Selected pesticide and trace organics monitoring studies, statewide context for observations from the Grand River

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In Cooperation with Michigan Department of Environmental Quality and Great Lakes Restoration Initiative

U.S. Department of the Interior
U.S. Geological Survey

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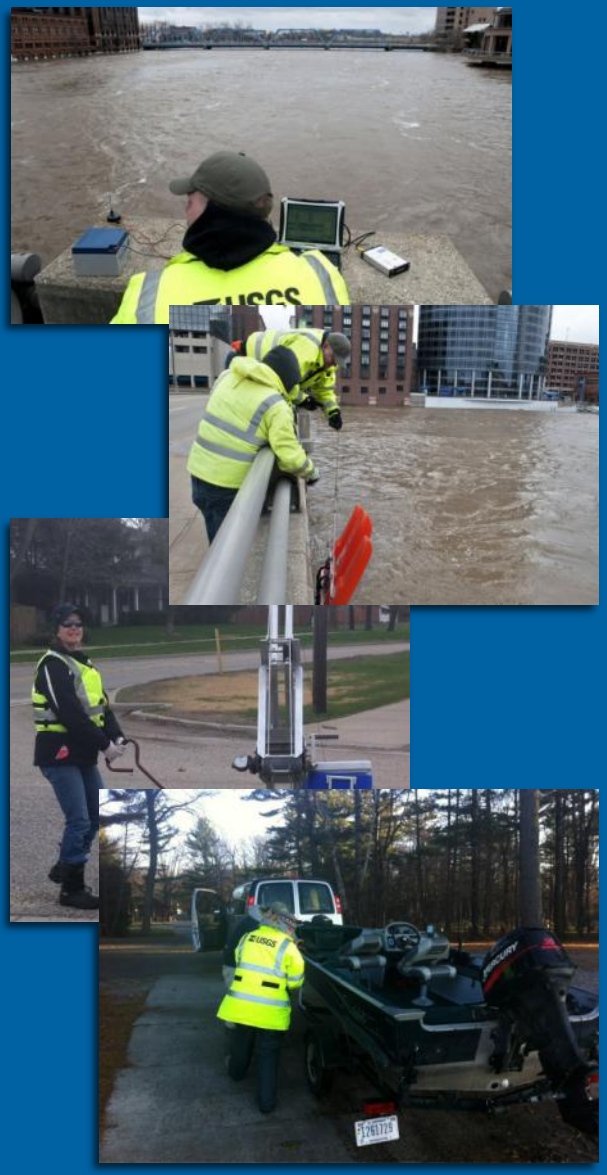
  - **Protect and enhance water resources for human health, aquatic health, and environmental quality**
  - **Contribute to wise physical and economic development of the nations water resources**



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Grand River Activities Overview

- Ongoing or past studies and activities
  - USGS Stream gages (NSIP/Local Cooperators)
  - Water Chemistry Monitoring Program (MDEQ WCMP)
  - Great Lakes Restoration Initiative Tributary Monitoring (USGS GLRI)
  - USGS Cooperative Water Program Studies (CWP)
- Expanded Studies
  - Grand River chemicals of emerging concern, spatial characterization (USGS GLRI)

Grand River Basin					
04109000	GRAND RIVER AT JACKSON, MI	11/06 17:30 EST	8.90	66	76.0
04111000	GRAND RIVER NEAR EATON RAPIDS, MI	11/06 18:00 EST	2.07	271	268
04111379	RED CEDAR RIVER NEAR WILLIAMSTON, MI	11/06 17:15 EST	3.95	48	54.0
04112000	SLOAN CREEK NEAR WILLIAMSTON, MI	11/06 17:45 EST	1.84	1.6	.78
04112500	RED CEDAR RIVER AT EAST LANSING, MI	11/06 17:30 EST	3.50	107	88.0
04112850	SYCAMORE CREEK AT HOLT ROAD NEAR HOLT, MI	11/06 17:15 EST	3.11	24	13.0
04113000	GRAND RIVER AT LANSING, MI	11/06 17:45 EST	2.89	478	433
04114000	GRAND RIVER AT PORTLAND, MI	11/06 17:45 EST	5.89	539	559
04114498	LOOKING GLASS RIVER NEAR EAGLE, MI	11/06 17:45 EST	2.93	98	72.0
04115000	MAPLE RIVER AT MAPLE RAPIDS, MI	11/06 17:15 EST	4.08	131	86.0
04115265	FISH CREEK NEAR CRYSTAL, MI	11/06 18:00 EST	2.89	41	30.0
04116000	GRAND RIVER AT IONIA, MI	11/06 17:45 EST	8.91	1,170	1,140
04116500	FLAT RIVER AT SMYRNA, MI	11/06 18:00 EST	3.90	--	---
04117000	QUAKER BROOK NEAR NASHVILLE, MI	11/06 18:00 EST	1.92	5.9	4.70
04117500	THORNAPPLE RIVER NEAR HASTINGS, MI	11/06 17:15 EST	3.34	178	174
04118000	THORNAPPLE RIVER NEAR CALEDONIA, MI	11/06 17:30 EST	3.83	--	---
04118105	GRAND RIVER AT ADA, MI	11/06 17:30 EST	7.78	--	---
04118500	ROGUE RIVER NEAR ROCKFORD, MI	11/06 17:00 EST	4.25	195	192
04119000	GRAND RIVER AT GRAND RAPIDS, MI	11/06 17:00 EST	3.51	2,730	2,230
04119055	PLASTER CREEK AT 28TH STREET AT GRAND RAPIDS, MI	11/06 17:00 EST	3.92	23	---
04119400	GRAND RIVER NEAR EASTMANVILLE, MI	11/06 17:48 EST	Dis	Dis	2,720

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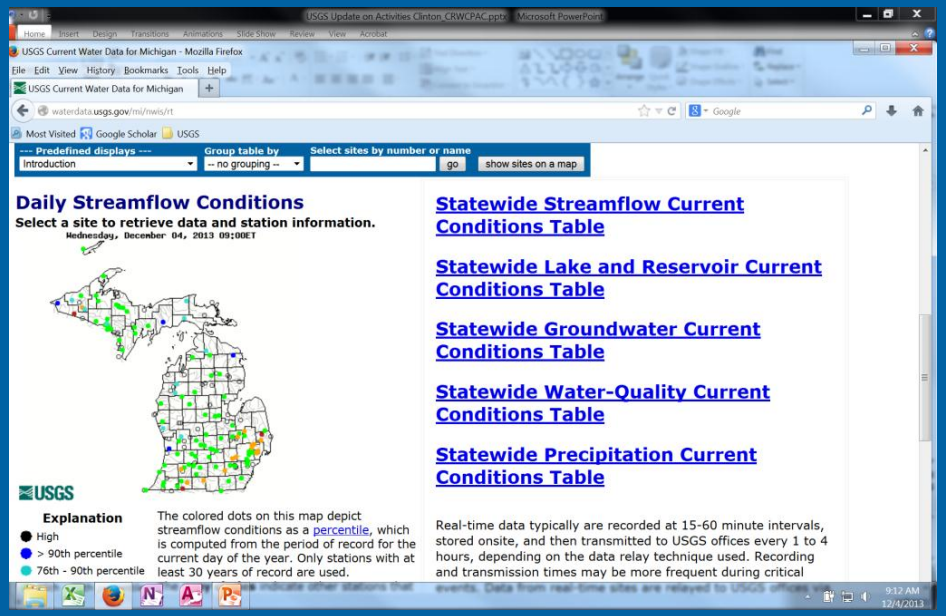
USGS Stream Gages



- [current conditions]
  - Grand: 20 gages
- 1 continuous water quality gage in the area [Eastmanville]
  - Customizable plots for all data since 2007
  - Useful to direct sampling efforts
  - Continued GLRI funding is currently uncertain, water quality data collection currently suspended

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USGS-MDEQ Cooperative Pesticide Monitoring

Use of immunoassay for the detection of atrazine, metolachlor, simazine, chlorpyrifos, and diazinon in streams

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Immunoassay- Pros and Cons

PROS	CONS
Inexpensive	Can only analyze one analyte at a time
High throughput	High detection limit
Quick screening	Non-specific

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Immunoassay Detection Limits

	Usage	Immunoassay detection limit	Lab analysis detection limit
Herbicides			
Atrazine	Several crops, majority on corn and soybeans	0.046 µg/L	0.001 µg/L
Metolachlor	Several crops, majority on corn and soybeans	0.05 µg/L	0.002 µg/L
Simazine	Several crops, primarily fruits and urban weed control	0.03 µg/L	0.005 µg/L
Insecticides			
Diazinon	Primarily urban insect control, little on field crops, being phased out	0.022 µg/L	0.002 µg/L
Chlorpyrifos	Widely used on field crops, being phased out as a urban use	0.1 µg/L	0.004 µg/L
Aldicarb	Primarily for soybean aphid control	4 µg/L	0.016 µg/L

Immunoassay vs. GS/MS

Triazine Concentration in ug/L

USGS station name	Date sampled	Triazine screen (Field)	Triazine screen (Lab)*
Pigeon River near Scott, Ind.	7/10/2001	2.00	0.655
Solomon Creek near Syracuse, Ind.	7/11/2001	.05	.126
East Branch Galien River, Mich.	9/2/2003	.12	.087
Galien River near Sawyer, Mich.	9/2/2003	.08	.051

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2005 Monitoring Study

1. Measure pesticide concentrations at selected stream sites throughout Michigan.
2. Provide data that will increase understanding as to when and where to sample most effectively for pesticides.
3. Provide data to aid in the development of a more comprehensive monitoring study.
4. Correlate pesticide concentrations with other water-quality constituents.

http://pubs.usgs.gov/sir/2007/5077/

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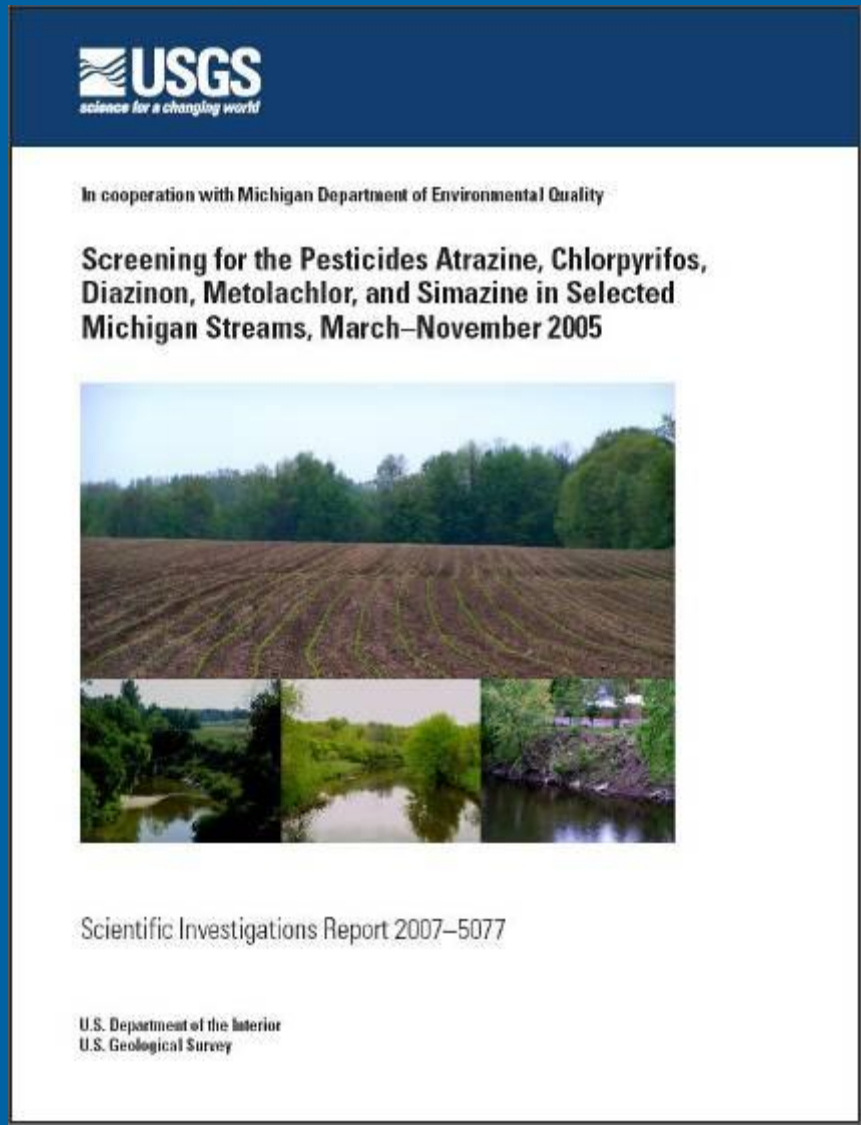
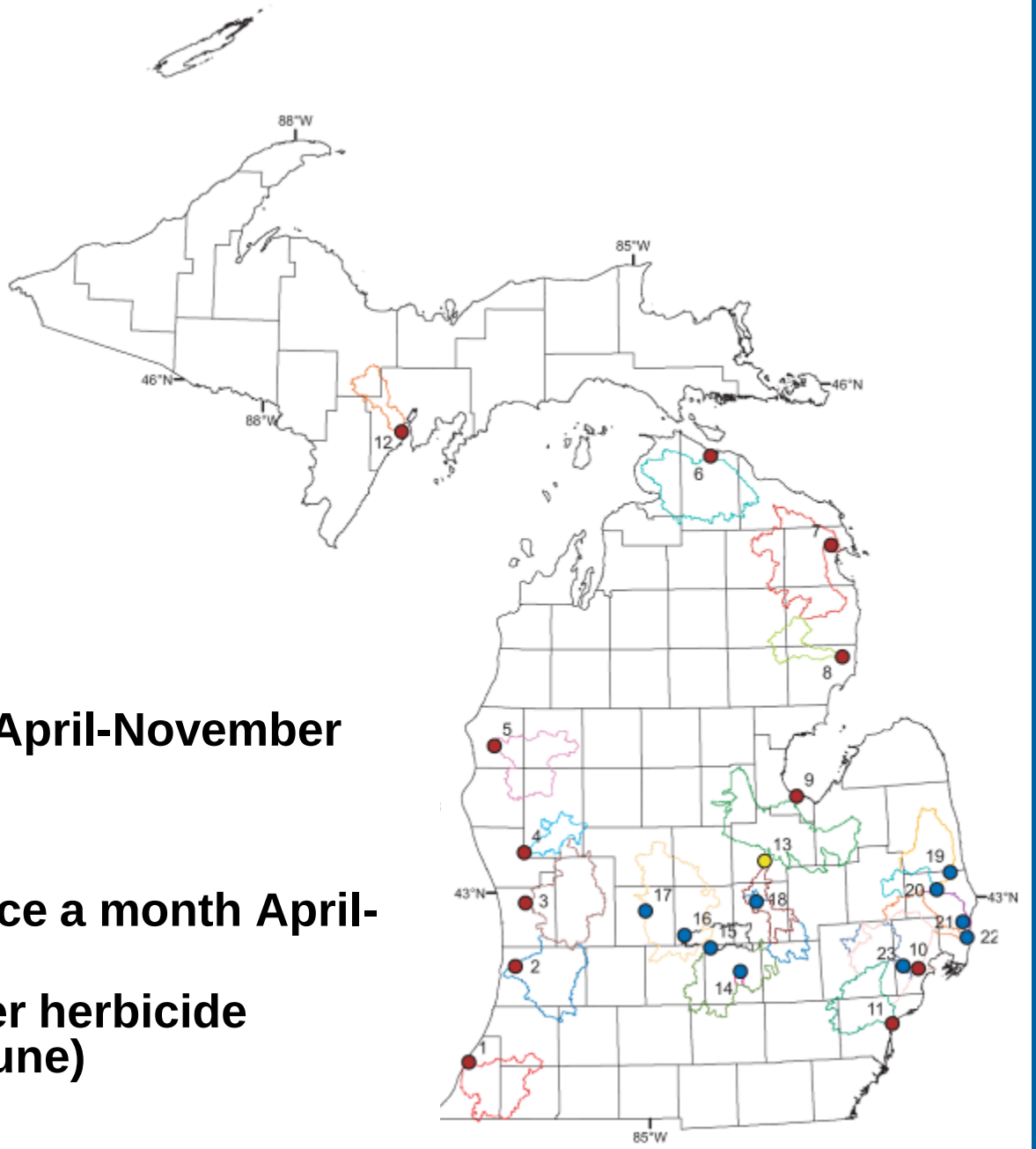
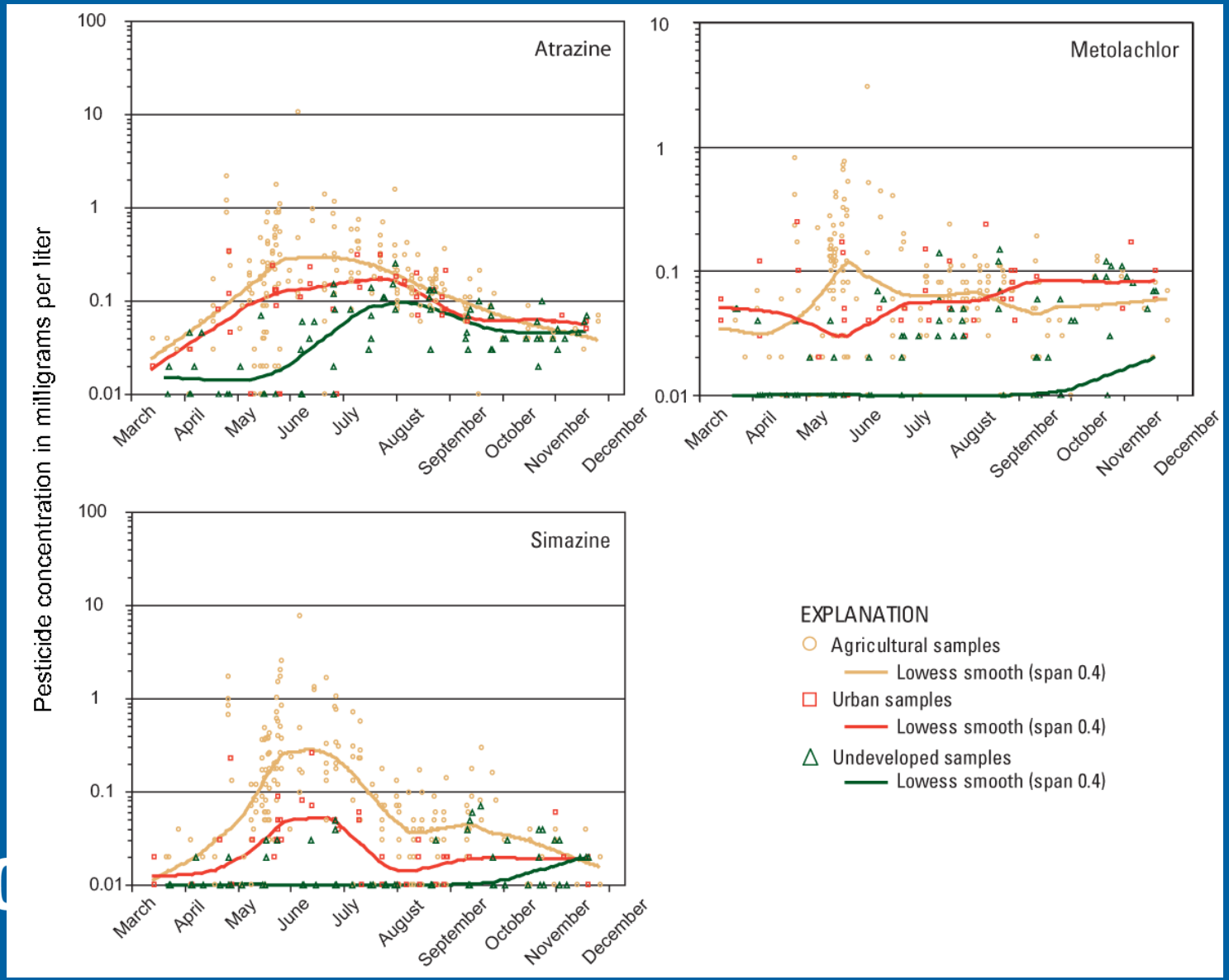


- **MDEQ WCMP**
  - **13 sites**
  - **Sampled 12 times April-November**
- **Focused Study**
  - **11 Sites**
  - **Sampled about twice a month April-September**
  - **Daily sampling after herbicide application (May/June)**

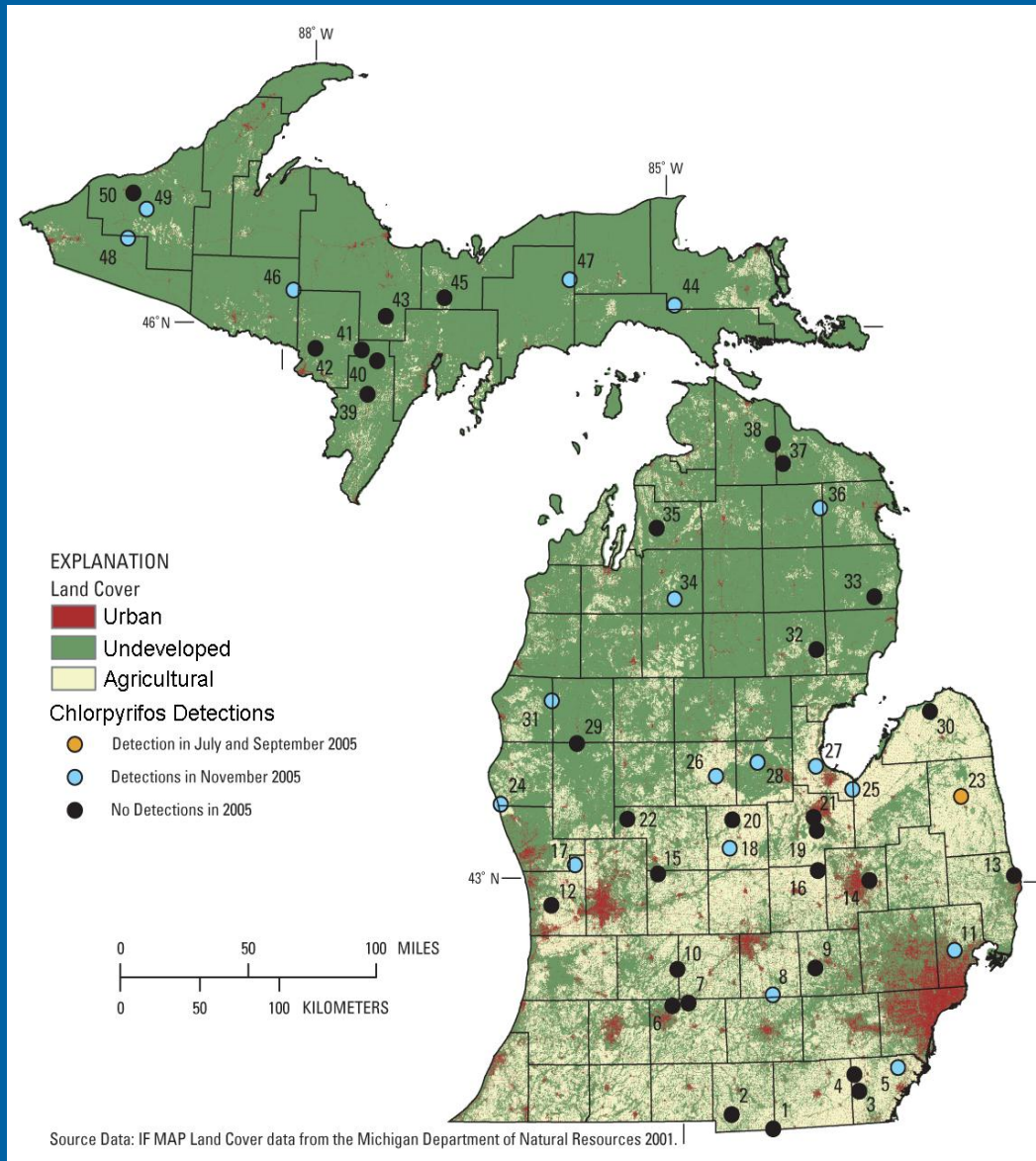


Seasonal Patterns in Herbicide Concentrations

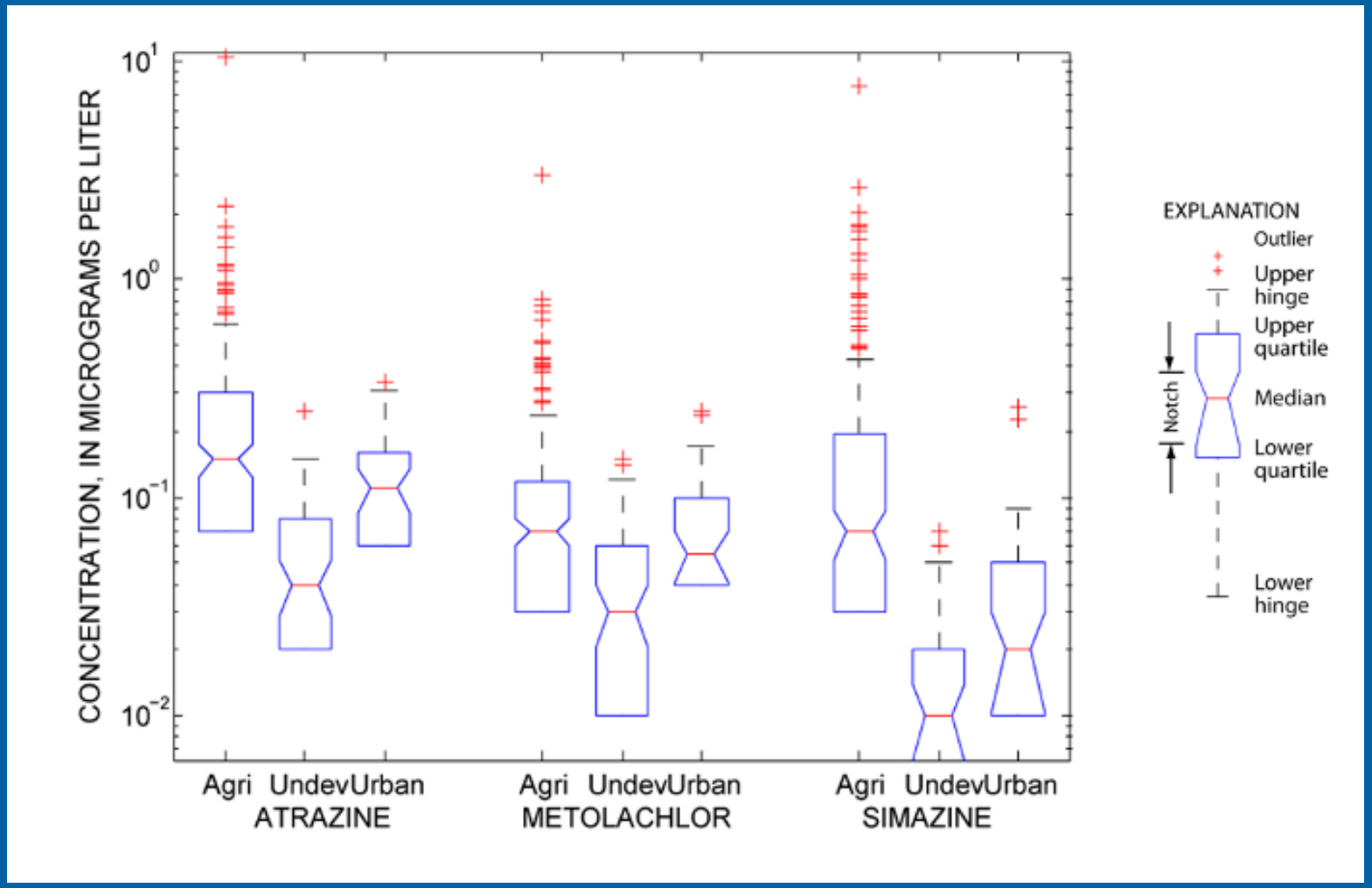


Seasonal Patterns in Insecticide Concentrations

- Diazinon was not detected in any samples
- Chlorpyrifos was not detected in samples from watershed monitoring study
- Chlorpyrifos was detected in MDEQ statewide assessment in 18 out of 50 sites in Nov. and 1 site in July and Sept., 2005



Influence of Land-Use



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Where does the Grand River fit?

[USGS, U.S. Geological Survey; MDL, method detection limit; µg/L, micrograms per liter]

USGS station number	Stream name (location)	Total number samples	Number detections above the MDL	Detected concentration (µg/L)		
				Maximum	Mean	Median
04102080	St. Joseph River	12	9	0.90	0.21	0.15
04108660	Kalamazoo River	12	9	.16	.09	.09
04111500	Deer Creek	14	10	.48	.16	.08
04113000	Grand River (Lansing)	14	14	.88	.26	.17
04114498	Looking Glass River	14	11	.30	.12	.11
04116000	Grand River (Ionia)	14	13	1.41	.24	.14
04119400	Grand River (Eastmanville)	12	7	.86	.17	.09
04122030	Muskegon River	12	6	.25	.06	.05
04122500	Pere Marquette River	12	3	.10	.04	.04
04132052	Cheboygan River	12	6	.12	.05	.05
04135020	Thunder Bay River	12	4	.15	.06	.05
04137500	Au Sable River	12	5	.14	.05	.04
04144500	Shiawassee River (Owosso)	14	12	.40	.15	.12
04145000	Shiawassee River (Fergus)	26	20	.97	.20	.13
04157065	Saginaw River	12	10	.71	.28	.27
04159492	Black River	16	15	10.55	1.04	.31
04159900	Mill Creek	15	12	.90	.25	.14
04160398	Pine River	16	14	1.75	.61	.45
04160625	Belle River	17	16	1.18	.36	.32
04161820	Clinton River (Sterling Heights)	19	14	.24	.09	.08
04165553	Clinton River (Mt. Clemens)	11	9	.34	.16	.15
04168550	River Rouge	11	9	.23	.11	.11
040590345	Escanaba River	11	6	.15	.06	.06

USGS

Conclusions

- Immunoassay are an inexpensive method to screen a large number of samples for select pesticides
- Monitoring studies in Michigan have shown:
  1. Atrazine, metolachlor, and simazine are usually only detected in low concentrations in stream water.
  2. Highest concentrations typically occur in late Spring
  3. Highest pesticide concentrations occurred in agricultural areas; however, there was little statistical difference in the overall concentrations between urban and agriculture land-use samples
  4. Areas with little development in MI, had very few pesticide detections

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GLRI Tributary Monitoring

- **Nutrients**, sediment, major ions, and continuous water quality
  - Temp, pH, Specific Conductance, DO, Turbidity
- Isco auto-sampler, automated virus sampler, flow integrated samples, & passive sampler
- Pathogens, fDOM, **emerging chemicals**
  - Goal: Develop relations with co-occurring contaminants and surrogates
  - Ongoing since 2010
  - Currently developing surrogate relations

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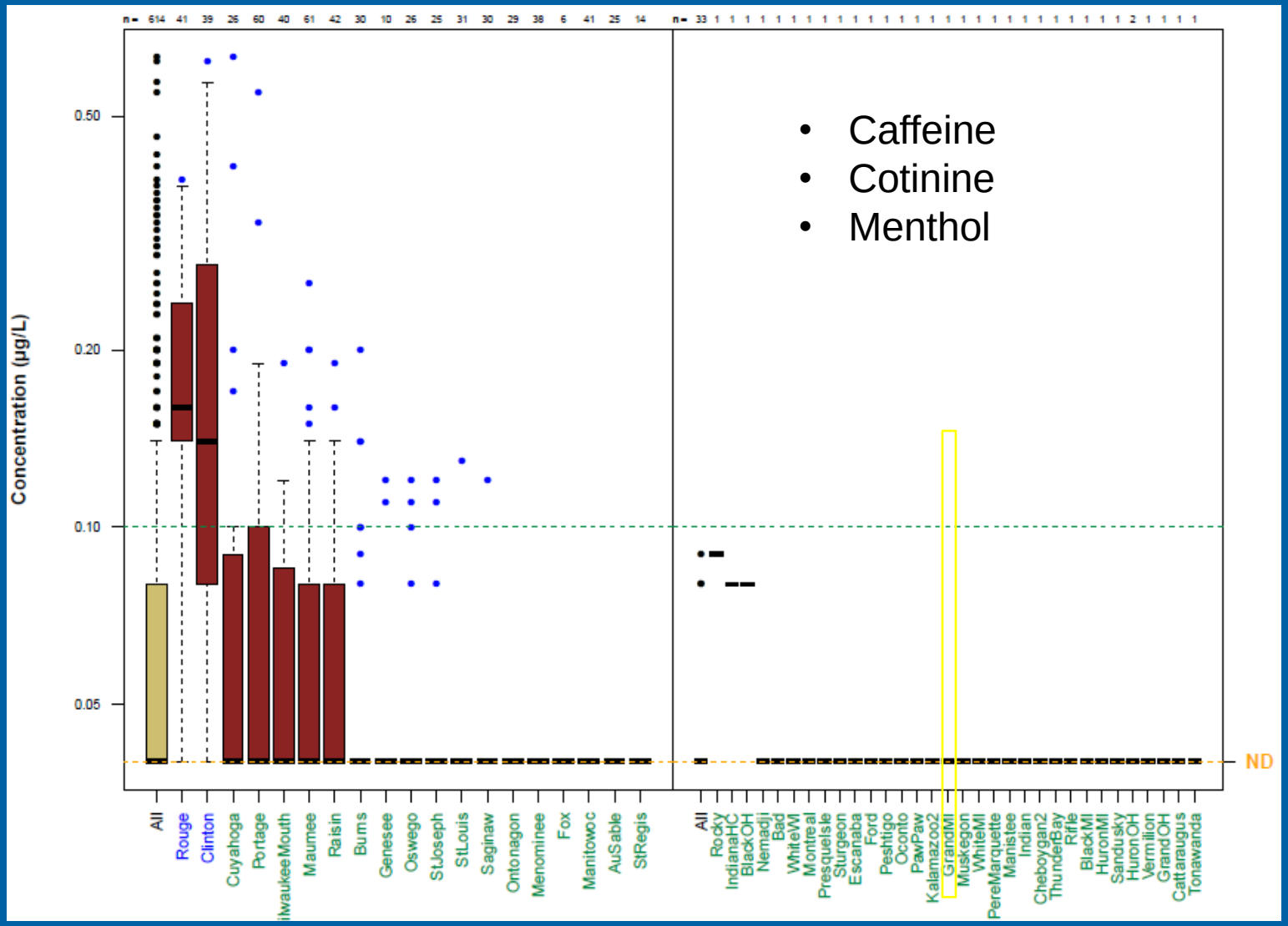
Example of Wastewater analysis



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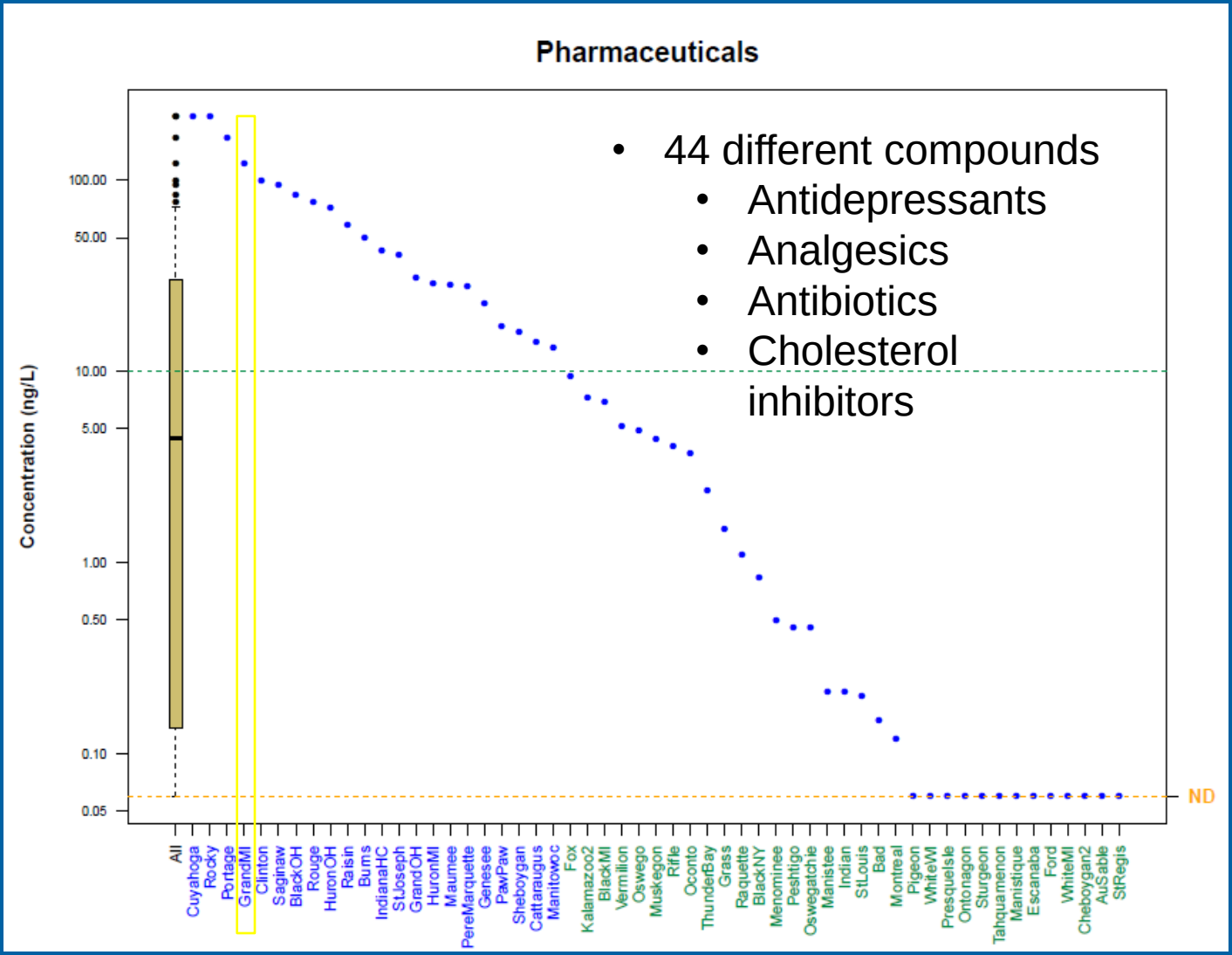
How does the Grand compare to other sites?



- 44 different compounds
  - Antidepressants
  - Analgesics
  - Antibiotics
  - Cholesterol inhibitors

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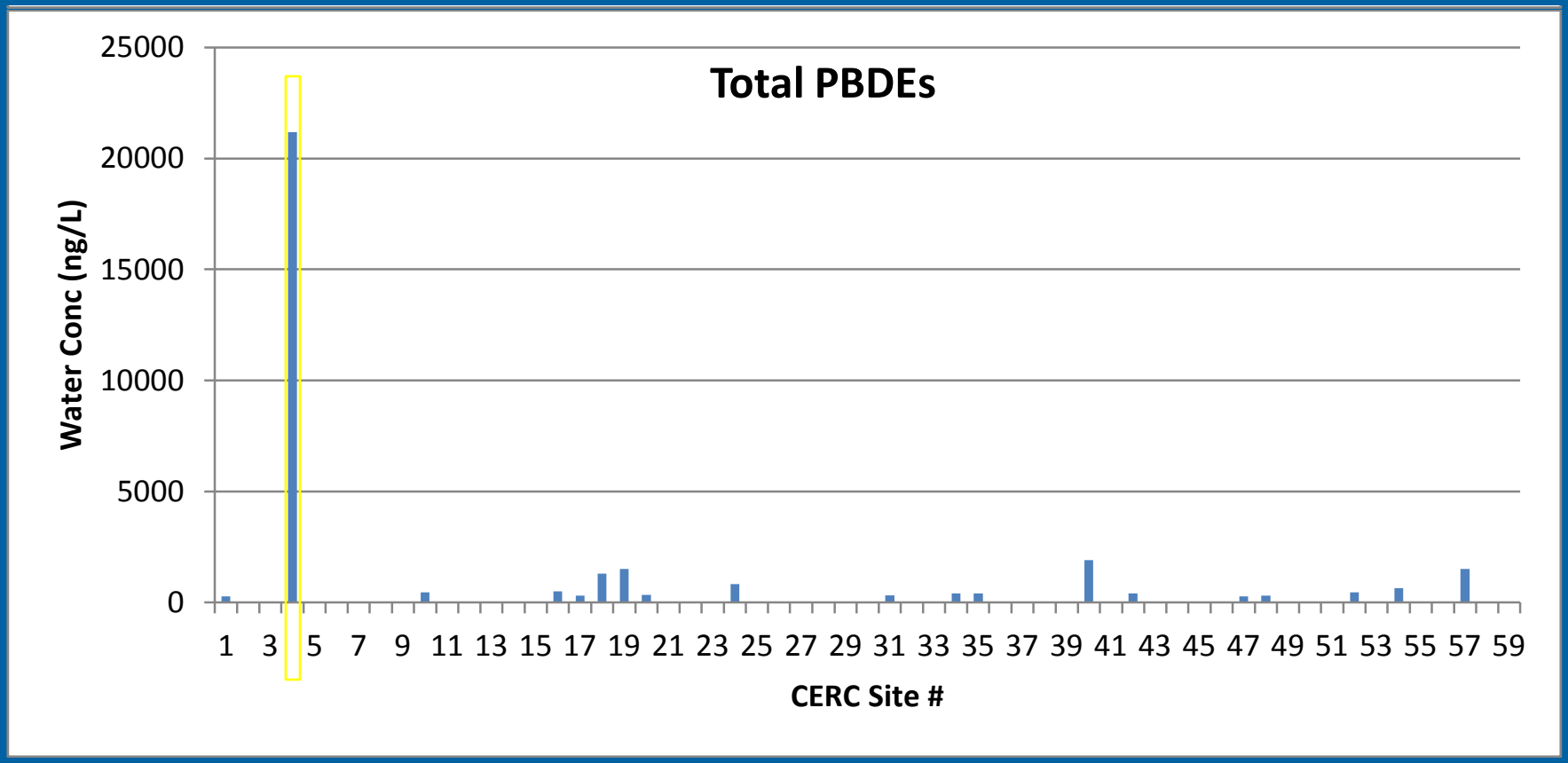
Elevated Total PBDEs (flame retardants)



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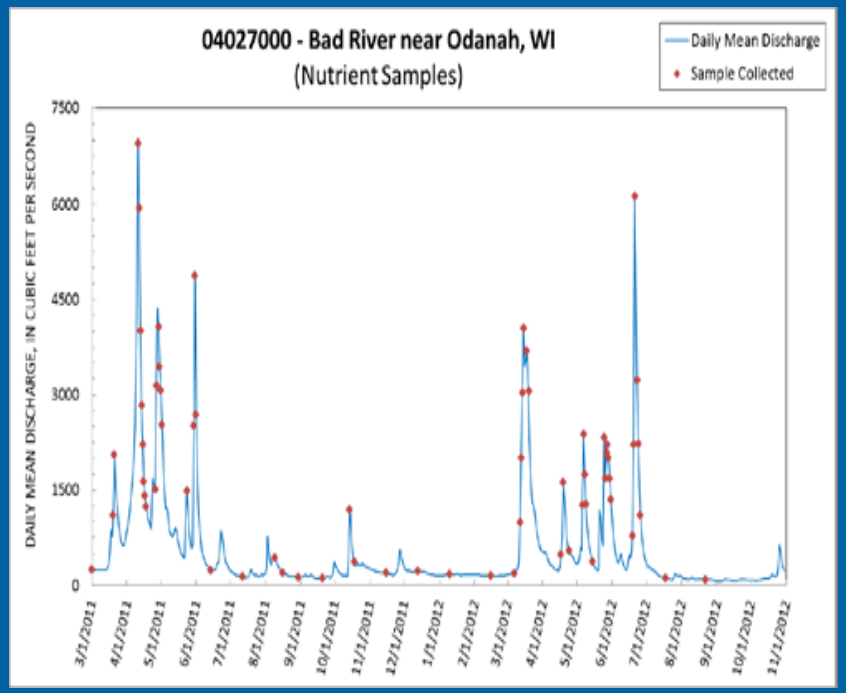
Original Tributary Monitoring Design

- 30 sites on tributaries to the Great Lakes
  - Automated samplers
  - Water-quality multi-sensor probes
- Monthly fixed-interval samples
- Plus up to 6 storm events per year, with up to 6 samples collected over the hydrograph during each event
- Most samples collected with ISCO samplers.



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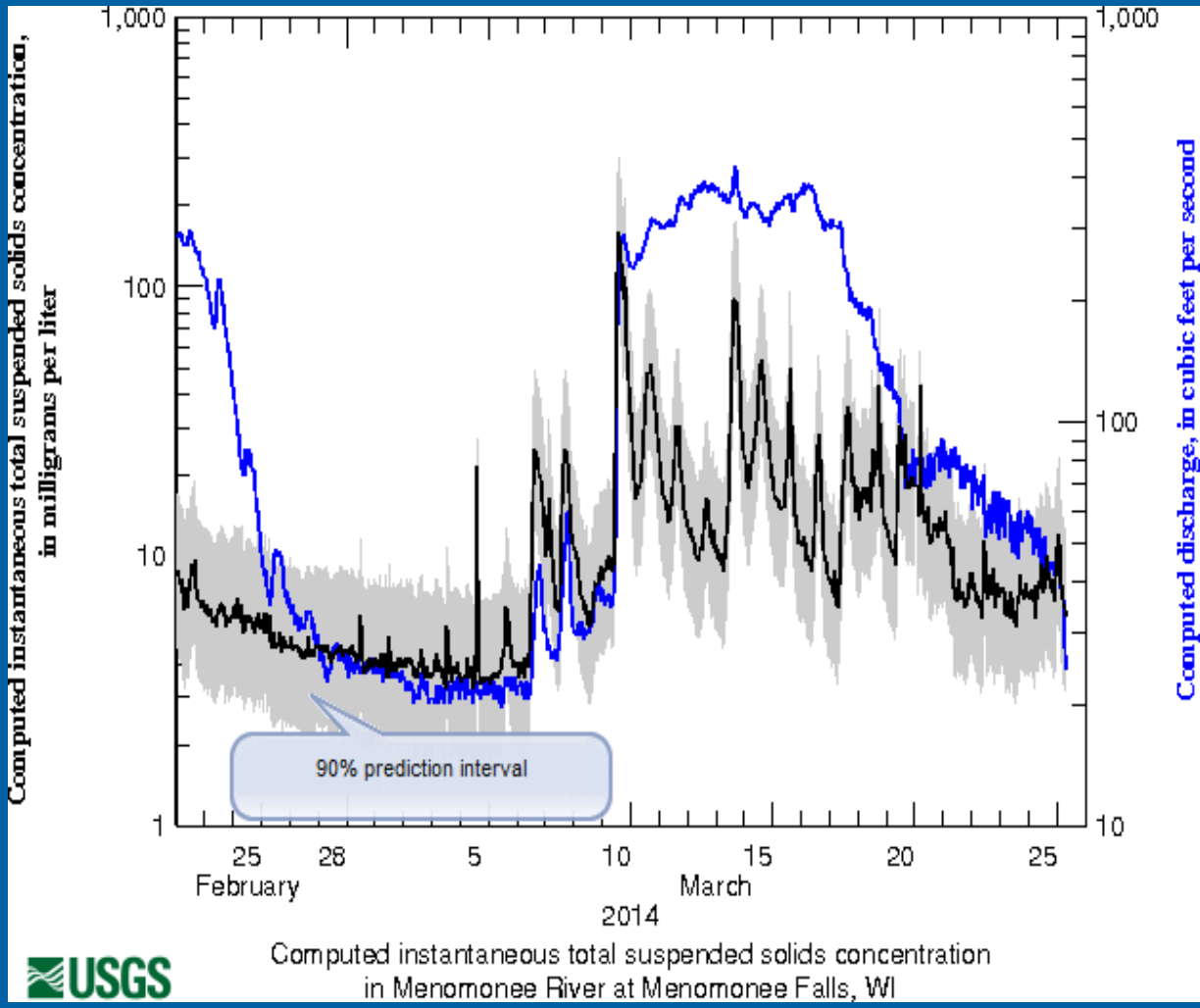
Planned Output for Each Tributary –

based on regressions with real-time surrogates

- TSS example
- Loads and Concentrations



USGS

Preliminary Load estimates for GRAND RIVER NEAR EASTMANVILLE, MI (USGS station 04119400)

- Loads were computed using streamflow and water quality data from the GLRI stations across the Great Lakes. An average daily load computed using the LOADEST code for statistical program R is presented by water year in the following tables. These load estimates are provisional and should not be considered approved.

USGS

Total Nitrogen Load
Grand River near Eastmanville, MI

Table of Nitrogen, mixed forms (NH3), (NH4), organic, (NO2) and (NO3) average daily load in kg/d.

Period	No. of Days	Load	Std. Error	Std. Error of Prediction	L95 CI	U95 CI
WY 2011	314					
WY 2012	366	29377	861	912	27630	31205
WY 2013	365	36389	978	1095	34289	38581
WY 2014	92					

USGS

Total Suspended Sediment Load Grand River near Eastmanville, MI

Table of Suspended sediment concentration (SSC) average daily load in kg/d.

Period	No. of Days	Load	Std. Error	Std. Error of Prediction	L95 CI	U95 CI
WY 2011	314					
WY 2012	366	152139	18445	19282	117850	193300
WY 2013	365	598311	132892	143655	365793	925290
WY 2014	92					

USGS

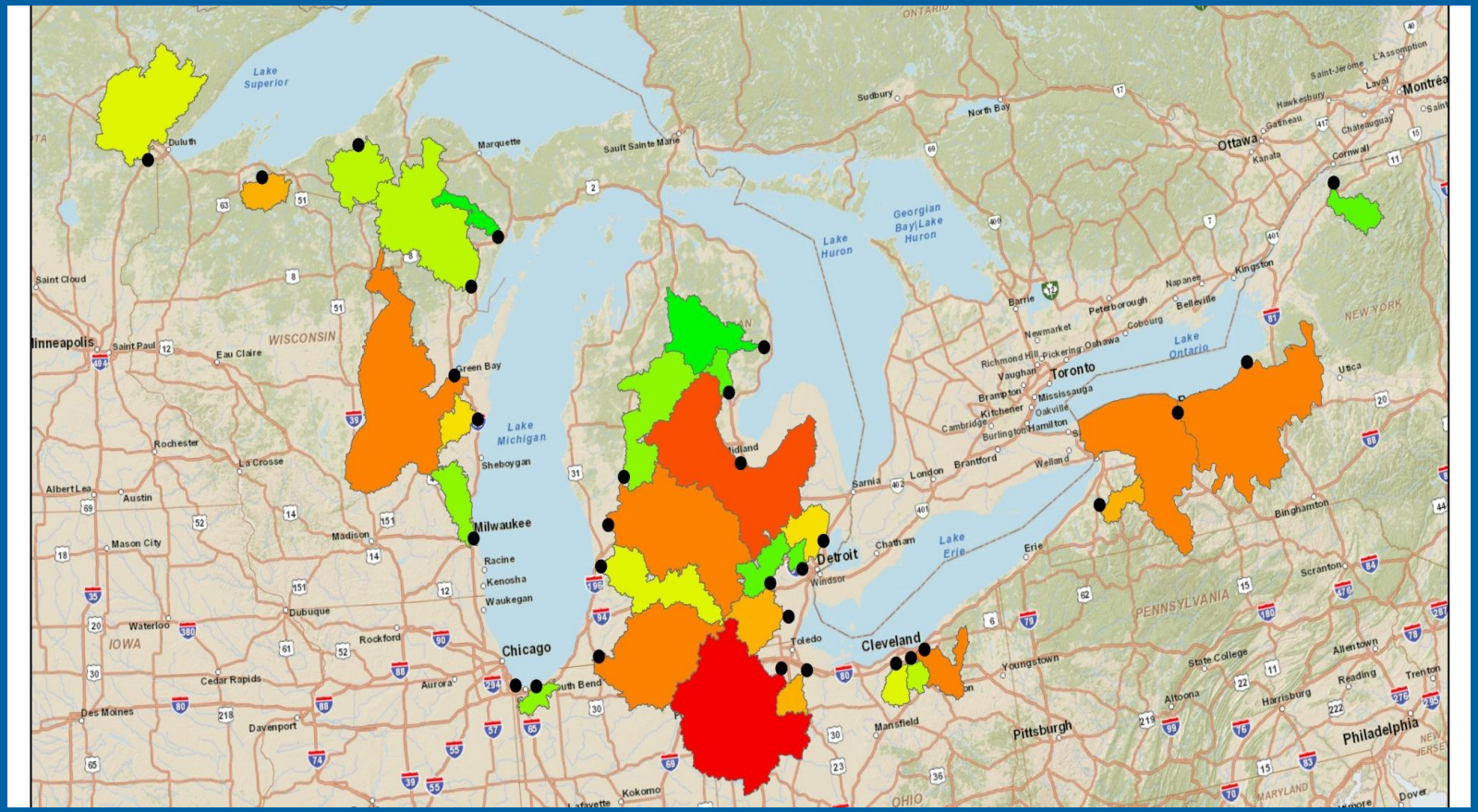
Total Phosphorus Load
Grand River near Eastmanville, MI

Table of Phosphorus average daily load in kg/d.

Period	No. of Days	Load	Std. Error	Std. Error of Prediction	L95 CI	U95 CI
WY 2011	314					
WY 2012	366	870	44	46	783	963
WY 2013	365	1640	129	136	1390	1922
WY 2014	92					

USGS

Relative Load of Orthophosphate



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"Preliminary Information—Subject to Revision. Not for Citation or Distribution"

Future Directions

- Grand River at Eastmanville, MI site is included in current plans for continued GLRI monitoring
  - GLRI Tributary monitoring
    - Nutrients, sediment, chloride, continuous sondes
  - GLRI toxic substances monitoring
    - Routine wastewater/chemical of emerging concern monitoring
    - Passive sampling to integrate over time
    - Focus contaminants by year
      - PCBs, Flame retardants, pharmaceuticals/antibiotics, etc.

USGS

Questions?

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