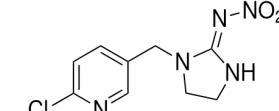
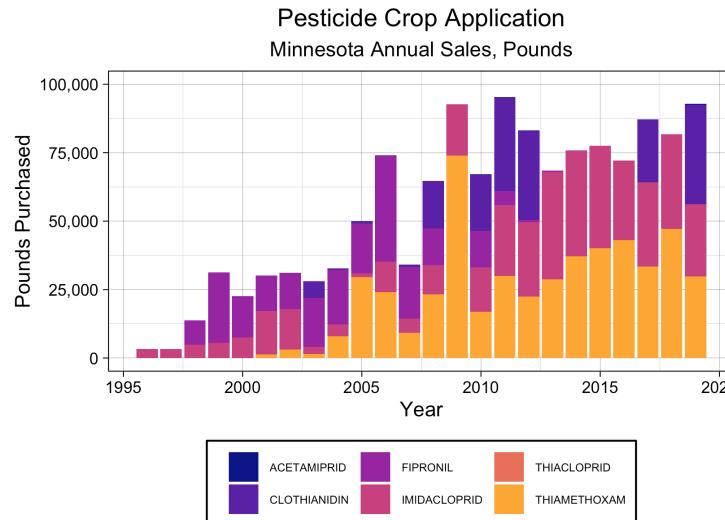
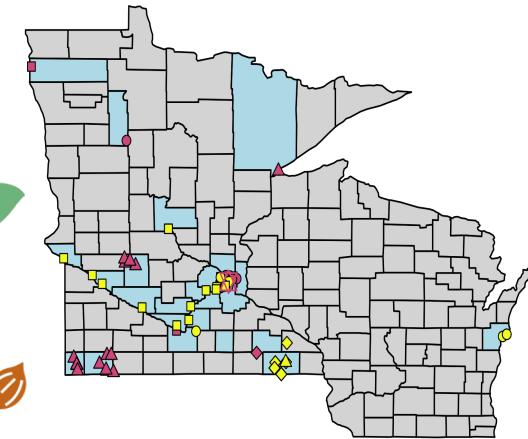


Pesticides in Minnesota's Surface and Groundwater:

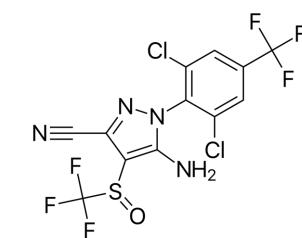
Neonicotinoids, Fipronil, and Key Transformation Products.

Grant Goedjen
University of Minnesota
Department of Civil, Environmental, and Geo-Engineering

March 24th, 2022



Imidacloprid



Fipronil



Acknowledgments



Predecessor:

Matthew Berens

Partner Agencies:



Undergrads:

Sylvia Doerr
Caroline Harrington
Sydney Olson



1

Background

2

Study Design

3

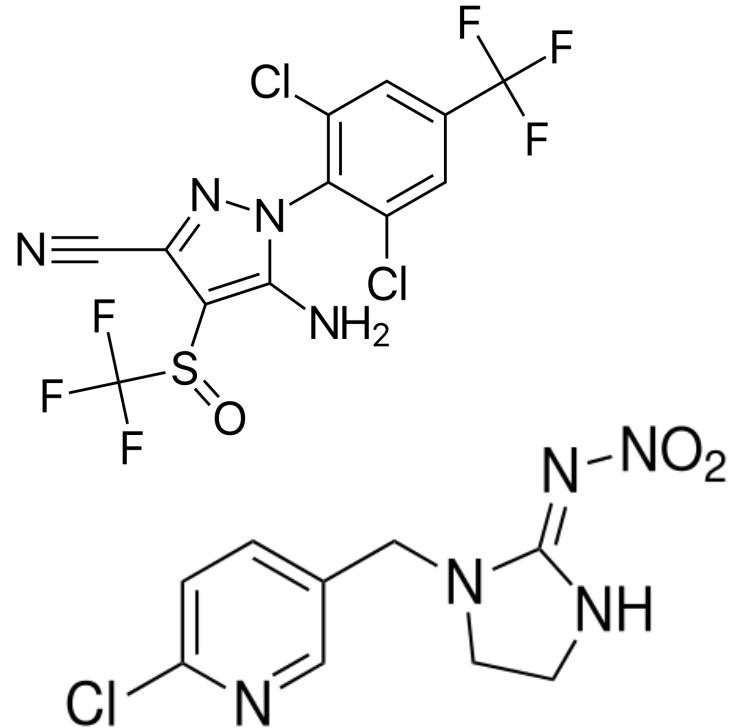
Results

4

Implications

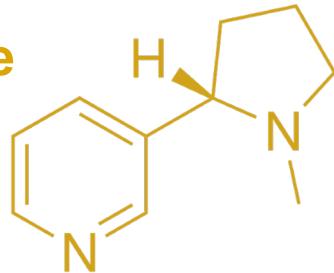
5

Questions

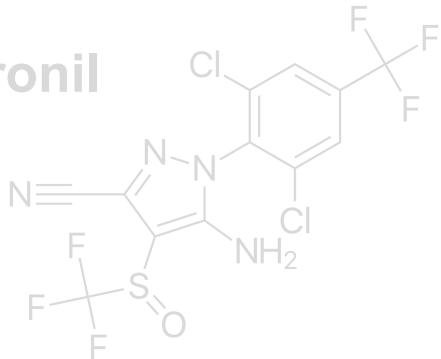


Target Compounds

Nicotine



Fipronil



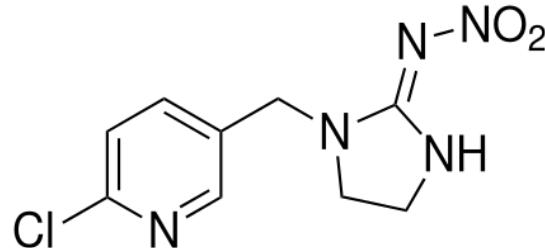
Neonicotiooids:

- Imidacloprid synthesized in **1991**.
- **Selective systemic** insecticide.
- Focuses on central nervous system.
 - Targets **nicotinic acetylcholine** receptor.

Fiproles:

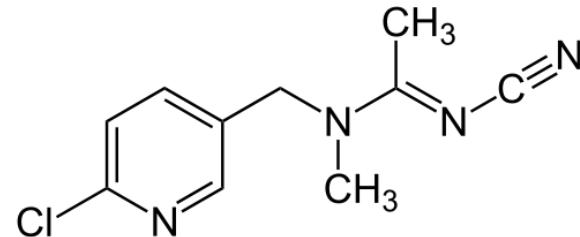
- First synthesized in **1996**.
- **Broad-spectrum** insecticide.
- Focuses on central nervous system.
 - Targets **GABA-gated Cl⁻ channels**.

The 5 “Classical” Neonicotinoids



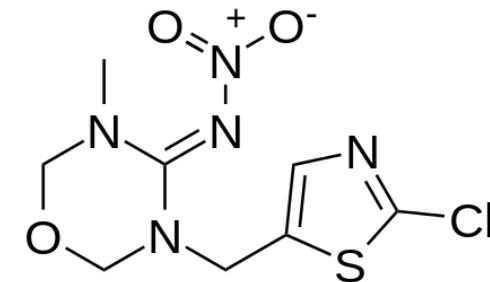
Imidacloprid

Imidacloprid Olefin
Imidacloprid Urea
Desnitro-Imidacloprid

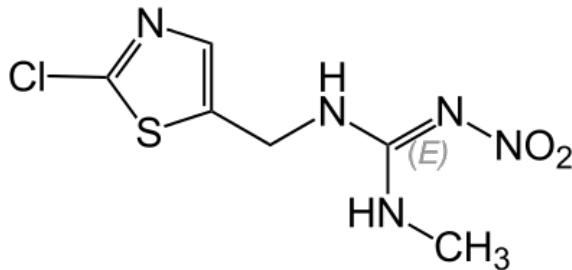


Acetamiprid

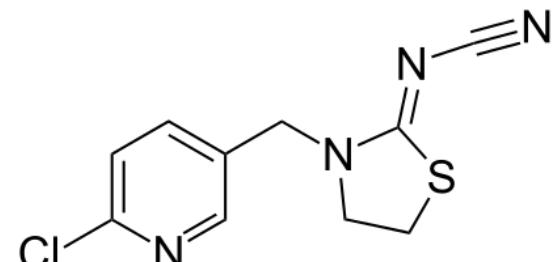
Acetamiprid-N-Desmethyl



Thiamethoxam

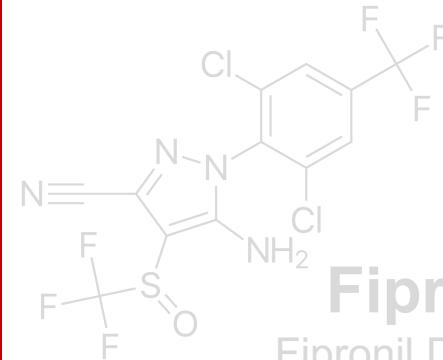


Clothianidin



Thiacloprid

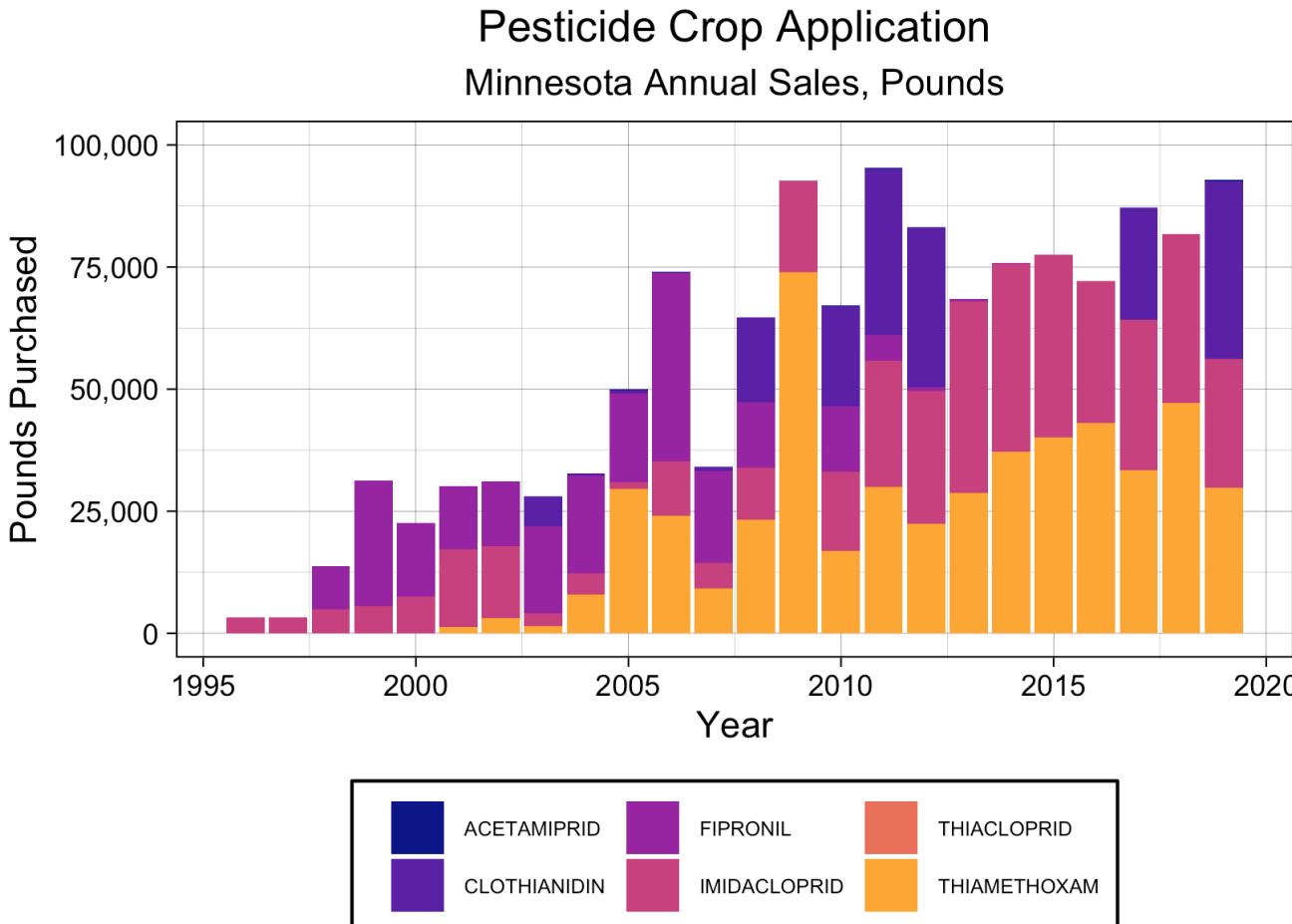
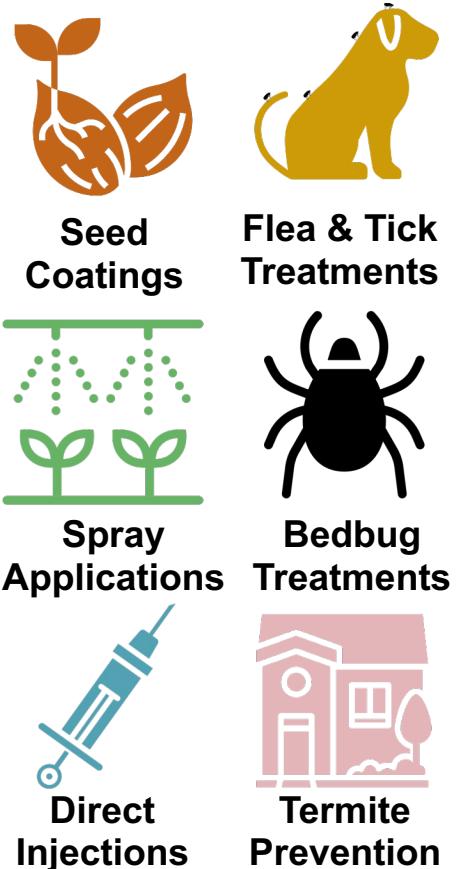
Thiacloprid Amide



Fipronil

Fipronil Desulfinyl Fipronil Sulfide Fipronil Sulfone

Neonicotinoids have high annual sales for crop applications.





Environmental Fate

- **Systemic** uptake into plants.
- **Persistent** in aquatic systems.
 - Moderate sorption to sediment.
 - High solubility in water.
- **Negatively-impacts pollinators** and non-target organisms.
- **Metabolized in mammals**, aquatic life, and humans.
- Observed **contaminating food supply**.
 - **Unknown harm / risk.**
- Identified in **surface and groundwater**.

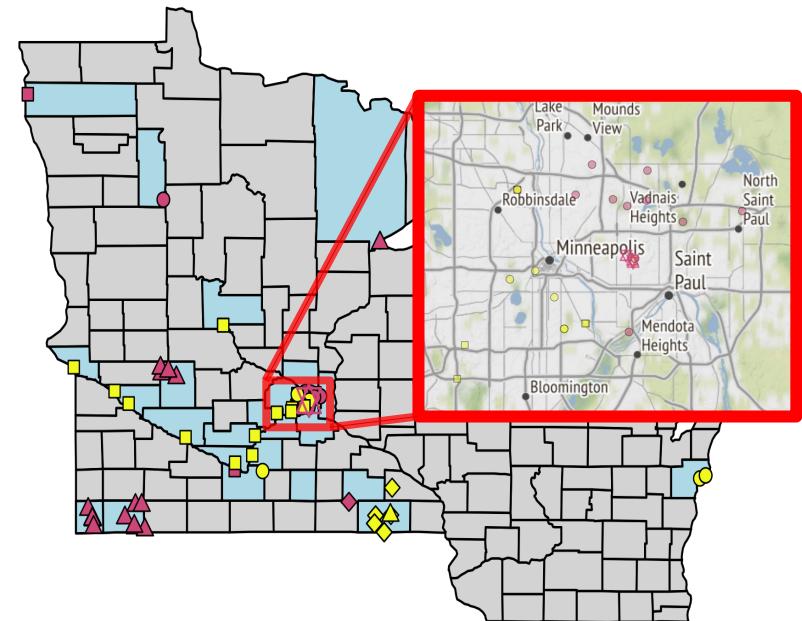
1 Background

2 Study Design

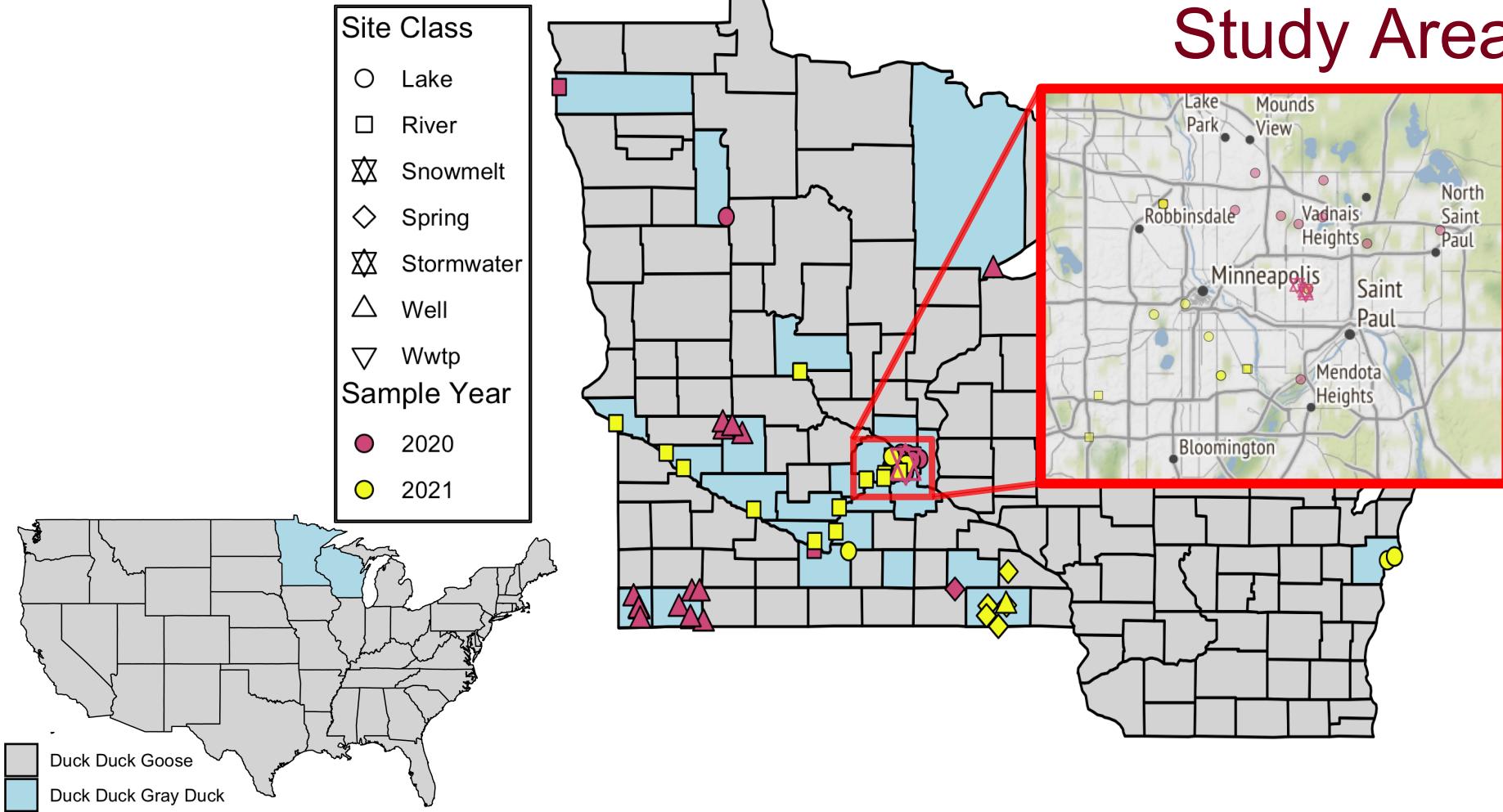
3 Results

4 Implications

5 Questions

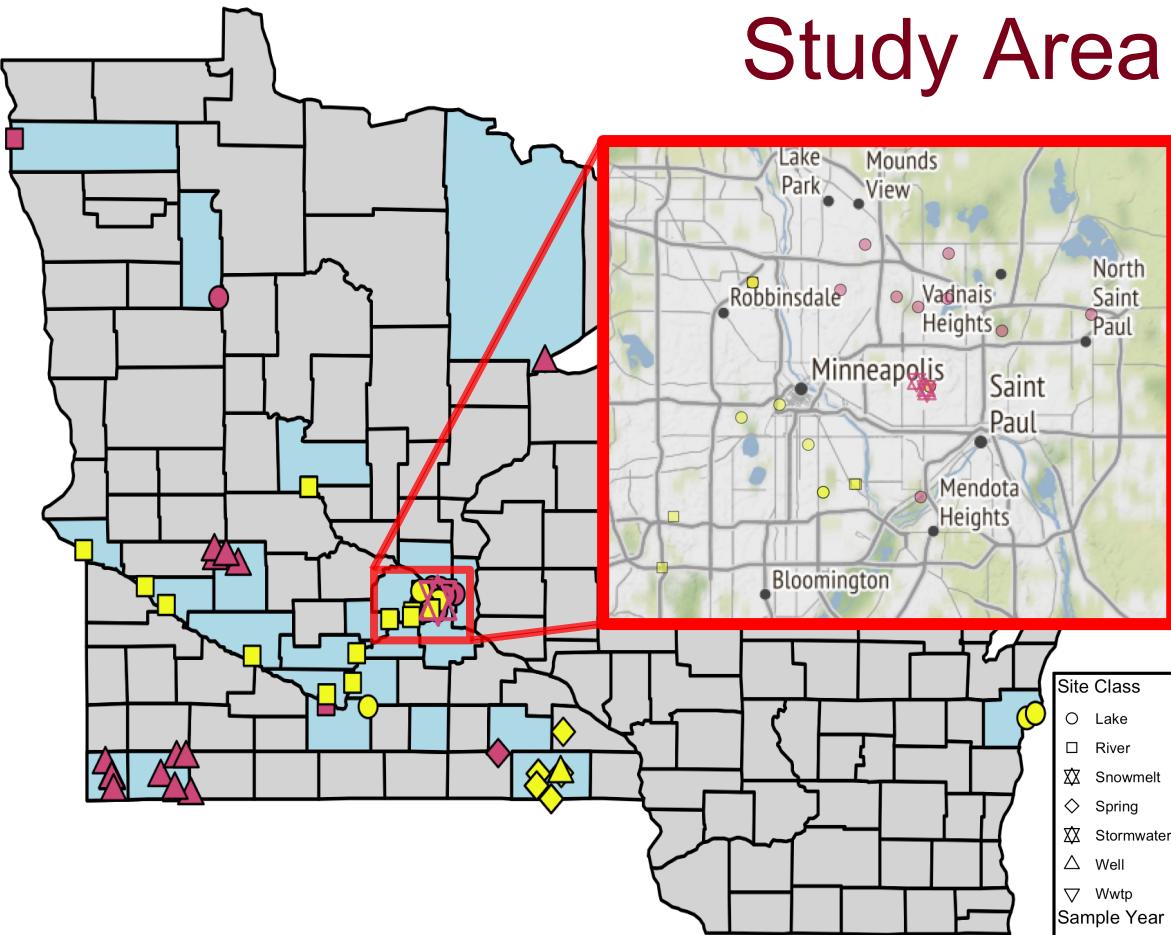


Study Area



Sample Collection

Class	Sites	Samples
Lake	22	198
River	19	105
Well	37	41
Spring	10	11
Runoff	5	50

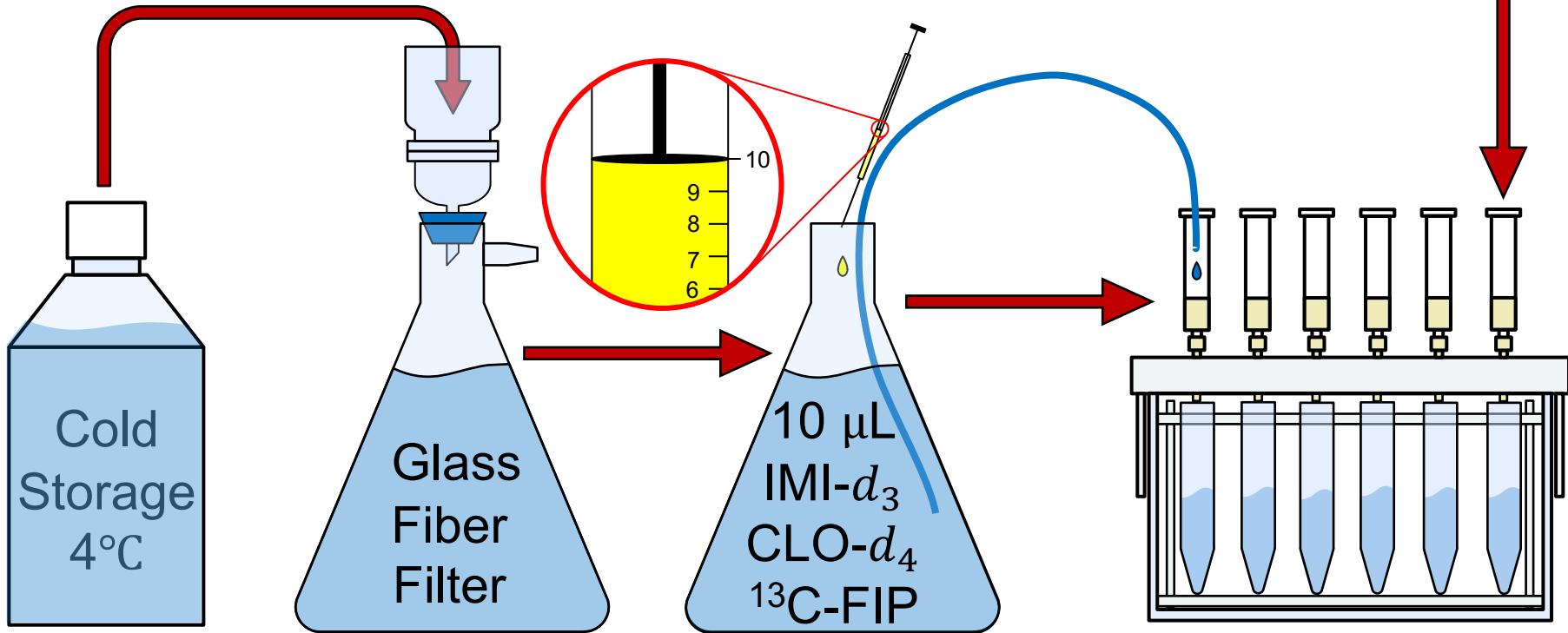
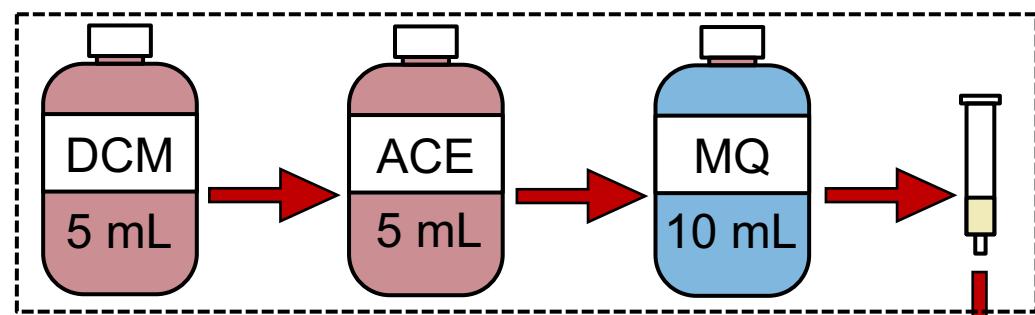


Study Area

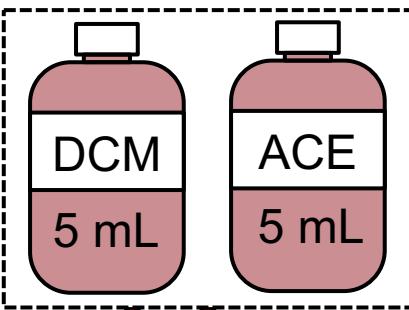


- Site Class
- Lake
 - River
 - △ Snowmelt
 - ◇ Spring
 - ◇ Stormwater
 - △ Well
 - ▽ Wwtp
- Sample Year
- 2020
 - 2021

Solid Phase Extraction

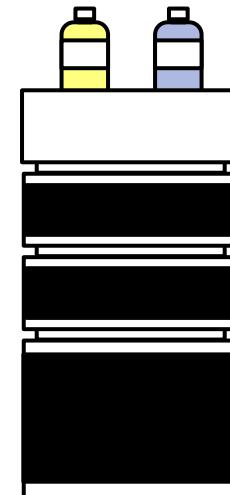


Reconstitution

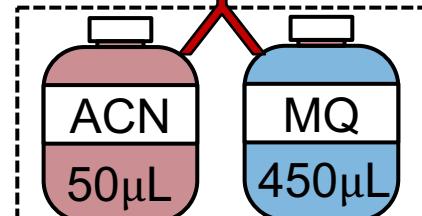
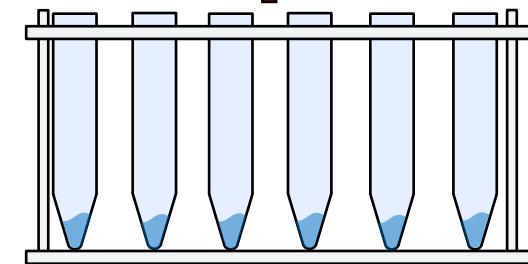
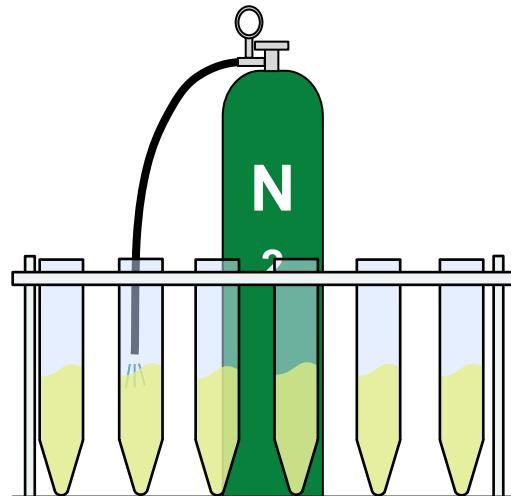
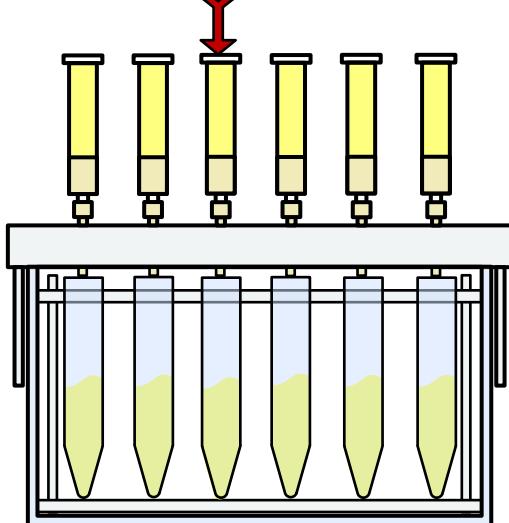
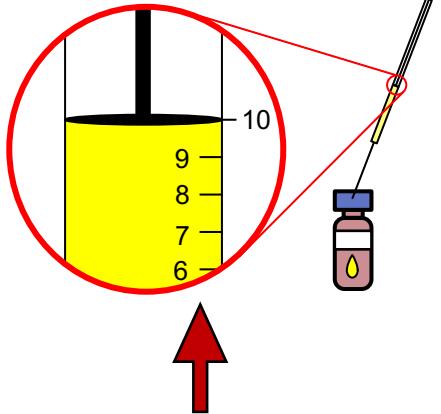


QQQ
LC/MS-MS

ESI
+ / -



¹³C-Caffeine ISTD



1

Background

2

Study Design

3

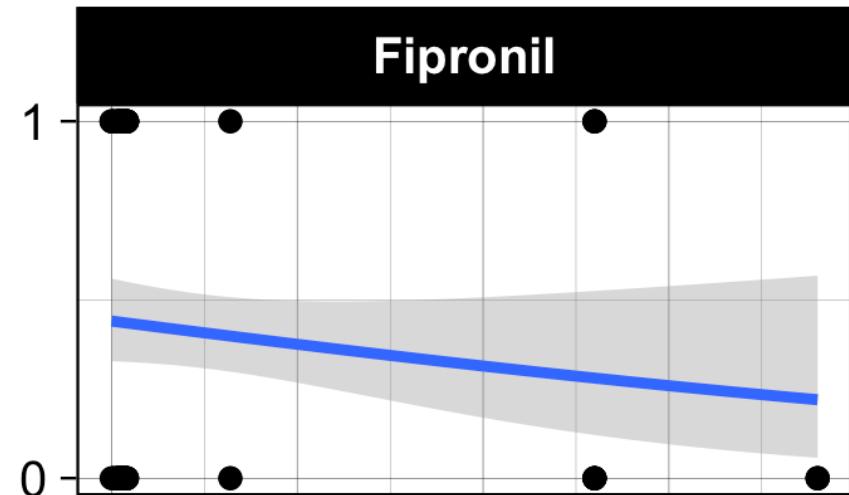
Results

4

Implications

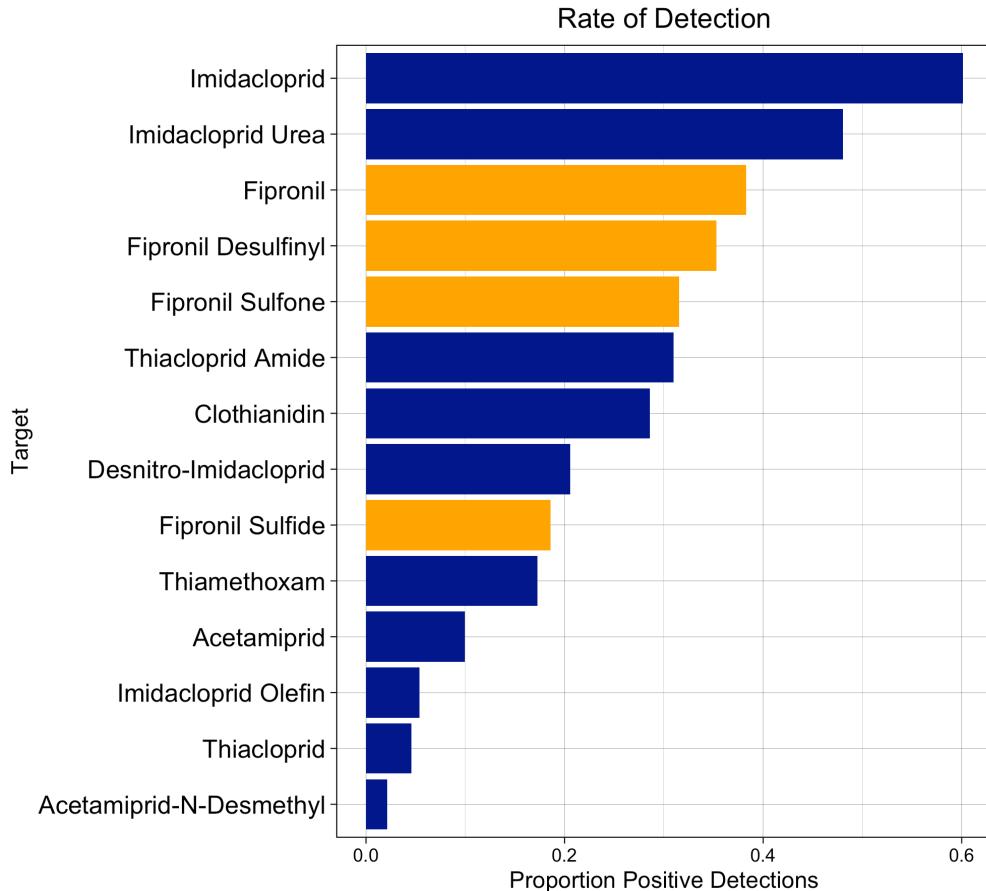
6

Questions

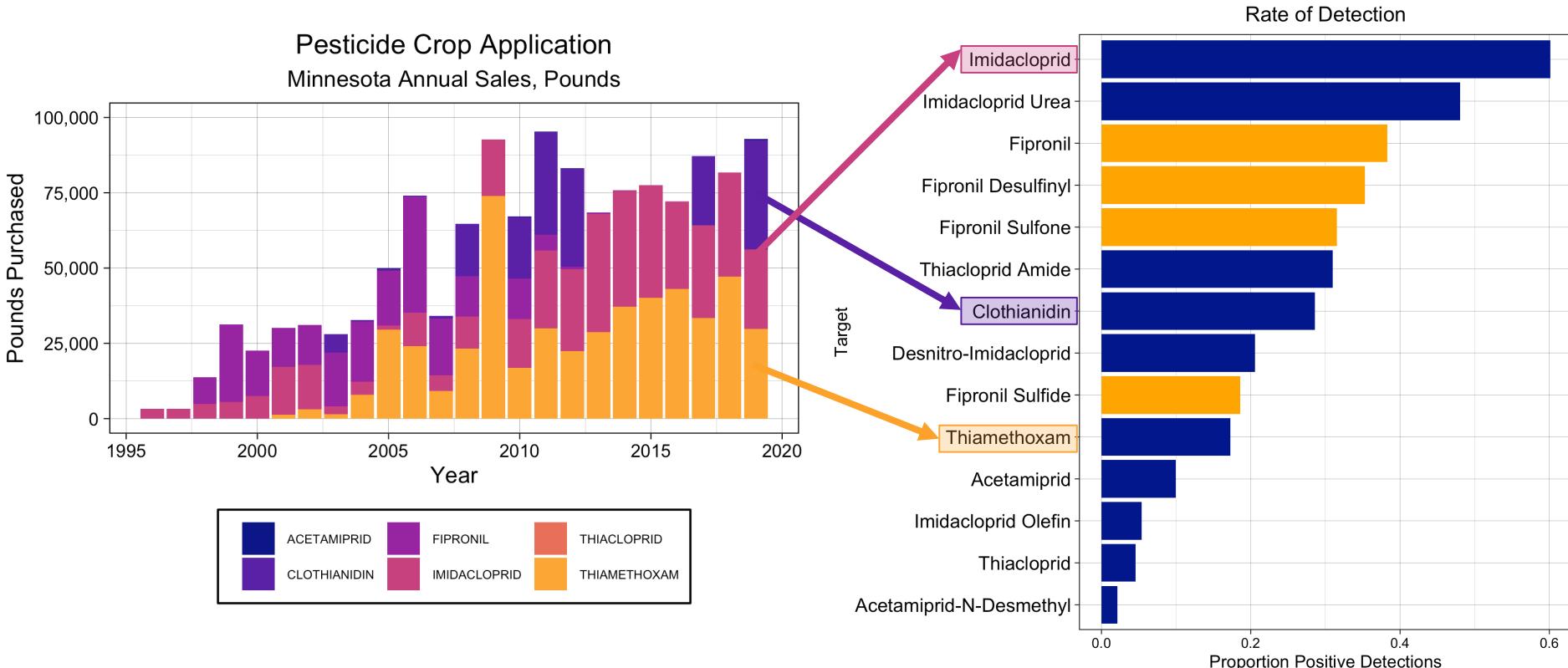


Purchase rate is a strong indicator of pesticide detection.

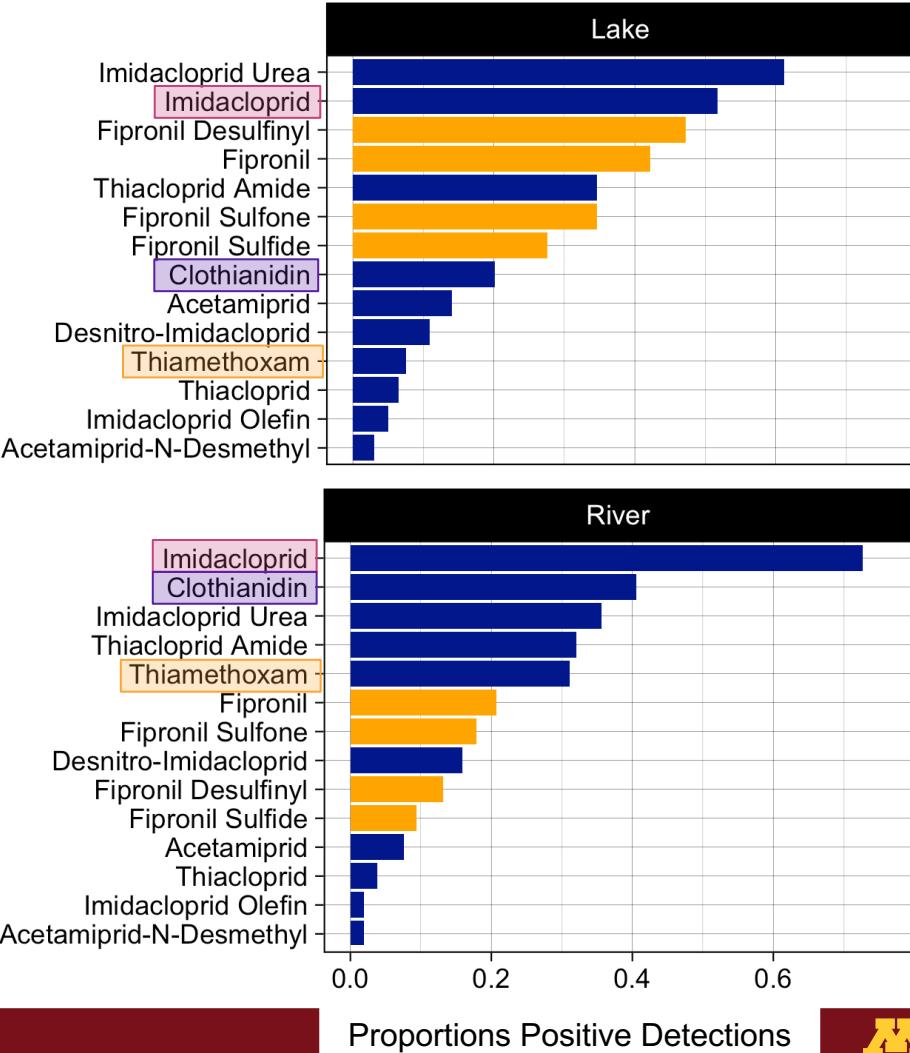
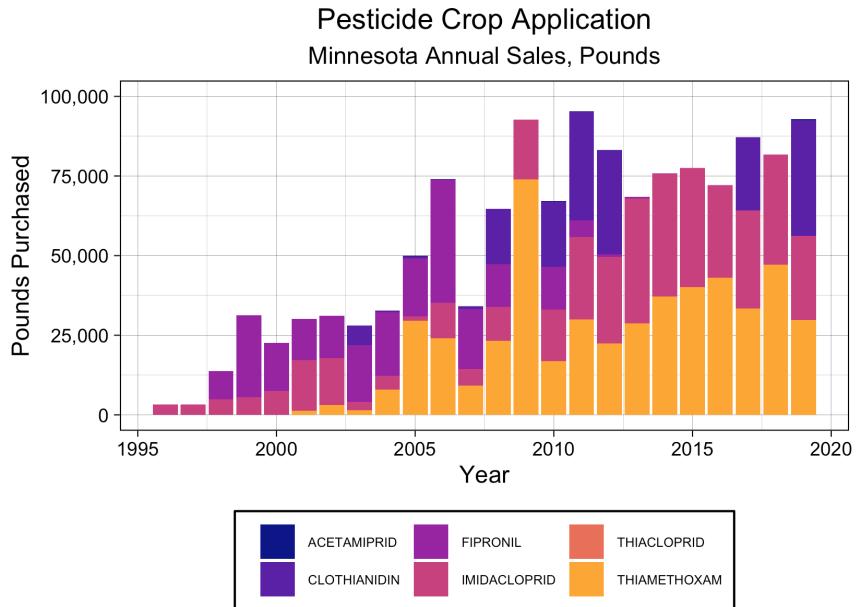
- **Imidacloprid** highest-detected neonicotinoid.
- **Fipronil** highest-detected fiprole.
- **Purchase rates** directly associated with **detection freq..**
 - All sites sampled
 - All matrices included



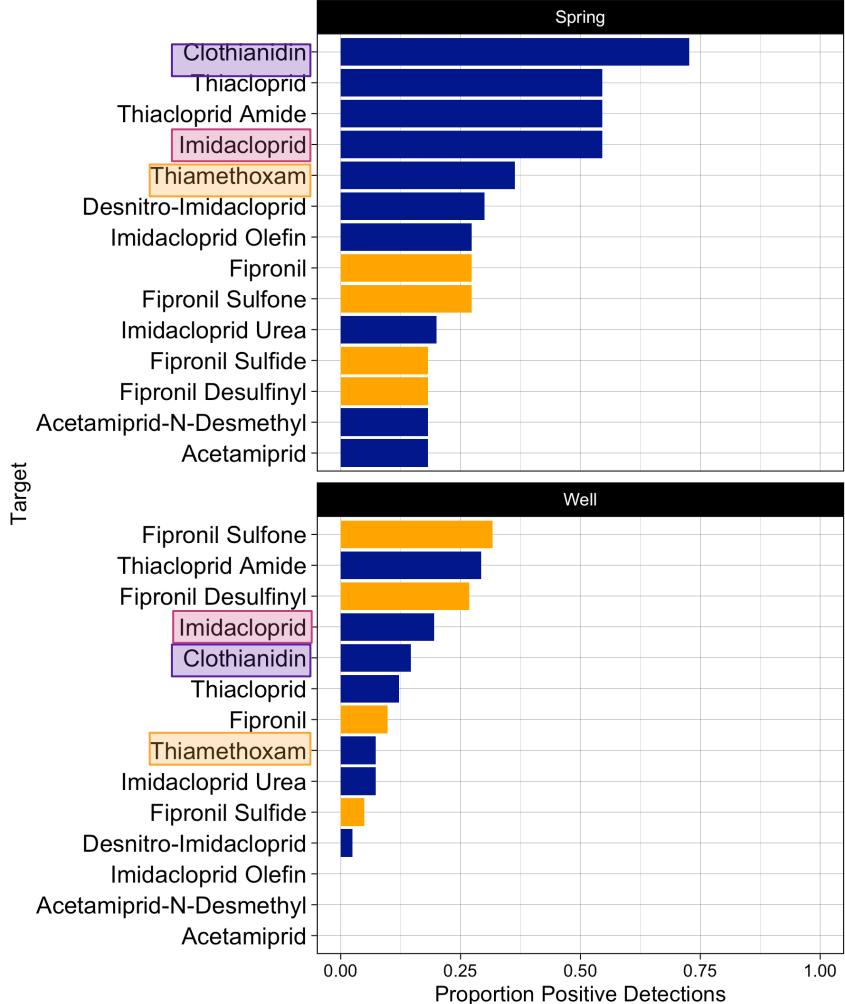
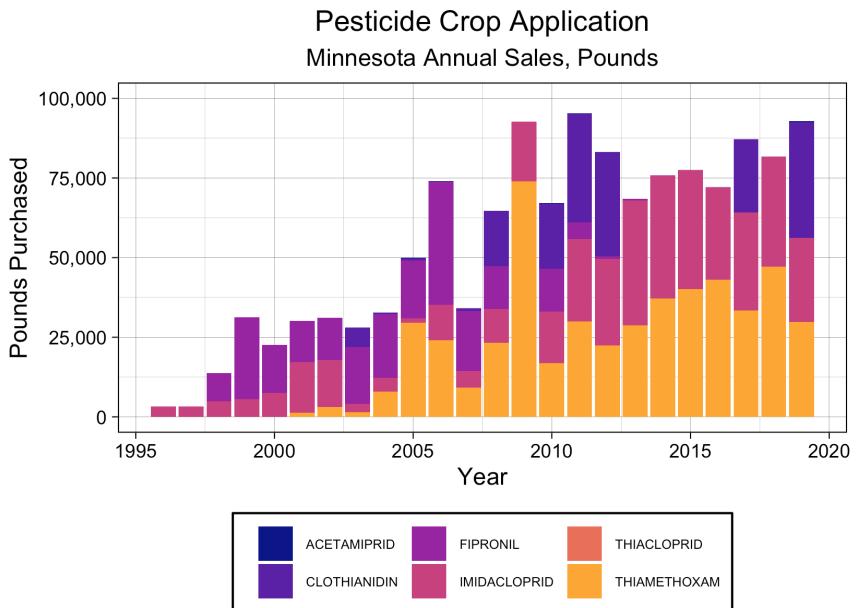
Purchase rate is a strong indicator of pesticide detection.



Purchase rate is a strong indicator of pesticide detection.



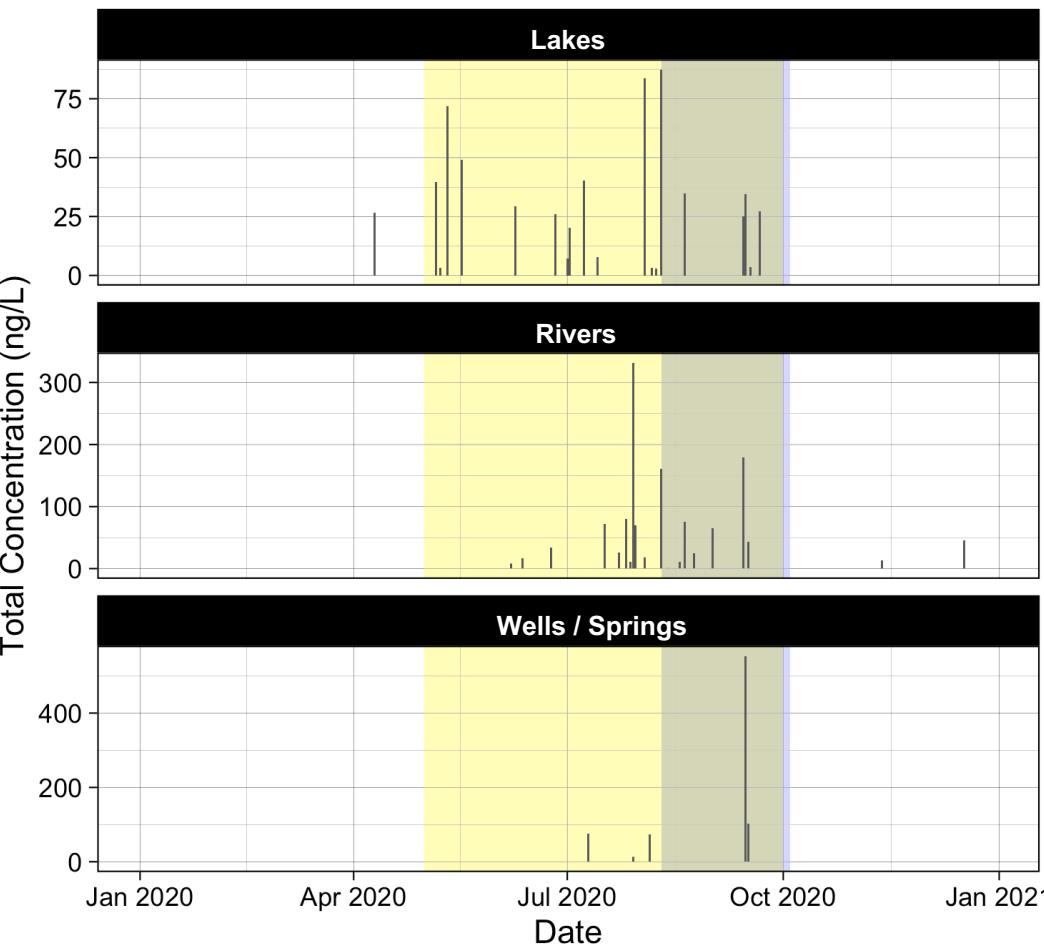
Purchase rate is a strong indicator of pesticide detection.



Total neonic concentrations highest during rainy and growing seasons.

- Concentrations peak during peak **growing season**
- Largest spring detections during **rainy season**.

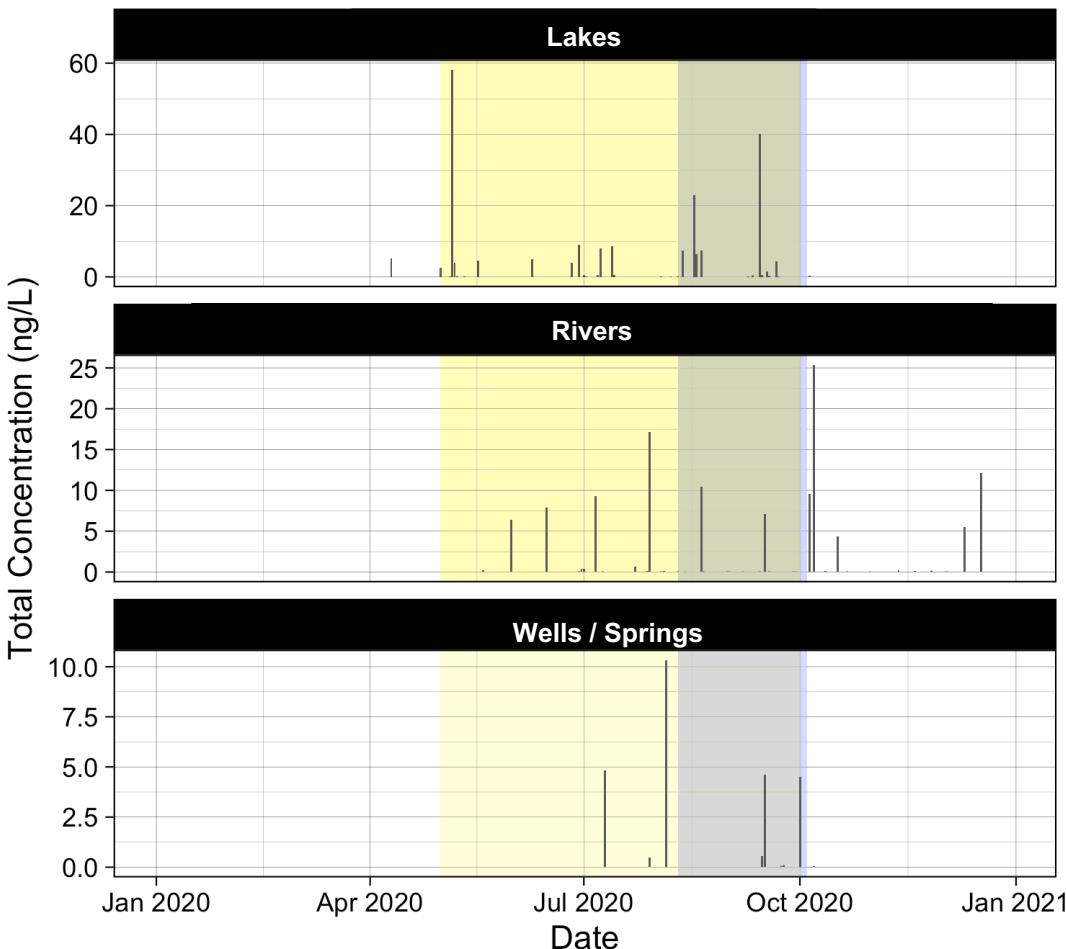
Total Neonicotinoid Concentration
2020 Sampling Season



Total fipronil concentrations highest during rainy and growing seasons.

- Concentrations peak during **growing season**.
- Rate of detection highest during **growing season**.
- Spring concentrations highest during late growing season / rainy season.

Total Fiprole Concentration
2020 Sampling Season



Shingle Creek Pesticide Concentration



Total pesticide concentrations highest during rainy and growing seasons

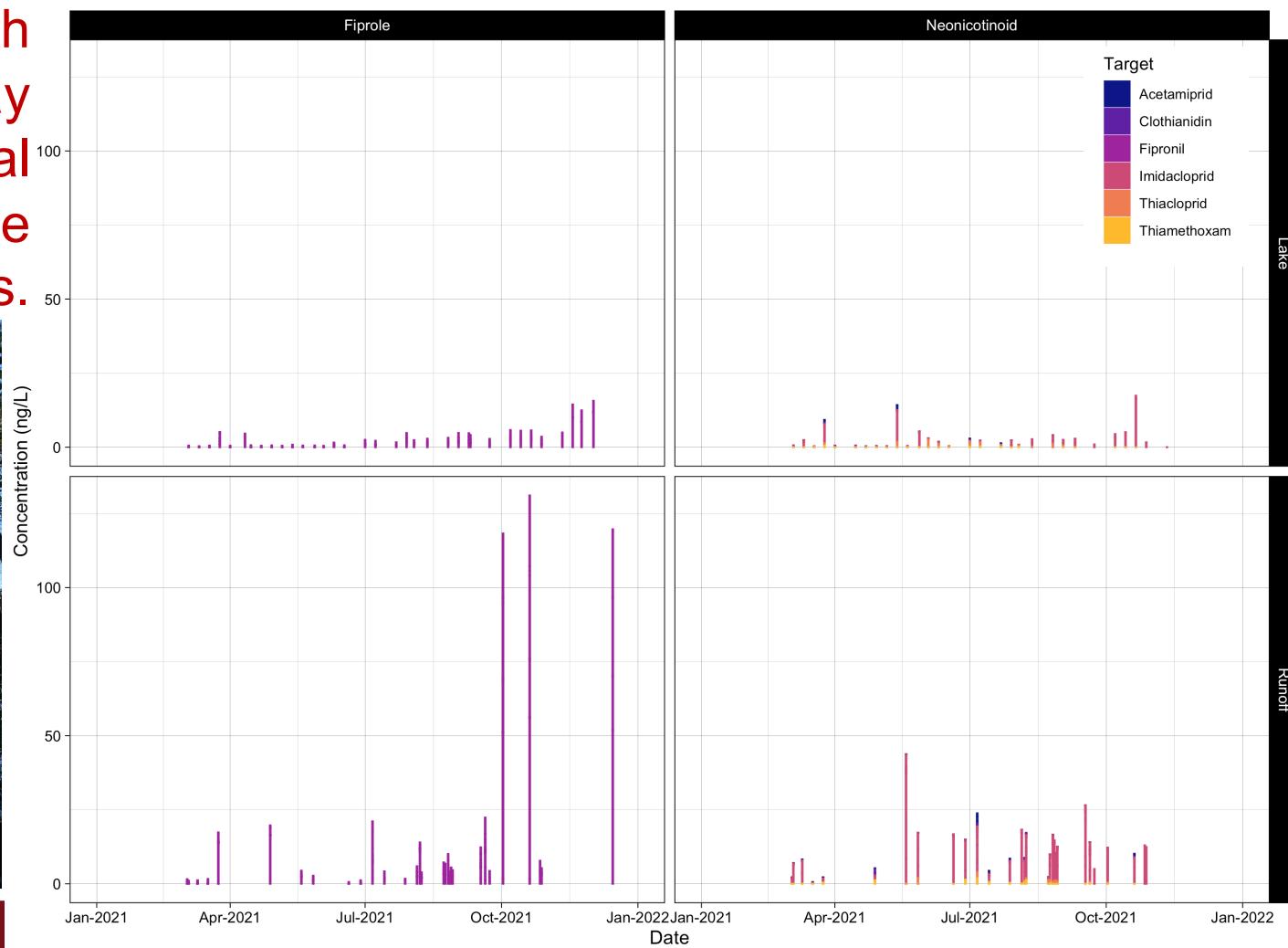
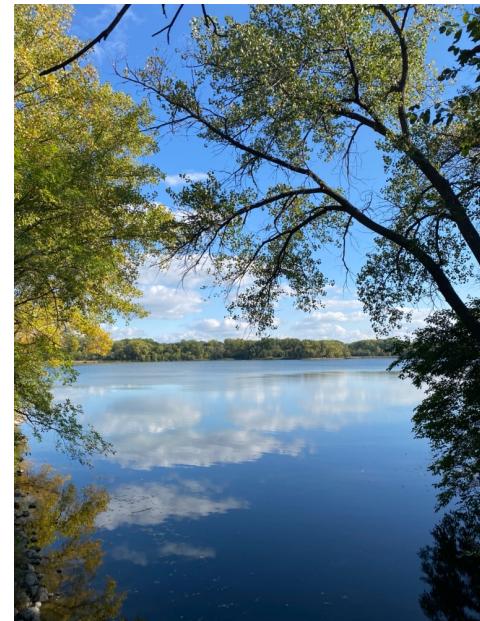
Target

- Acetamiprid
- Acetamiprid-N-Desmethyl
- Clothianidin
- Desnitro-Imidacloprid
- Fipronil
- Fipronil Desulfanyl
- Fipronil Sulfide
- Fipronil Sulfone
- Growing
- Imidacloprid
- Imidacloprid Olefin
- Imidacloprid Urea
- Thiacloprid
- Thiacloprid Amide
- Thiamethoxam



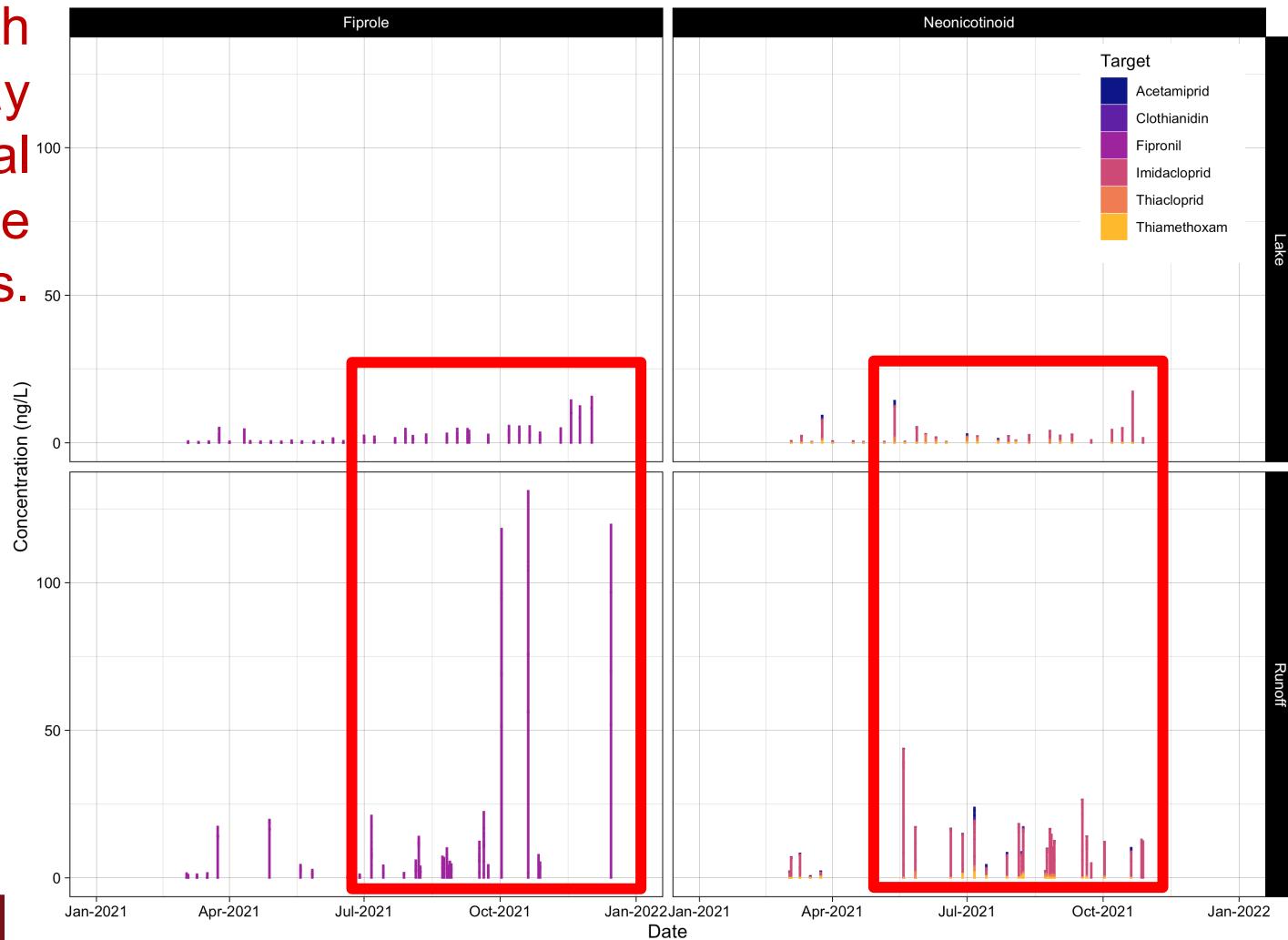
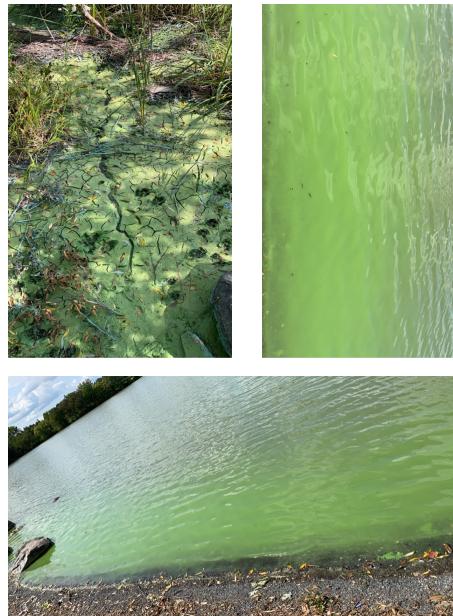
Lake Como Runoff Pesticide

High-strength runoff may influence total pesticide concentrations.

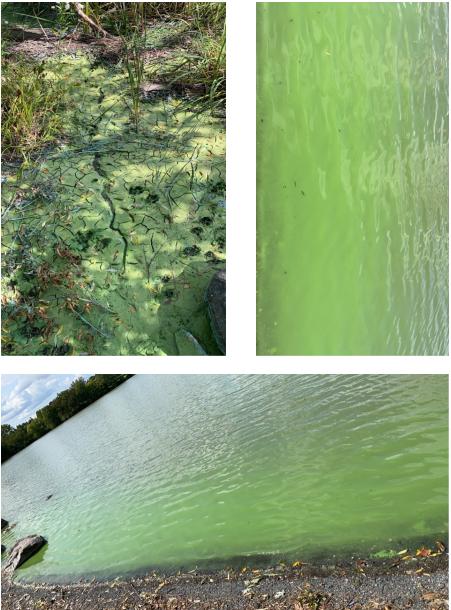


Lake Como Runoff Pesticide

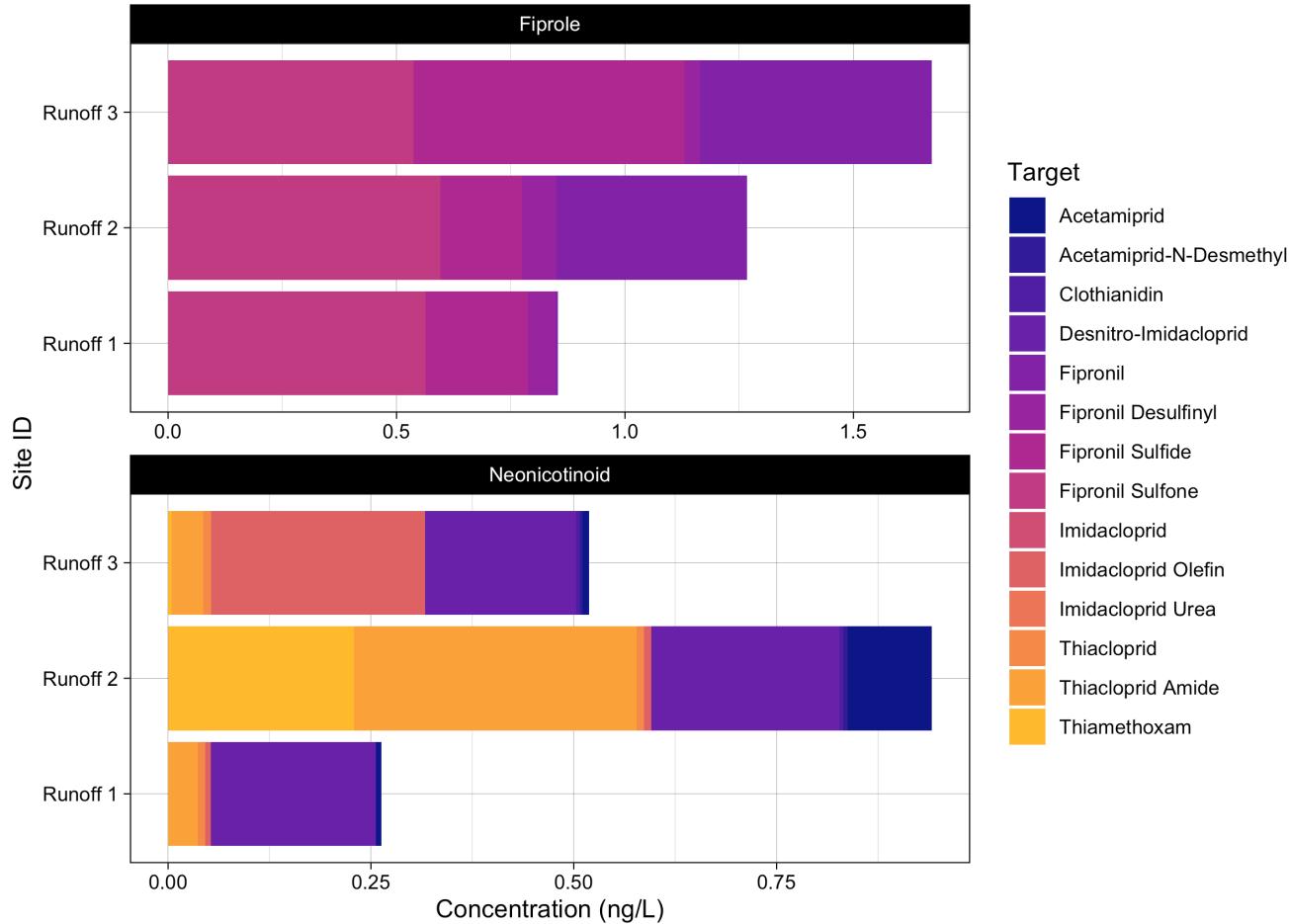
High-strength runoff may influence total pesticide concentrations.



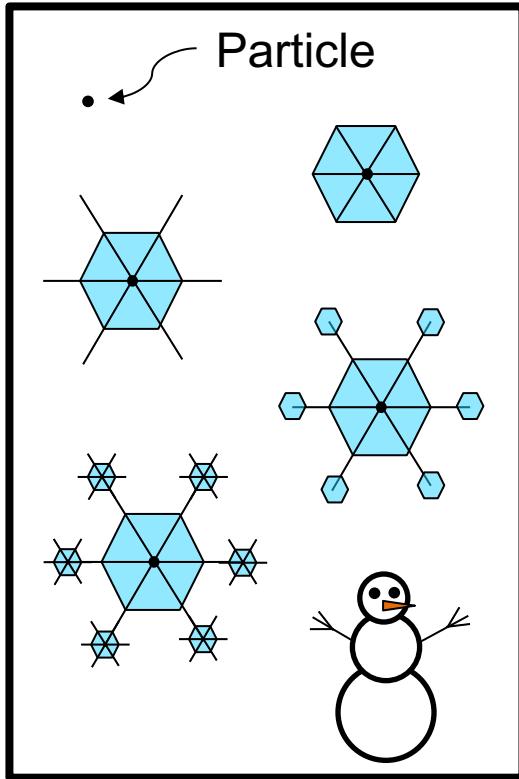
High-strength runoff may influence total pesticide concentrations



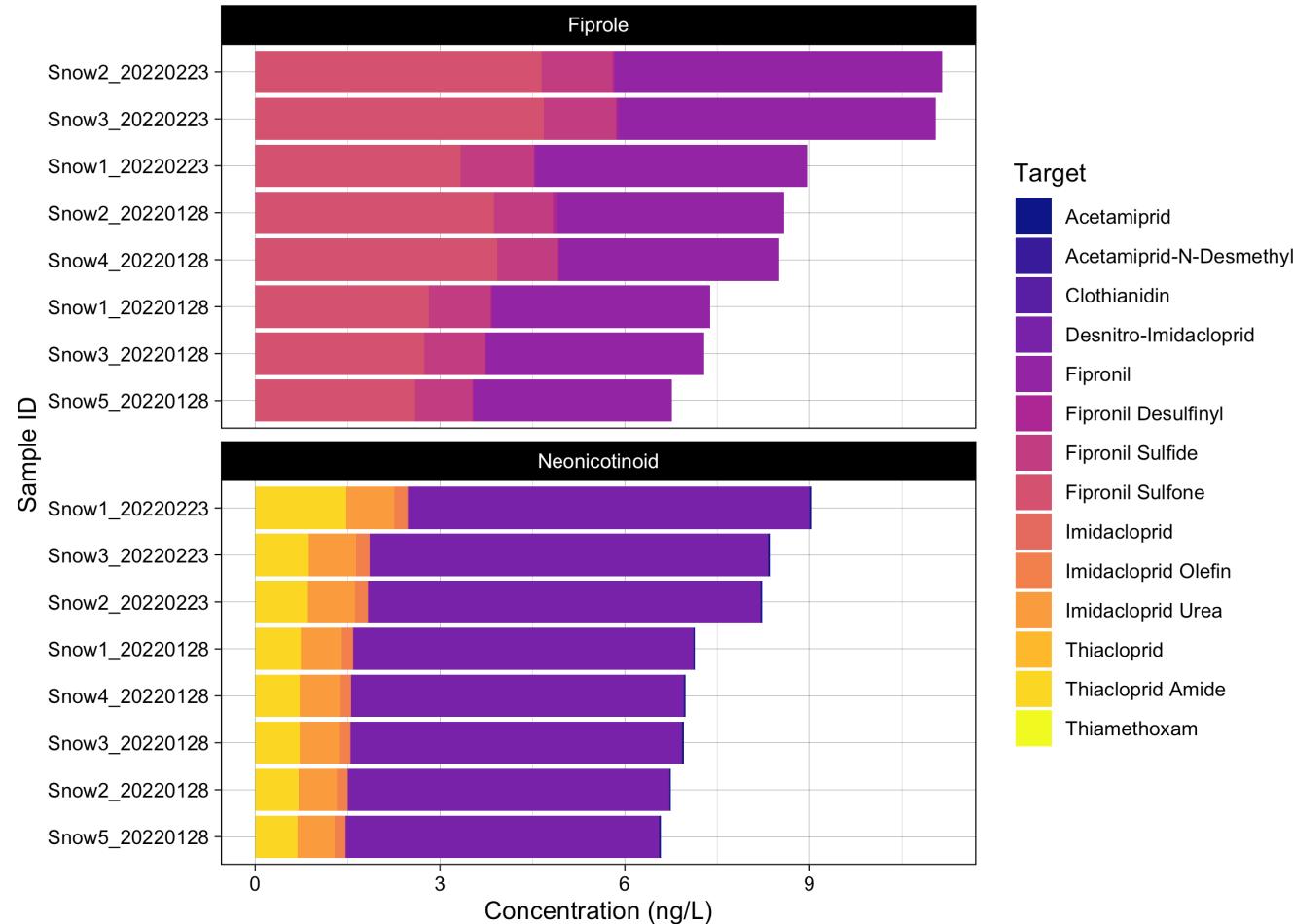
Pesticide Accumulation in Surface Runoff



Snowfall acts as secondary transport for pesticides.

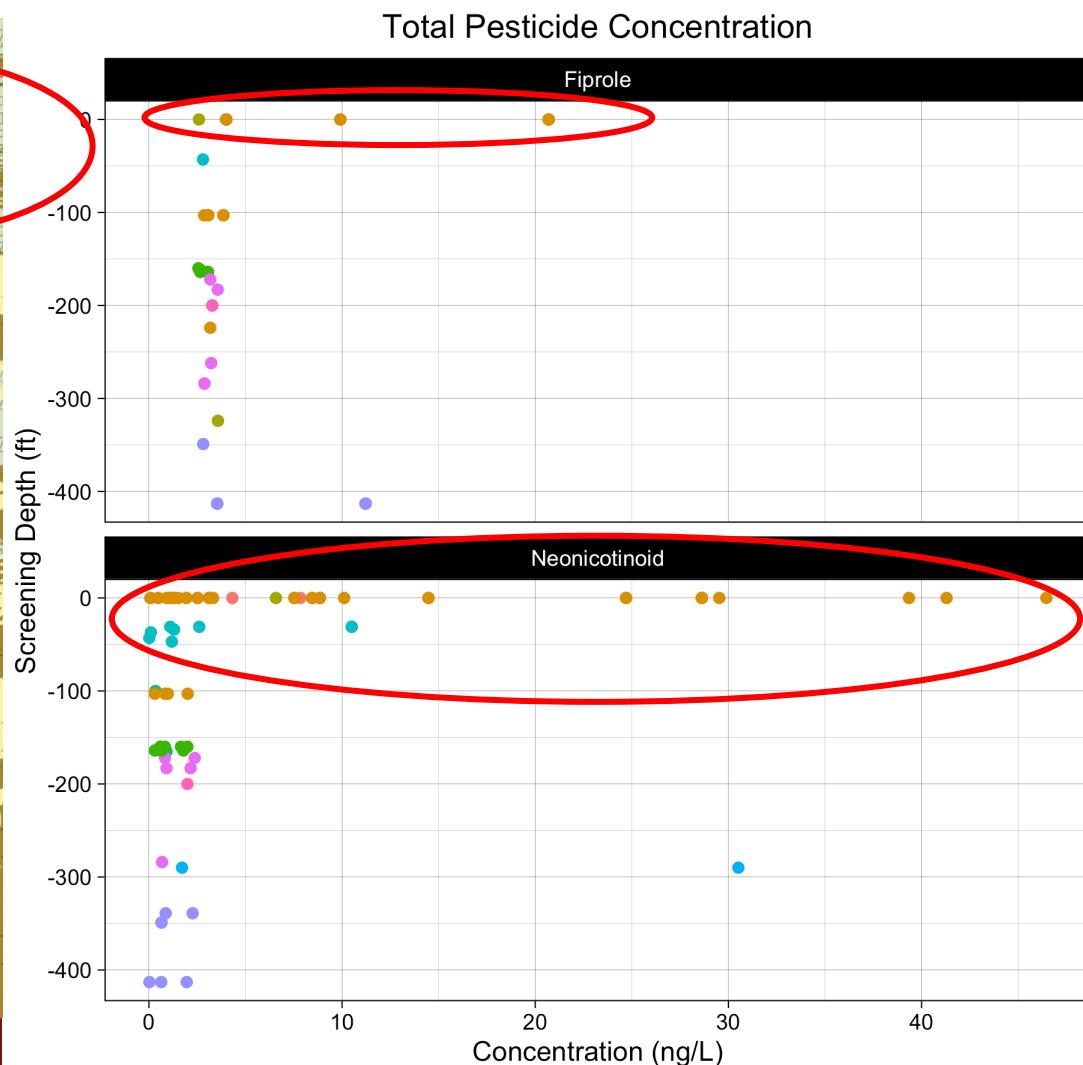
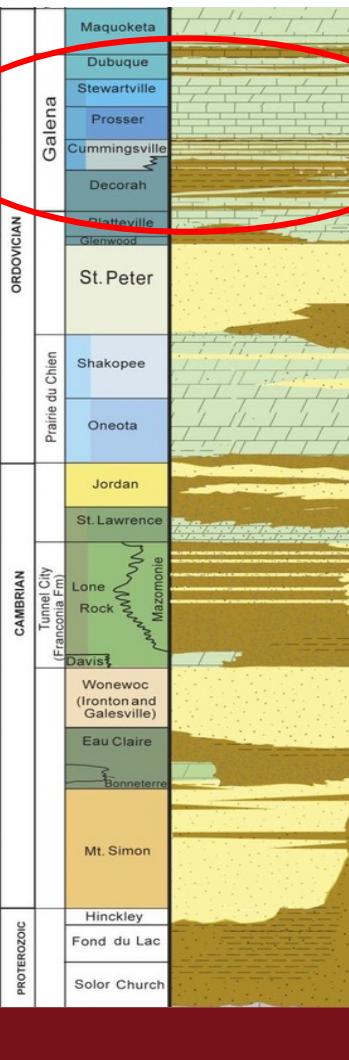


Pesticide Accumulation in Fresh Snow



Fipronil and neonicotinoid concentrations increase exponentially with casing depth.

- Aquifer
- Dubuque-Galena
 - Galena
 - Jordan
 - KRET
 - Prairie Du Chien
 - Prosser-Cummingsville
 - QBAA
 - QBUA
 - QWTA
 - SIOUX QUARTZITE
 - St. Peter
 - Stewartville-Prosser
 - Below LOD
 - Above LOD



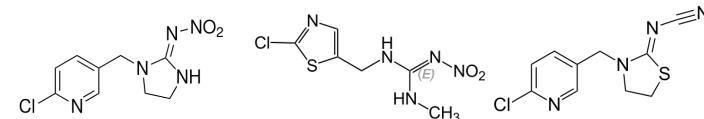
1 Background

2 Study Design

3 Results

4 Implications

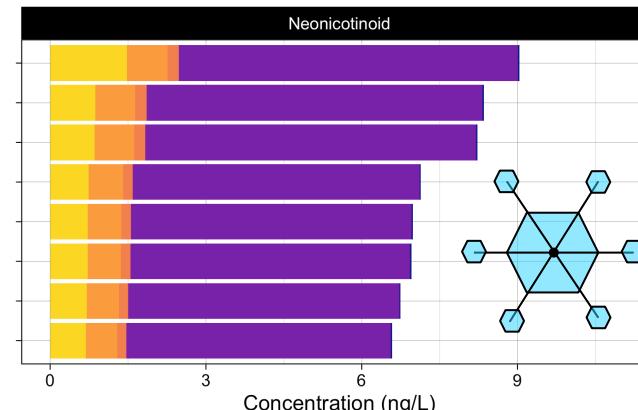
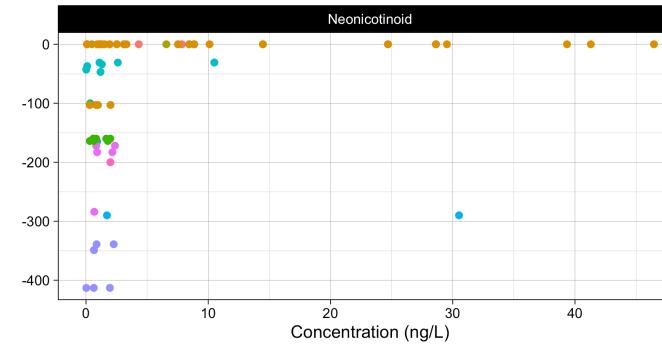
5 Questions



Imidacloprid

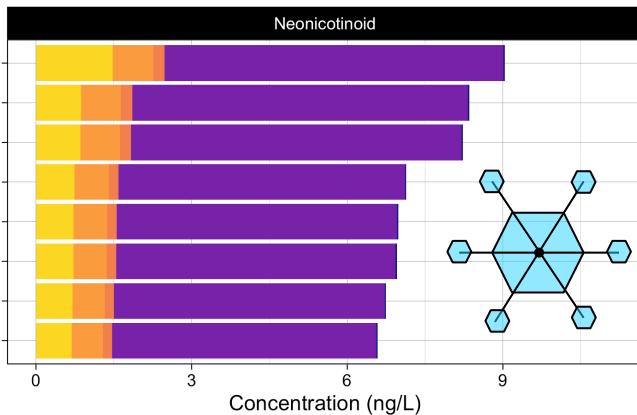
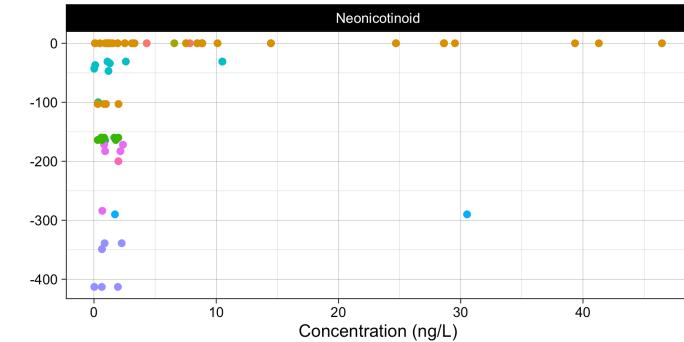
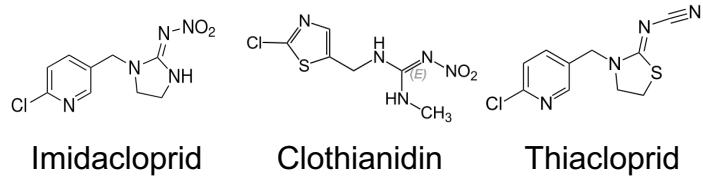
Clothianidin

Thiacloprid



Key Takeaways:

- Lakes and groundwater act as long-term **reservoirs for longer-term degradation.**
- **Seasonality, Application Rate** increase concentration and rate of detection.
- **Shallow, unconfined aquifers** highest risk for groundwater contamination.
- Previously overlooked forms of **precipitation** may be **key transport mechanism.**





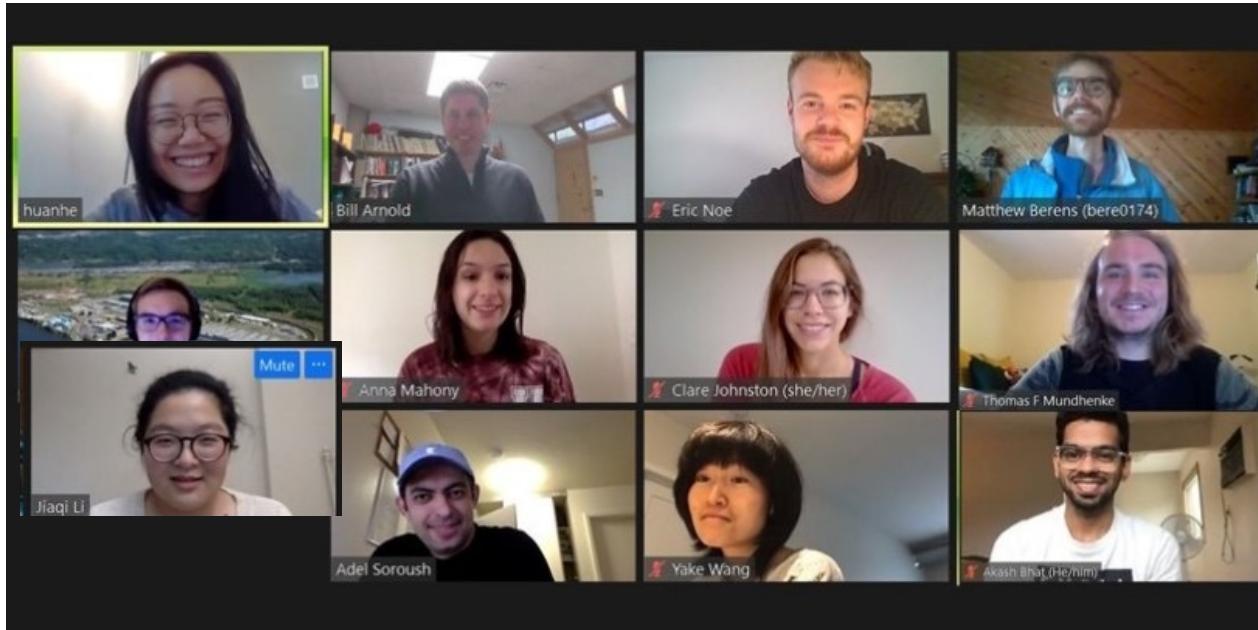
UNIVERSITY OF MINNESOTA

Driven to Discover®

Crookston Duluth Morris Rochester Twin Cities

The University of Minnesota is an equal opportunity educator and employer.

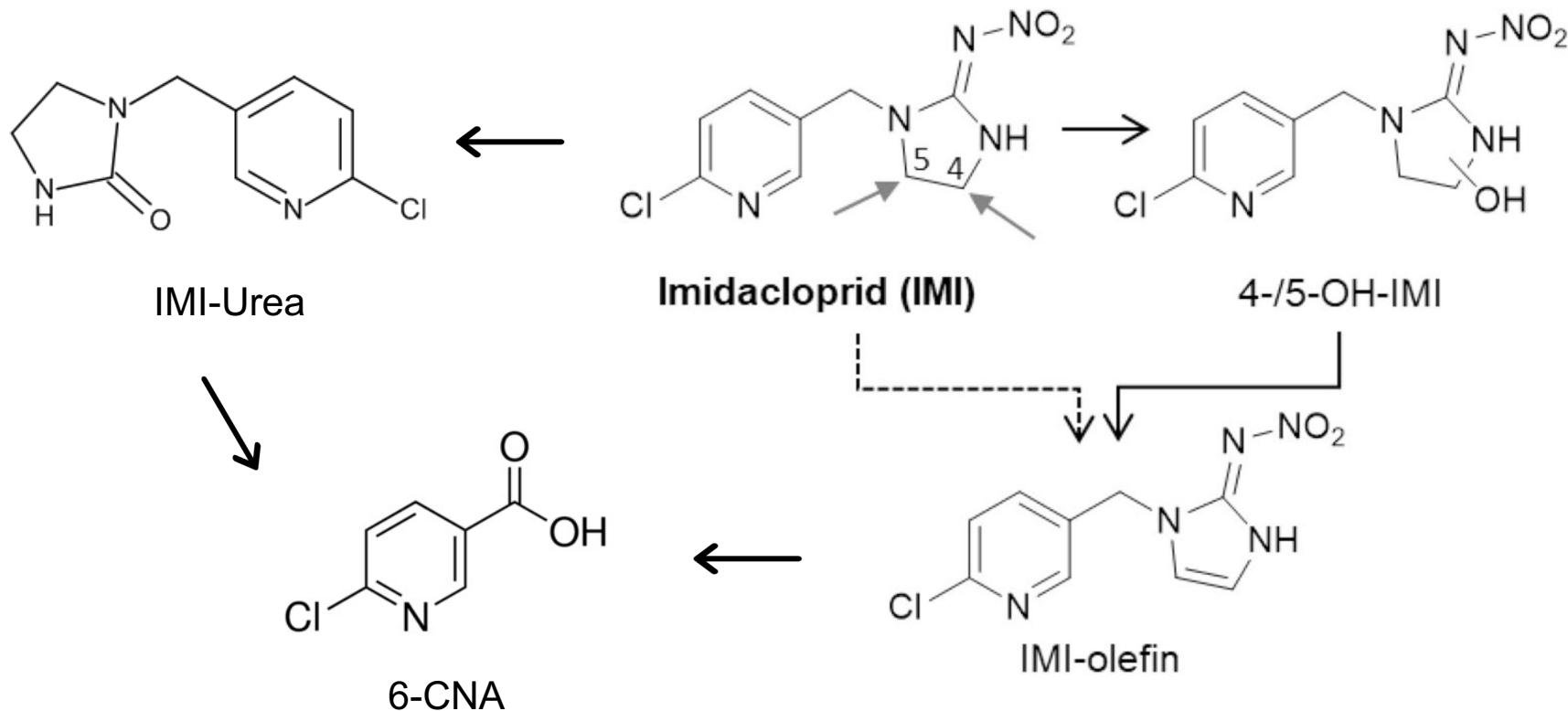
Grant Goedjen
University of Minnesota
Dept. of Civil, Environmental, and Geo-Engineering
Goedj011@umn.edu
(832) 445-7265



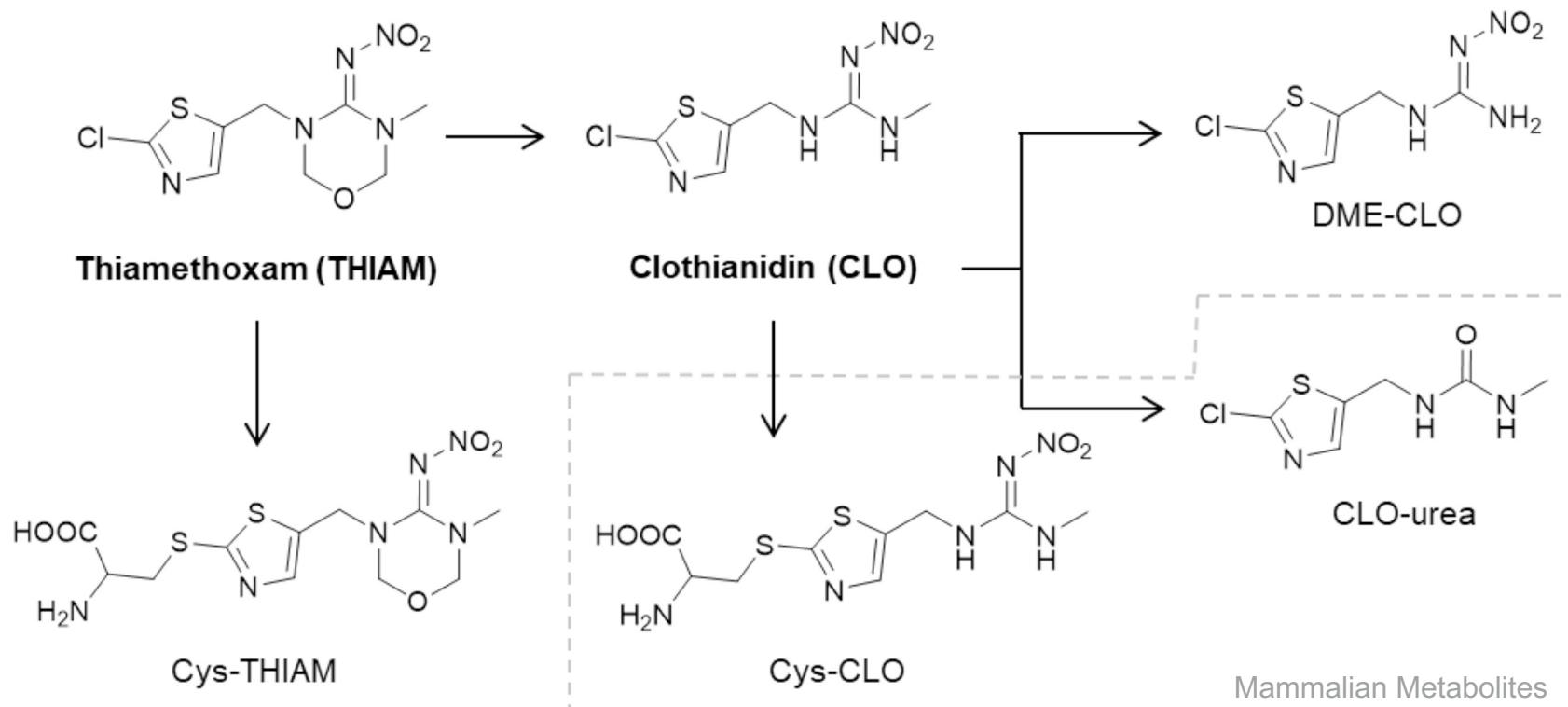
<https://WilliamArnold.org>



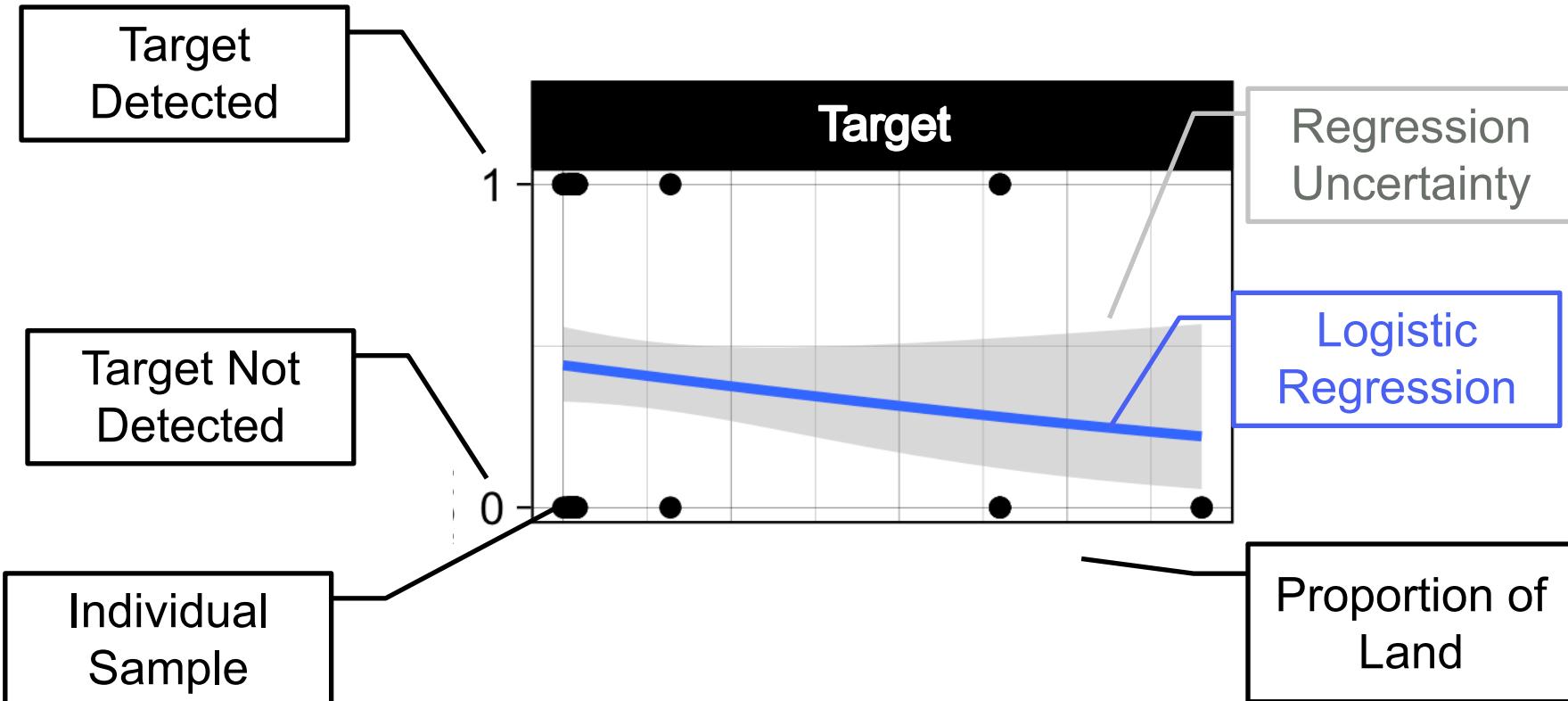
TPs: Imidacloprid



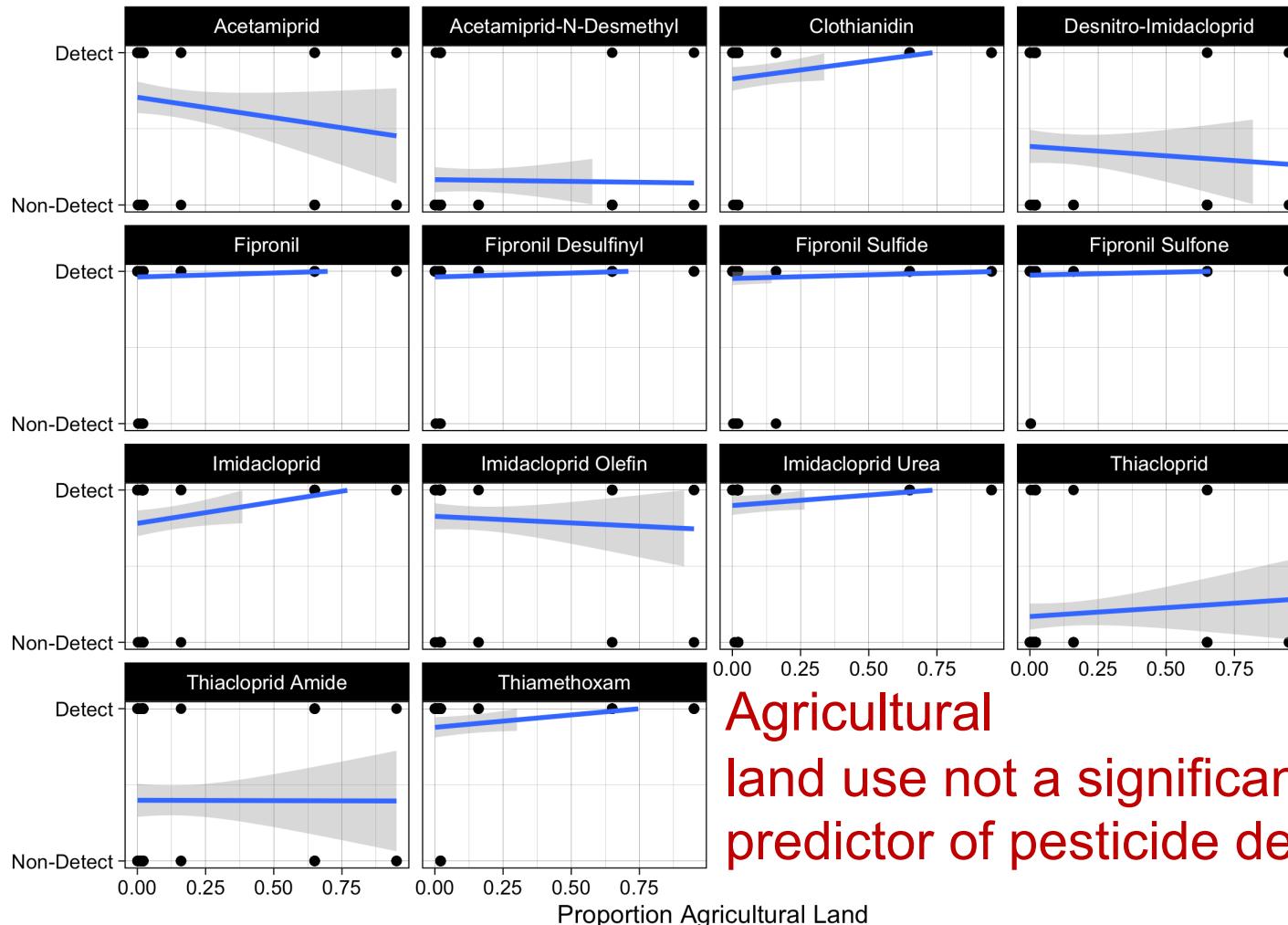
TPs: Thiamethoxam /Clothianidin



Effect of Land Use: Logistic Regression

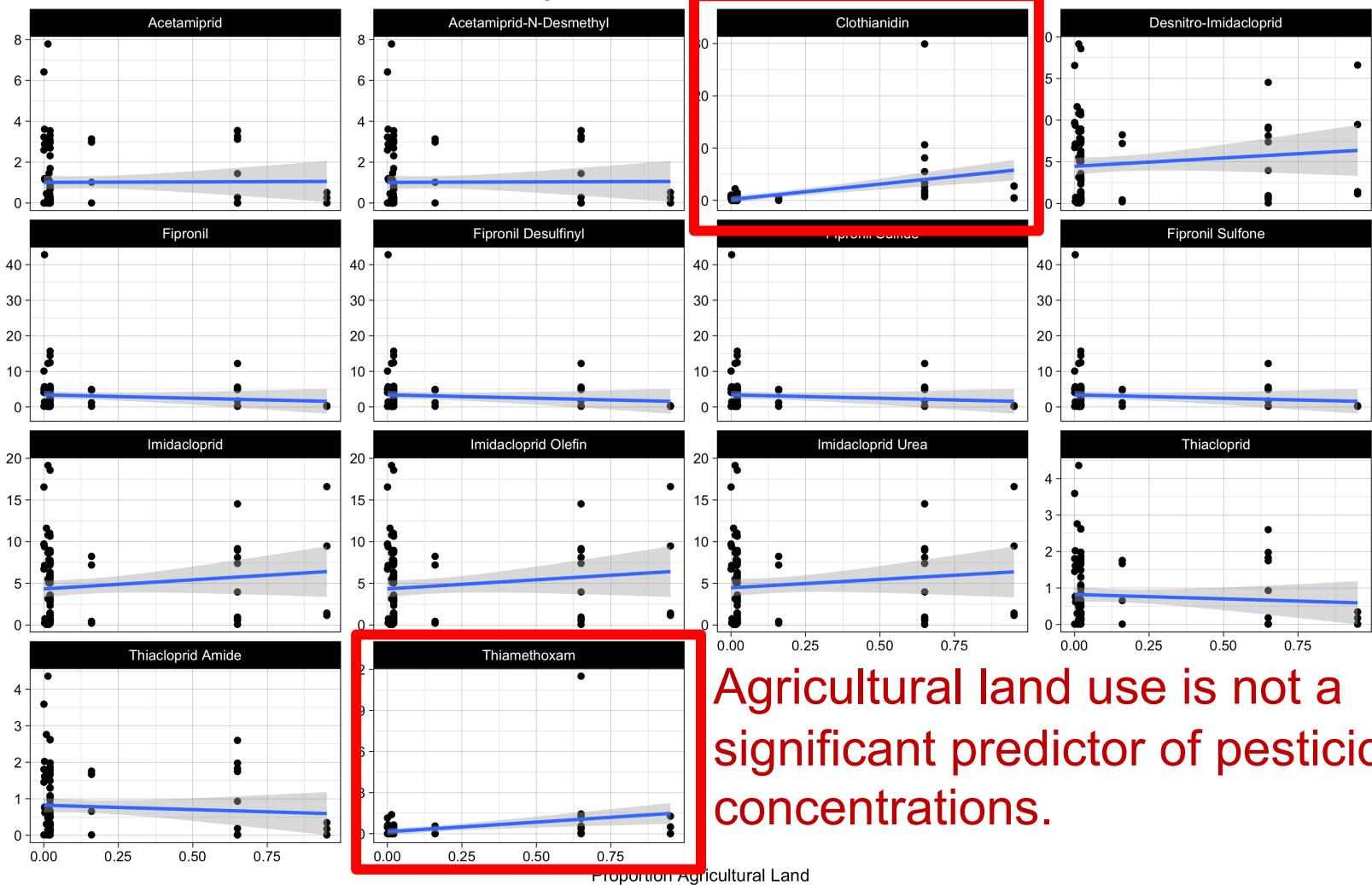


Influence of Agricultural Land Use on Pesticide Detections



Agricultural land use not a significant predictor of pesticide detection.

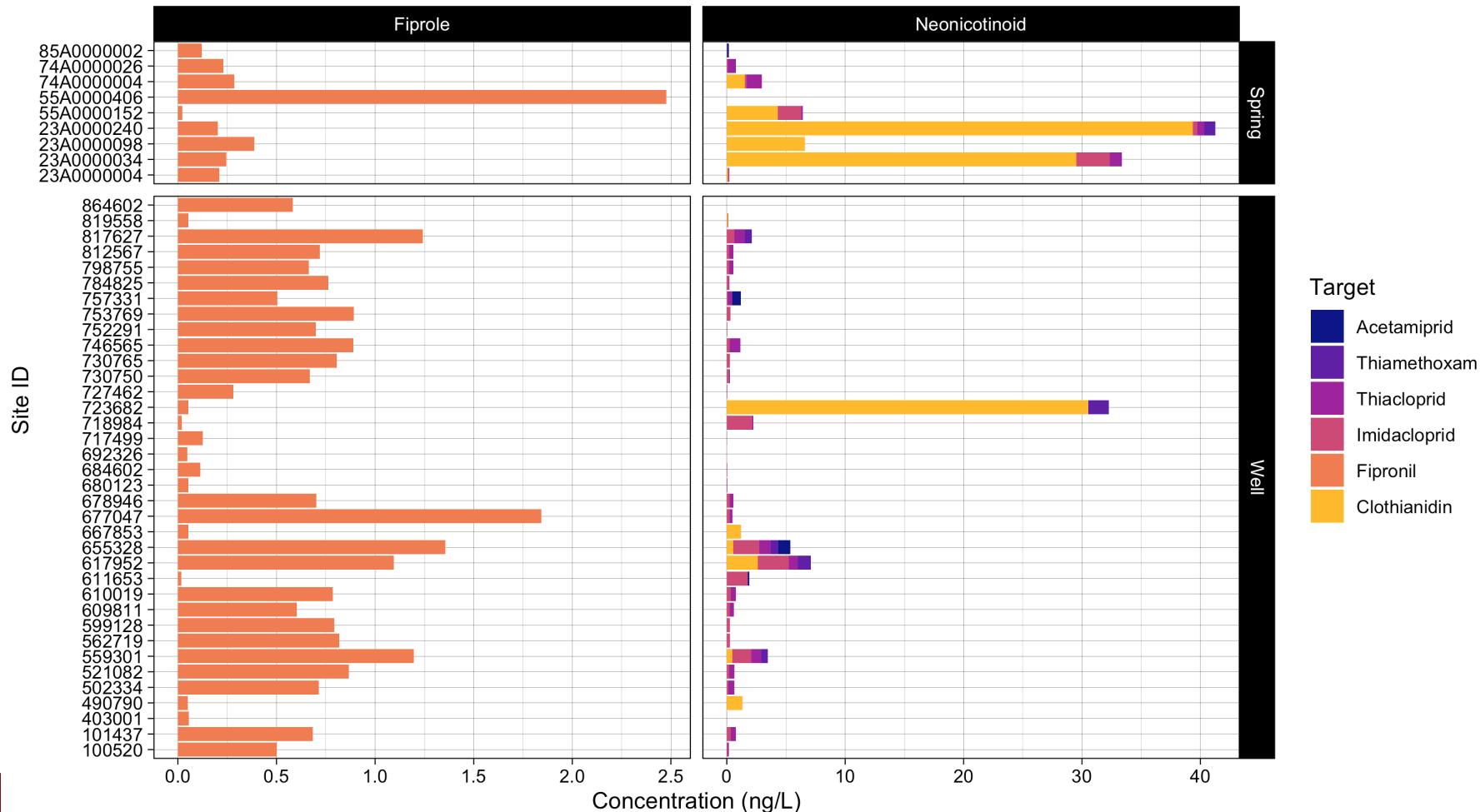
Influence of Agricultural Land Use on Pesticide Concentration



Agricultural land use is not a significant predictor of pesticide concentrations.

Mean Pesticide Concentrations

Groundwater



Median Pesticide Concentrations

Surface Water

