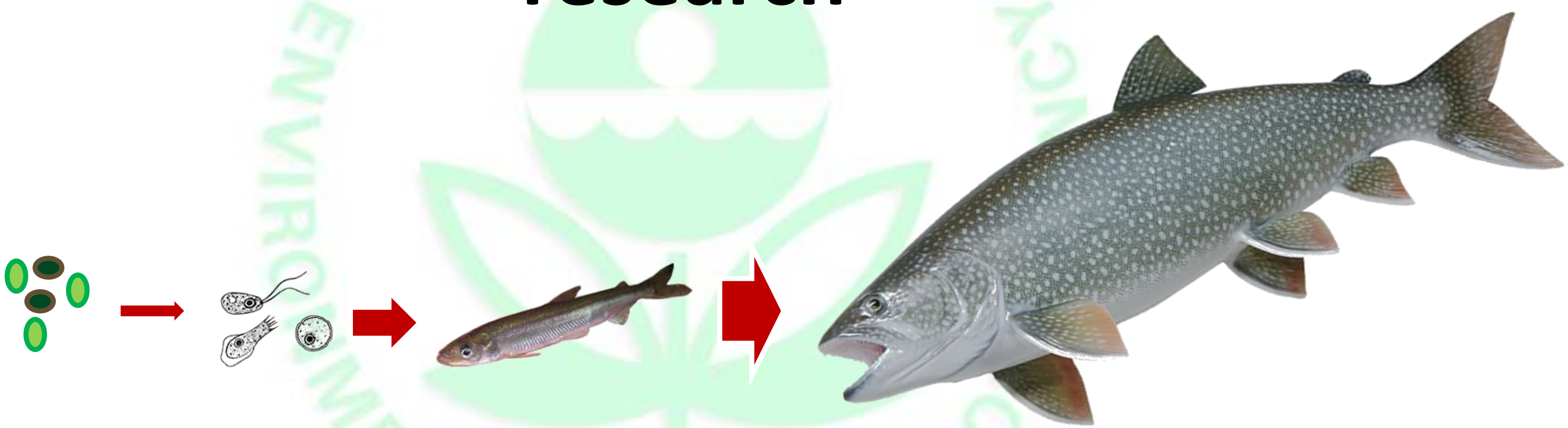
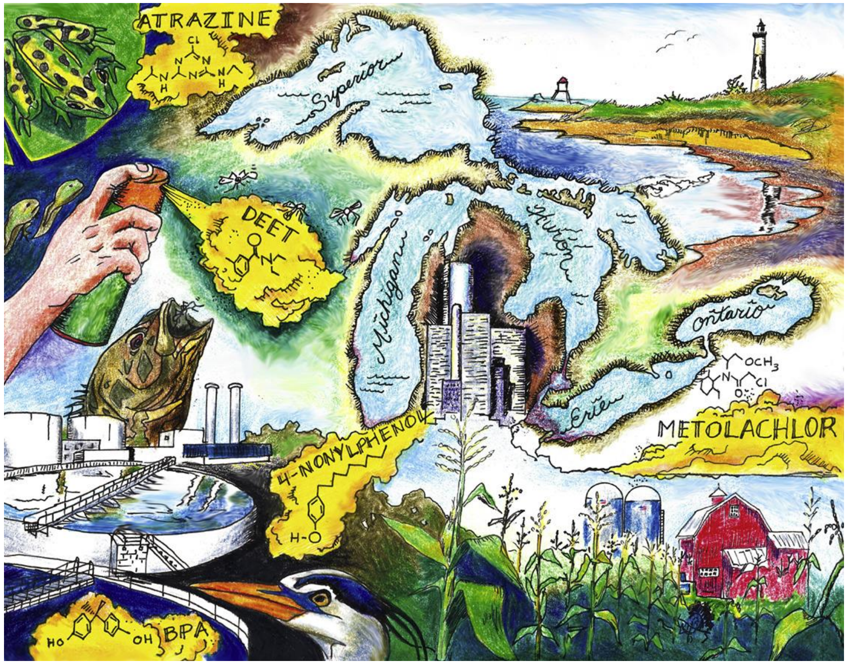
Food web energy transfer in Lake Superior to support contaminant research



Ryan Lepak, Brett Blackwell, Joel Hoffman, Anne Cotter, Morgann Gordan, Daniel Villeneuve, Gerald Ankley

Scope of talk

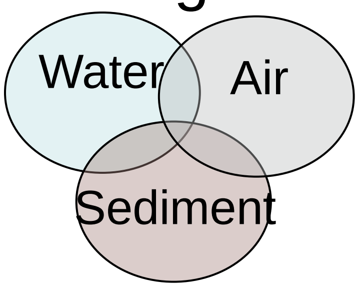
- Problem
  - Contaminant interactions with environment and biology – temporal & spatial trends
- New concepts/approaches
  - Biomarkers that hold potential to better understand aquatic ecosystems
- Preliminary finds
  - Concluding thoughts and future direction

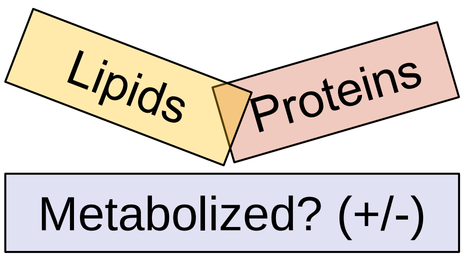


A shortlist of complications - contaminants

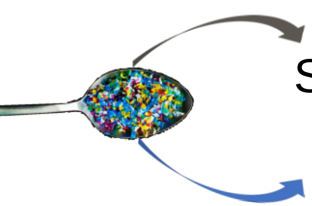
Contaminant diversity

Organic contaminants





“Inorganic” contaminants

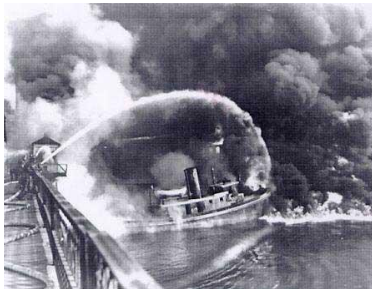


Secondary releases

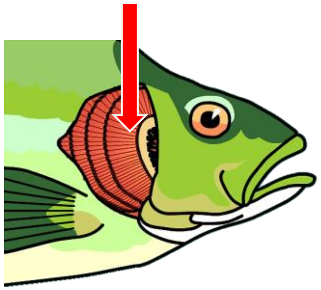
Cadmium, lead and mercury

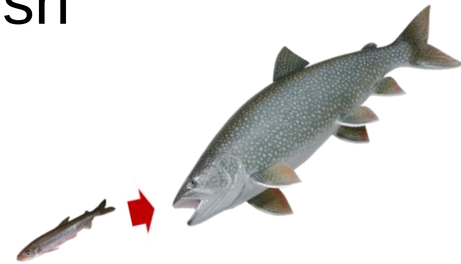
Contaminant delivery

- to the Great Lakes



- to fish

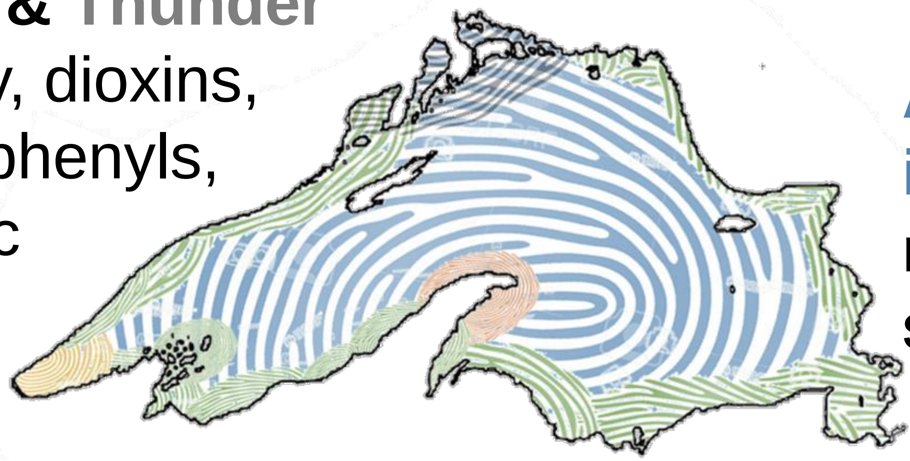




Spatial variation in contaminants

Non-point coastal inputs: e.g., mercury, erosional inputs

St Louis Estuary & **Thunder Bay:** e.g., mercury, dioxins, polychlorinated biphenyls, polycyclic aromatic hydrocarbons

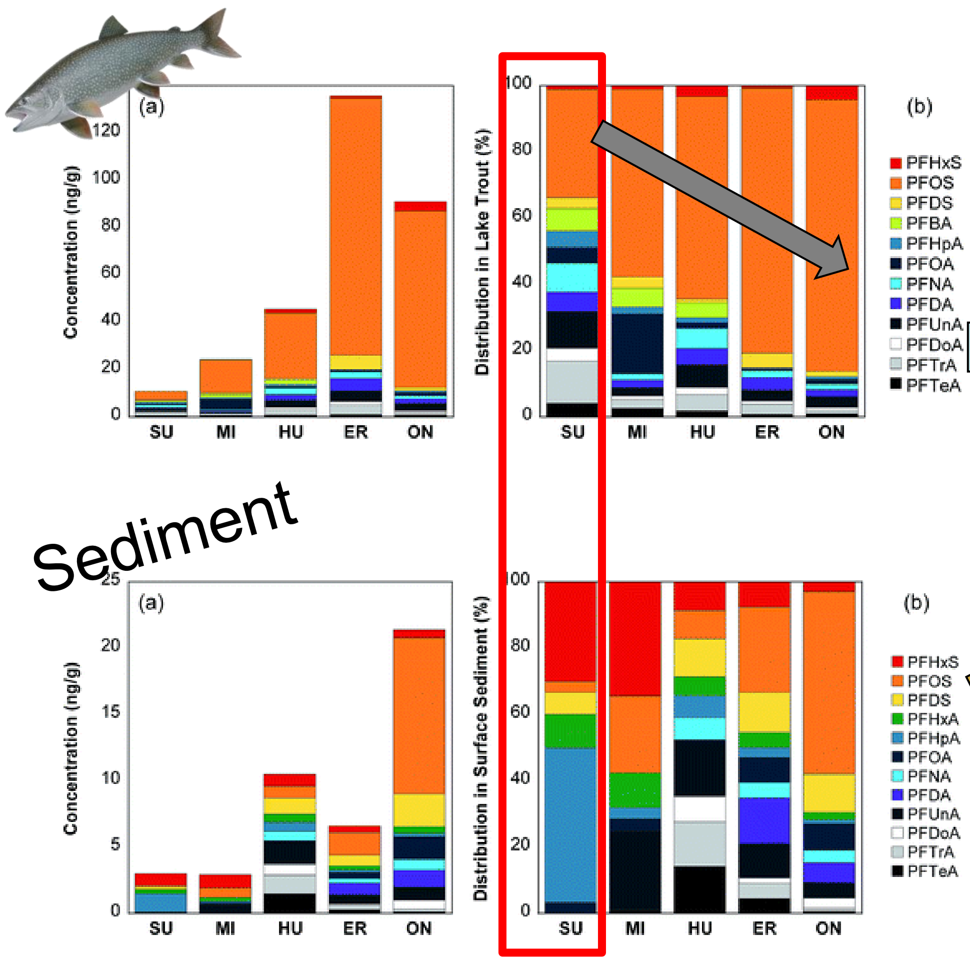


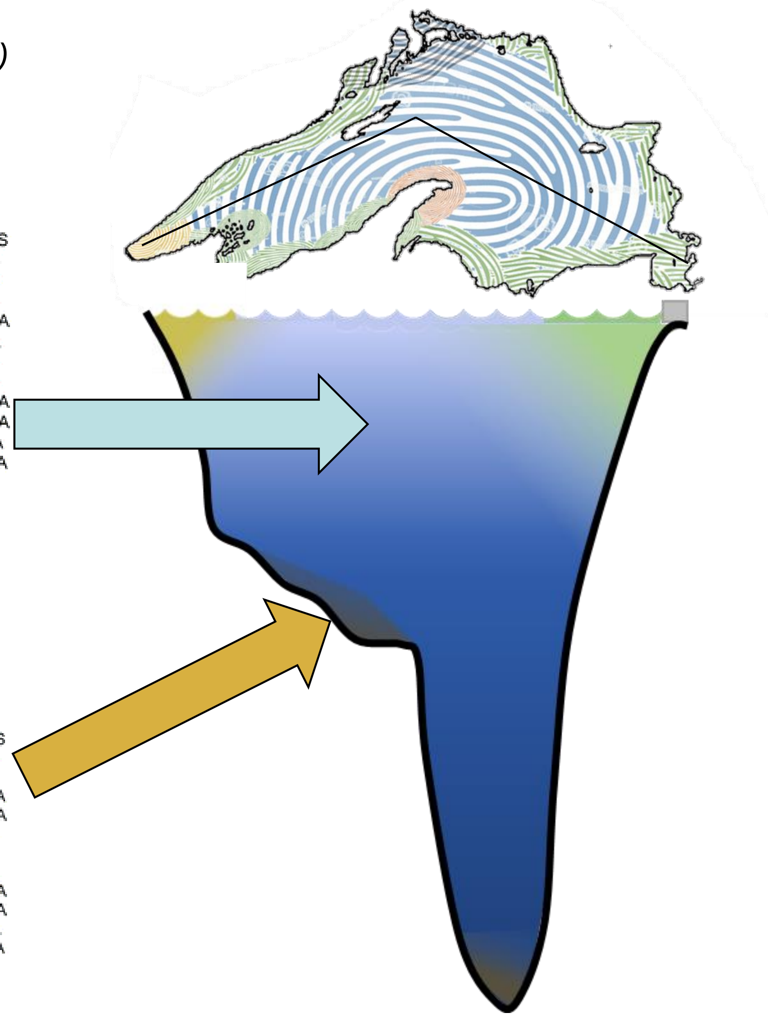
Atmospheric inputs: e.g., mercury, some PFAS's

Keweenaw Peninsula: PFAS's incl. AFFFs

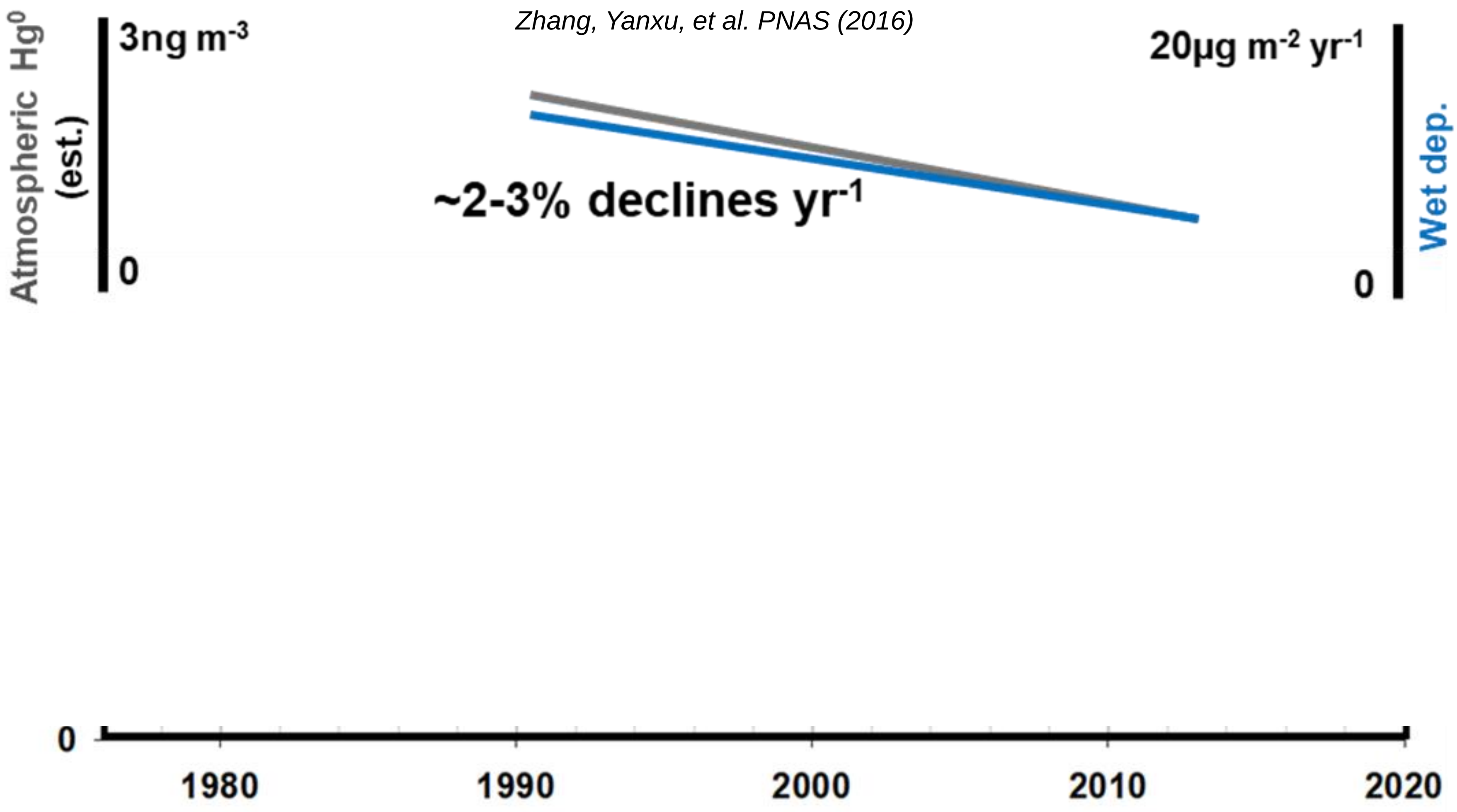
Vertical variation in contaminants – PFAS's

Remucal Environmental Science: Processes & Impacts (2019)



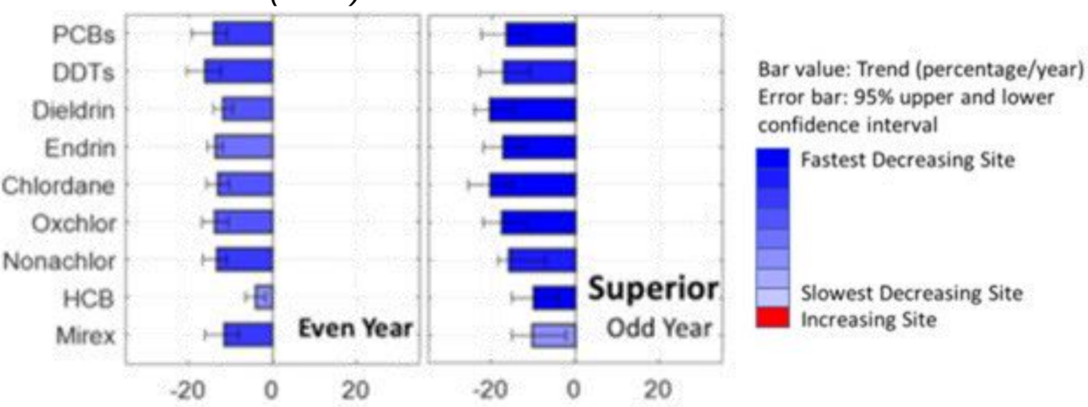


Temporal trends in contaminants



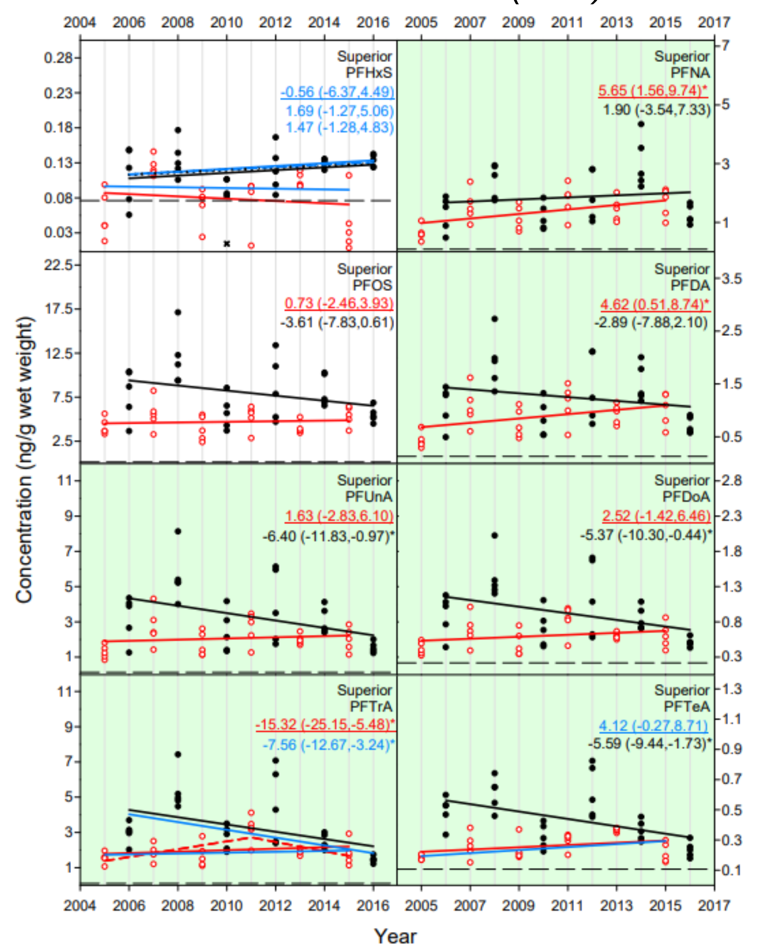
Temporal trends in contaminants

Zhou et al. JGLR (2018)

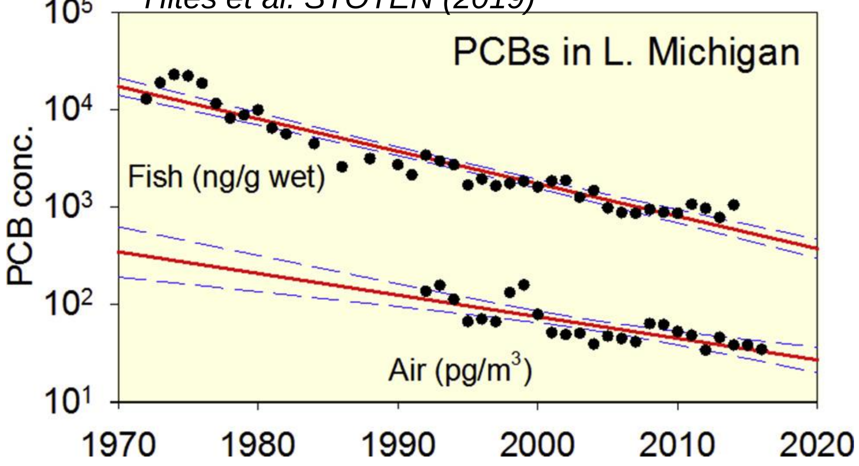


% change

Point et al. STOTEN (2021)

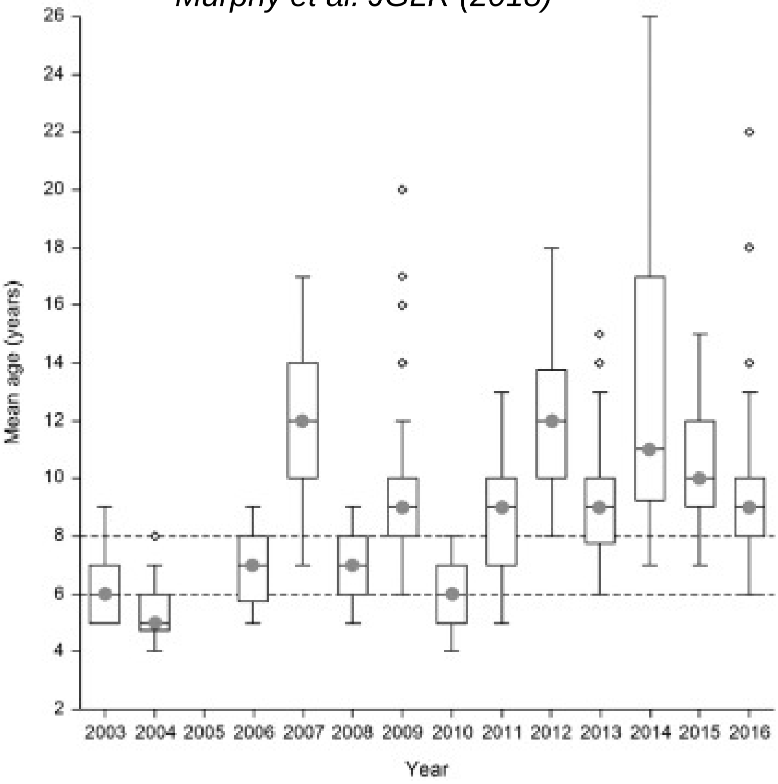


Hites et al. STOTEN (2019)

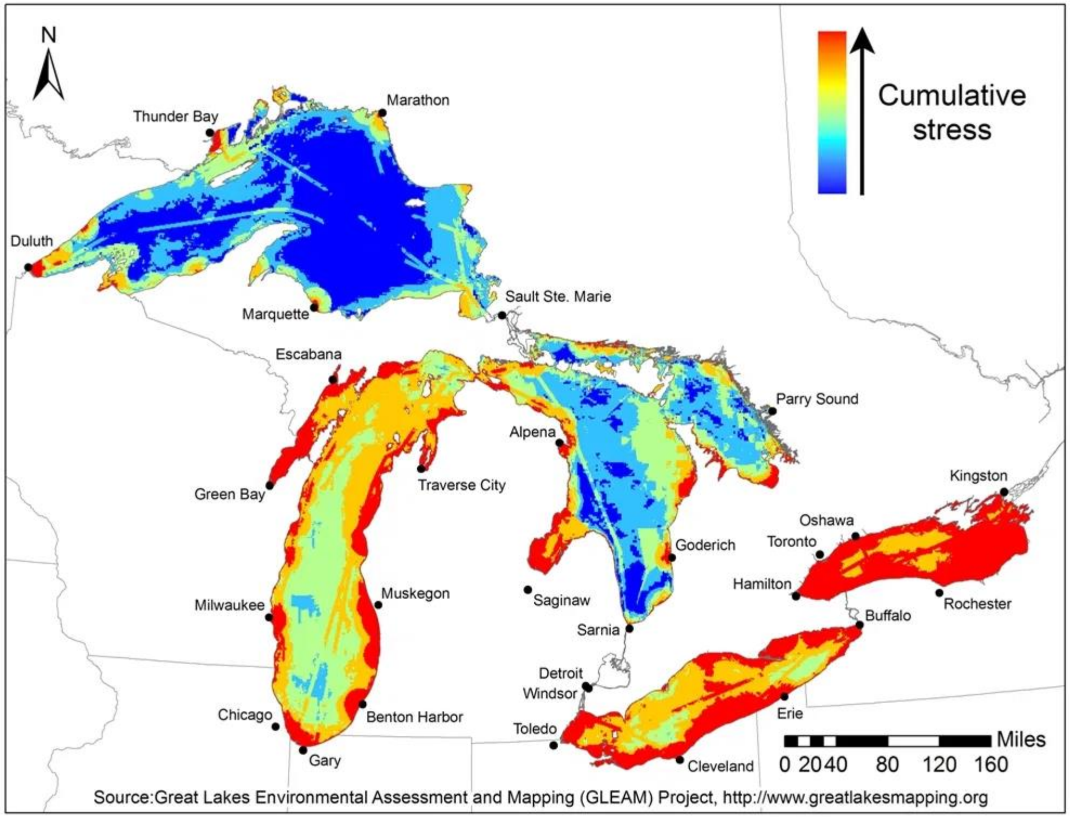


Stressors have changed the GLs and will continue to

Murphy et al. JGLR (2018)



Allan et al. PNAS (2013)



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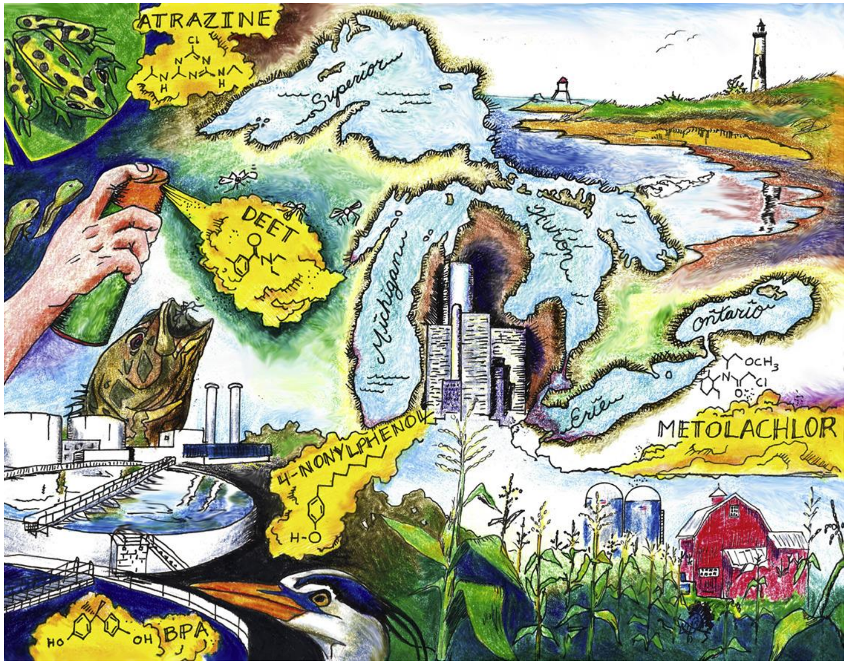
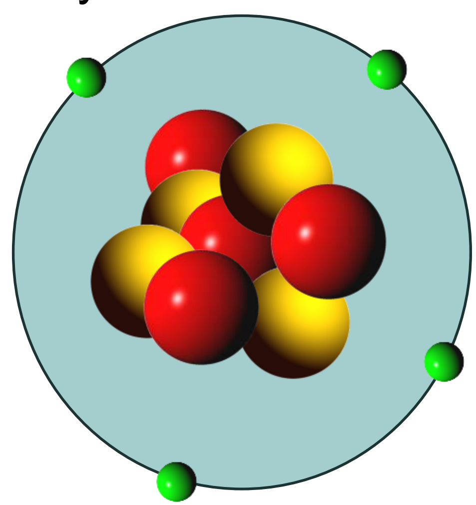


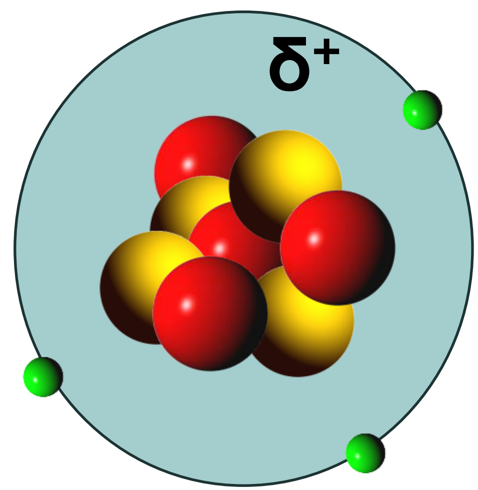
Isotope basics

+ charge subatomic particle - critical to defining an element

- charge subatomic particle - critical to defining an element’s outward facing reactivity

0 charge subatomic particle - builds an element’s mass and core size





Think iron redox
Iron - 26 electrons
Rusted iron - 23 electrons

Same element, different reactivity and charge

Isotope basics

+ charge subatomic particle - critical to defining an element

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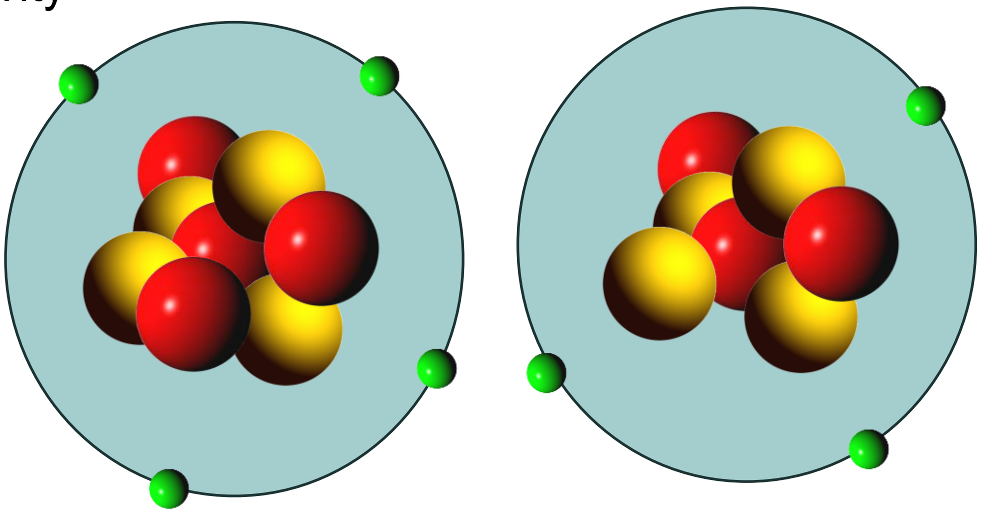
0 charge subatomic particle - builds an element's mass and core size



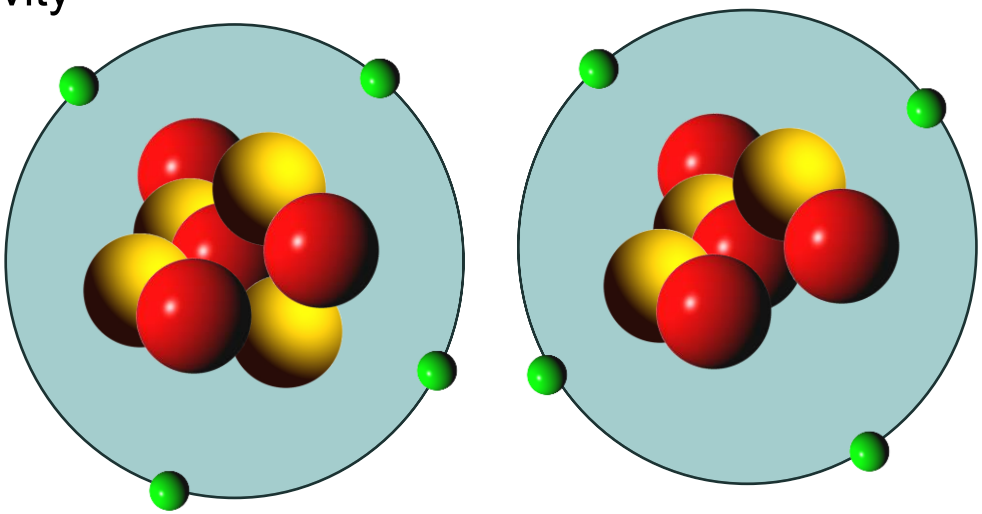
Different elements

Isotope basics

+ charge subatomic particle - critical to defining an element

- charge subatomic particle - critical to defining an element's outward facing reactivity

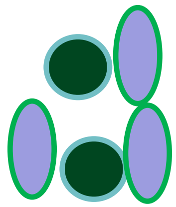
0 charge subatomic particle - builds an element's mass and core size

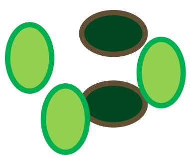


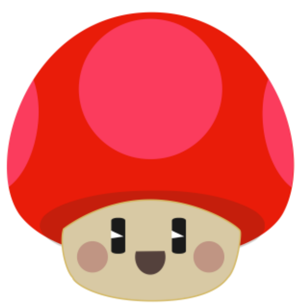
Different isotopes of the same element

Reaction rates of the same element differ due to kinetic mass differences

An example: Carbon isotope values



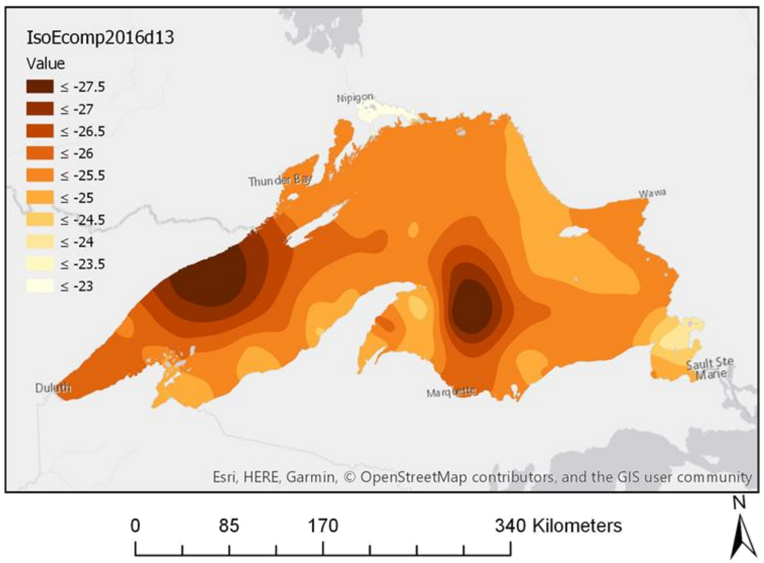




- Each “type” of primary producer “harvests” CO_2 in its own way
  - A carbon isotope value
  - But sometimes they overlap

- CO_2 isotope values also change spatially/temporally
  - “isoscape”

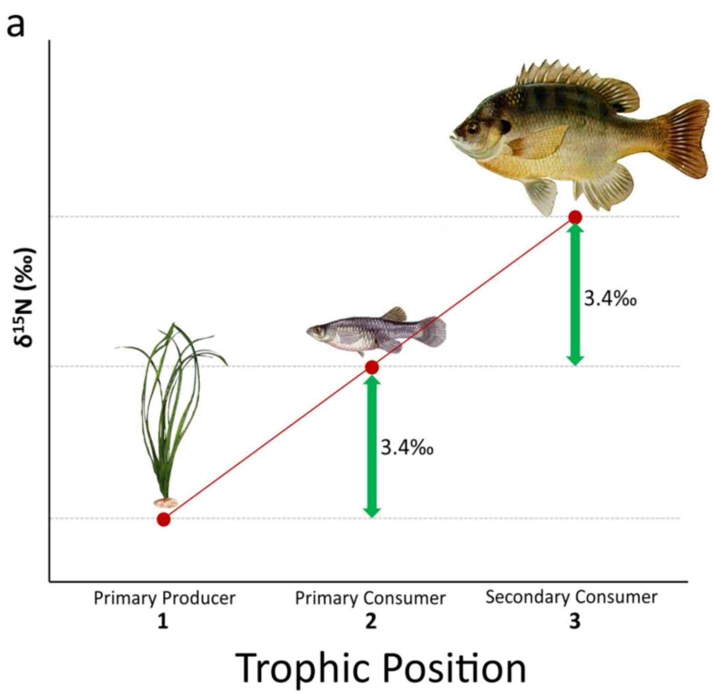
An example: Carbon isotope values



Hoffman: Preliminary Information-Subject to Revision. Not for Citation or Distribution.

- Each "type" of primary producer "harvests" CO_2 in its own way
  - A carbon isotope value
  - But sometimes they overlap
- CO_2 isotope values also change spatially/temporally
  - "isoscape"
- Nitrogen undergoes similar phenomenon but with quirks

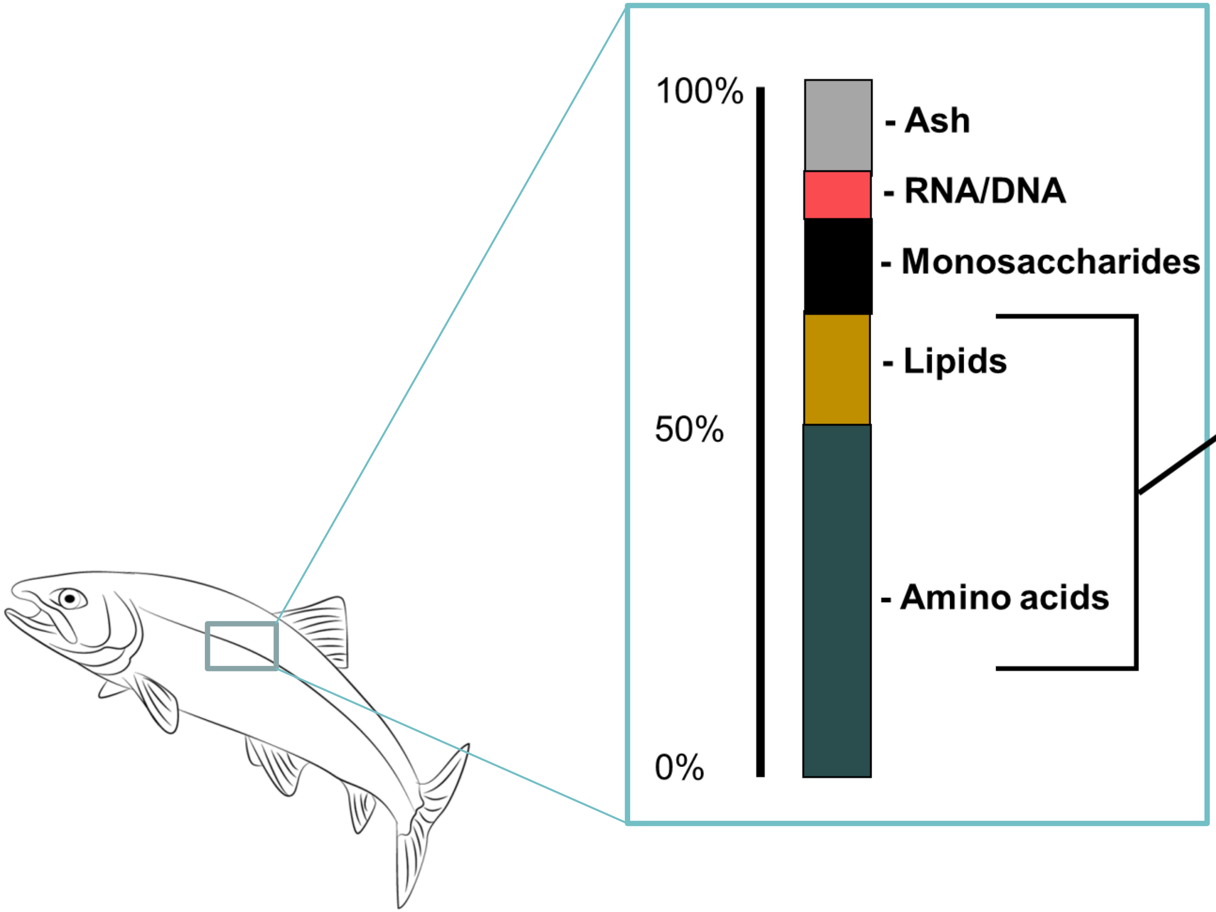
Nitrogen isotope values



- Nitrogen isotopes increase up the food chain
  - $\delta^{15}N$ can signal relative trophic position
- Together, delineate energy sources and pathways for this sampling design

Bowes and Thorp. Ecosphere 2015.

What comprises fish tissue?



Essential or “dietary”

-produced by primary organisms

Non-essential or “non-dietary”

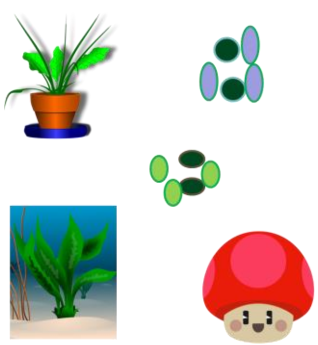
-synthesized by the organism

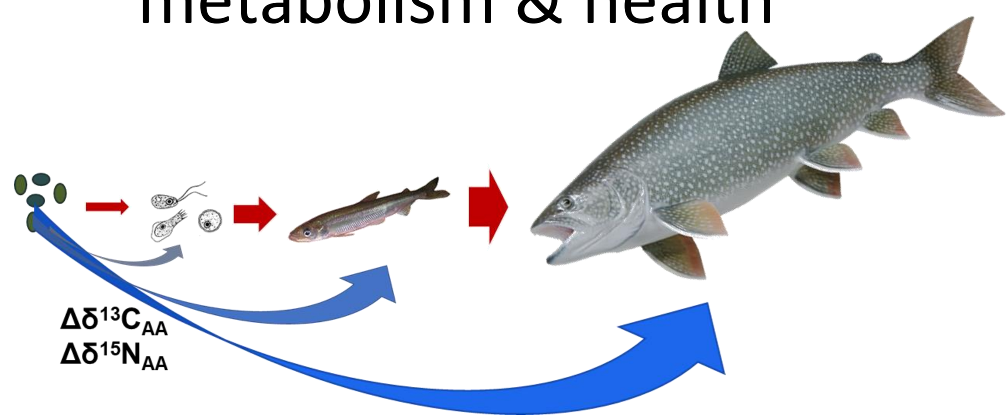
Essential or dietary

- Produced by novel machinery of primary producers
- Macromolecule integrity conserved in food web

Nonessential or non-dietary

- Biochemically reworked or synthesized directly
- Macromolecules can represent organism metabolism & health



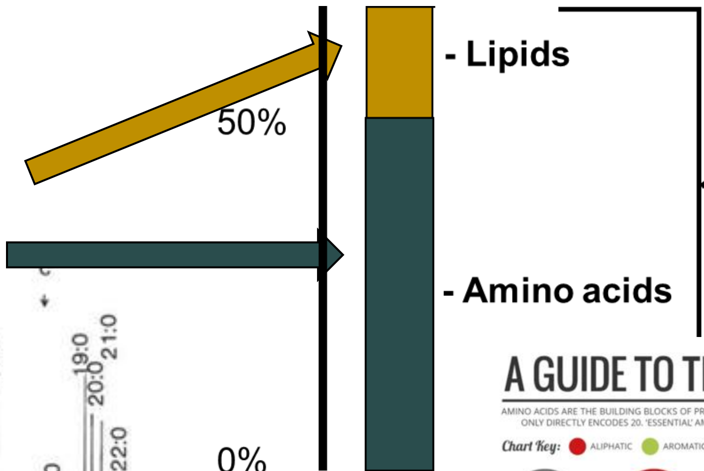


Extracting out the good stuff?

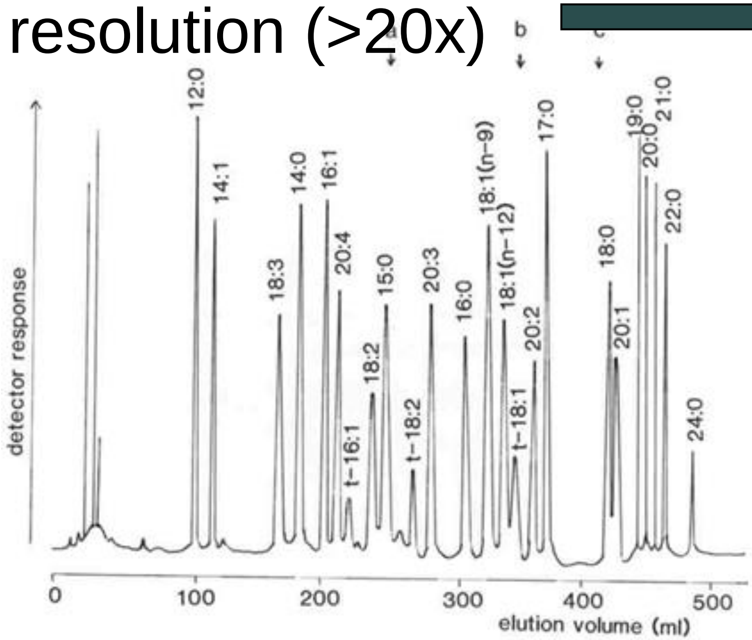
δ^2H & $\delta^{13}C$ values

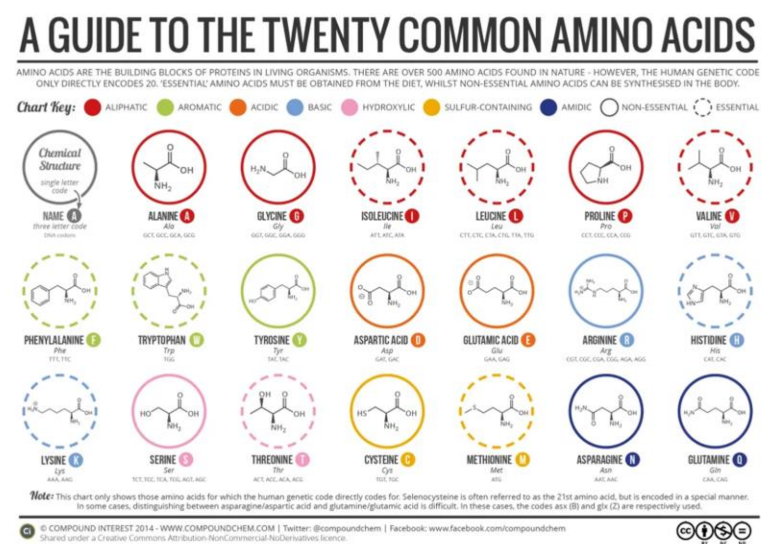
Omega-3s & 6s

More analytes = resolution (>20x)

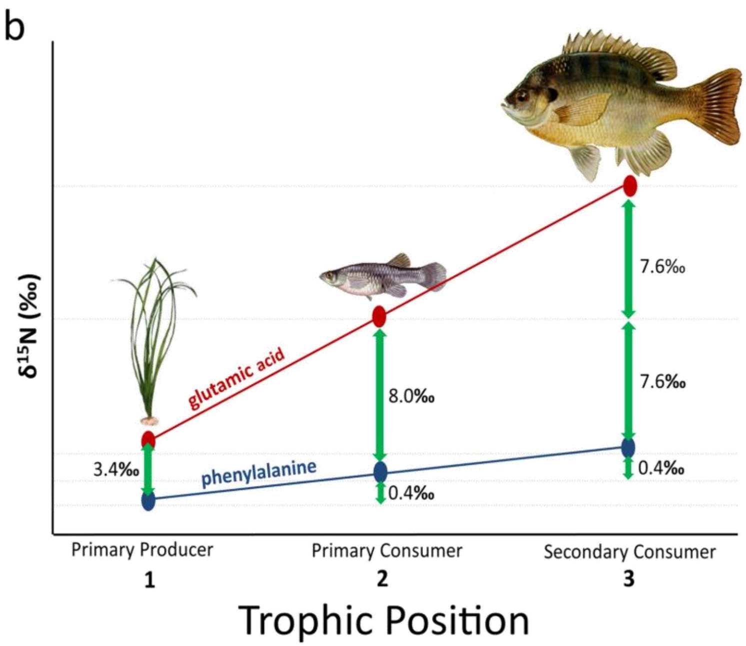


$\delta^{15}N$ & $\delta^{13}C$ values

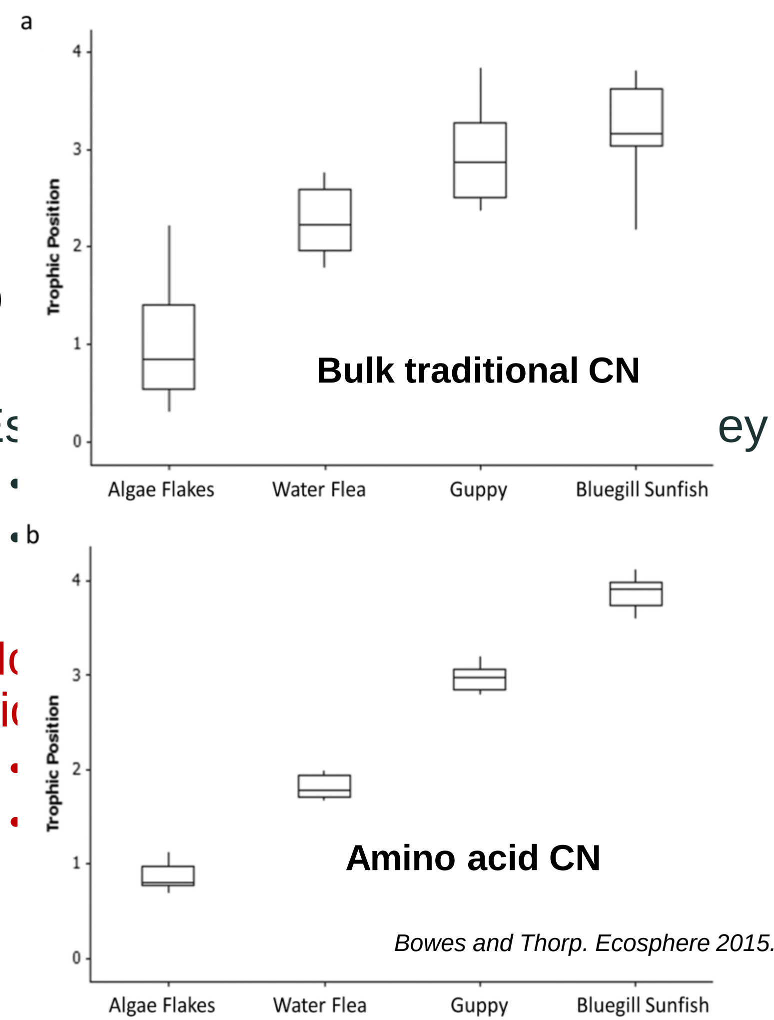




CN stable isotopes ratios in extracted amino acids

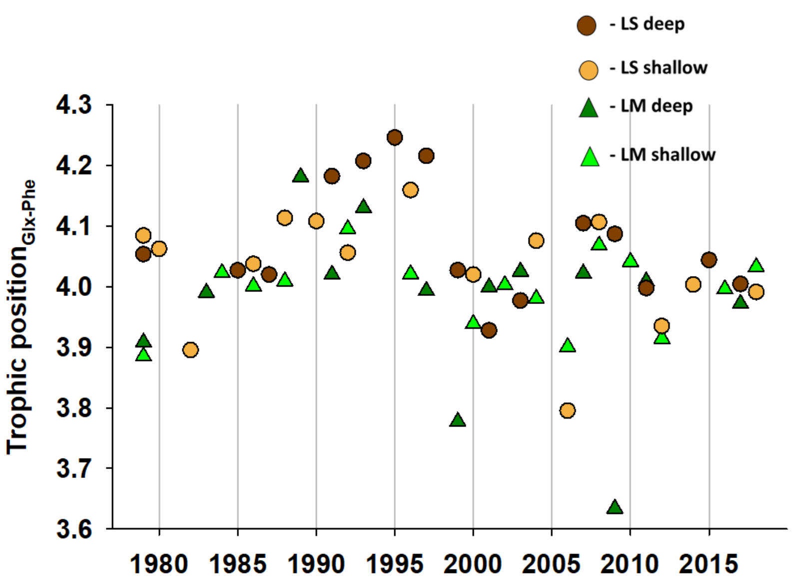


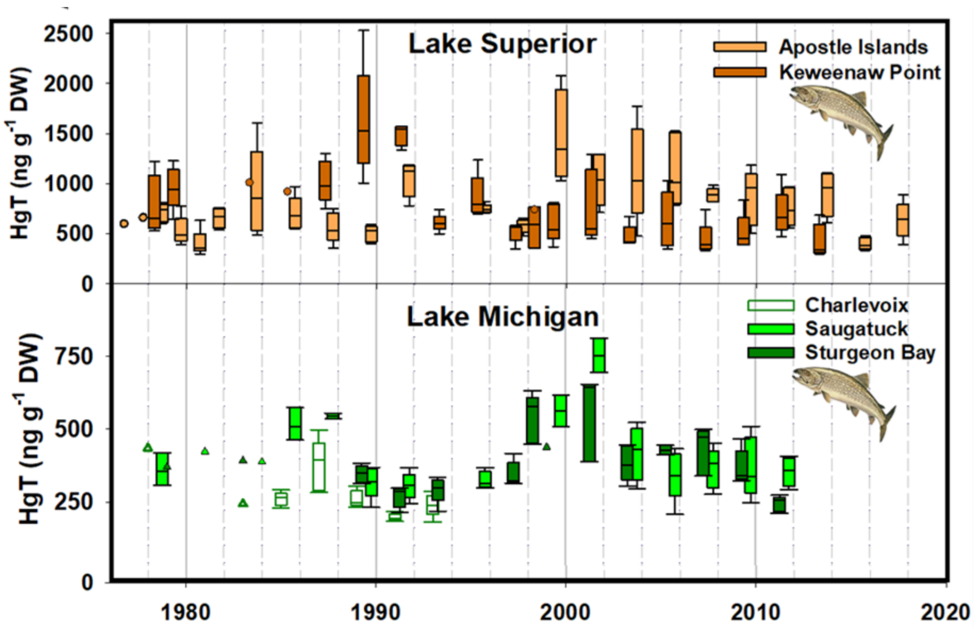
- Two
  - Es ... ey
- No bi



Bowes and Thorp. Ecosphere 2015.

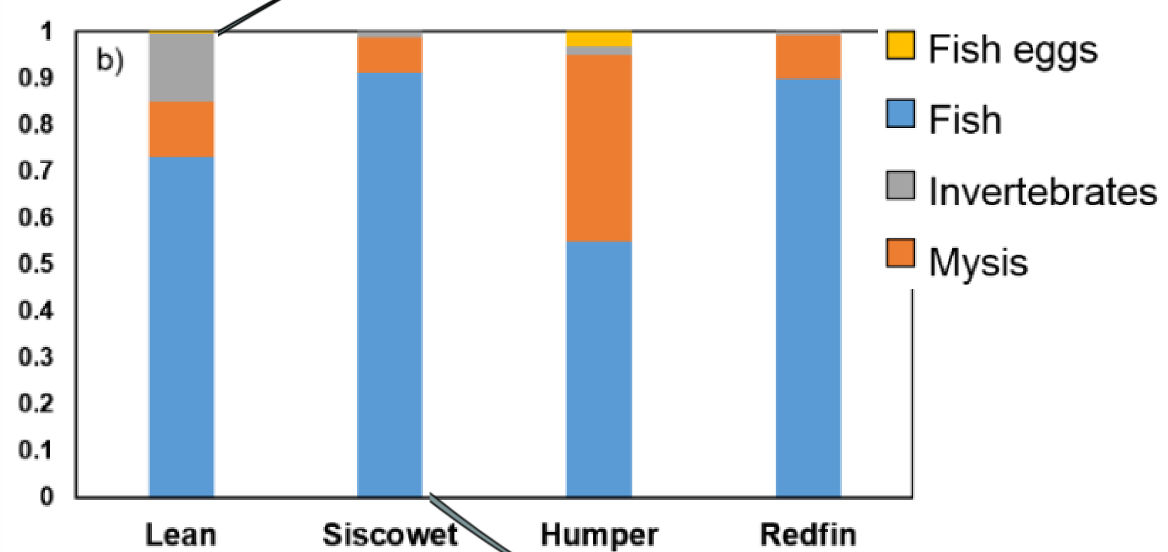
Amino acids - take away from preliminary work





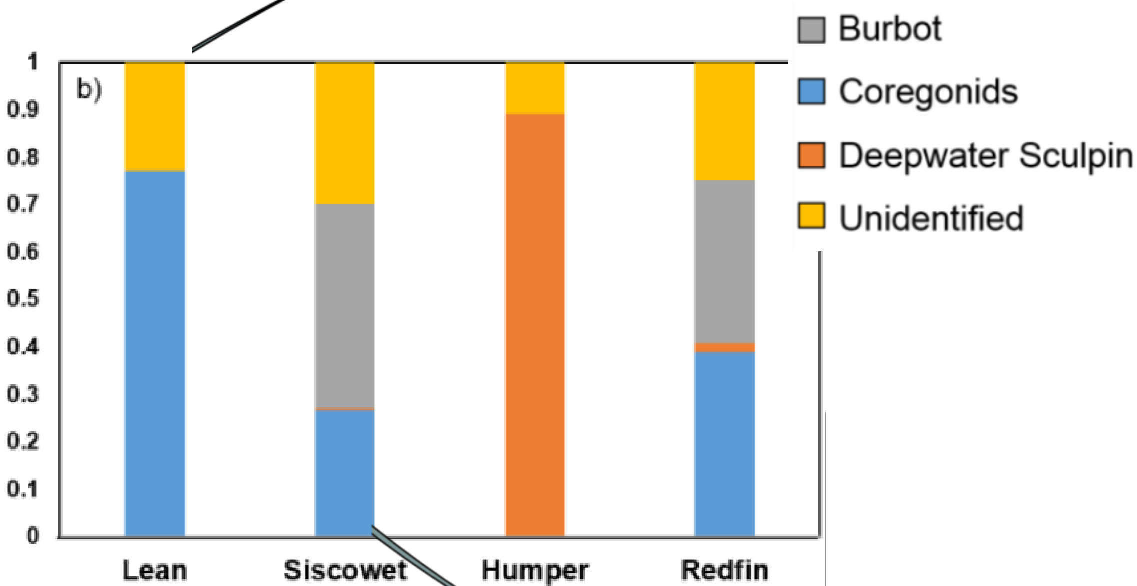
Preliminary Information-Subject to Revision. Not for Citation or Distribution.

Fish diets vary



Hoffman U. Waterloo (2017)

Fish diets vary



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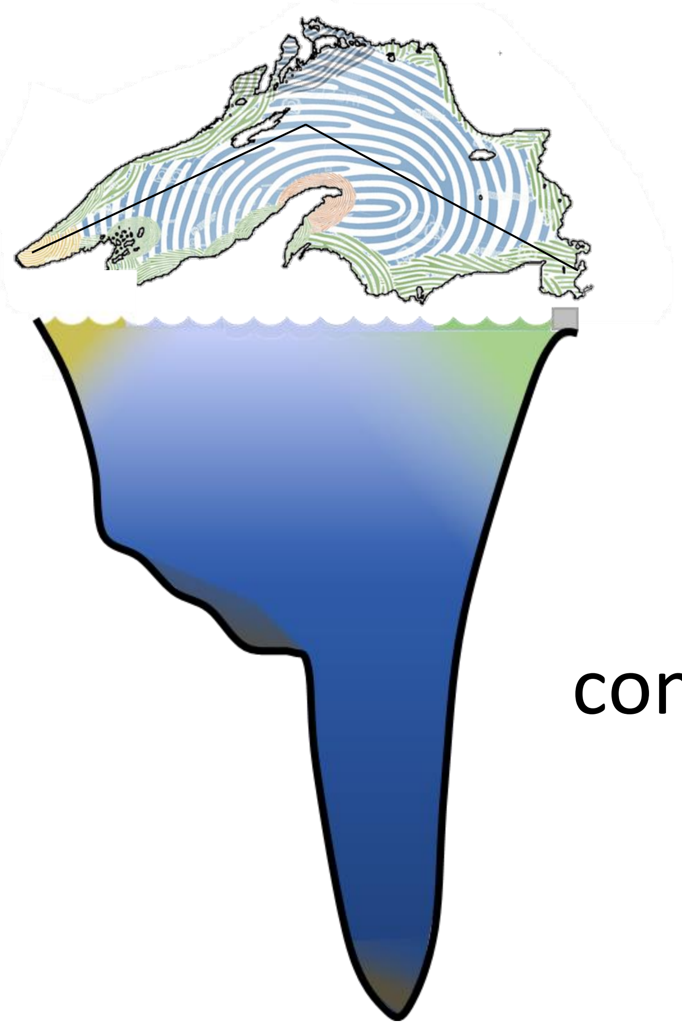

Fish habits vary

Fish habitats vary

and route of contaminant exposures do too

Scope of talk

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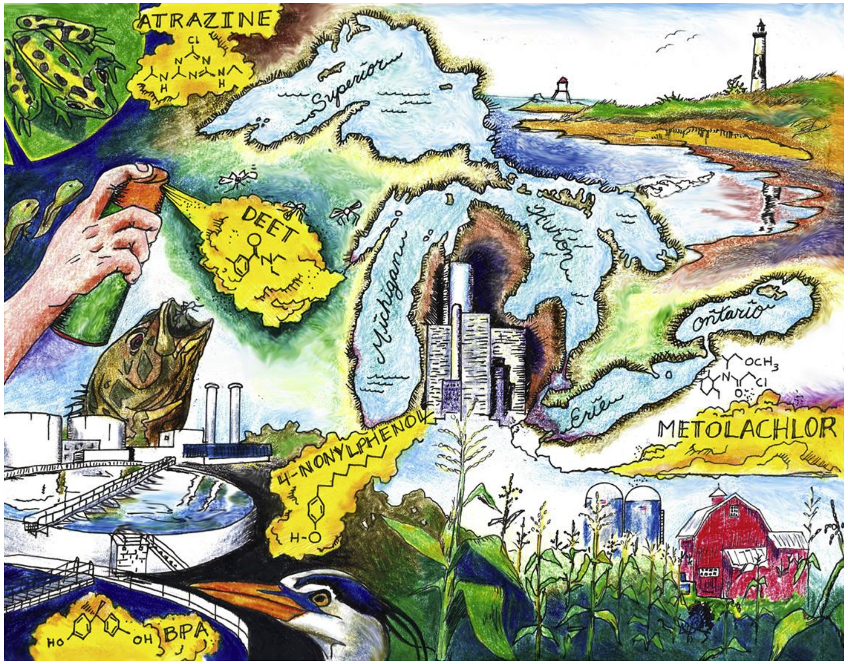
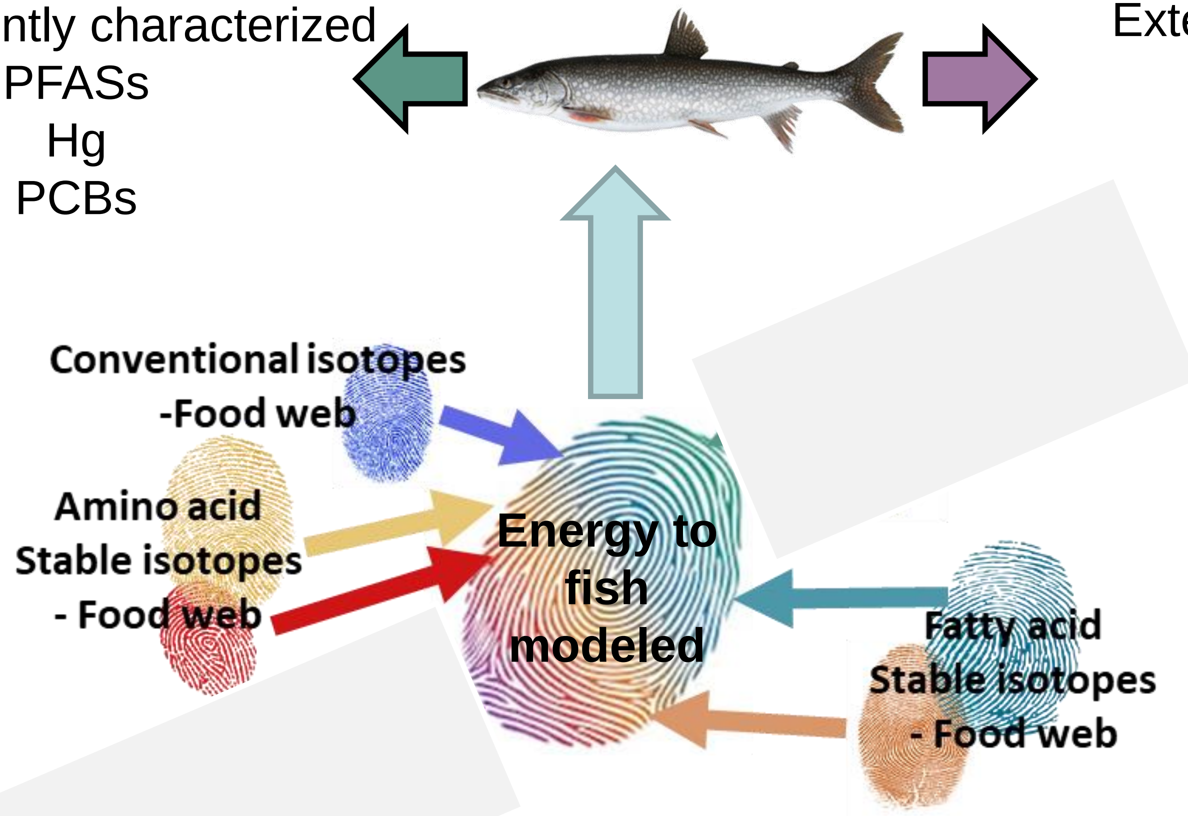


Food web energy transfer in Lake Superior to support contaminant research

Contaminant(s) “A”
Independently characterized
PFASs
Hg
PCBs

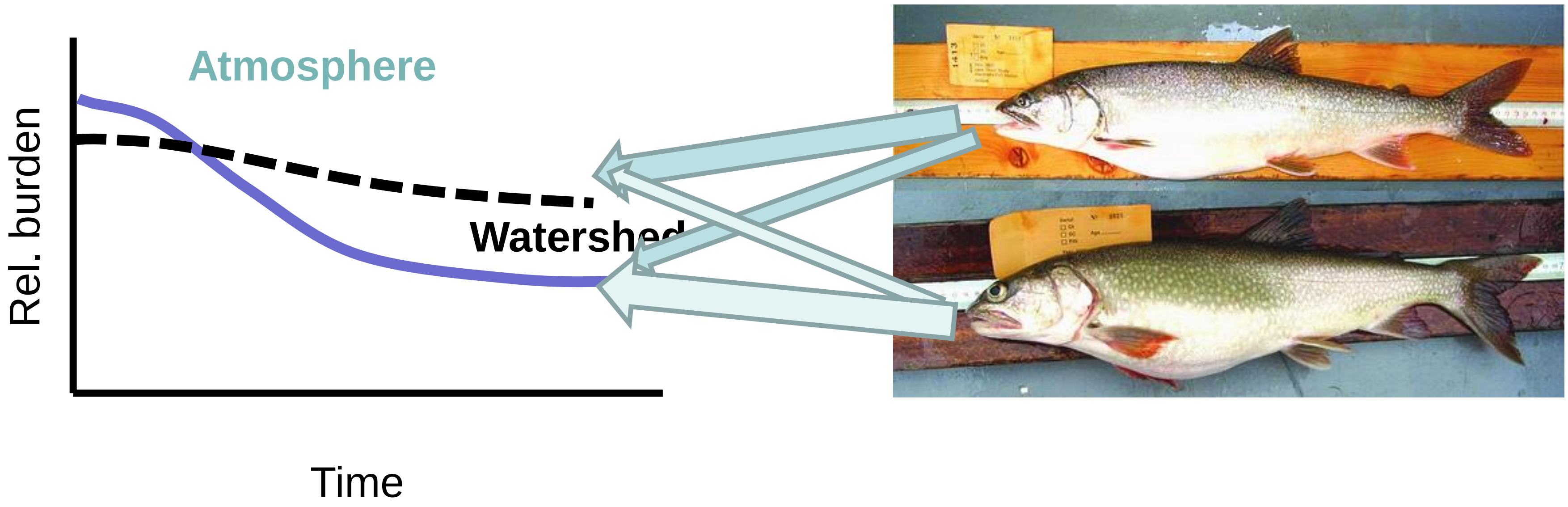
Contaminant(s) “B”
Extent of burden
PFASs
HBCDDs
Virus?



Hypothetical benefits

Contaminant work

- PFAS - burdens and delineation of the congeners of PFASs can be better understood
- Energetic coupling supports better understood food webs which support better understood contaminant trends in those complex scenarios (Hg, PFASs, etc)



Hypothetical benefits

Contaminant reconstructions

- PFAS reconstruction – temporal burdens and delineation of the congeners of PFASs can be better understood
- Energetic coupling supports better understood food webs which support better understood contaminant trends in those complex scenarios (Hg, PFASs, etc)

Forward looking values

- Fish health – Human health
  - Quantifying the amount of beneficial nutrients in fish and where they come from.
  - Closer linking markers of health, contaminants etc with habitat

Hypothetical benefits

Forward looking values

- Fish oddities – i.e. smelt
  - Understanding whether this is a habitat niche phenomenon – smelt diet or habitat preference facing toward PFAS concentrations spots (like surface layer)
  - Understanding whether smelt biochemistry (fatty acids) render them at enhance susceptibility to PFASs

NEW SMELT CONSUMPTION ADVISORY FOR LAKE SUPERIOR

ELEVATED LEVELS OF PFAS FOUND IN RAINBOW SMELT

Smelt "had PFOS concentrations of 24.1 to 118 with an average of 63.4 ppb", higher than multiple SLR fish that "did not warrant a change from current advisories." - 2021

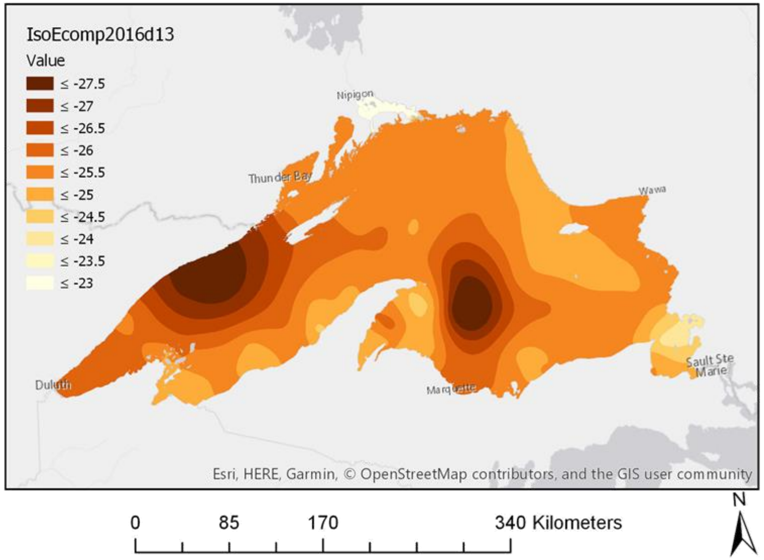
Scope of talk

- Problem
  - Contaminant inte[…] environment and […] spatial trends

What can be said of temporal trends?

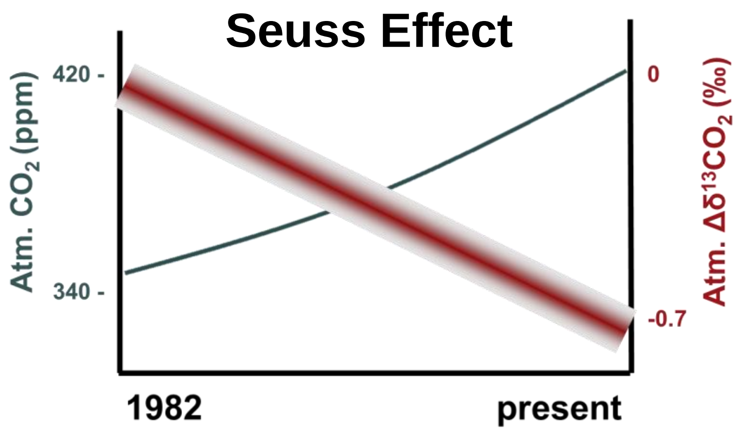
- New concepts/approaches
  - Biomarkers that hold potential to better understand aquatic ecosystems

- Preliminary finds
  - Unexpected excitement from data driven by basal level producers but measured in <u>fish</u>

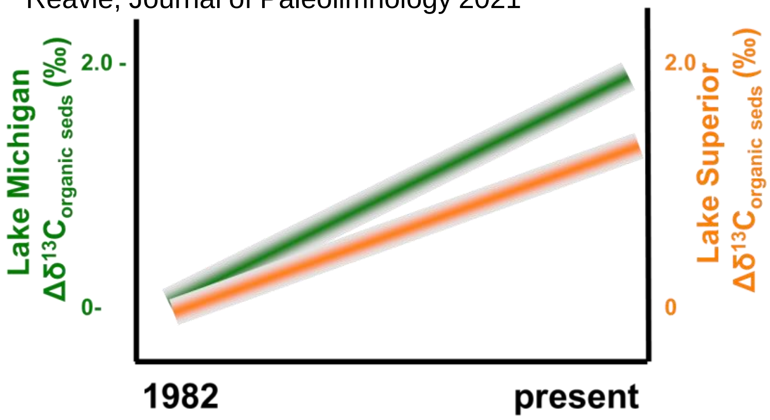


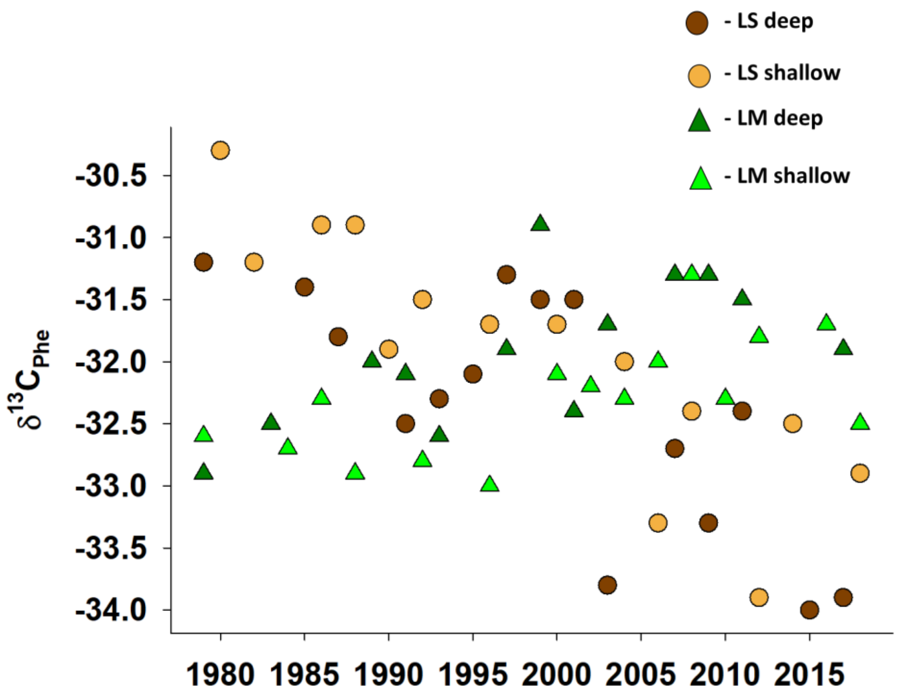
Basal - item C sources

Keeling, Science 1979



Reavie, Journal of Paleolimnology 2021





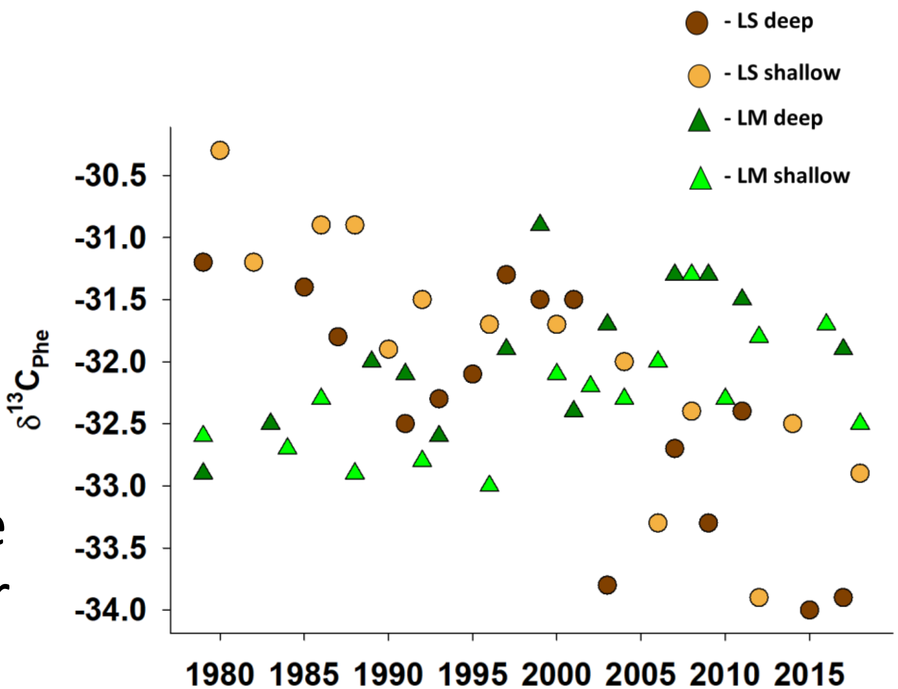
Preliminary Information-Subject to Revision. Not for Citation Distribution.

Basal - item C sources

- Surprising differences in values

  Lake Superior (-) Lake Michigan (+)

  - Carbon - traces physical lake or planktonic phenomena or habitat movement?



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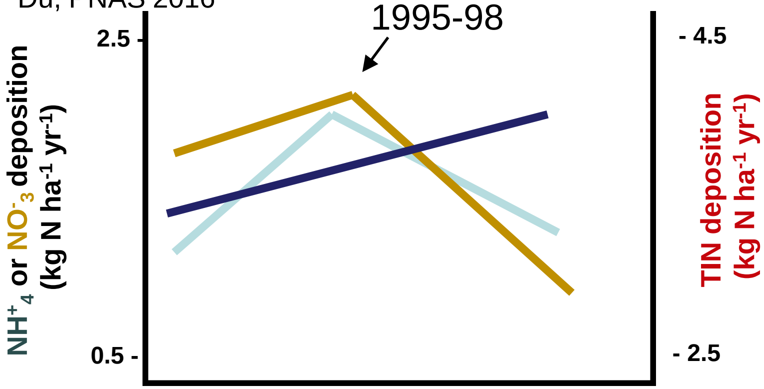
<u>**Basal**</u> - item N sources

Du, PNAS 2016



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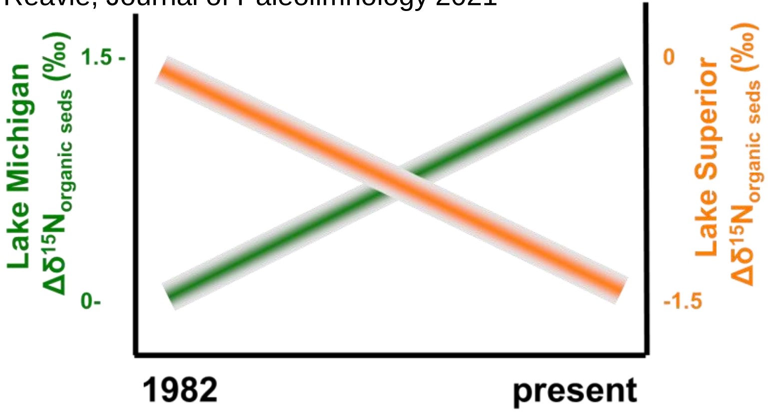

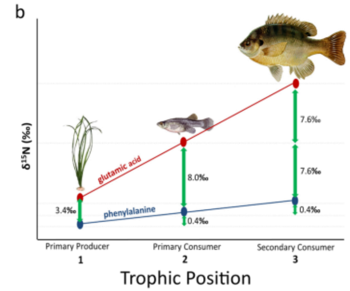

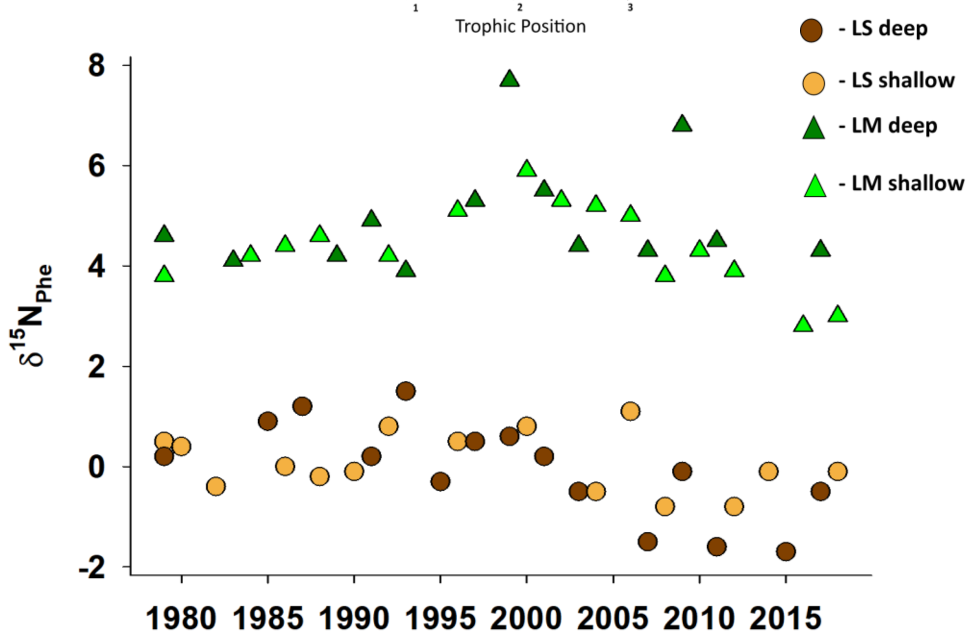

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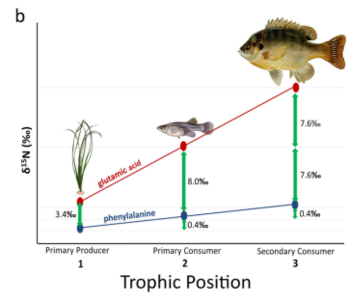
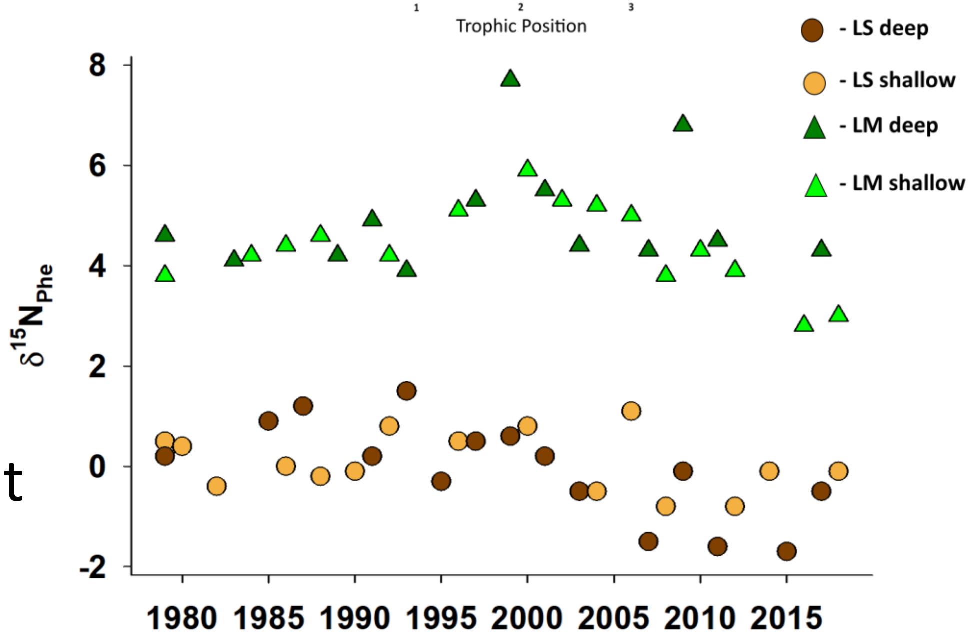
<u>Basal</u> - item N sources



- Surprising similarities in trend
  - Nitrogen - traces the incoming sources of nitrogen?
  - N cycles are quite different between lakes



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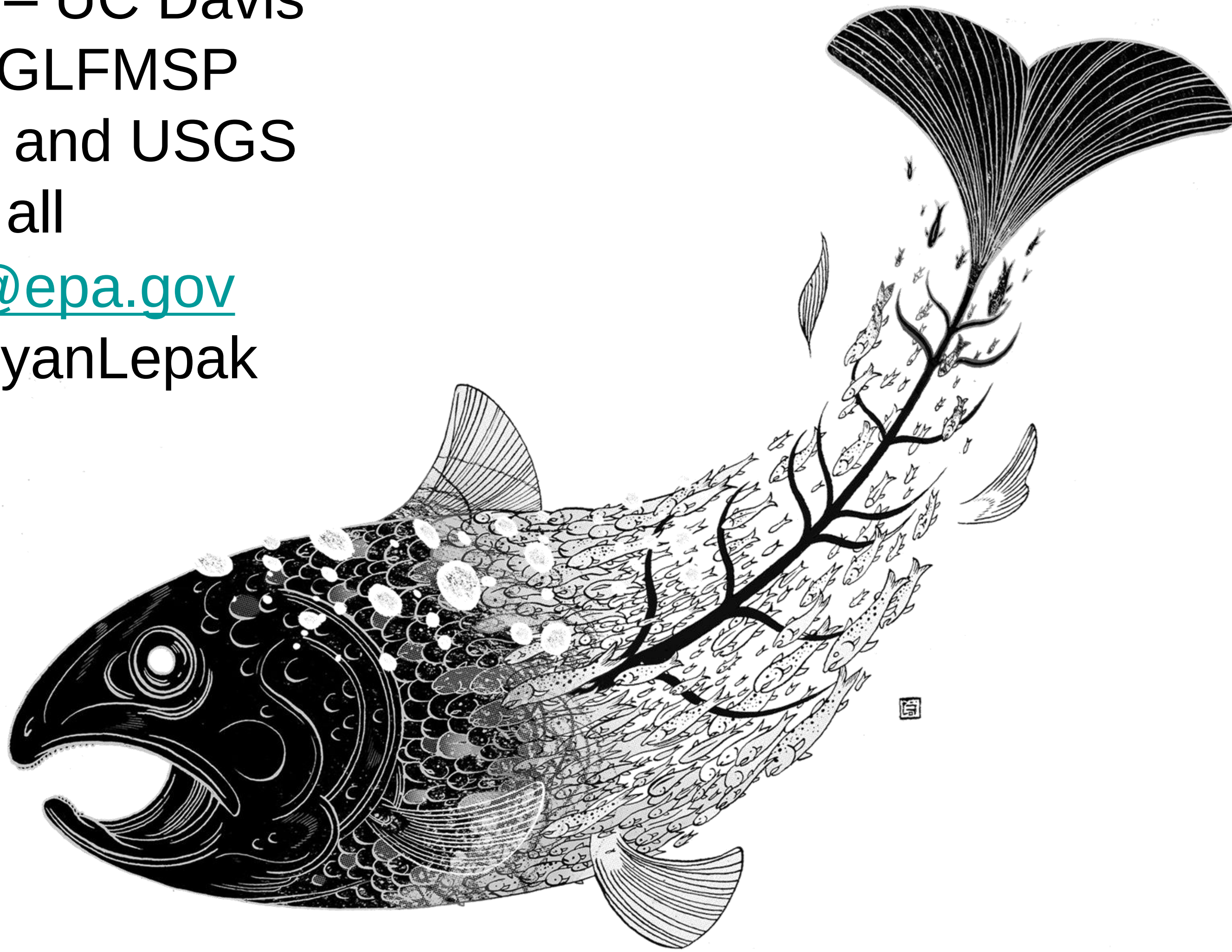
Thank you

Chris Yarnes – UC Davis
GLNPO & GLFMSP
UW Madison and USGS
You all

lepak.ryan@epa.gov
Twitter: @RyanLepak



• Mercury inputs

Sources

- Lake-lake coherence in $\delta^{202}Hg$ - response (and source)
- Increasing ~0.6 per mille, away from point/local source contamination