

May 2023

Virtual WQS Academy

Nutrient Criteria

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U.S. Environmental Protection Agency
Office of Water, Office of Science and Technology

Disclaimer

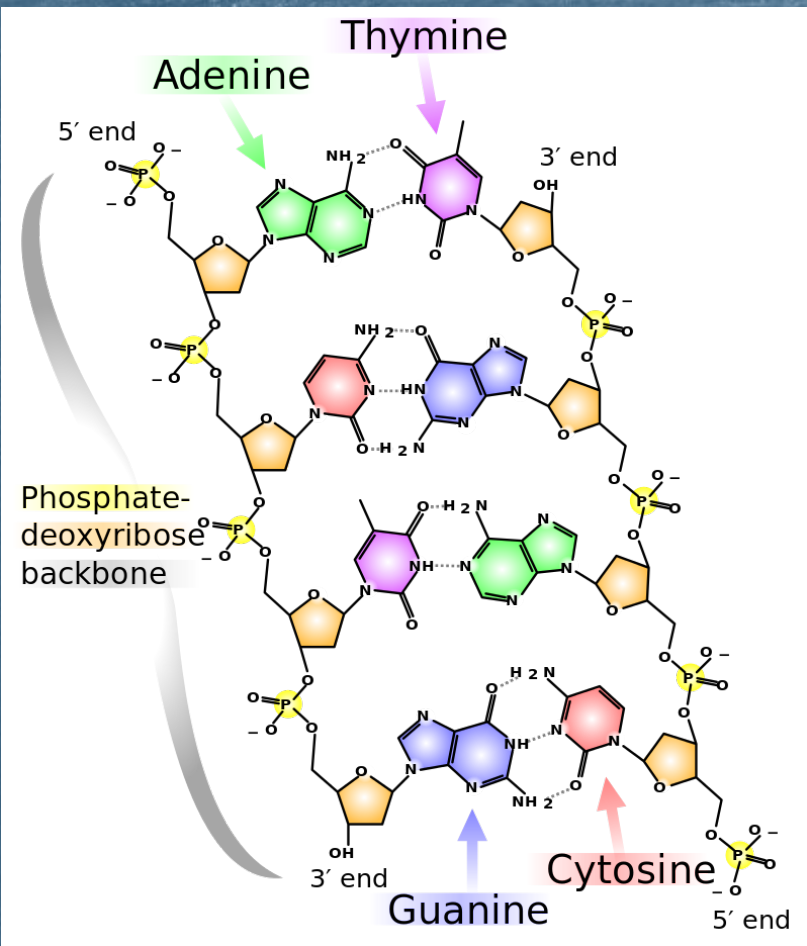
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 - ▶ Determine the obligation of the regulated community.
 - ▶ Change or substitute for any statutory provision or regulatory requirement.
 - ▶ Change or substitute for any Agency policy or guidance.
 - ▶ Control in any case of conflict between this discussion and statute, regulation, policy, or guidance.

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Outline

- ❖ Pollutants: Nitrogen and phosphorus
- ❖ Effects: Widespread degradation of water quality in the U.S.
- ❖ Governance: Authorization, regulations, and technical support
- ❖ Management: Developing numeric nutrient criteria
- ❖ Making a difference: EPA-State partnerships (N-STEPS Program)

Pollutants: Nitrogen and Phosphorus



Twenty-One Amino Acids

⊕ Positive ⊖ Negative
• Side chain charge at physiological pH 1

A. Amino Acids with Electrically Charged Side Chains

Positive

Arginine (Arg) R <p>pKa 2.03 pKa 9.00 pKa 12.10</p>	Histidine (His) H <p>pKa 1.70 pKa 6.05 pKa 6.04</p>	Lysine (Lys) K <p>pKa 2.15 pKa 9.16 pKa 10.57</p>
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Negative

Aspartic Acid (Asp) D <p>pKa 1.95 pKa 9.05 pKa 3.71</p>	Glutamic Acid (Glu) E <p>pKa 2.16 pKa 9.55 pKa 4.15</p>
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B. Amino Acids with Polar Uncharged Side Chains

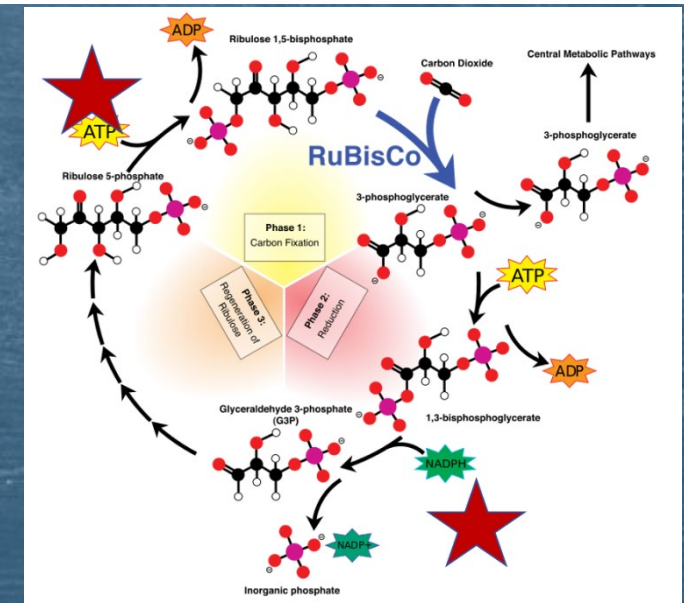
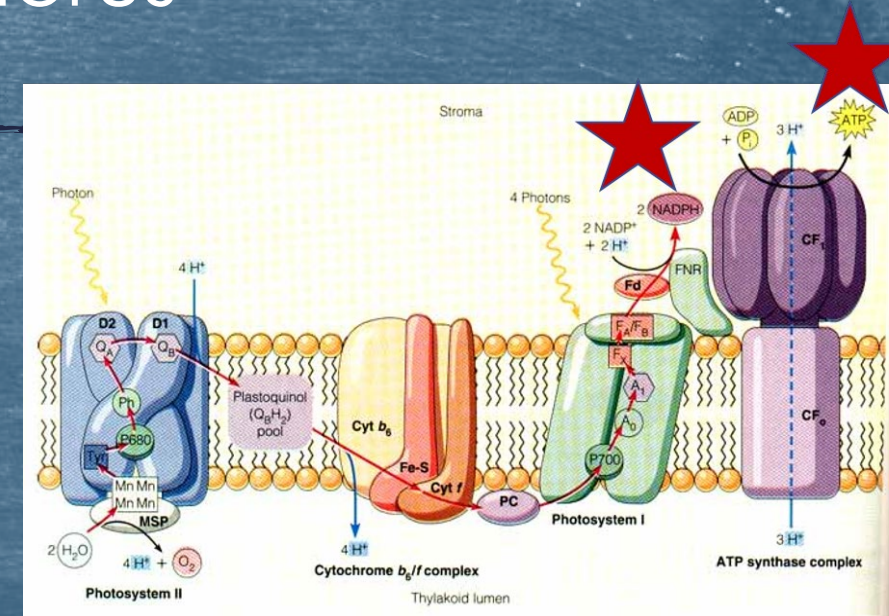
Serine (Ser) S <p>pKa 2.15 pKa 9.05</p>	Threonine (Thr) T <p>pKa 2.20 pKa 9.05</p>	Asparagine (Asn) N <p>pKa 2.16 pKa 8.70</p>	Glutamine (Gln) Q <p>pKa 2.18 pKa 9.00</p>
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C. Special Cases

Cysteine (Cys) C <p>pKa 1.91 pKa 10.28 pKa 8.14</p>	Selenocysteine (Sec) U <p>pKa 1.55 pKa 10 pKa 5.98</p>	Glycine (Gly) G <p>pKa 2.34 pKa 9.55</p>	Proline (Pro) P <p>pKa 1.95</p>
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D. Amino Acids with Hydrophobic Side Chain

Alanine (Ala) A <p>pKa 2.35 pKa 9.71</p>	Valine (Val) V <p>pKa 2.27 pKa 9.52</p>	Isoleucine (Ile) I <p>pKa 2.36 pKa 9.60</p>	Leucine (Leu) L <p>pKa 2.32 pKa 9.59</p>	Methionine (Met) M <p>pKa 2.16 pKa 9.16</p>	Phenylalanine (Phe) F <p>pKa 2.18 pKa 9.29</p>	Tyrosine (Tyr) Y <p>pKa 2.24 pKa 9.04 pKa 10.10</p>	Tryptophan (Trp) W <p>pKa 2.38 pKa 9.34</p>
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EUTROPHICATION

Competition Pathway



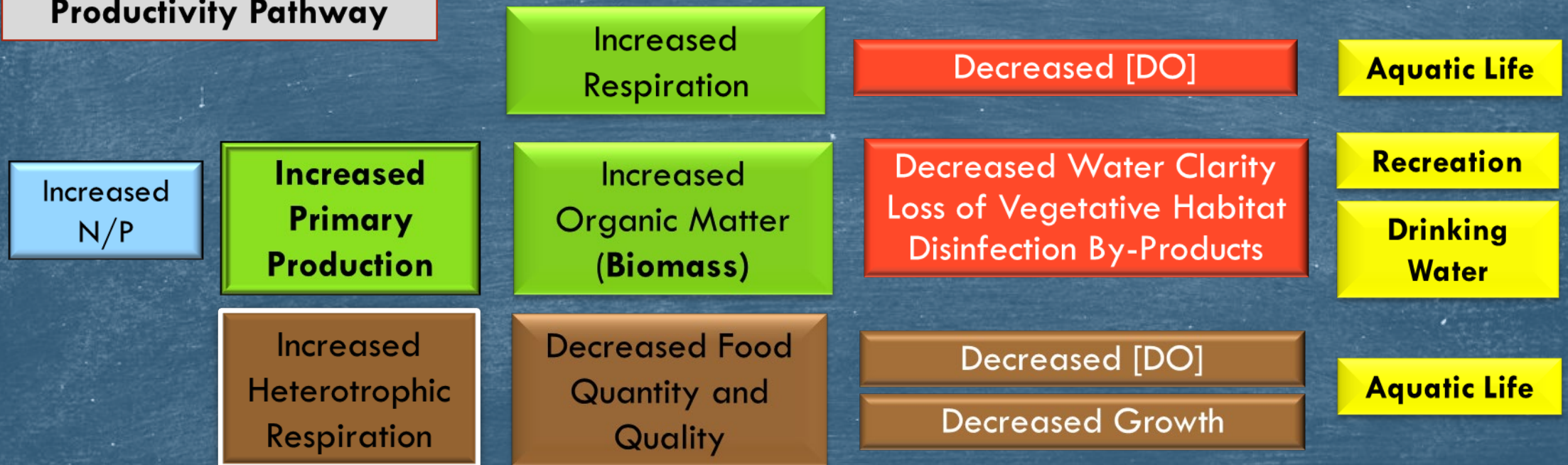
Productivity Pathway



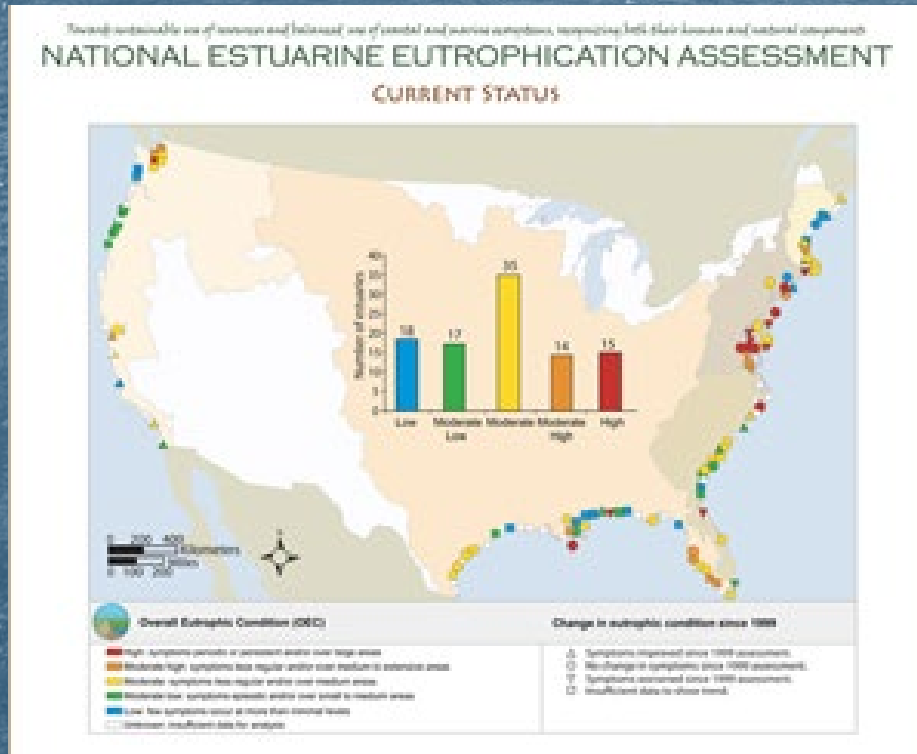
Competition Pathway



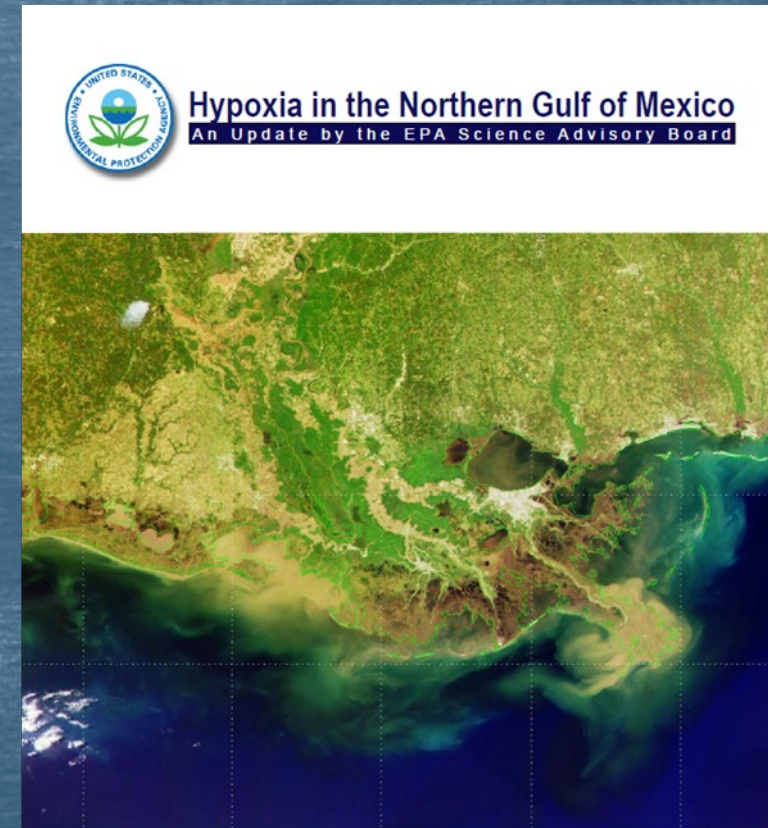
Productivity Pathway



Effects: Widespread degradation of water quality in the U.S. (1)

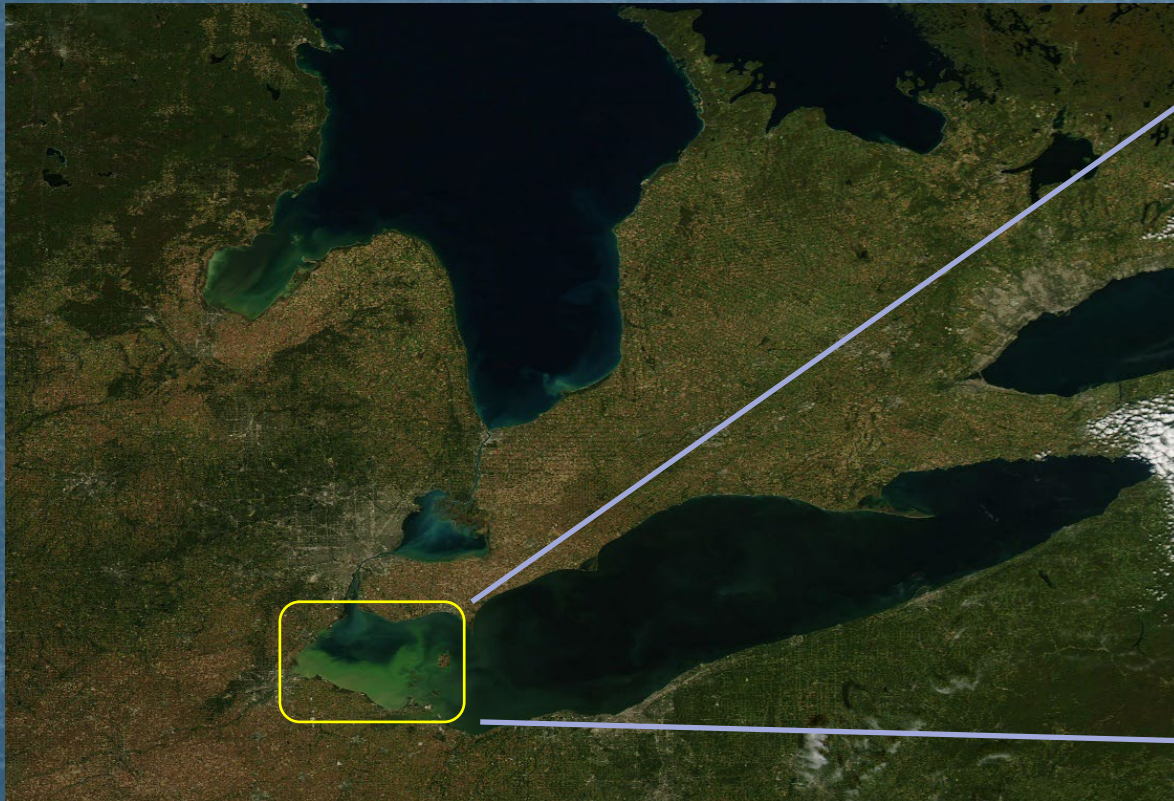


Suzanne Bricker et al., 2007



U.S. EPA, 2007, EPA-SAB-08-003

Effects: Widespread degradation of water quality in the U.S. (2)



Effects: Widespread degradation of water quality in the U.S. (3)

Diagnosis

Impaired waters¹ (303(d) list)

Wetlands: 672,924 acres

Rivers and streams: 588,173 miles

Lakes, reservoirs, ponds: 13,208,917 acres

Bays and estuaries: 44,625 miles²

Diagnosis

Nutrient-Impaired waters¹

Wetlands: 10%, 67,849 acres (6th)

Rivers and streams: 20%, 118,831 miles (3rd)

Lakes, reservoirs, ponds: 30%, 3,943,395 acres (2nd)

Bays and estuaries: 40%, 18,279 miles² (2nd)

Remediation

Total maximum daily loads¹ (TMDLs) = 74,001

Nutrient TMDLs¹ = 6,685 (4th)

¹U.S. EPA ATTAINS accessed on November 8, 2018

Governance: Authorization, regulations, and technical support (1)

Federal Water Pollution Control Act (Clean Water Act)

33 U.S.C. Section 1251 (CWA Section 101)

- ❖ “integrity”, “protection and propagation”, “recreation”

33 U.S.C. Section 1313 (CWA Section 303)

- ❖ State and tribal authority to adopt water quality standards (WQS) Federal authority to review, approve/disapprove state and tribal WQS
- ❖ Federal authority to promulgate WQS for a state or tribe

33 U.S.C. Section 1314 (CWA Section 304)

- ❖ Federal authority to publish technical support

Federal Regulations

Title 40 Code of Federal Regulations, Part 131

- ❖ Part 131.4(a) – State authority to develop WQS
- ❖ Part 131.5(a) – EPA authority to review WQS
 - ❖ (2) “protect the designated uses”
 - ❖ (4) “appropriate technical and scientific data and analyses”
- ❖ Part 131.6
 - ❖ (b) “methods and analyses”
 - ❖ (c) “protect the designated uses”
 - ❖ (f) “scientific basis”
- ❖ Part 131.11(a)(1)
 - ❖ “criteria must protect designated uses”,
 - ❖ “based on a sound scientific rationale”,
 - ❖ “must contain sufficient parameters and constituents”
- ❖ Part 131.10(b) – Downstream protection
- ❖ Part 131.20(a) – Triennial review by states

Governance: Authorization, regulations, and technical support (2)

State Regulations: Narrative Criteria

*“Plant nutrients from other than natural causes shall not be present in concentrations which will produce **undesirable aquatic life** or result in a **dominance of nuisance species** in surface waters of the state.”*

–State of New Mexico Standards for Interstate and Intrastate Surface Waters (Subsection E of 20.6.4.13 NMAC)

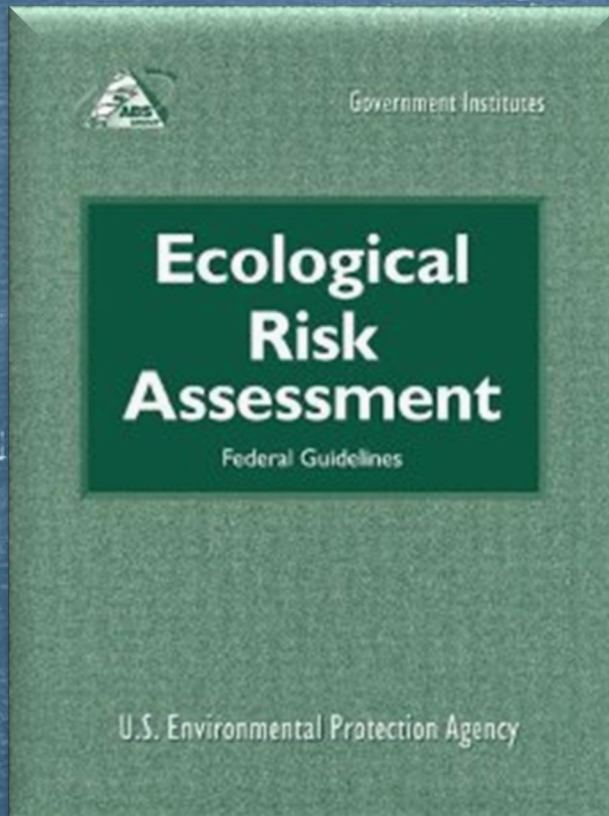
EPA Strategy and Technical Support

National Strategy for the Development of Regional Nutrient Criteria (1998)

Technical support documents (pursuant to 33 USC 1314, CWA Section 304)

- ❖ Nutrient criteria = nitrogen, phosphorus, chlorophyll-a, and water clarity
- ❖ Waterbody-specific technical support documents (2000, 2001, 2006)
- ❖ Recommended criteria for most lakes/reservoirs, rivers/streams (2000-1)
- ❖ Stressor-response approaches (2010)
- ❖ Revised recommendations for lakes and reservoirs (2021)

Management: Developing numeric nutrient criteria (1)



Guidelines for Ecological Risk Assessment (1998)

Term	Definition
Management Goal ★	Narrative criteria or statement reflective of protecting a designated use
Assessment Endpoint ★	Ecological entity and its attributes to be protected to support designated use
Measure ★	Measurable attributes of an assessment endpoint
Water Quality Target ★	Numeric value that indicates attainment of the management goal

Management: Developing numeric nutrient criteria (2)

- ❖ Range of waterbody types
- ❖ Conceptual models
- ❖ Data
 - ❖ Surveys vs. experiments (spatial and temporal scales)
 - ❖ Discrete vs. continuous (data quantity)
- ❖ Analysis
 - ❖ Classification: Parsimonious techniques to reduce variability
 - ❖ Stressor-response models (empirical)
 - ❖ Reference condition models (empirical)
 - ❖ Mechanistic numerical models (deterministic)
 - ❖ Nutrient criteria duration and frequency

Competition Pathway

Increased
N/P

**Primary
Producer
Species Shifts**

**Nuisance Algae
Harmful Algae
(Biomass)**

Poor Food Quality
Toxins
Degraded Aesthetics
Taste/Odor Alterations
Disinfection By-Products

Aquatic Life

Recreation

**Drinking
Water**

Term	Definition
Management Goal ★	Narrative criteria or statement reflective of protecting a designated use
Assessment Endpoint ★	Ecological entity and its attributes to be protected to support designated use
Measure ★	Measurable attributes of an assessment endpoint
Water Quality Target ★	Numeric value that indicates attainment of the management goal

Competition Pathway



	Term	Definition
Recreation	Management Goal	Narrative criteria or statement reflective of protecting a designated use
Toxins	Assessment Endpoint	Ecological entity and its attributes to be protected to support designated use
Harmful Algae	Measure	Measurable attributes of an assessment endpoint
(Biomass) Chlorophyll-a	Water Quality Target	Numeric value that indicates attainment of the management goal
[Chlorophyll-a]		
[Nitrogen]		
[Phosphorus]		

Recreation

Toxins

Harmful
Algae

(Biomass)
Chlorophyll-a

[Chlorophyll-a]

Management Goal



Assessment Endpoint



Measure



Water Quality Target



Recreation

Toxins

Harmful
Algae

(Biomass)
Chlorophyll-a

[Chlorophyll-a]

Management Goal



Assessment Endpoint



Measure

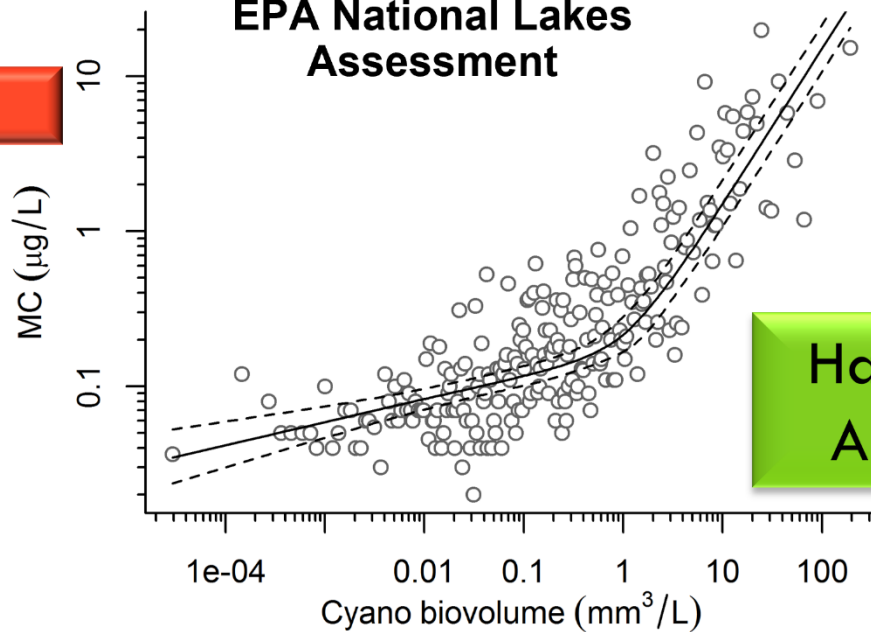


Water Quality Target



Toxins

EPA National Lakes Assessment



Harmful
Algae

Recreation

Toxins

Harmful
Algae

(Biomass)
Chlorophyll-a

[Chlorophyll-a]

Harmful
Algae

(Biomass)
Chlorophyll-
a

Management Goal



Assessment Endpoint



Measure

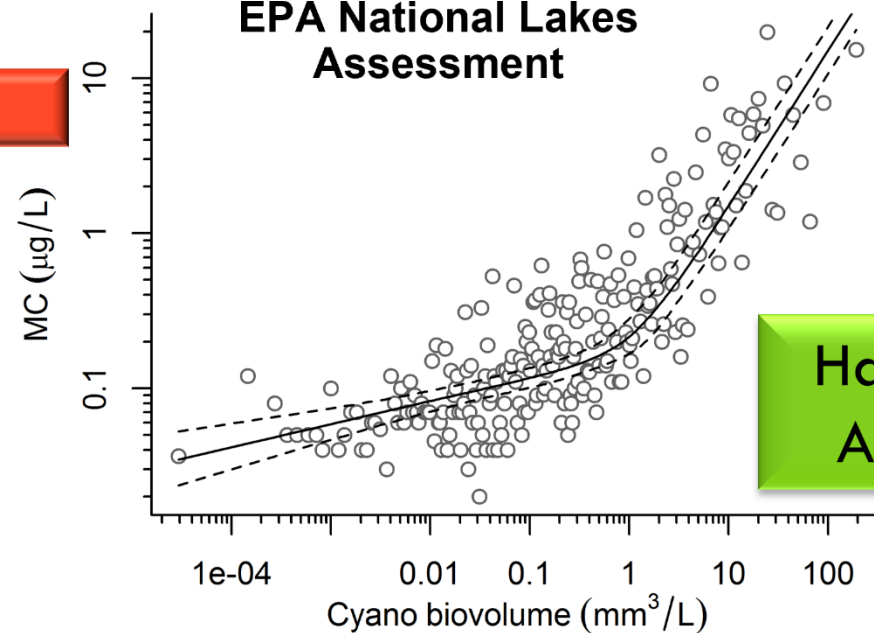


Water Quality Target



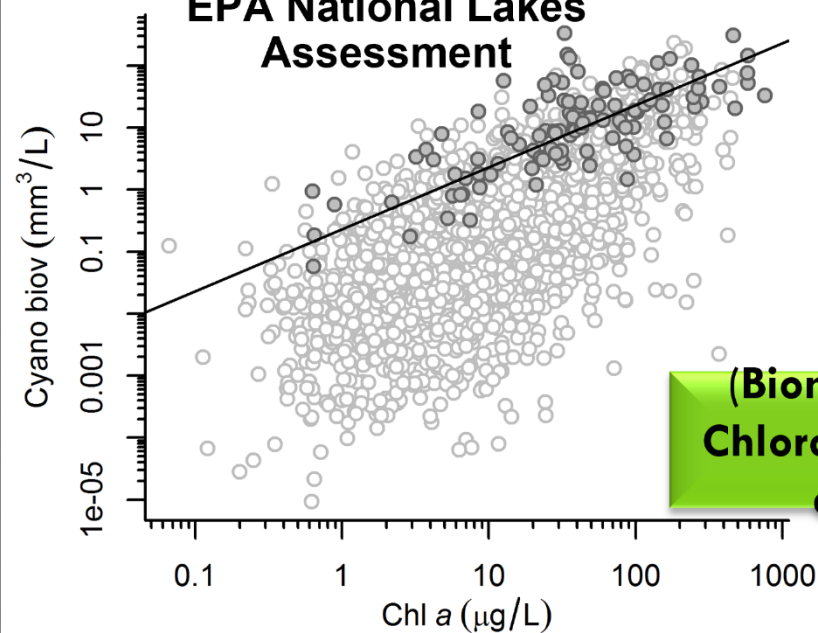
Toxins

EPA National Lakes Assessment



Harmful
Algae

EPA National Lakes Assessment



Recreation

Toxins

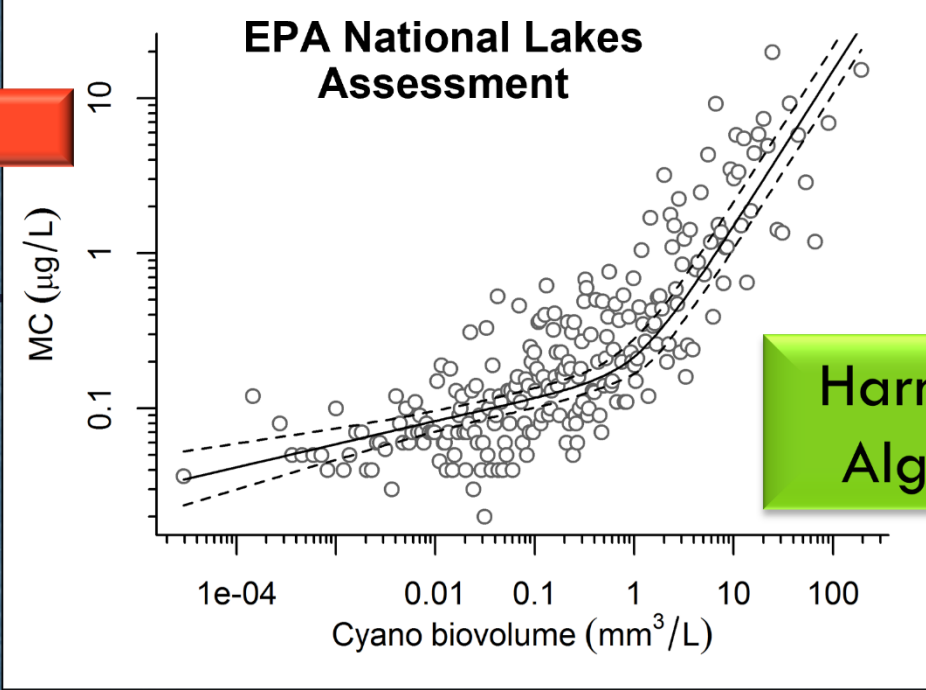
Harmful
Algae

(Biomass)
Chlorophyll-a

Management Goal	★
Assessment Endpoint	★
Measure	★
Water Quality Target	★

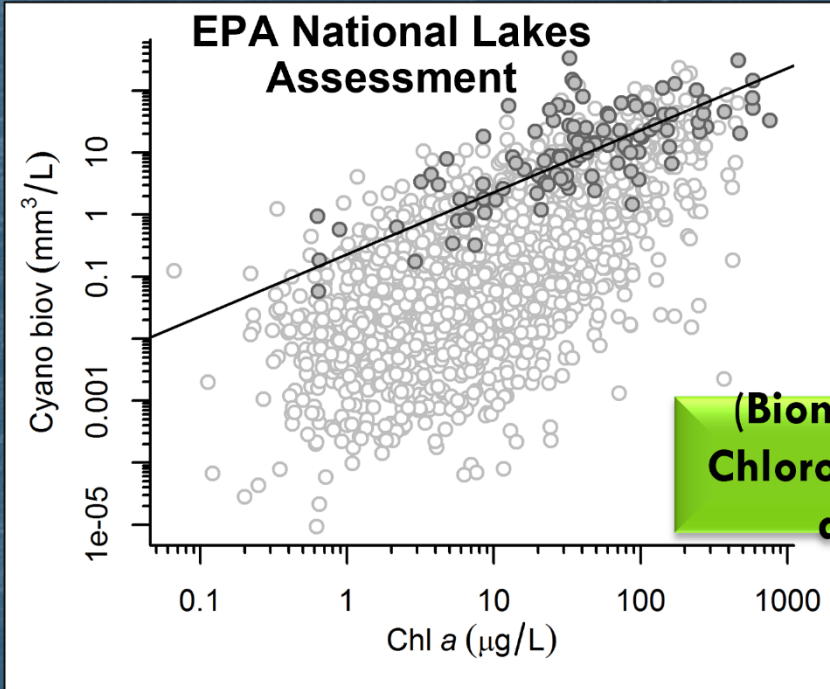
[Chlorophyll-a]

Toxins



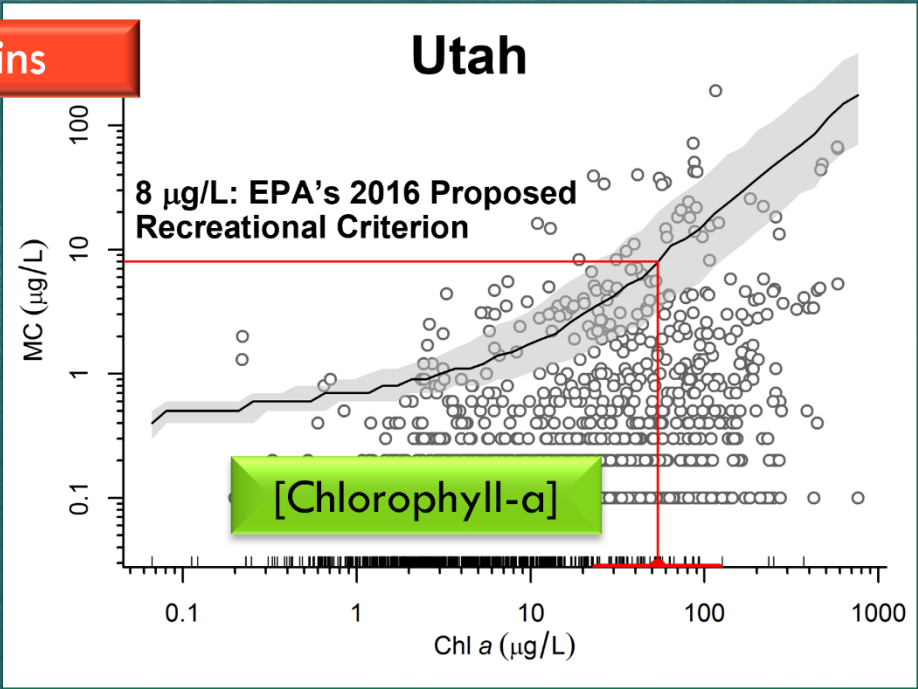
Harmful
Algae

Harmful
Algae



(Biomass)
Chlorophyll-
a

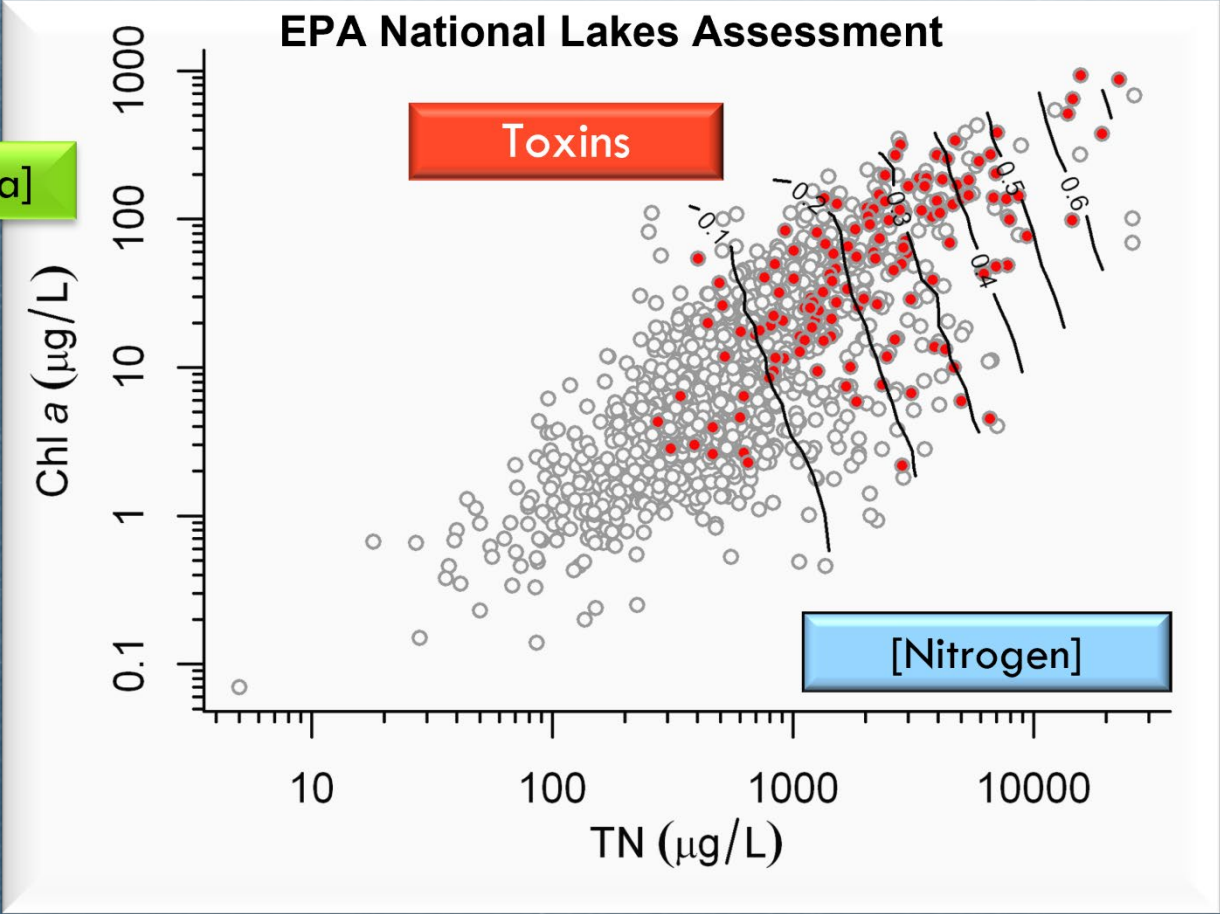
Toxins



[Chlorophyll-a]

Recreation	Management Goal
Toxins	★
Harmful Algae	Assessment Endpoint
	★
(Biomass) Chlorophyll-a	Measure
	★
[Chlorophyll-a]	Water Quality Target
	★
[Nitrogen]	

[Chlorophyll-a]



L. Yuan *et al.* 2014, *Freshwater Biology*

Productivity Pathway

Increased
N/P

Increased
Primary
Production

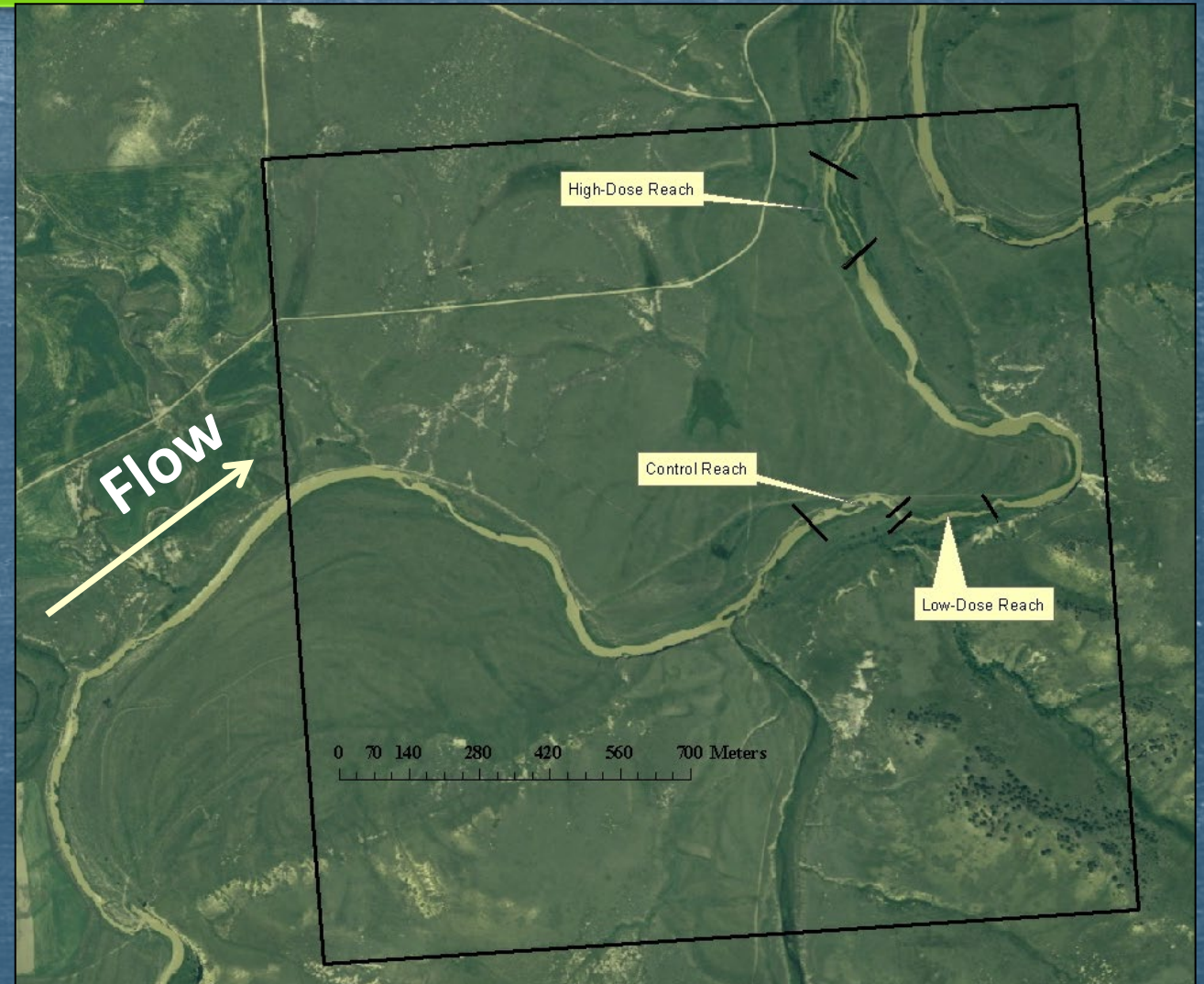
Increased
Respiration

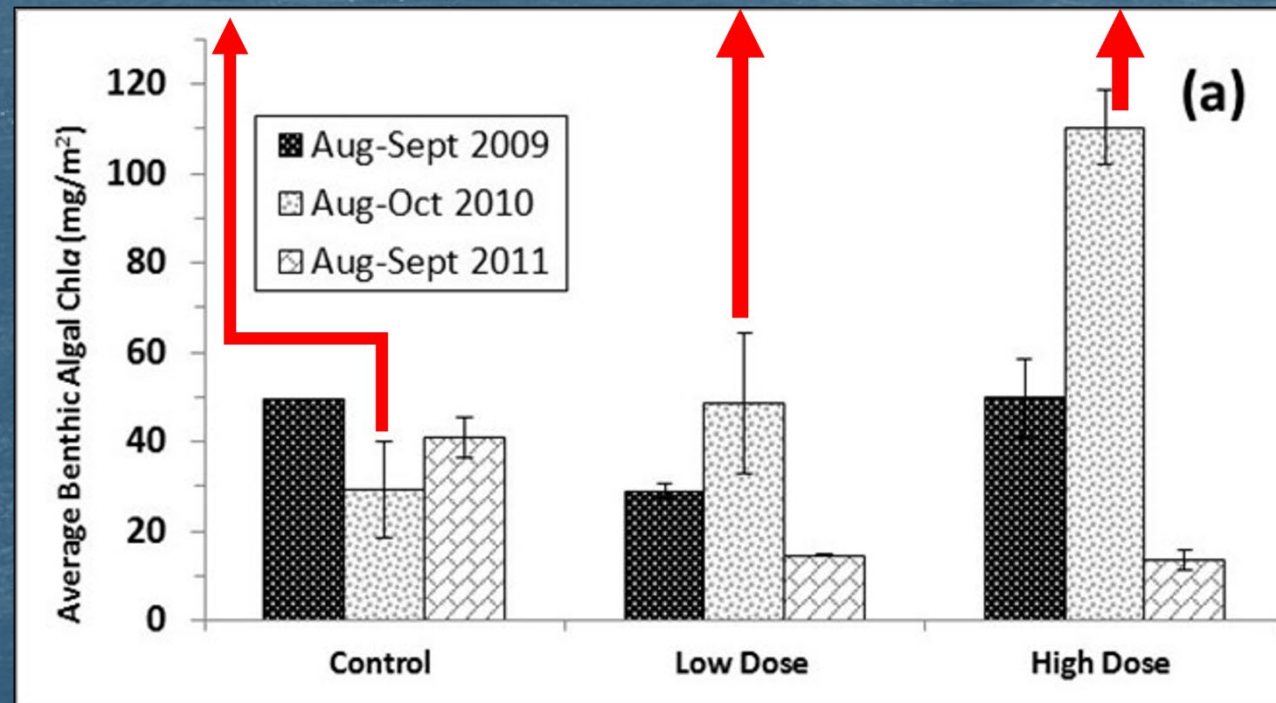
Decreased [DO]

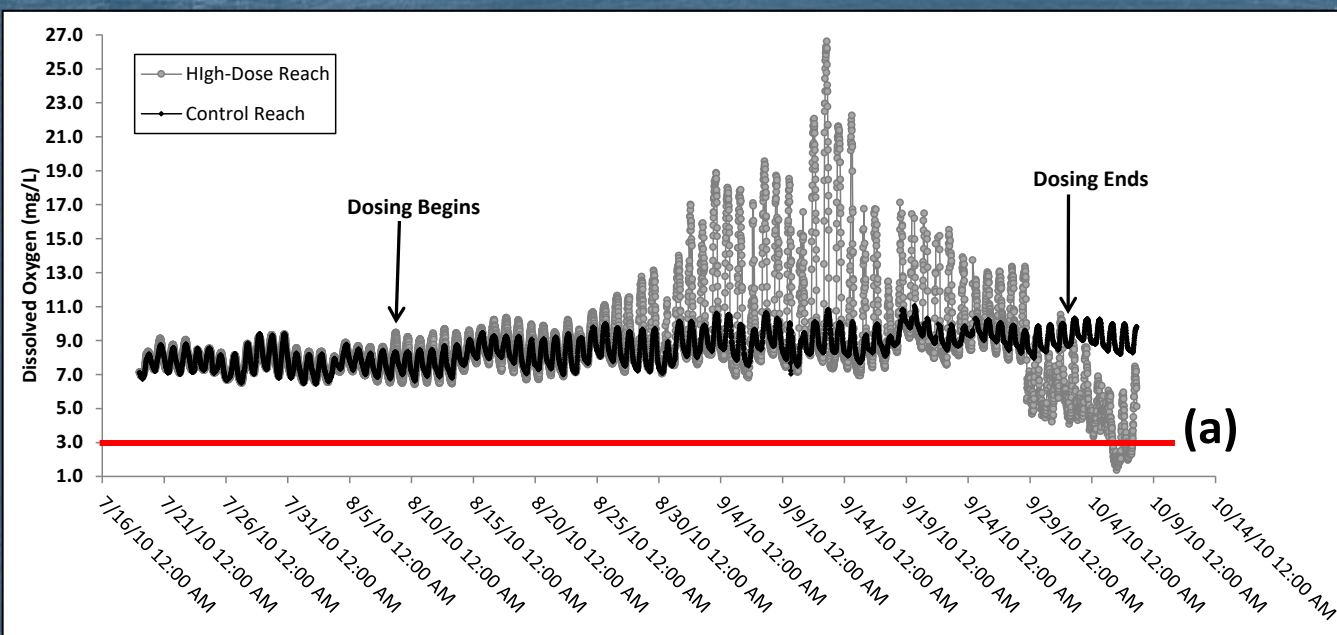
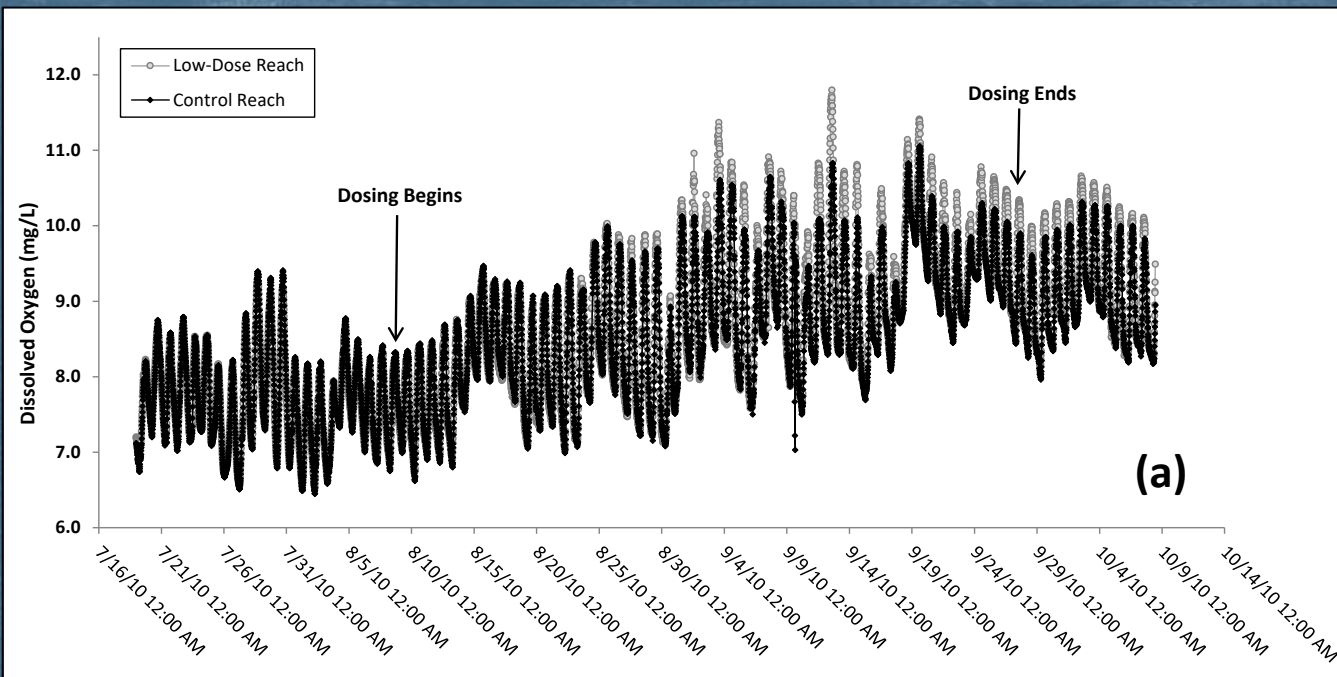
Aquatic Life



M. Suplee, Montana DEQ







Reference condition model and data quantity

Selection criteria (examples):

Forested land cover

No human hydrologic alterations (e.g., dams, canals)

No NPDES discharges

No documented CWA 303(d) listings

Biological evidence of aquatic life support

Reference condition model and data quantity

Selection criteria (examples):

- Forested land cover
- No human hydrologic alterations (e.g., dams, canals)
- No NPDES discharges
- No documented CWA 303(d) listings
- Biological evidence of aquatic life support

U.S. EPA, 2000.
Rivers and Streams.

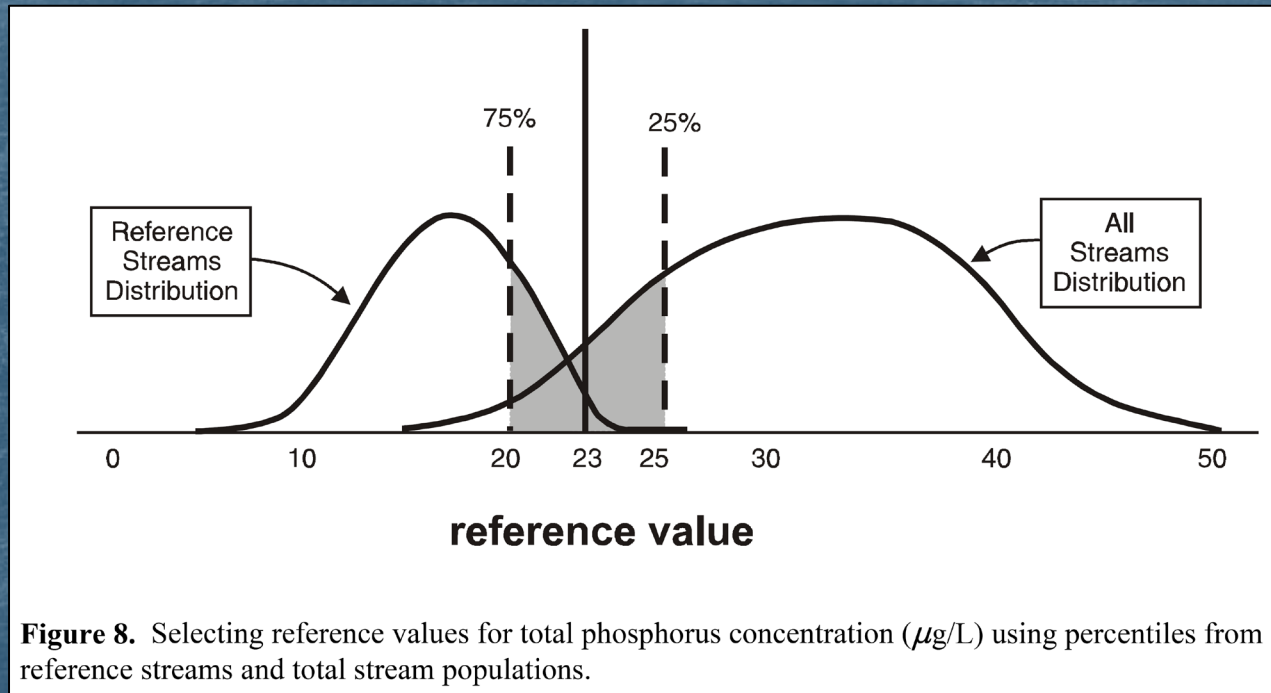


Figure 8. Selecting reference values for total phosphorus concentration ($\mu\text{g/L}$) using percentiles from reference streams and total stream populations.

Reference condition model and data quantity

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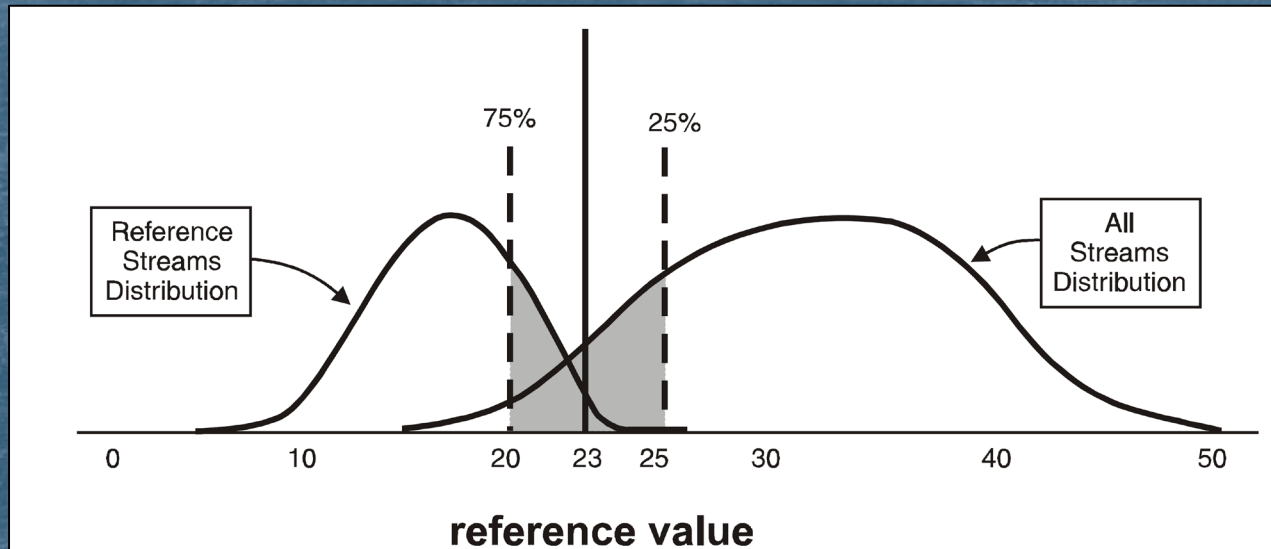
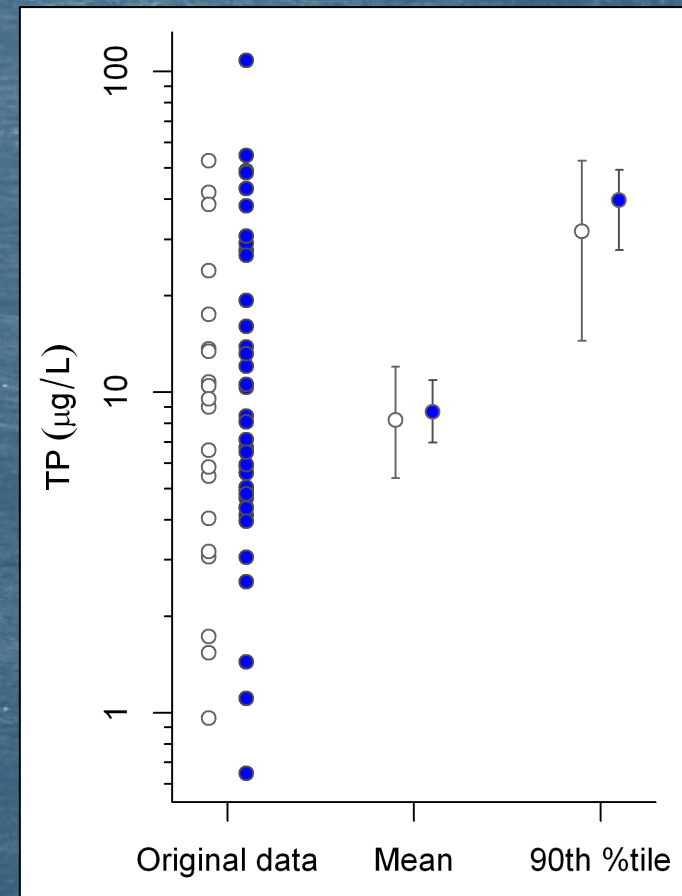
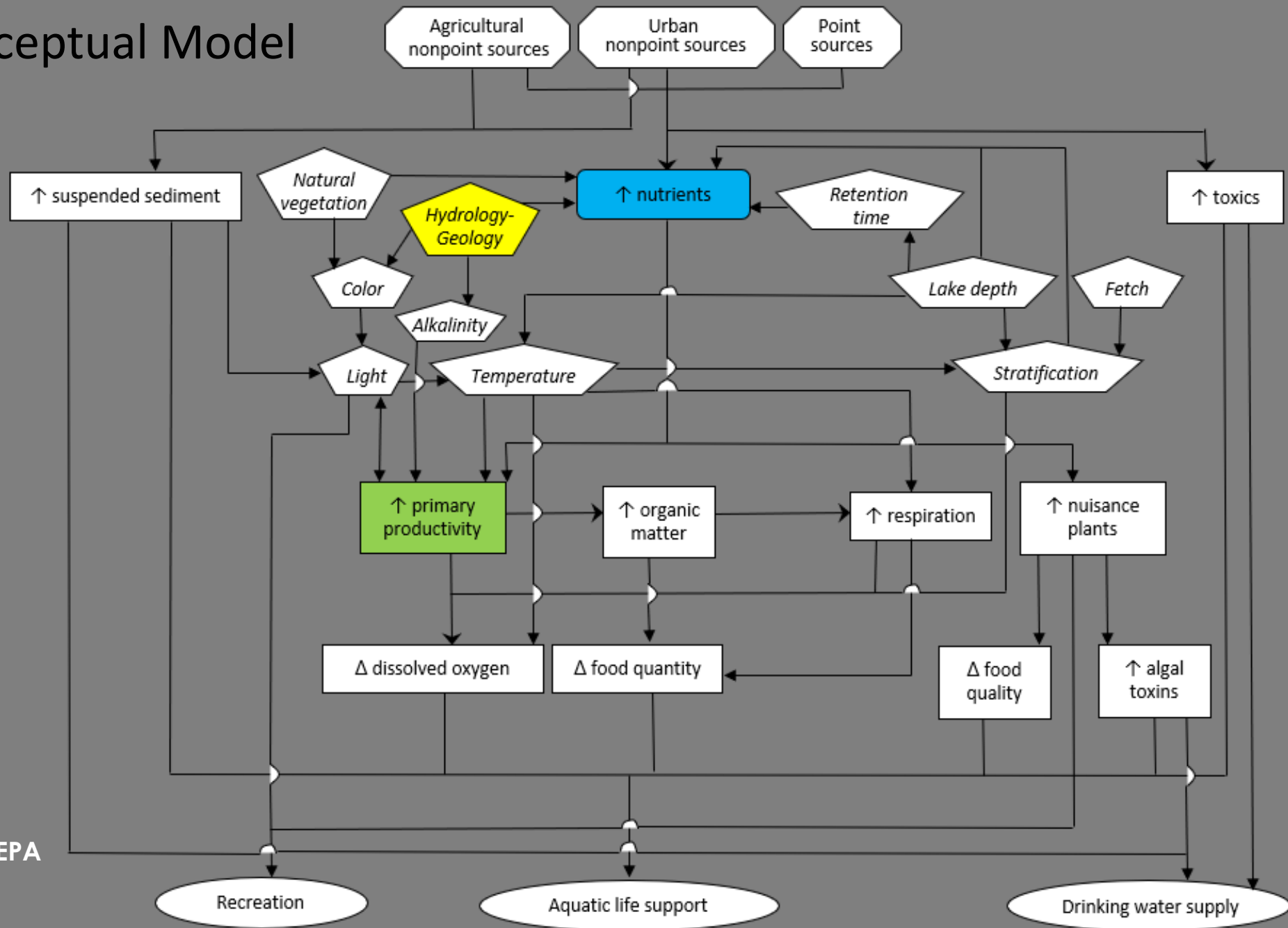


Figure 8. Selecting reference values for total phosphorus concentration ($\mu\text{g/L}$) using percentiles from reference streams and total stream populations.

L. Yuan, U.S. EPA

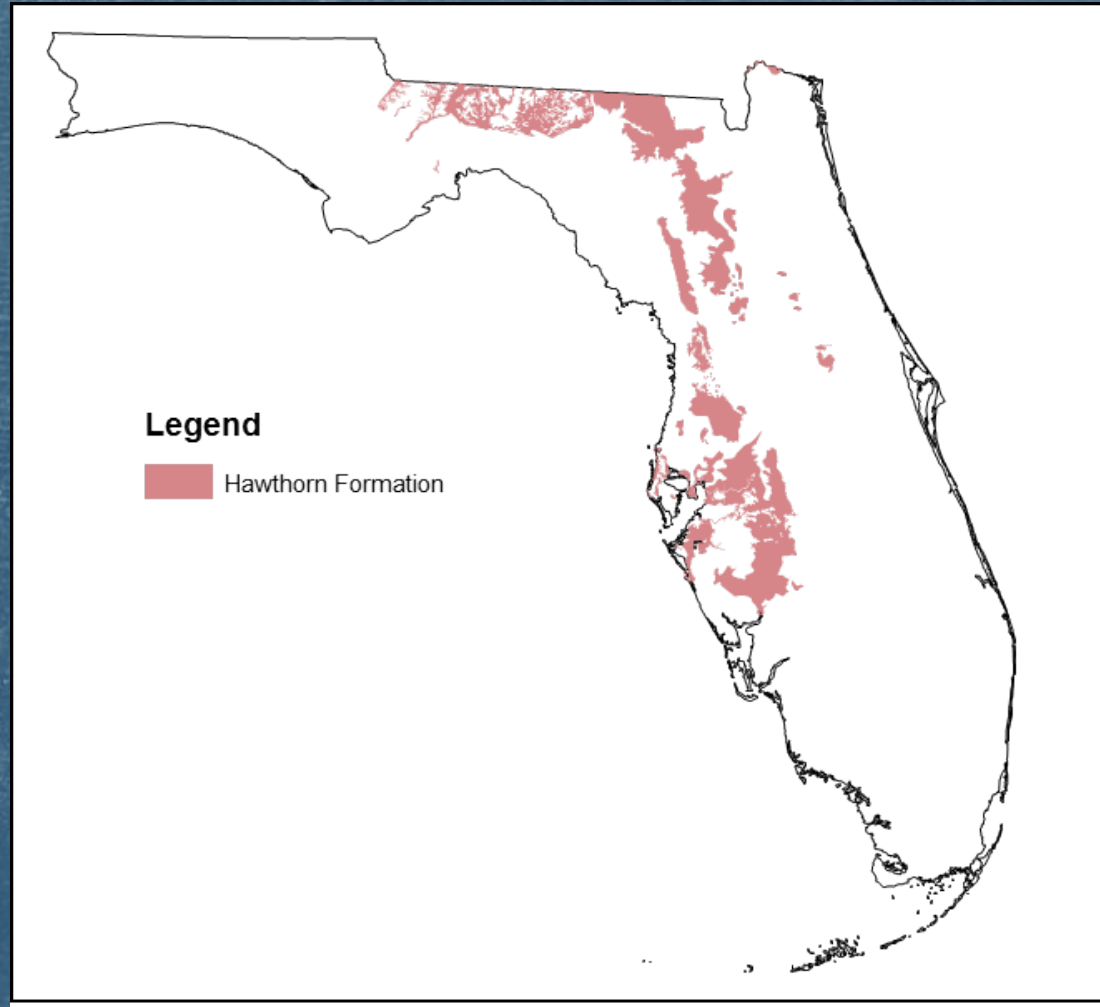


Lake Conceptual Model

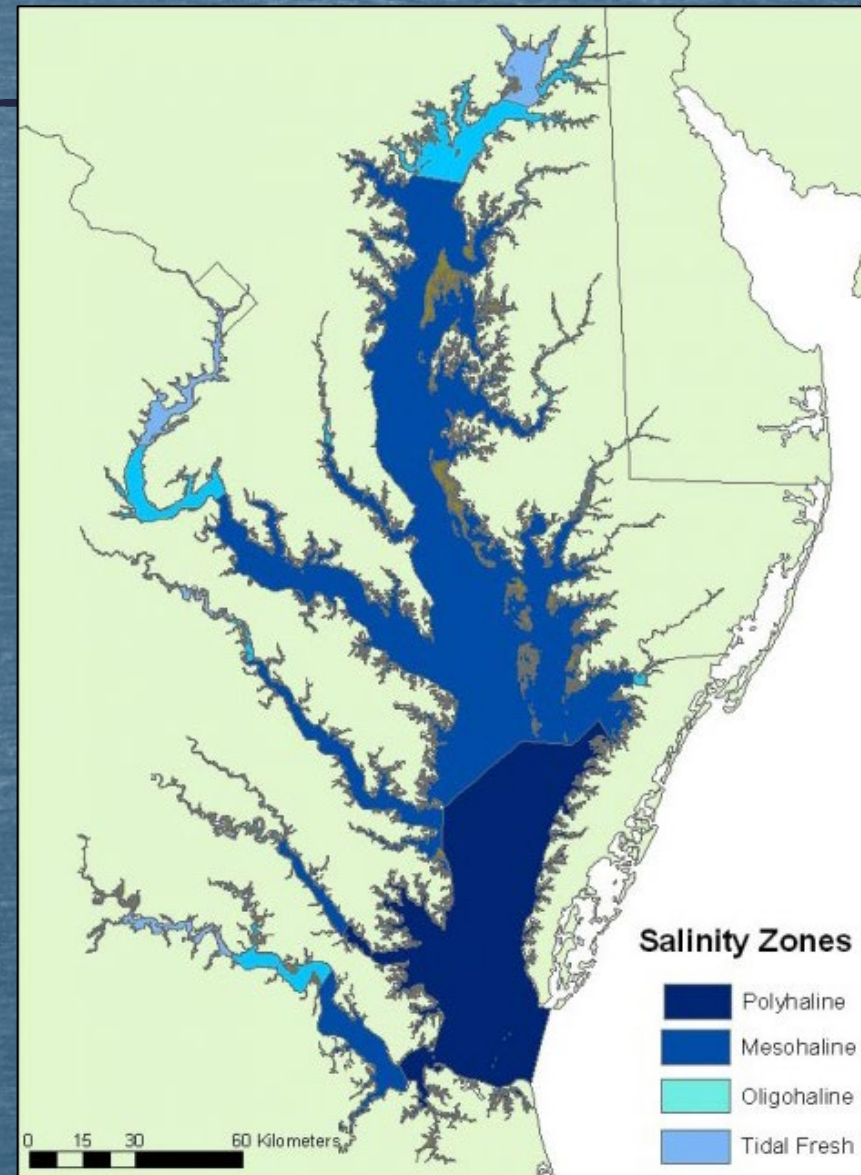
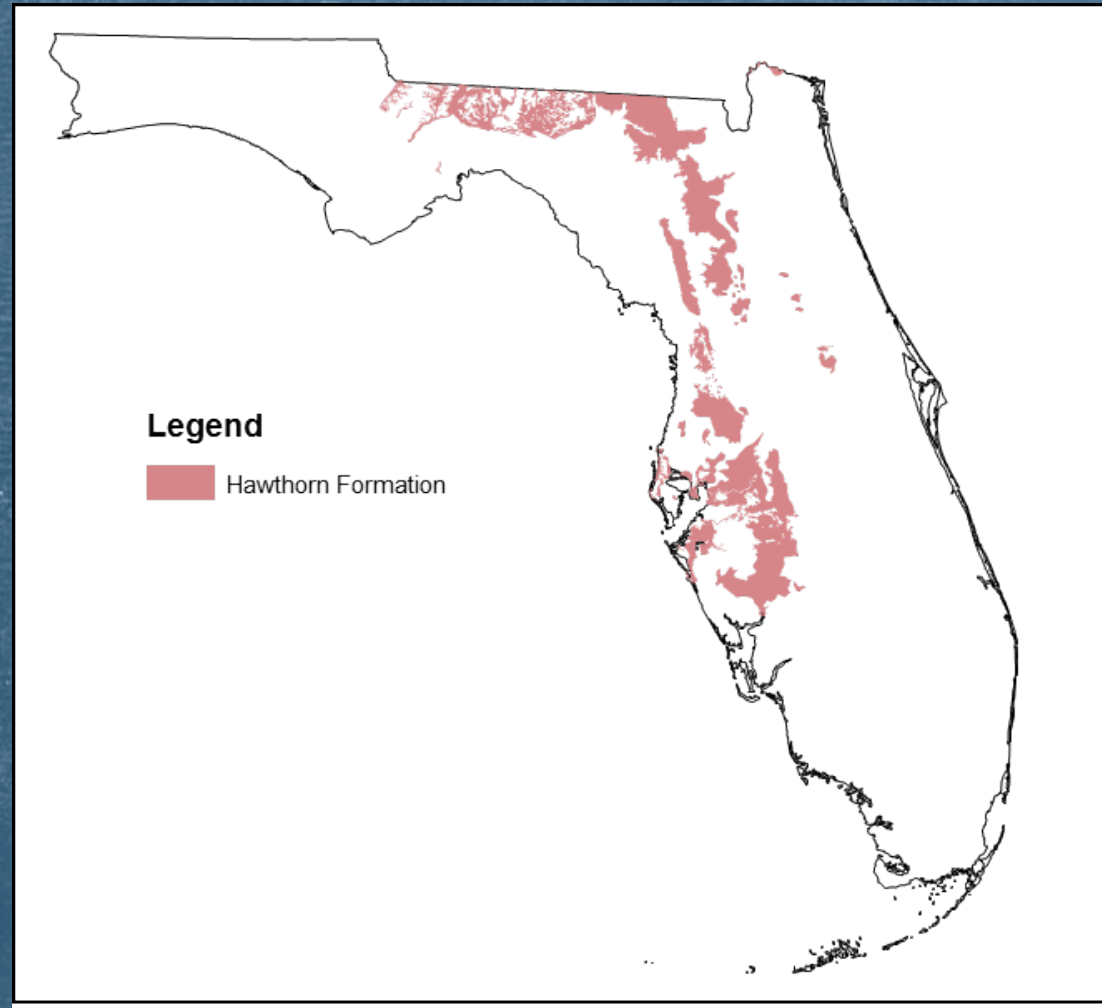


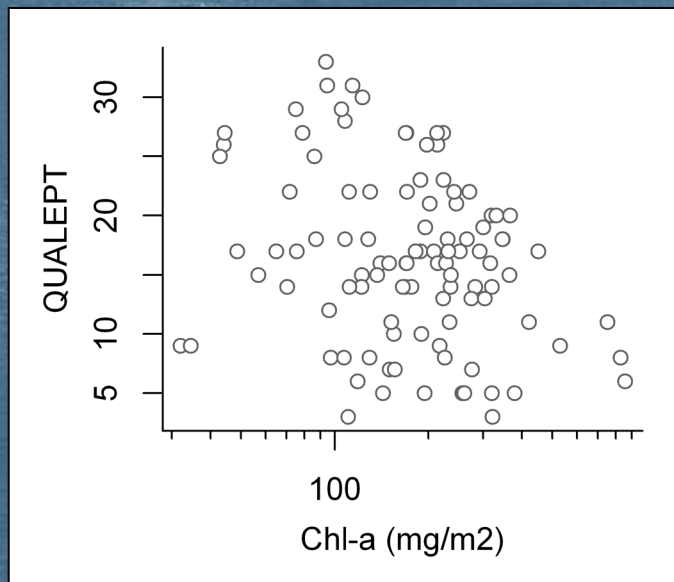
L. Yuan, U.S. EPA

Classification: Geographic (spatially-variable factors)



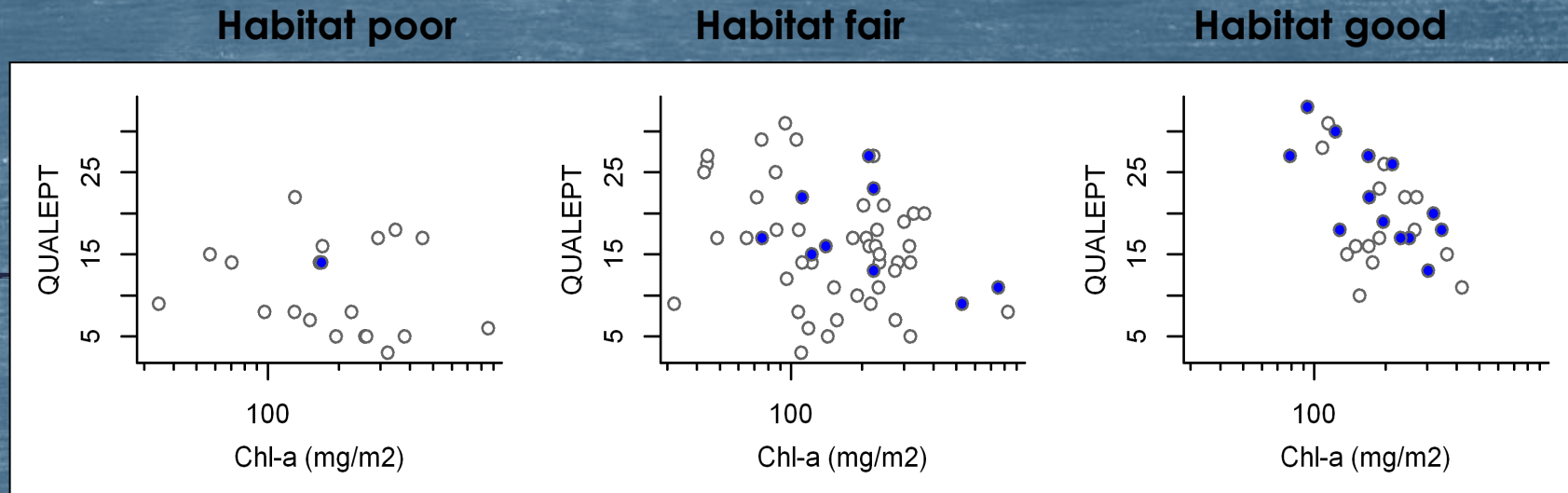
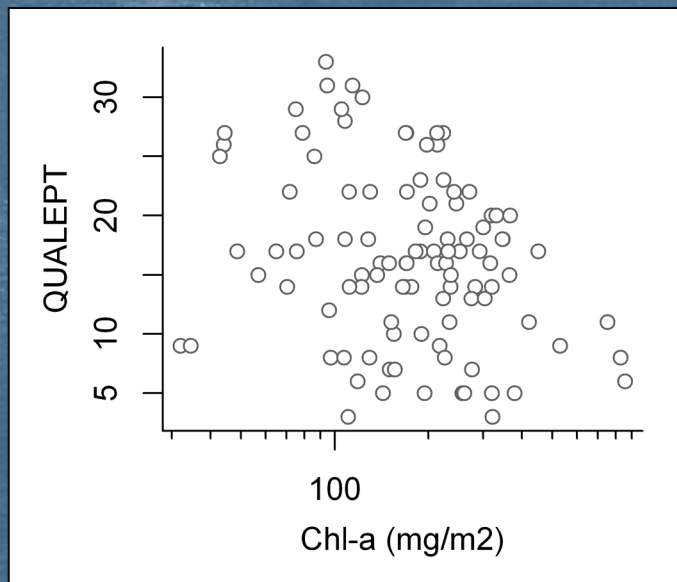
Classification: Geographic (spatially-variable factors)





Classification:
Functional

L. Yuan, U.S. EPA

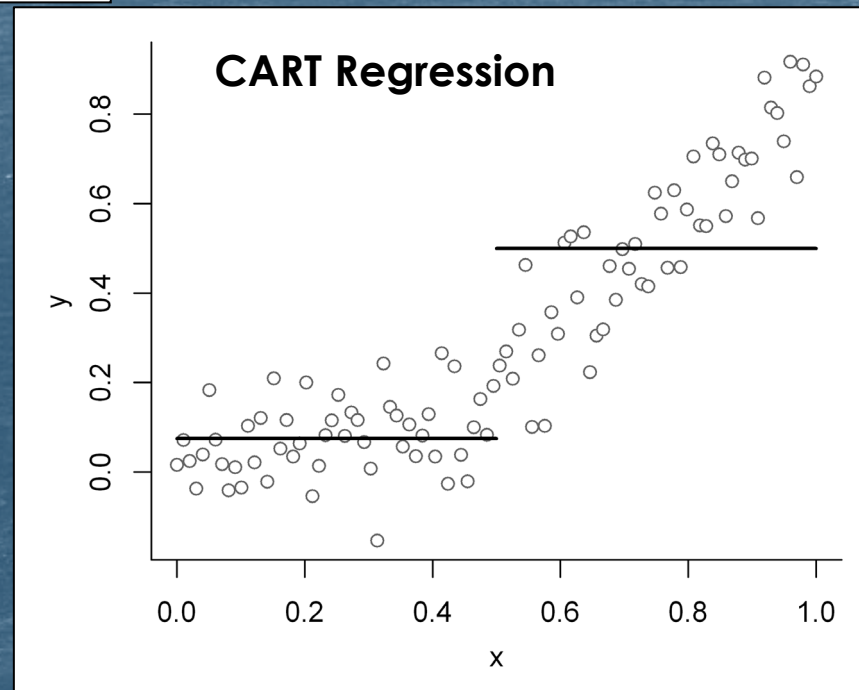
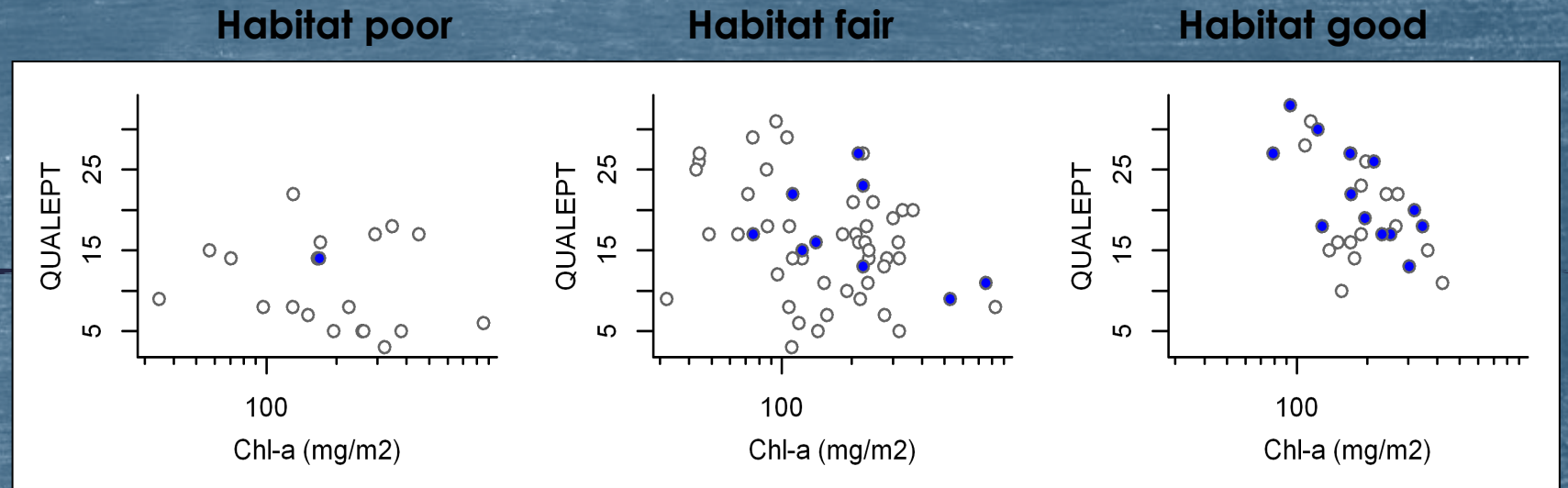
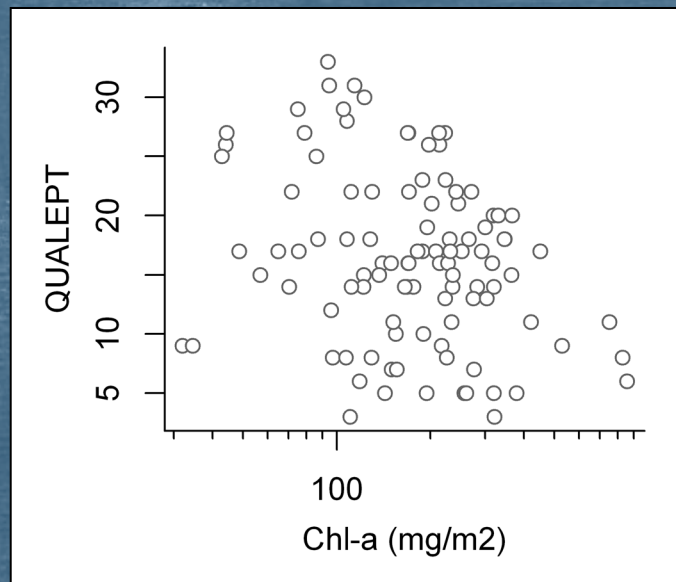


Classification:
Functional

L. Yuan, U.S. EPA

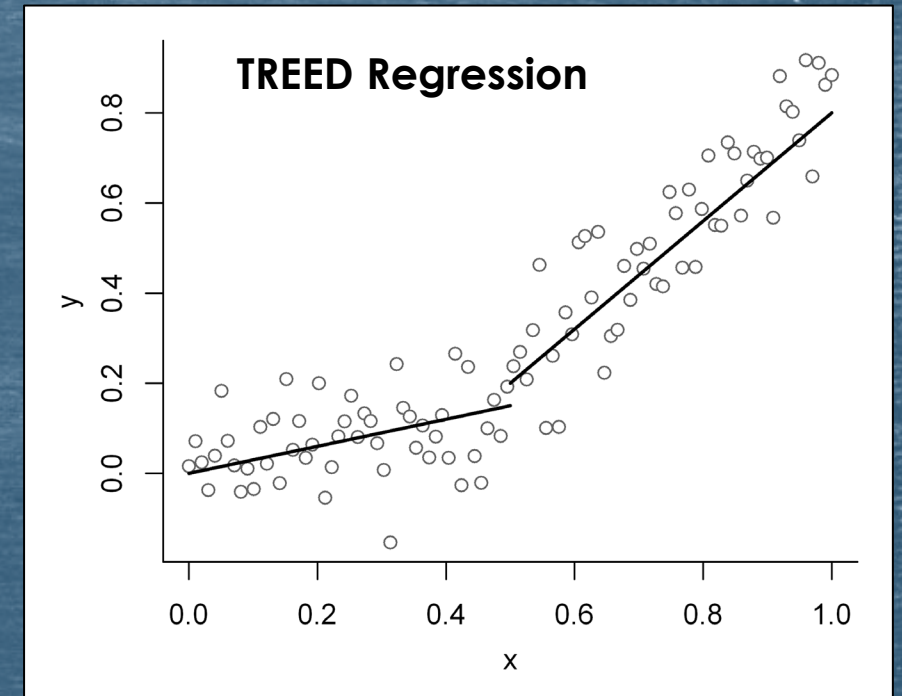
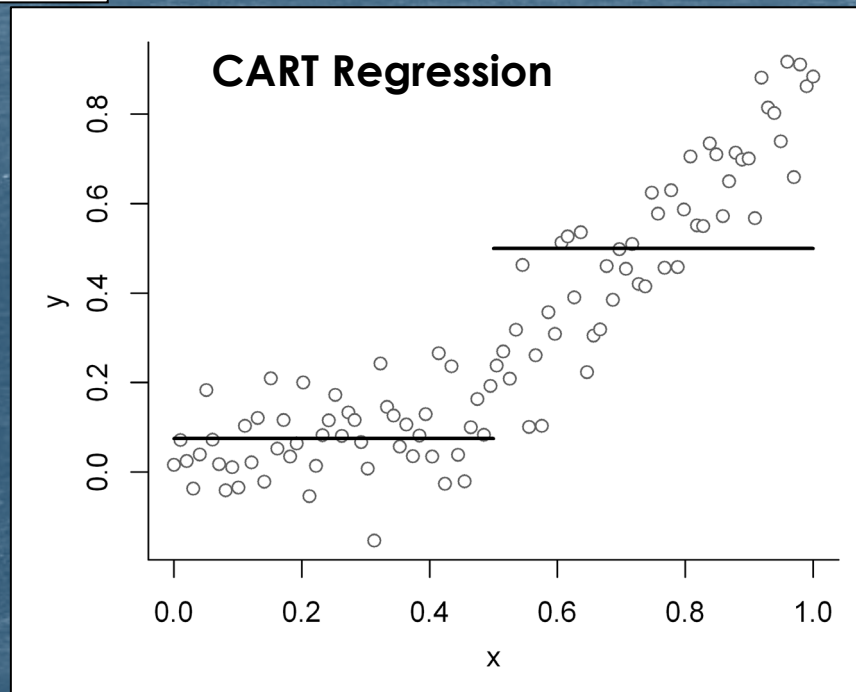
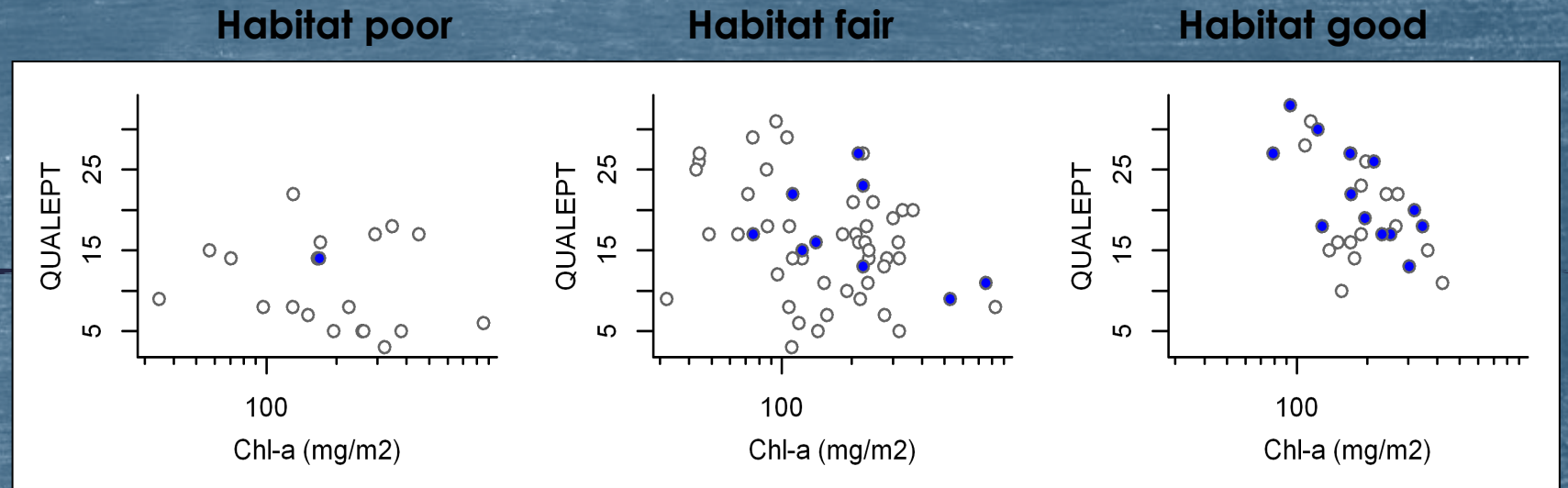
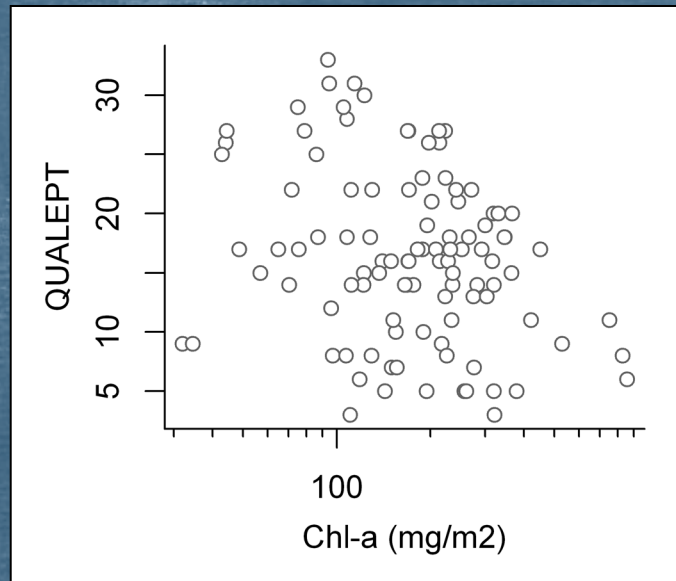
Classification: Functional

L. Yuan, U.S. EPA



Classification: Functional

L. Yuan, U.S. EPA



Estimating duration and frequency

Toxic pollutants

- ❖ Controlled laboratory experiments (removes confounding variables)
- ❖ Dose-response (gradient)
- ❖ Lethal effects
- ❖ Length of exposure: hours–days
- ❖ Frequency of exposure: weeks–months (recovery time)

Estimating duration and frequency

Toxic pollutants

- ❖ Controlled laboratory experiments (removes confounding variables)
- ❖ Dose-response (gradient)
- ❖ Lethal effects
- ❖ Length of exposure: hours–days
- ❖ Frequency of exposure: weeks–months (recovery time)

Nutrient pollution

- ❖ **Field monitoring of WQ (includes confounding variables)**
- ❖ **Correlations, not dose-response**
- ❖ **Sub-lethal effects**
- ❖ **Length of exposure: weeks–months+**
- ❖ **Frequency of exposure: months–years (recovery time)**

Distinguishing criteria duration and frequency

Criteria (defines protection)

Length and frequency of **exposure** to a pollutant, or pollutant parameter, magnitude

WQ Monitoring/Sampling

Length of time and frequency of **observations needed to detect** exceedance of the criteria

Assessment Period

Length of time and frequency over which **exceedance of the criteria is concluded**

Distinguishing criteria duration and frequency

Criteria (defines protection)

Length and frequency of **exposure** to a pollutant, or pollutant parameter, magnitude

WQ Monitoring/Sampling

Length of time and frequency of **observations needed to detect** exceedance of the criteria

Assessment Period

Length of time and frequency over which **exceedance of the criteria is concluded**

Nutrient Criteria Duration/Frequency

Instantaneous [chl-a] shall not exceed 40 µg/L over the **year, more than 10% of the time**

Magnitude: 40 µg/L
Duration: Year (365 days)
Frequency: ≤ 10%

Criteria Monitoring Period (Index Period) Sampling Frequency

Monitor over growing season (140 days)
Sample once per week (n=20)

Criteria Assessment Period

303(d) Assessment: Every two years
Multiple annual assessment periods

Making a difference: EPA-State partnerships (N-STEPS Program)

State Projects

- ✓ Data acquisition and preparation
- ✓ Classification analysis
- ✓ Modeling
 - ✓ Conceptual
 - ✓ Stressor-response
 - ✓ Reference condition
 - ✓ Mechanistic
- ✓ Technical reports
- ✓ Technical literature reviews
- ✓ Peer reviews

Making a difference: EPA-State partnerships (N-STEPS Program)

State Projects

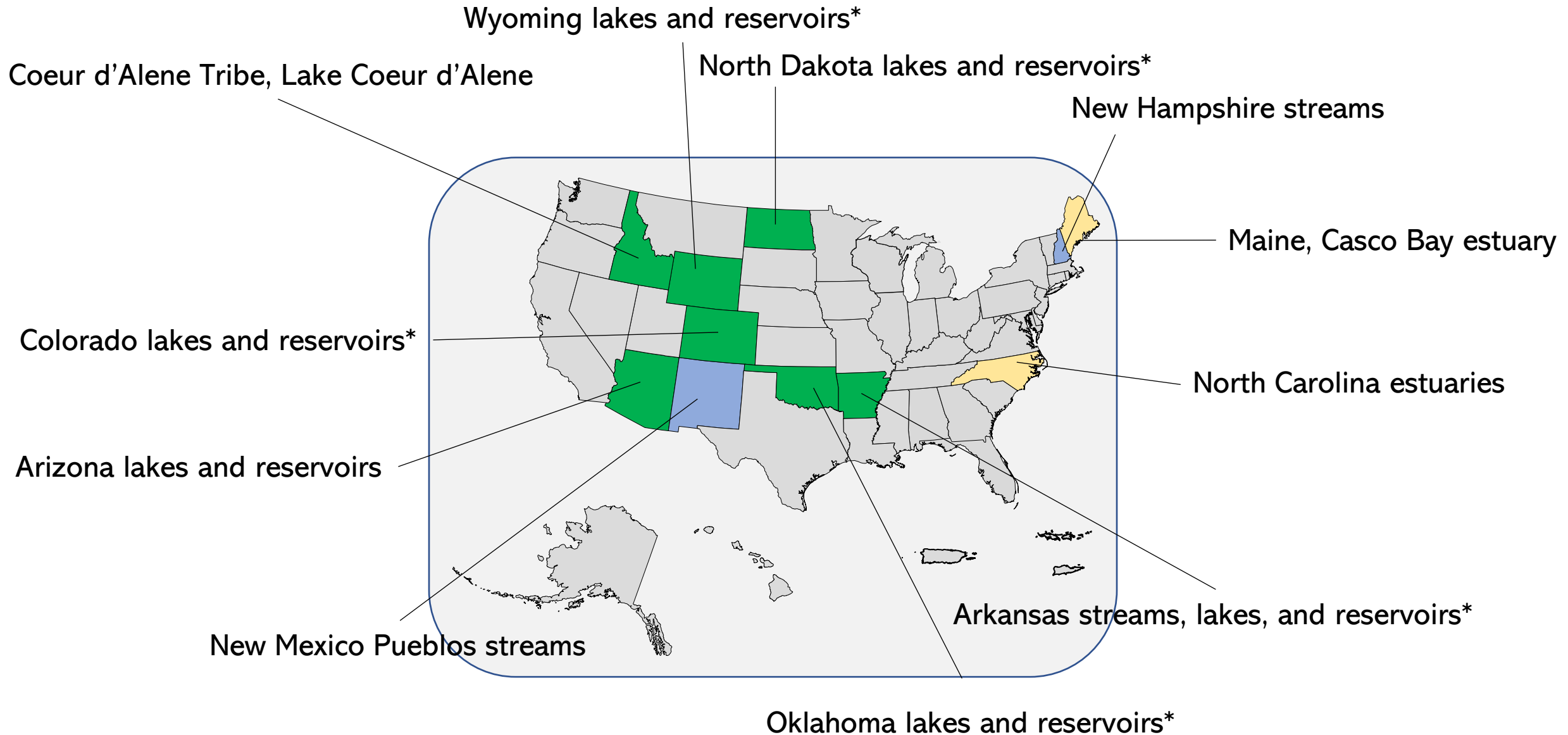
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- ✓ Classification analysis
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 - ✓ Stressor-response
 - ✓ Reference condition
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- ✓ Technical reports
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National and Regional Projects

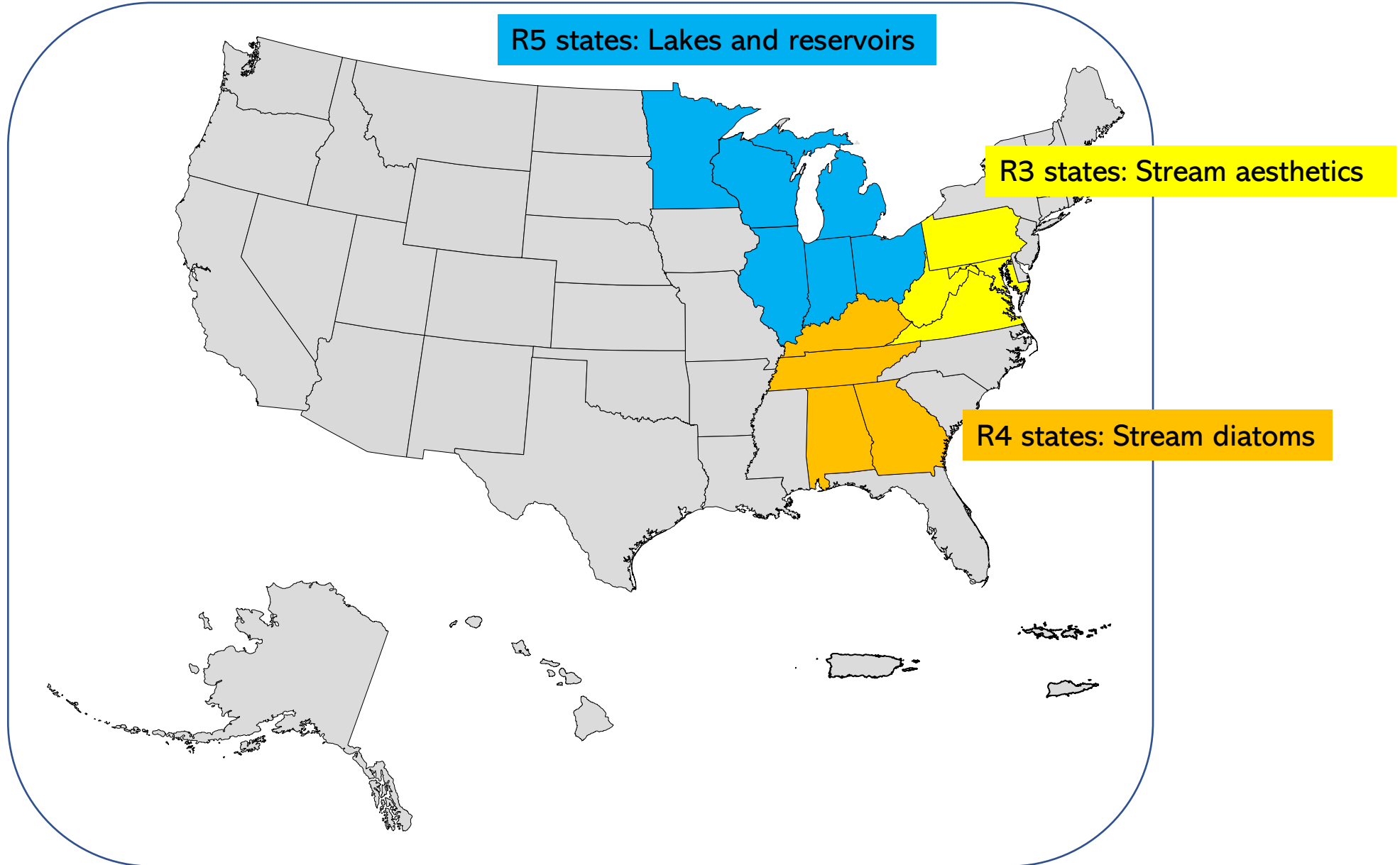
- ✓ Webinars
- ✓ White papers
- ✓ Online technical resources
- ✓ National meetings
- ✓ Regional workshops
- ✓ 304(a) criteria recommendations
- ✓ Consultations with CWA 303(d), 402 programs

FY22-23 State and Tribal Projects - Completed

*Includes application of EPA's 304(a) national lake models

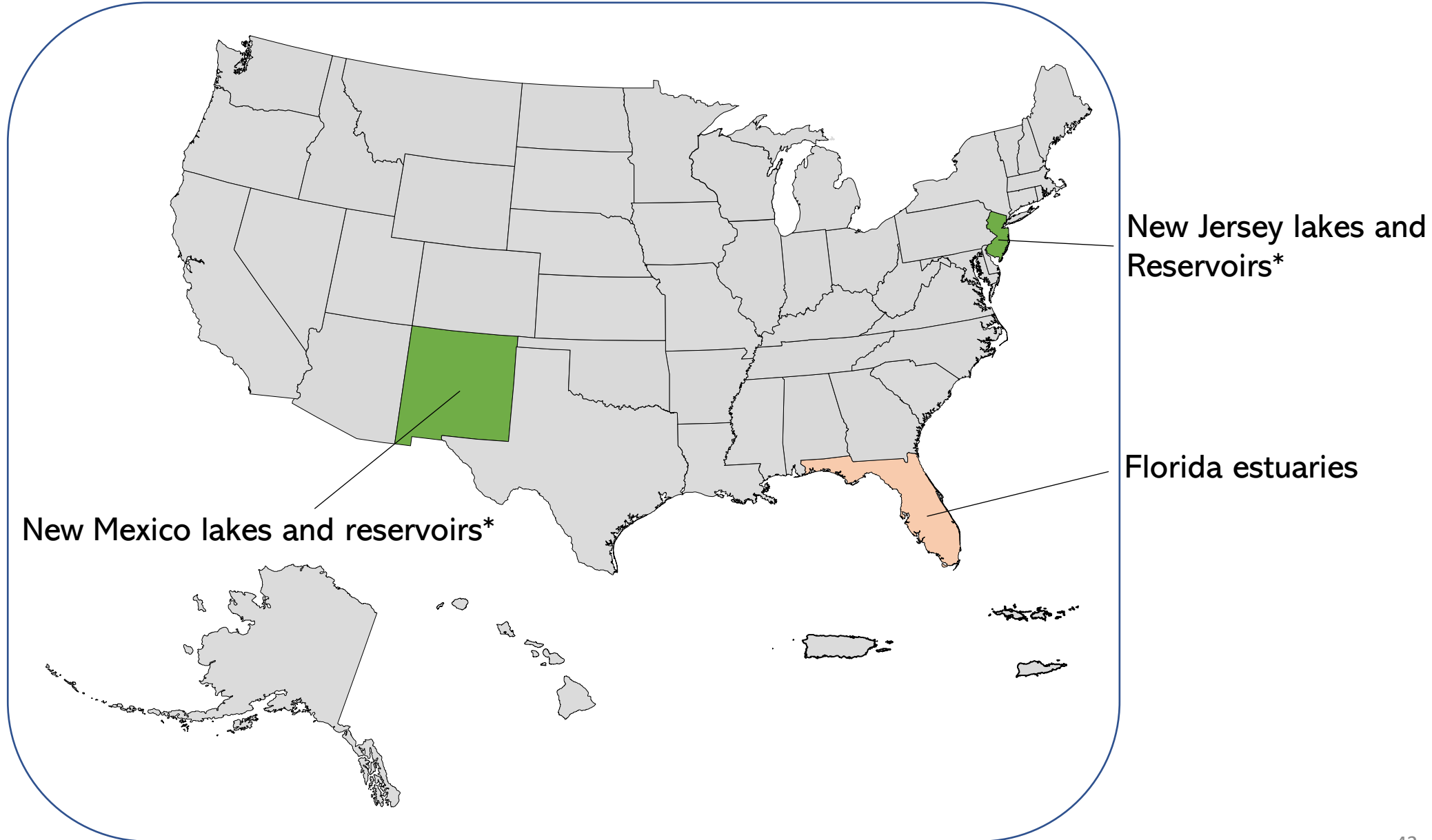


FY22 Region-wide State Projects - Completed



FY23 State Projects – New Starts

*Includes application of EPA's 304(a) national lake models



Additional technical resources

N-STEPS Online (2021)

Primer on user perception surveys (2021)

Ambient Water Quality Criteria to Address Nutrient Pollution in Lakes and Reservoirs (2022)

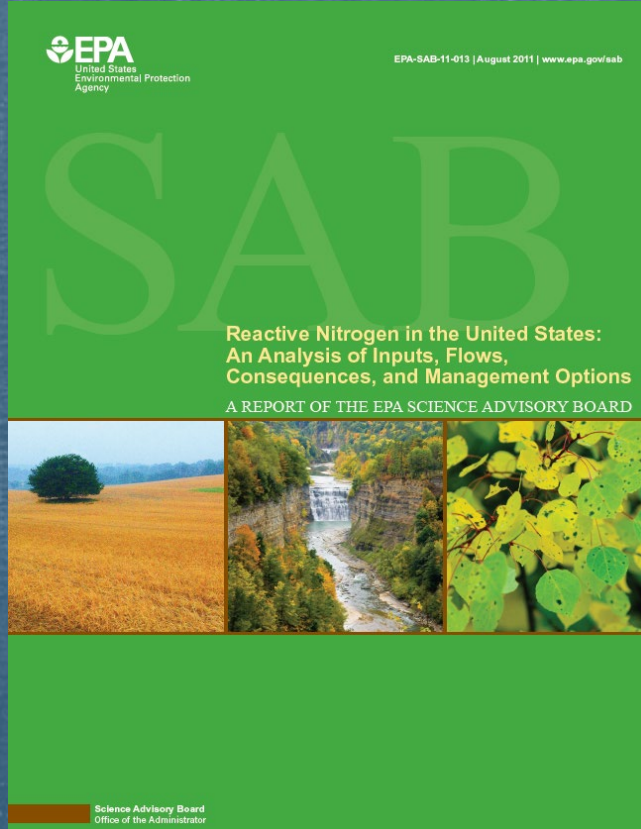
Acknowledgments

- ❖ Michael Paul, Ph.D., U.S. EPA, Office of Water
- ❖ Lester Yuan, Ph.D., U.S. EPA, Office of Water
- ❖ Michael Suplee, Ph.D., Montana Department of Environmental Quality

Questions and Discussion

Jacques L. Oliver, (202) 566-0630, oliver.jacques@epa.gov

Further Reading (1)



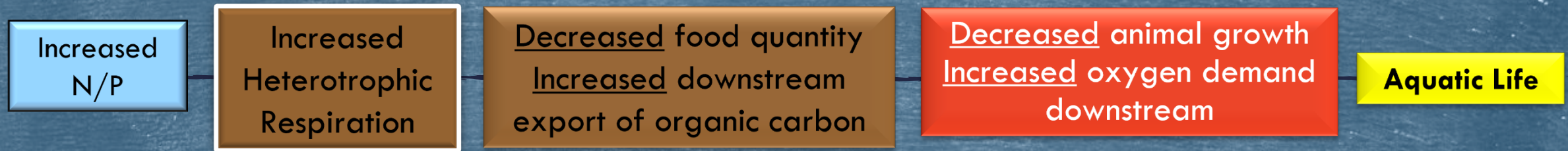
The Nitrogen Bomb, by James Worrell, David E. and Marshall Jon Fisher

The Swamp: The Everglades, Florida, and the Politics of Paradise, by Michael Grunwald

Cooperative Federalism, Nutrients, and the Clean Water Act: Three Cases Revisited, by Oliver Houck

U.S. EPA, 2011, EPA-SAB-11-013

Productivity Pathway: Brown Pathway



Experimental nutrient additions accelerate terrestrial carbon loss from stream ecosystems

Amy D. Rosemond,^{1*} Jonathan P. Benstead,² Phillip M. Bumpers,¹ Vladislav Gulis,³ John S. Kominoski,^{1†} David W. P. Manning,¹ Keller Suberkropp,² J. Bruce Wallace¹

Nature, 2015

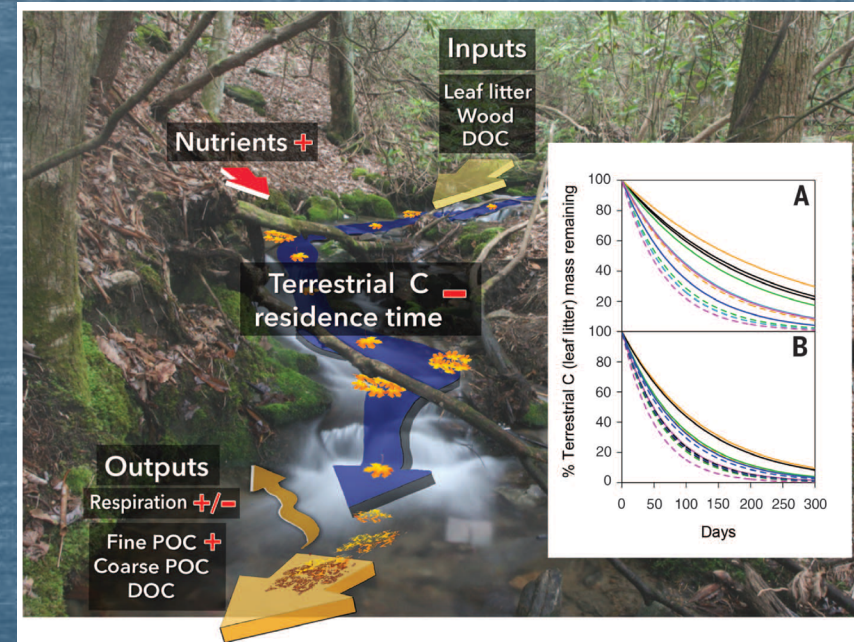


Fig. 1. Terrestrial C residence time was approximately halved with experimental nutrient enrichment. Increased nutrient inputs (+) reduced terrestrial particulate C residence time (–) and increased export of fine detrital particles (+) and respiration rates [which increased on C substrates (II) but decreased at reach scales; +/–]. Inset graph: Reach-scale leaf litter loss rates were faster in enriched (dashed lines) than in reference (solid lines) streams; the inverse of these rates is residence time. Colors correspond to the same years in (A) (reference versus enriched streams; N+P experiment; $n = 12$ annual rates) and to the same streams in (B) (pretreatment versus enriched years; N×P experiment; $n = 15$ annual rates). Data shown for litter loss are untransformed but were natural log-transformed for analyses and the calculation of loss rates (k , per day). The larger image depicts terrestrial organic C inputs, which enter as leaf litter, wood, and dissolved organic carbon (DOC), and outputs as hydrologic export (fine and coarse particles, DOC) and respired CO_2 in deciduous forest streams, using an image of one of the N×P experimental stream sites.

Coastal eutrophication as a driver of salt marsh loss

Nature, 2012

Linda A. Deegan¹, David Samuel Johnson^{1,2}, R. Scott Warren³, Bruce J. Peterson¹, John W. Fleeger⁴, Sergio Fagherazzi⁵ & Wilfred M. Wollheim⁶

Reference



Nutrient-enriched



Figure 1 | Comparison photos of the marshes from the ecosystem nutrient-enrichment experiment. a–c, Reference. d–f, Nutrient-enriched. Photo credits: a, b, d and e, L.A.D.; c and f, Google Earth (19 June 2010 image, copyright 2012 Google).

Further Reading (3)

Productivity Pathway

Increased
N/P

Changes in
Primary
Production

Increased shoot height
Decreased below-ground biomass
Increased marsh fractures
Increased marsh slumps
Increased fine organic matter

Loss of Habitat
Loss of Food
Increased Predation

Aquatic Life

Further Reading (4)

Estimating nutrient criteria magnitude and duration: An experimental approach adapted from M. Pace et al., 2017, *PNAS*

Recovery time after exposure to a nutrient supply

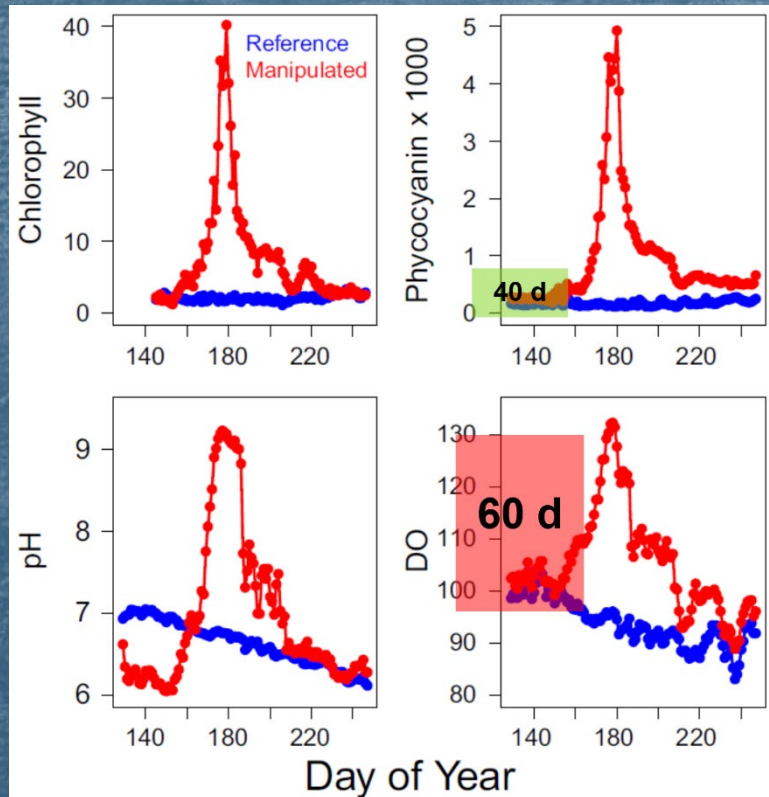


Fig. 1. Dynamics of (Upper Left) chlorophyll *a* ($\mu\text{g}\cdot\text{L}^{-1}$), (Upper Right) phycocyanin (fluorescence units), (Lower Left) pH, and (Lower Right) dissolved oxygen (DO; percent saturation) in the unenriched reference and enriched manipulated lakes. Nutrients were added to the manipulated lake from day of year 151–180.

Exposure to a nutrient supply over time

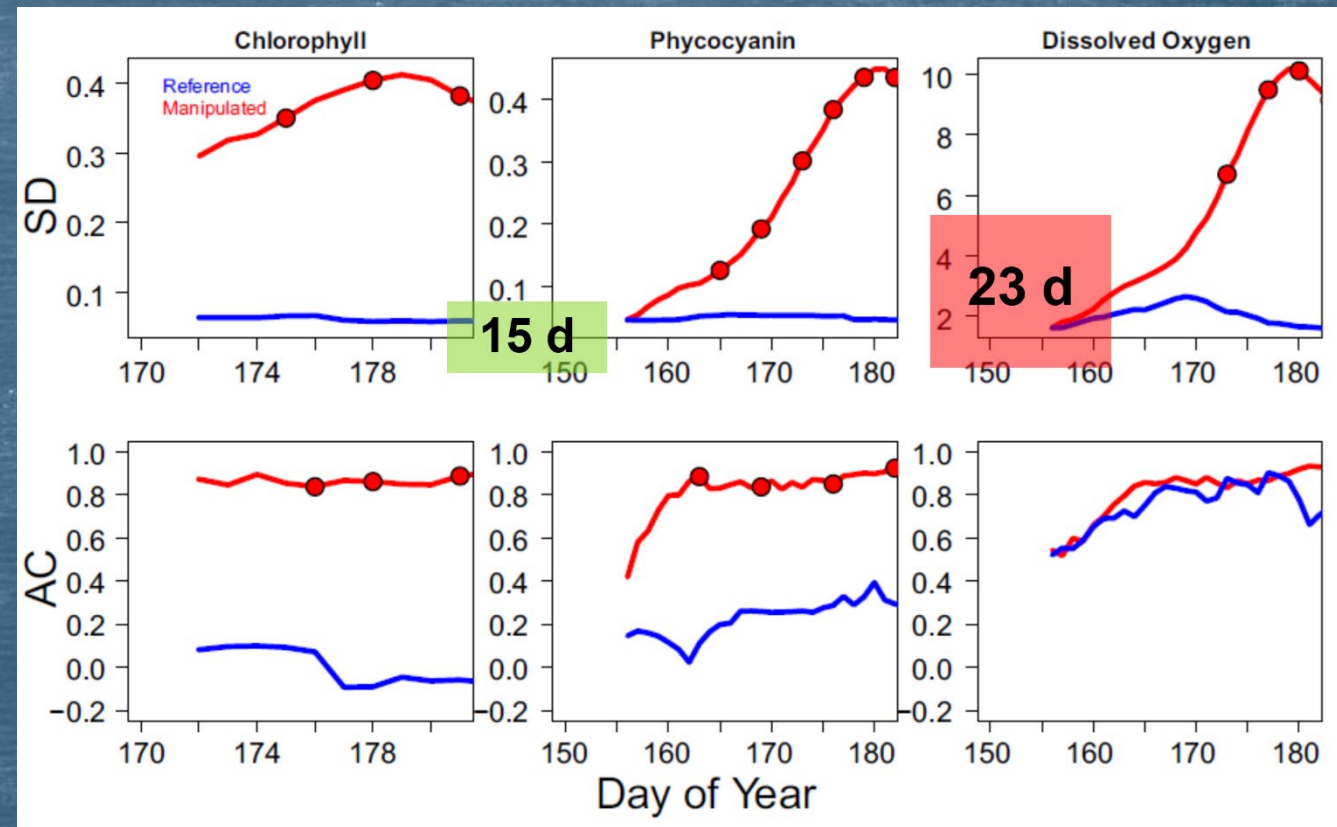


Image Credits

❖ Slides 8-12

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- ❖ Slides 28/29

- ❖ [2017 Gulf of Mexico dead zone](#), NOAA media release

- ❖ Slides 30-32

- ❖ Lake Erie algal bloom: NASA Earth Observatory, image taken on Sept. 13, 2013 by MODIS on NASA's Aqua satellite
 - ❖ *Microcystis cf. aeruginosa*: (Kützing) Kützing. Sample from epilimnion of Lake Mahopac, NY. Source: John D. Wehr, Professor, Fordham University
 - ❖ Microcystin biosynthesis: Dittmann et al., 2013, *FEMS Microbiol. Rev.* 37:23-43