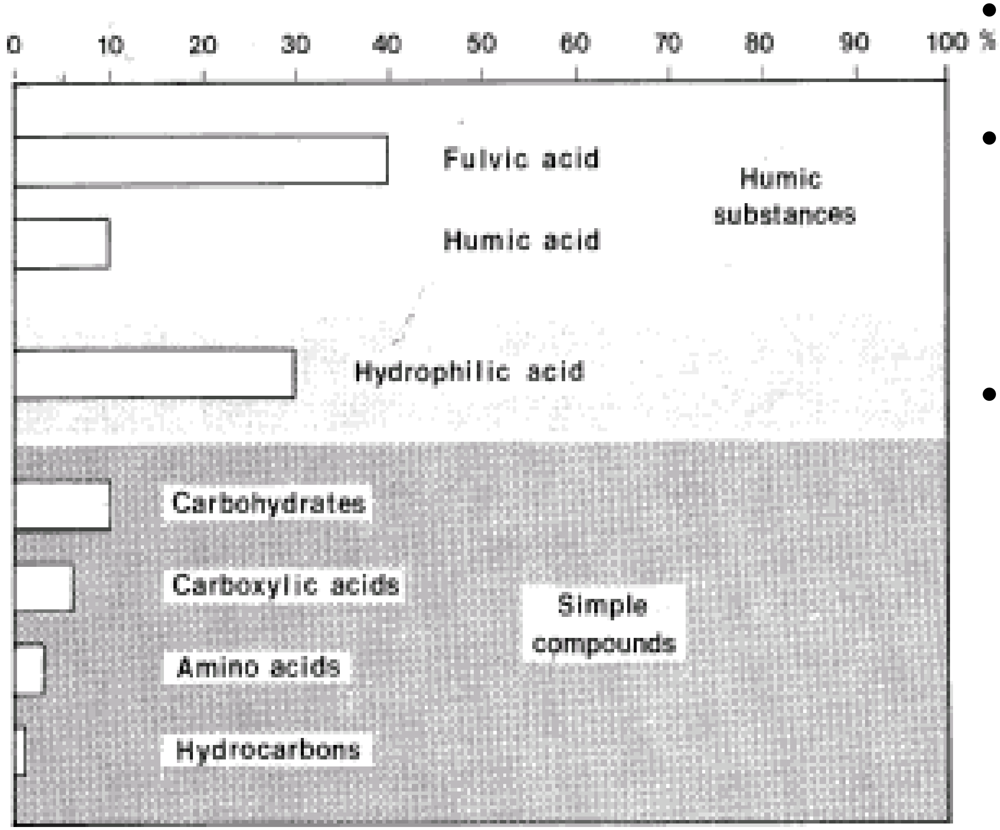
Carbon Cycle

What exactly is Dissolved OM?

- DOM is composed of reduced carbon-based molecules that pass through a 0.5 µm filter.
- DOM is 40 to 50% C and is typically measured as dissolved organic carbon (DOC)

Carbon Cycle

- DOM Compounds Classes in Streams



- Plant, microbial, & animal products in various stages of decomp.
- Biological & chemically synthesized from degradation products and of microorganisms in stages of decomposition
- Two primary categories:
  - Nonhumic – carbohydrates, proteins, peptides, amino acids, fats, waxes, resins, pigments, other low-molecular-weight substances
  - Humics – fulvic and humic acids, hydrophilic acids

Image source: unknown

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Operational Definitions

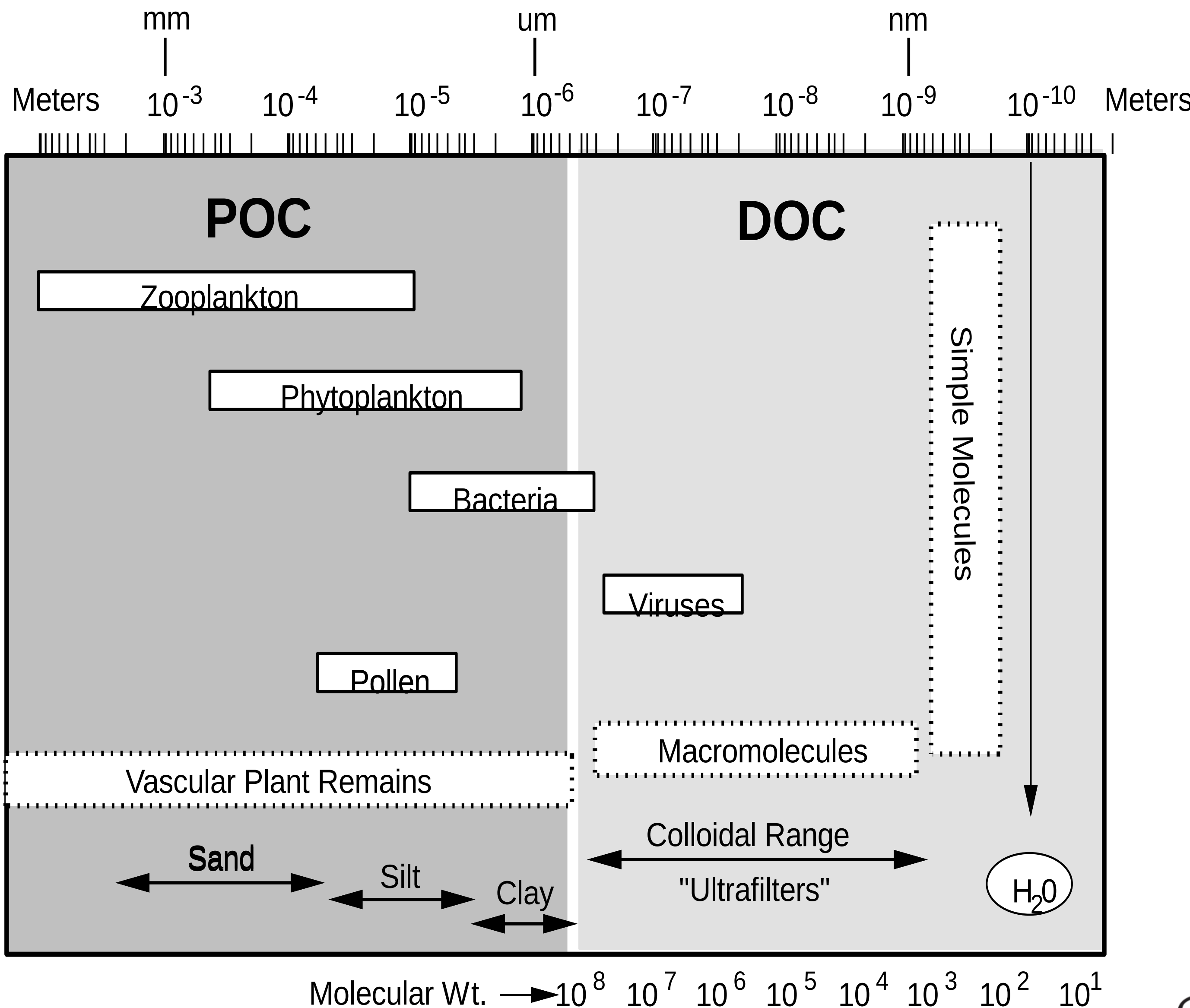

Image source: adapted from Thurman. 1985. Organic Geochemistry of Natural Waters. Nijhoff/Junk, Dordrecht.

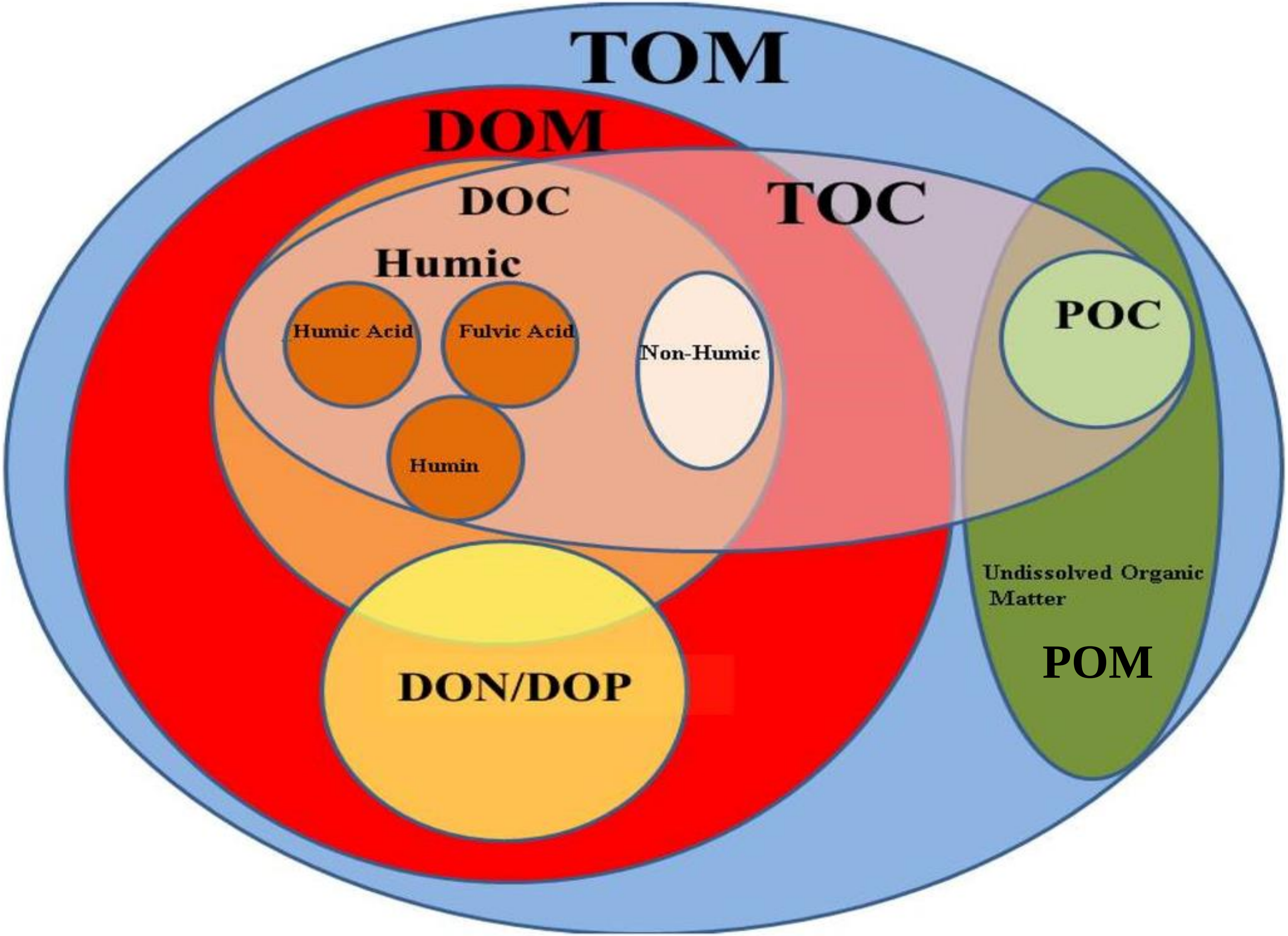

Image source: Pagano et al. 2014. Trends in levels of allochthonous dissolved organic carbon in natural water: a review of potential mechanisms under a changing climate. Water. 6:2862-2897

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Fates of CPOM/FPOM in Streams

- Transport, deposition, re-suspension
- Colonization by microorganisms
- Shredding by macroinvertebrates
- Metabolism
- Burial
- Abrasion and disintegration

Leaf litter in stream

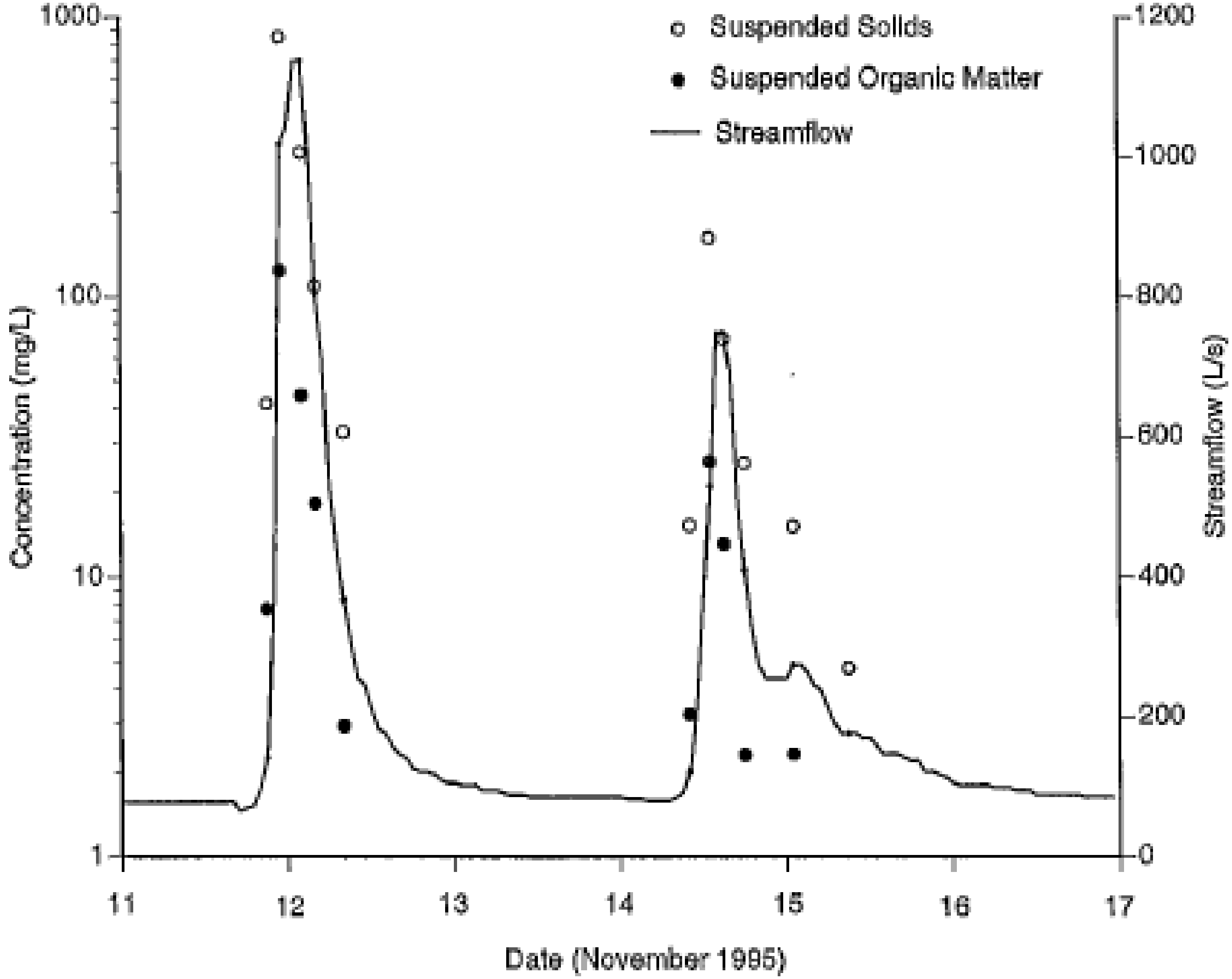
Image source:
https://watershed.ucdavis.edu/education/classes/tuolumne-river/pages/detailed-conceptual-model-clavey

Variability in CPOM/FPOM Concentrations

- Storm flows
- Diel patterns
- Seasonal patterns

White Clay Creek at SWRC (9/7/2011)
Photo credit: S. Hicks

POM and Sediment Loads Increase with Storm Flows



Data source: SWRC (Kaplan)

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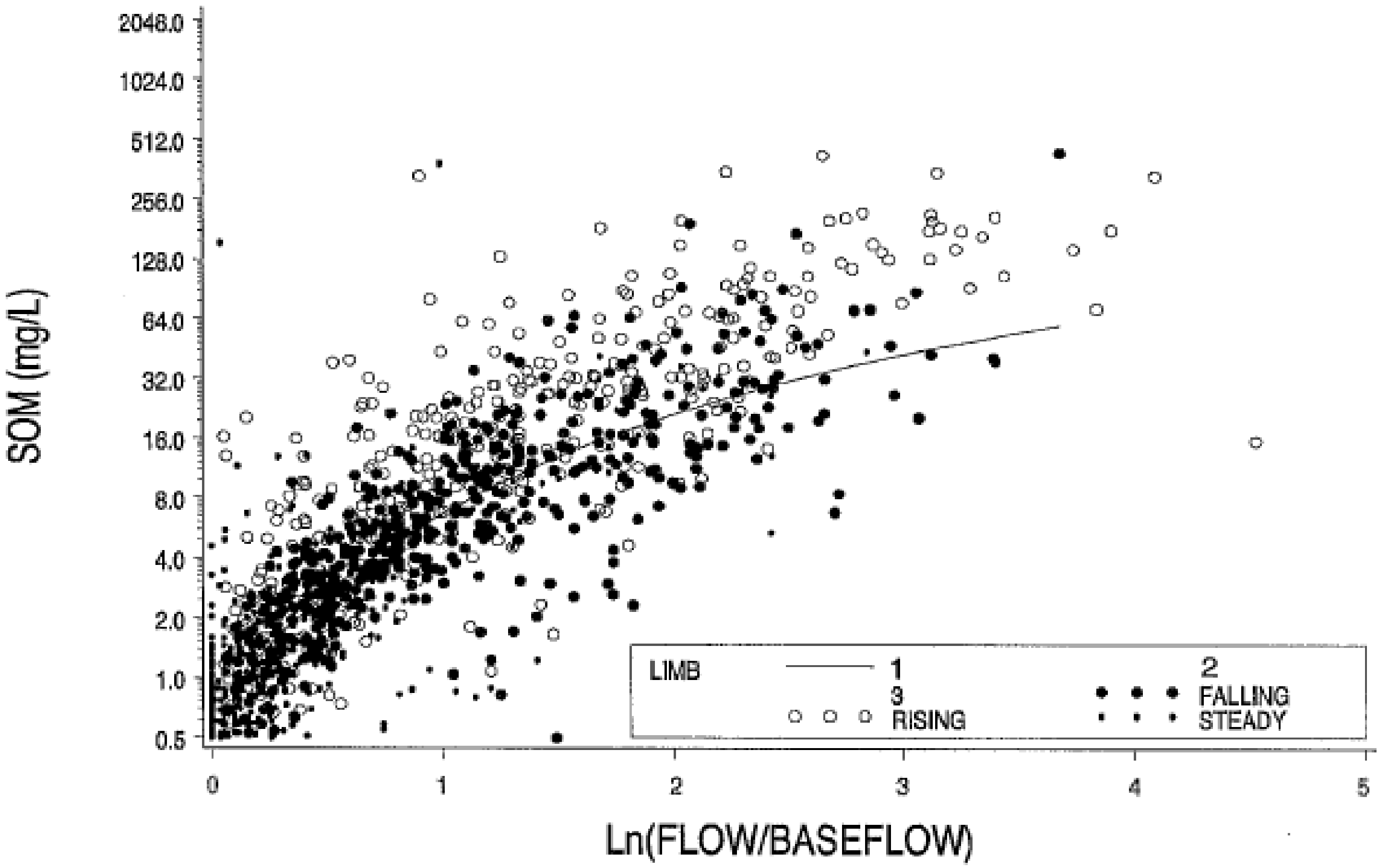
POM Concentrations Keep Increasing with Elevated Discharge

SOM=Suspended POM



Data source: SWRC (Kaplan)

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Processes Controlling DOM Delivery to Streams

- Forest canopy
- Forest floor
- Soil biogeochemistry
- Flow paths

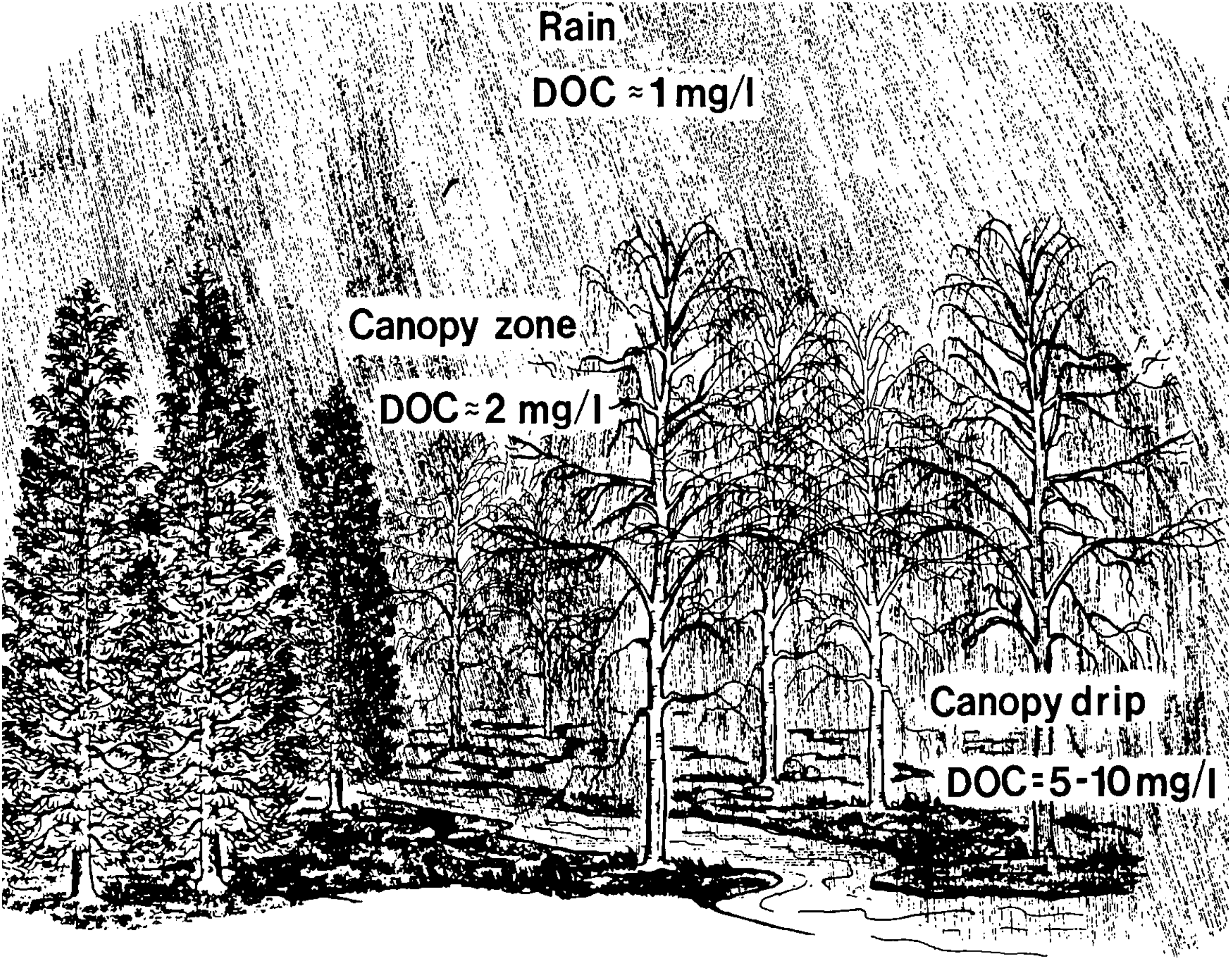

Figure 1.5 Dissolved organic carbon in precipitation and canopy drip.

Image source: unknown

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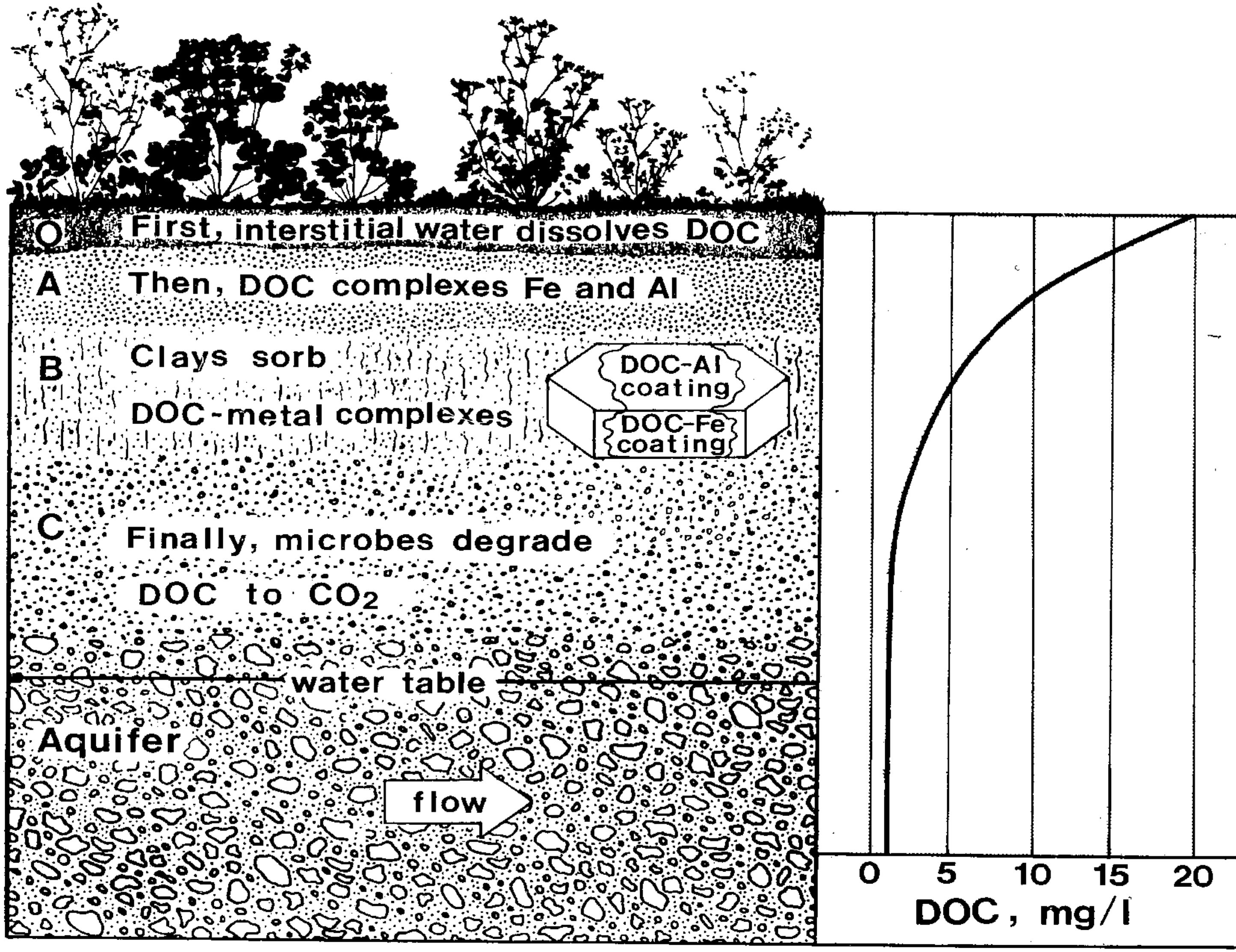


Figure 1.2 Podzolization and decrease of organic carbon in interstitial water of soils.

Image source: unknown

DOC Concentration

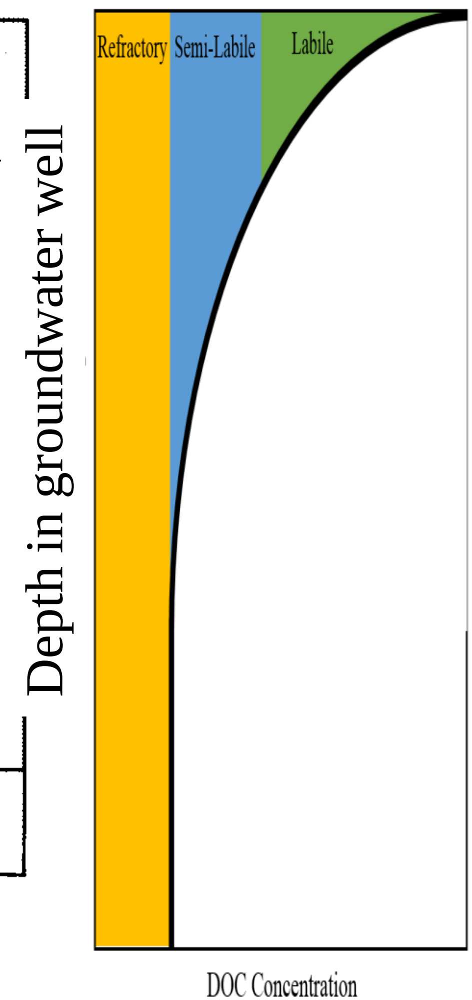
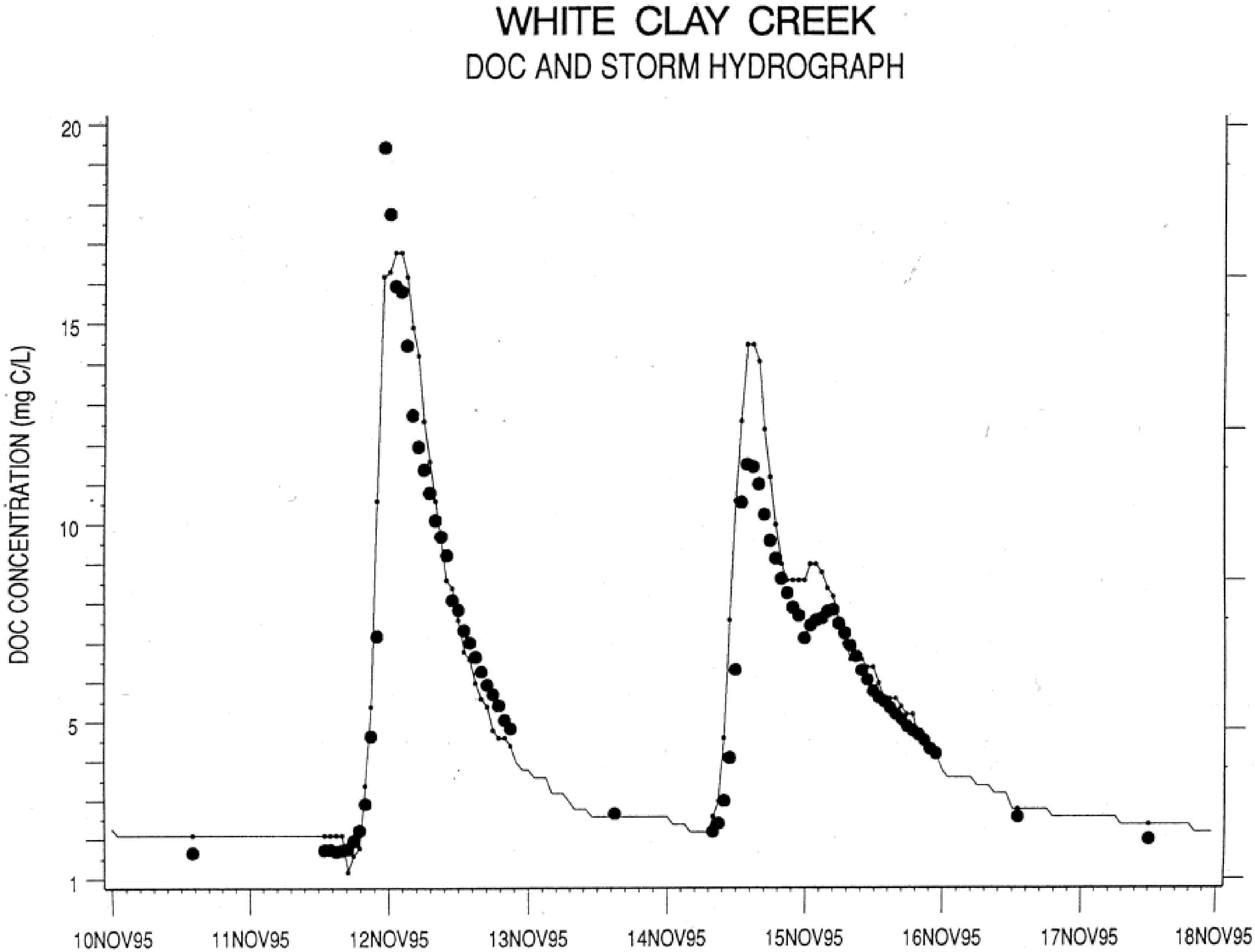


Image credit: Siegeofjones -CC BY-SA 4.0 https://en.wikipedia.org/wiki/Dissolved_organic_carbon



Data source: SWRC (Kaplan)

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Fates of DOC in Streams

- Photolysis
  - Chemical process by which molecules are broken down into smaller units through the absorption of light energy
- Adsorption
  - Capability of all solid substances to attract to their surfaces molecules of gases or solutions with which they are in contact. Adsorption can be either physical or chemical in nature
- Metabolism
  - Sum of the chemical reactions that take place within each cell of a living organism and that provide energy for vital processes and for synthesizing new organic material

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LAND USE AND STORMWATER DYNAMICS INFLUENCE WATER CHEMISTRY

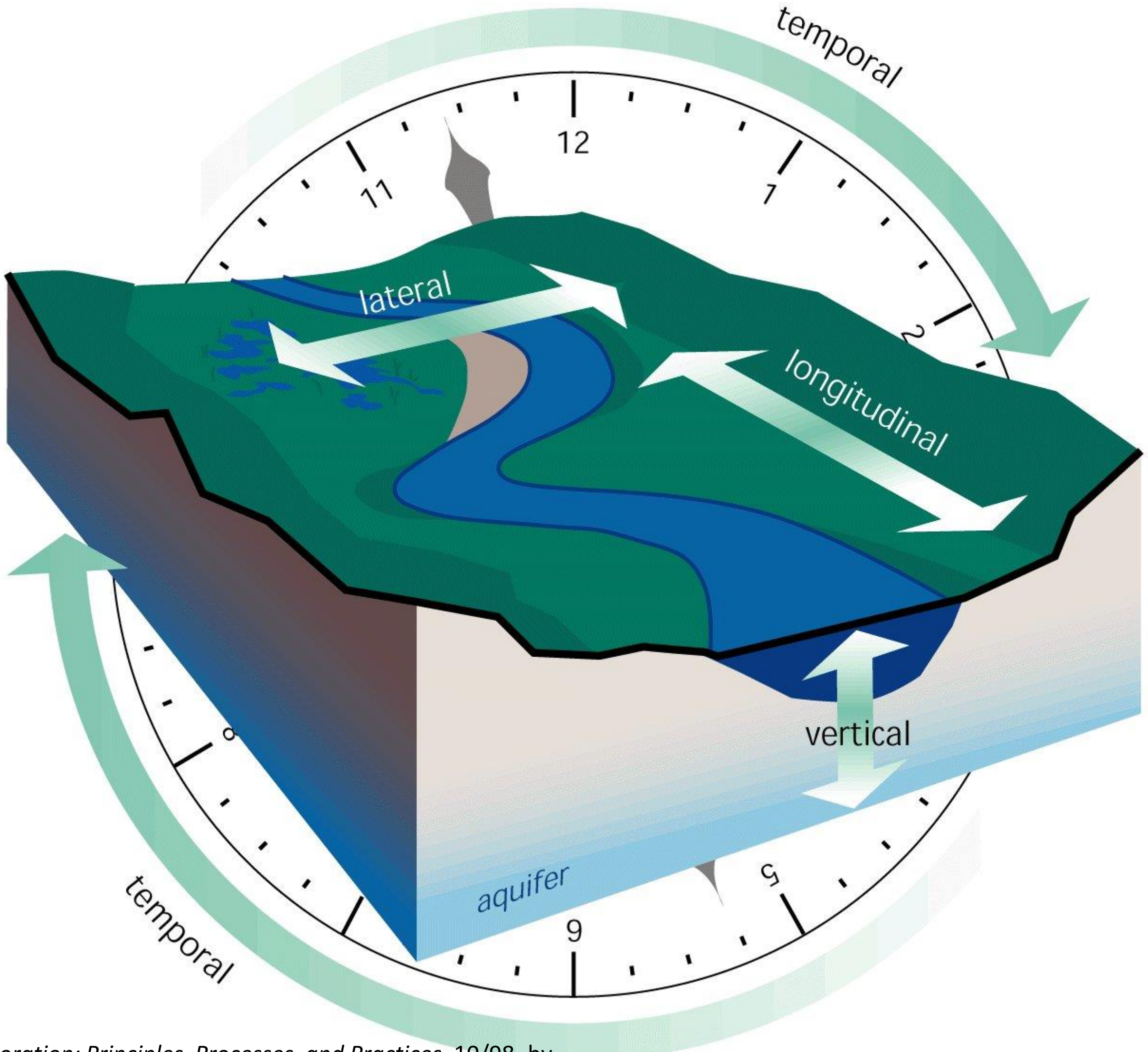
Learning objectives:

Understand land use influences on chemical delivery to streams

Understand what a pollutograph or first flush is?

If time allows, introduction to Model My Watershed

Four Dimensional Nature of Rivers



Stream Corridor Restoration: Principles, Processes, and Practices, 10/98, by the Federal Interagency Stream Restoration Working Group (FISRWG).

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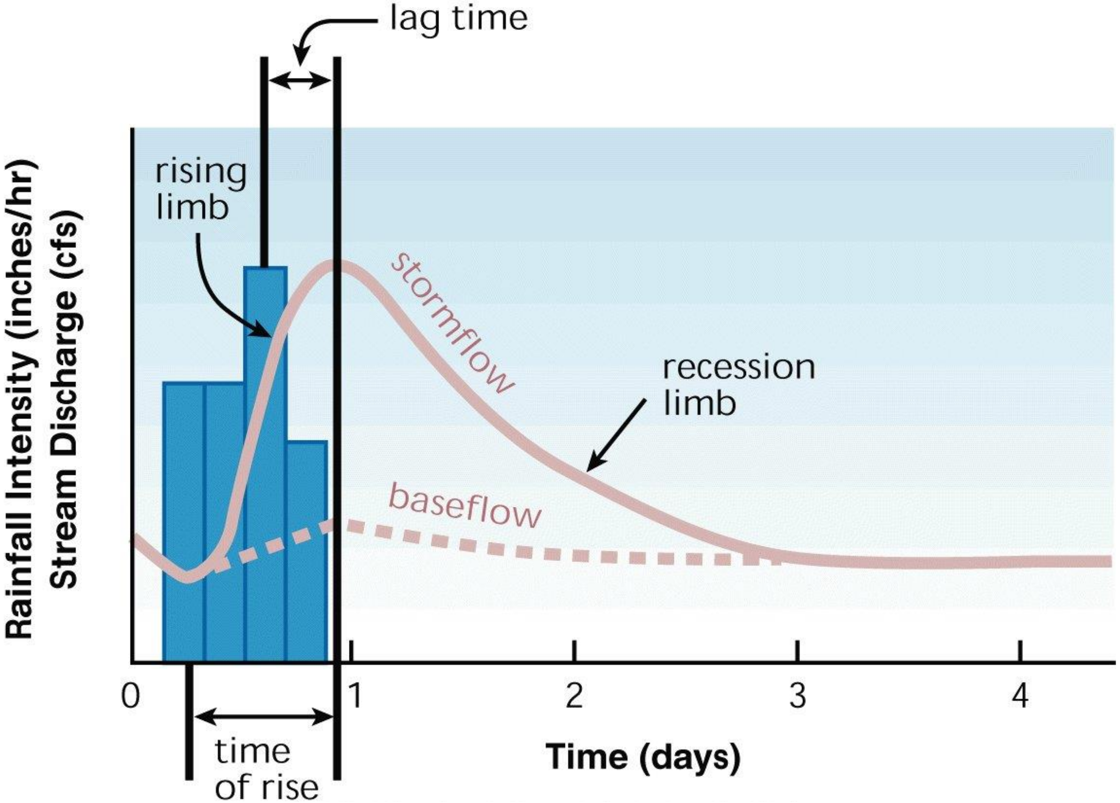
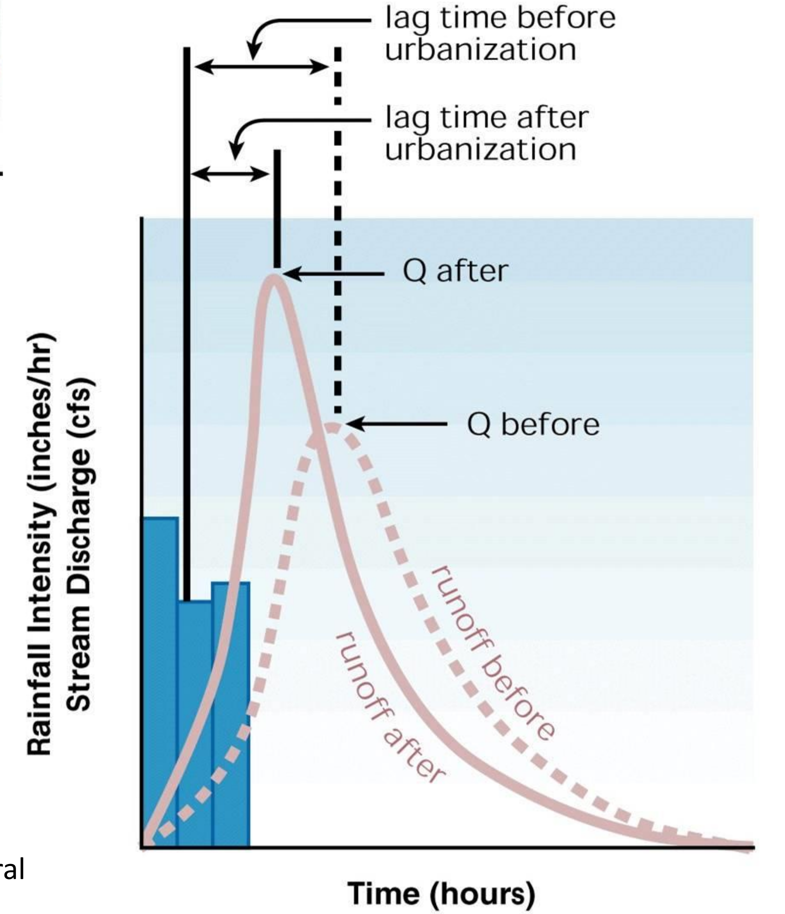
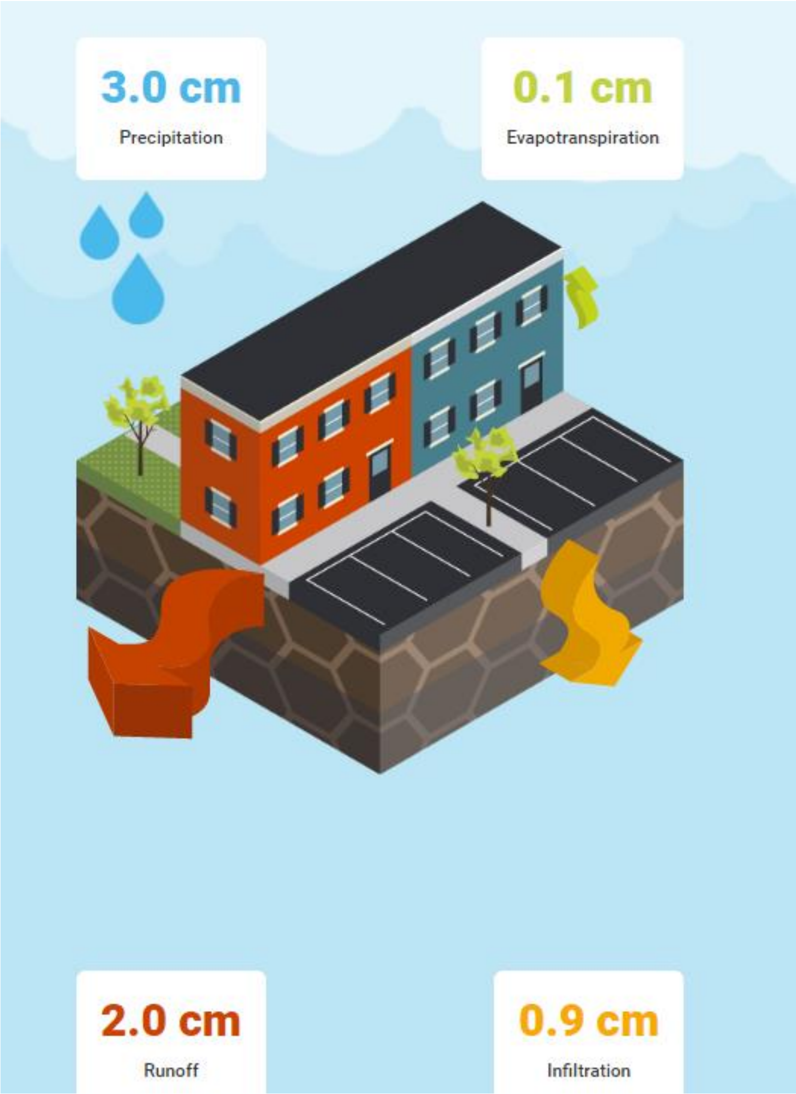




Stream Corridor Restoration: Principles, Processes, and Practices, 10/98, by the Federal Interagency Stream Restoration Working Group (FISRWG).

Land Use Influences Hydrologic Setting



From Wikiwatershed.org: https://app.wikiwatershed.org/micro/

Pollutant Loads Are Impacted by Land Cover

Table 2-2. Wet Weather Event Mean Concentration, (Derived from EPA, 1981; Cahill et al, 1978, 1984, and 1997; Philadelphia Water Department 2000, and other references - see Appendix A).

LAND COVER CLASSIFICATION	POLLUTANT						
	Total Suspended Solids, *(mg/l)*	Total Phosphorus, *(mg/l)*	Nitrate, *(mg/l as N)*	Chemical Oxygen Demand, *(mg/l)*	Total Petroleum Hydrocarbons, *(mg/l)*	Lead, *(mg/l)*	Copper, *(mg/l)*
Pervious Surfaces							
Forest	39	0.15	0.17	40	0.0	0.0015	0.008
Cleared Woodland	47	0.19	0.30	40	0.0	0.0015	0.008
Fert. Planting Area	55	1.34	0.73	53	0.0	0.0050	0.010
Rough Grass	180	0.40	0.44	53	0.0	0.0050	0.010
Lawn	180	2.22	1.46	60	0.0	0.0050	0.010
Playfield	200	1.07	1.01	65	0.0	0.0050	0.010
Impervious Surfaces							
Rooftops	21	0.13	0.32	1	0.6	0.0027	0.024
Roads & pavements	135	0.43	0.60	85	9.0	0.0110	0.047
Walks & misc.	60	0.46	0.47	50	0.4	0.0090	0.014

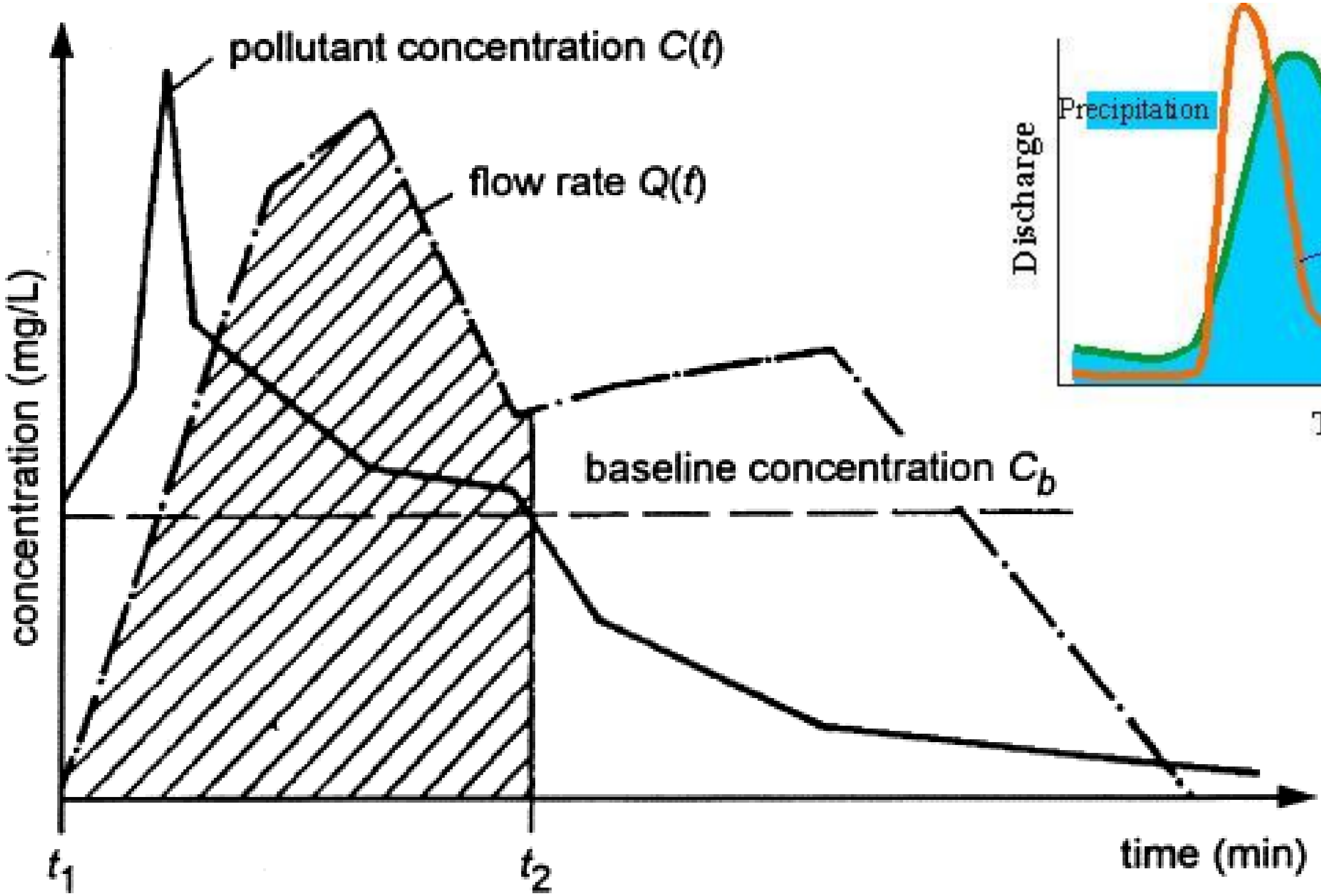
Stormwater Impacts

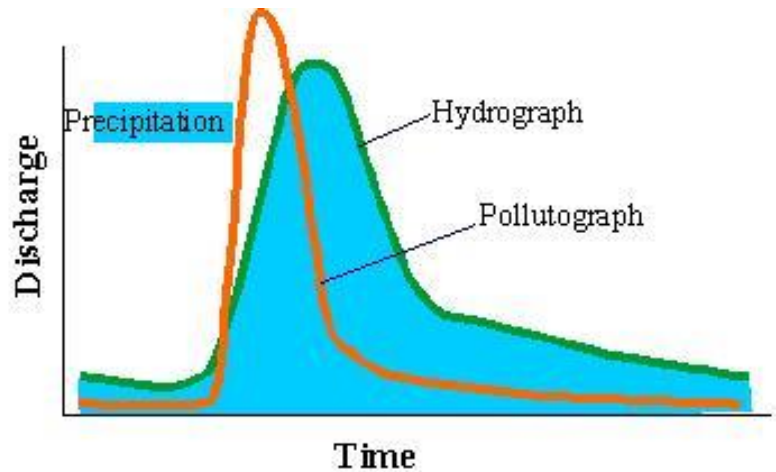
- Increased runoff volume from impervious surfaces and compacted soils
- Decreased evapotranspiration and groundwater recharge
- Increased frequency and intensity of runoff events
- Faster conveyance of water
- Erosion and stream channel changes
- Decreased baseflow
- Impacted aquatic Life
- Pollutants and temperature impacts

Pollutant Loading Can Include:

- Oil and grease from roadways
- Pesticides and nutrients from lawns
- Sediment from construction sites
- Sediments and nutrients from farming activities

First Flush Carries Significant Pollutant Load





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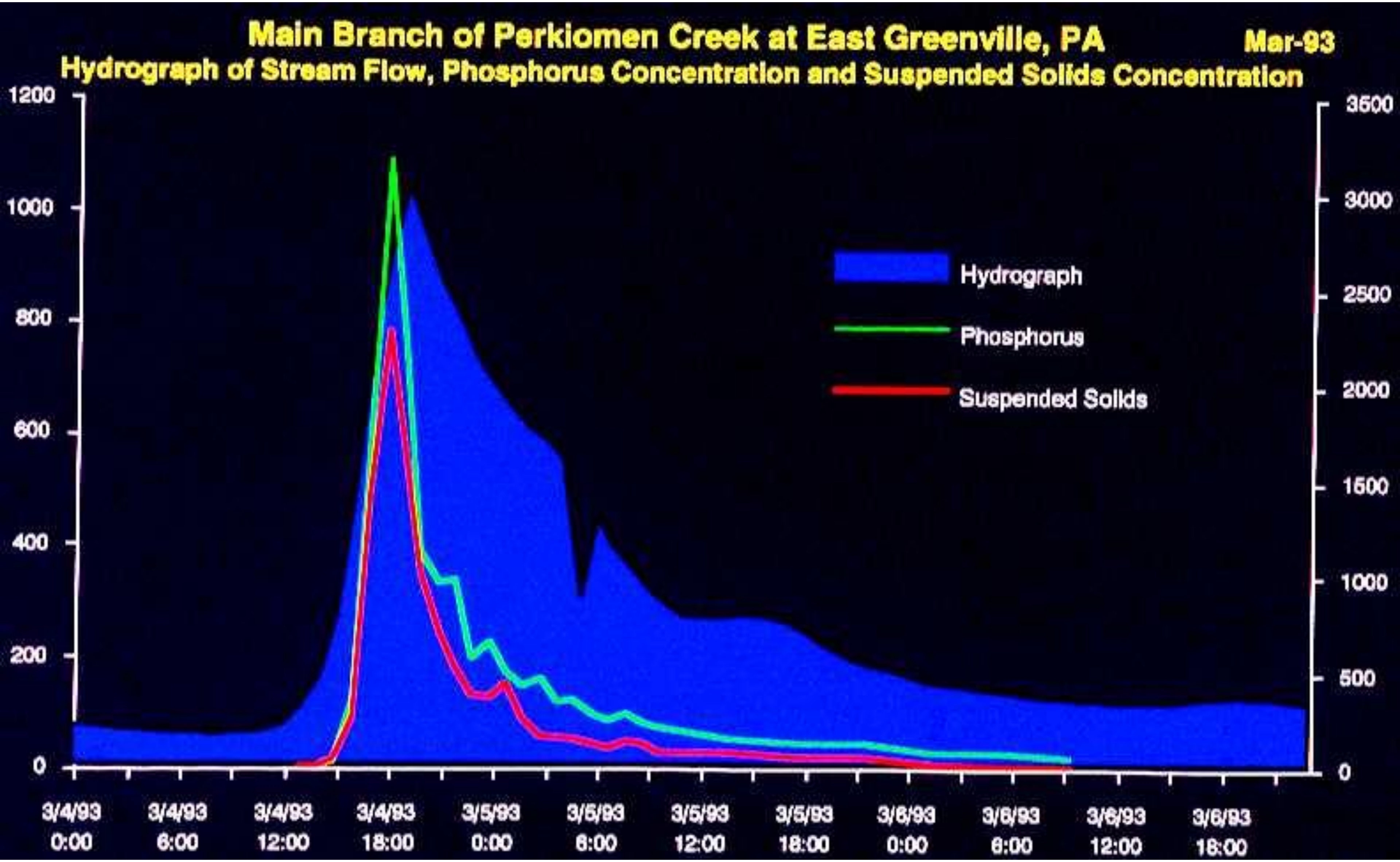
Mass First Flush Ratio (MFF) for Pollutants

Table 4.1 Ranked mass first flush ratios for MFF_{20}

Rank	7-201		7-202		7-203		Combined Sites	
	Parameters	Median	Parameters	Median	Parameters	Median	Parameters	Median
1	COD	1.740	Dissolved Ni	2.086	DOC	2.511	Dissolved Ni	1.943
2	Total P	1.706	DOC	2.005	Dissolved Ni	2.405	DOC	1.942
3	Dissolved P	1.688	NH_3-N	2.000	COD	2.326	TKN	1.895
4	TKN	1.589	Total Zn	1.999	TKN	2.180	COD	1.883
5	Dissolved Ni	1.577	Dissolved Cu	1.982	Dissolved Cu	2.122	NH_3-N	1.882
6	Oil & Grease	1.567	COD	1.948	NH_3-N	2.099	Dissolved P	1.748
7	TSS	1.559	TKN	1.944	TSS	1.980	TSS	1.718
8	NH_3-N	1.558	Dissolved Zn	1.927	Total Ni	1.864	Total P	1.717
9	DOC	1.522	Dissolved P	1.862	Total Cu	1.792	Oil & Grease	1.699
10	Total Ni	1.489	Total Ni	1.845	Oil & Grease	1.787	Dissolved Cu	1.680
11	Total Zn	1.484	Total Cu	1.714	Dissolved P	1.747	Total Ni	1.680
12	Dissolved Zn	1.428	Oil & Grease	1.709	Total P	1.747	Total Zn	1.666
13	Conductivity	1.416	Total P	1.703	Conductivity	1.741	Dissolved Zn	1.657
14	Dissolved Cu	1.401	NO_3-N	1.486	Dissolved Zn	1.661	Total Cu	1.644
15	Total Cu	1.396	Total Cd	1.459	Total Zn	1.652	Conductivity	1.538
16	NO_2-N	1.392	Turbidity	1.429	Hardness	1.607	Hardness	1.484
17	Total Cr	1.358	TSS	1.416	NO_3-N	1.573	NO_2-N	1.371
18	Turbidity	1.299	Dissolved Pb	1.377	NO_2-N	1.369	NO_3-N	1.345
19	Total Pb	1.225	PO_4-P	1.366	Dissolved Pb	1.339	Turbidity	1.288
20	Hardness	1.200	Dissolved Cr	1.349	Total Cd	1.269	Total Cd	1.264
21	Dissolved Cr	1.152	Total Pb	1.323	Total Cr	1.224	Total Pb	1.230
22	Total Cd	1.074	Dissolved Cd	1.307	Total Pb	1.131	Total Cr	1.223
23	Dissolved Cd	1.001	NO_2-N	1.251	Turbidity	1.093	Dissolved Pb	1.206
24	Dissolved Pb	1.000	Hardness	1.227	Dissolved Cd	1.091	Dissolved Cr	1.172
25	PO_4-P	1.000	Conductivity	1.214	Dissolved Cr	1.040	Dissolved Cd	1.087
26	NO_3-N	0.983	Total Cr	1.200	PO_4-P	1.000	PO_4-P	1.000

Values > 1 indicate normalized mass discharged faster than normalized volume



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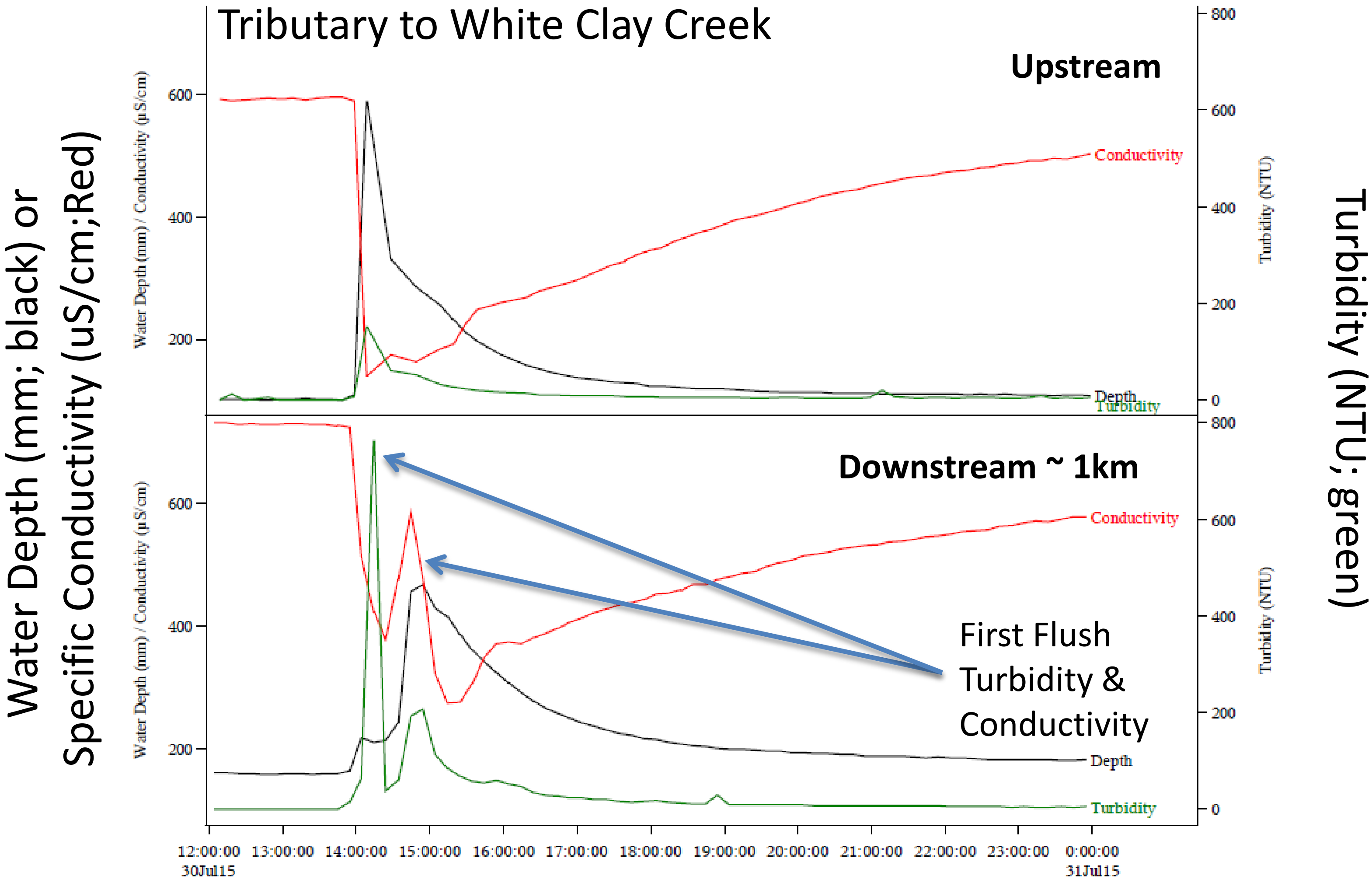
First Flush Hydrograph



Data source: SWRC (D. Arscott) 2015 – from location in White Clay
Data are provisional (not final and subject to change)
n = 513; (75 PK; 53 UL; 62 SH; 54 NJH; 92 MS; 136 BC; 38 SP; 3 KCA)

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Appendix and Reference Material

Unique character of H_2O

- Water, physically unique (Emerson and Hedges 2008)

Property	**Comparison**	**Importance**
Heat capacity (1 cal/g °C) (energy needed to raise temp of 1 kg by 1 ^{o}K)	Highest of all solids & liquids	Regulates thermal change (thermostating), energy transfer
Heat of fusion (79 cal/g) (energy needed to convert solid to liquid)	Highest except for NH_3	Regulates thermal change (thermostating), energy transfer
Heat of vaporization (540 cal/g) (energy needed to convert liquid to gas)	Highest of all substances	Regulates thermal change (thermostating), energy transfer
Surface tension	Highest of all liquids	Wave and drop formation
Dielectric constant (charge insulation) (ability to store electrical energy)	Highest of all substances	Solubility of salts & ion reactions

Image: SilverV/iStock

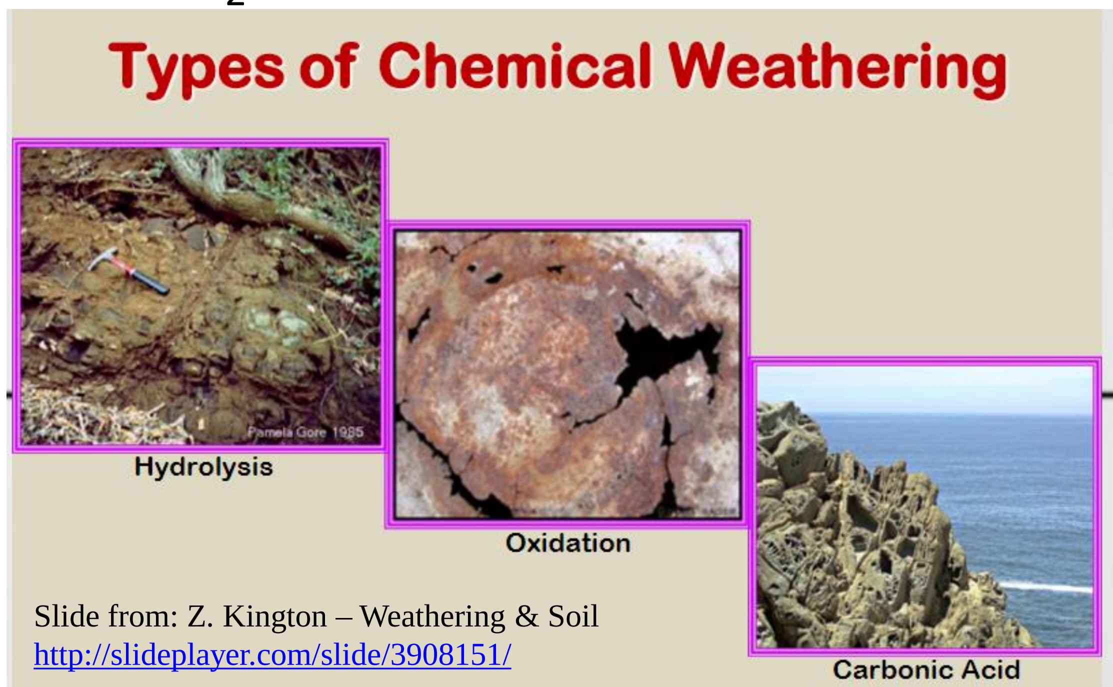
Cation and Anion Valences

Ion Name	Symbol	Valence
Aluminum	Al	+3
Ammonium	NH_4	+1
Barium	Ba	+2
Calcium	Ca	+2
Carbon	C	+4
Cesium	Cs	+1
Chromium (Chromic)	Cr	+3
Chromium (Chromus)	Cr	+2
Copper (Cuprium)	Cu	+2
Hydrogen	H	+1
Iron (Ferric)	Fe	+3
Iron (Ferrous)	Fe	+2
Lead (Plumbic)	Pb	+4
Lead (Plumbus)	Pb	+2
Magnesium	Mg	+2
Manganese	Mn	+2
Nickel	Ni	+2
Phosphorus	P	+5
Potassium	K	+1
Silicon	Si	+4
Silver	Ag	+1
Sodium	Na	+1
Zinc	Zn	+2

Ion Name	Symbol	Valence
Bicarbonate	HCO_3	-1
Bisulfate	HSO_4	-1
Bisulfide	HS	-1
Bisulfite	HSO_3	-1
Bromate	BrO_3	-1
Bromide	Br	-1
Carbonate	CO_3	-2
Chloride	Cl	-1
Chromate	CrO_4	-2
Dichromate	Cr_2O_7	-2
Fluoride	F	-1
Hydroxide	OH	-1
Hypochlorite	ClO	-1
Nitrate	NO_3	-1
Nitrite	NO_2	-1
Perchlorate	ClO_4	-1
Phosphate	PO_4	-3
Sulfate	SO_4	-2
Sulfide	S	-2
Sulfite	SO_3	-2

Chemical Weathering

- Simple (congruent) dissolution occurs when rock salts (e.g., NaCl, called halite) formed by seawater evaporation are uplifted on the continents and exposed to rainwater:
  - $NaCl(s) + H_2O \Leftrightarrow Na^+ + Cl^- + H_2O$



Slide from: Z. Kington – Weathering & Soil
http://slideplayer.com/slide/3908151/

Chemical – Geochemistry – geology as the foundation

- Silicate weathering (with many mineral types involved) has the general form:
- $2NaAlSi_3O_4 + 2CO_2 + 11H_2O \Leftrightarrow Al_2Si_2O_5(OH)_4 + 2Na+ + 2HCO_3^- + 4H_4SiO_4$
  - In this case, the mineral reactant is albite (a feldspar) and the mineral product is kaolinite (a clay mineral and common chemical weathering product)
  - Both feldspar and kaolinite are solid aluminosilicates minerals, but the latter clay mineral has been hydrated in the process of weathering and also stripped of its sodium (lost as dissolved Na^+) and most of its silicon (lost as dissolved silicic acid)
  - Many other **aluminosilicate minerals** undergo **similar weathering reactions**, all of which **take up carbon dioxide gas and water and give off dissolved bicarbonate, cations and silicic acid** as products

Carbonate Buffering System

Major CBS species in natural waters include:

- $CO_2(aq)$ → dissolved (unhydrated) carbon dioxide: ~ 99.9% of $[CO_2(aq)] + [H_2CO_3] \equiv CO_2^*$
- H_2CO_3 → carbonic acid (from hydrolysis $CO_2(aq)$): ~ 0.1% of $[CO_2(aq)] + [H_2CO_3] \equiv CO_2^*$
- HCO_3^- → bicarbonate ion (the conjugate base of H_2CO_3)
- CO_3^{2-} → carbonate ion (the conjugate base of HCO_3^-)
- ΣCO_2^- → Total CO_2, or Dissolved Inorganic Carbon (DIC), is by definition:

  $$\Sigma CO_2 \equiv [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$$
- $CaCO_3(s)$ → solid calcium carbonate minerals calcite or aragonite

Table 3. Composition of river water

[Date under sample number is date of collection. Sources of data: 1, Oltman (1968, p. 13); 2, U.S. Geological Survey Water-Supply Paper 1964; 3, Livingstone (1963, p. G41); 4, Maybeck (1979)]

Constituent	1		2		3		4	
	July 16, 1963		Oct. 1, 1964 – Sept. 30, 1965					
	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
Silica (SiO_2)	7.0		7.9		13		10.4	
Aluminum (Al)	.07							
Iron (Fe)	.06		.02					
Calcium (Ca)	4.3	.215	38	1.896	15	.749	13.4	.669
Magnesium (Mg)	1.1	.091	10	.823	4.1	.337	3.35	.276
Sodium (Na)	1.8	.078	20	.870	6.3	.274	5.15	.224
Potassium (K)			2.9	.074	2.3	.059	1.3	.033
Bicarbonate (HCO_3)	19	.311	113	1.852	58	.951	52	.852
Sulfate (SO_4)	3.0	.062	51	1.062	11	.239	8.25	.172
Chloride (Cl)	1.9	.054	24	.677	7.8	.220	5.75	.162
Fluoride (F)	.2	.011	.3	.016				
Nitrate (NO_3)	.1	.002	2.4	.039	1	.017		
Dissolved solids	28.		232		89		73.2	
Hardness as $CaCO_3$	15		138		54		47	
Noncarbonate	0		45		7		5	
Specific conductance (micromhos at 25°C).	40		371					
pH	6.5		7.4					
Color			10					
Dissolved oxygen	5.8							
Temperature (°C)	28.4							

1. Amazon at Obidos, Brazil. Discharge, 216,000 m^3/s (7,640,000 cfs) (high stage).
2. Mississippi at Luling Ferry, La. (17 mi west of New Orleans). Time-weighted mean of daily samples.
3, 4. Mean composition of river water of the world (estimated). Dissolved-solids computed as sum of solute concentrations, with HCO_3 converted to equivalent amount of CO_3.

World averages

From 3- Livingstone (1963)
4 -Maybeck (1979)

Data of Geochemistry
Sixth Edition
MICHAEL FLEISCHER, *Technical Editor*
Chapter G. Chemical Composition of Rivers and Lakes
By DANIEL A. LIVINGSTONE
GEOLOGICAL SURVEY PROFESSIONAL PAPER 440-G

REVUE DE GÉOLOGIE DYNAMIQUE ET DE GÉOGRAPHIE PHYSIQUE VOL. 21, FASC. 3, p. 215-246, PARIS, 1979
Concentrations des eaux fluviales en éléments majeurs et apports en solution aux océans
par Michel MEYBECK *

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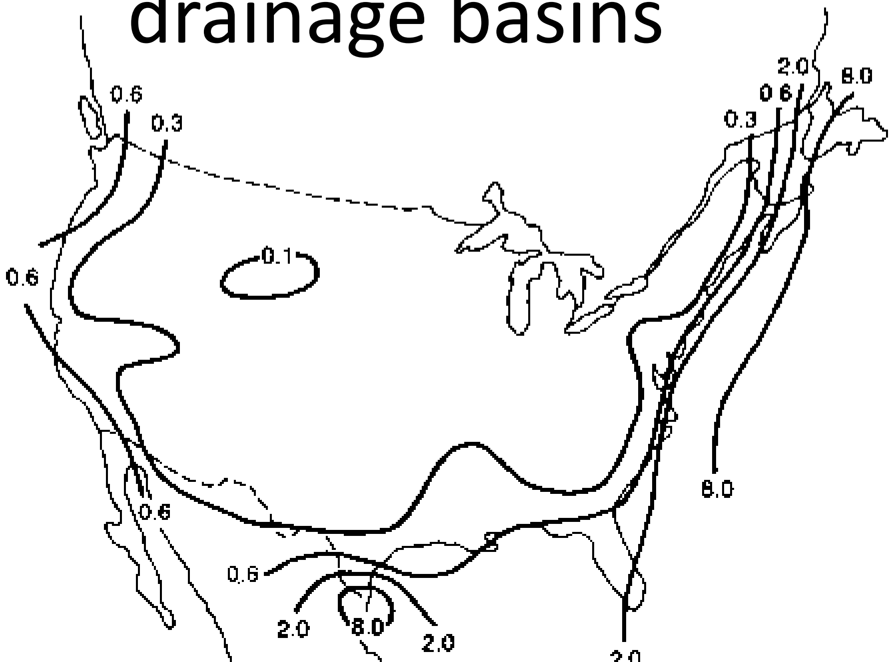
Geologic Weathering Results in

- Dissolved composition of river water records the types of chemical weathering (both substrates and rates) that occur on in their drainage basins



One complication is "**cyclic salts**" in rivers that are derived from sea-surface aerosols, as opposed to recent continental weathering

Spatial distributions of sodium (Na^+) concentrations (ppm) in rain, as an example of cyclic salts from marine aerosols entering freshwater systems (Garrels and Mackenzie1971).

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Chemical – Geochemistry – geology as the foundation

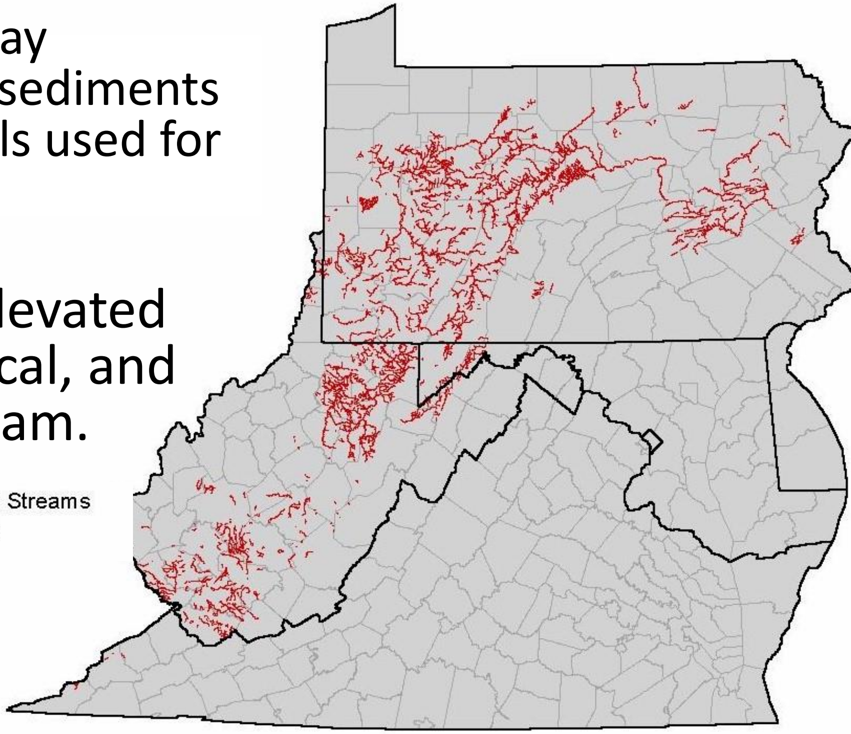
- Sulfide weathering (acid mine drainage)
  - Produces acid mine drainage (AMD) when sulfides are oxidized (oxygen and water) to hydrogen ions and sulfuric acid. Almost all base metals are mined from sulfide ores (pyrite=iron sulfide=FeS_2), and there is often substantial sulfide in coal.
- $2FeS_2$ (s) + $7O_2$ + $2H_2O$ –> $2Fe^{+2}$ + $4SO_4^{-2}$ + $4H^+$
- Fe^{+2} can precipitate to red-orange flock/crust

Suggested Citation: Jennings, S.R., Neuman, D.R. and Blicker, P.S. (2008). "Acid Mine Drainage and Effects on Fish Health and Ecology: A Review". Reclamation Research Group Publication, Bozeman, MT.

https://www.epa.gov/polluted-runoff-nonpoint-source-pollution/abandoned-mine-drainage
http://www.sosbluewaters.org/epa-what-is-acid-mine-drainage%5B1%5D.pdf

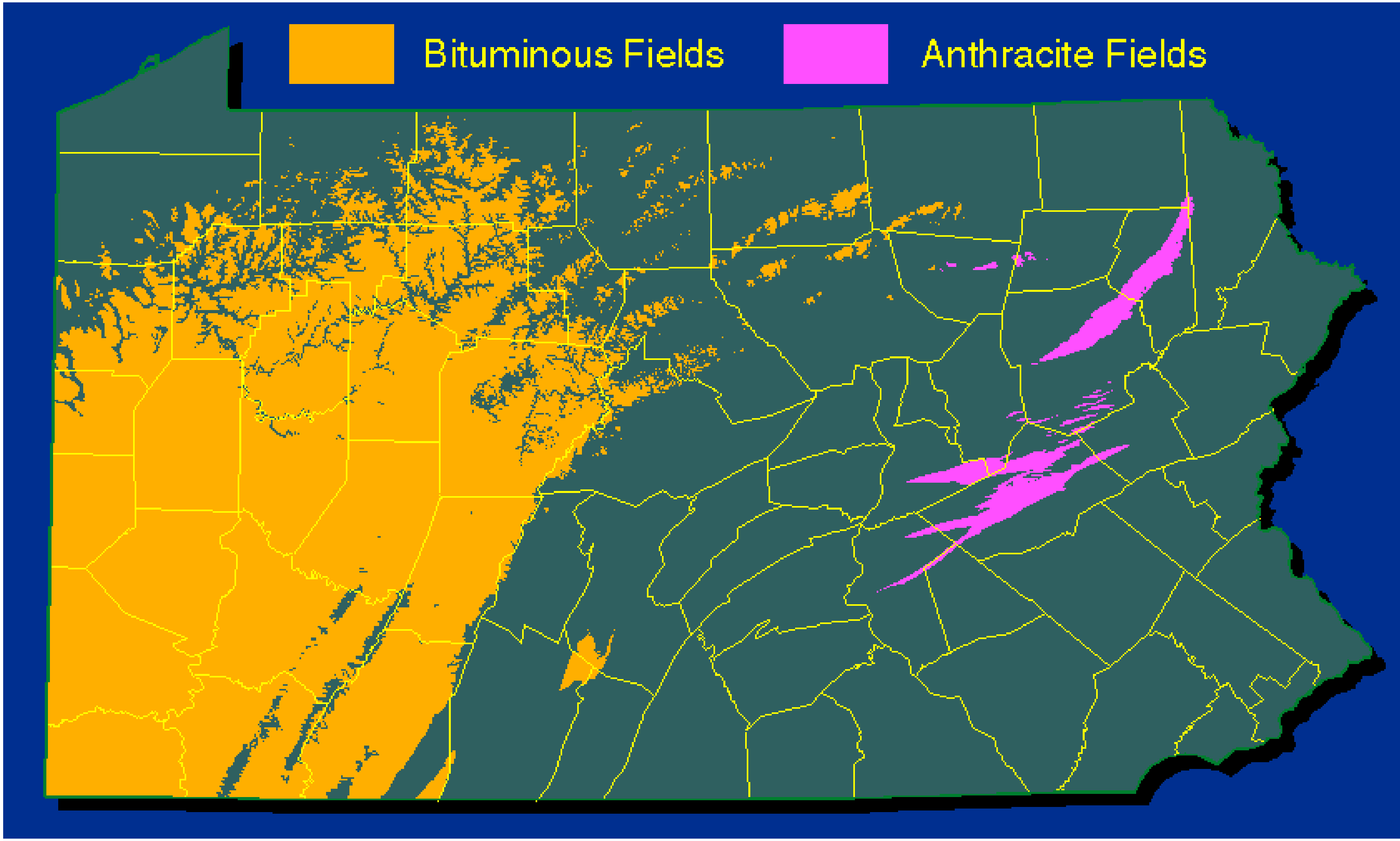
Acid Mine Drainage Impacts

- Metals released, available to biological organisms
  - fish exposed directly to metals and H^+ ions through gills, impaired respiration results from chronic and acute exposure
  - Indirect exposure via ingestion of contaminated sediments and food
- Weathering product of sulfide oxidation = iron hydroxide ($Fe(OH)_3$), a red/orange colored precipitate found in streams affected by AMD.
  - Iron hydroxides and oxyhydroxides may physically coat the surface of stream sediments and streambeds covering clean gravels used for spawning, reduces fish food (benthic macroinvertebrates).
- AMD, characterized by acidic metal-elevated conditions, can cause physical, chemical, and biological change/degradation to stream.



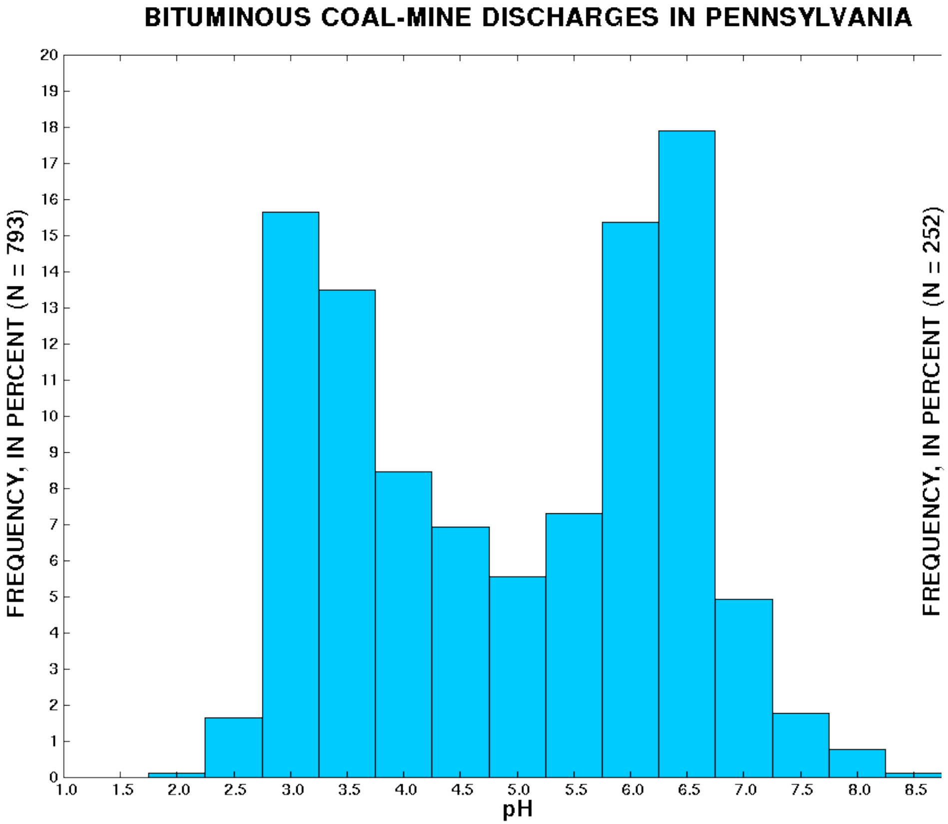
Suggested Citation: Jennings, S.R., Neuman, D.R. and Blicker, P.S. (2008). "Acid Mine Drai
Health and Ecology: A Review". Reclamation Research Group Publication, Bozeman, MT.

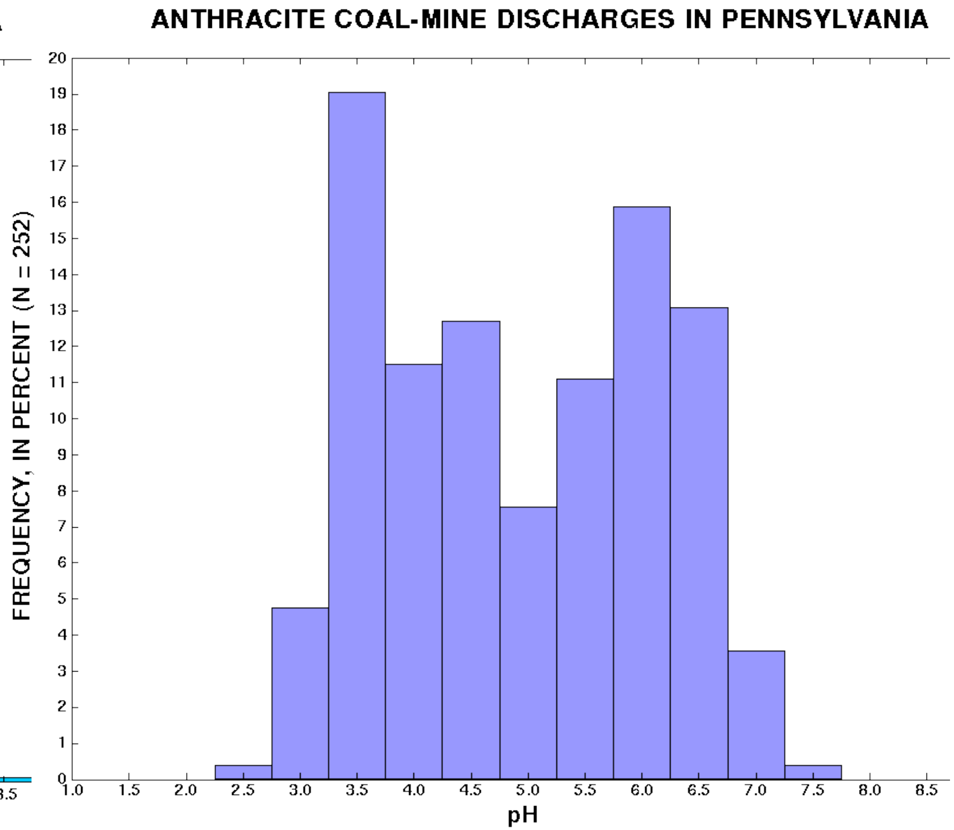
Image from: http://www.ei.lehigh.edu/envirosci/enviroissue/amd/links/graphs.html



"Drainage from thousands of abandoned coal mines has contaminated more than 3,000 miles of streams and associated ground waters in Pennsylvania…"

Image from: USGS website on Coal-mine drainage projects in PA: http://pa.water.usgs.gov/projects/energy/amd/





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Conemaugh River showed marked improvement after remediation.

Photo: Courtesy Rosebud Mining Company (June 2004)

http://archive.alleghenyfront.org/story/mining-company-invests-big-treat-acid-mine-drainage.html

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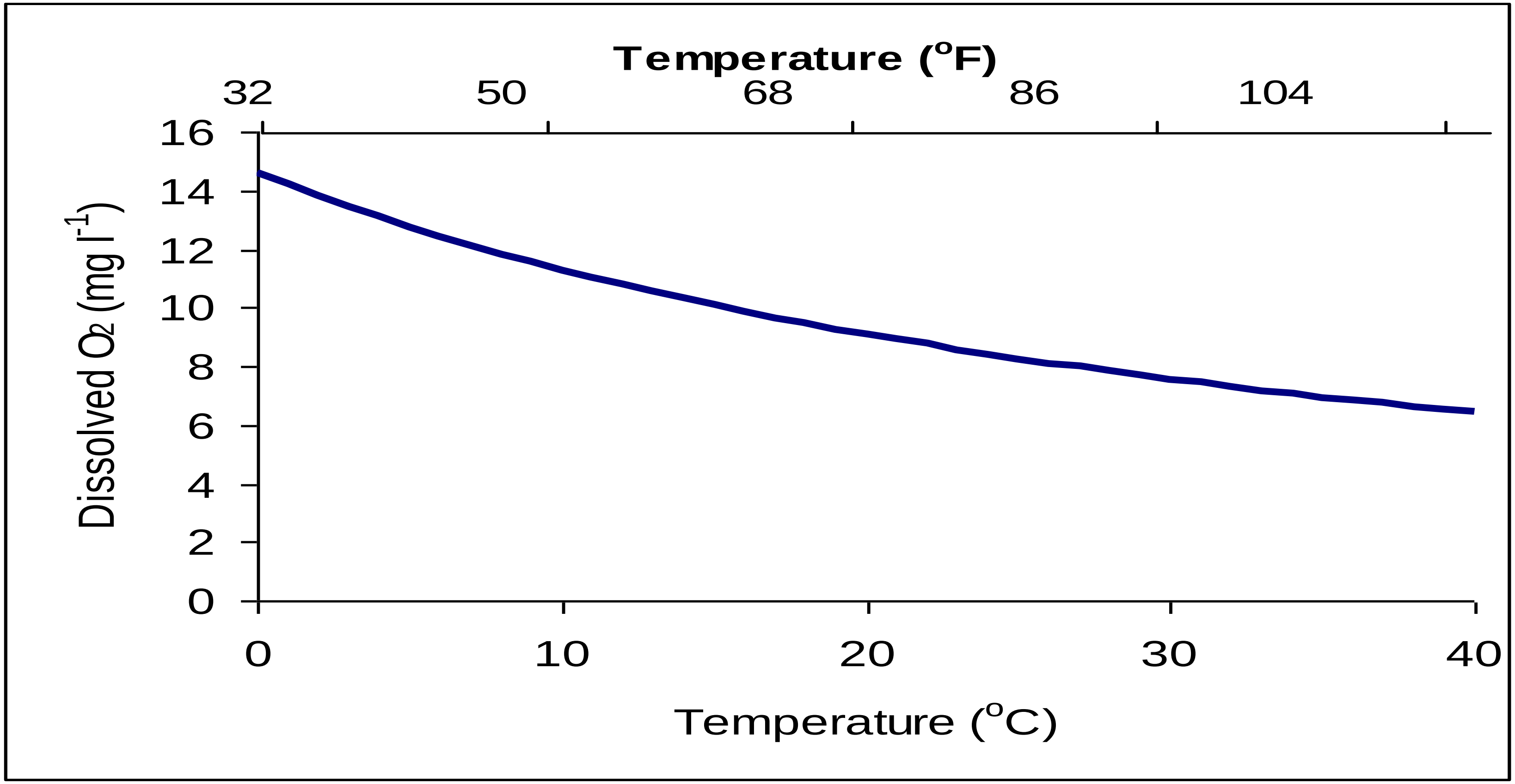
AMD Impacts

- Distribution of fish in PA streams affected by AMD (Cooper and Wagner 1973) severely impacted at pH 4.5 to 5.5
- Ten species with some tolerance to pH 5.5 and below; 38 were at pH from 5.6 to 6.4; 68 species only at pH > 6.4.
- Complete loss of fish in 90% of streams with waters of pH 4.5 and total acidity of 15 mg/L.

Maximum Dissolved Oxygen Saturation vs Water Temperature



Turbidity

- Turbidity (NTU, FNU JTU,)
  - Measure of water cloudiness caused by suspended sediment
  - Can result from soil erosion, runoff and algal blooms
  - NTU – Nephelometric Turbidity Units – particles scattering light beam in front of detector photodiode (90^{o} angle) – light source 400-680 nm range
  - FNU – Formazin Nephelometric Units- measuring incident light scattered at right angles from sample (photodiode) – light source 780-900 nm range
  - Jackson Candle method (Jackson TU) – inverse measure of length of water column need to completely obscure candle flame viewed through it
  - Importance:
    - High turbidity limits sunlight penetration=inhibits growth of aq.plants
    - High levels indicate soil erosion

***No Pa State Standards for Turbidity; EPA has recommended water quality criteria for NTU – some states LA, VT, WA**

https://www.epa.gov/wqc/aquatic-life-ambient-water-quality-criteria

http://or.water.usgs.gov/grapher/fnu.html

Turbidity	
O JTU	Excellent
>0 to 40 JTU	Good

Turbidity

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  - Measure of water cloudiness caused by suspended sediment
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  - FNU – Fomazin TU right angles from sample (photodiod
  - Jackson Candle me f length of water column need to co through it

Turbidity	
O JTU	Excellent
>0 to 40 JTU	Good
>40 to 100 JTU	Fair/storm
>100 JTU	Poor/storm

***No Pa State Standards for Turbidity; EPA has recommended water quality**

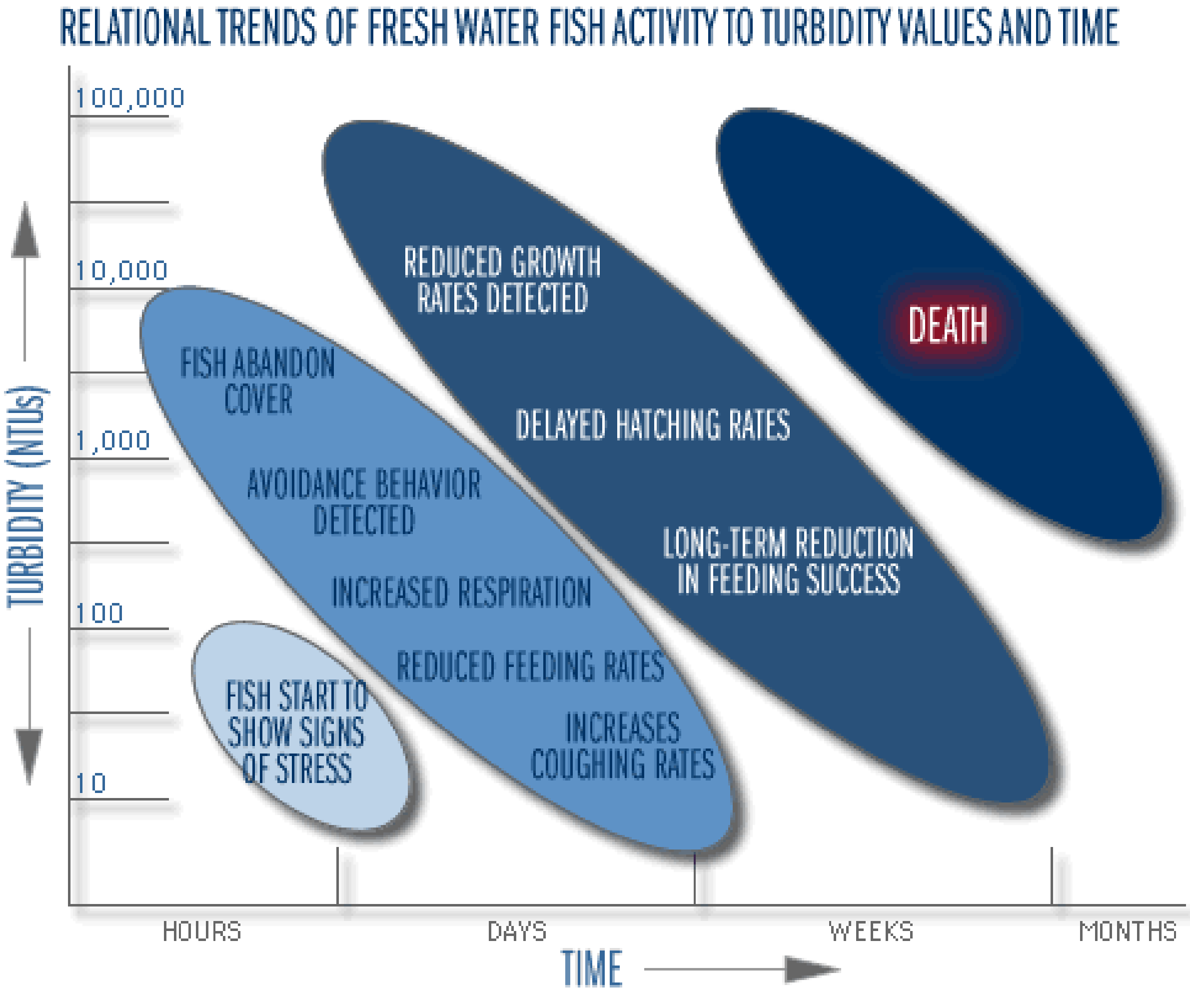
criteria for NTU – some states LA, VT, WA

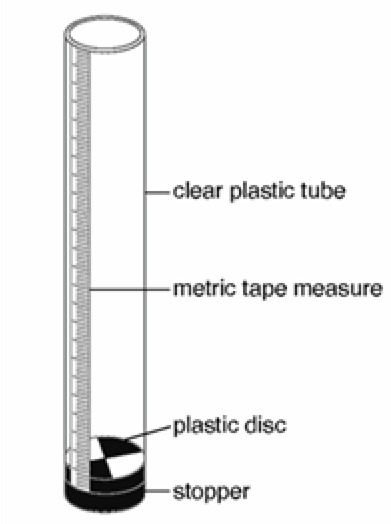
https://www.epa.gov/wqc/aquatic-life-ambient-water-quality-criteria

http://or.water.usgs.gov/grapher/fnu.html

Turbidity

- Turbidity (NTU, FNU JTU)





Is Turbidity Related to Total Suspended Solids?

- Yes
- But differences in relationship among rivers due to different kinds (quality) of particles in matrix
  - Albert Canada Agency
    - TSS = 3.4216(xNTU)
  - French Cr and Brandywine
    - (next slide)

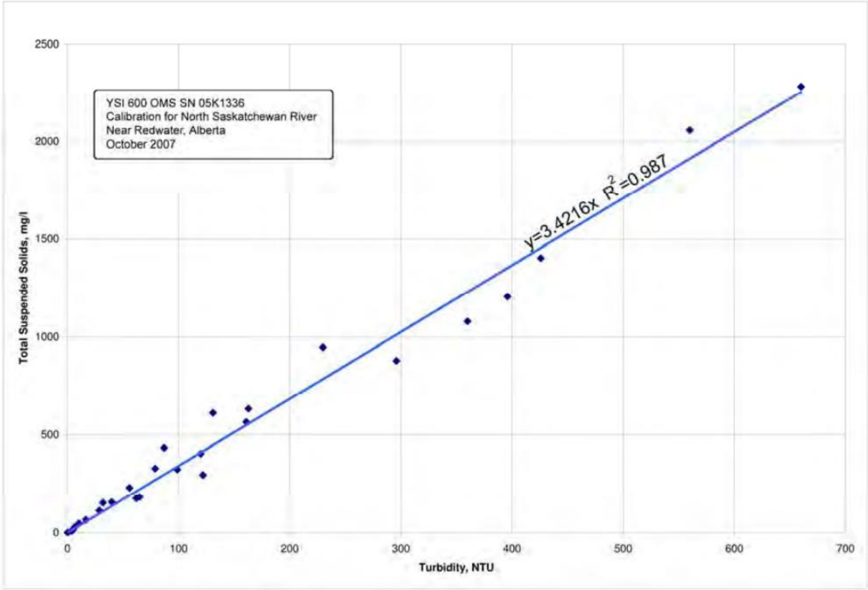


Figure 1 The TSS-NTU Relationship

Alberta CA example -
http://www.transportation.alberta.ca/content/doctype245/production/the%20conversion%20of%20nephelometric%20turbidity%20units.pdf

Sloto, R.A., and Olson, L.E., Estimated suspended-sediment loads and yields in the French and Brandywine Creek Basins, Chester County, Pennsylvania, water years 2008–09: U.S. Geological Survey Scientific Investigations Report 2011–5109, 31 p.

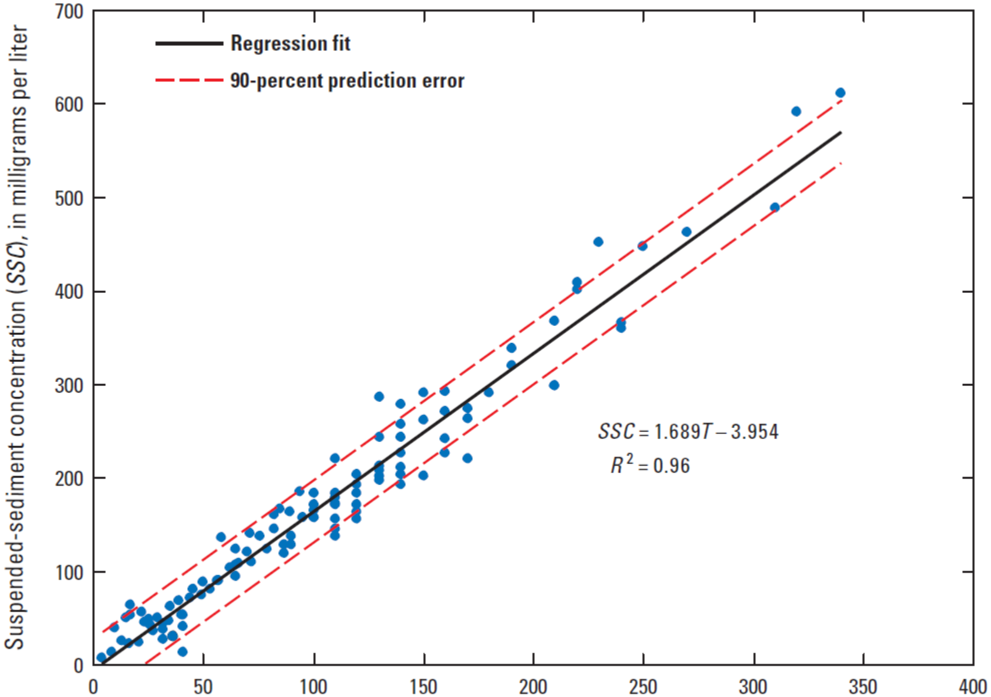


Figure 3. Regression relations of turbidity and suspended-sediment concentration for French Creek near Phoenixville, Pennsylvania.

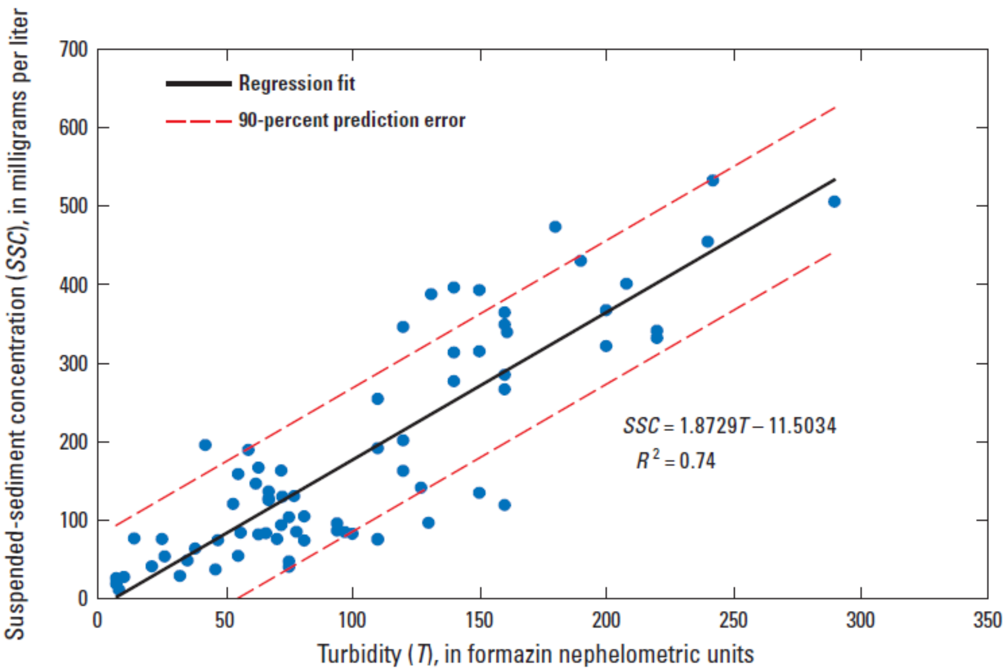


Figure 4. Regression relations of turbidity to suspended-sediment concentration for West Branch Brandywine Creek near Honey Brook, Pennsylvania.

Sloto, R.A., and Olson, L.E., Estimated suspended-sediment loads and yields in the French and Brandywine Creek Basins, Chester County, Pennsylvania, water years 2008–09: U.S. Geological Survey Scientific Investigations Report 2011–5109, 31 p.

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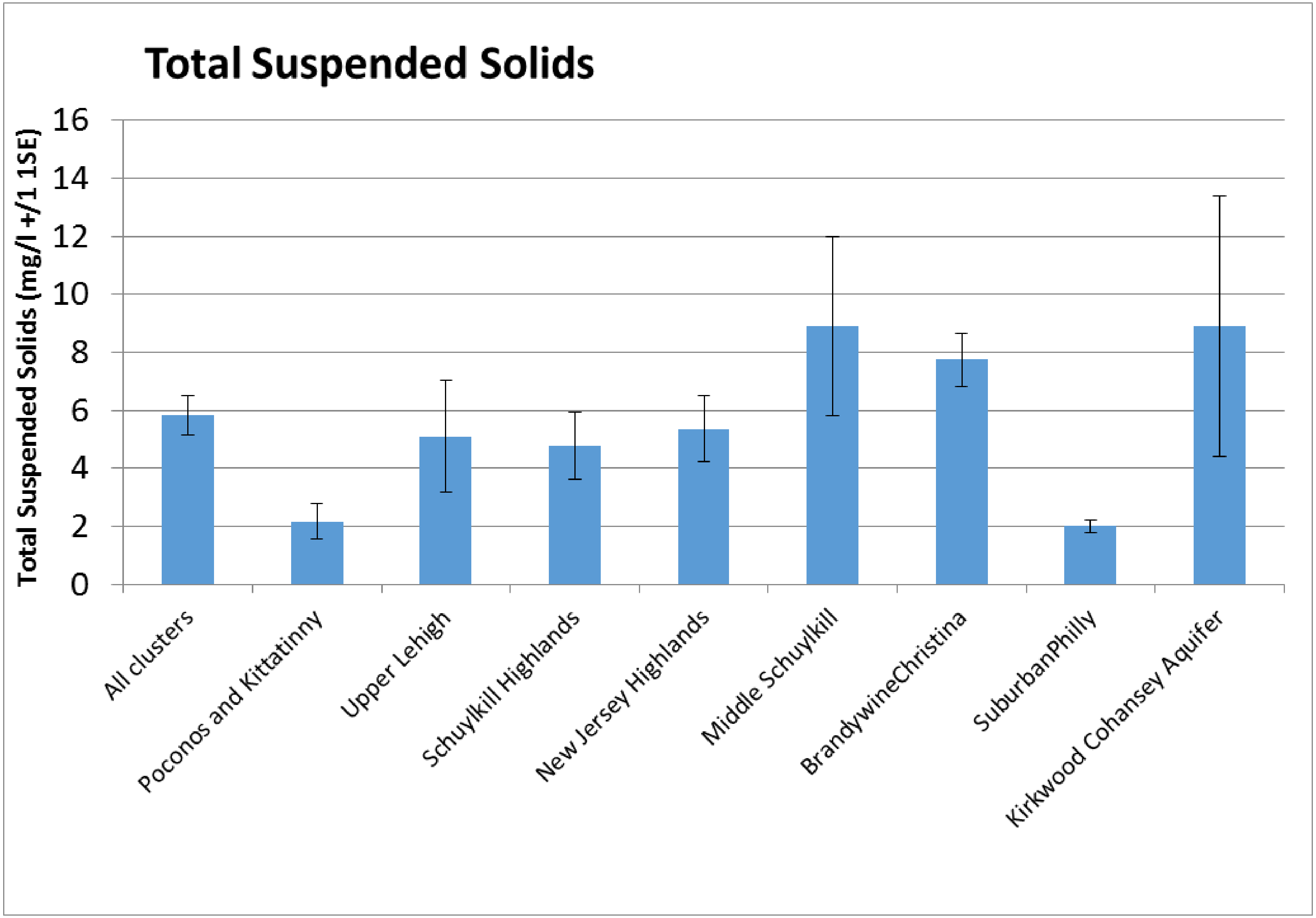

Data source: ANSD (M. Kurz) 2013-15 (ANSD + Cluster Partners)
Data are provisional (not final and subject to change)
n = 513; (75 PK; 53 UL; 62 SH; 54 NJH; 92 MS; 136 BC; 38 SP; 3 KCA)

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Table 2. Analytical methods, detection limits and errors.

Nutrient form		Method	Reference	Detection limit ($\mu g\ L^{-1}$)	CV^1 %
Total phosphorus	TP	Persulphate digestion	Valderrama, 1981	10	3.5
Total dissolved phosphorus	TDP	Persulphate digestion	Valderrama, 1981	5	3.2
Dissolved inorganic phosphorus	DIP	Ascorbic acid + molybdate blue	Parsons et al., 1984	21.8	
Total particulate phosphorus	TPP	TP – TDP	—	—	6.7
Dissolved organic phosphorus	DOP	TDP – DIP	—	—	5.0
Total nitrogen	TN	Persulphate digestion	Valderrama, 1981	10	4.4
Total dissolved nitrogen	TDN	Persulphate digestion	Valderrama, 1981	5	2.4
Nitrate + nitrite	NO_x	Cadmium reduction + sulphanilamide + NED	Parsons et al., 1984	21.9	
Ammonium	NH_4^+	Hypochlorite + phenol + nitroprusside	Parsons et al., 1984	5	5.4
Total particulate nitrogen	TPN	TN – TDN	—	—	6.8
Dissolved organic nitrogen	DON	$TDN - NO_x - NH_4^+$	—	—	9.7
Chlorophyll-a	Chl-a	0.45 μm filter, 90% acetone	APHA, 1995	1	3.1
				$g\ kg^{-1}$	
Sediment nitrogen	SN	Kjeldahl digestion	APHA, 1995	0.2	6.0
Sediment phosphorus	SP	Ash (550 °C), HCl extraction, ascorbic acid, molybdate blue	Eyre, 1993	0.1	4.7
Organic carbon	OC	Weighing dried and crushed sample, ash at 550 °C and reweighing	APHA, 1995	1.0	—

[1]Coefficient of variation (CV).

McKee et al. 2000, Biogeochemistry

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Cation Exchange Capacity (CEC) in Soils

- Soil CEC = ability of soil to hold and release various positively charged elements and compounds
- Clay particles have (-) charge, so attract and hold (+) charged ions
- Soil organic matter (SOM or OM) has both (+) and (-) charges (depending on exact composition of OM), so can potentially hold both cations and anions
- 2 types of cations of concern here: acidic or acid-forming cations, and basic, or alkaline-forming cations
  - H^+ and Al^{3+} are acid-forming. Neither are plant nutrients. A soil with high levels of H^+ or Al^{3+} is an acid soil, with a low pH
  - Ca^{2+}, Mg^{2+}, K^+ and Na^+ are all alkaline or basic cations or bases

Cation Exchange Capacity (CEC) in Soils

- Both types of cations may be sorbed onto clay particles or SOM
- Nutrients need to be held in soil for use by plants, or they will wash away during rain storms (e.g., PO_4)

- Cation Exchange Capacity is the measure of how many negatively-charged sites are available in the soil.
- Some soils have high CEC and some have low CEC. Generally:
  - sandy soil with low OM = very low CEC
  - clay soil with high OM (e.g., humus) = high CEC
  - OM (as humus) has high CEC; for clay soils, CEC depends on clay type

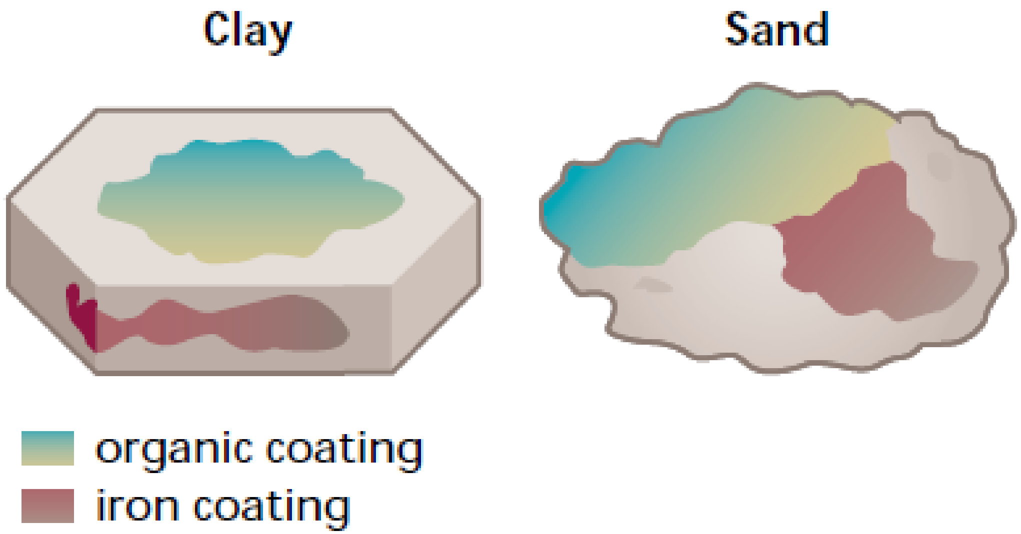

Figure 2.19: The organic coatings on suspended sediment from streams. *Water chemistry determines whether sediment will carry adsorbed materials or if stream sediments will be coated.*

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	Samples					
Constituent	1	2	3	4	5	6
SiO_2	0.0		1.2	0.3		0.1
Al	.01					
Fe	.00					.015
Ca	.0	.65	1.2	.8	1.41	.075
Mg	.2	.14	.7	1.2		.027
Na	.6	.56	.0	9.4	.42	.220
K	.6	.11	.0	.0		.072
NH_4	.0					
HCO_3	3		7	4		
SO_4	1.6	2.18	.7	7.6	2.14	1.1
Cl	.2	.57	.8	17	.22	
NO_2	.02		.00	.02		
NO_3	.1	.62	.2	.0		
Total dissolved solids	4.8		8.2	38		
pH	5.6		6.4	5.5		4.9

1. Snow, Spooner Summit. U.S. Highway 50, Nevada (east of Lake Tahoe) (Feth, Rogers, and Roberson, 1964).
2. Average composition of rain, August 1962 to July 1963, at 27 points in North Carolina and Virginia (Gambell and Fisher, 1966).
3. Rain, Menlo Park, Calif., 7:00 p.m. Jan. 9 to 8:00 a.m. Jan 10, 1958 (Whitehead and Feth, 1964).
4. Rain, Menlo Park, Calif., 8:00 a.m. to 2:00 p.m. Jan 10, 1958 (Whitehead and Feth, 1964).
5. Average for inland sampling stations in the United States for 1 year. Data from Junge and Werby (1958), as reported by Whitehead and Feth (1964).
6. Average composition of precipitation, Williamson Creek, Snohomish County, Wash., 1973-75. Also reported: As, 0.00045 mg/L; Cu 0.0025 mg/L; Pb, 0.0033 mg/L; Zn, 0.0036 mg/L (Deithier, D.P., 1977, Ph.D. thesis. University of Washington, Seattle).

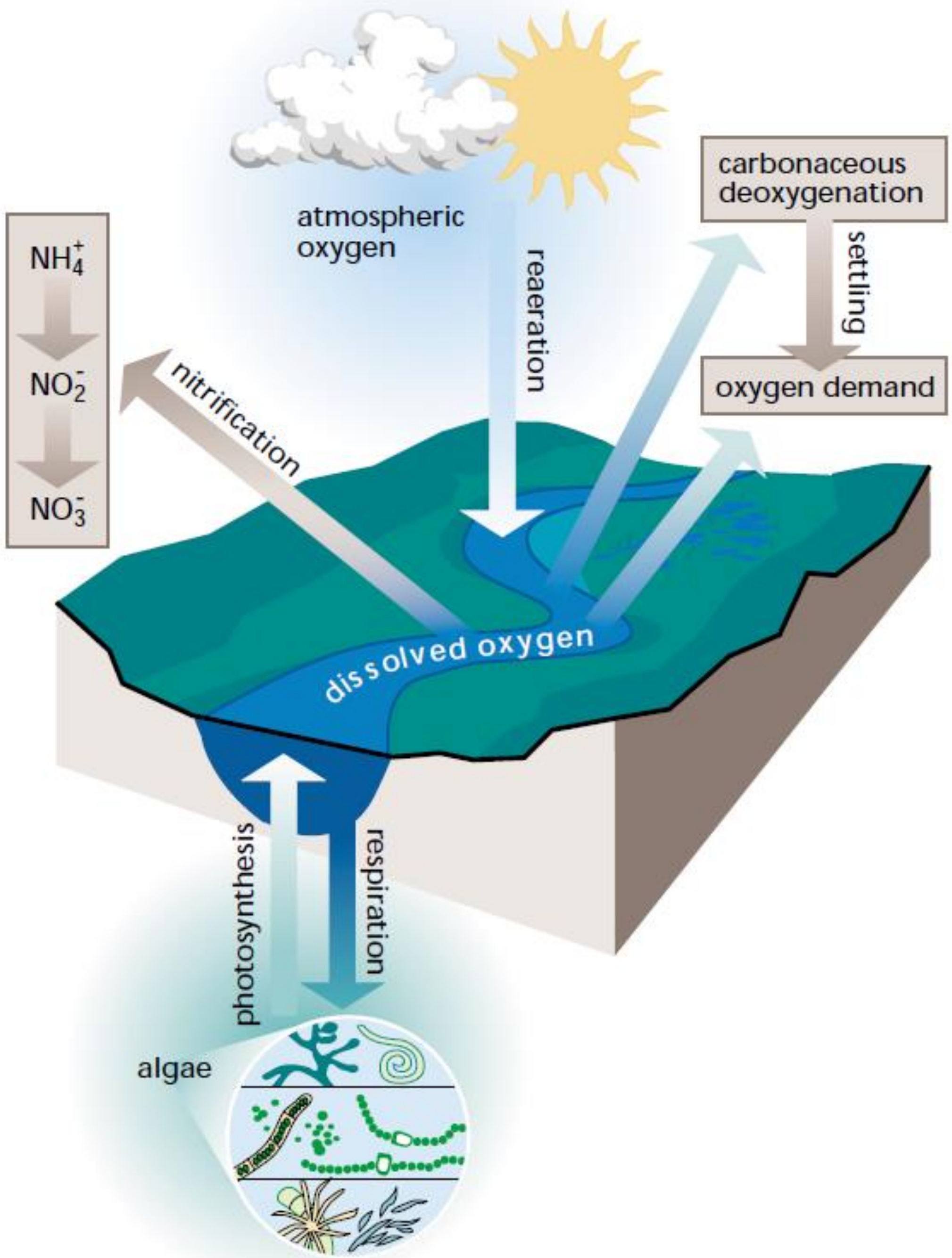

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Table 2.6: Sources and concentrations of pollutants from common point and nonpoint sources.

Source	Total Nitrogen (mg/L)	Total Phosphorus (mg/L)
Urban runoff[a]	3–10	0.2–1.7
Livestock operations[a]	6–800[b]	4–5
Atmosphere (wet deposition)[a]	0.9	0.015[c]
90% forest[d]	0.06–0.19	0.006–0.012
50% forest[d]	0.18–0.34	0.013–0.015
90% agriculture[d]	0.77–5.04	0.085–0.104
Untreated wastewater[a]	35	10
Treated wastewater[a,e]	30	10

[a] Novotny and Olem (1994).
[b] As organic nitrogen.
[c] Sorbed to airborne particulate.
[d] Omernik (1987).
[e] With secondary treatment.

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Toxic Organic Chemicals

- Synthetic compounds that contain carbon such as PCBs, most pesticides and herbicides
- Originate from both point and non-point sources
- Movement from land to water primarily determined by chemical characteristics
  - Sorption to soil particles (eroding sediments)
  - Solubility of compound
    - Aromaticity – delocalized bonding structure of ringed compound like benzene
  - Volatilization
  - Degradation
    - Phtolysis – degradation due to energy of light
    - Hydrolysis – splitting of organic molecule by water

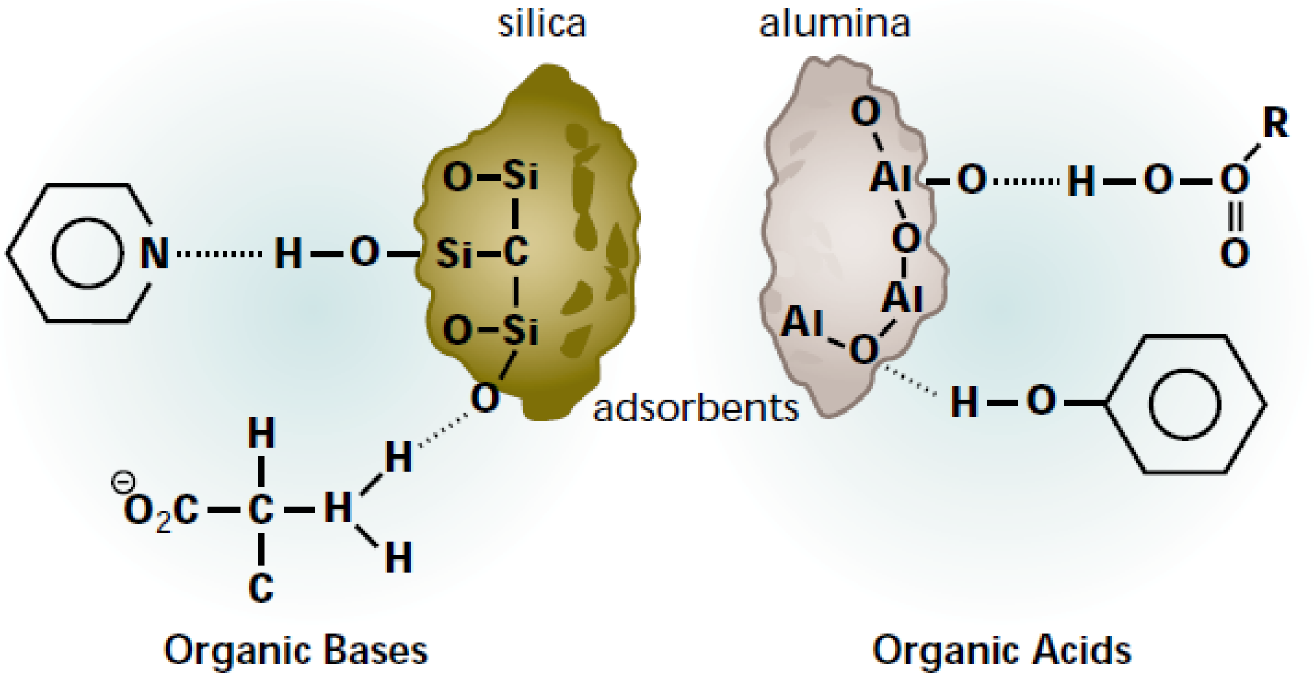

Figure 2.27: Two important types of hydrogen bonding involving natural organic matter and mineral surfaces. *Some contaminants are carried by sediment particles that are sorbed onto their surfaces by chemical bonding.*

Figure 2.22: Relative aqueous solubility of different functional groups. *The solubility of a contaminant in water largely determines the extent to which it will impact water quality.*

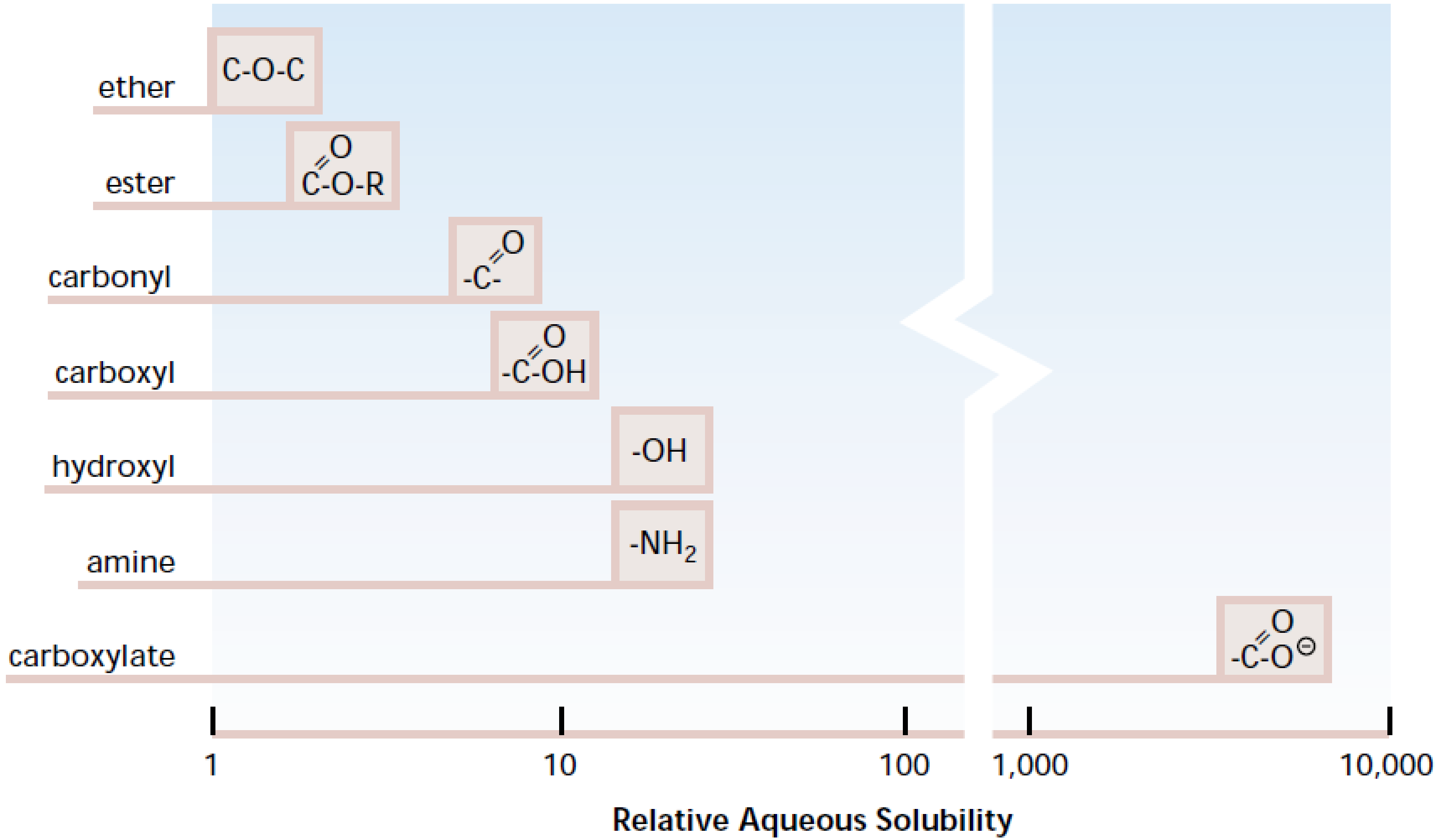

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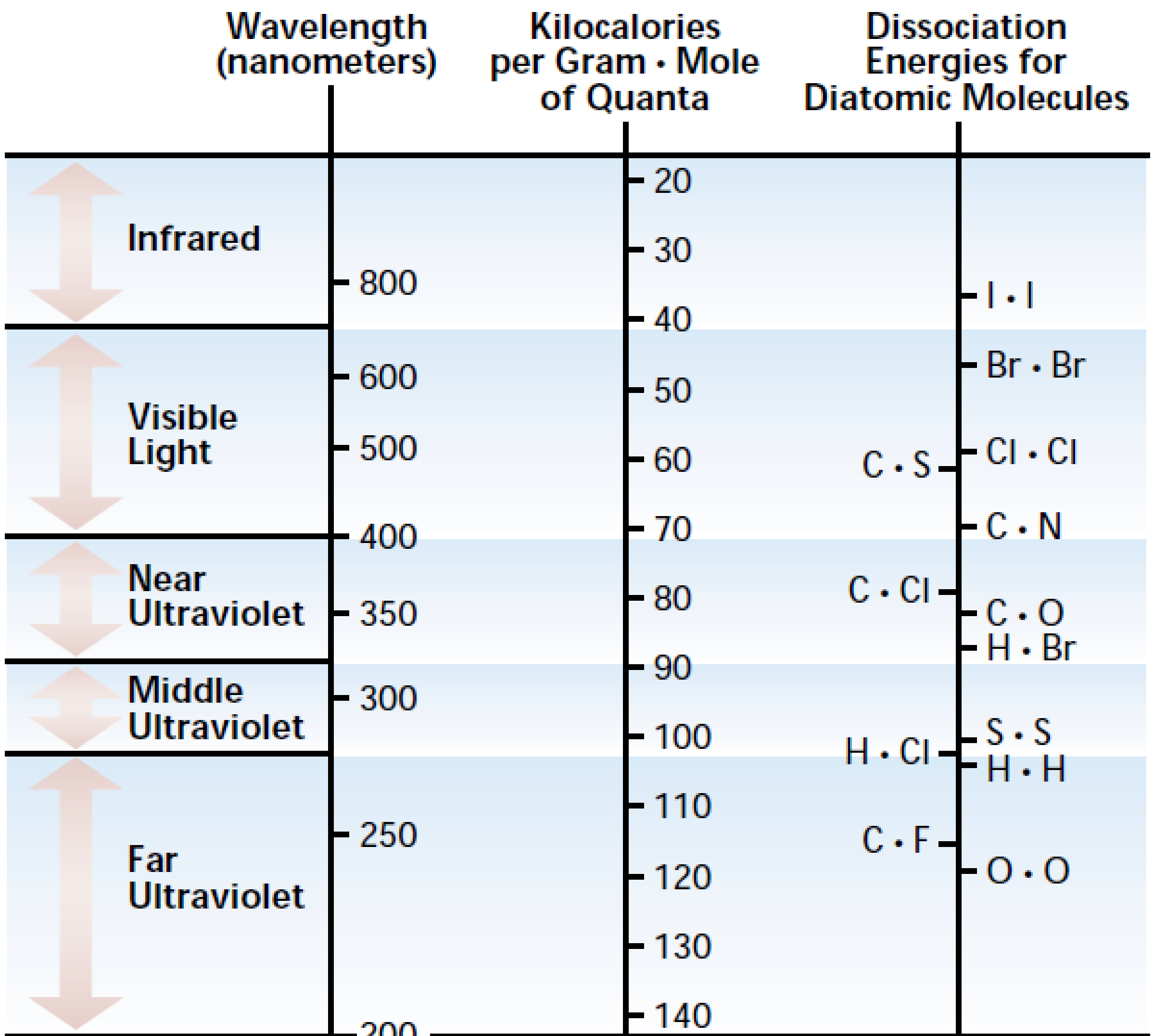
Figure 2.28: Energy of electromagnetic radiation compared with some selected bond energies. *Light breaks chemical bonds of some compounds through photolysis.*



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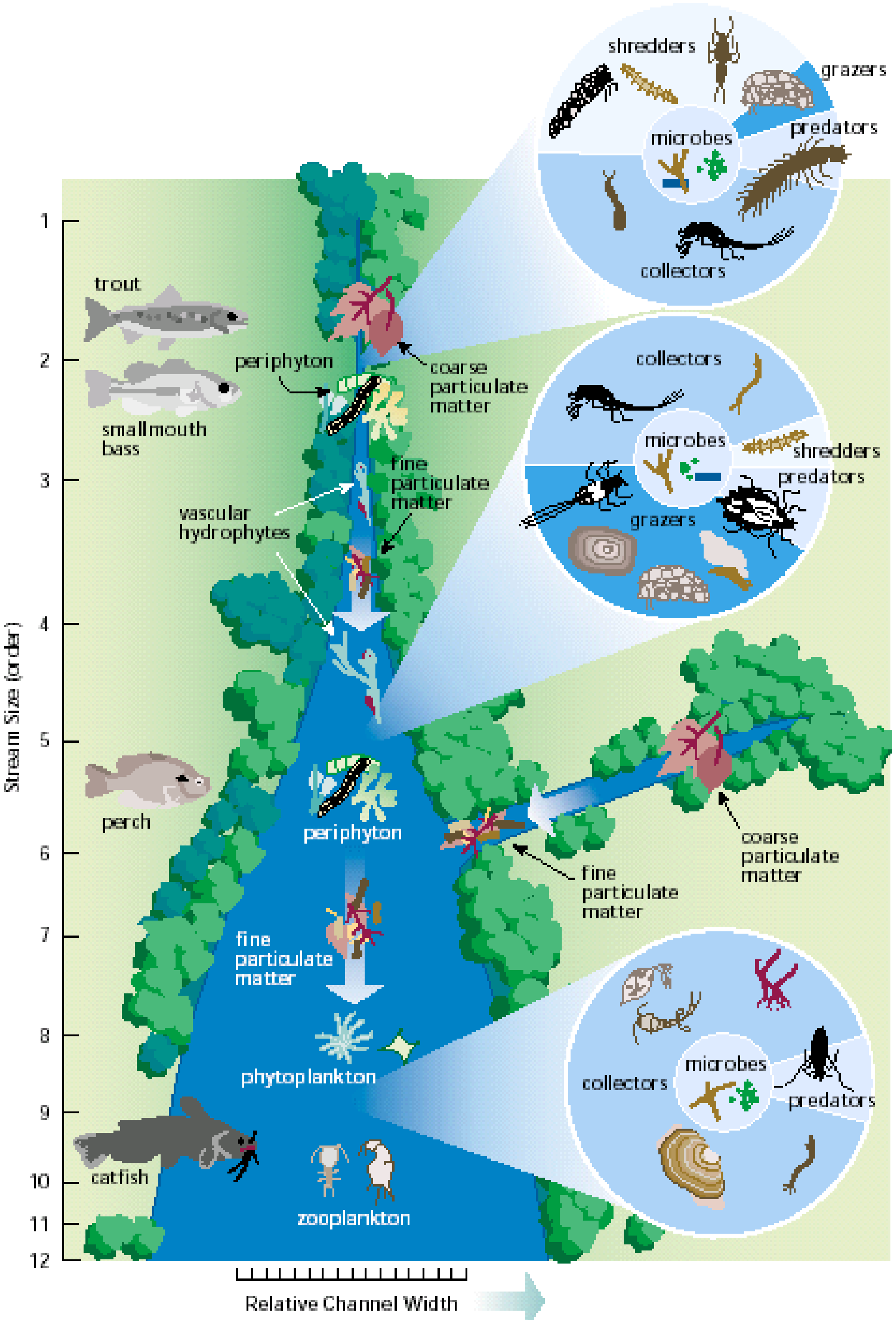

The River Continuum Concept

Vannote, R.L.,
G.W. Minshall,
K.W. Cummins,
J.R. Sedell, and
C.E. Cushing.
(1980)

Canadian Journal of Fisheries and Aquatic Sciences 32:130-137

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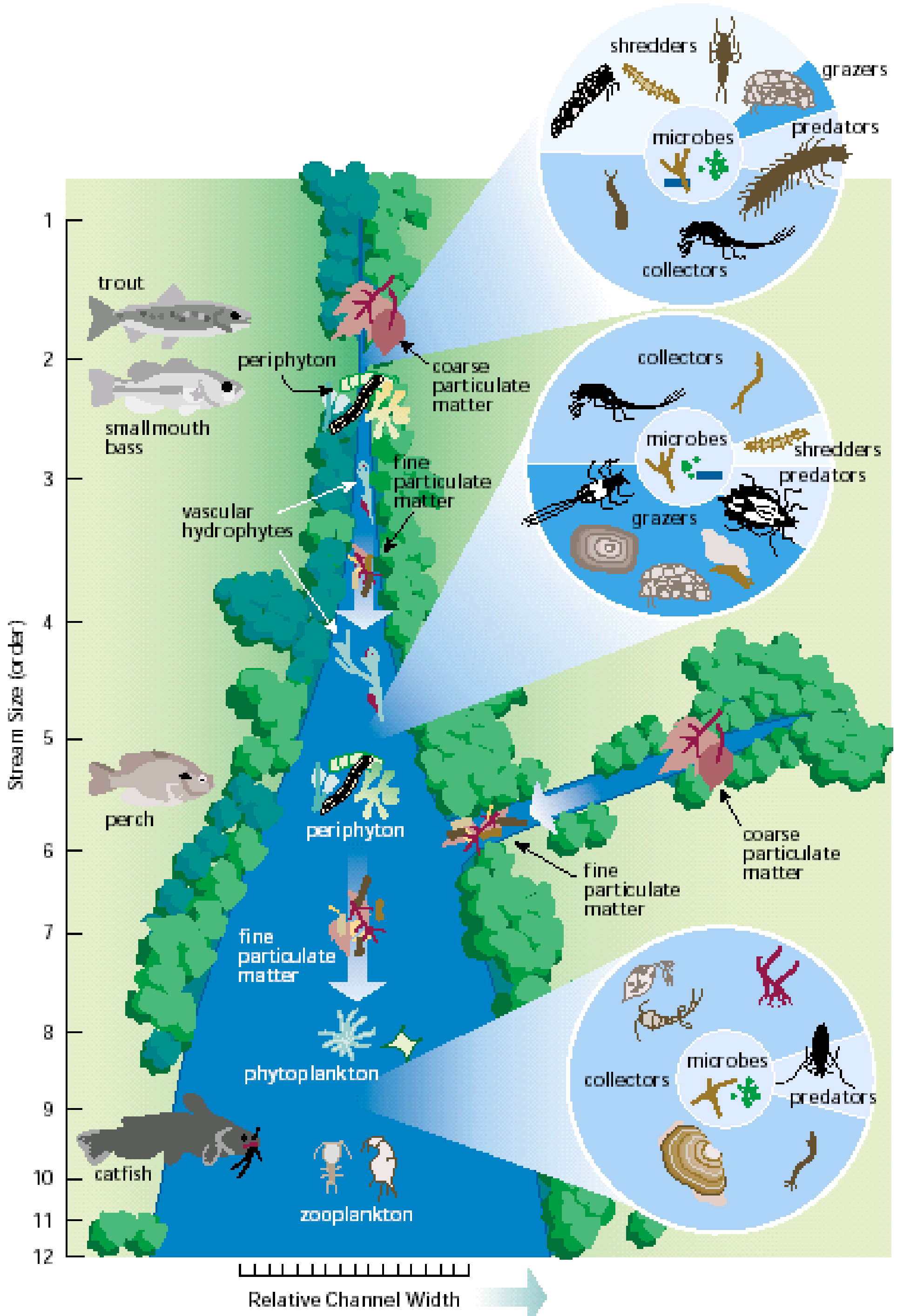

The River Continuum Concept describes how biological processes vary from headwaters to large rivers

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