

Indicators of
Contaminant Mixtures
and Their Sources in an
Urbanized Watershed

Jonathan Behrens, Emily Bernhardt,
Lee Ferguson, Abigail Joyce, Brooke
Hassett

Duke University

SUSE6, May 2023

Duke

Challenge: 1000s of Contaminants Persist in US Waterways

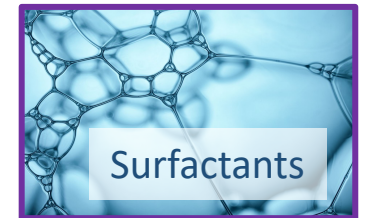
Land-Use

Stormwater

Wastewater

Non-Point Sources

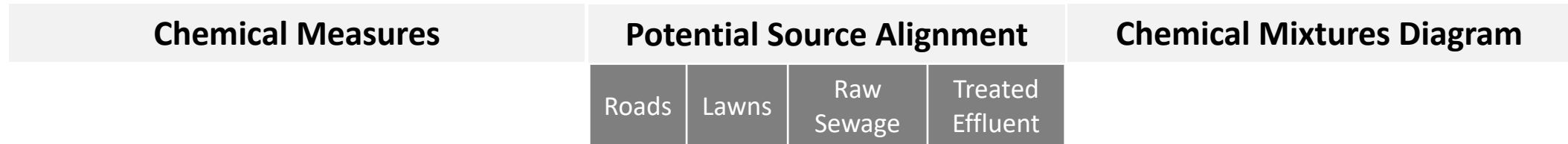
Point Sources



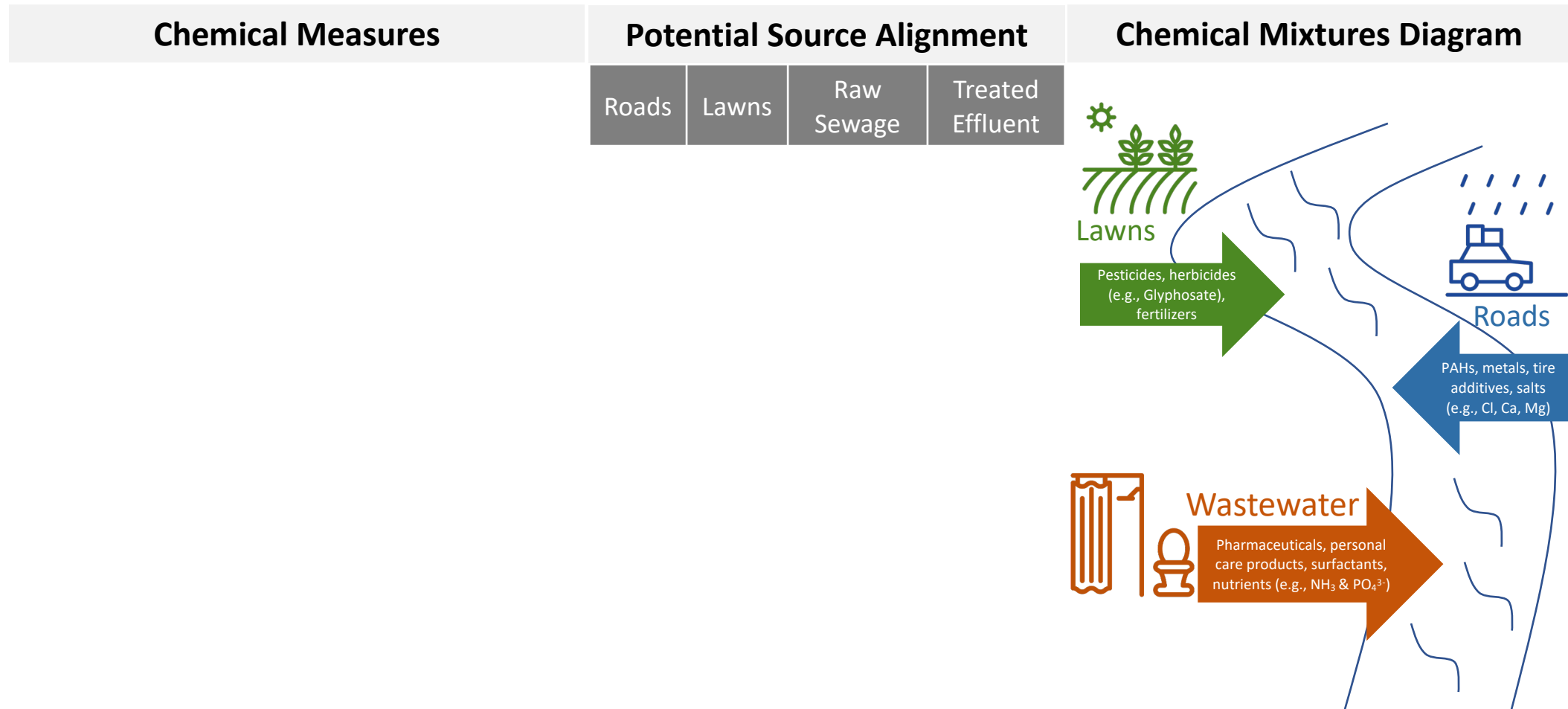
Masoner et al., 2019; "Urban Stormwater: An Overlooked Pathway of Extensive Mixed Contaminants..."

Focazio et al., 2008; "A National Reconnaissance for Pharmaceuticals and Other Organic Wastewater Contaminants in the US..."

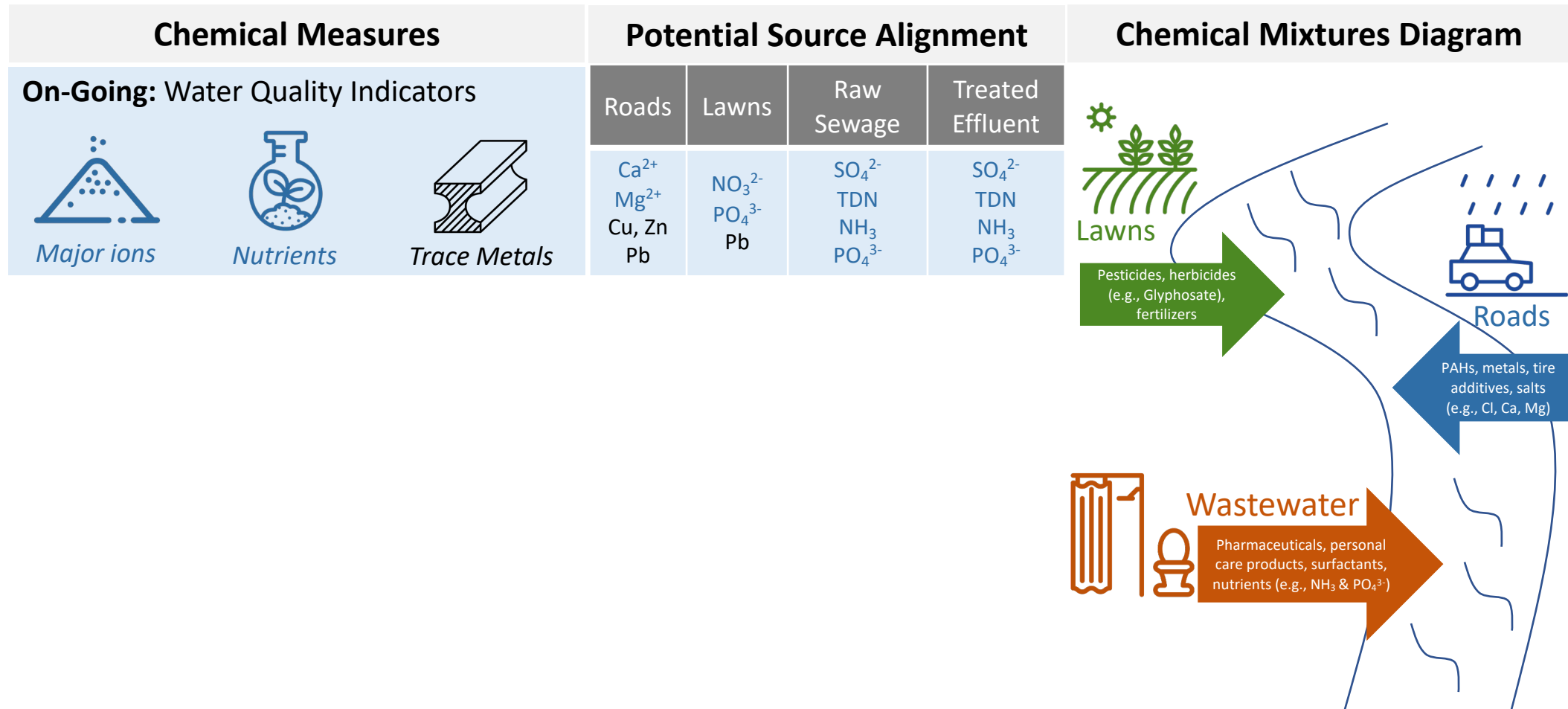
A Tiered Approach to Contaminant Mixture Analysis





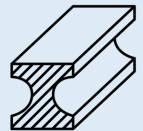
A Tiered Approach to Contaminant Mixture Analysis



A Tiered Approach to Contaminant Mixture Analysis



A Tiered Approach to Contaminant Mixture Analysis



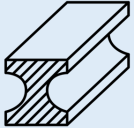
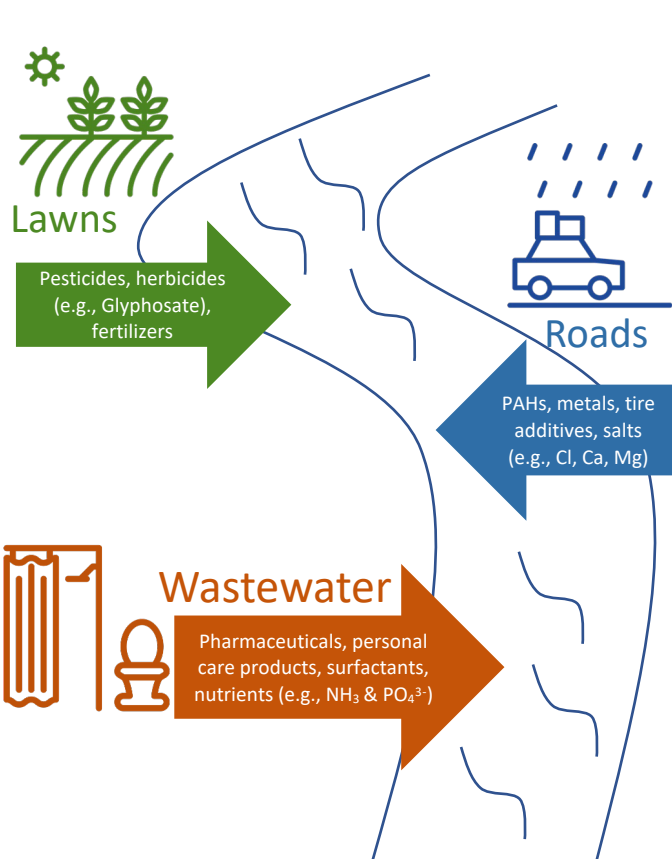






Chemical Measures	Potential Source Alignment				Chemical Mixtures Diagram
On-Going: Water Quality Indicators  <i>Major ions</i>  <i>Nutrients</i>  <i>Trace Metals</i>	Roads	Lawns	Raw Sewage	Treated Effluent	
	Ca^{2+} Mg^{2+} Cu, Zn Pb	NO_3^{2-} PO_4^{3-} Pb	SO_4^{2-} TDN NH_3 PO_4^{3-}	SO_4^{2-} TDN NH_3 PO_4^{3-}	
On-Going: Source-Specific Indicators					


Specific to a Source


Persistent in Environment


Relatively Low Toxicity

A Tiered Approach to Contaminant Mixture Analysis

Chemical Measures	Potential Source Alignment				Chemical Mixtures Diagram
<p>On-Going: Water Quality Indicators</p>  <p><i>Major ions</i></p>  <p><i>Nutrients</i></p>  <p><i>Trace Metals</i></p>	Roads	Lawns	Raw Sewage	Treated Effluent	
<p>On-Going: Source-Specific Indicators</p>  <p><i>Diphenyl guanidine</i></p>  <p><i>Glyphosate & AMPA</i></p>  <p><i>Sucralose</i></p>	DPG	Gly & AMPA	Sucralose	Sucralose	
<p>Planned: PFAS (“Forever Compounds”)</p>   	?	?	?	?	

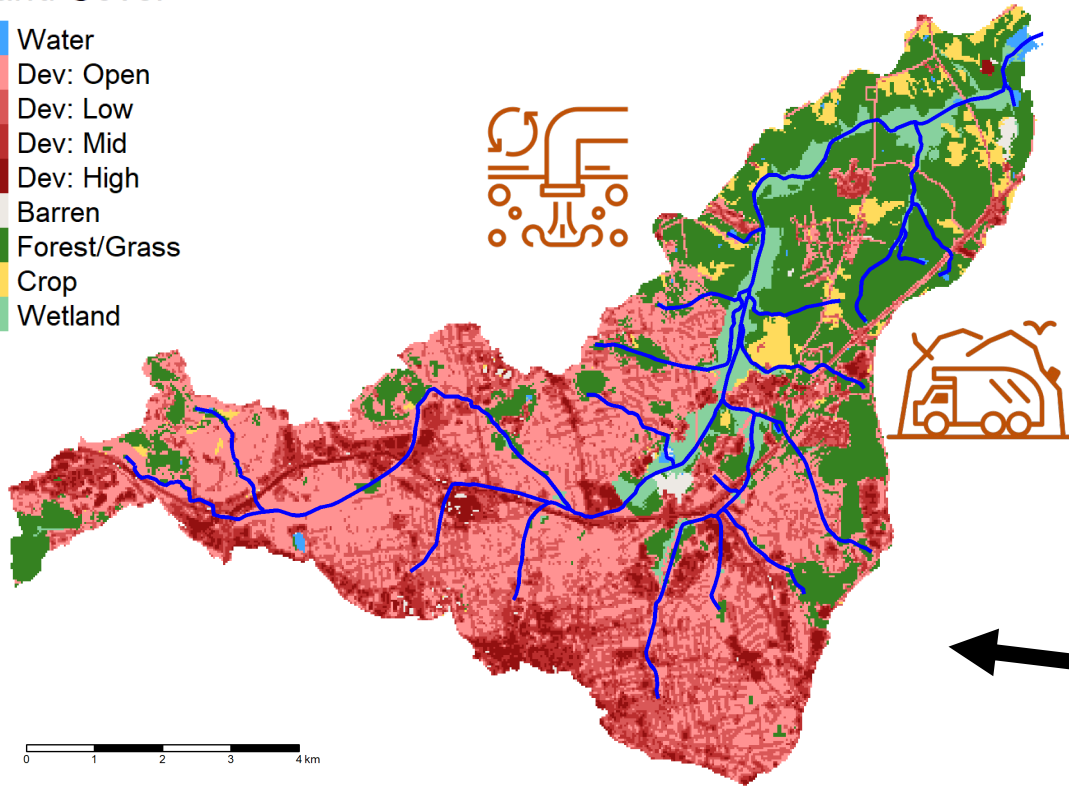
Site Selection: Ellerbe Creek & Tributaries



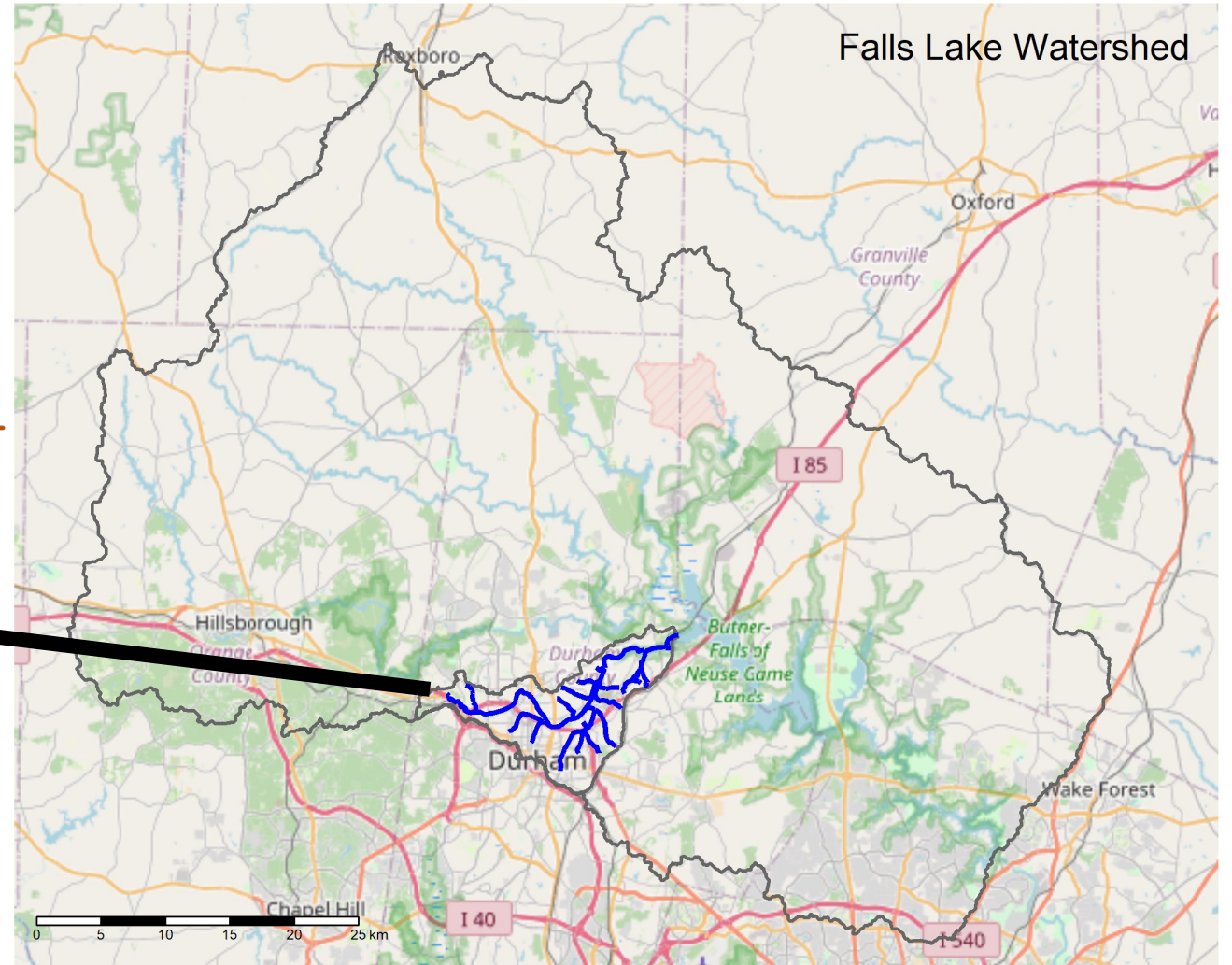
Site Selection: Ellerbe Creek & Tributaries

Land Cover

- Water
- Dev: Open
- Dev: Low
- Dev: Mid
- Dev: High
- Barren
- Forest/Grass
- Crop
- Wetland



~20mi²
(50km²)



Sample Collection: Water

Seasonal (4x) Baseflow Sampling (35 sites)

Biweekly Sampling (3 sites)

Sampling
Approach

Seasonal



Tributaries



Main Branch



Great opportunity for community science!

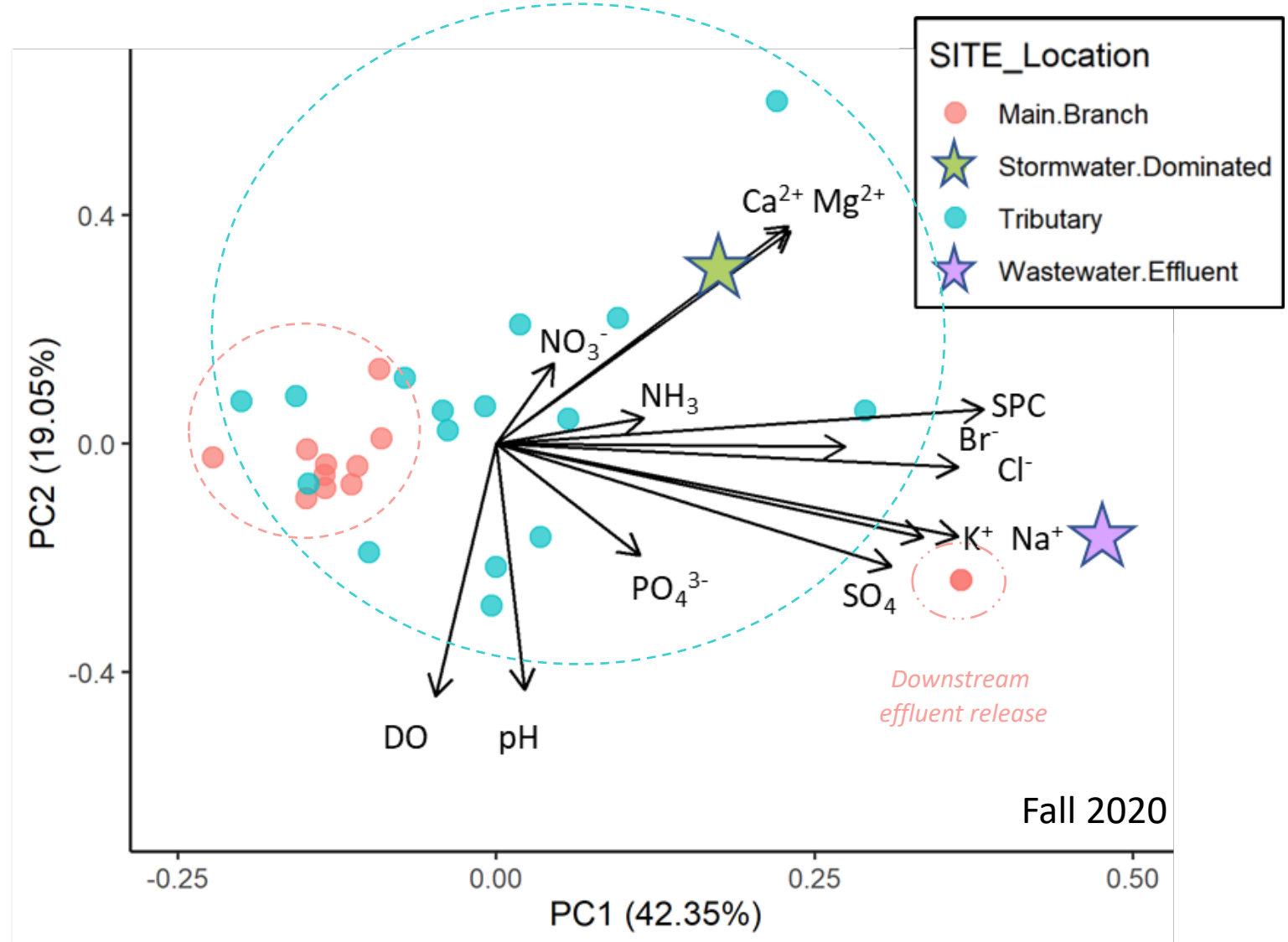
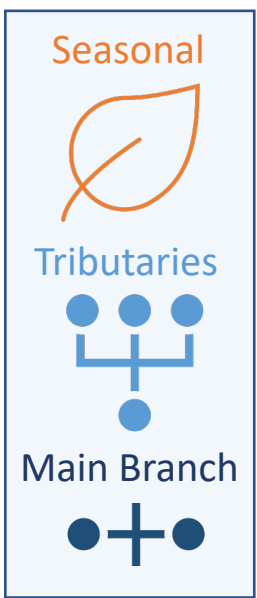
Research Questions

1. *How do chemical mixture indicators vary across an urban watershed?*
2. *What point and non-point (sub-watershed landcover attributes) predict variation in associated contaminant signature?*



Heterogeneous Loading of “Low-Cost” Indicators

Sampling Approach





Indicator 1: Sucralose (Wastewater)

Sampling Approach

Seasonal



Tributaries



Main Branch



62%

Detection





Indicator 1: Sucralose (Wastewater)

Sampling Approach

Seasonal



Tributaries

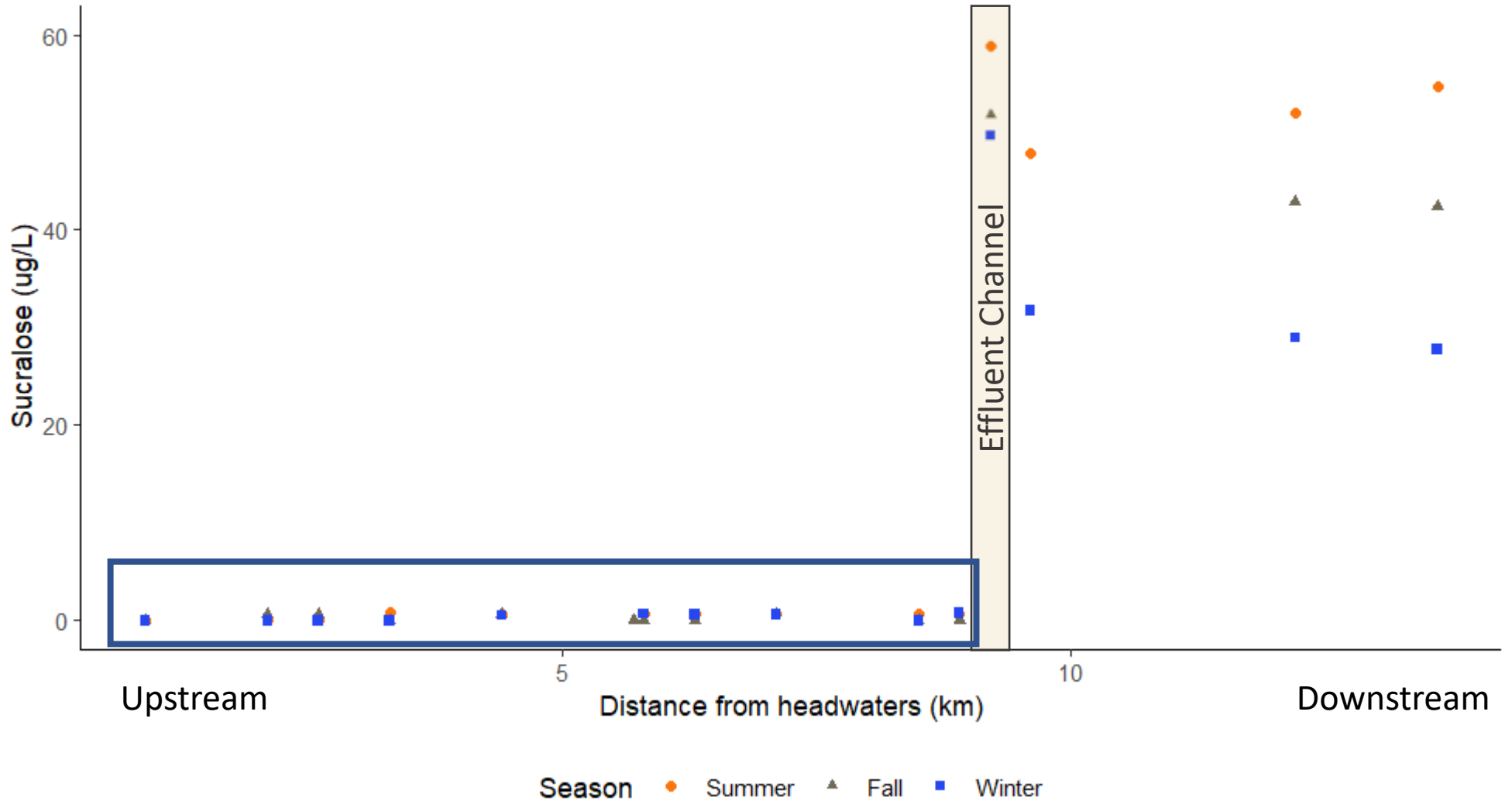


Main Branch



62%

Detection

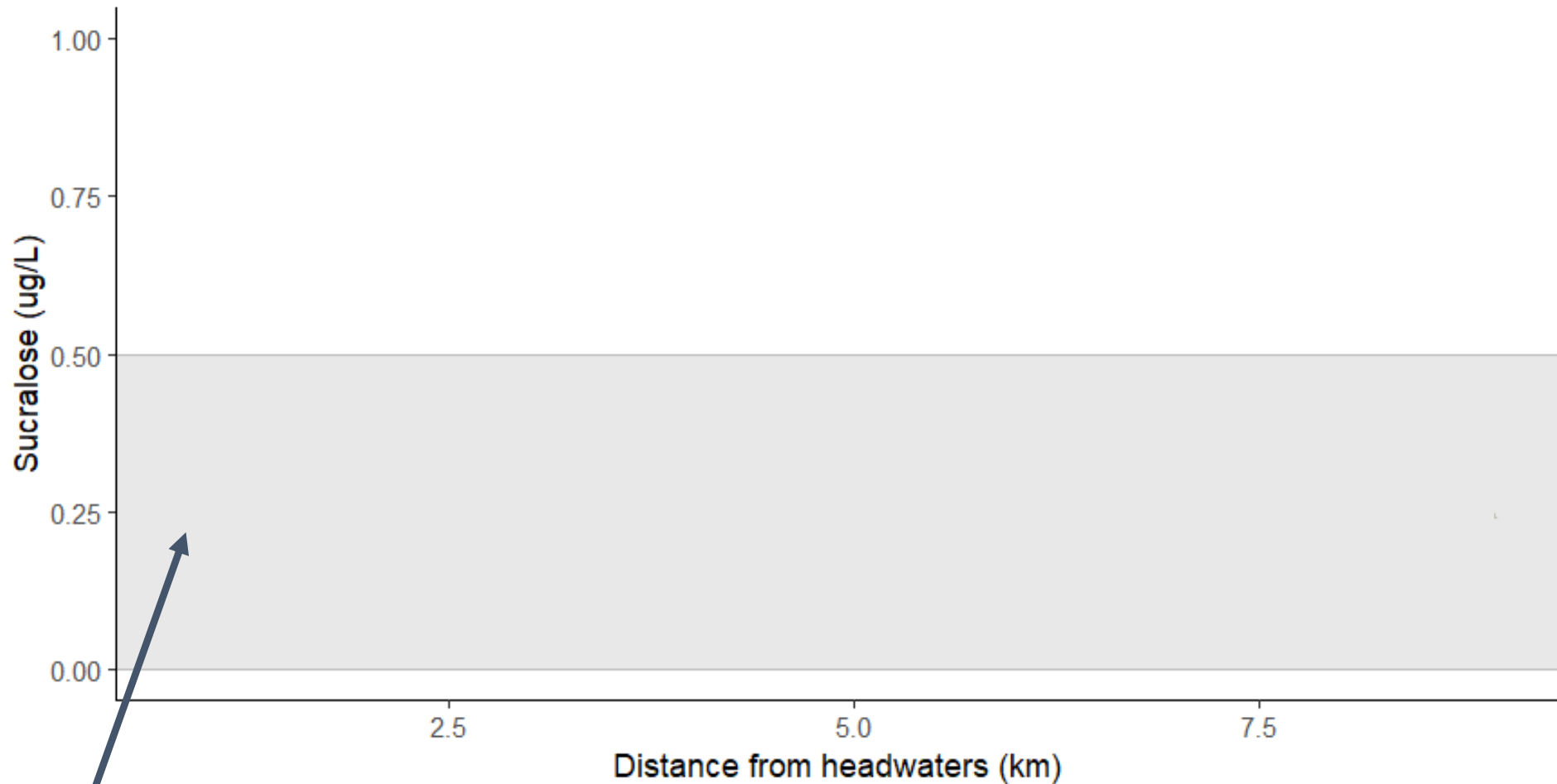




Sucralose

Indicator 1: Sucralose (Wastewater)

Values below detection are depicted at 1/2 detection limit for visualization



Sampling Approach

Seasonal



Tributaries



Main Branch



52%

Detection

Season ● Summer ▲ Fall ■ Winter



Sucralose

Indicator 1: Sucralose (Wastewater)

Values below detection are depicted at 1/2 detection limit for visualization

Sampling Approach

Seasonal



Tributaries

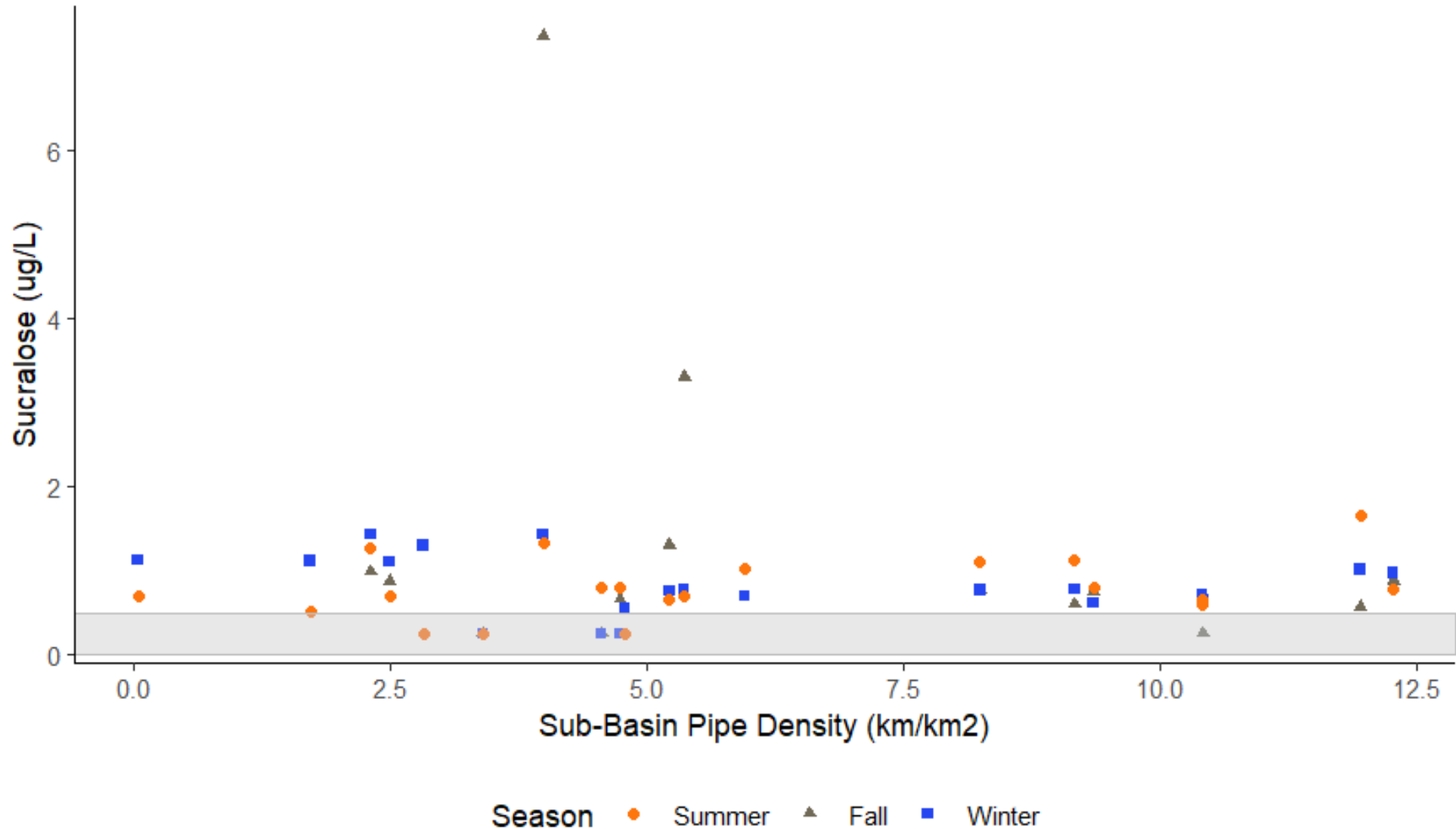


Main Branch



74%

Detection



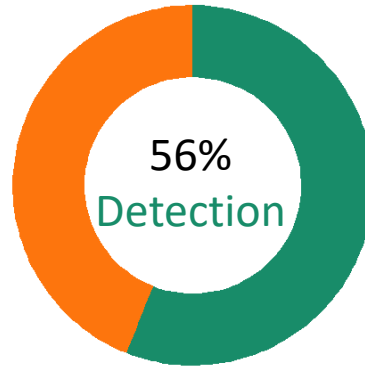
Indicator 2: Glyphosate & AMPA (Lawncare)

Main Branch

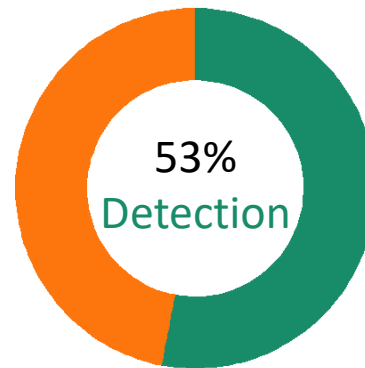
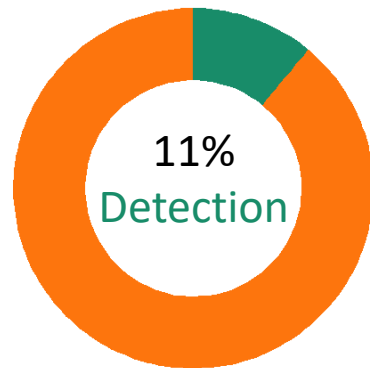

Glyphosate



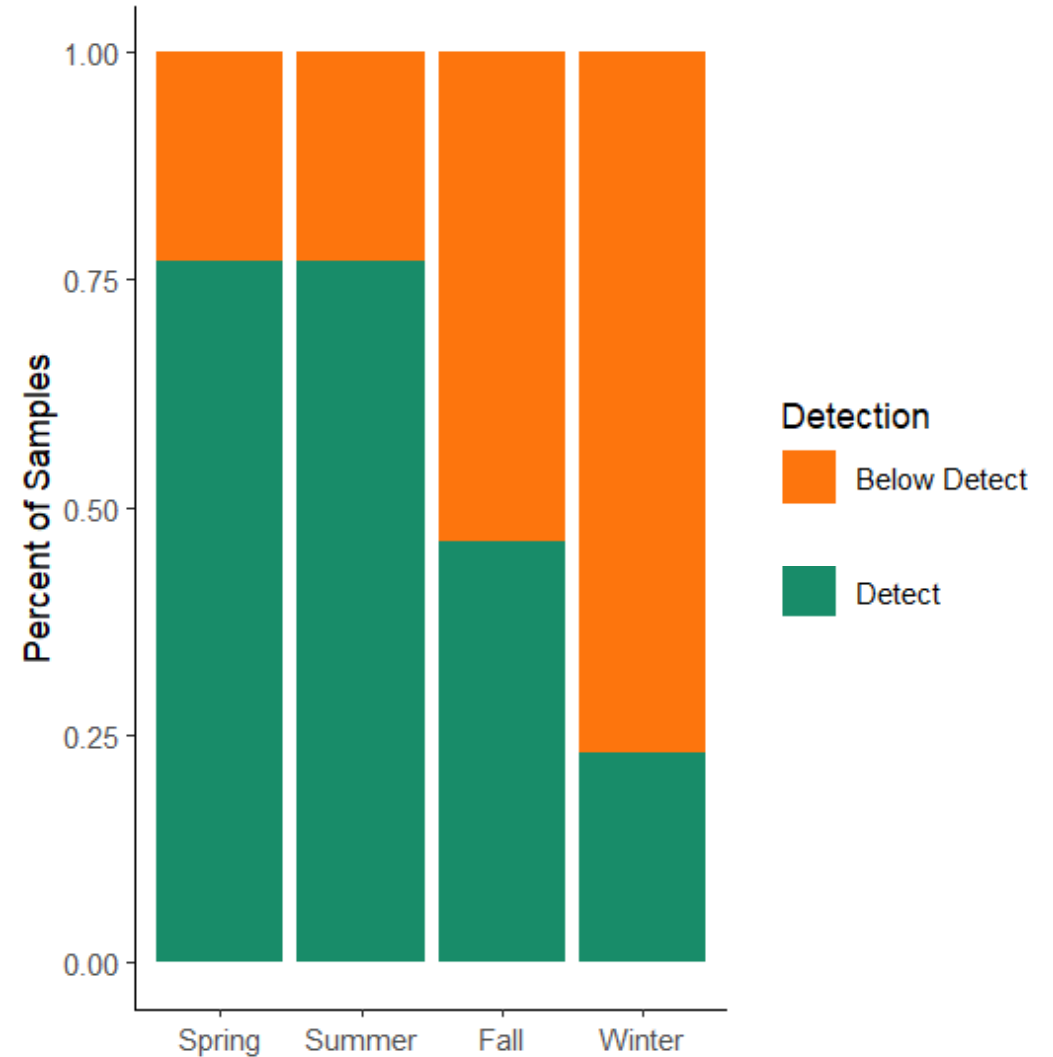
AMPA



Tributaries

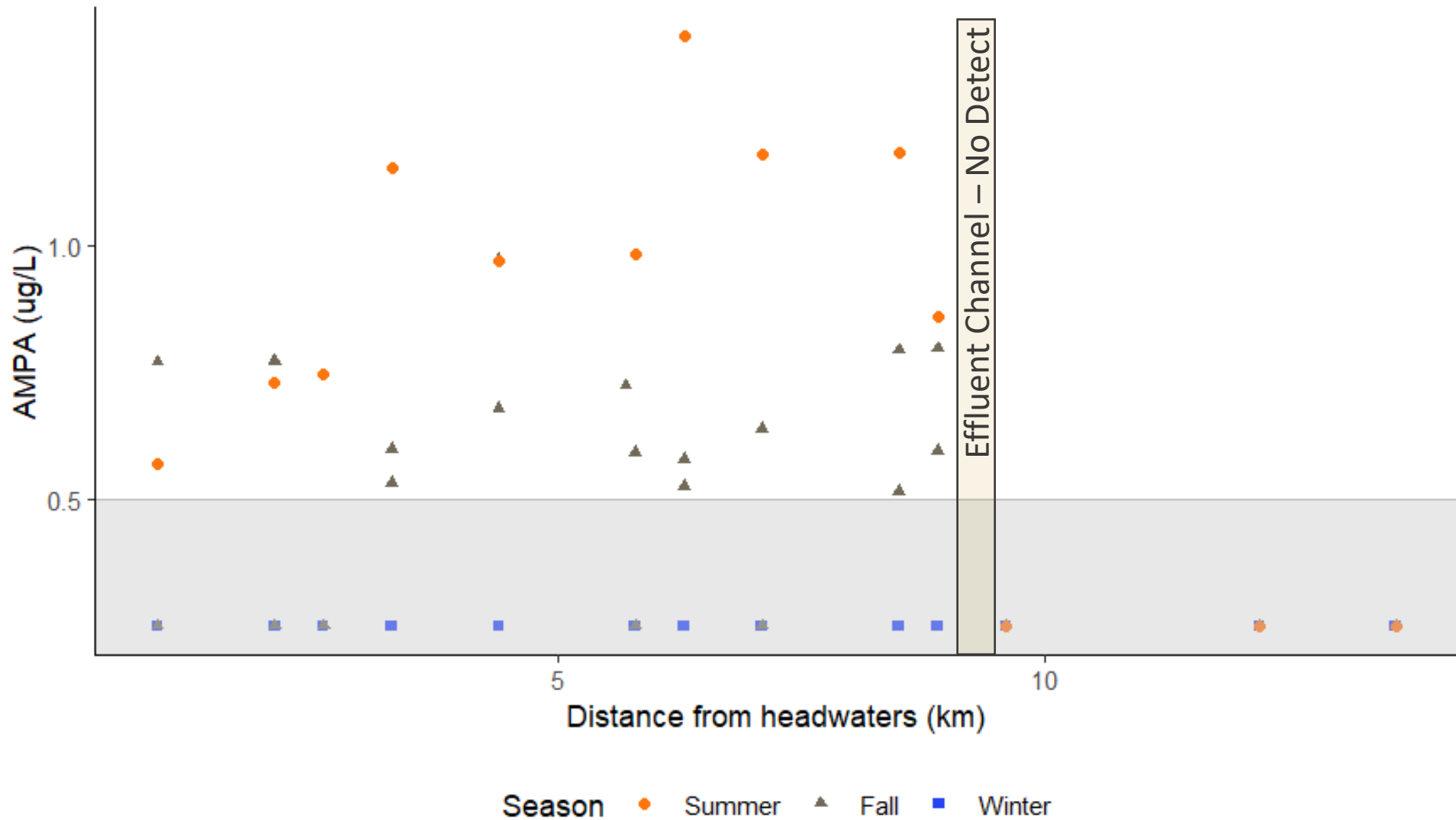



Detection of AMPA: Main Branch



Indicator 2: AMPA (Lawncare)

Values below detection are depicted at 1/2 detection limit for visualization

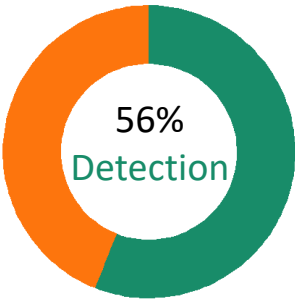


Sampling Approach

Seasonal

Tributaries

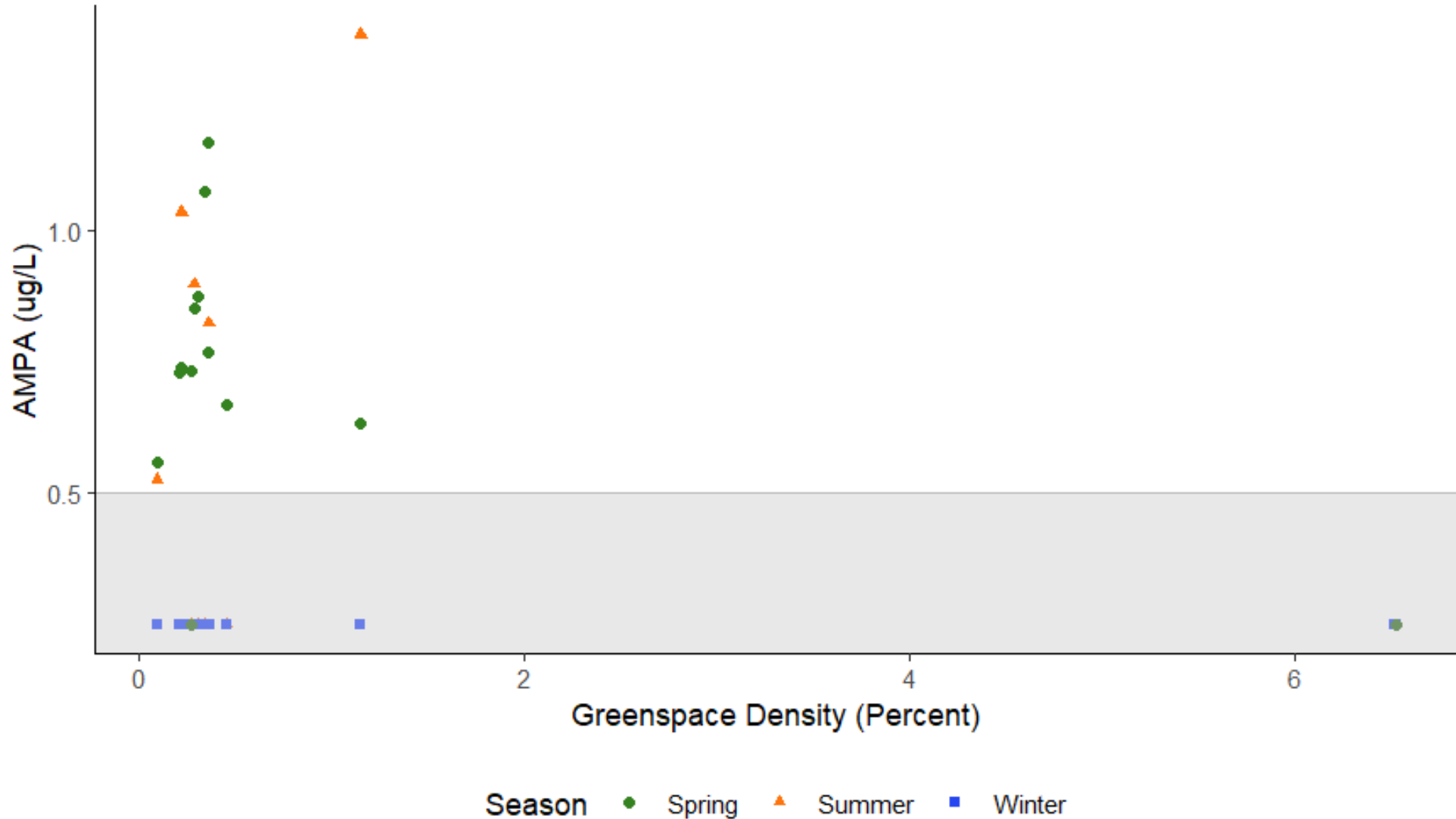
Main Branch



Season ● Summer ▲ Fall ■ Winter

Indicator 2: AMPA (Lawncare)

Values below detection are depicted at 1/2 detection limit for visualization

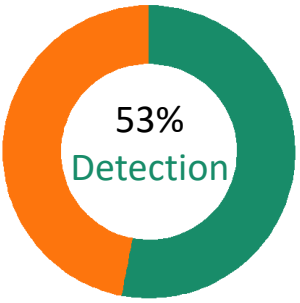


Sampling Approach

Seasonal

Tributaries

Main Branch





Diphenyl guanidine

Indicator 3: Diphenyl Guanidine (Roads)

Sampling Approach

Seasonal



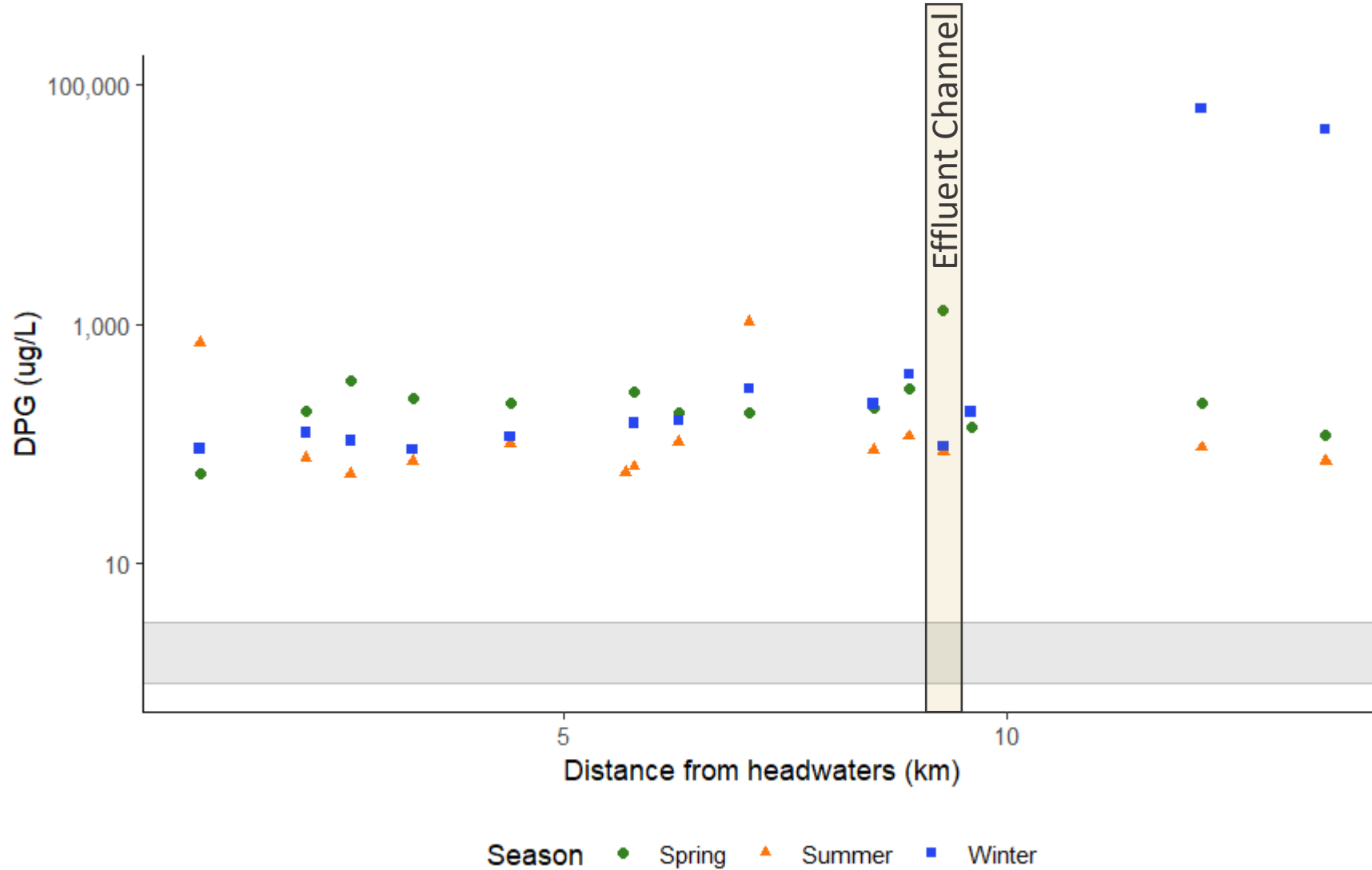
Tributaries



Main Branch



100%
Detection





Diphenyl guanidine

Indicator 3: Diphenyl Guanidine (Roads)

Sampling Approach

Seasonal



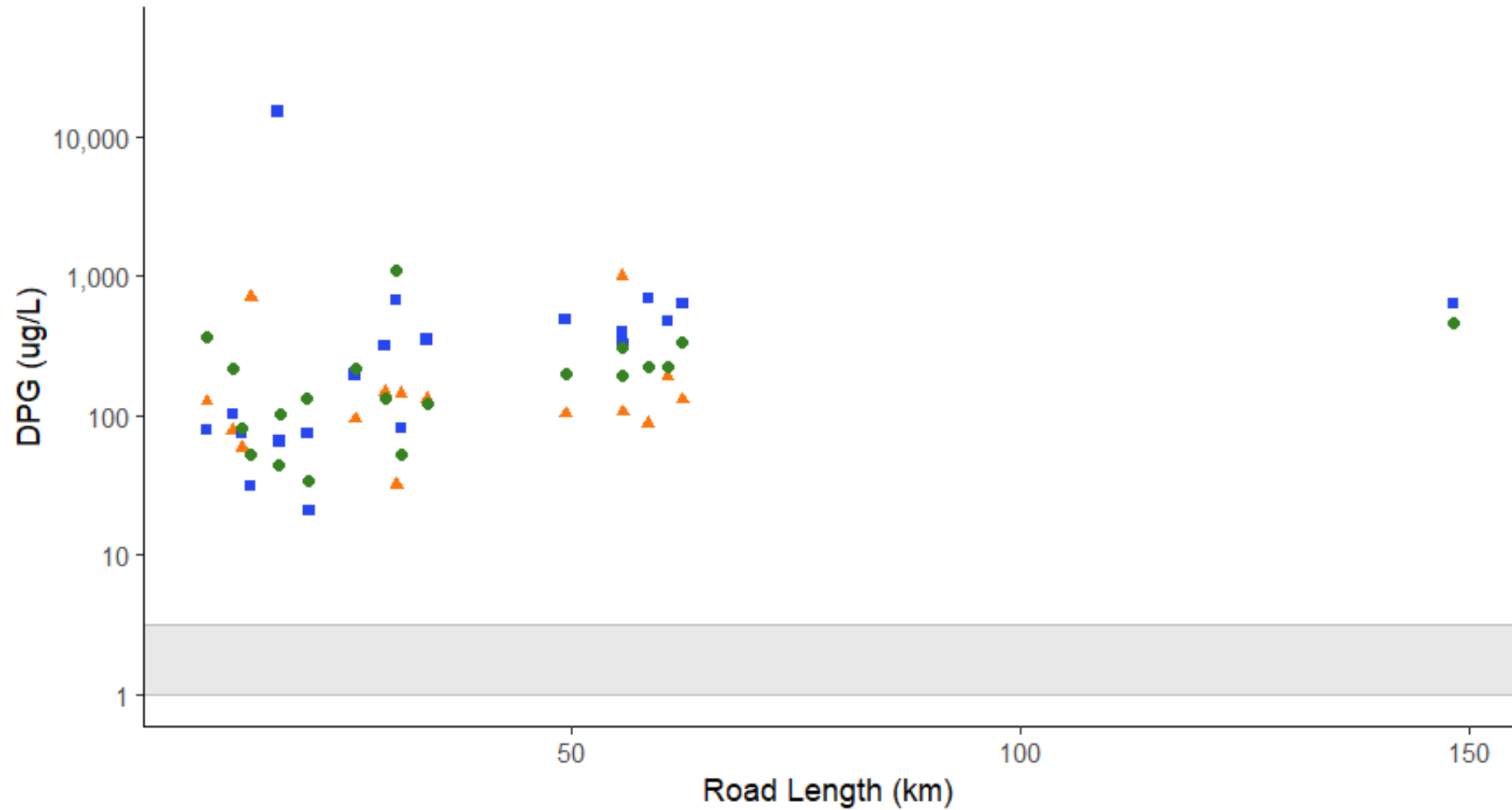
Tributaries



Main Branch



100%
Detection



Season ● Spring ▲ Summer ■ Winter

Conclusion & Next Steps

Chemical Measures

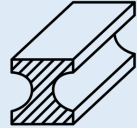
On-Going: Water Quality Indicators



Major ions



Nutrients



Trace Metals

On-Going: Source-Specific Indicators



Sucralose



Glyphosate
& AMPA



Diphenyl
guanidine

Planned: PFAS (“Forever Compounds”)



Main Findings

Tributaries:

- Non-point sources likely drive heterogeneity in mixtures

Main Branch:

- Point source drives main variation

Drivers of Variation:

- Sucralose: Infrastructure (non-point) & WWTP (point)
- AMPA: Seasonality & greenspace density
- DPG: Infrastructure

**Outliers indicate interesting multi-variate landscape processes!*

Forthcoming!

Research Team & Funders

Collaborators



Emily Bernhardt



Lee Ferguson



Abigail Joyce



Brooke Hassett



Bass Student Researchers

Funding



Questions?



Contact:
jrb146@duke.edu
@Jonny_Behrens

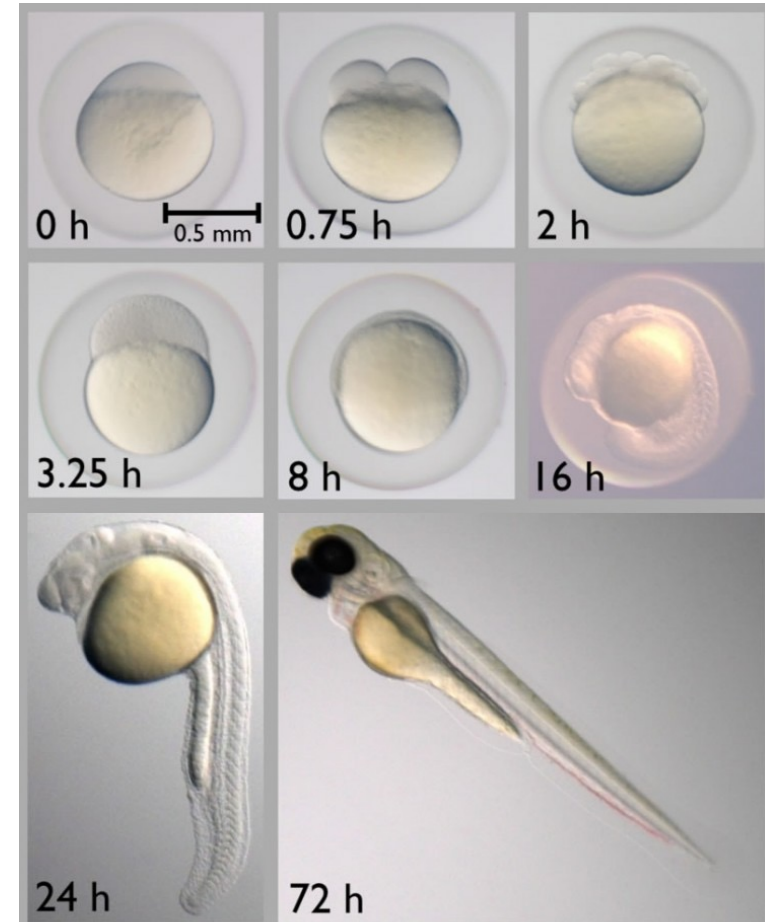
Photos from Ellerbe Creek (J.Behrens)

Back-Up Slides

Tier 1: Zebrafish EcoTox Experiments

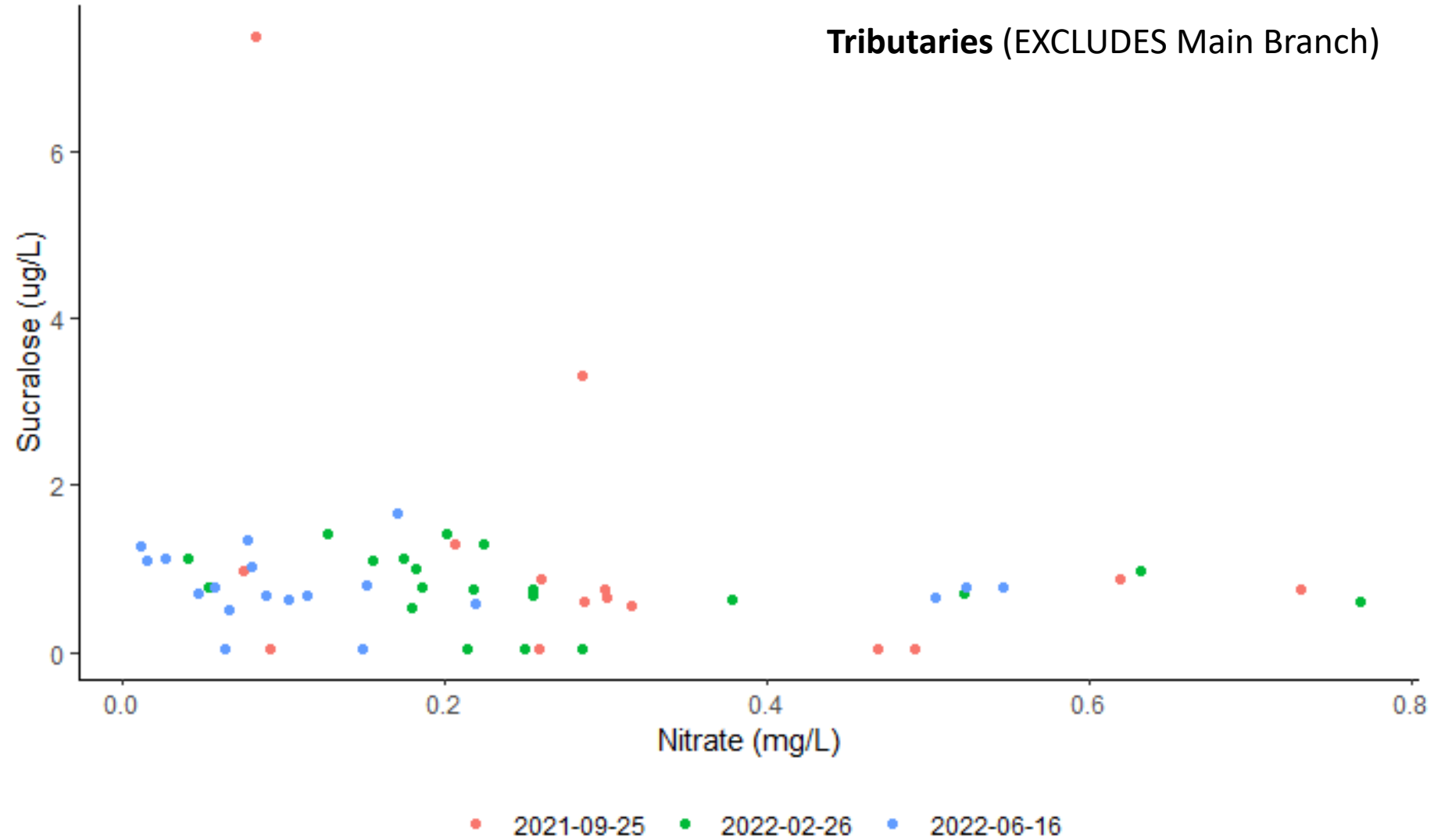
What stress do contaminants place on aquatic life?

- ✓ Zebrafish help us explore this!
 - ❖ Survival as larvae
 - ❖ Deformities developed (if any)
 - ❖ Ability to swim
 - ❖ Energy needed for normal function (mitochondrial respiration)

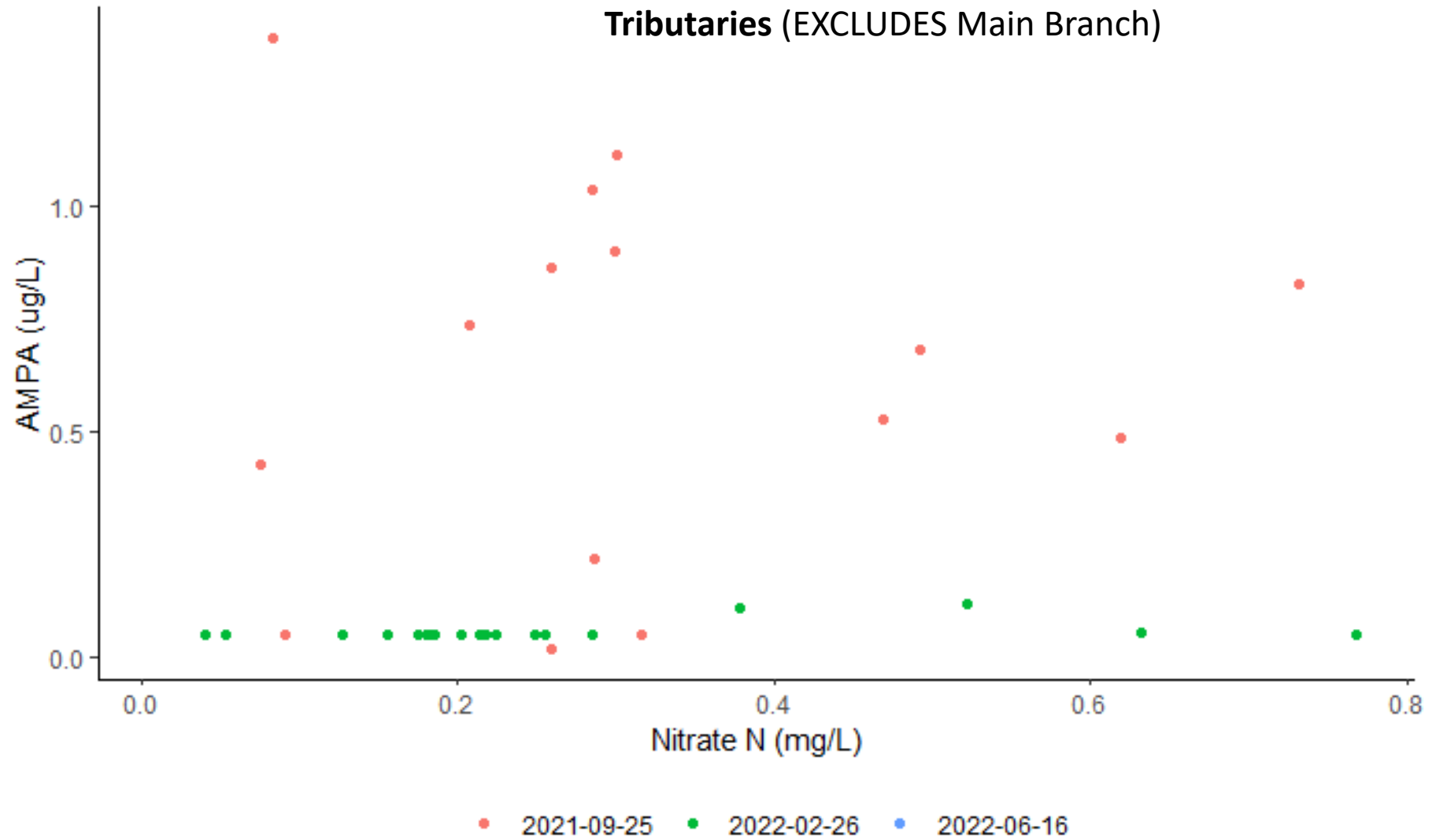


PC: [Ed Hendel/Wikimedia Commons](#)

Indicator 1: Wastewater



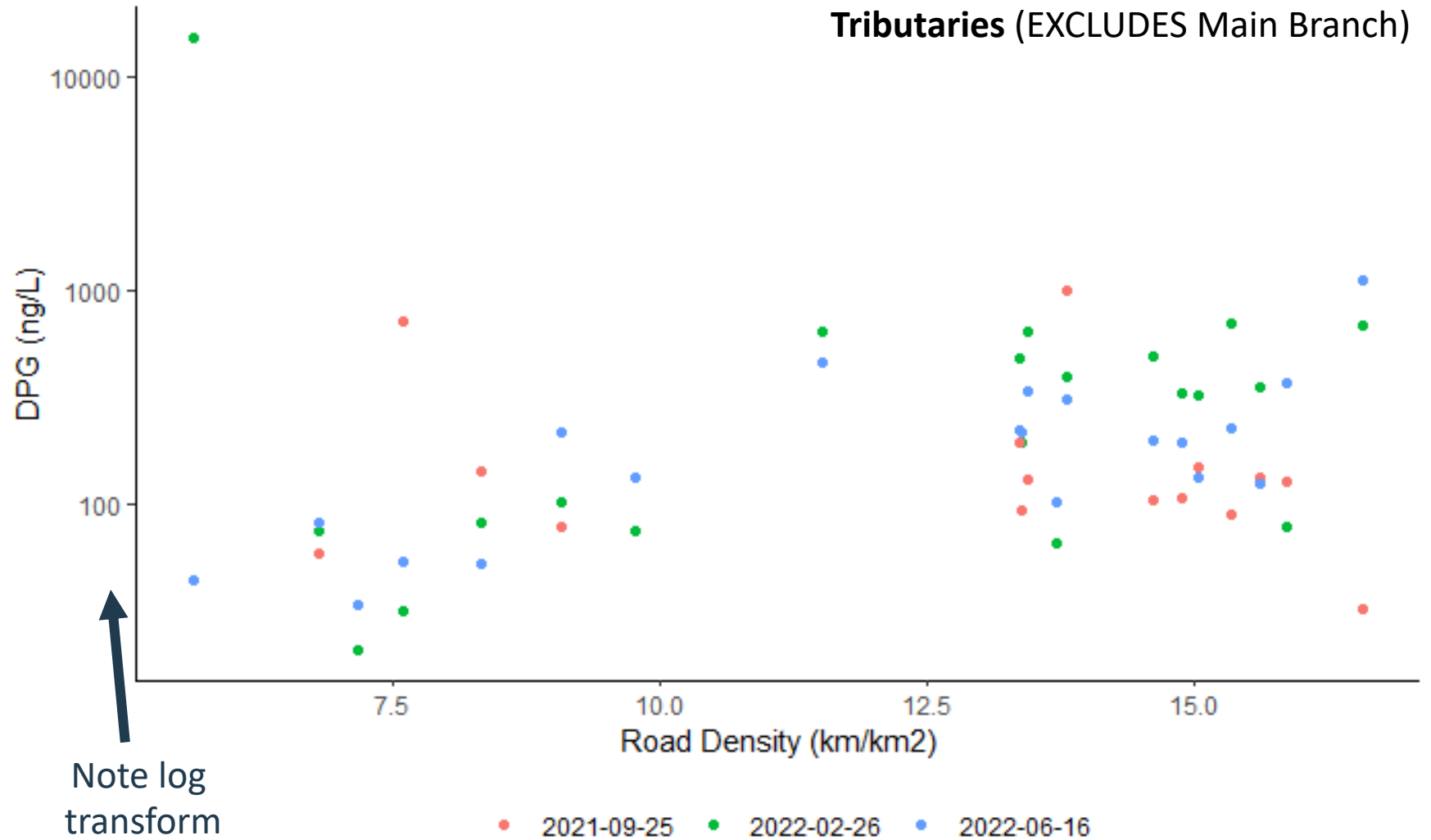
Indicator 2: Lawncare



Indicator 2: Road Runoff



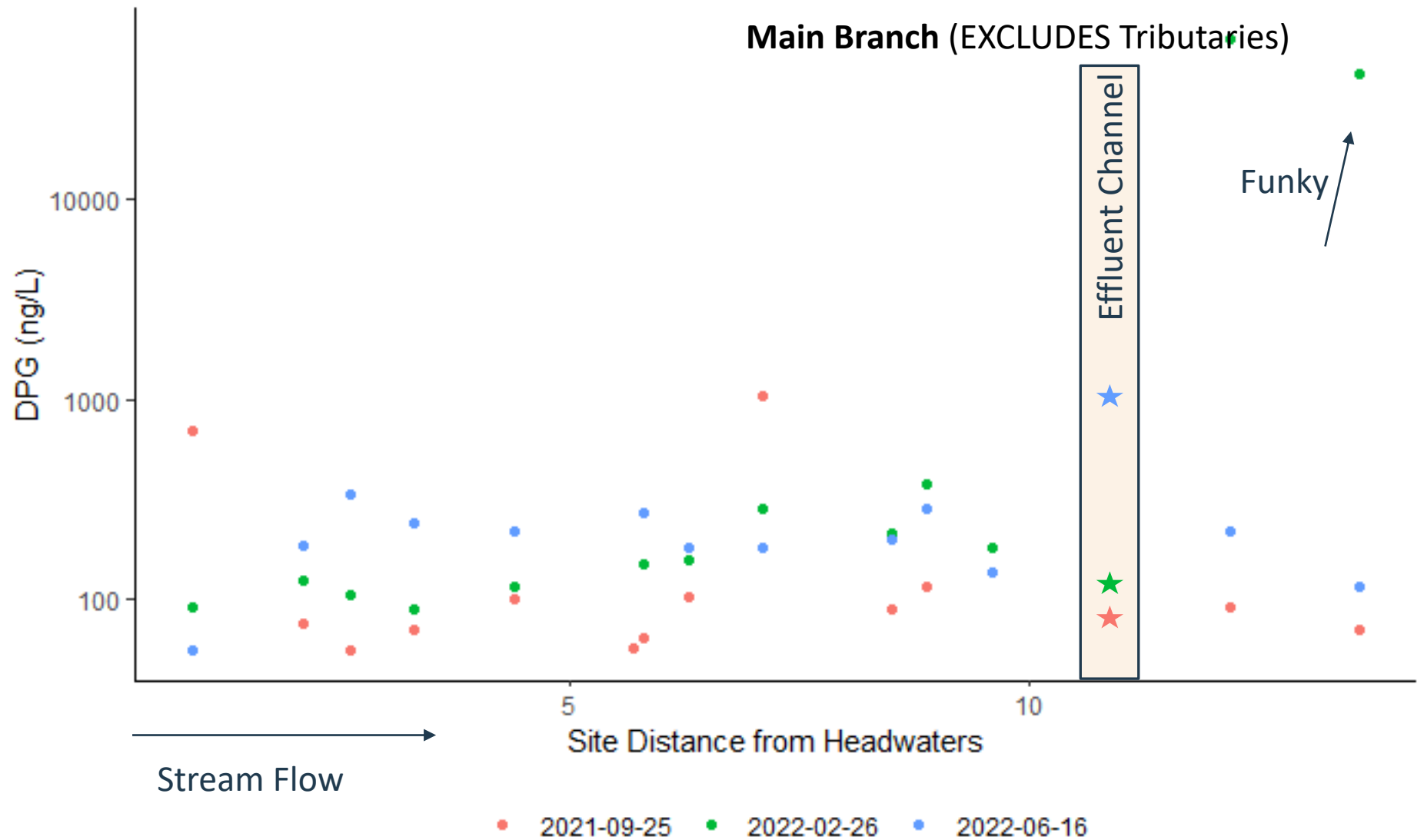
Created by Andrejs Kirma



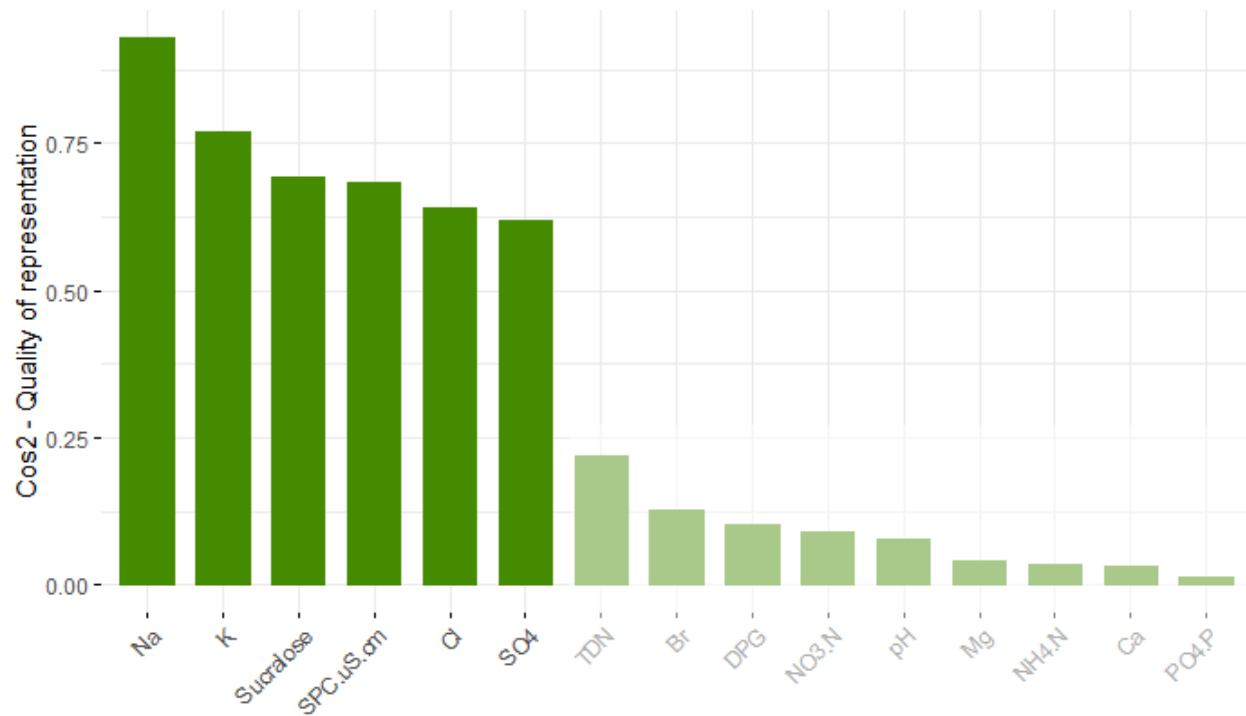
Indicator 2: Road Runoff



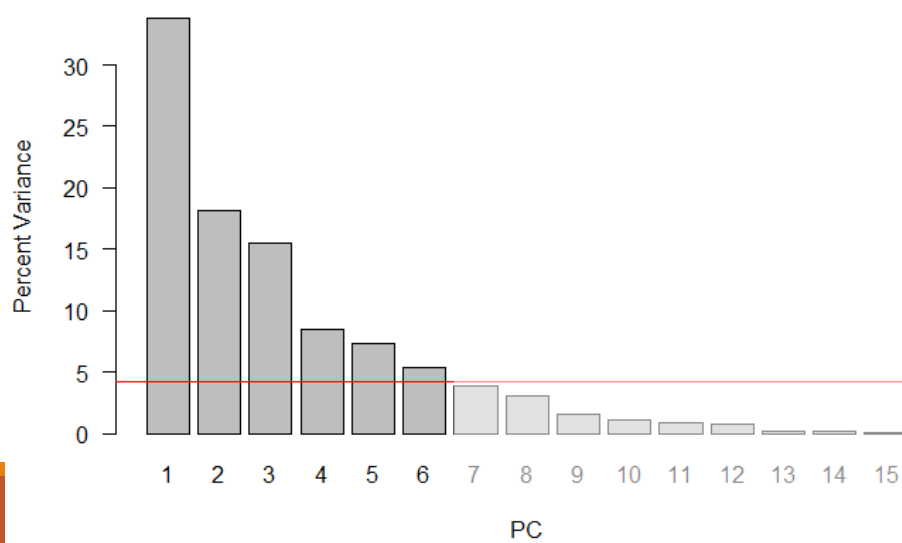
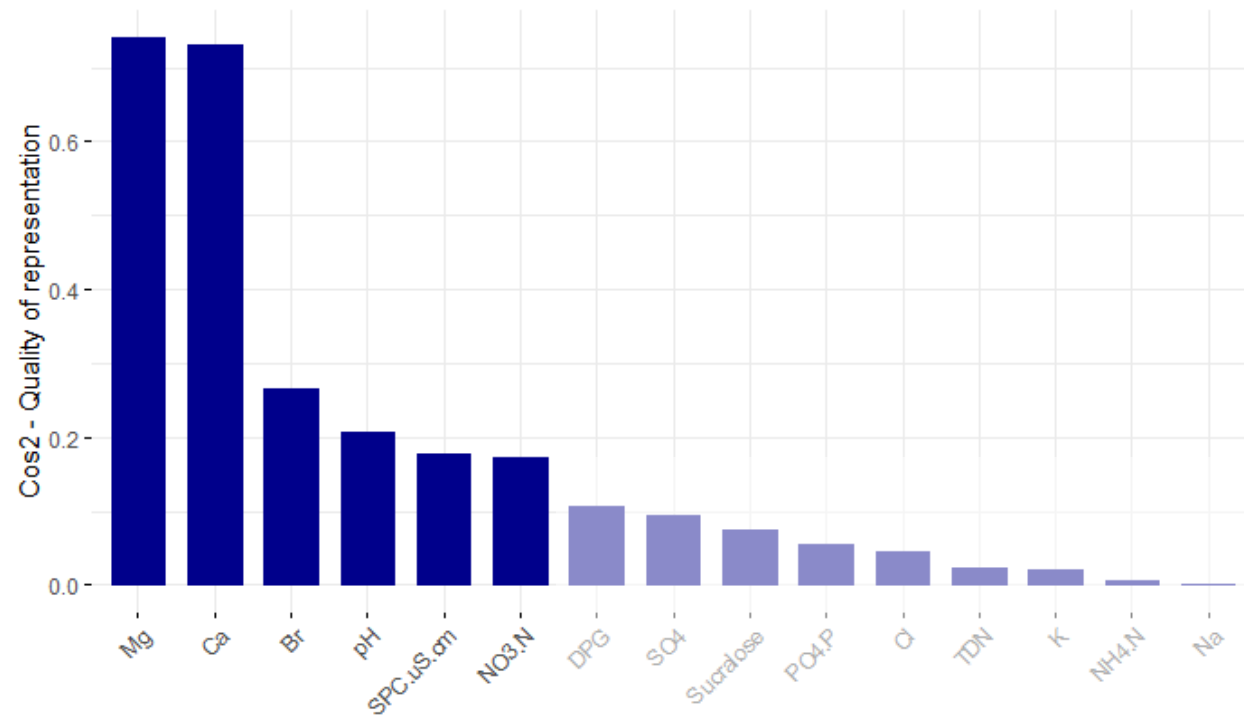
Created by Andrejs Kirma



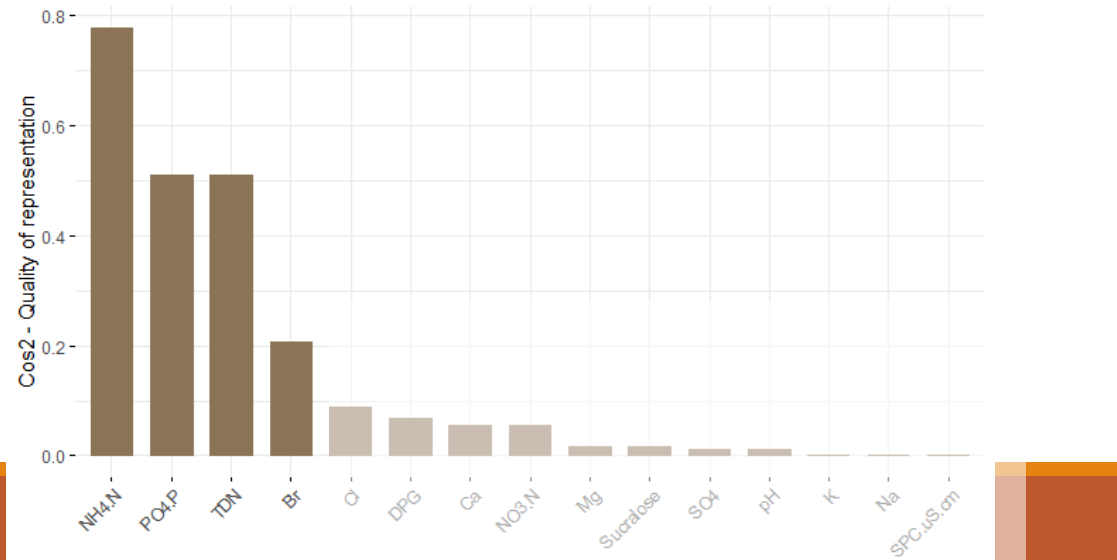
Cos2 of variables to Dim-1



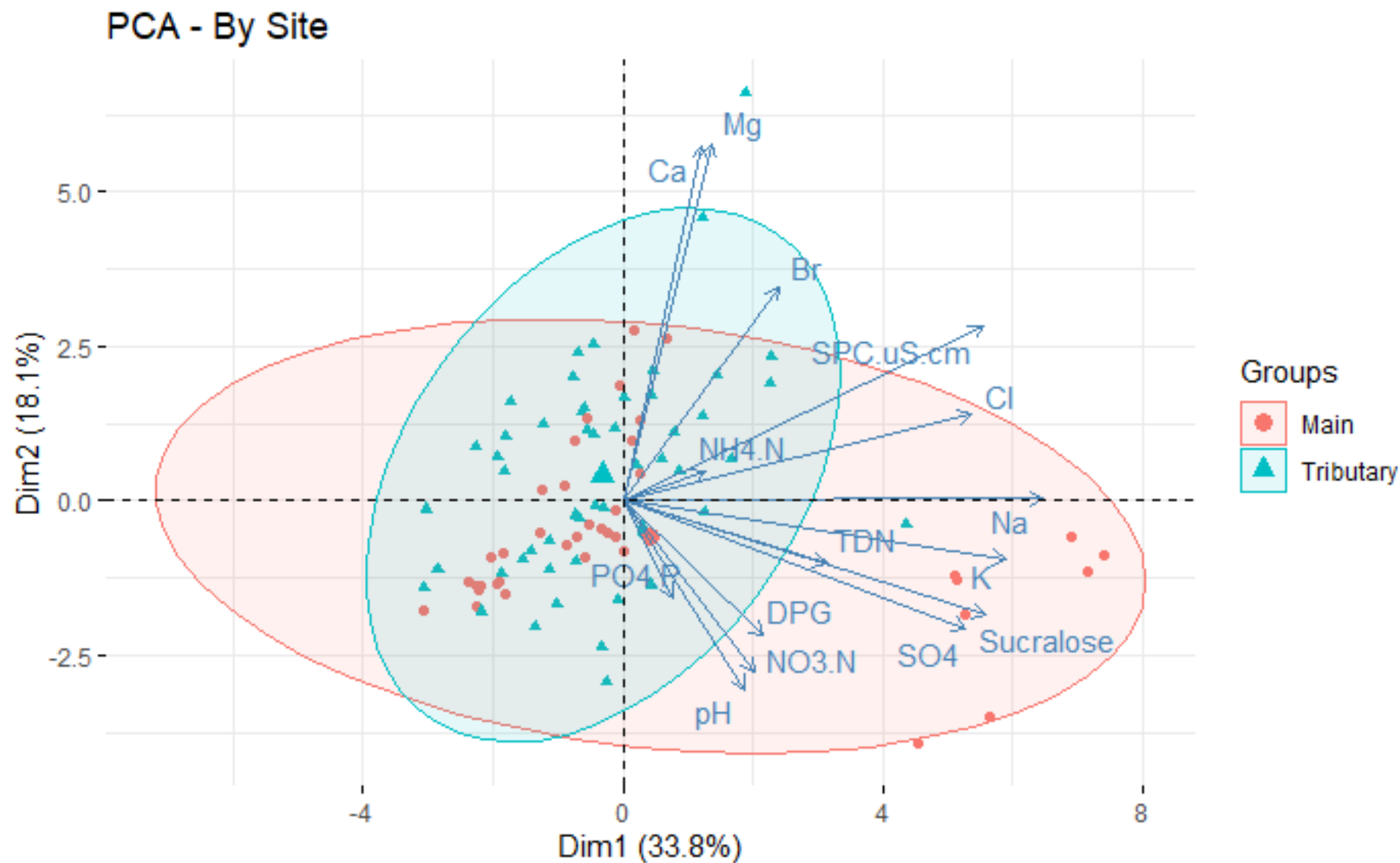
Cos2 of variables to Dim-2



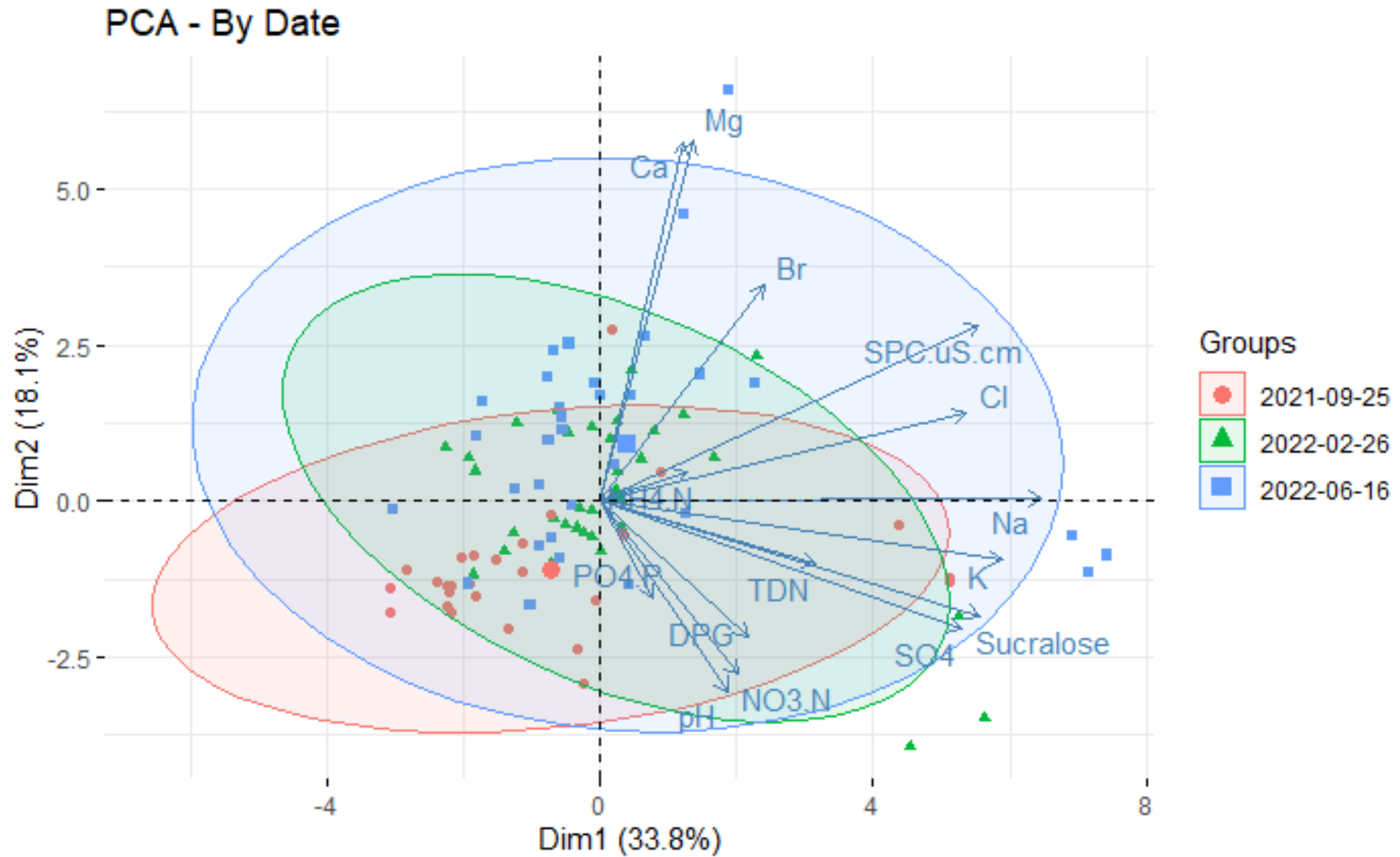
Cos2 of variables to Dim-3



PCA Time!

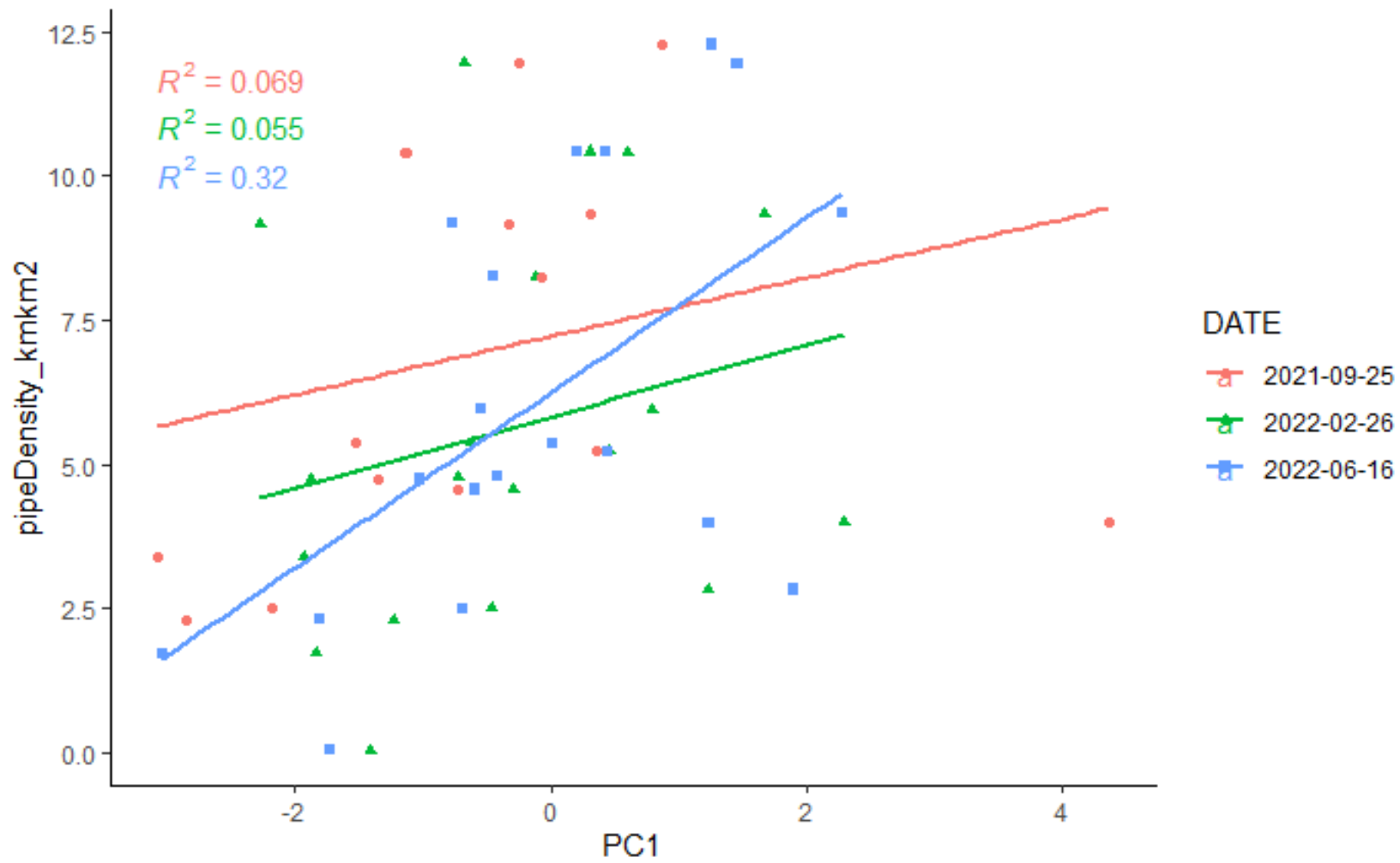


PCA Time!



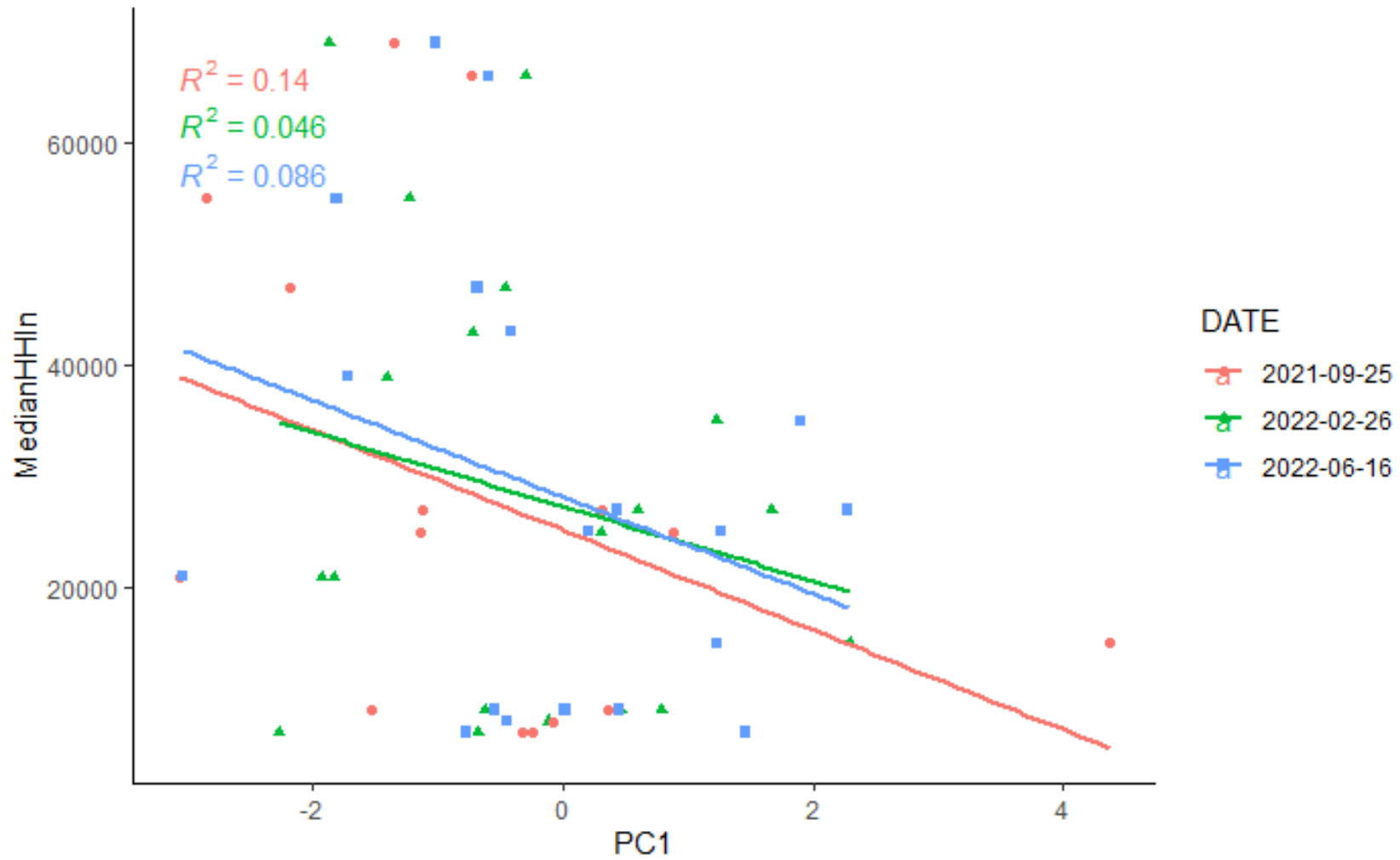
Pipe Density in Tribes...

Maybe something in summer, if we squint? Non-detects might through things off



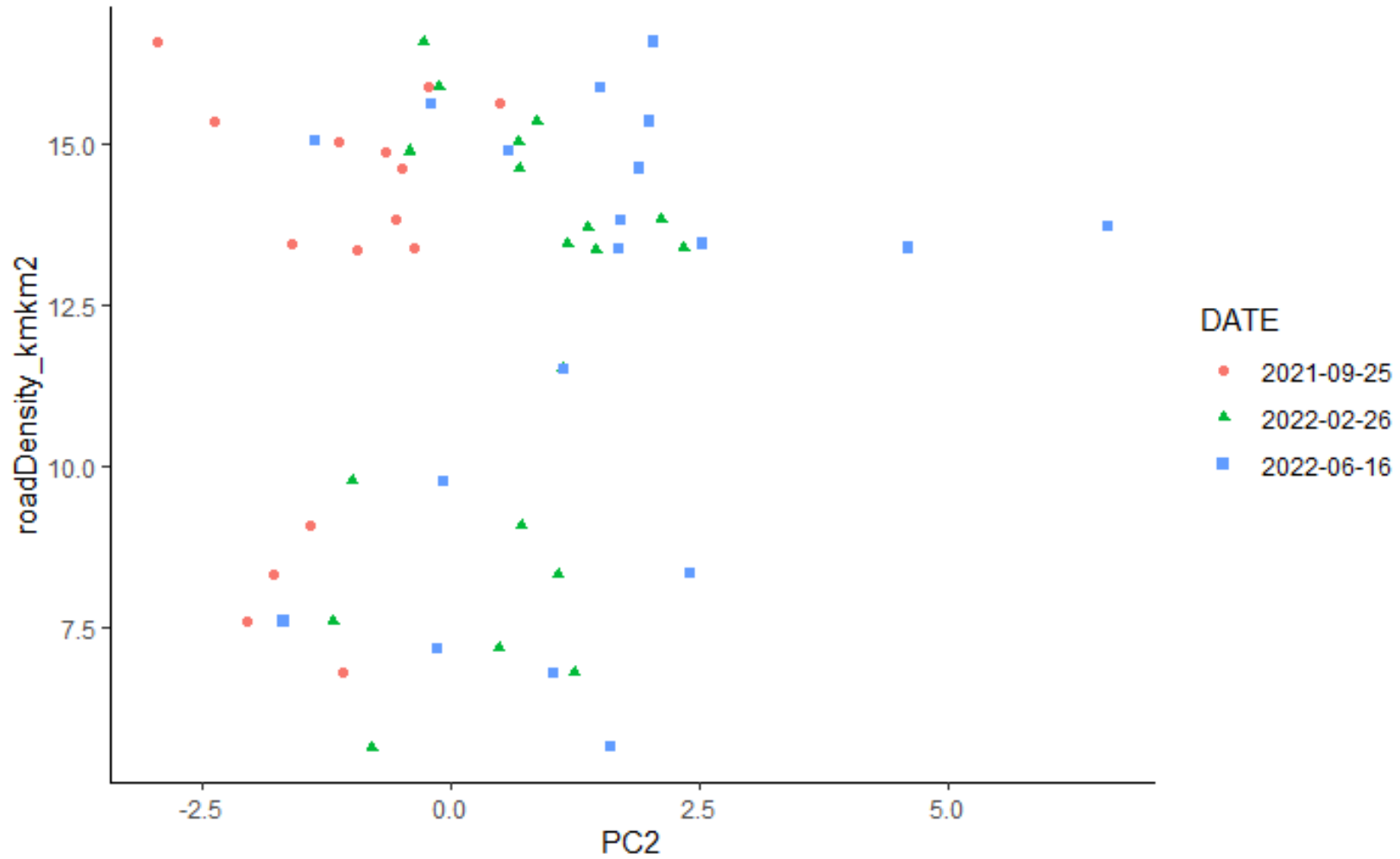
Income in Tribes...

Not much relationship, good news?

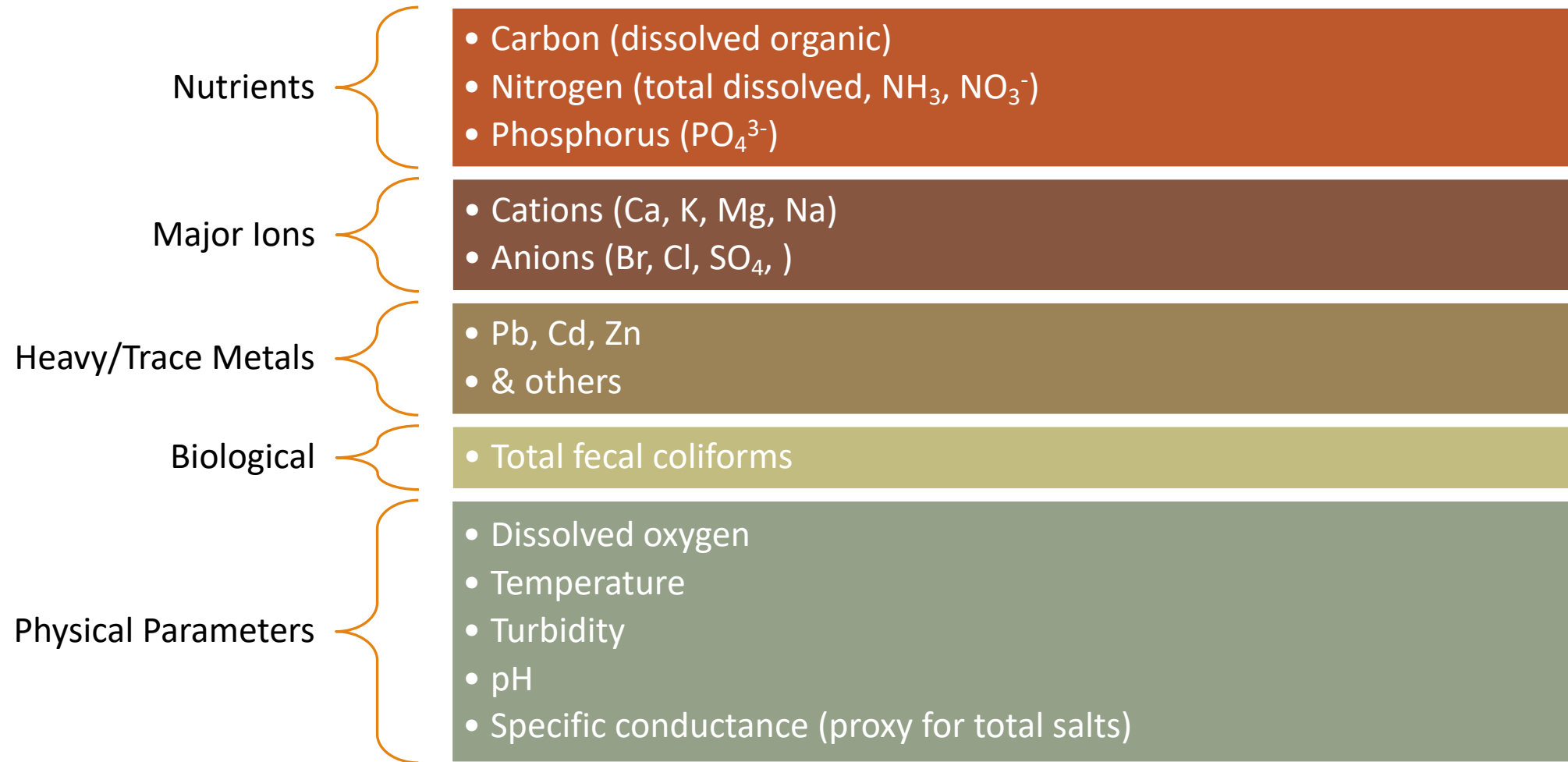


Road Density in Tribs...

Maybe something, if we squint? Non-detects might through things off

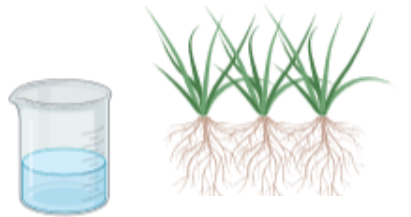


Tier 1: Chemical and Physical Parameters



Tiers 2 & 3: Attributing to Source + Chemical

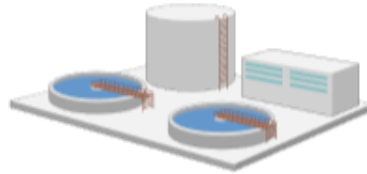
TIER 2: INDICATOR COMPOUNDS



Pesticide
(Glyphosate)



Tire Additive
(n,n-diphenyl-
guanidine)



Wastewater
(sucralose)

TIER 3: FINGERPRINT + BIOACCUMULATION



Non-targeted analysis (screen for 2000+ compounds)



Metals



Micro-
plastics

+ Indicator Compounds