Insecticide and Fungicide Residue Monitoring from Treated Seed Recycling near a Nebraska Bioethanol Facility

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Outline

- Increasing use of pesticides in treated seed
- Disposal or recycling seed corn
- AltEN facility history & 2021 spill
- Waste product disposal methods
- Recent and projected response to pesticide release
- Long term monitoring needs

PESTICIDES DETECTED: The AltEn plant near Mead, which was shut down earlier this year, is shown on Aug. 25. Byproducts have now been detected in groundwater 6 miles from the site. (Lincoln Journal Star Photo)

Pesticide seed treatment

- Difficult to identify all active ingredients currently used
- Likely over 40-50 chemical treatments generally classified as fungicides, insecticides, nematicides and plant growth regulators
- Multiple neonicotinoid insecticides, strobularin and azole fungicides used in corn

Clothiandin a.i. ~160 gm/35# bag enough for ~2.5 acres or ~64 gm/acre

What's on your seed?

Seed treatments have been used for a number of years, mostly for protection against seedling diseases. However, there are a number of new seed treatments marketed for protection against a range of pests, including seedling diseases, insects and nematodes, and even improving plant health.

The purpose of this publication is to take some of the confusion of seed treatments away, giving you a better understanding of what is on your seed. The list covers seed treatments registered in the state of Wisconsin for use on corn, soybean, small grain and/or alfalfa seed. The seed treatments are grouped by the number of active ingredients (1-6), treatment type (fungicide, insecticide, nematicide or plant growth regulator) and then alphabetically by the product trade name. The list is not based on efficacy of the seed treatments and is not an endorsement or criticism of one product over another. You are responsible for using pesticides according to the manufacturer's current label directions.

Damon Smith, Associate Professor of Plant Pathology

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NPM

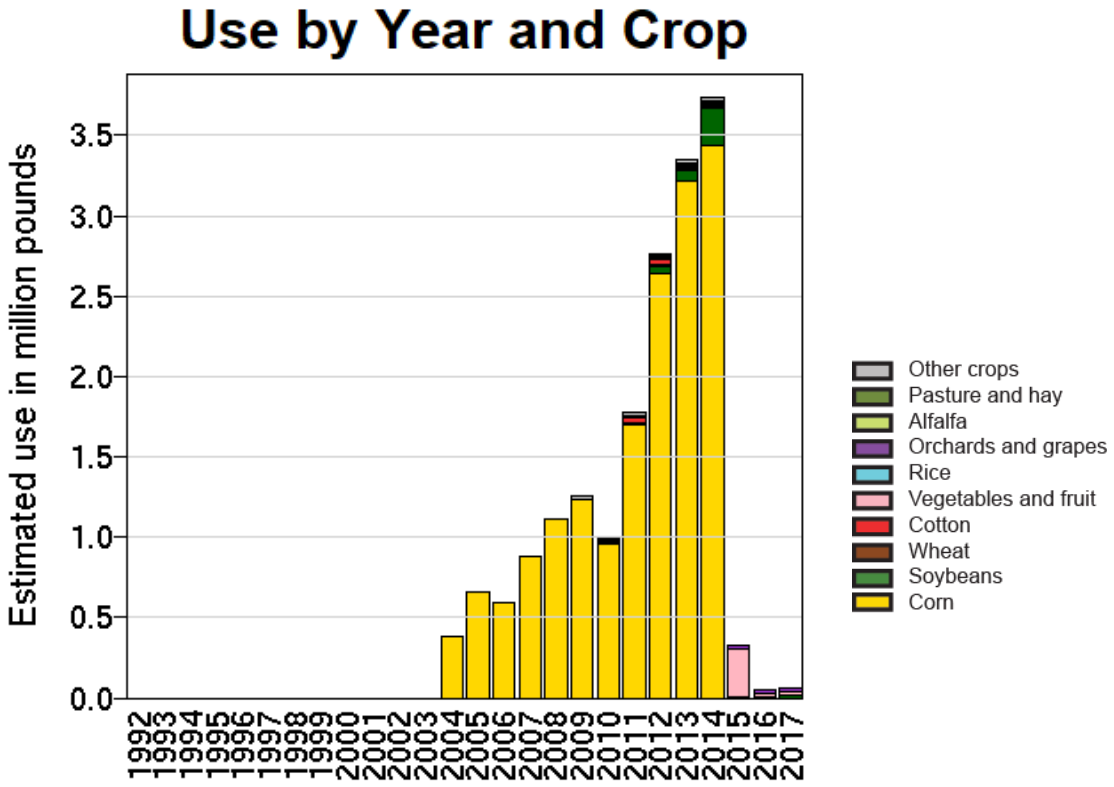
College of Agricultural & Life Sciences
UNIVERSITY OF WISCONSIN–MADISON

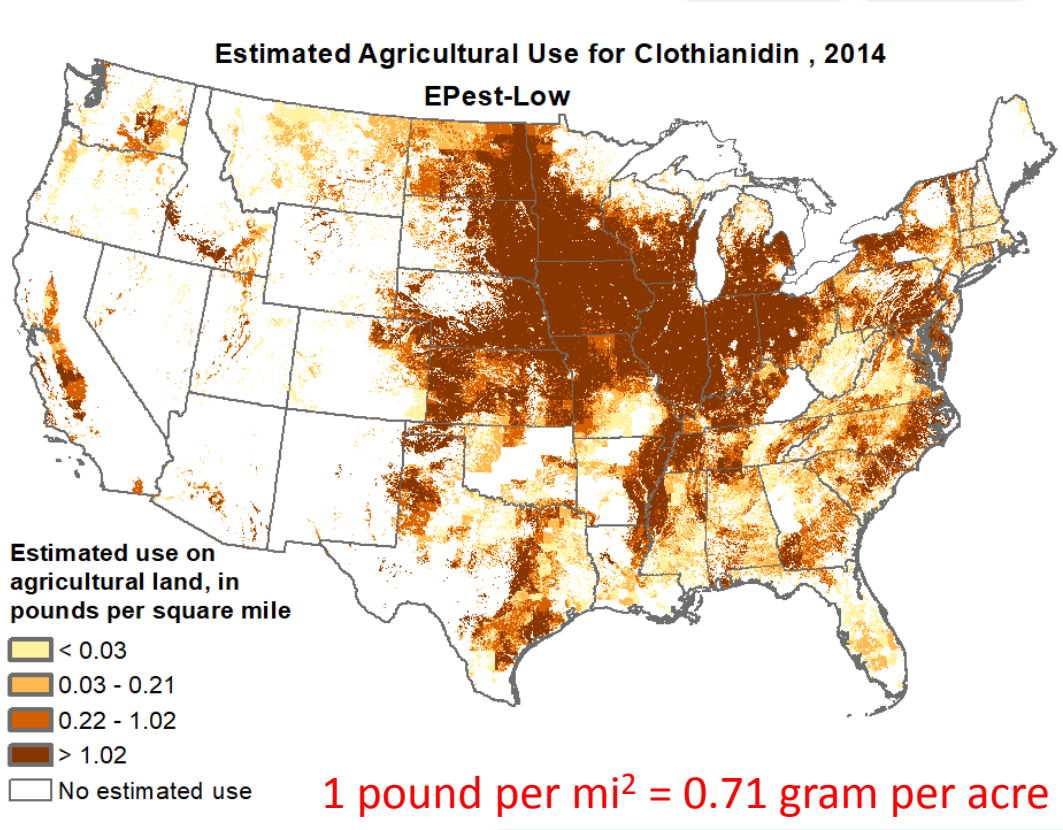
Treatment Type Legend

- F Fungicide
- I Insecticide
- N Nematicide
- P Plant Growth Regulator

	Active Ingredient(s)	Product Trade Name	Crop
F	azoxystrobin	**Agri Star Azoxystrobin 100 ST**	Corn, Soybean, Small Grains
		A-Zox 25SC	Corn, Soybean
		Dynasty®	Corn, Soybean, Small Grains
		Start UP AZOXY	Corn, Soybean, Small Grains
F	*Bacillus amyloliquefaciens*, strain MBI 600	**HiStick® N/T Soybean**	Soybean
		Integral®	Soybean
		L-2013 P	Corn

Neonicotinoid Insecticides

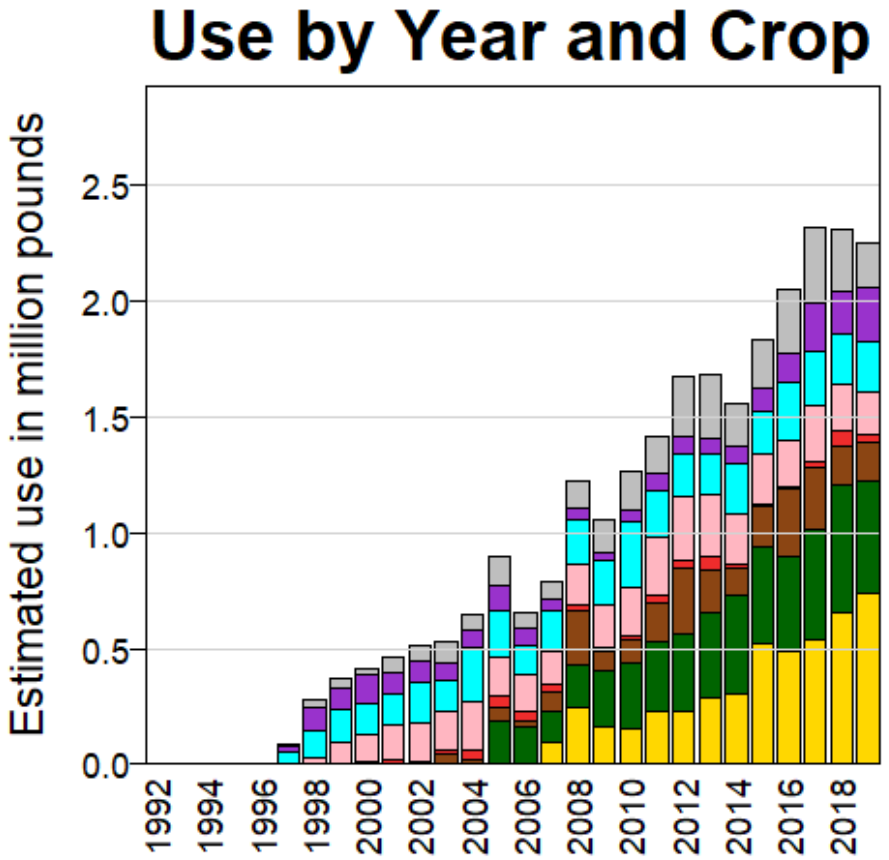


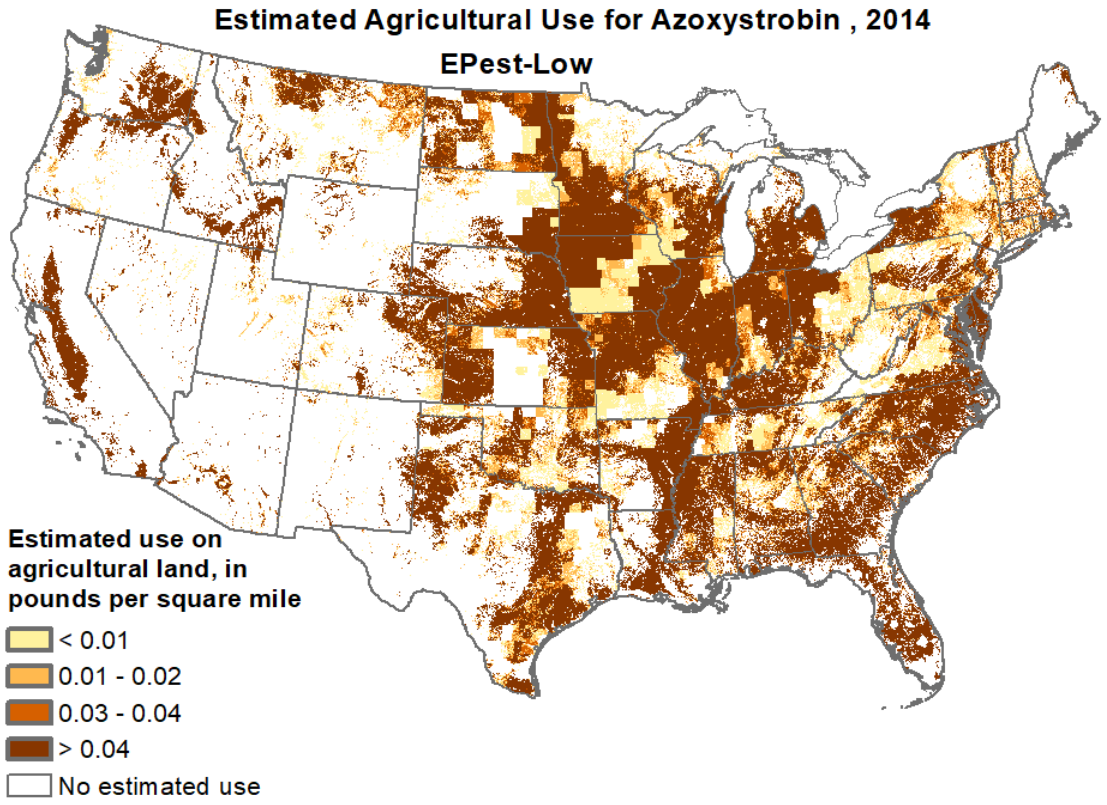


1 pound per mi^2 = 0.71 gram per acre

https://water.usgs.gov/nawqa/pnsp/usage/maps/show_map.php?year=2011&map=CLOTHIANIDIN&hilo=L&disp=Clothianidin

Strobularin fungicides





https://water.usgs.gov/nawqa/pnsp/usage/maps

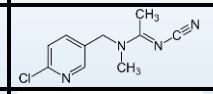
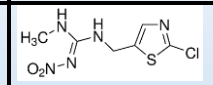
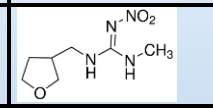
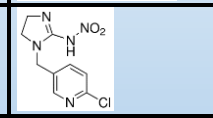
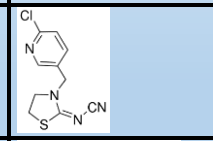
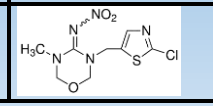
Disposing excess treated seed product

1. Municipal Landfill
2. Fuel Source for Power Plants or Cement Kilns
3. High-Temperature Incineration by a Waste Management Facility
4. Fermentation in an Alcohol-Producing Process at an Ethanol Plant

https://www.lsuagcenter.com/profiles/truffin/articles/page1565288428524

Neonicotinoid insecticides

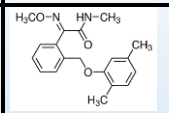
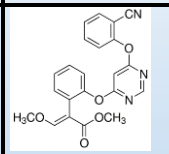
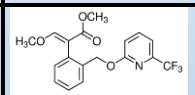
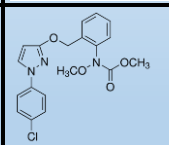
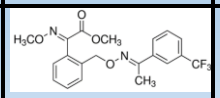
Table 1. Analyte Physical Parameters

Analyte	CAS Number	Mol. Formula	Mol. Weight (g/mol)	Solubility in water	pKa	Log Kow pH = 7	Structure
Acetamiprid	135410-20-7	$C_{10}H_{11}ClN_4$	222.67	2.95 g/L @ 20ºC	0.7	0.80 @20ºC	
Clothianidin	210880-92-5	$C_6H_8ClN_5O_2S$	249.68	0.340 g/L @ 20ºC	11.1	0.905 @20ºC	
Dinotefuran	165252-70-0	$C_7H_{14}N_4O_3$	202.21	39.8 g/L @ 20ºC	12.6	-0.549 @20ºC	
Imidacloprid	138261-41-3	$C_9H_{10}ClN_5O_2$	255.66	0.61 g/L @ 20ºC	NA	0.57 @20ºC	
Thiacloprid	111988-49-9	$C_{10}H_9ClN_4S$	252.72	0.184 g/L @ 20ºC	NA	1.26 @20ºC	
Thiamethoxam	153719-23-4	$C_8H_{10}ClN_5O_3S$	291.71	4.10 g/L @ 20ºC	NA	-0.13 @20ºC	

- Generally low mammalian toxicity
- Water soluble and persistent
- Some ecological effects

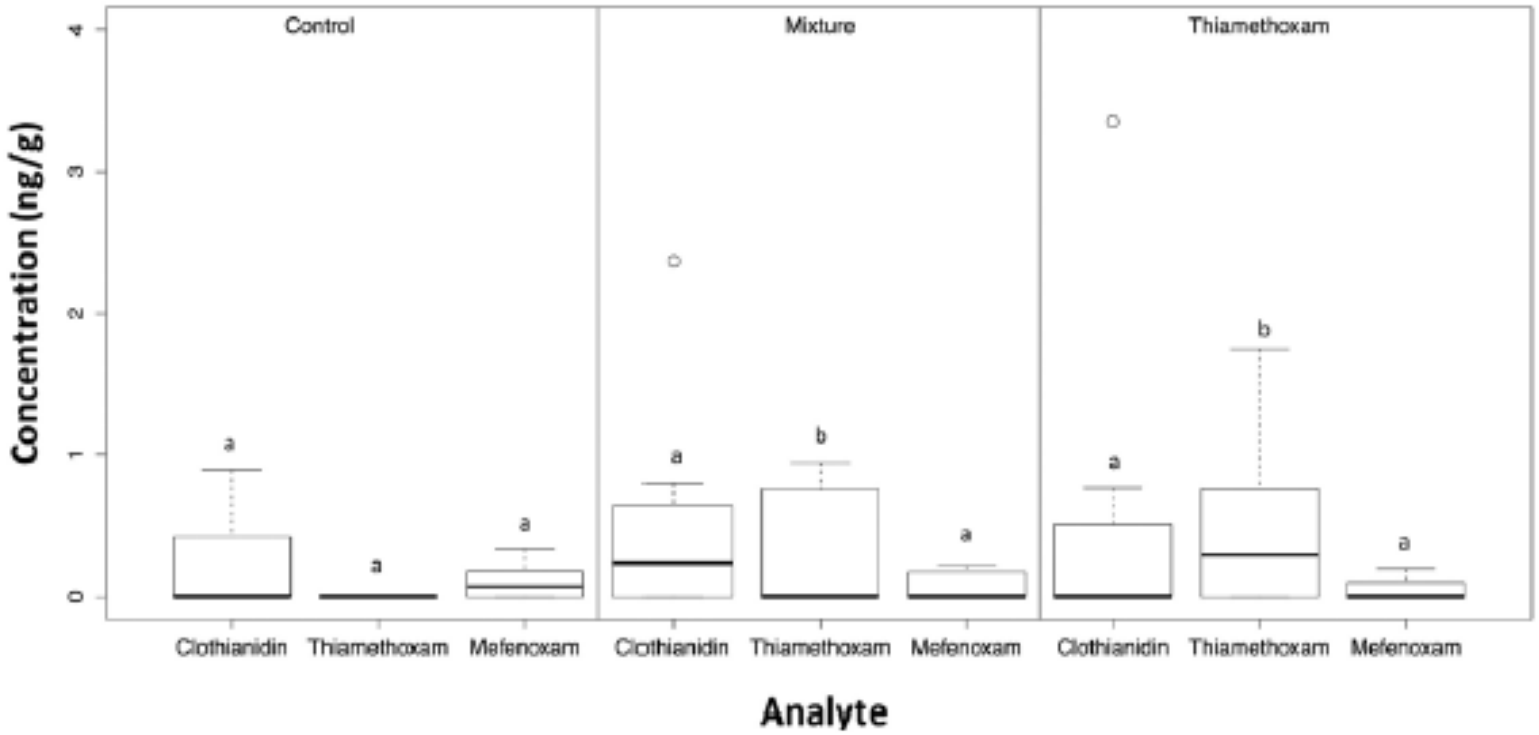
Strobularin fungicides

Table 1. Analyte Physical Parameters

Analyte	CAS Number	Mol. Formula	Mol. Weight (g/mol)	Solubility in water	pKa	Log Kow pH = 7	Structure
Dimoxystrobin	149961-52-4	$C_{19}H_{22}N_2O_3$	326.39	.0043 g/L @ 20ºC	NA	3.59 @20ºC	
Azoxystrobin	131860-33-8	$C_{22}H_{17}N_3O_5$	403.39	0.0067 g/L @ 20ºC	NA	2.5 @20ºC	
Picoxystrobin	117428-22-5	$C_{18}H_{16}F_3NO_4$	367.32	0.0031 g/L @ 20ºC	NA	3.6 @20ºC	
Pyraclostrobin	175013-18-0	$C_{19}H_{18}ClN_3O_4$	387.82	0.0019 g/L @ 20ºC	NA	3.99 @20ºC	
Trifloxystrobin	141517-21-7	$C_{20}H_{19}F_3N_2O_4$	408.37	0.00061 g/L @ 20ºC	NA	4.5 @20ºC	

- Generally low mammalian toxicity
- Less soluble and persistent
- Ecological effects to amphibians

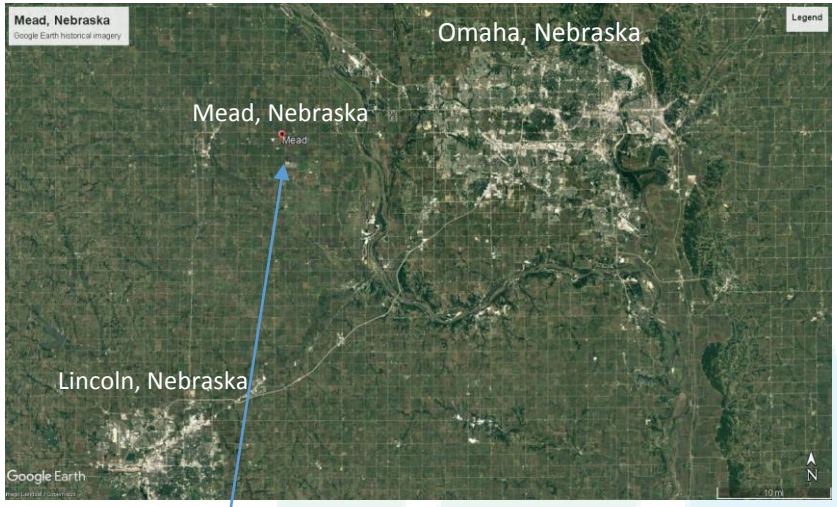
Exposure of honeybees to pesticide mixtures



Camargo, C., Snow, D. D., Onanong, S., Hunt, T. E., & Siegfried, B. D. (2019). Residues of thiamethoxam and mefenoxam in vegetative and floral tissue of soybean at the early reproductive stage resulting from seed treatments. *Crop Protection*, *119*, 134-140.

AltEN Facility Background

- Ethanol production facility since 2004
- Began receiving and processing treated seed corn in 2015
- Estimated production of ~200,000 tons per year of wet distiller's grain w/solubles (WDGS)
- Maximum 70,000 cu yds storage
- Permit to compost WDGS on-site and land-apply
- Located adjacent to cattle operation
- Used anaerobic digesters to reduce solids content of wastewater

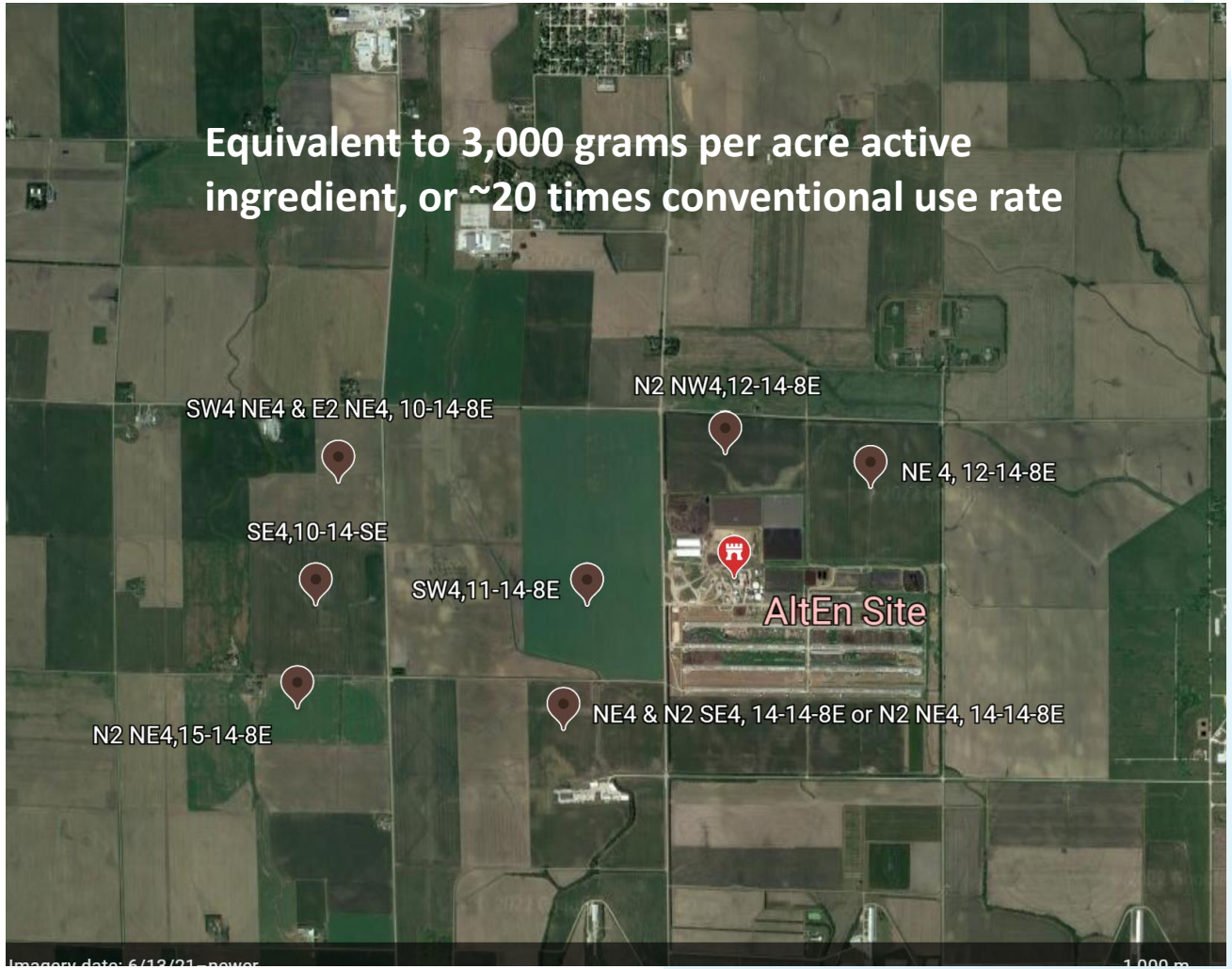


AltEN Facility Background - Continued

- Combined treated livestock bioenergy wastewater product applied to cropland through center pivots
- On-site lagoon wastewater storage
  - Three lagoons 165 million gallons total
  - Provision to apply wastewater to cropland
- Wastewater and spent distiller's byproducts applied to cropland starting in 2018
- Pesticides measured in distiller's byproducts 2019 (example 427,000 ng/g clothianidin)
- Wastewater up to 312,000 µg/L imidacloprid
- Lagoon structures and liners allowed leakage and run-off

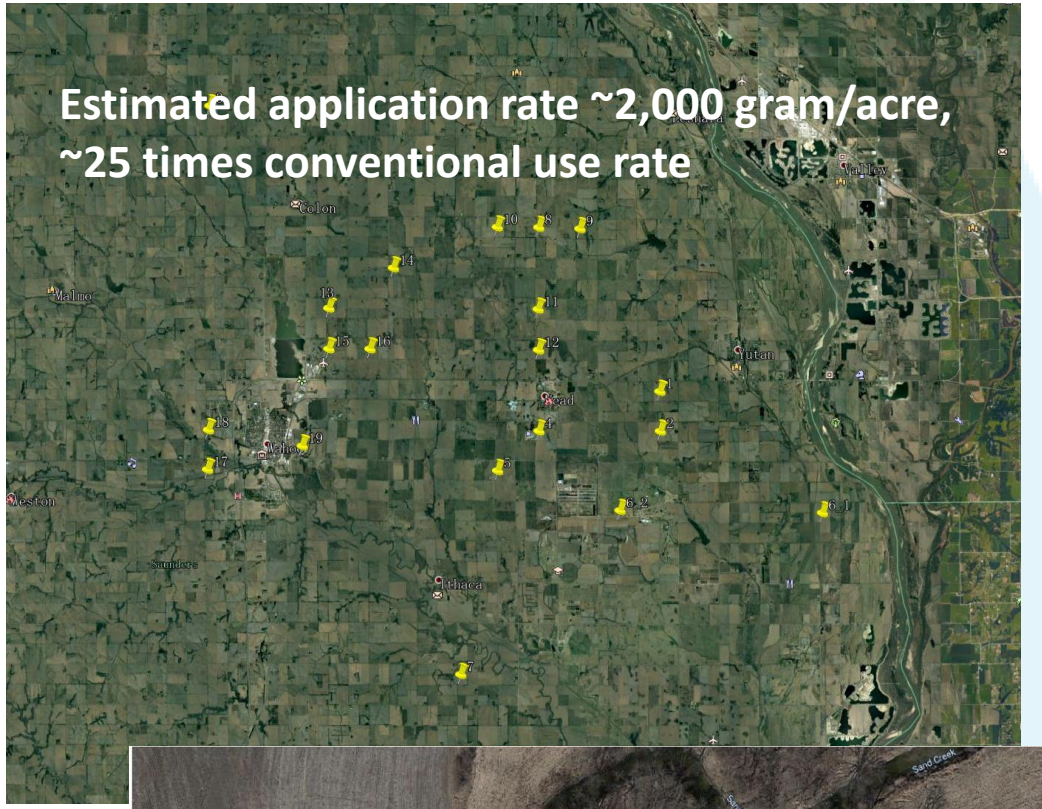
Wastewater application

- Over 30 million gallons wastewater applied to adjacent fields, some fields received 2-3 applications
- Grab samples show highest levels (>1,000 µg/L) for clothianidin, thiabendazole, thiamethoxam
- Detectable levels of 12 other residues
- Estimated average application 740,000 gallons per acre



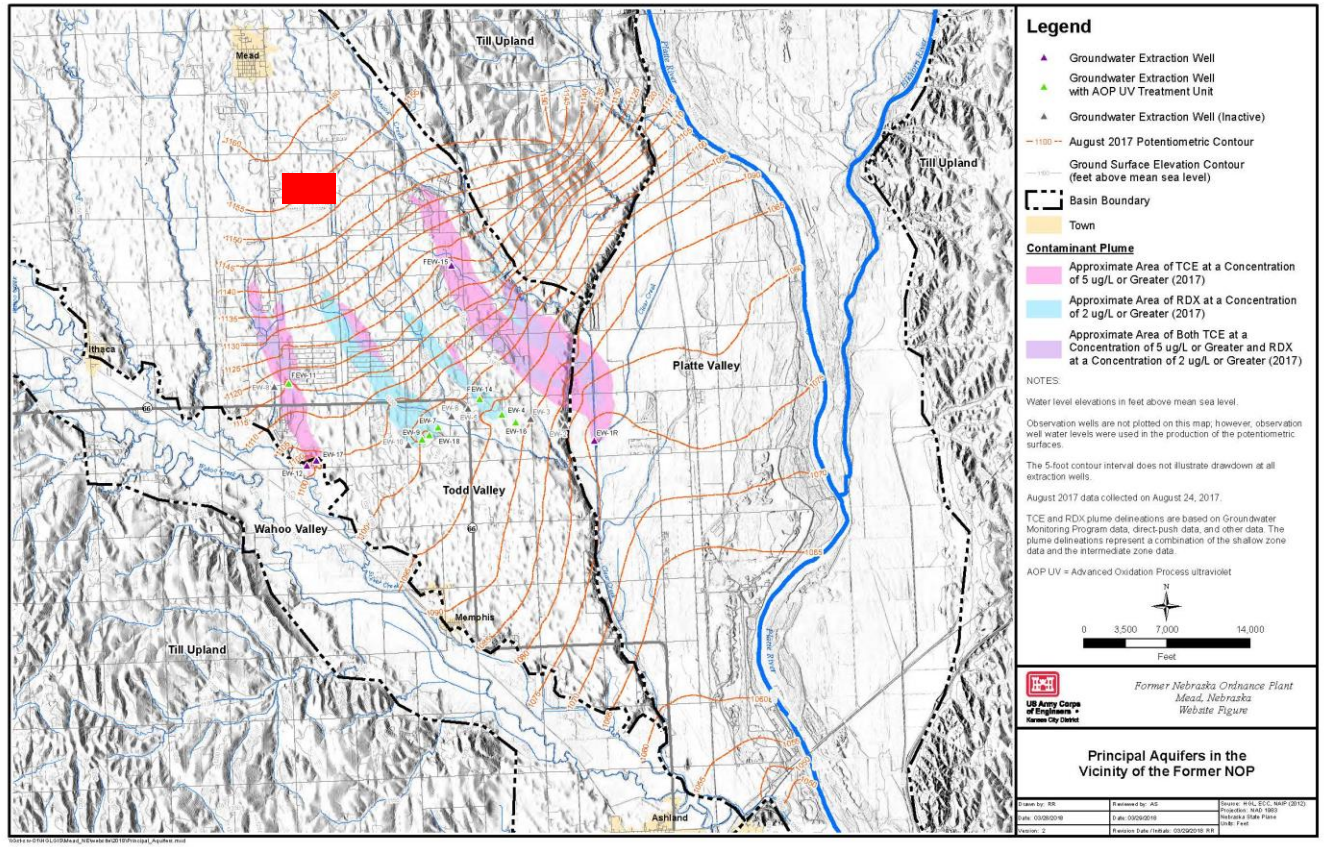
Solids application areas

- Nearly 33,000 tons of WDGS applied in surrounding region (~20-30 mi^2)
- WDGS piles stored near houses, streams, often left for many weeks or months
- Includes towns of Mead, Ithaca, Yutan, and Wahoo (~7,000 residents)
- Application rate 20-25 tons per acre
- Higher potential for exposure through surface application and runoff



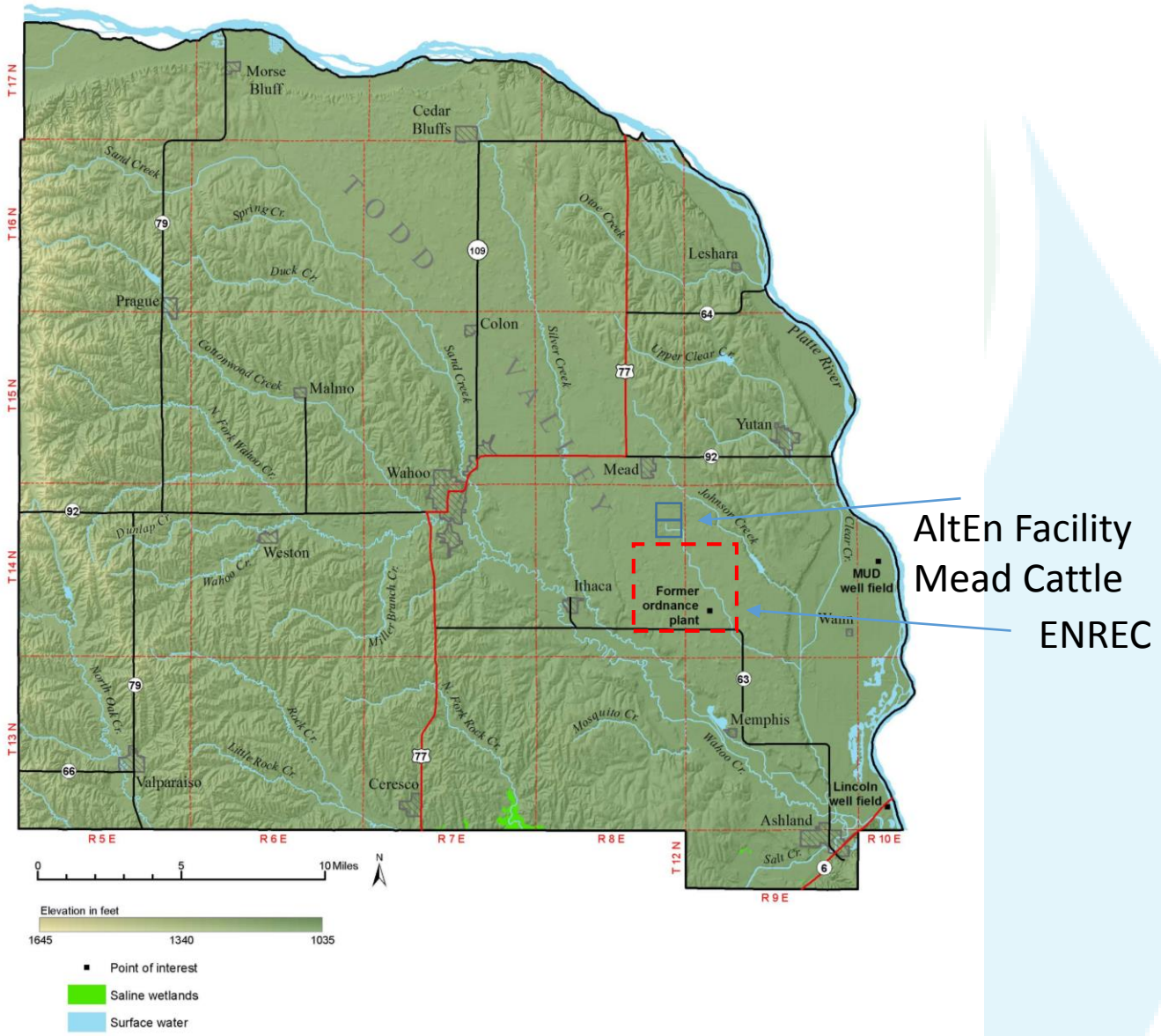
Hydrogeology

- USACE remediation projects for Nebraska Ordnance Plant now occupied by Eastern Nebraska Research and Extension Center
- Todd Valley alluvial aquifer (Platte River)
- Topsoil, loess, sand and gravel
- Groundwater flow to southeast (35-65 feet below surface)



Surface drainage

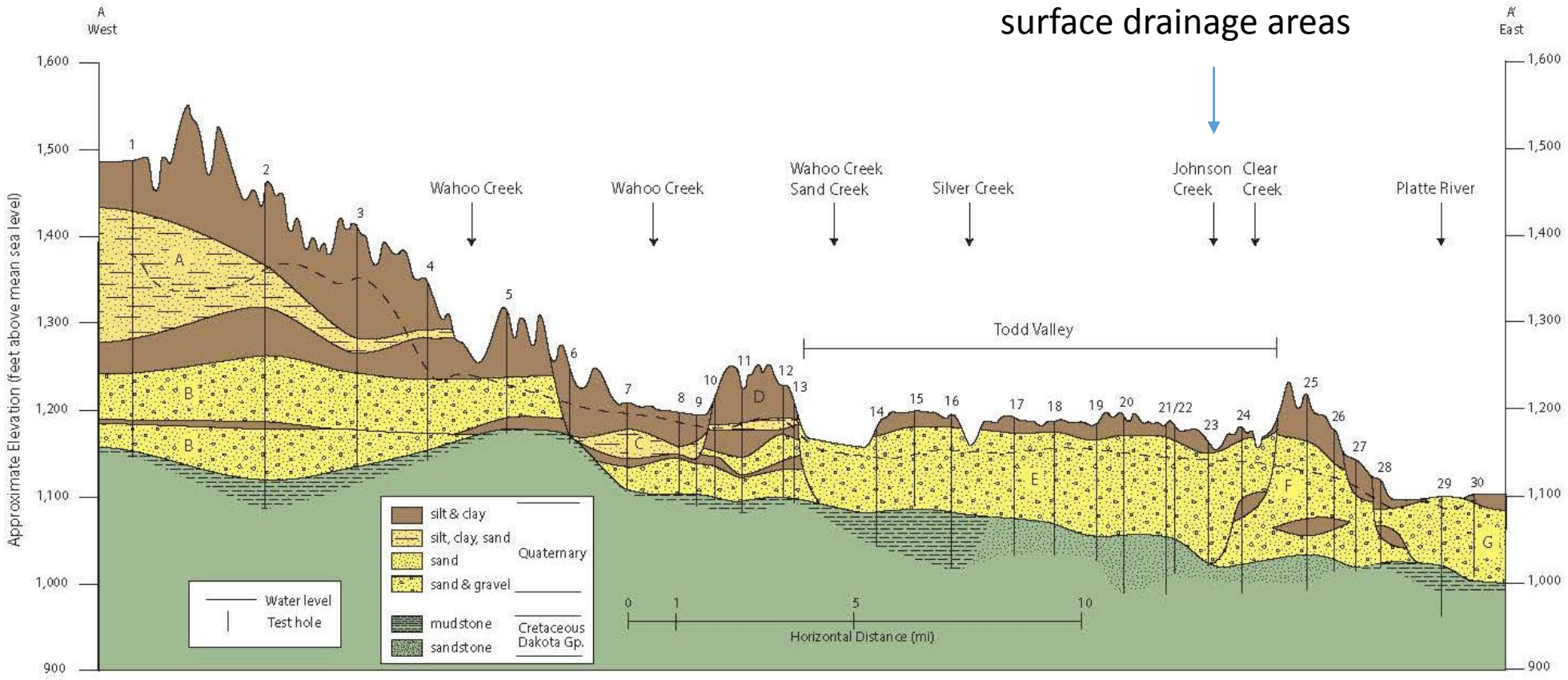
- Topography slopes to southeast
- Soils well-drained silty-clay loam over silts, alluvial sand and clay deposits
- One perennial stream – Johnson Creek
- An unnamed intermittent drainage way flows on the eastern edge of facility into ENREC
- Johnson Creek and “ENREC” creek flow into Clear Creek and into Platte River near Ashland, Nebraska



Davine, 2015, Groundwater Atlas of Saunders County, Nebraska CSD Resource Atlas 9.

Cross section through Todd Valley Alluvium

Higher leaching potential around surface drainage areas



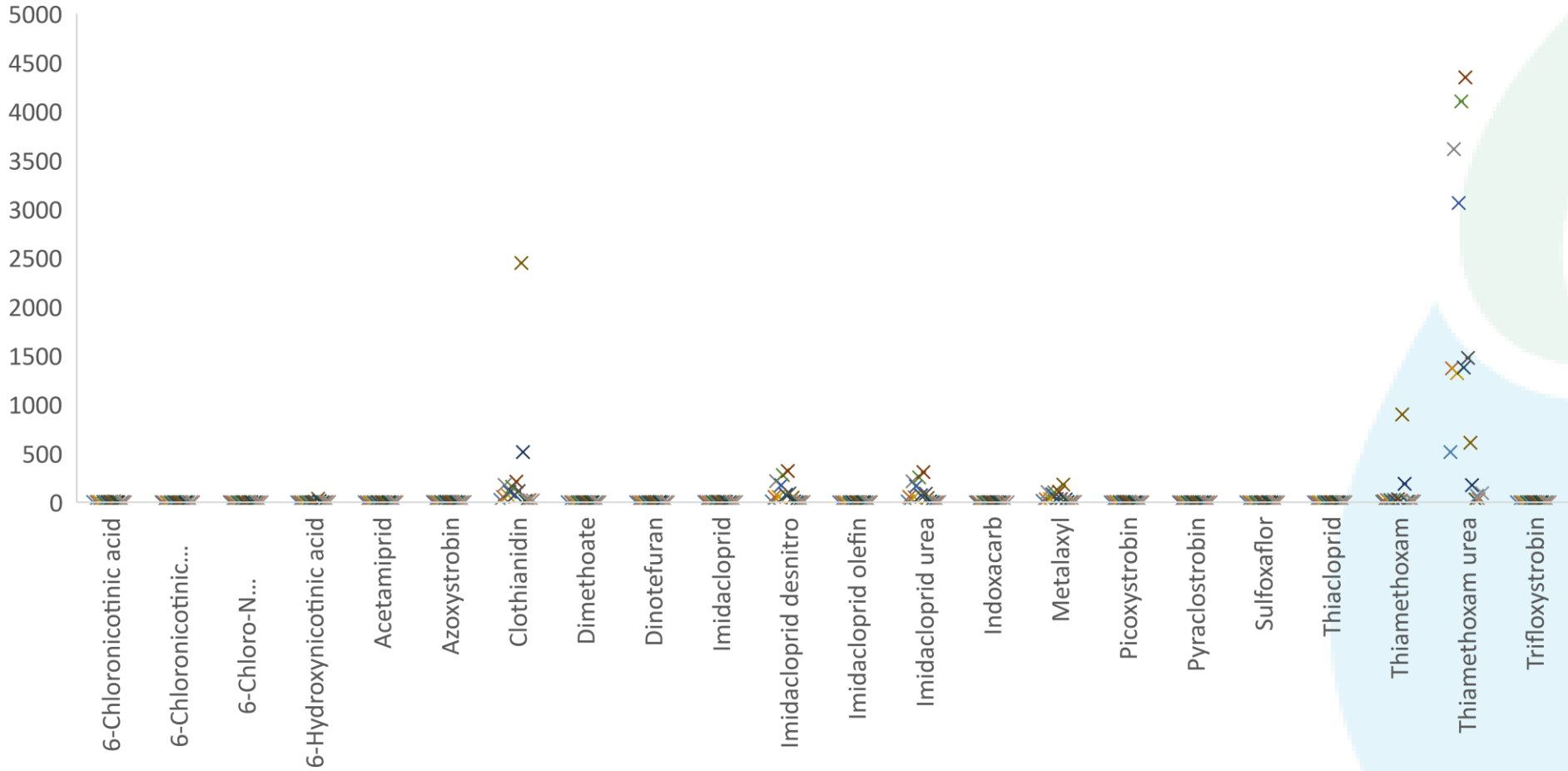
Devine, D. P. 2015. The Groundwater Atlas of Saunders County, Nebraska. Resource Atlas No. 9. Conservation and Survey, University of Nebraska. 48p.

Wastewater spill & spring flooding

- February 12, 2021 rupture of valve cause release of ~4 million gallons of wastewater
- Wastewater flowed off of the AltEN facility and on to Eastern Nebraska Research and Extension Center
- Heavy rains in March lead to additional flooding
- NDEE report shows >1,000 µg/L of prothioconazole, thiabendazole, and abamectin

Photos by Judy Wu-Smart

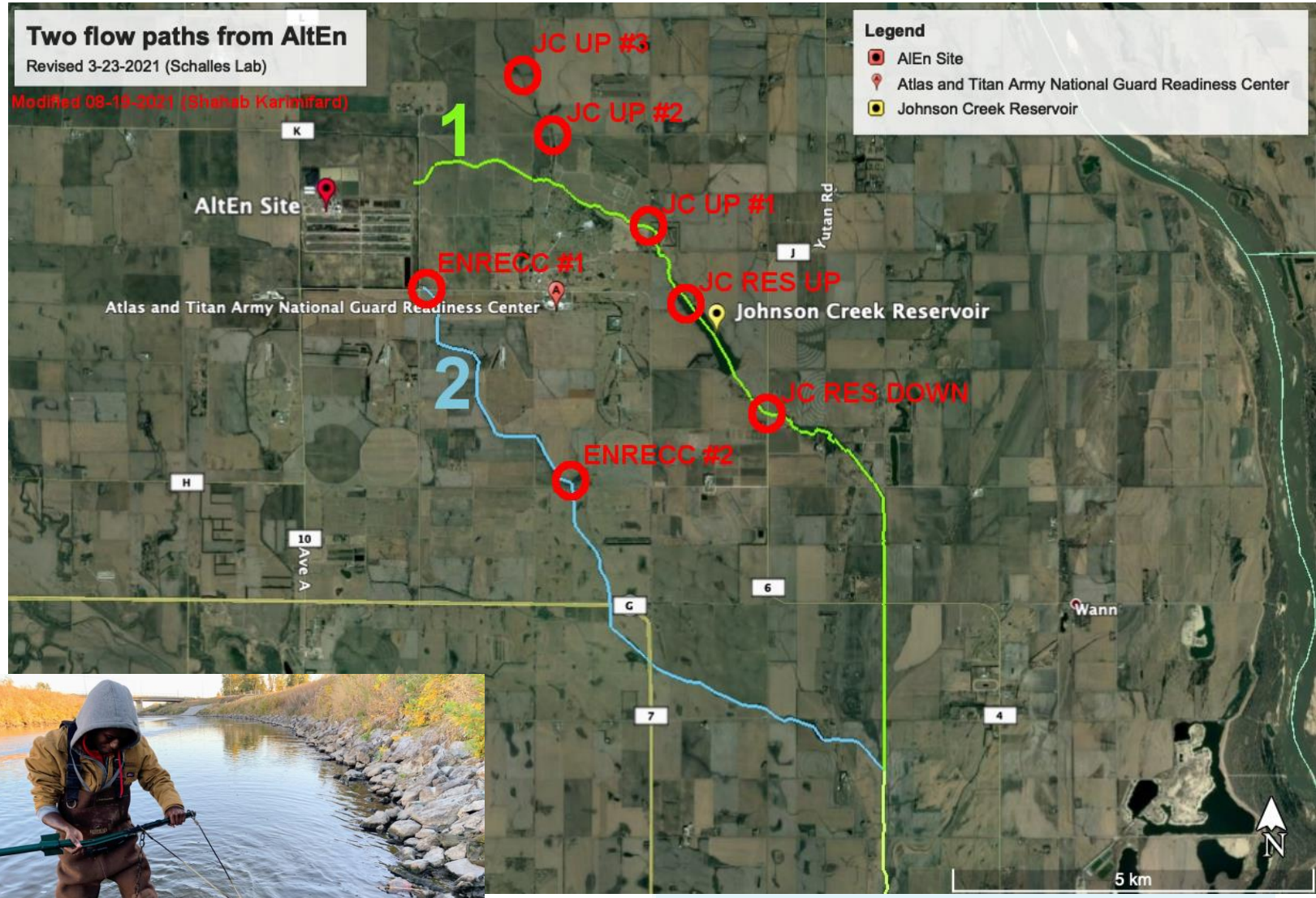
WSL analysis Feb 12- March 3 spill samples



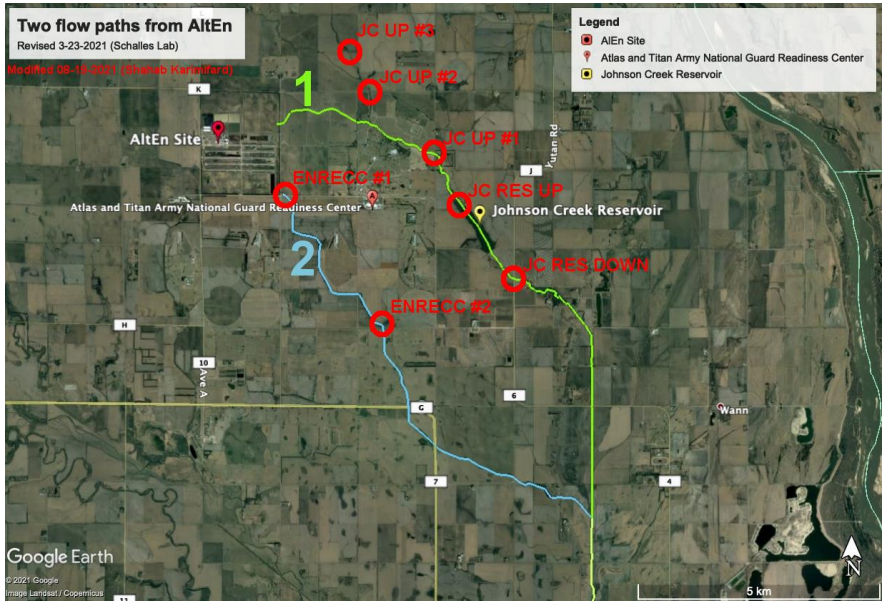
- Several thousand ppb clothianidin, thiamethoxam, thiamethoxam urea
- Several hundred ppb metaxyl, imidacloprid desnitro and imidacloprid urea

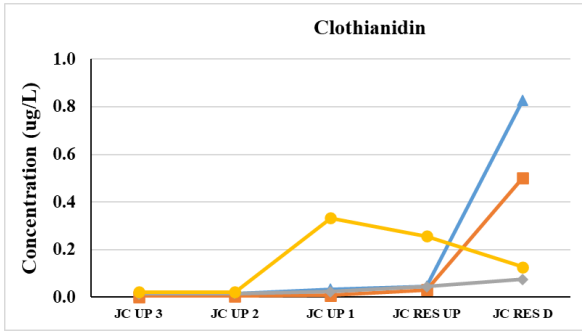
Surface water Monitoring

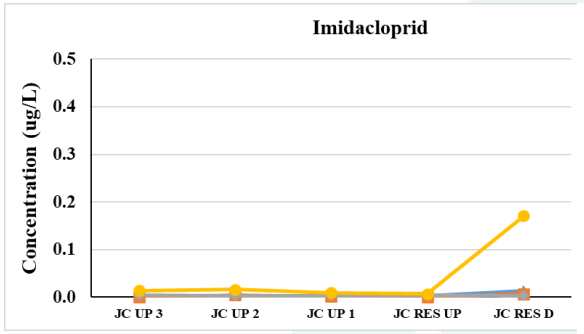
- Monthly sampling of 7 locations initiated in April 2021
- Grab samples plus installation of polar organic contaminant integrative samplers (POCIS)

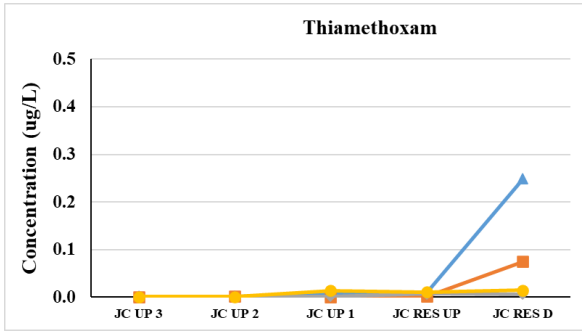


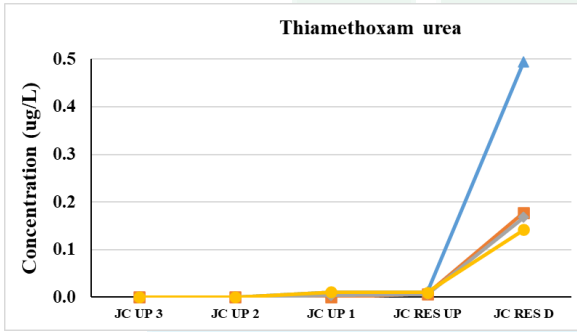
Grab Sampling Results from Johnson Creek April-August 2021

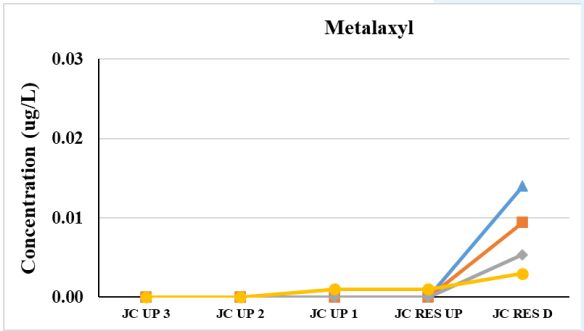






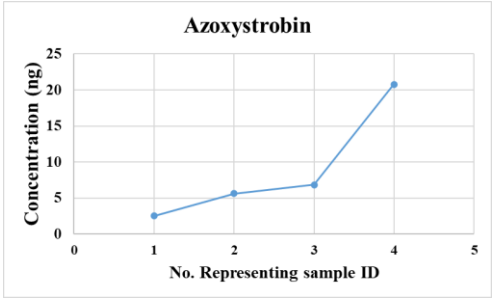


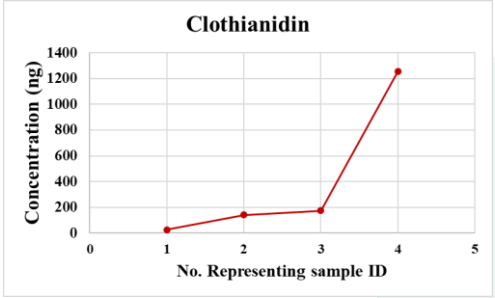


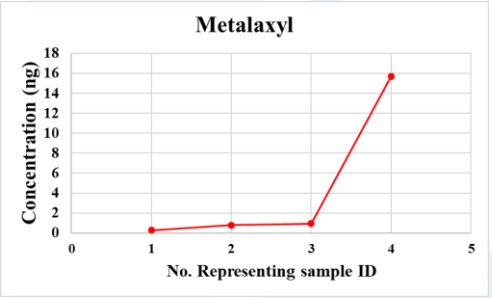


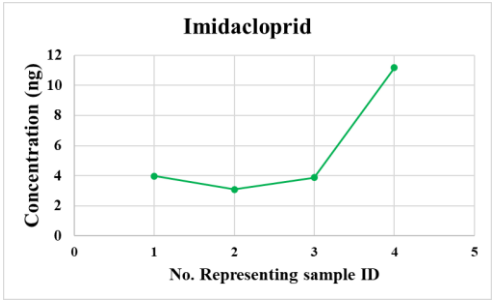
Passive Sampler Results from Johnson Creek 2021

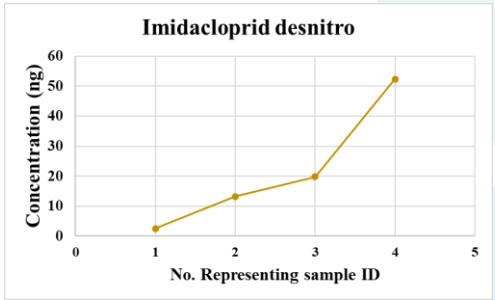
- 8 contaminants showed an increasing trend of concentration from upstream to downstream of Johnson Creek

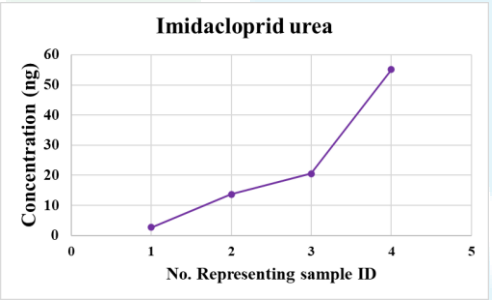


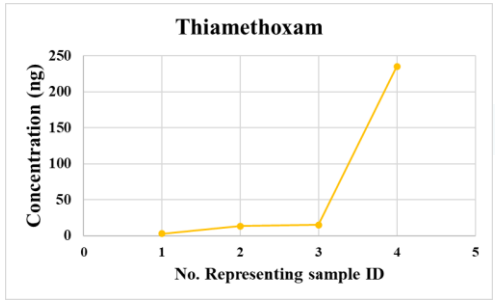


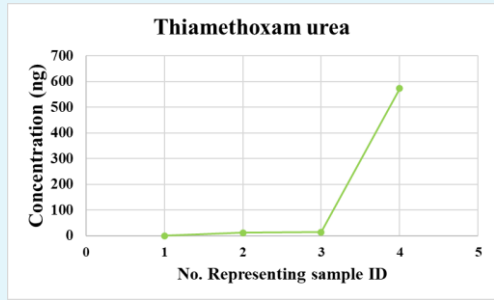






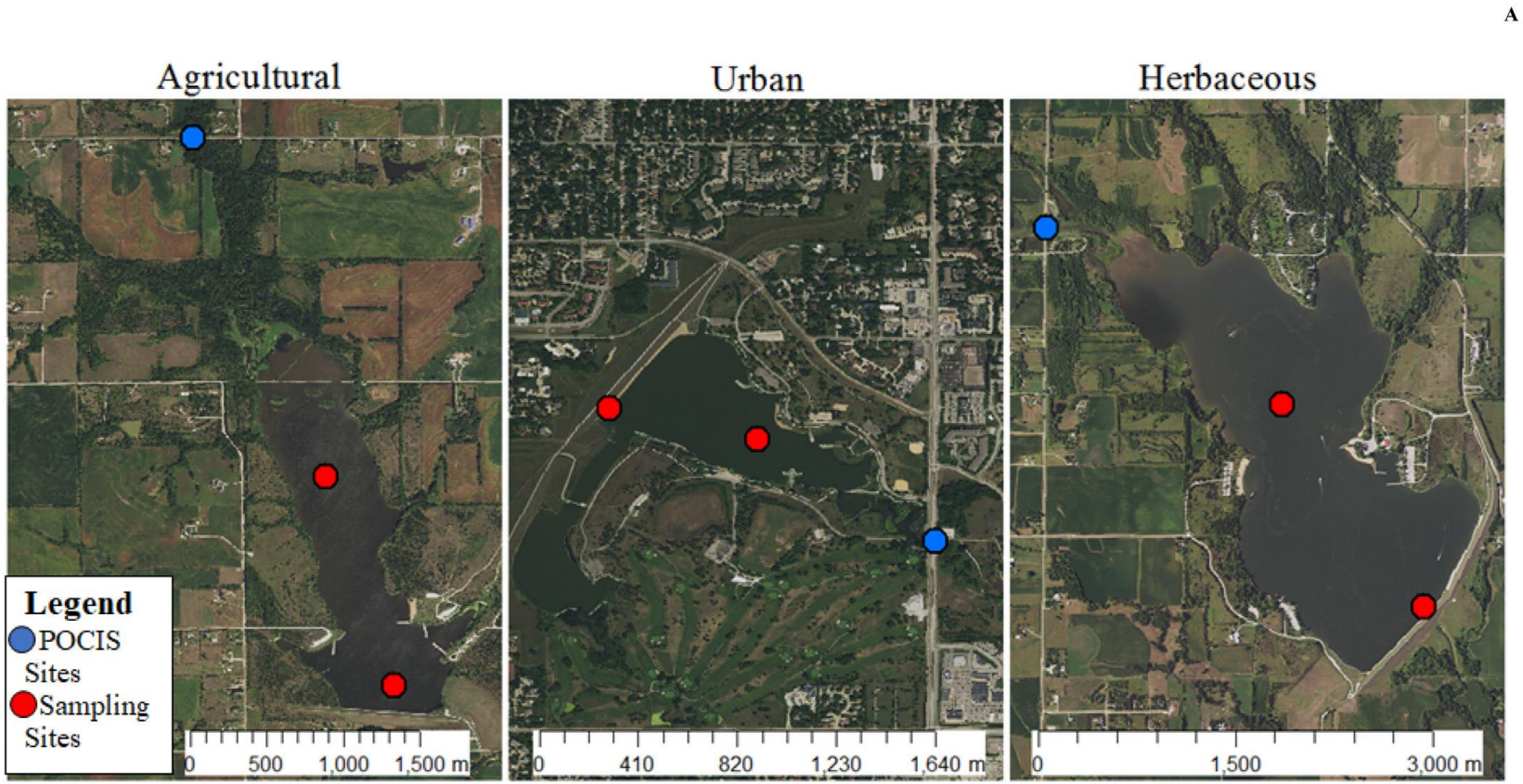


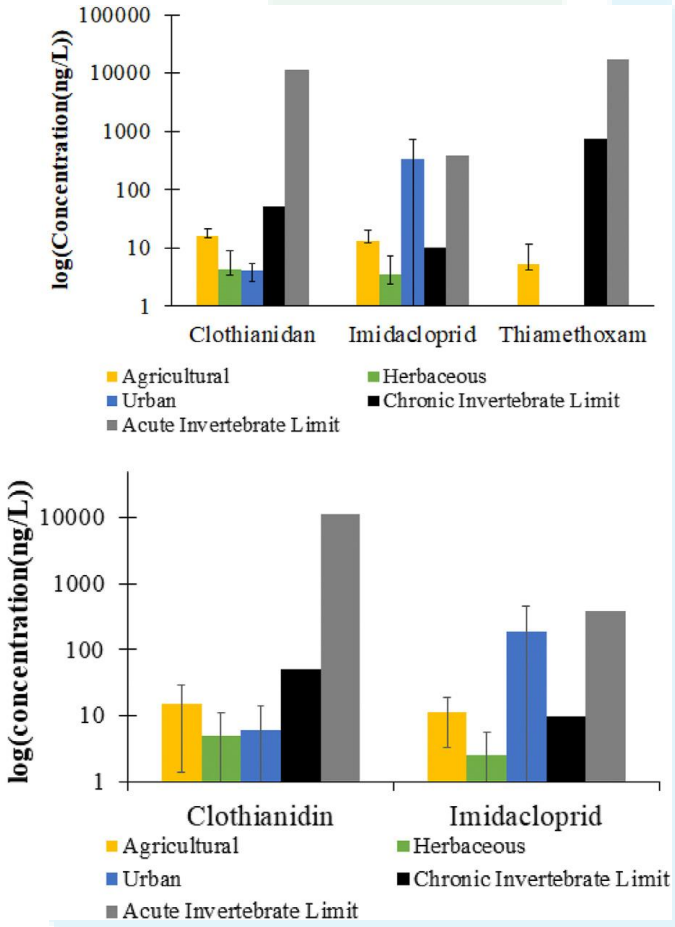




Sample IDs: 1 = JC UP #3 2 = JC UP #2 3 = JC UP #1 4 = JC Res Down

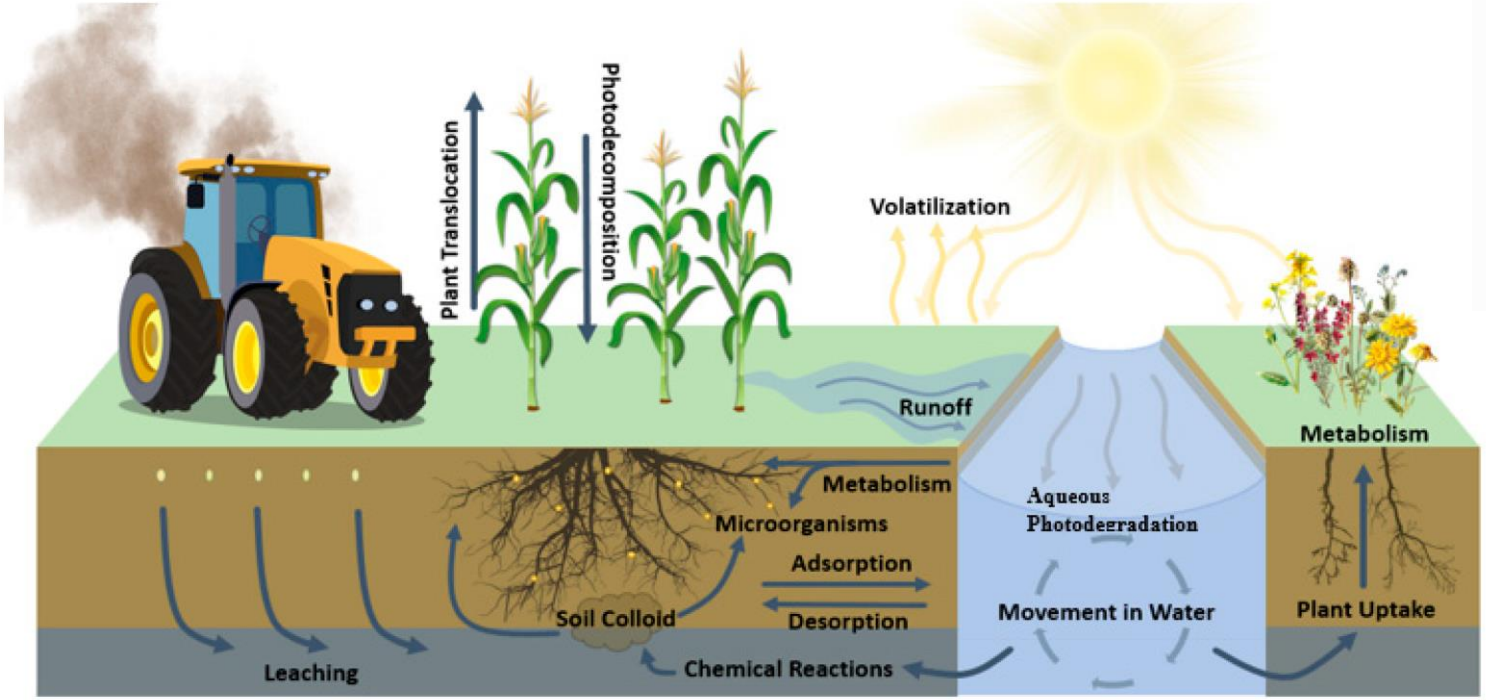
Comparison to other studies

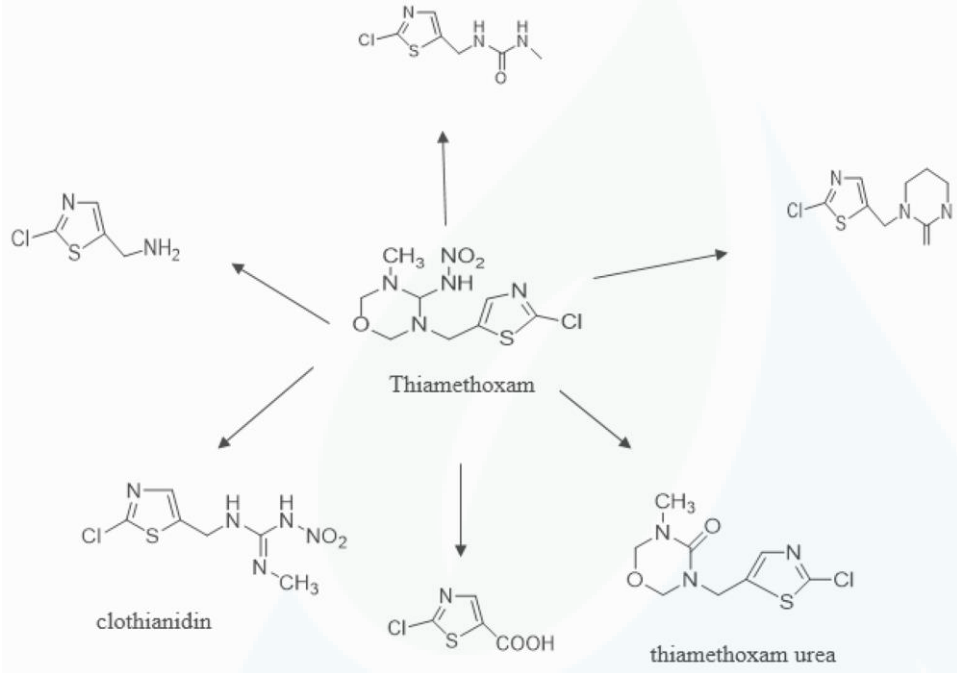


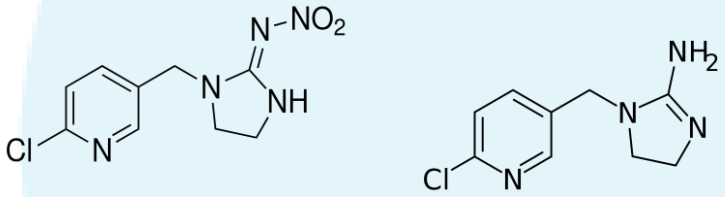


Satiroff, J.A., Messer, T.L., Mittelstet, A.R. and Snow, D.D., 2021. Pesticide occurrence and persistence entering recreational lakes in watersheds of varying land uses. *Environmental Pollution*, *273*, p.116399.

Neonicotinoid Insecticides







Imidacloprid → Imidacloprid desnitro

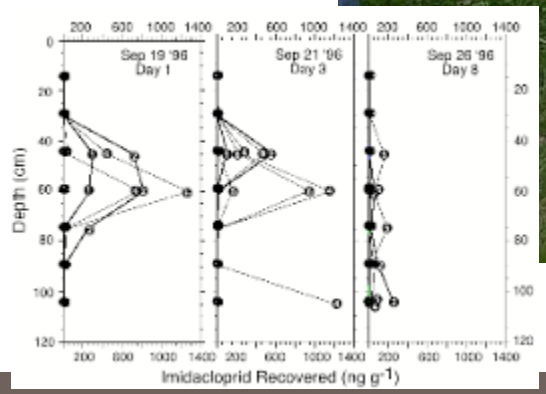
Imidacloprid desnitro may have greater mammalian toxicity

Borsuah, J.F.; Messer, T.L.; Snow, D.D.; Comfort, S.D.; Mittelstet, A.R. Literature Review: Global Neonicotinoid Insecticide Occurrence in Aquatic Environments. *Water* **2020**, *12*, 3388.

Loser, D., Grillberger, K., Hinojosa, M.G. *et al.* Acute effects of the imidacloprid metabolite desnitro-imidacloprid on human nACh receptors relevant for neuronal signaling. *Arch Toxicol* **95,** 3695–3716 (2021).

2022 Deep soil coring

- Direct-push coring on wastewater and biosolids application area
- Grab samples of groundwater near the water table
- Process and analyze for HYDRUS 1-D transport modeling of pesticides and degradation products



Felsot, A.S., Evans, R.G. and Ruppert, J.R., 2003, January. Field studies of imidacloprid distribution following application to soil through a drip irrigation system. In *ACS Symposium Series* (Vol. 842, pp. 189-205). Washington, DC; American Chemical Society; 1999.

2022 Surface water sampling

- Monthly surface water sampling will continue in 2022 and include additional sites requested by USGS collaborators
- WSL Laboratory testing will be expanded to include azole fungicides
- Bottom sediments are being tested from Johnson Creek, Clear Creek and Downstream from ENREC unnamed creek
- Aquatic organisms sampled and tested by USGS

One-Health Organism sampling

Undergraduate researcher Abi Schoup setting frog recorders at an agricultural pond/wetland to assess local frog species present in the area. Tadpoles and blackbird eggs collected for insecticide testing

University of Nebraska

Water for Food
Daugherty Global Institute
at the University of Nebraska

Proposed Health Response

Multilayered Environmental & Human Health Project

- **Environment**
  - Analysis of neonicotinoids/fungicides and transformation products in the **solid byproduct and wastewater, surface soil, surface water and groundwater**
  - Analysis of neonicotinoids/fungicides and transformation products in **air and dust samples**
- **Human Health**
  - Collection of blood/urine samples from residents
  - Community Assessment for Public Health Emergency Response (CASPER) survey of people living in Mead and surrounding area
  - Review of hospital records
  - Establish a Medical Registry
- **Animal Health**
  - Collection of blood/urine samples from animals (companion, production, wildlife)
  - Data on the decline of the bee population

Long term needs

- Site cleanup limited to AltEn facility property
- Limited funding
  - Small grant from Claire M. Hubbard Foundation for initial site assessment and analysis at the UNL Water Sciences Laboratory
  - Grant from USDA Multistate Hatch program for student training
- USGS providing sampling and analytical support (M. Hladik, D. Kolpin, P. Bradley)
- USEPA (Advanced Analytical Chemistry Methods Branch) providing support for untargeted mass spectrometry and ecological risk assessment

Temporary wastewater storage tanks installed June 28, 2021, LJS

AltEn Facility

Temporary wastewater storage tanks installed June 28, 2021

Treated wastewater scheduled to be applied to surrounding cropland

Covers applied to remaining piles of distiller's product February 2022

Long term monitoring plans uncertain

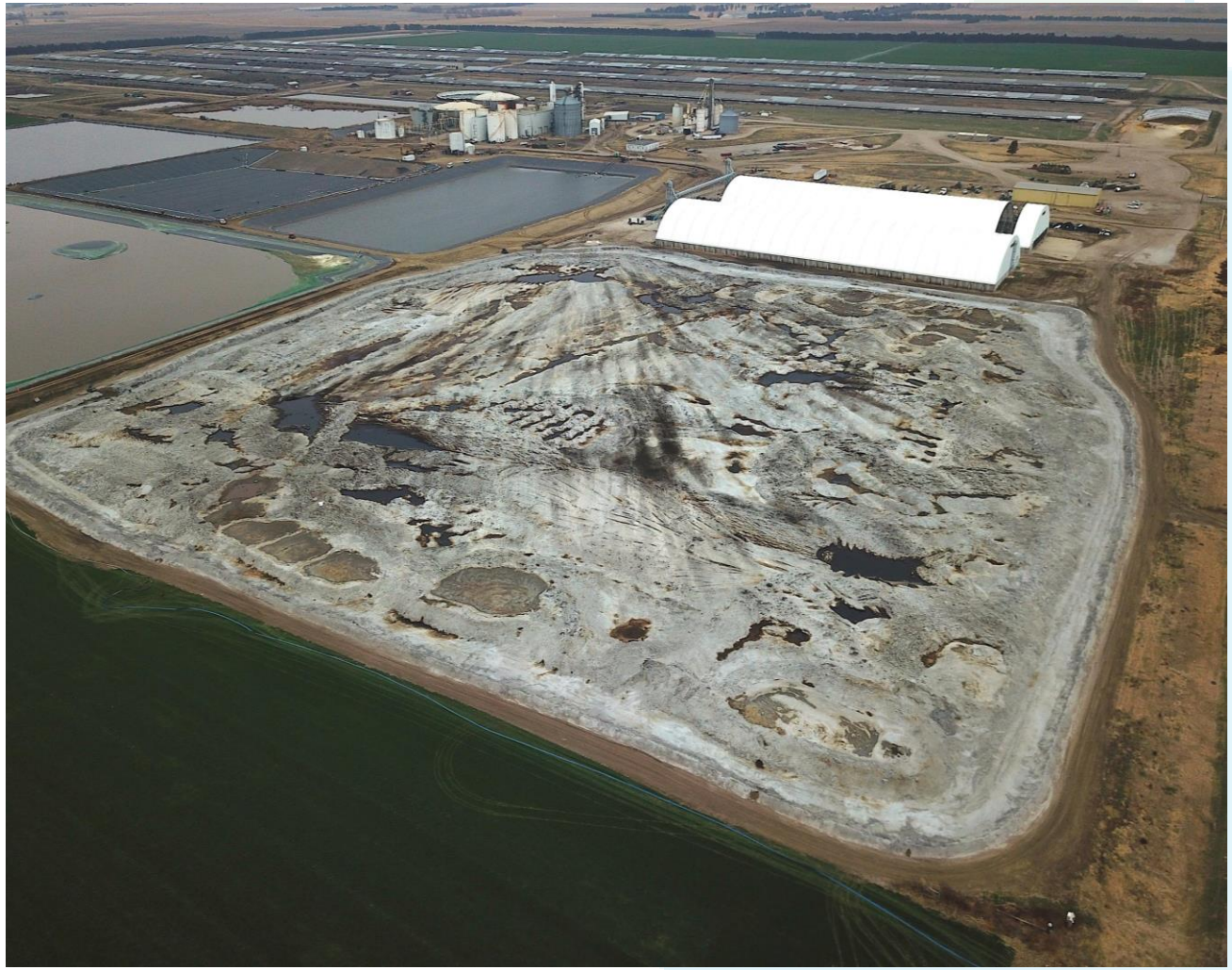


Photo John Schalles, April 5, 2022

Water for Food
ROBERT B. DAUGHERTY INSTITUTE
at the University of Nebraska

Thank you!

https://www.unmc.edu/publichealth/departments/environmental/mead/

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