Occurrence and potential biological effects of pesticides in tributaries of the Great Lakes

Samantha Oliver, Hydrologist

U.S. Geological Survey Upper Midwest Water Science Center (Madison)











FIGURE 1: Map of sampling locations for the Great Lakes Restoration Initiative—Contaminants of Emerging Concern collaborative project.



Background

GLRI Phase I: Identified a few contaminant classes as priorities

- Monitored at 57 Great Lakes tributaries
- 69 compounds 15 chemical classes
- Priority chemical classes based on concentrations and comparison to water quality benchmarks
 - Pesticides
 - PAHs
 - Pharmaceuticals

GLRI Phase II, Water Year 2016: Pesticides

What questions did we want to answer about pesticides in the Great Lakes?

What and where:

• What pesticides are present in Great Lakes tributaries? How does land use impact the presence of pesticides in tributaries?

Prioritization:

 Which compounds are the most likely to negatively impact aquatic biota? Which sites should we prioritize for further investigation or management actions?

Seasonality:

Are pesticides an episodic (growing season) or year-round threat to aquatic biota?



Summary of Data Collected

Pesticides

- 232 compounds: Herbicides, Insecticides, Fungicides
 - Parent compounds and (some) degradates
- 16 Great Lakes tributaries
 - Watershed
 characteristics: Gradient
 of agriculture to urban to
 forest/wetland
- Monthly surface water sampling:
 October 2015 September 2016



* All results can be found in <u>Oliver</u> et al. 2022 or <u>Loken et al. 2022</u>



Transformation Transport



Concentration relevance

ToxCast/Tox21

Concentration that induced cellular or molecular response to chemicals (*in vitro* assay)

Aquatic Life Benchmarks

Concentration that induced organismal response to chemicals (*in vivo* assay)

- Relatively inexpensive & fast (many compounds, many biological endpoints)
- Cannot directly translate to biological impacts

- Relatively expensive & slow (few compounds, few target species)
- Directly related to organism-level impacts





Negative impacts on aquatic communities

How prevalent are pesticides in tributaries of the Great Lakes?

- Pesticides were detected in 190/198 (96%) samples
- Pesticides were detected in all 16 tributaries
- Of the 232 compounds measured, 104 were detected
- 80% of samples had 10 or more pesticides detected



Sites from low to high median concentration

Oliver et al. 2022

When are pesticides present in tributaries of the Great Lakes?

- Pesticides are detected year-round at all sites
- Concentrations and the number of detected compounds peak June through August



In which tributaries of the Great Lakes are pesticides present?

- Pesticides are detected year-round at all sites
- Concentrations and the number of detected compounds peak June through August
- Between 6-72 unique compounds detected per site across the study duration
- Few compounds detected at the wetland and forested sites



What pesticides are present in tributaries of the Great Lakes?

- Herbicides and related transformation products (TPs) were the most frequently detected class of pesticides
 - Atrazine and two TPs
 were present in 75% of
 samples at all sites
- Neonicotinoid insecticides imidacloprid and clothianidin were most frequently detected insecticides (44% of samples)

Metolachlor 2.4-D Diuron Atrazine Acetochlor *Deisopropylatrazine Sulfentrazone Simazine Triclopyr Chlorimuron-ethyl Dimethenamic *Metribuzin DK Ametryn Metribuzin *Deethylatrazine Bentazor Herbicide Propazine · Flumetsulam Dicamba Linuror *Metolachlor SA Prometon Oryzalin EPTC *Hydroxyatrazine *Metolachlor OA *Monomethyldiuron *Metribuzin DA Tebuthiuron Glyphosate -*Aminomethylphosphonic acid *Deethylhydroxyatrazine · *Dechlorometolachlor *Didealkvlatrazine -*Hydroxymetolachlor *Acetochlor OA Not measured Imidacloprid Fiproni Clothianidin Insecticide Carbary *Dichlorvos 🚩 Thiamethoxam Dimethoate Diflubenzuror Bifenthrin Propiconazole *Carbendazim Fungicide Azoxystrobin Tebuconazole · Metalaxyl Myclobutanil -Pyraclostrobin -

50

100

Number of samples

150

200

Detected

Not detected

neonics

Pesticides are in all Great Lakes tributaries where we sampled.

Is this biologically meaningful?



We can estimate potential for negative biological impact by dividing our measured concentration by a benchmark value reported from either ToxCast or ALB

> Measured Concentration ----- = Exposure Activity Ratio (EAR) Benchmark or Toxicity Quotient (TQ) concentration

Concentration relevance ToxCast/Tox21 Concentration that induced cellular or molecular response to chemicals (in vitro assay) **Aquatic Life Benchmarks** Concentration that induced organismal response to chemicals (*in vivo* assay)

* We used EAR > 0.001 and TQ > 0.1 as conservative thresholds for potential negative impact

Pesticide exceedances of water quality benchmarks

Number of sites w/ exceedances



potentially negatively impacted by pesticides year-round

~Half of sites

In any given month, ~5 or more chemicals contributing to exceedances.

Which pesticides may negatively impact aquatic biota?

- 65/104 detected chemicals had Aquatic Life Benchmarks
- 15 chemicals had TQ > 0.1 (exceeded our conservative ALB)
- Insecticides imidacloprid (44%), clothianidin (28%), and fipronil (17%) had high ALB exceedances
- Herbicides atrazine and metolachlor also had ALB exceedances in 16% and 11% of samples, respectively

What if we consider all information? (missing info, transformation products, etc?)





Which pesticides may negatively impact aquatic biota?



We identified 16 priority parent compounds based on:

- Occurrence (if no toxicity information but at 50% sites or 20% samples)
- TQ > 0.1 or EAR > 0.001 (>25% sites and >10% samples)
- Compound contributed to mixture with EAR > 0.001 (>25% sites and >10% of samples)

Which sites are likely to have negative impacts to biota?

Sites with the highest human disturbance in the watershed (ag + urban) had the highest potential negative impacts from pesticides



Oliver et al. 2022

Loken et al. 2022

Which tributaries have the greatest potential for negative effects from pesticides?

Many sites had year-round exceedances.

The Maumee & Vermillion (row crops) and Clinton, Cuyahoga, and Rouge (urban) were prioritized based on ranking metrics.



Conclusions

- High potential for biota in tributaries of the Great Lakes to be negatively impacted by pesticides
 - Potential increases with % ag + % urban in watershed
- Pesticides likely impacting biota in GL tributaries year-round
 - Highlights the importance of transformation + transport/storage
- These screening tools (ALB and ToxCast) suggest that neonics (particularly imidacloprid and clothianidin) are a few of many pesticides that have potential for negative biological impacts



Thanks! Questions?

Feel free to reach out: soliver@usgs.gov