Developing a Method for the Analysis of Chemical Waste Markers in Groundwater and Identifying Sources of Nitrate Contamination

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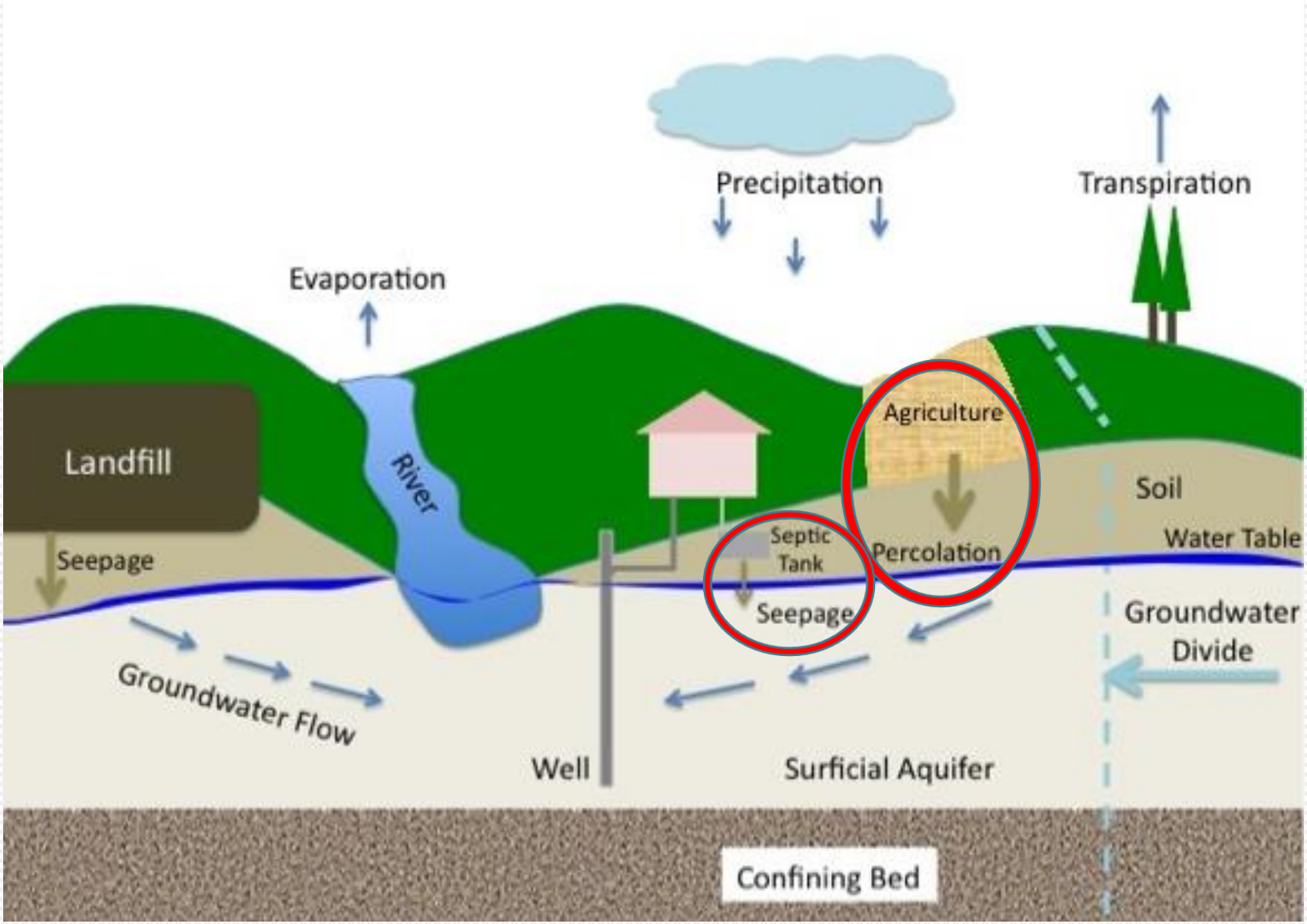
Outline

- Introduction
  - Sources of Nitrate Contamination
  - Chemical Waste Markers
- Analytical Method Development
  - Solid Phase Extraction
- Field Study
  - Town of Hull (Portage County, WI)
  - Results
- Conclusions/Future Work
- Questions

Sources of Nitrate Contamination



Identifying Sources of Nitrate Contamination

- Agricultural
  - Nitrogen and phosphorus containing pesticides
  - Chloroacetanilide metabolites (CAAMs)

Nitrogen and Phosphorus Containing Pesticides

Acetochlor
Atrazine
De-ethyl atrazine
De-isoprophyl atrazine
Alachlor (Lasso)
Ametryn
Atraton
Bromacil
Butachlor
Butylate
Carbofuran
Chloropropham
Chlorthalonil
Cyanazine (Bladex)
Cycloate
Dimethinamid
Diphenamid
Dyfonate
EPTC (Eptam)
Etridiazole
Hexazinone
MGK (a + b)
Metolachlor (Dual)
Metribuzin (Sencor)
Molinate
Napropamide
Norflurazon
Pebulate
Prometon
Prometryne
Pronamide
Propachlor
Propazine
Simazine
Simetryn
Terbacil
Terbutryn
Trifluralin
Vernolate

Chloroacetanilide Metabolites (CAAMs)

Acetochlor ESA
Acetochlor OA
Alachlor ESA
Alachlor OA
Metolachlor ESA
Metolachlor OA

Identifying Sources of Nitrate Contamination

- Agricultural
  - Nitrogen and phosphorus containing pesticides
  - Chloroacetanilide metabolites (CAAMs)

- Septic
  - Analyze for human waste markers (HWM)

Human Waste Markers

- Chemical compounds unique to human use
  - Pharmaceuticals
  - Personal care products
  - Food products, e.g., artificial sweeteners

Human Waste Markers of Interest

Acesulfame

Sucralose

Cotinine

Caffeine

Paraxanthine

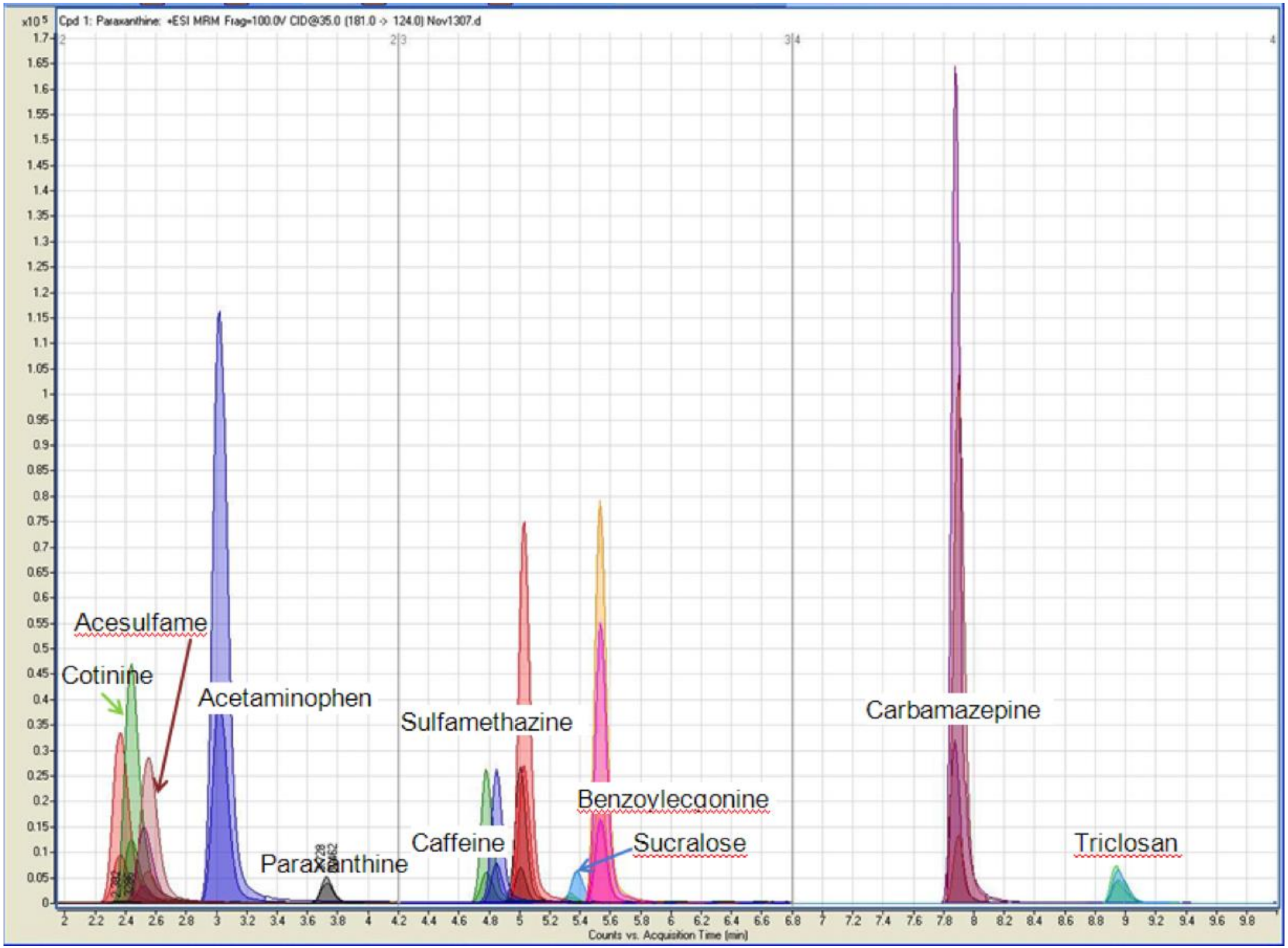
Acetaminophen

Carbamazepine
(anti-convulsant/
mood stabilizer)

Triclosan

Method Development for Waste Markers

- **Identification/Quantitation**
  - ESI-LC/MS/MS
    - Optimization
- **Chromatography**
  - Calibration


Cpd 1: Paraxanthine: +ESI MRM Frag=100.0V CID@35.0 (181.0 -> 124.0) Nov1307.d
x10 5
Acesulfame
Cotinine
Acetaminophen
Paraxanthine
Sulfamethazine
Caffeine
Benzoylecgonine
Sucralose
Carbamazepine
Triclosan
Counts vs. Acquisition Time (min)

Method Development for Waste Markers

- **Identification/Quantitation**
  - ESI-LC/MS/MS
    - Optimization
- **Chromatography**
  - Calibration
- **Sample Preparation**
  - Sample Extraction

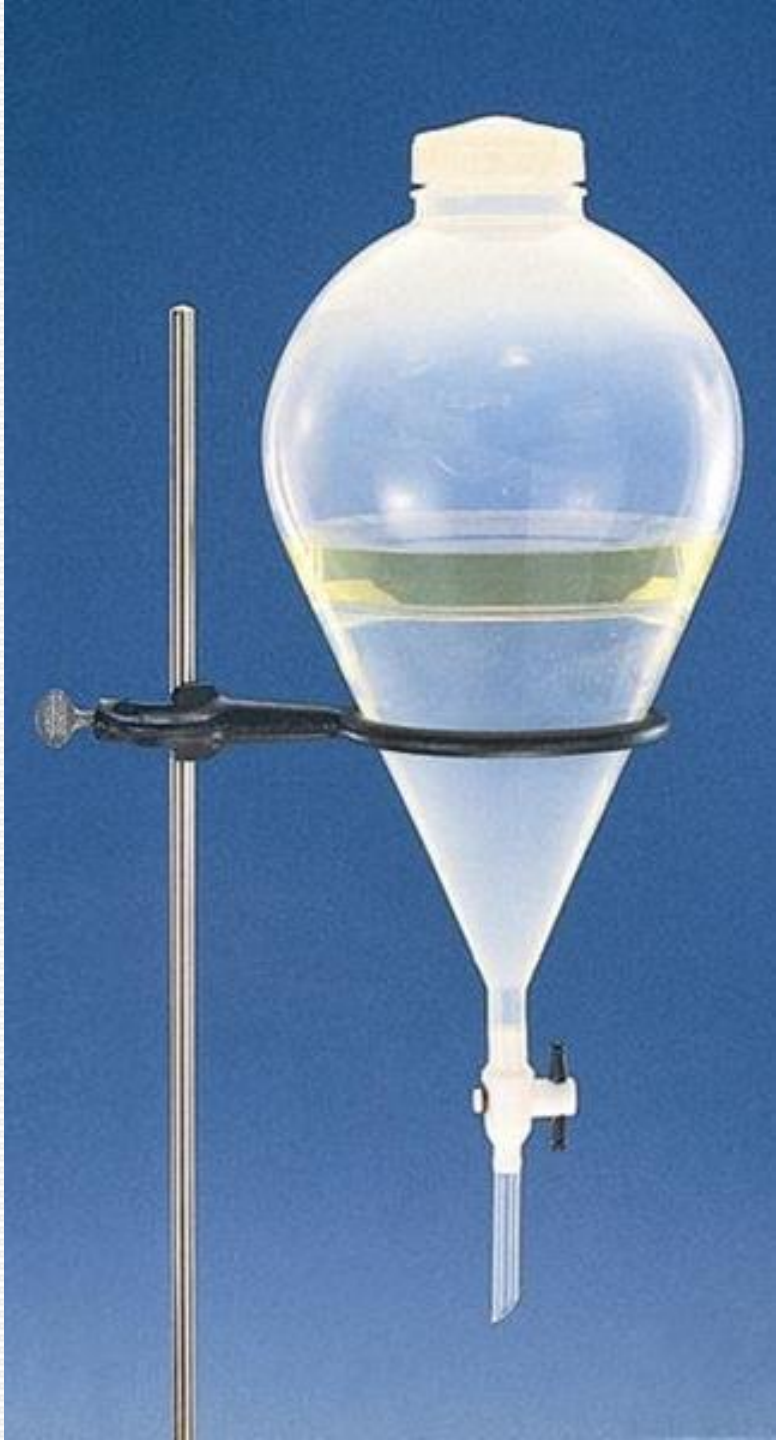
Method Development for Waste Markers

Sample Extraction

- Remove/reduce interferences to improve detection and quantitation of analytes of interest.
- Increase the concentration (i.e. 200-fold) for better detection and more accurate quantitation.
  - Detection limit without extraction = 1.0 part per billion
  - Detection limit after extraction = 5.0 parts per trillion

Sample Extraction

- Liquid-Liquid vs Solid Phase
  - Solvent waste
  - Time
  - Cost



SPE: How it works

Method Development

- Considered
  - Cartridges
  - Sample pH
  - Elution schemes

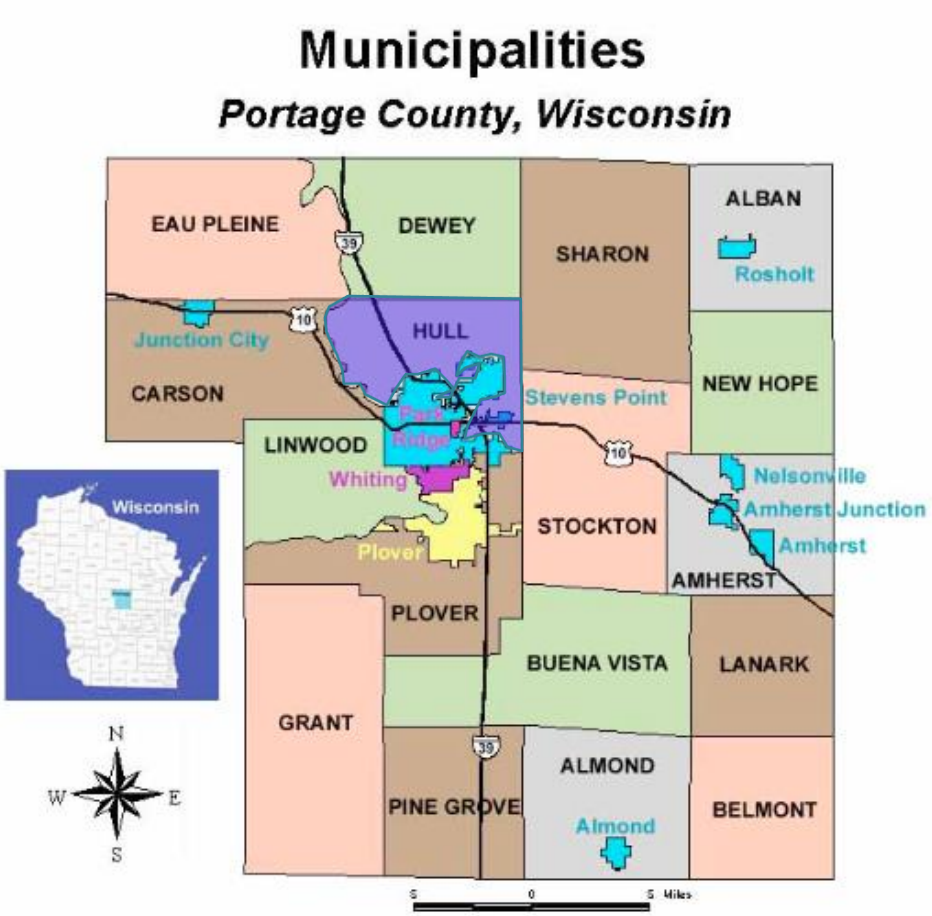
Proposed Extraction Method

- No pH adjustment to sample
- Cartridge: Waters Oasis HLB
- Elution Scheme: methanol, water

Method Detection Limit Study

	Spike Concentration (ng/L)	N	Average Percent Recovery	Limit of Detection (ng/L)
Cotinine	7.5	13	84%	2.8
Acesulfame	15	10	9%	6.6
Acetaminophen	15	4	106%	3.6
Paraxanthine	7.5	13	105%	4.2
Caffeine	7.5	13	172%	11.7
Sucralose	37.5	14	63%	22.9
Carbamazepine	3.75	14	80%	1.9
Triclosan	37.5	10	124%	52.5

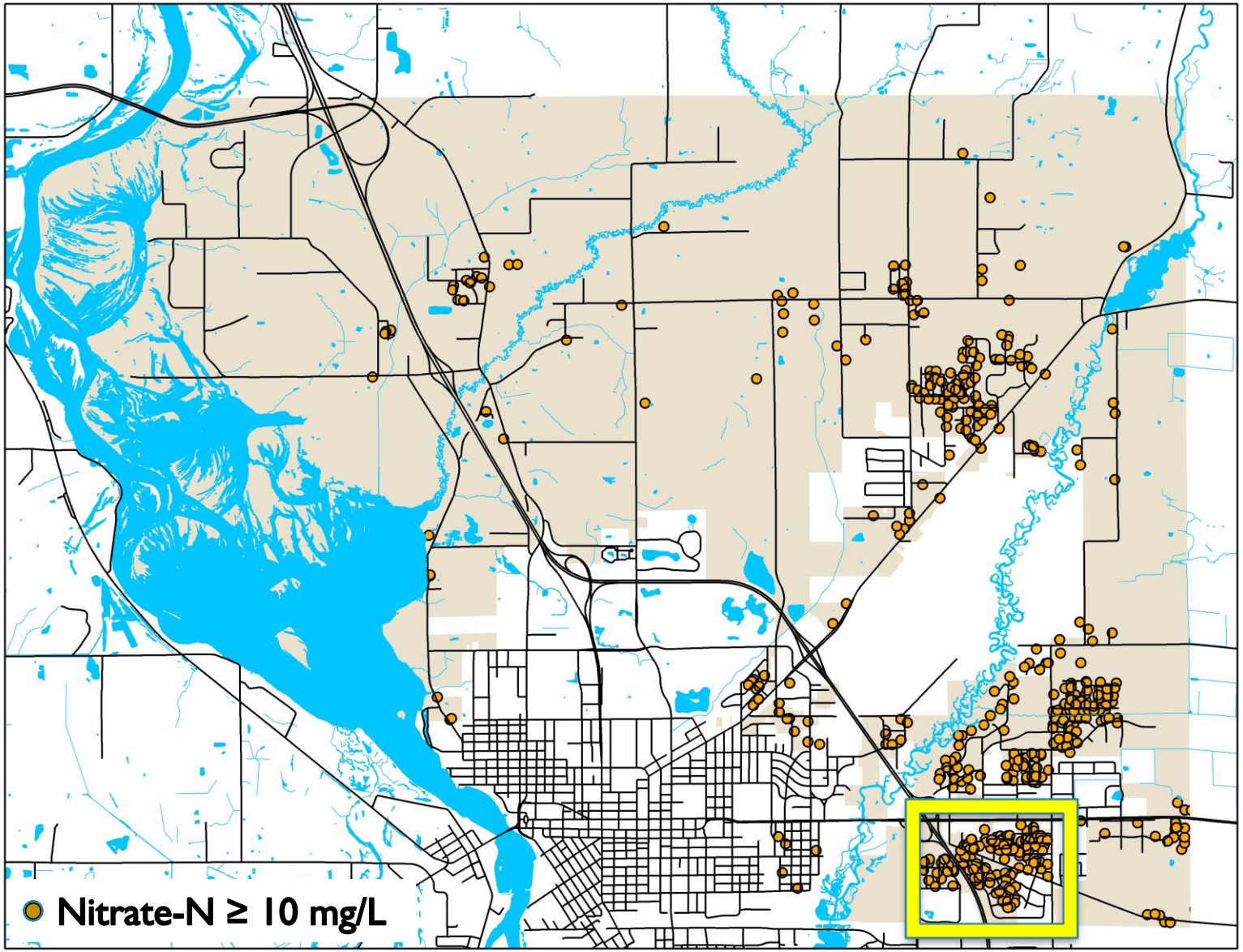
Town of Hull Background



- 5,700 residents/2,200 septic systems
- 20,088 acres
- Single-family residential
- Agricultural land
- Drinking water from private wells
- Shallow wells in sand and gravel, as well as bedrock

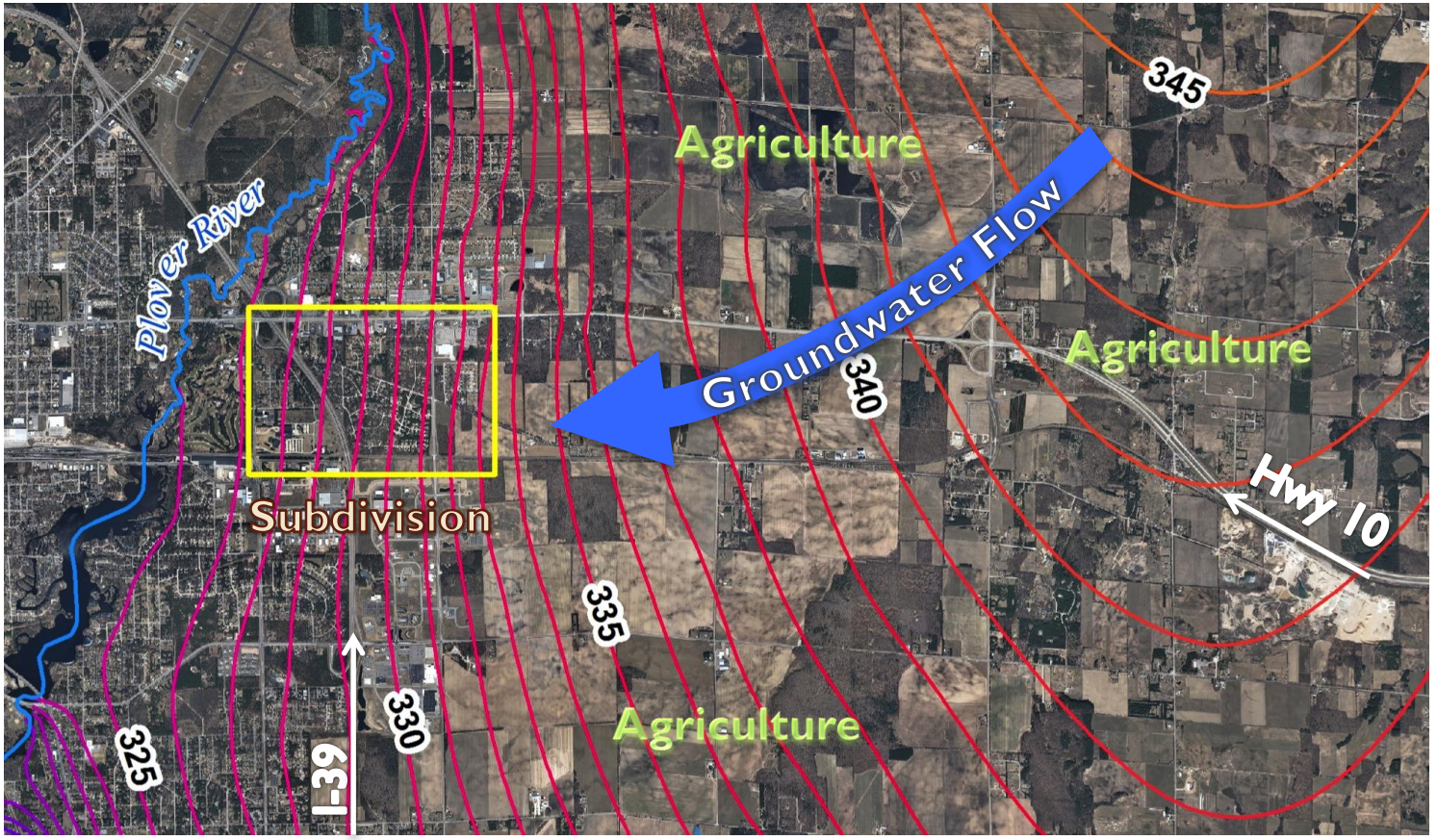
Source: *http://www.co.portage.wi.us/groundwater/undrstnd/pcmap.htm*

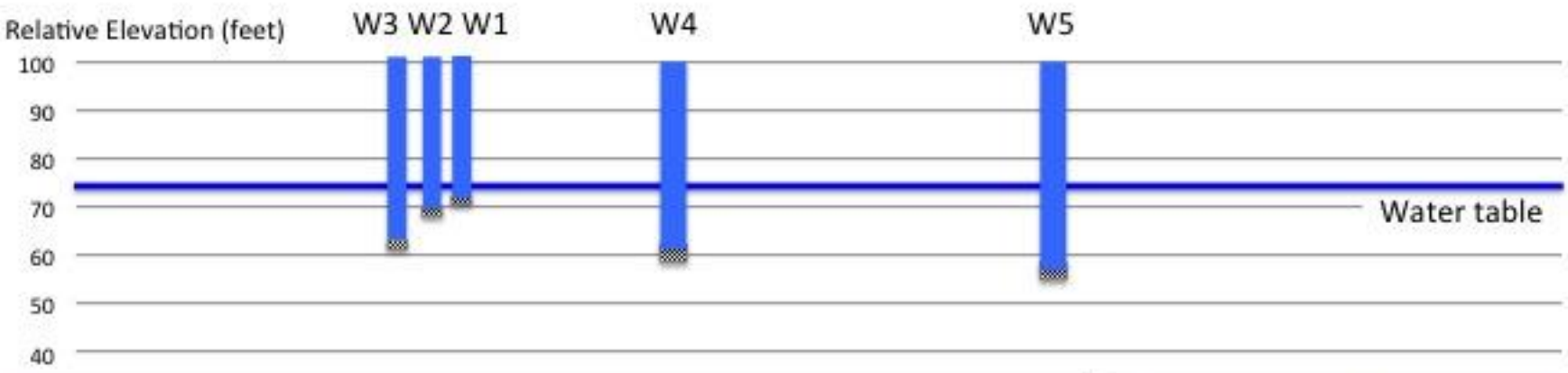
Nitrate in the Town of Hull

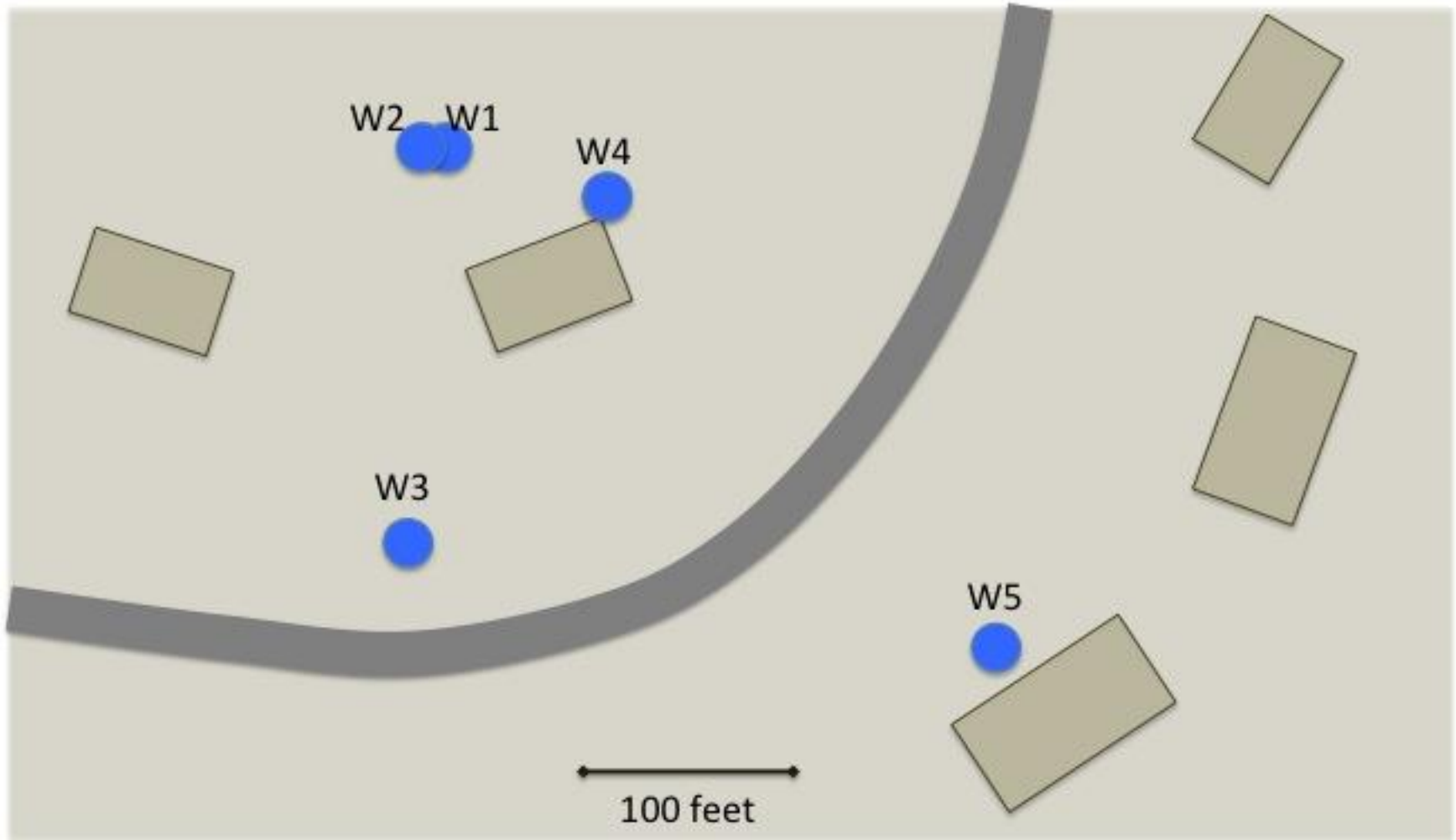


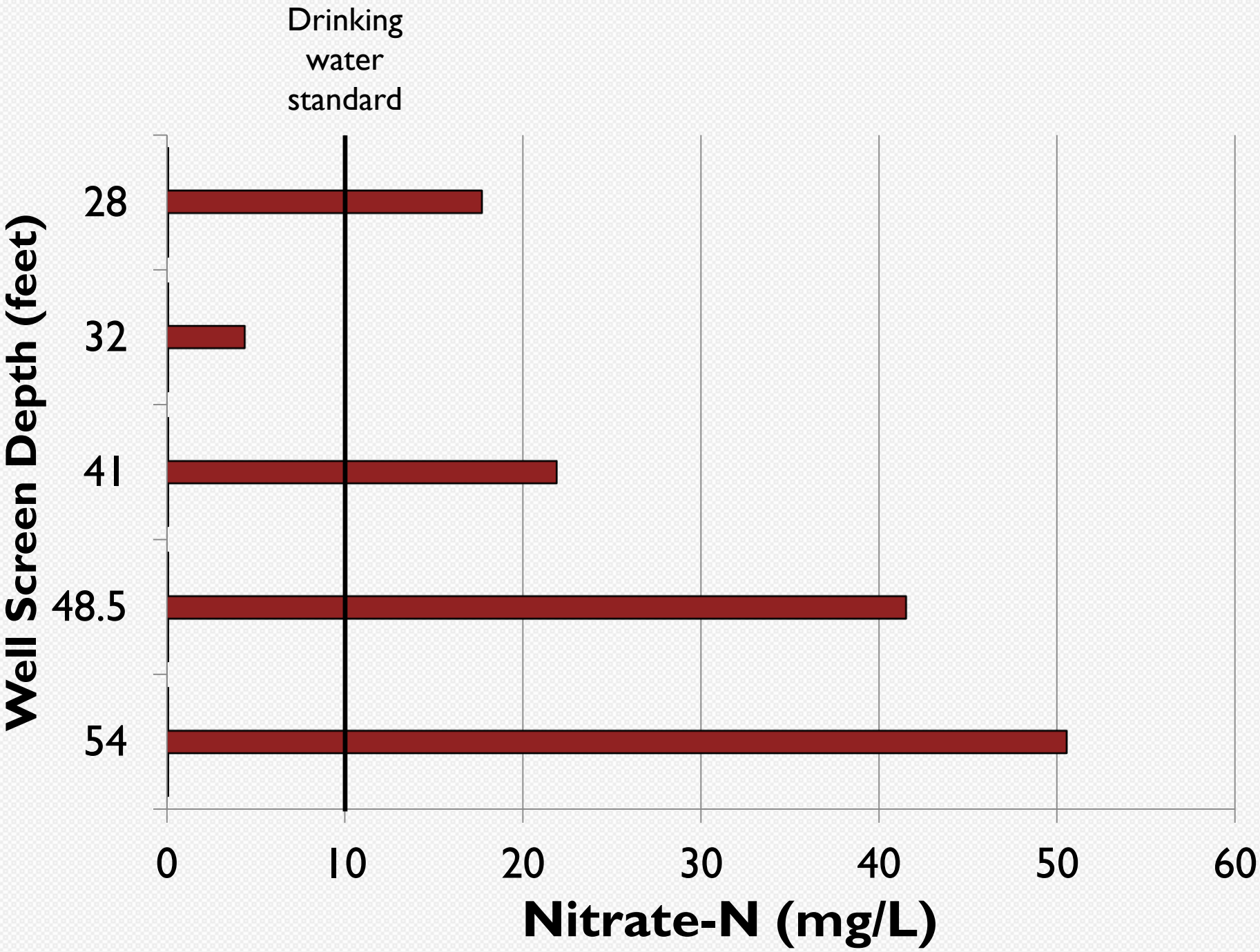
Study Site Selection

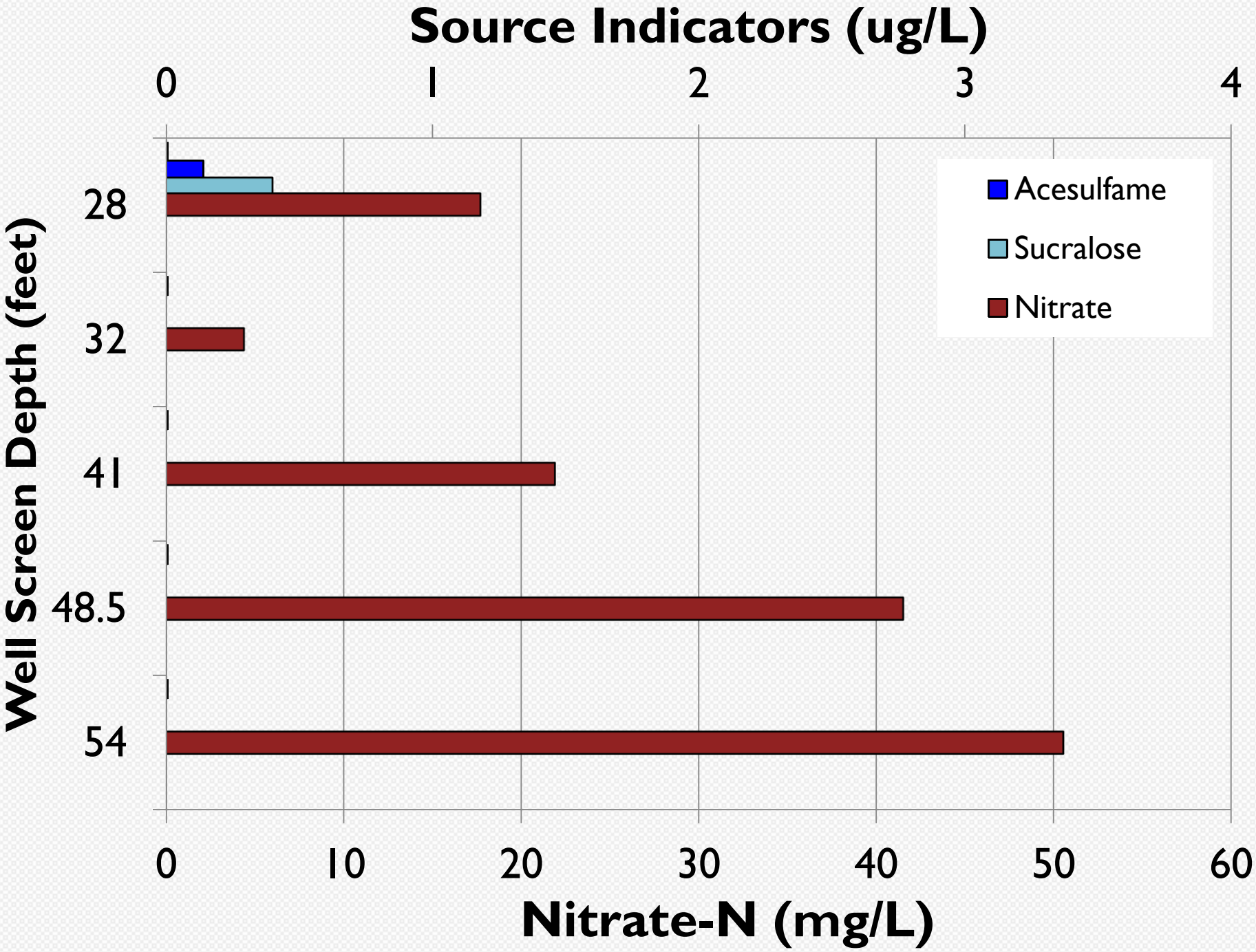
- Targeted area that previously had nitrate-N levels >10 ppm (mg/L)
  - to identify sources of nitrate contamination

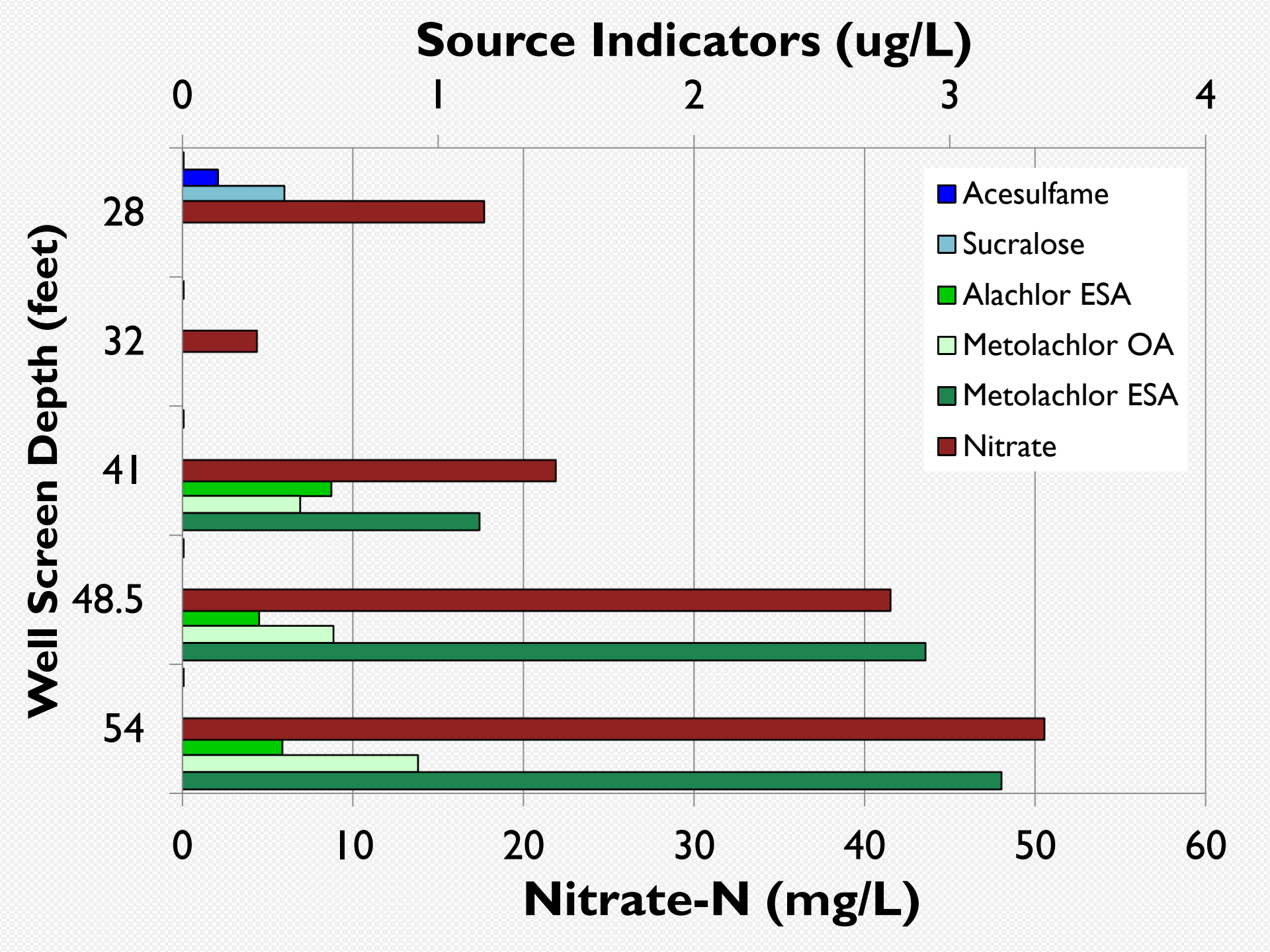



Relative Elevation (feet)
W3 W2 W1
W4
W5
100
90
80
70
60
50
40
Water table


W2
W1
W4
W3
W5
100 feet


Drinking water standard
Well Screen Depth (feet)
28
32
41
48.5
54
0
10
20
30
40
50
60
Nitrate-N (mg/L)


Source Indicators (ug/L)
0
1
2
3
4
Acesulfame
Sucralose
Nitrate
Well Screen Depth (feet)
28
32
41
48.5
54
0
10
20
30
40
50
60
Nitrate-N (mg/L)

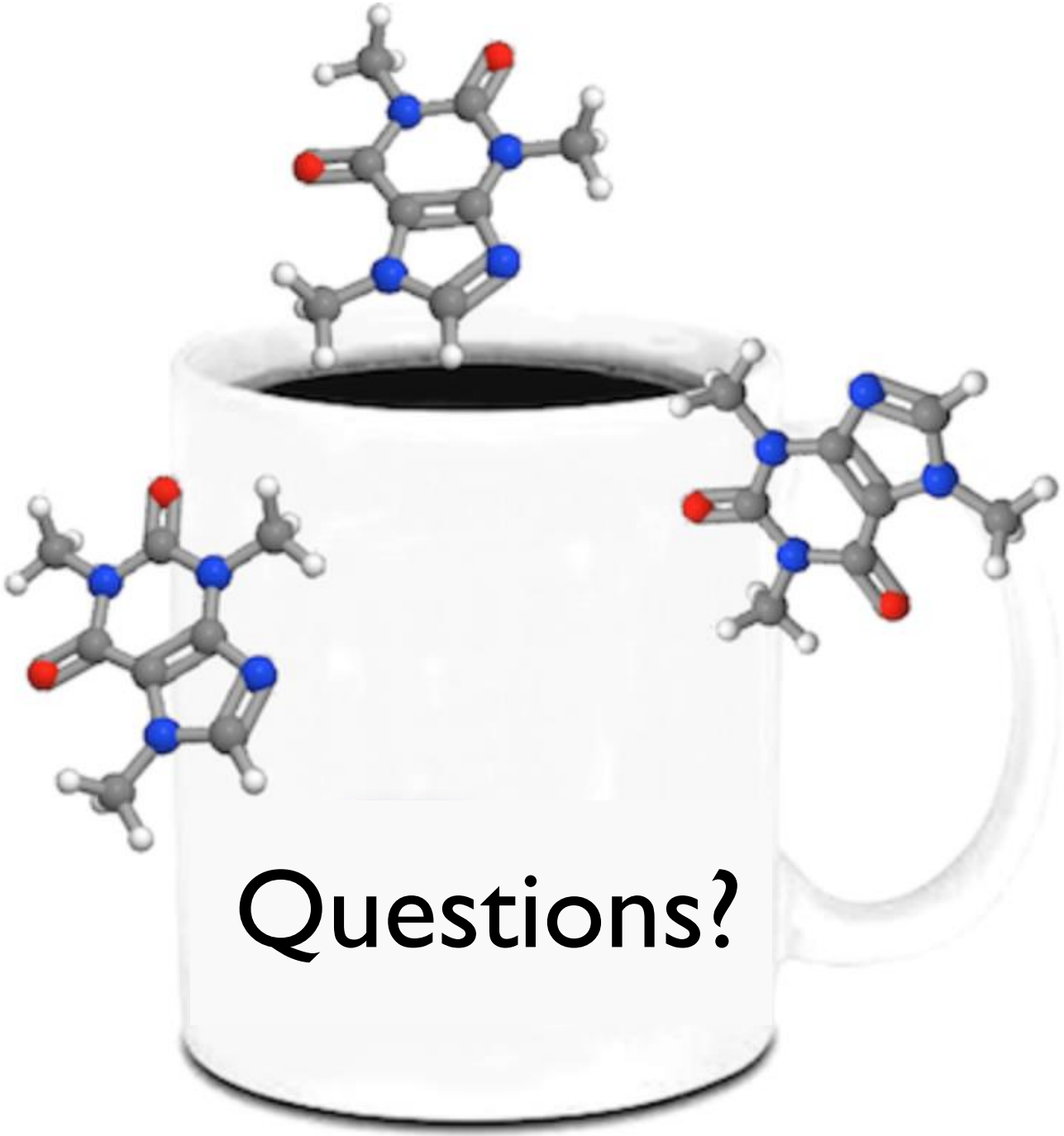

Source Indicators (ug/L)
0
1
2
3
4
Well Screen Depth (feet)
28
32
41
48.5
54
Acesulfame
Sucralose
Alachlor ESA
Metolachlor OA
Metolachlor ESA
Nitrate
0
10
20
30
40
50
60
Nitrate-N (mg/L)

Conclusions/Future Work

- Single method/simple extraction scheme useful in identifying multiple compounds
- Reliable indicators used to determine nitrate sources / Understanding the source can direct remediation and planning for the future
- Add other chemical indicators / Combine with fecal sterol analysis / Additional sampling

Acknowledgements

- Water & Environmental Analysis Lab (UWSP)
- Dave Mechenich
- Portage County Planning & Zoning
- Town of Hull
- Wisconsin DNR


Questions?