


Analysis and detection of cyanazine-specific degradates in Minnesota groundwater using LC-MS/MS.

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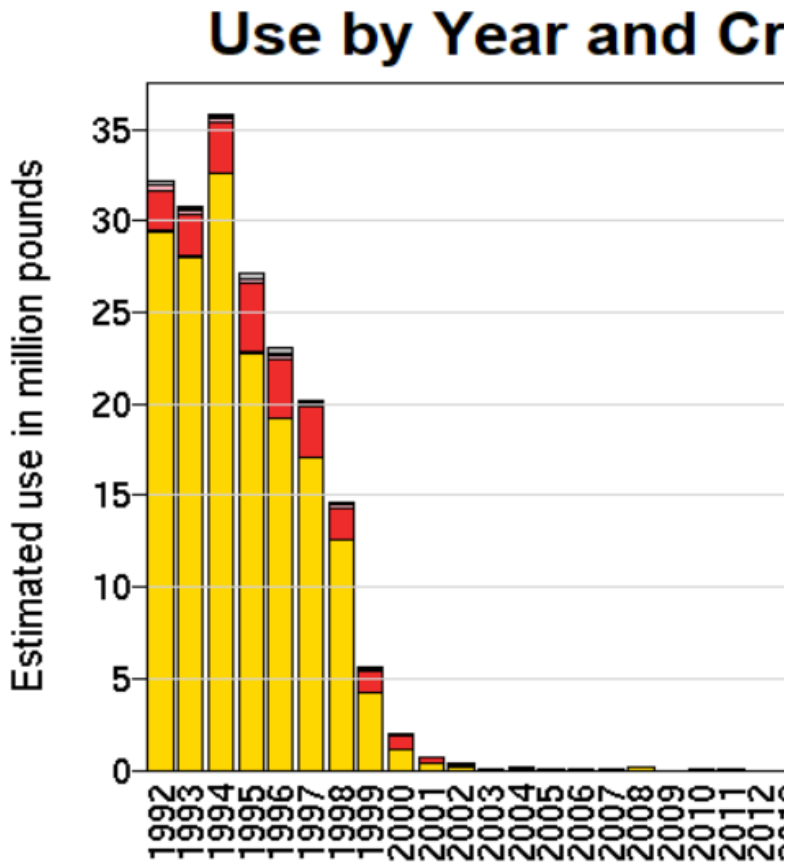
DEPARTMENT OF AGRICULTURE

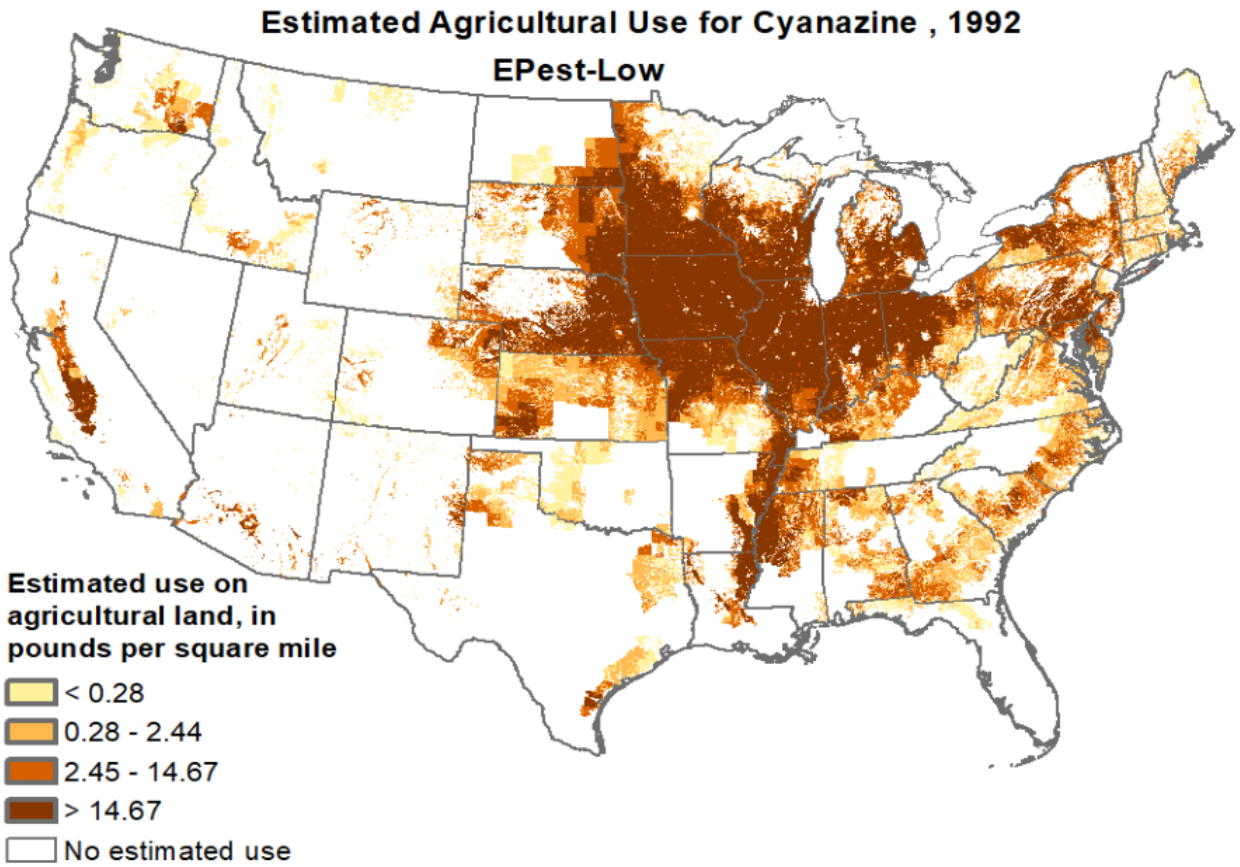
CLEAN WATER LAND & LEGACY AMENDMENT

Cyanazine History

- Heavily used corn herbicide (Bladex) from 1971 through 1990s throughout the corn belt.
- Registration of this pesticide voluntarily cancelled in 2000 and use ceased nationally in 2002, because of potential “unreasonable adverse effects on the environment” risk concerns.
- Limited analysis of the degradates in water in years since due to limited availability of analytical standards.

Estimated National Cyanazine Use

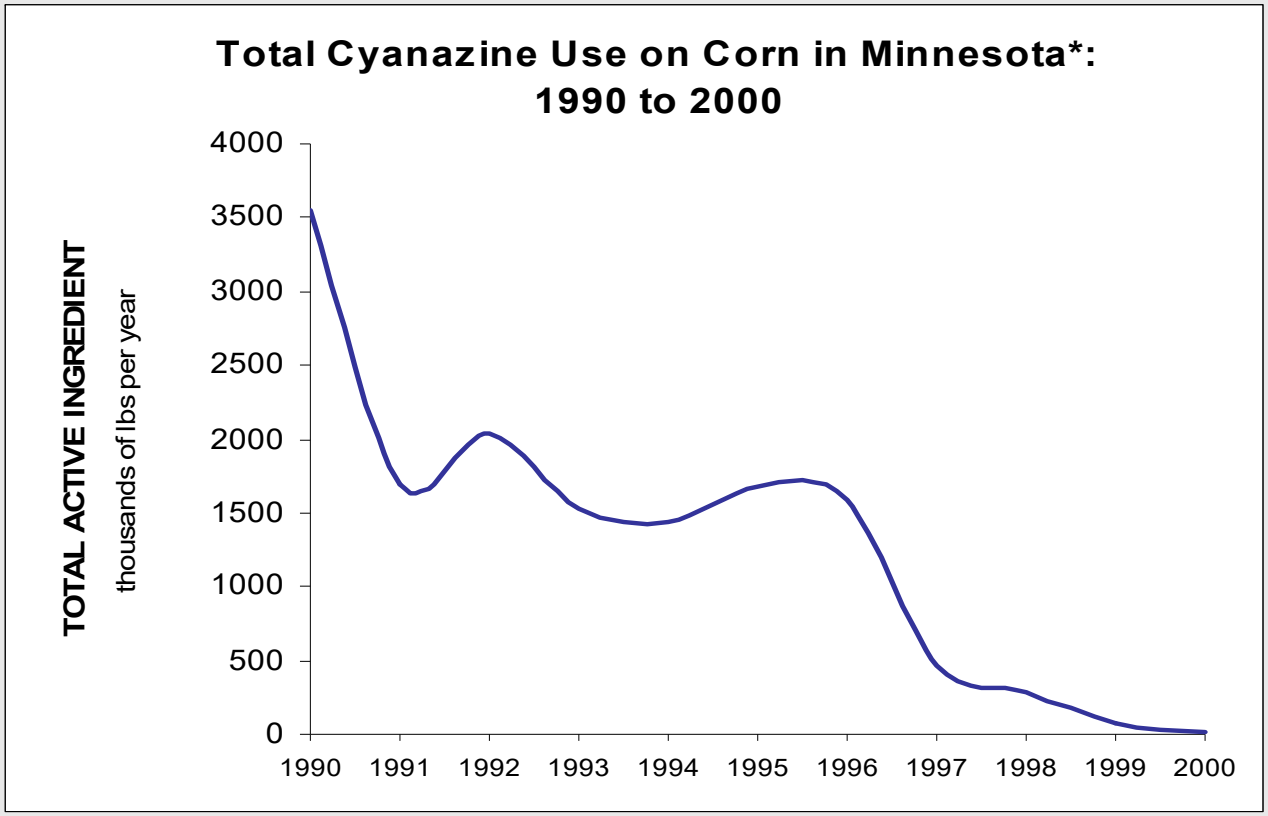




* Source- USGS Pesticide National Synthesis Project: https://water.usgs.gov/nawqa/pnsp/usage/maps/ /

Cyanazine Use in MN

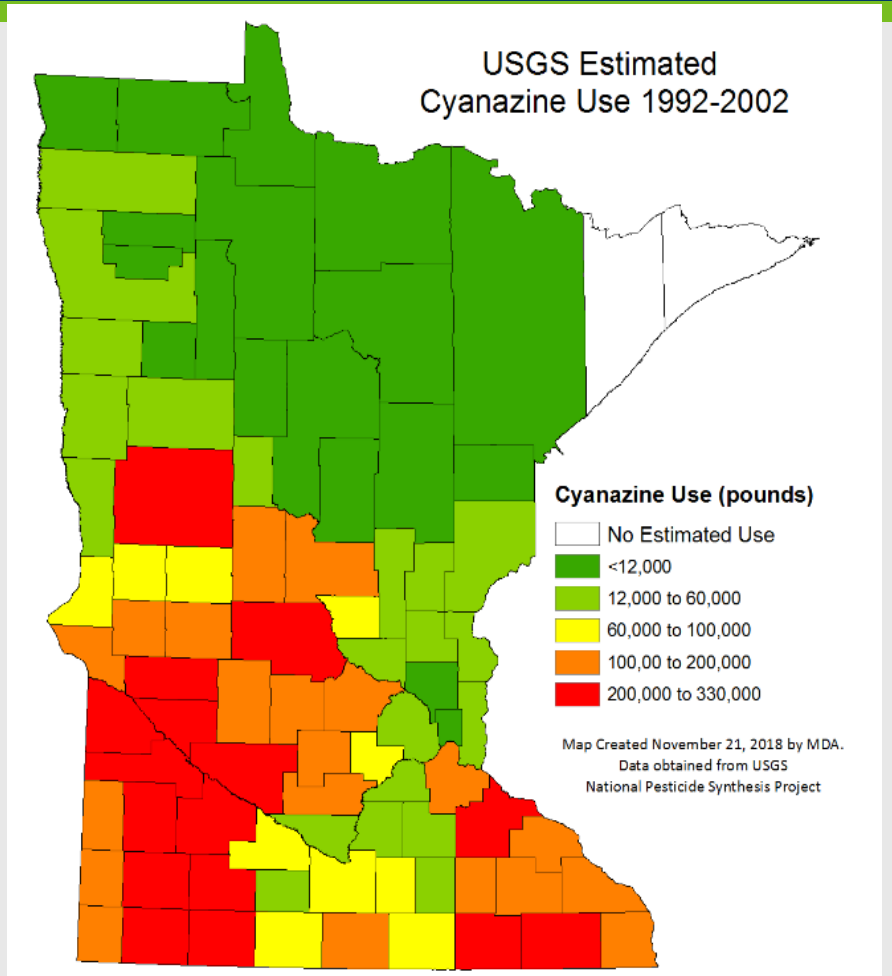
- **Estimated 3.5 million lbs used in 1990 in MN.**
- **Use declining through the 1990s.**



* Source- National Agricultural Statistics Service: http://www.pestmanagement.info/nass/

Minnesota Cyanazine Use Estimates

- **USGS estimates based on National Agricultural Statistics Service (NASS) data.**
- **Use was widespread but higher in certain regions.**
- **Potentially useful for targeting monitoring.**



* Source- USGS Pesticide National Synthesis Project: https://water.usgs.gov/nawqa/pnsp/usage/maps/ /

Cyanazine Degradation

- **Five cyanazine specific degradates have been identified.**
- **Two additional degradates are common to atrazine, which is still in use.**
- **All are added to compare with the cyanazine Health Risk Limit (1.0 ppb) in MN.**

- **Deethylcyanazine acid is the most frequently detected cyanazine specific degradate in groundwater.**

From: Kolpin DW, Thurman EM, Linhart SM. Occurrence of cyanazine compounds in groundwater. Environ Sci Technol. 2001 Mar 15;35(6):1217-22.

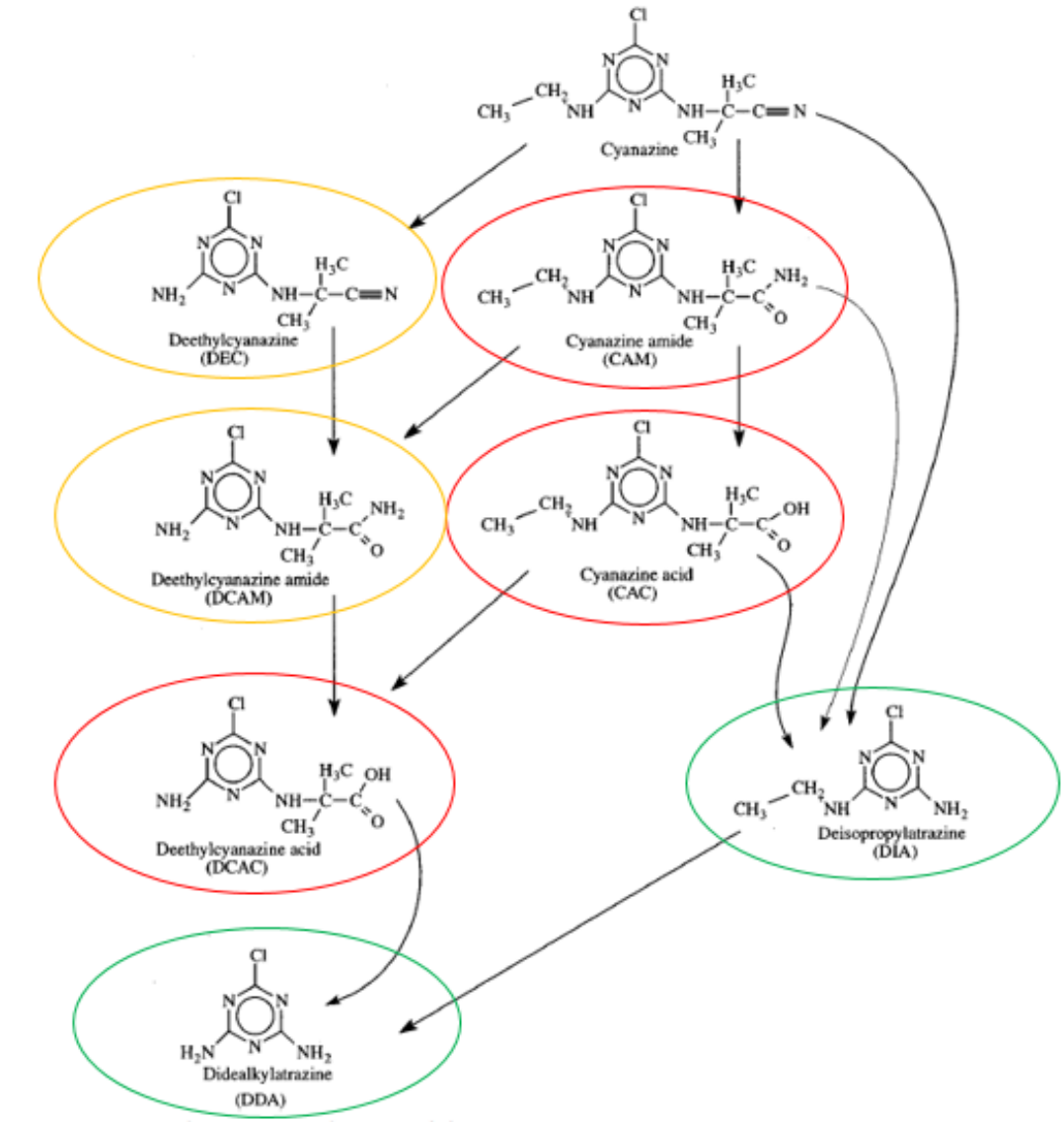


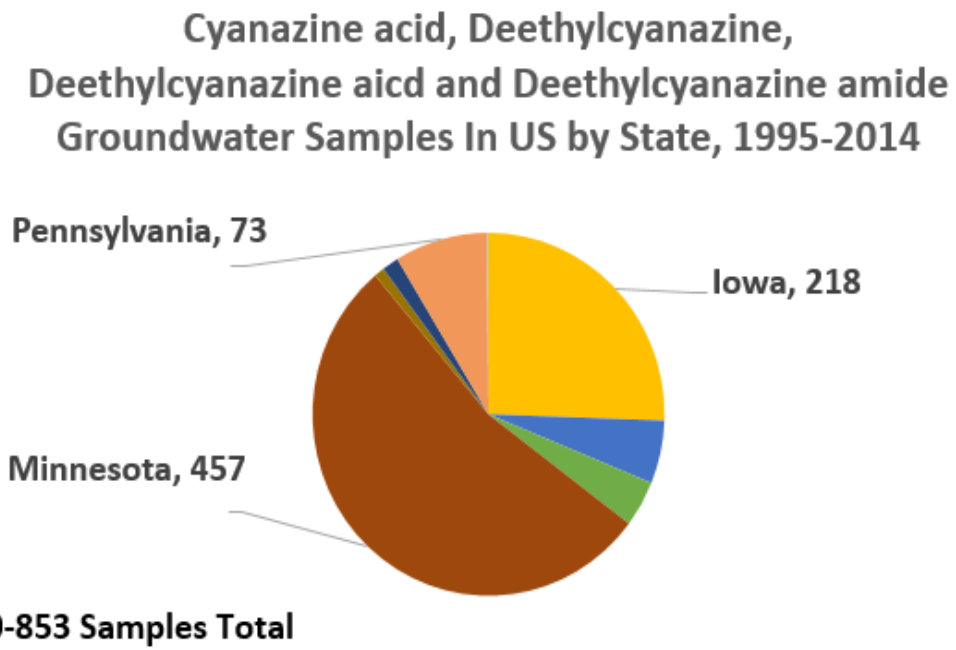
FIGURE 1. Pathways for degradation of cyanazine (17).

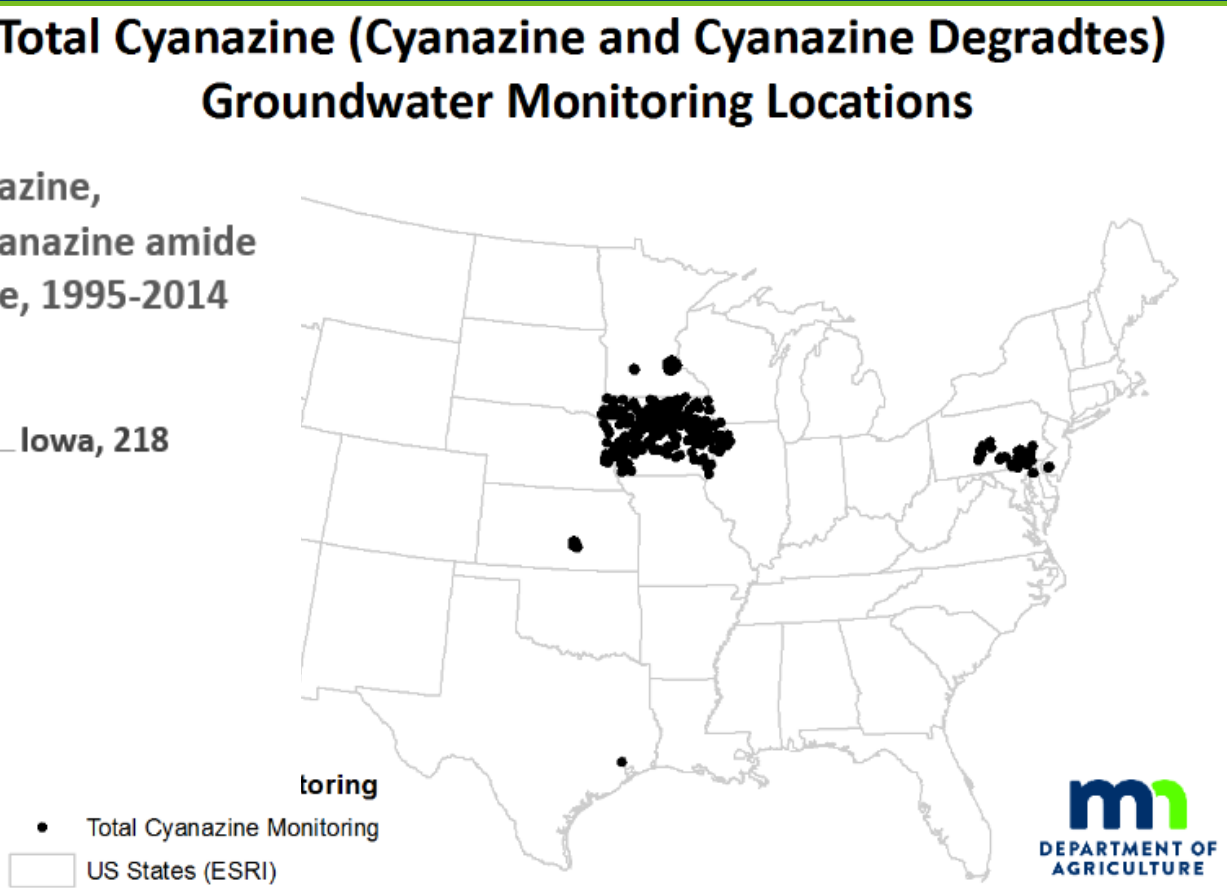
Cyanazine Degradate Analytical Methods

- Historically only the USGS Organics Geochemistry Research Lab (OGRL) had analytical standards and a method.
- In 2019 MDA contracted for synthesis of analytical standards (now available commercially).
- Data from three laboratories are presented:

➢ USGS Organics Geochemistry Research Lab – LCEA Method SPE LC-MS/MS ➢ Triazine and Phenylurea ➢ Cyanazine degradate method Reporting Limit (MRL) ~20 ng/L	➢ Minnesota Department of Agriculture – SPE LC-MS/MS ➢ MDA Polar Pesticides and Metabolites in Water ➢ Cyanazine degradates MRL 10 – 25 ng/L	➢ Weck Laboratories – Large Volume Direct Aqueous Injection (DAI) LC-MS/MS ➢ EPA Method 538 ➢ Cyanazine degradates MRL 10 – 25 ng/L

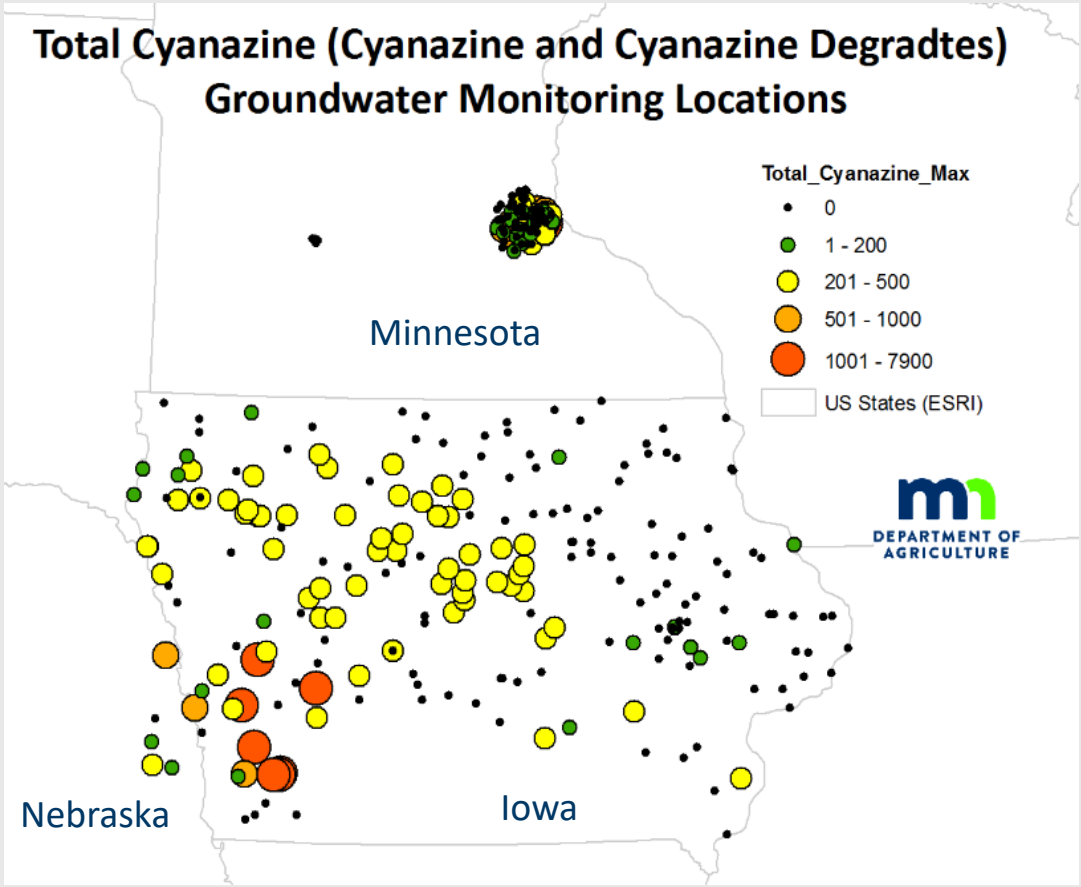
Historic Groundwater Cyanazine Degradate Monitoring





Source National Water Quality Portal: https://www.waterqualitydata.us/

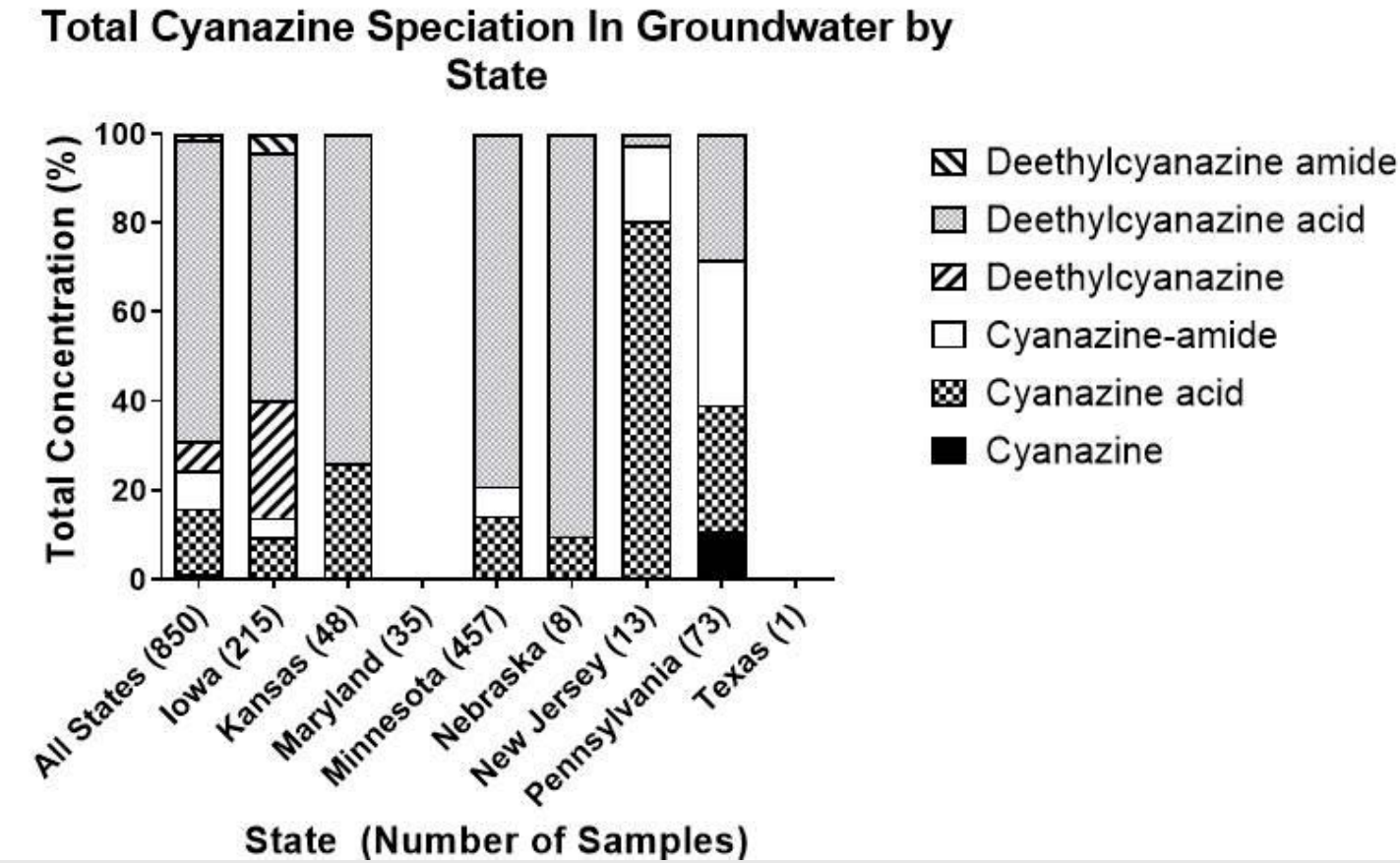
Total Cyanazine Concentration Ranges (MN, IA and NE)



Source National Water Quality Portal: https://www.waterqualitydata.us/

National Groundwater Speciation of Cyanazine and Degradates

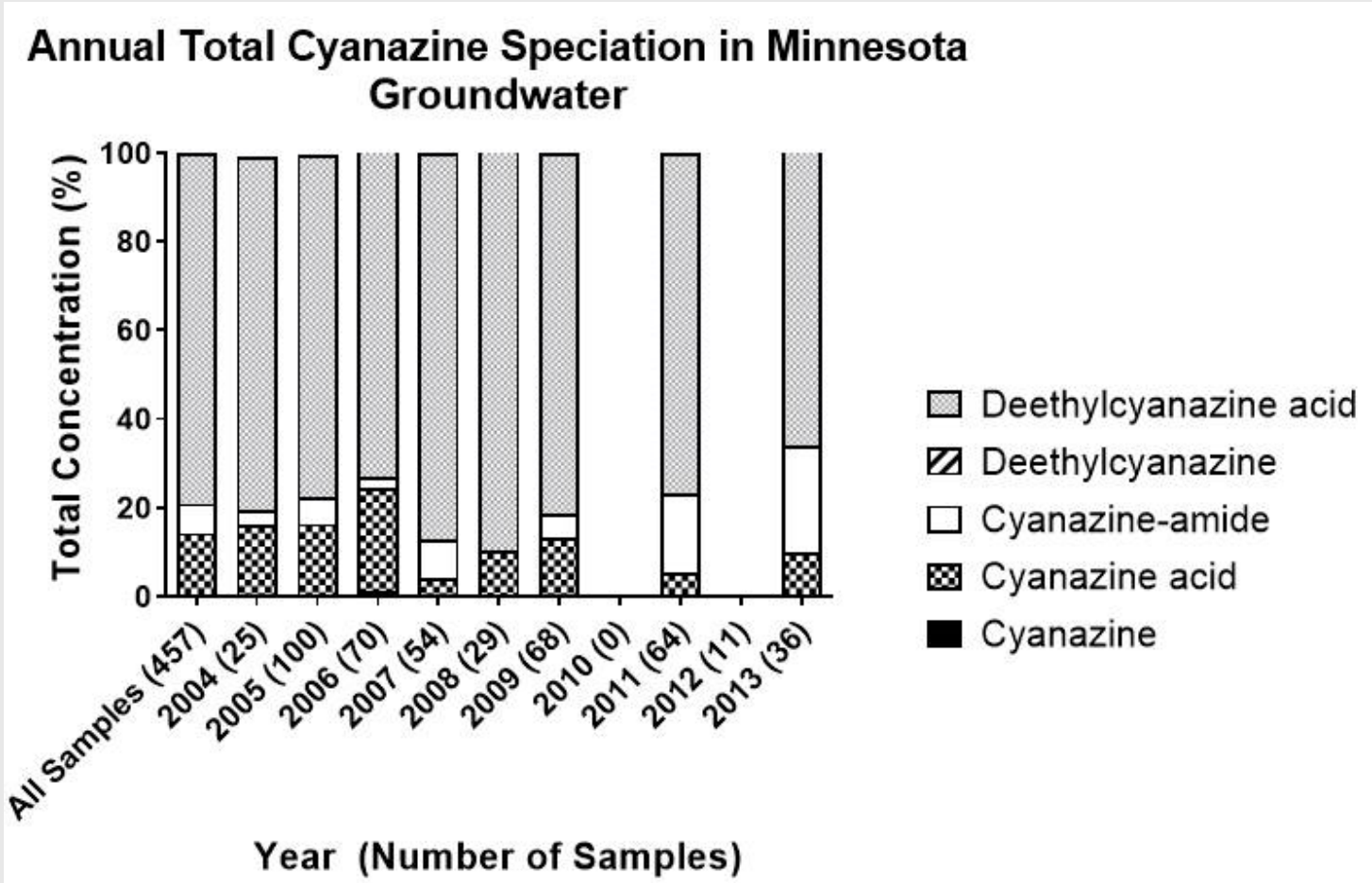
- **All data from USGS OGRL.**
- **Data from 2002 to 2014.**



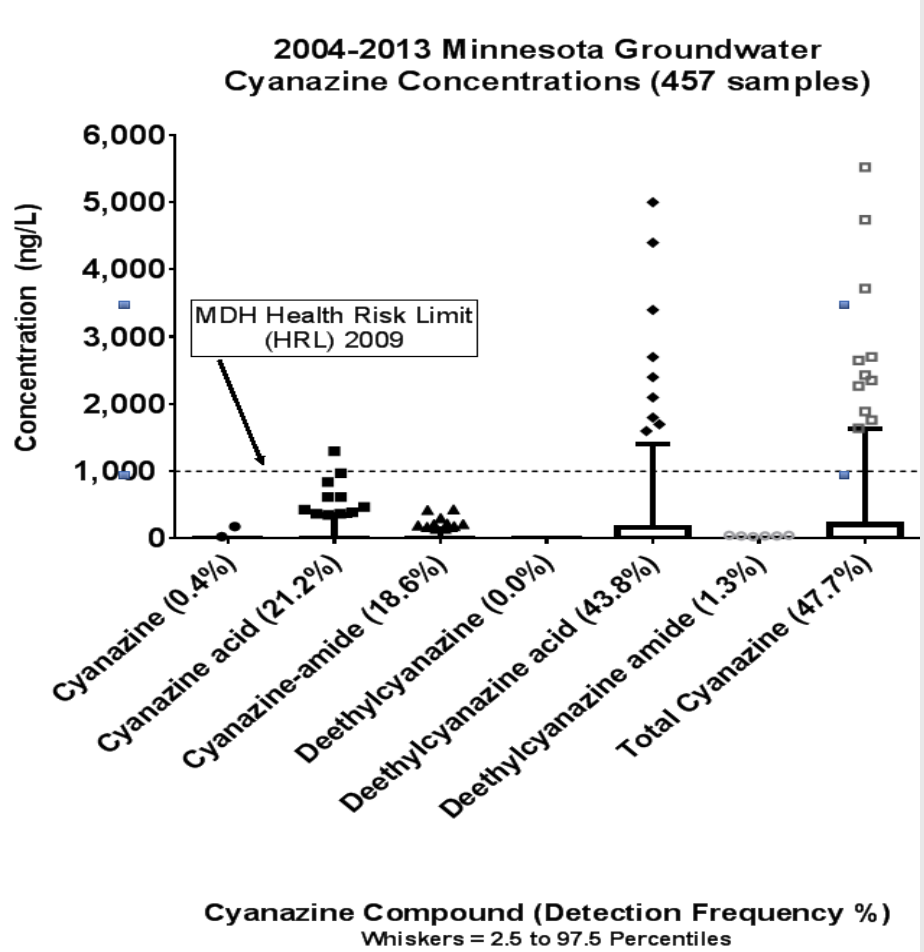
Source National Water Quality Portal: https://www.waterqualitydata.us/

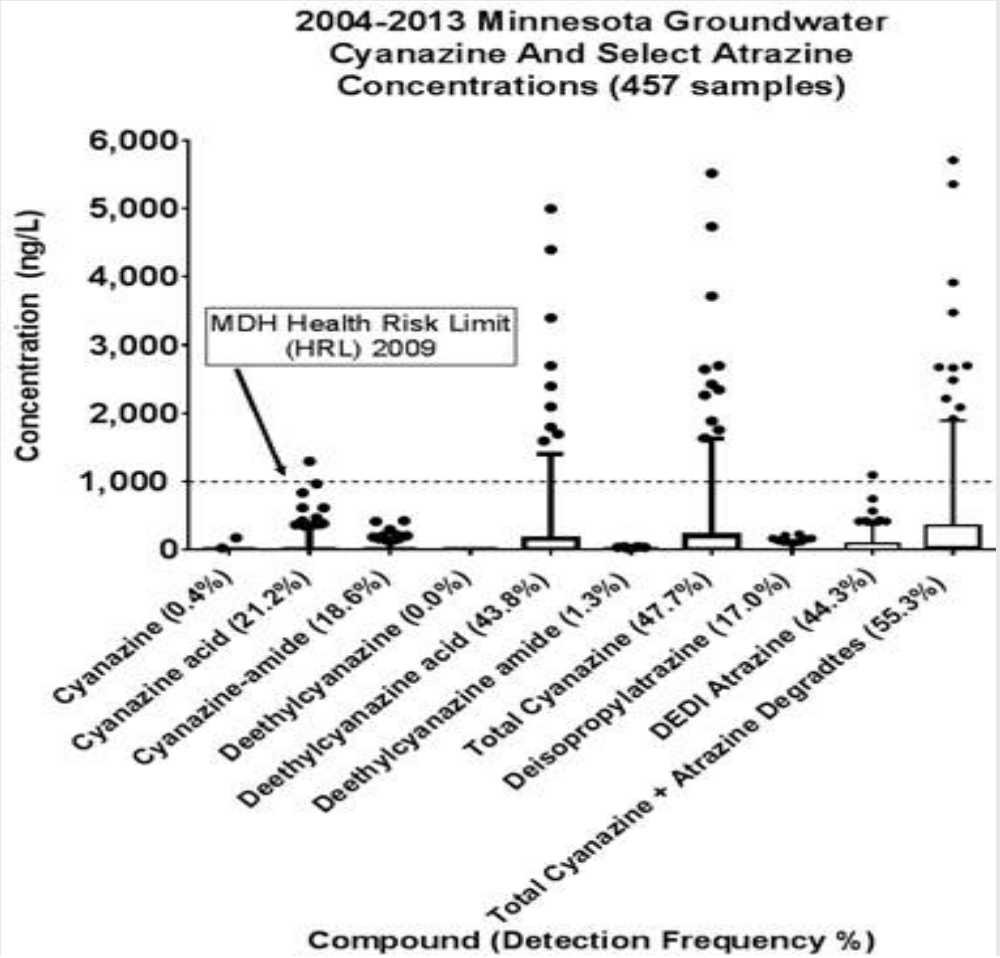
Minnesota Groundwater Speciation of Cyanazine and Degradates

- **All data from USGS OGRL.**
- **Samples represent limited geographic area.**
- **Population of sampled wells varies by year.**



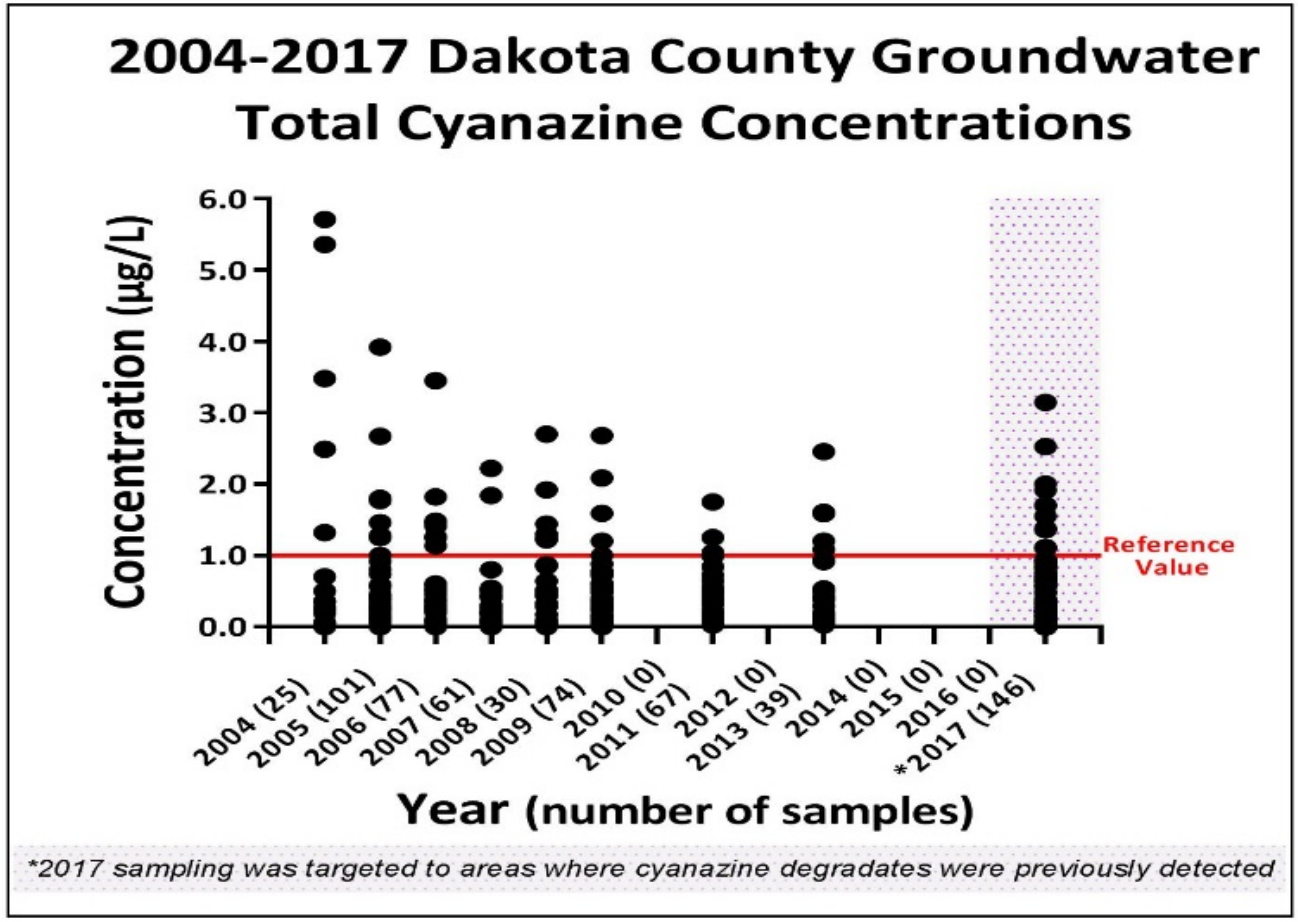
Minnesota Groundwater Concentration of Cyanazine and Degradates





Historic Data in Dakota County MN

- All samples analyzed by USGS OGRL.
- Sampled by Dakota County Environmental Res. Dept.
- Samples from private drinking water wells.
- General decline in total cyanazine concentration.
- 2017 sampling targeted to areas with historic detections.

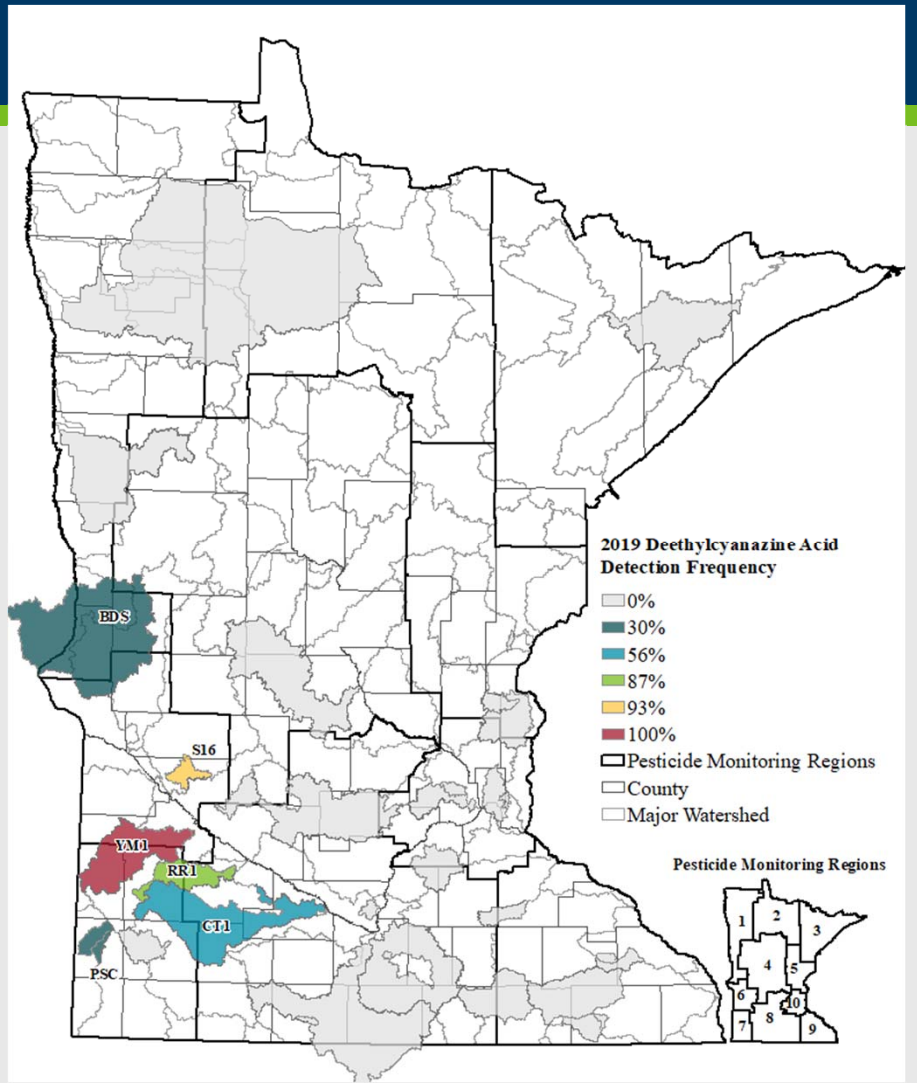


2019 MDA Cyanazine Degradate Sampling

1. **MDA ambient surface water and groundwater sites (~600 SPE LC-MS/MS samples).**
2. **Private Well Pesticide Sampling (PWPS) samples (~1,100 DAI LC-MS/MS).**
3. **Dakota County Study including 84 private drinking water wells (DAI and SPE LC-MS/MS).**

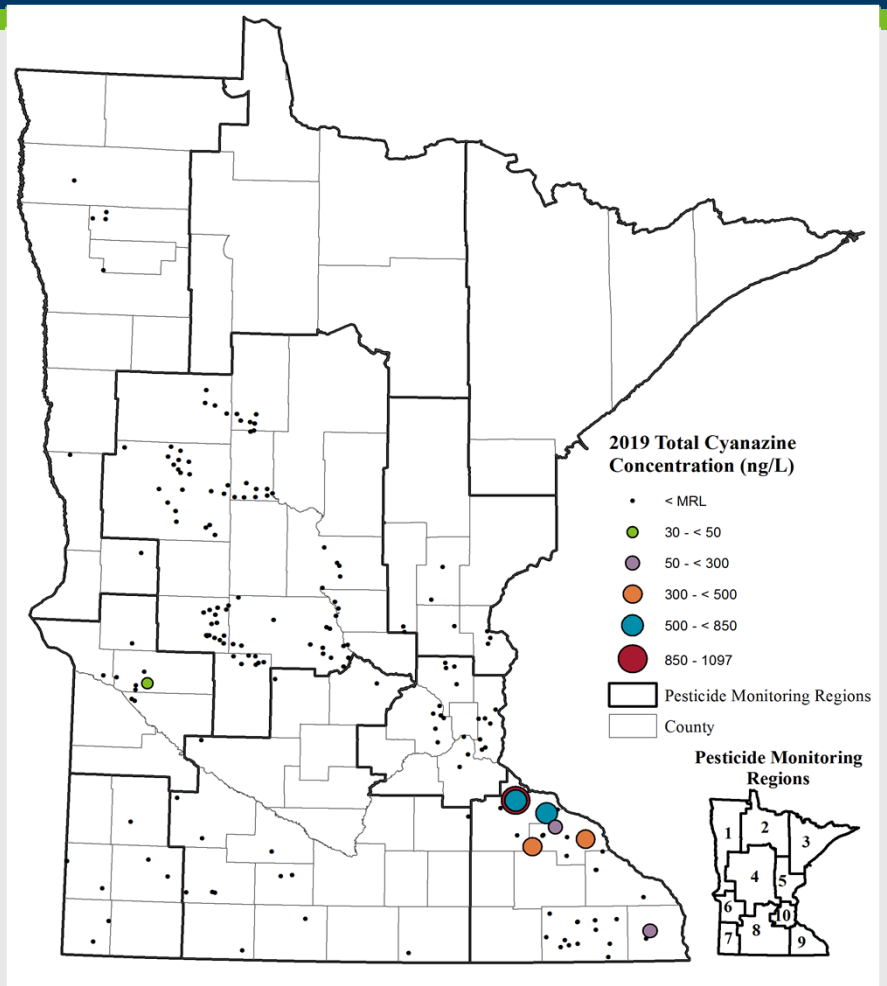
MDA 2019 surface water data for cyanazine degradates
SPE LC-MS/MS

- **373 samples for cyanazine degradates.**
- **Deethylcyanazine acid was detected in 15% of samples.**
- **Maximum concentration was 104 ng/L.**
- **No aquatic life benchmarks for cyanazine degradates.**
- **Detections likely related to groundwater baseflow contribution.**



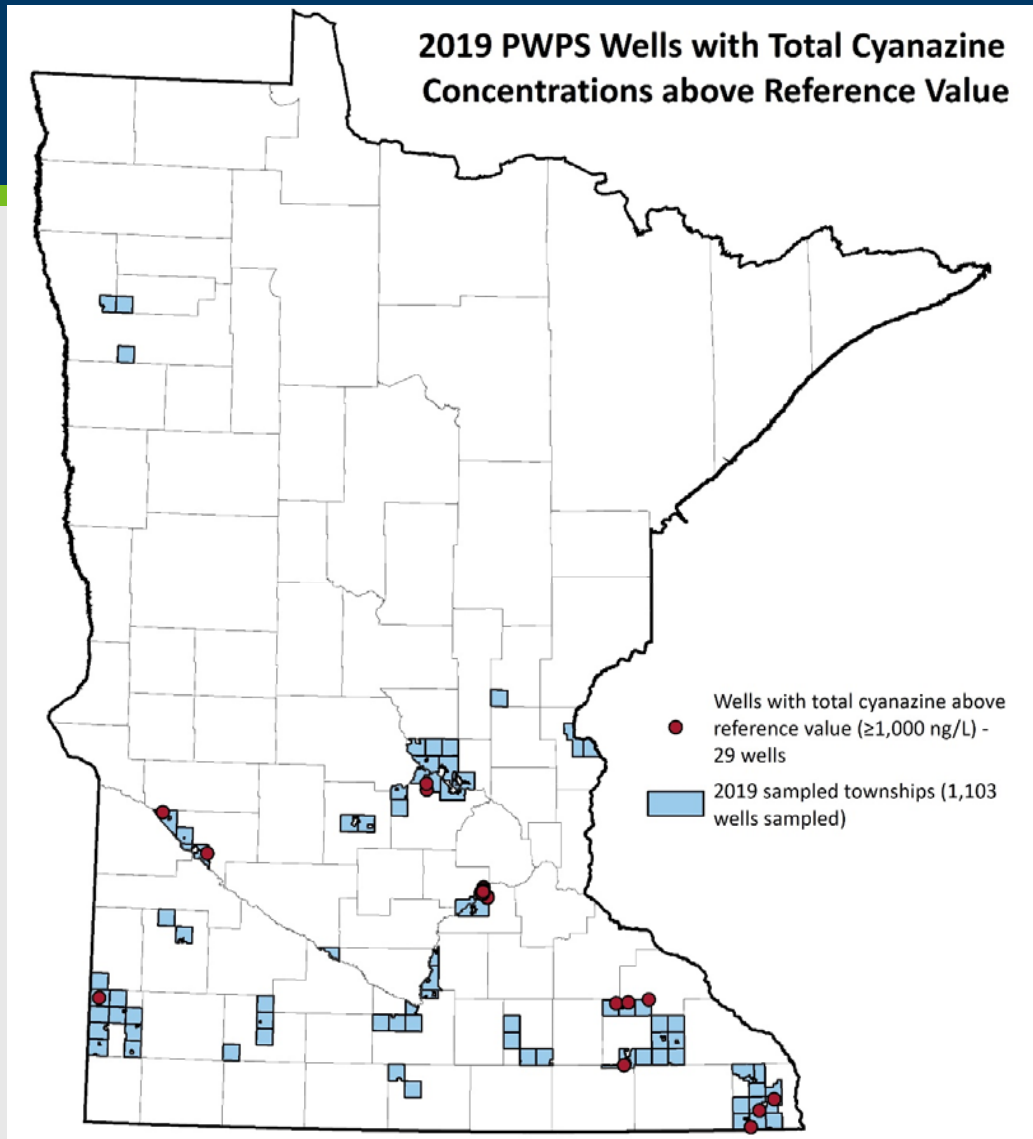
MDA 2019 ambient groundwater results
SPE LC-MS/MS

- 166 sites sampled, most are monitoring wells.
- Target shallow groundwater, uppermost aquifer.
- Limited detections:
  - Three springs in SE MN
  - Three private wells in SE MN
  - One shallow water table well
  - One total cyanazine concentration above 1,000 ng/L drinking water HRL of 222 samples.
- Compounds detected:
  - Cyanazine acid and cyanazine amide
  - Deethylcyanazine acid (max 653 ng/L)



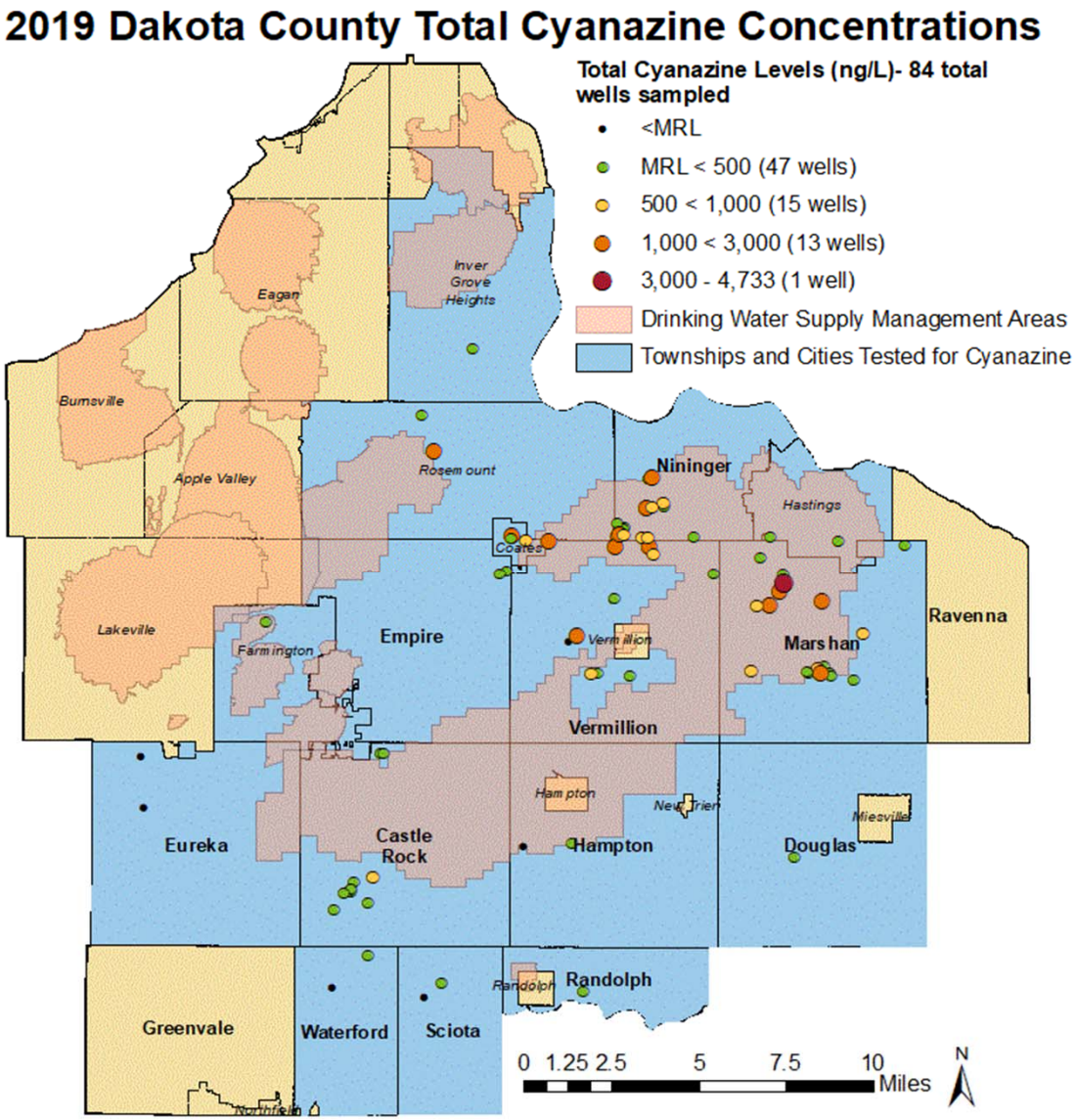
MDA 2019 total cyanazine results – Private Wells (DAI LC-MS/MS)

- 1,103 samples collected, from 23 counties.
- Targeted areas with vulnerable groundwater and row crop agriculture.
- Detects below 1,000 ng/L not presented on map.
- 29 samples over 1,000 ng/L total cyanazine HRL drinking water standard.
- Of those 7 samples over 3,000 ng/L.



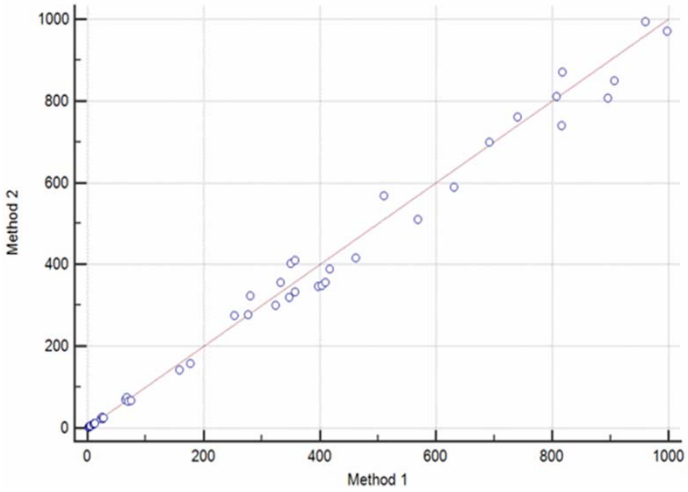
MDA 2019 Dakota County Results

- Targeted sampling effort
- 84 total sites collected in July-August 2019
  - 84 samples DIA LC-MS/MS
  - 46 samples MDA SPE LC-MS/MS
  - 41 samples to USGS OGRL (results pending)
- 14 wells over the 1,000 ng/L HRL



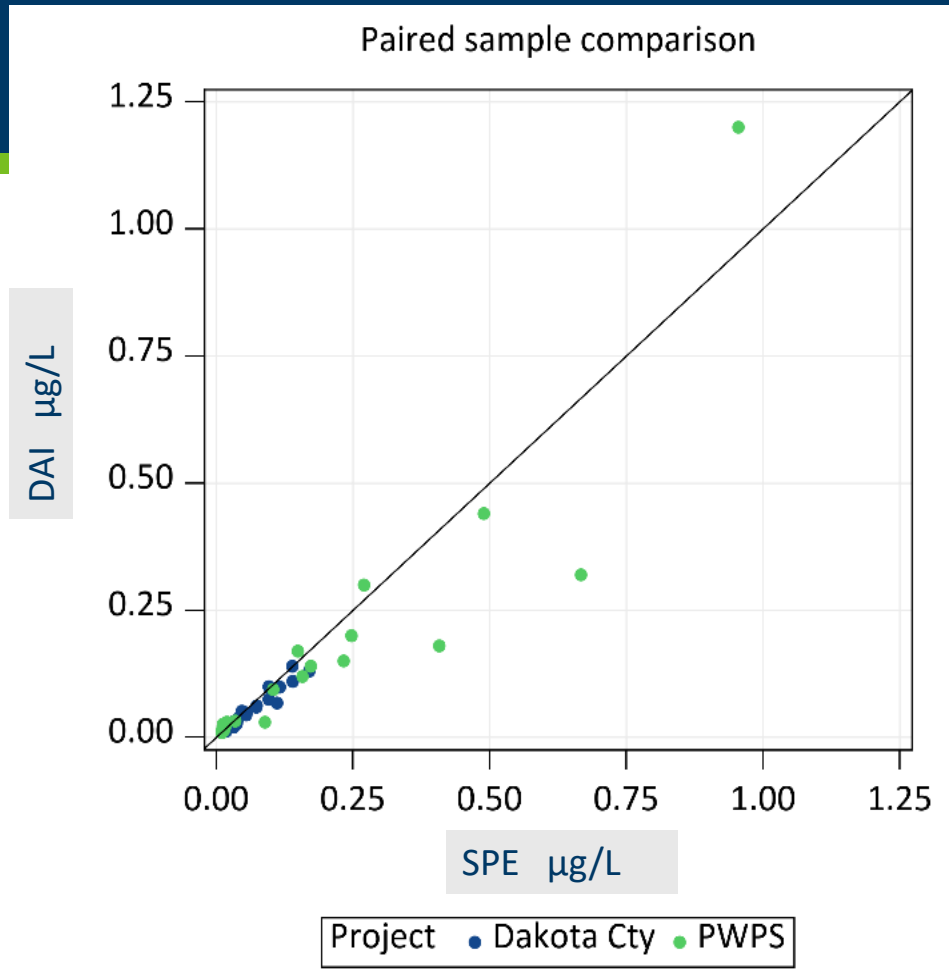
Lab method comparison DAI vs. SPE LC-MS/MS

- Typical to see random error
- Typical to see consistent or proportional bias
  - Consistent bias: one method's values stay above or below the other by fixed amount (e.g., 1 vs. 2 µg/L and 5 vs. 6 µg/L)
  - Proportional bias: one method's values consistently a % higher (e.g., 5%: 3 vs. 3.15 µg/L and 10 vs. 10.5 µg/L)
  - How much bias is acceptable? May depend on how close values are to health-based guidance value.



Cyanazine acid ("CAC", MRL=0.01 µg/L)

- 48% of pairs had ≥1 detect (49/102)
- SPE result higher in 34/49 samples
- In 5/49 pairs, ≥2-fold diff. in concentration (e.g., 320 vs. 670 ng/L)
- Low levels; no major issues seen

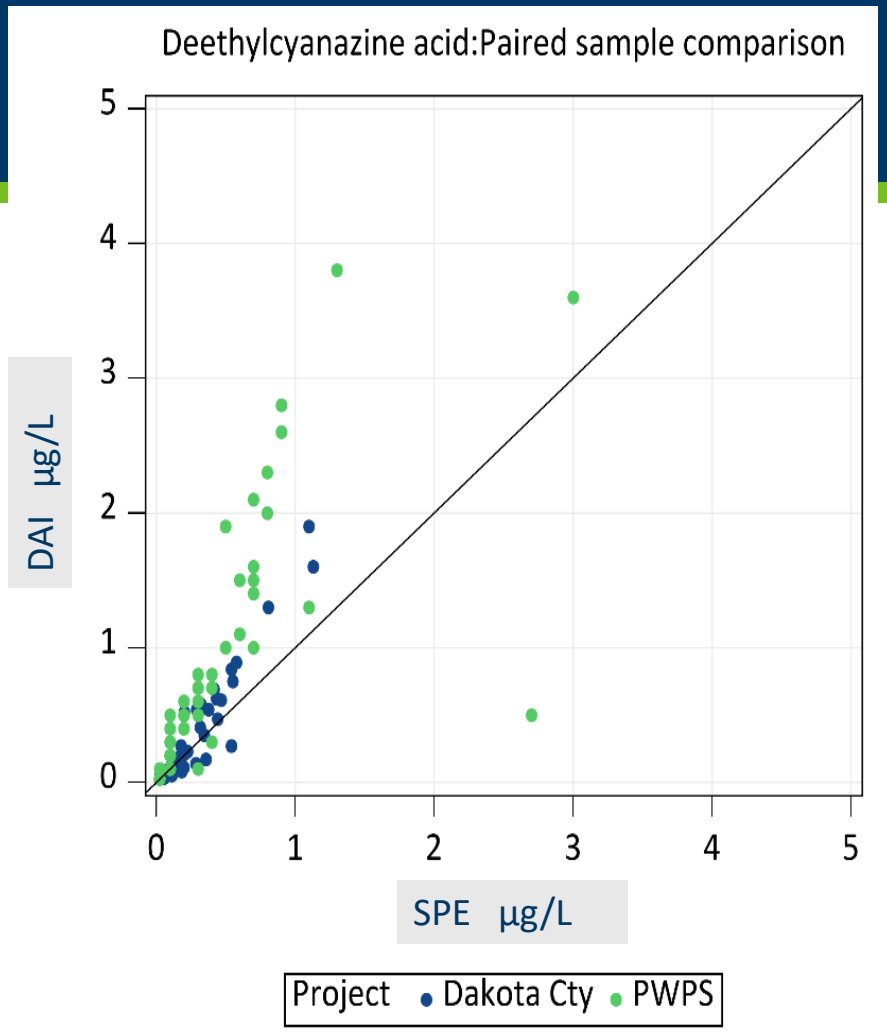


	Mean (Std Dev)	25th Pctl	50 Pctl	75th Pctl	95th Pctl
DAI	0.064 (0.176)	<MRL	<MRL	0.032	0.200
SPE	0.085 (0.283)	<MRL	<MRL	0.041	0.270

Deethylcyanazine acid ("DCAC", MRL=0.025 µg/L)

- 87% of pairs had ≥ 1 detect (89/102).
- DAI result higher in 72/89 samples.
- In 44/89 pairs (49%), ≥2-fold diff. in concentration.
- Proportional bias seen; follow-up recommended since it is a driver in total cyanazine concentration.

	Mean (Std Dev)	25th Pctl	50 Pctl	75th Pctl	95th Pctl
DAI	1.13 (3.72)	0.10	0.38	0.80	3.6
SPE	0.59 (1.51)	0.10	0.20	0.50	2.7



Lab/Method Comparison Summary

Differences between labs/methods are expected – not just a cyanazine analyte issue.

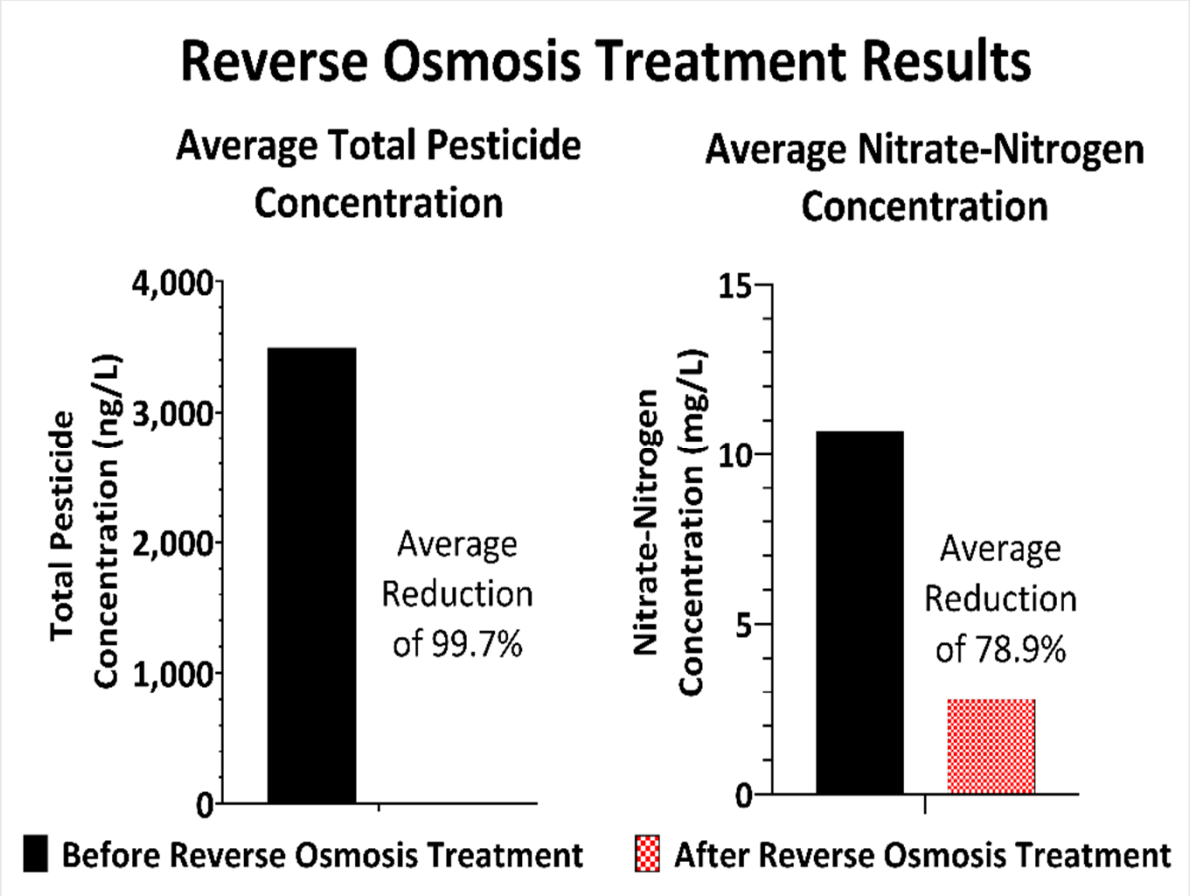
Bias between lab methods for deethylcyanazine acid and atrazine DEDI has potential to impact interpretation of results due to higher detection frequencies and concentrations.

- Matrix interference suspected and confirmed with deethylcyanazine acid.

- 2020 Response - To optimize the DAI chromatography and minimize coeluting matrix effects, each sample injection is “sandwiched” between two solvent aliquots.

Pre and post treatment in private water systems

- 44 samples collected pre and post treatment in private water systems from 2017-2019.
- Pre-treatment total pesticide range: 745 to 11,762 ng/L
- Post-treatment total pesticide range: Non-detect to 153 ng/L
- All cyanazine degradates removed.



Primary Findings

- Total cyanazine is present in vulnerable drinking water wells in agricultural areas of Minnesota at concentrations above the established Health Risk Limit of 1,000 ng/L indicating long-term persistence.
- Measured concentrations are similar to historical values reported by USGS.
- Deethylcyanazine acid generally dominates among the cyanazine specific degradates both with respect to concentration and detection frequency.
- DAI LC-MS/MS deethylcyanazine acid results indicated proportional bias related to matrix interference when compared to SPE LC-MS/MS.
- Homeowner maintained point-of-use reverse osmosis water treatment systems were effective at reducing total pesticide concentrations.

Additional Information

Funding provided by:
- MN Clean Water, Land and Legacy Amendment
- Pesticide Regulatory Account – Fees paid by pesticide dealers and users.

For additional information:

- https://www.mda.state.mn.us/cyanazine-monitoring
- https://www.mda.state.mn.us/pesticide-fertilizer/water-monitoring-reports-resources (2019 Water Quality Monitoring Report)
- https://www.health.state.mn.us/communities/environment/water/docs/contaminants/cyanazine.pdf

Contributions from: Heather Johnson, Brennon Schaefer, Kathy Reynolds, Dave Tollefson, Matt Ribikawskis, Mike MacDonald and Deanna Scher, Dakota County Environmental Resources Dept., MN Dept. of Agriculture Lab, Weck Laboratories

Questions

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