Understanding patterns in pesticide detection across a non-irrigated agricultural landscape

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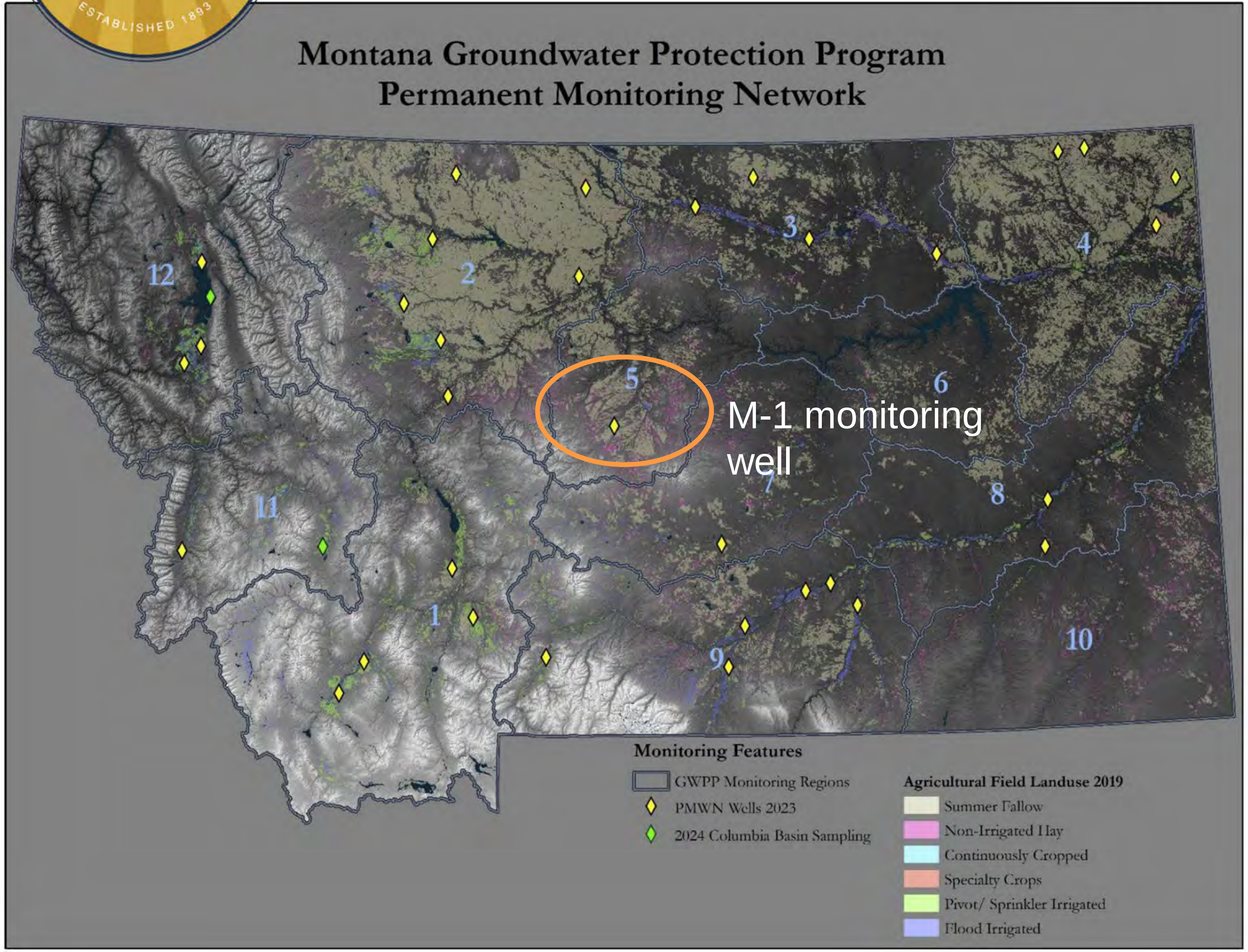


Increased fertilizer and pesticide usage over the decades

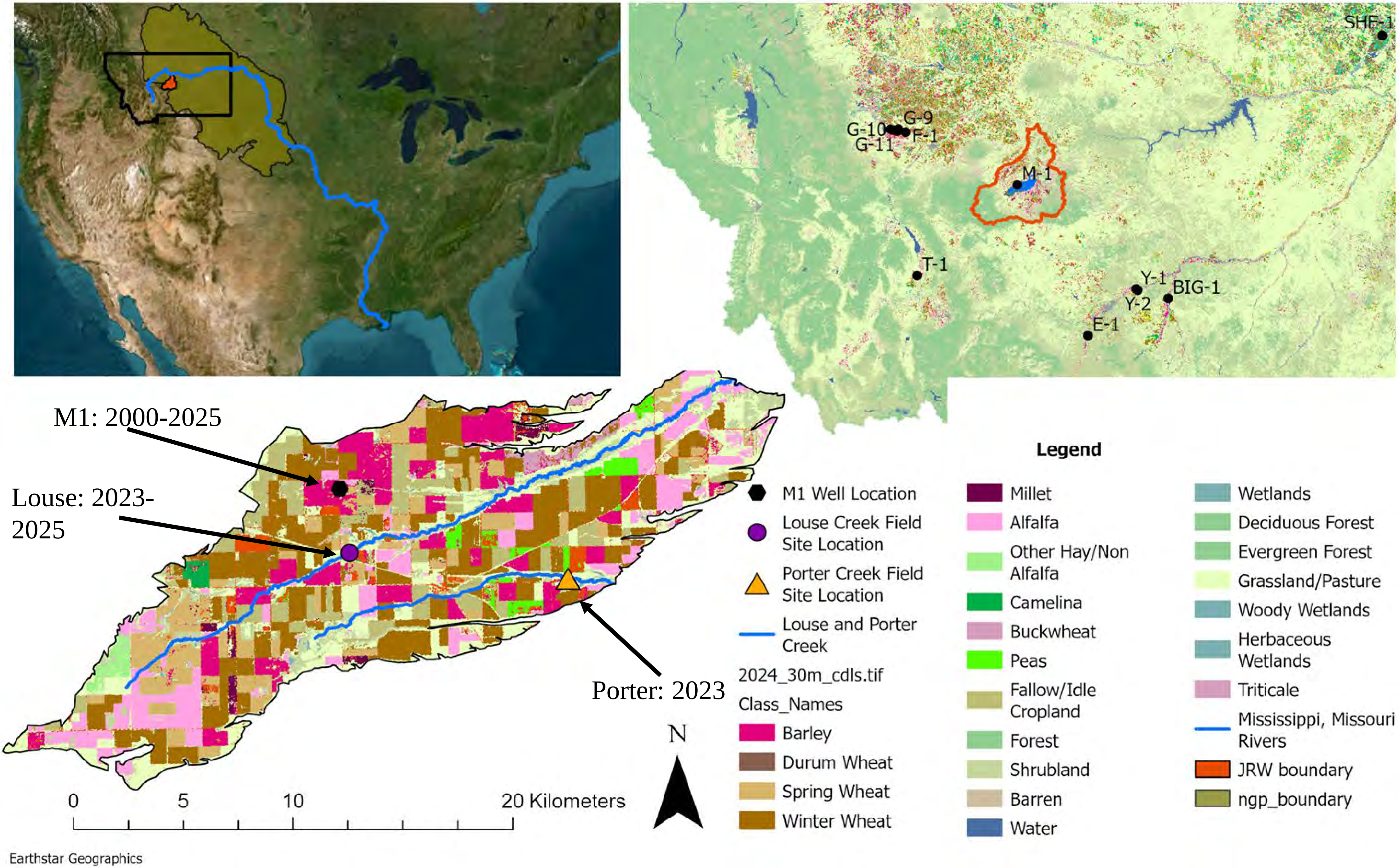
Importance of pesticides

- No-till systems
- Maintain crop yields quality
- Sustain growing global population

- 1989 Montana Agricultural Chemical Groundwater Protection Act

- MDA GWPP tasked with monitoring groundwater for pesticides and fertilizers

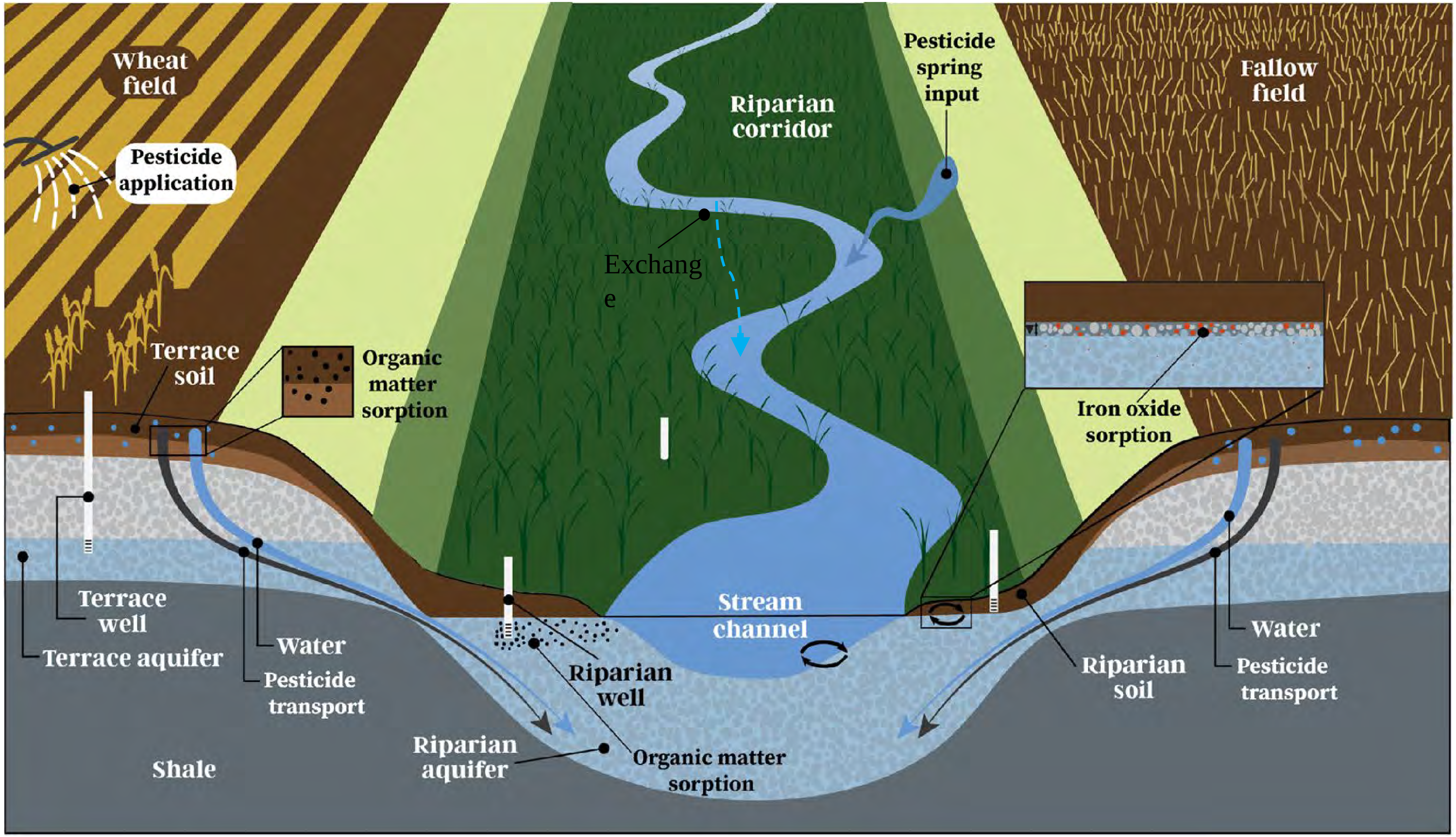
- Network of monitoring wells installed across Montana


SHE-1
G-9
G-10
F-1
G-11
M-1
T-1
Y-1
BIG-1
Y-2
E-1
M1: 2000-2025
Louse: 2023-2025
Porter: 2023
0 5 10 20 Kilometers
N
Earthstar Geographics
Legend
M1 Well Location
Louse Creek Field Site Location
Porter Creek Field Site Location
Louse and Porter Creek
2024_30m_cdls.tif
Class_Names
Barley
Durum Wheat
Spring Wheat
Winter Wheat
Millet
Alfalfa
Other Hay/Non Alfalfa
Camelina
Buckwheat
Peas
Fallow/Idle Cropland
Forest
Shrubland
Barren
Water
Wetlands
Deciduous Forest
Evergreen Forest
Grassland/Pasture
Woody Wetlands
Herbaceous Wetlands
Triticale
Mississippi, Missouri Rivers
JRW boundary
ngp_boundary

Questions:

- How are pesticides transported and transformed along flow paths from terrace soil application to riparian corridors?
- How might application history and usage influence detections?

Conceptual flow path: sorption to soil organic matter, iron oxides and degradation



Methods

Questions:

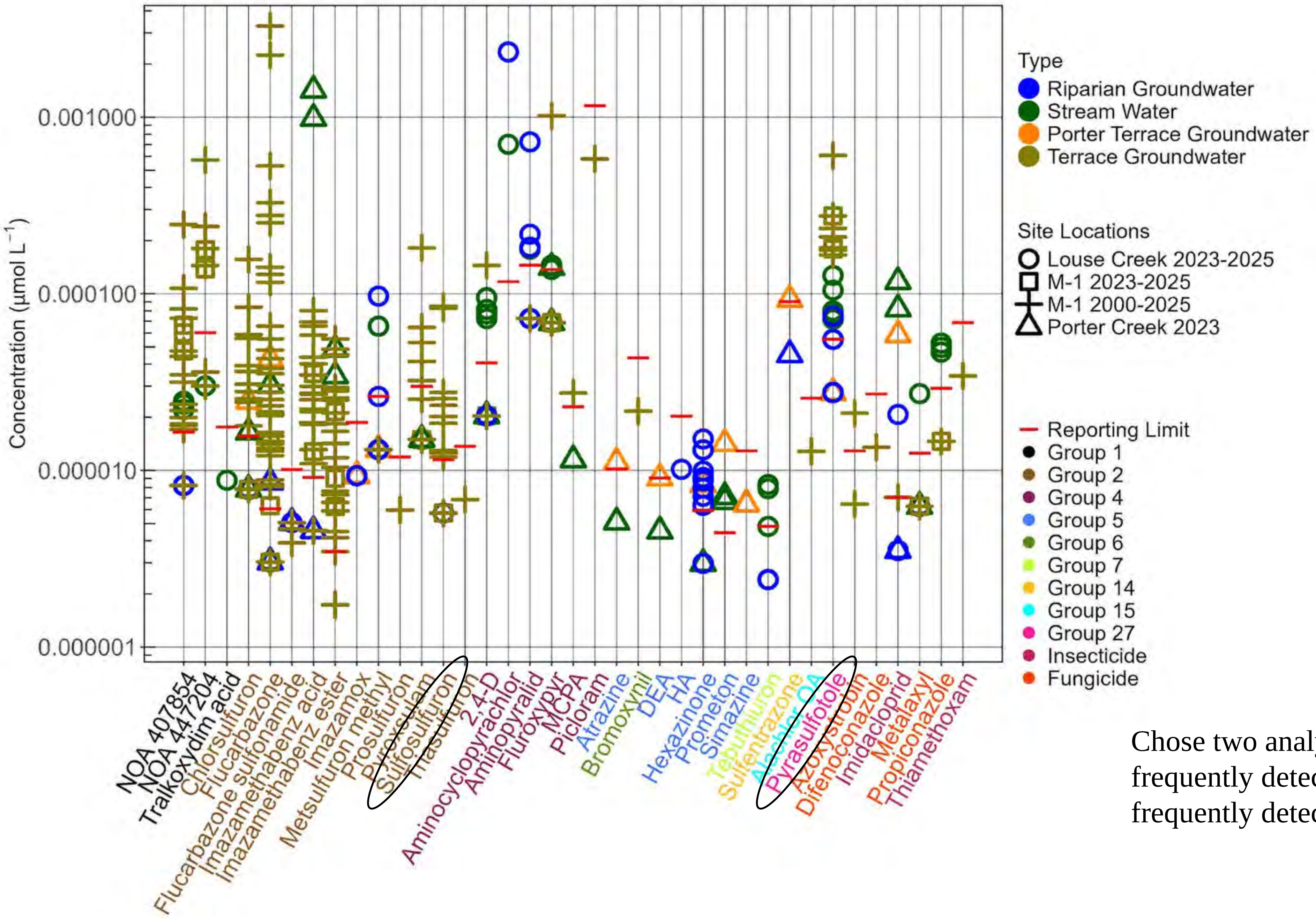
- How are pesticides transported and transformed along flow paths from terrace soil application to riparian corridors?
- How might application history and usage influence detections?

- Sampling Louse, Porter Creek
  M-1 2000-2025
  Louse Creek 2023-2025
  Porter Creek 2023
  (what are detection patterns? What does this say about transport and transformation?)

- M-1 data comparison to other monitoring wells (how long after usage until detections?)

- Batch equilibrium experiments that study sorption (how much is transport delayed?)

All M1, Louse, Porter detections

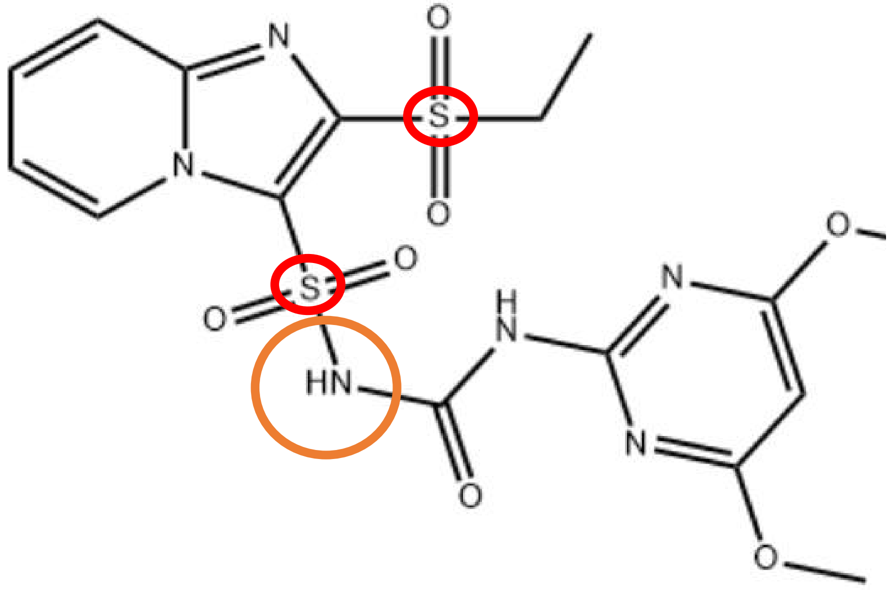


Many weak acid compounds detected
Concentrations generally well below DEQ drinking water human health standards

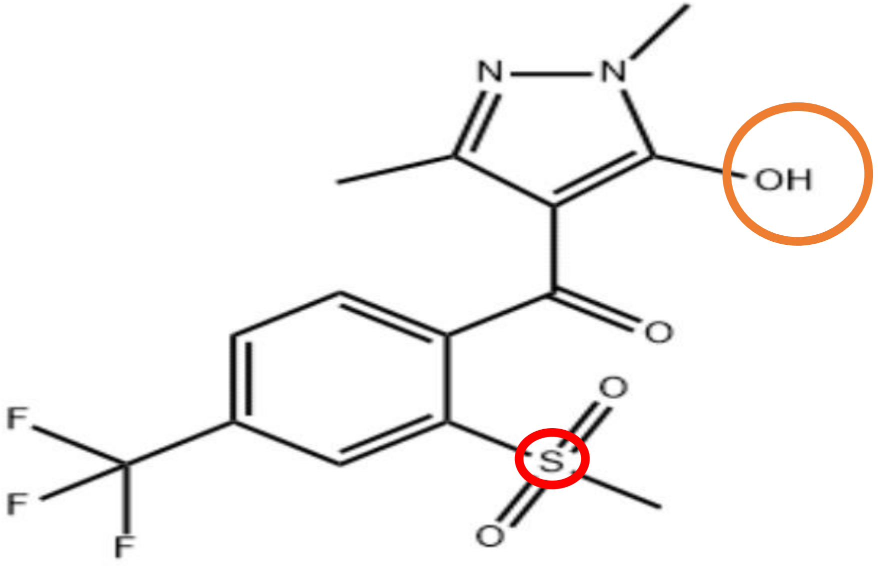
Chose two analytes: one older compound more frequently detected and one newer compound less frequently detected

Molecular characteristics of sulfosulfuron and pyrasulfotole

Sulfosulfuron



Pyrasulfotole

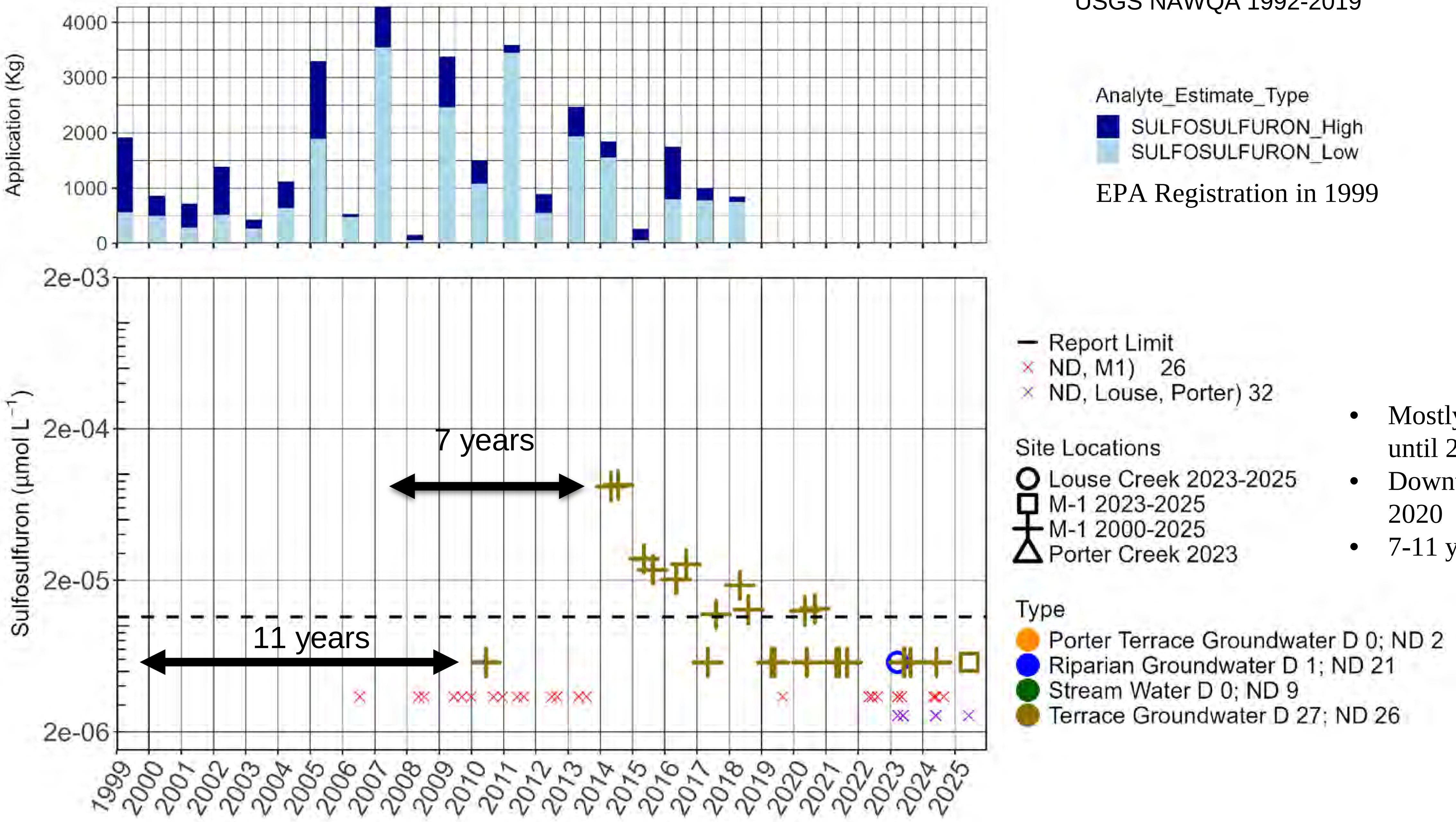


- Good record of non detects and detects for both analytes
- Some differences in molecular properties

Analyte	Molecular weight g mol^{-1}	Solubility mg L^{-1} (pH 7)	pKa	K_{oc} ml g^{-1}	DT_{50} day (aerobic)	DT_{50} day (water-sediment)	DT_{50} day (water phase)
Sulfosulfuron	470.48	1627	3.51	5.3-89	63.8	26.8	17.8
Pyrasulfotole	362.32	69100	4.2	21.6-715	55.5	365	140

Sulfosulfuron applications in Montana and detections in the JRW

USGS NAWQA 1992-2019

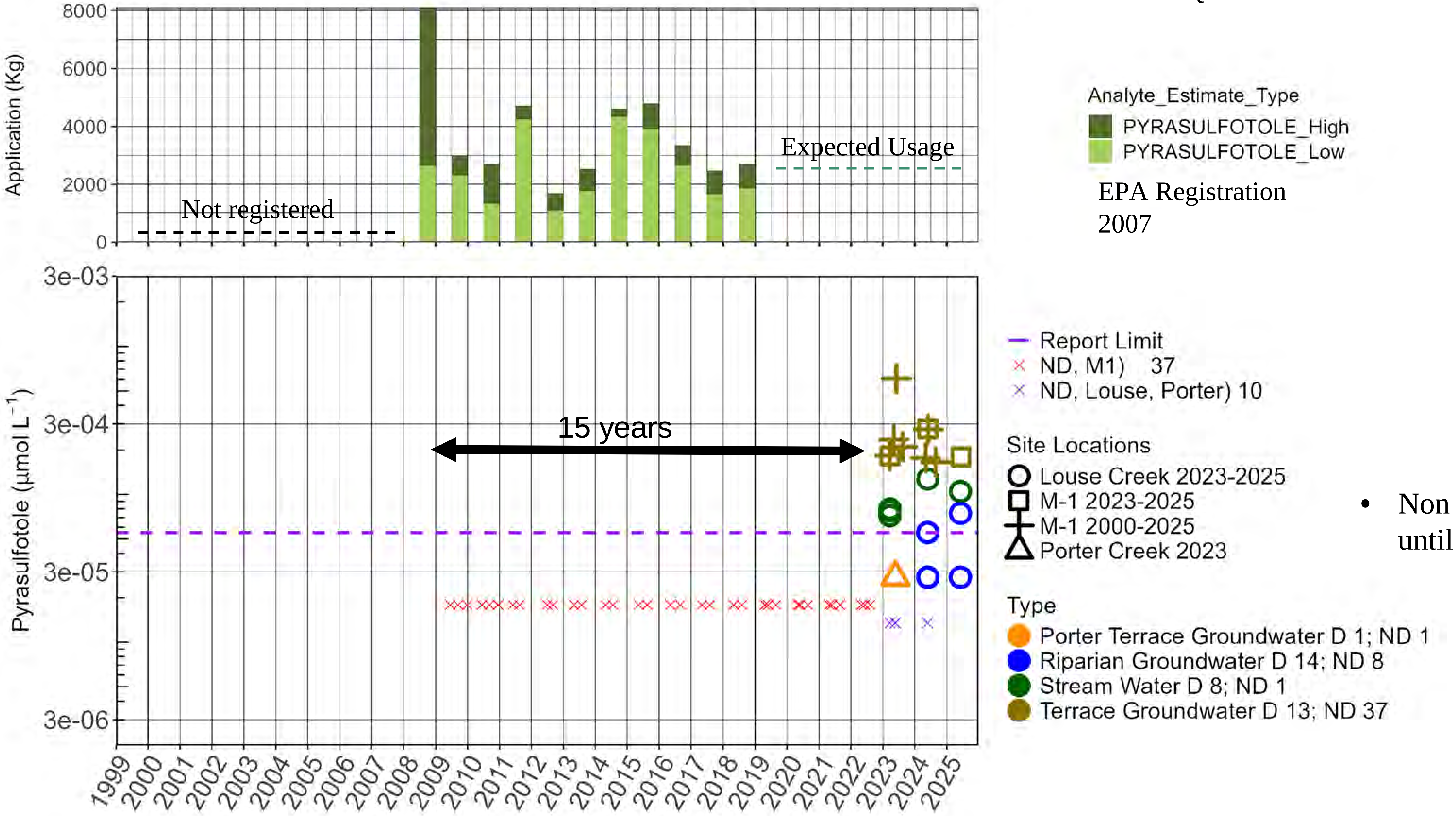


EPA Registration in 1999

- Mostly non detects until 2014
- Downtrend through 2020
- 7-11 year lag?

Pyrasulfotole applications in Montana and detections in the JRW

USGS NAWQA 1992-2019



EPA Registration
2007

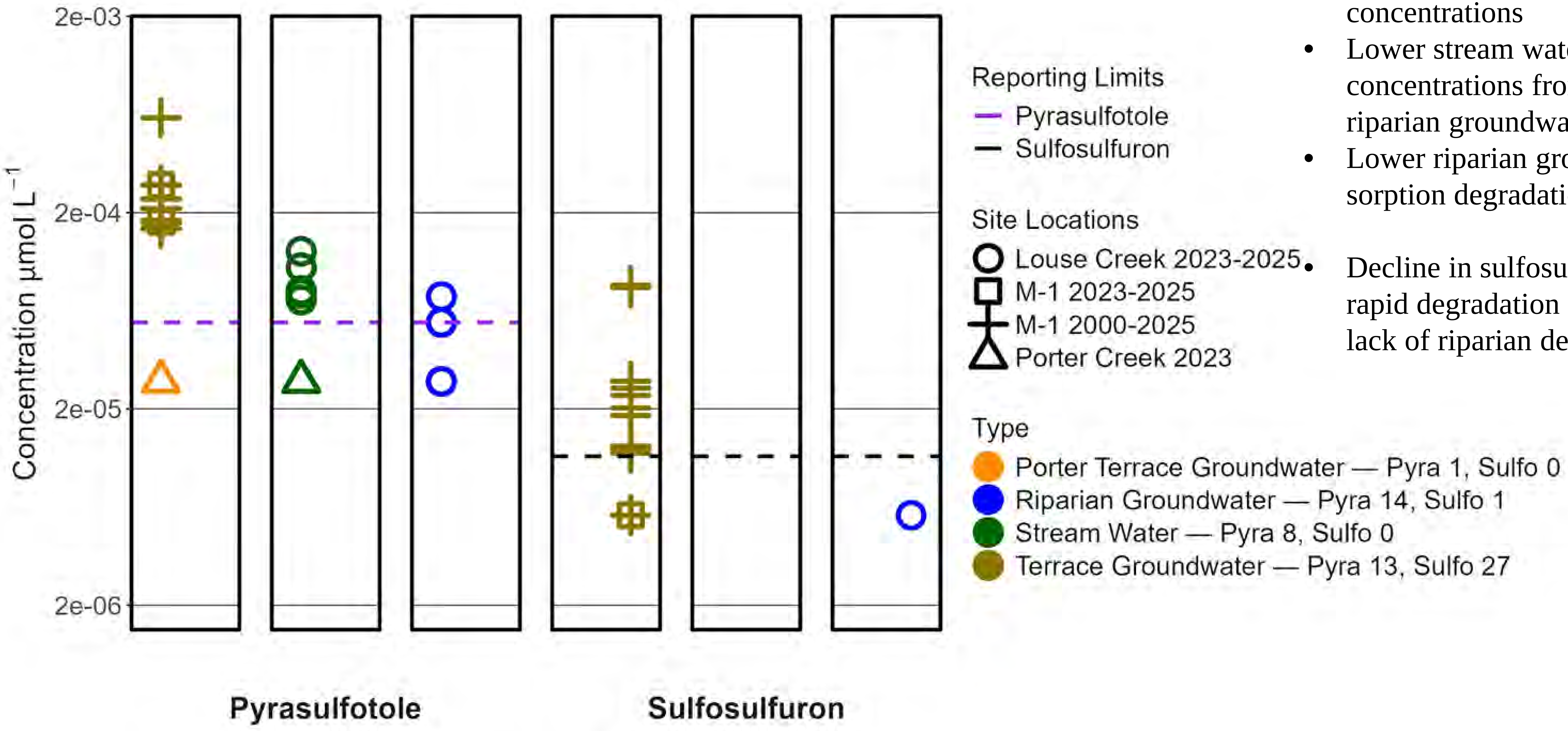
- Non detects until 2023

Detections at other monitoring wells compared to M1

Site	MBMG #	Install Yr	Analyte	Apparent Lag (Yr)	Irrigation	Aquifer Type
BIG-1	236086	2007	NOA 407854	3	Irrigated	Unconfined
BIG-1	236086	2007	**Pyrasulfotole**	**4**	Irrigated	Unconfined
E-1	122340	1991	NOA 407854	3	Irrigated	Unconfined
F-1	122338	1990	Clopyralid	9	Irrigated	Unconfined
F-1	122338	1990	Pyroxsulam	4	Irrigated	Unconfined
G-10	76565	1949	Tralkoxydim	4	Irrigated	Unconfined
G-10	76565	1949	Tralkoxydim Acid	4	Irrigated	Unconfined
G-11	149990	1995	**Pyrasulfotole**	**4**	Irrigated	Confined?
G-11	149990	1995	Tralkoxydim Acid	5	Irrigated	Confined?
G-15	166838	1981	NOA 407854	2	Irrigated	Unconfined
G-9	76555	1975	Aminopyralid	7	Irrigated	Unconfined
G-9	76555	1975	Tralkoxydim Acid	6	Irrigated	Unconfined
M-1	133047	1993	Imazamethabenz acid	18	Nonirrigated	Unconfined
M-1	133047	1993	Imazamethabenz ester	18	Nonirrigated	Unconfined
M-1	133047	1993	NOA 407854	6	Nonirrigated	Unconfined
M-1	133047	1993	**Pyrasulfotole**	**16**	Nonirrigated	Unconfined
M-1	133047	1993	Pyroxsulam	3	Nonirrigated	Unconfined
M-1	133047	1993	**Sulfosulfuron**	**11**	Nonirrigated	Unconfined
SHE-1	235955	2007	Aminopyralid	9	Nonirrigated	Confined?
T-1	130432	1992	Imazamethabenz acid	10	Irrigated	Unconfined
T-1	130432	1992	Imazamethabenz ester	19	Irrigated	Unconfined
T-1	130432	1992	NOA 407854	6	Irrigated	Unconfined
Y-1	166069	1997	NOA 407854	5	Irrigated	Unconfined
Y-2	166070	1997	NOA 407854	3	Irrigated	Unconfined

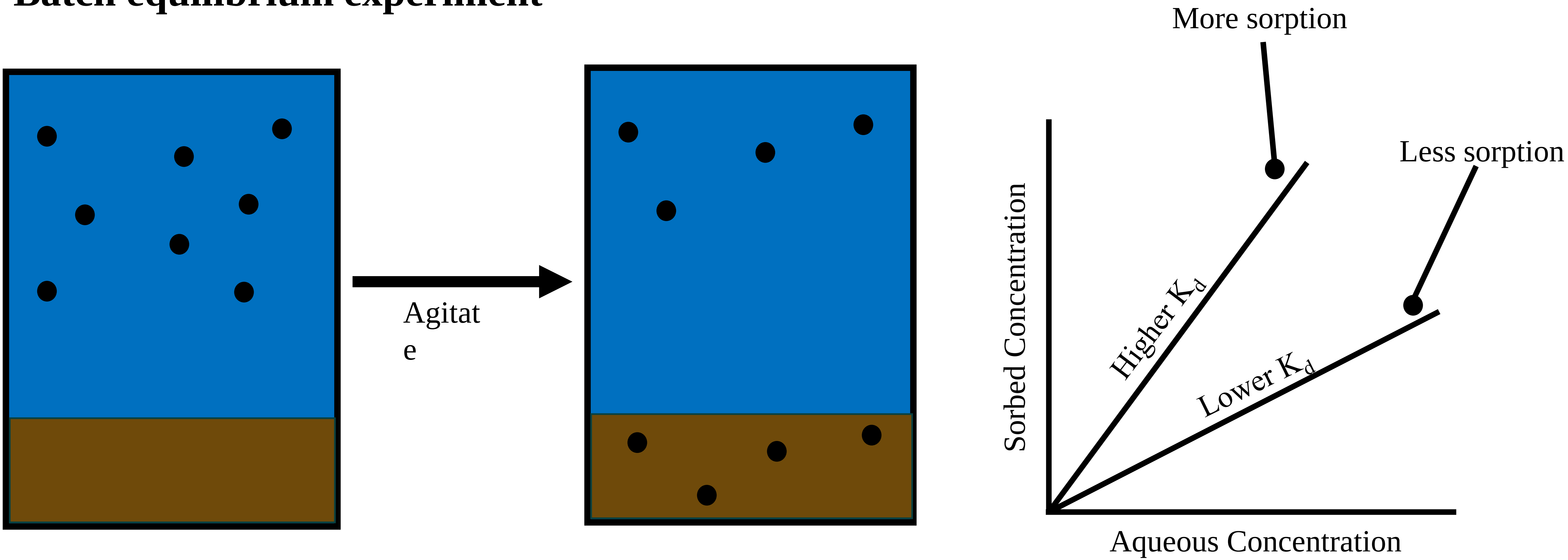
Pyrasulfotole
apparent lag times lower
under irrigated
conditions

Patterns in detections between M1 terrace groundwater, riparian stream water, and riparian groundwater

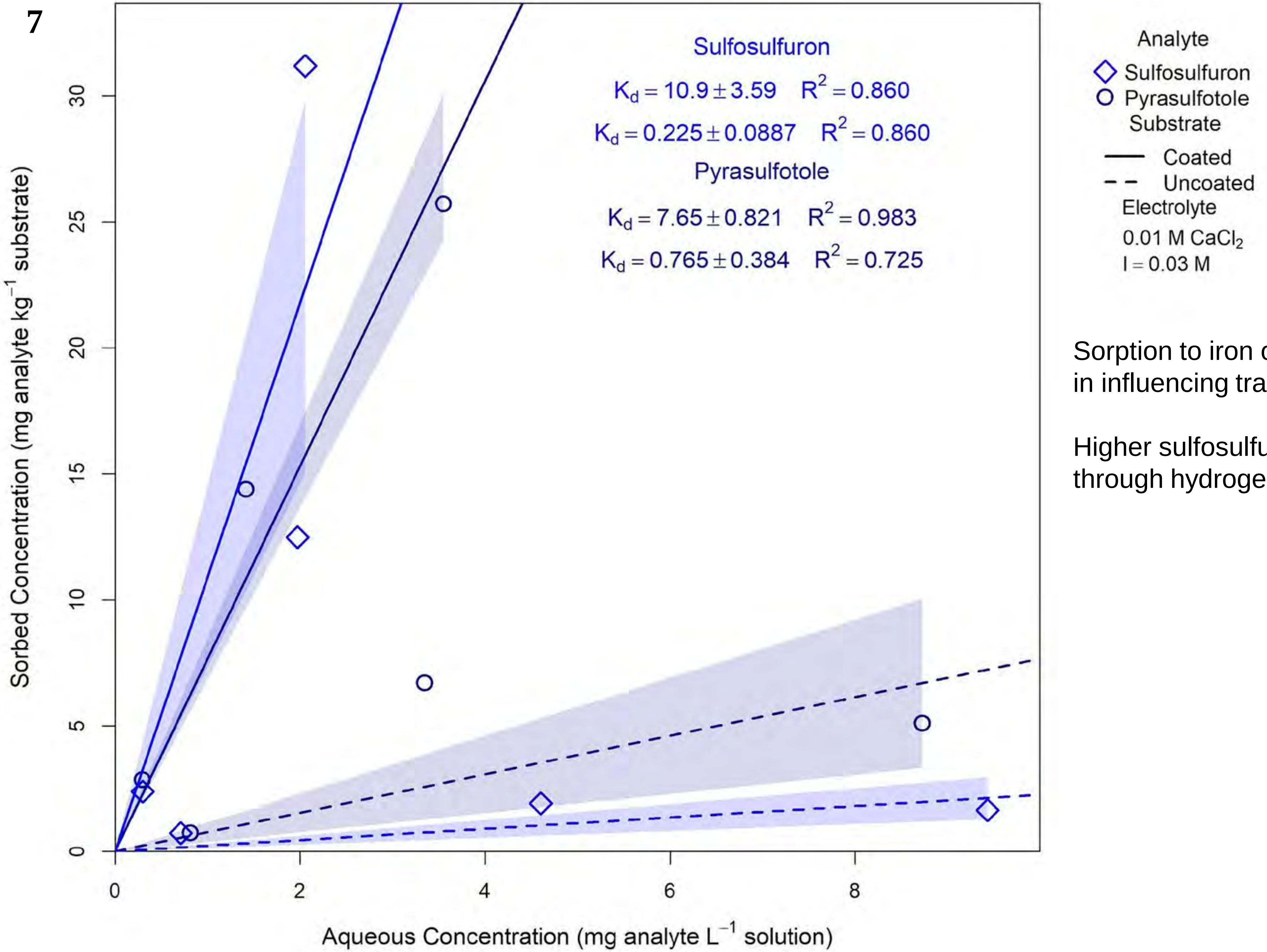


- Higher pyrasulfotole concentrations
- Lower stream water concentrations from mixing with riparian groundwater
- Lower riparian groundwater from sorption degradation
- Decline in sulfosulfuron and more rapid degradation could explain lack of riparian detections

Batch equilibrium experiment



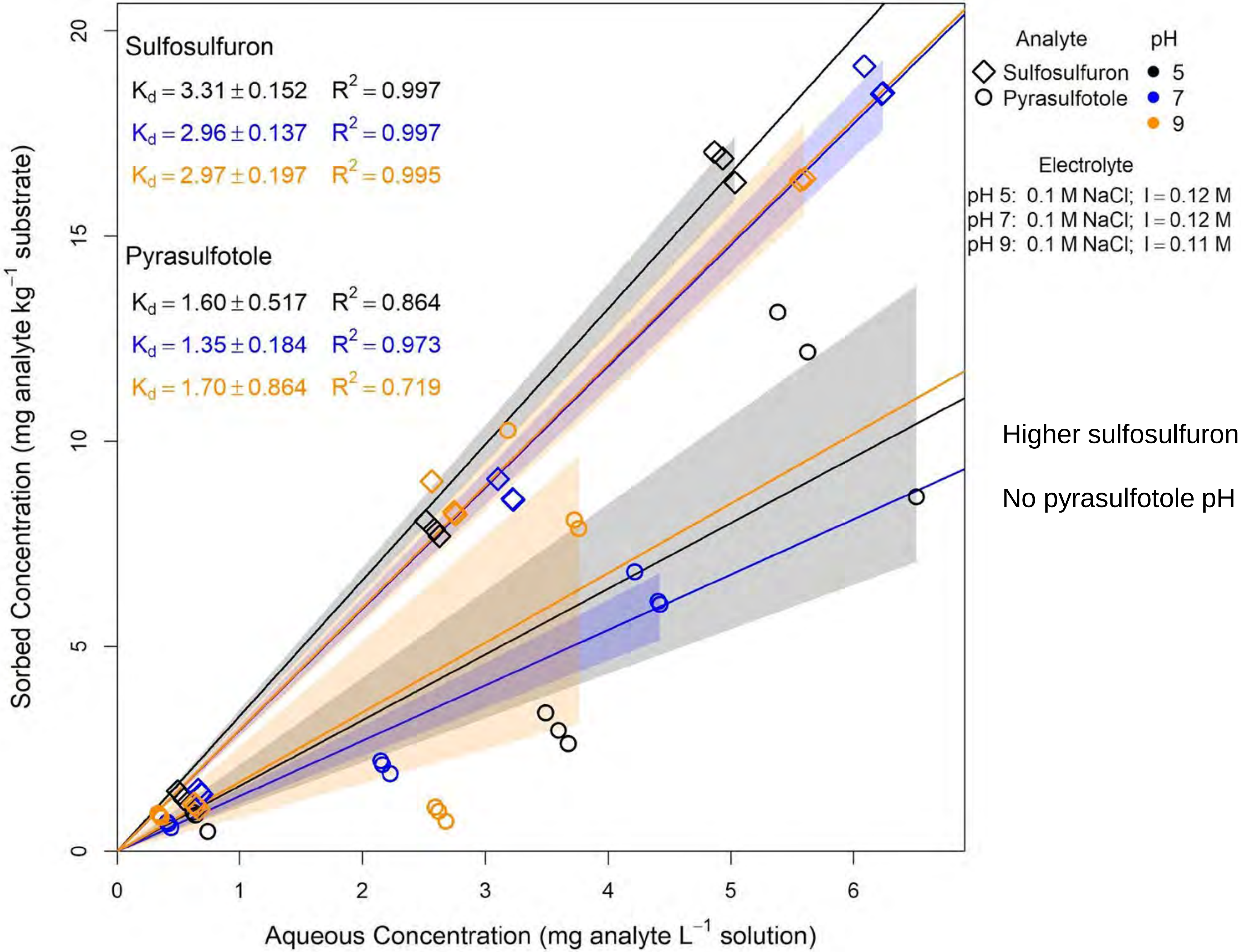
Sorption to iron oxides at pH 7



Sorption to iron oxides indicates importance of iron oxides in influencing transport

Higher sulfosulfuron sorption on iron oxide coated sand through hydrogen bonding

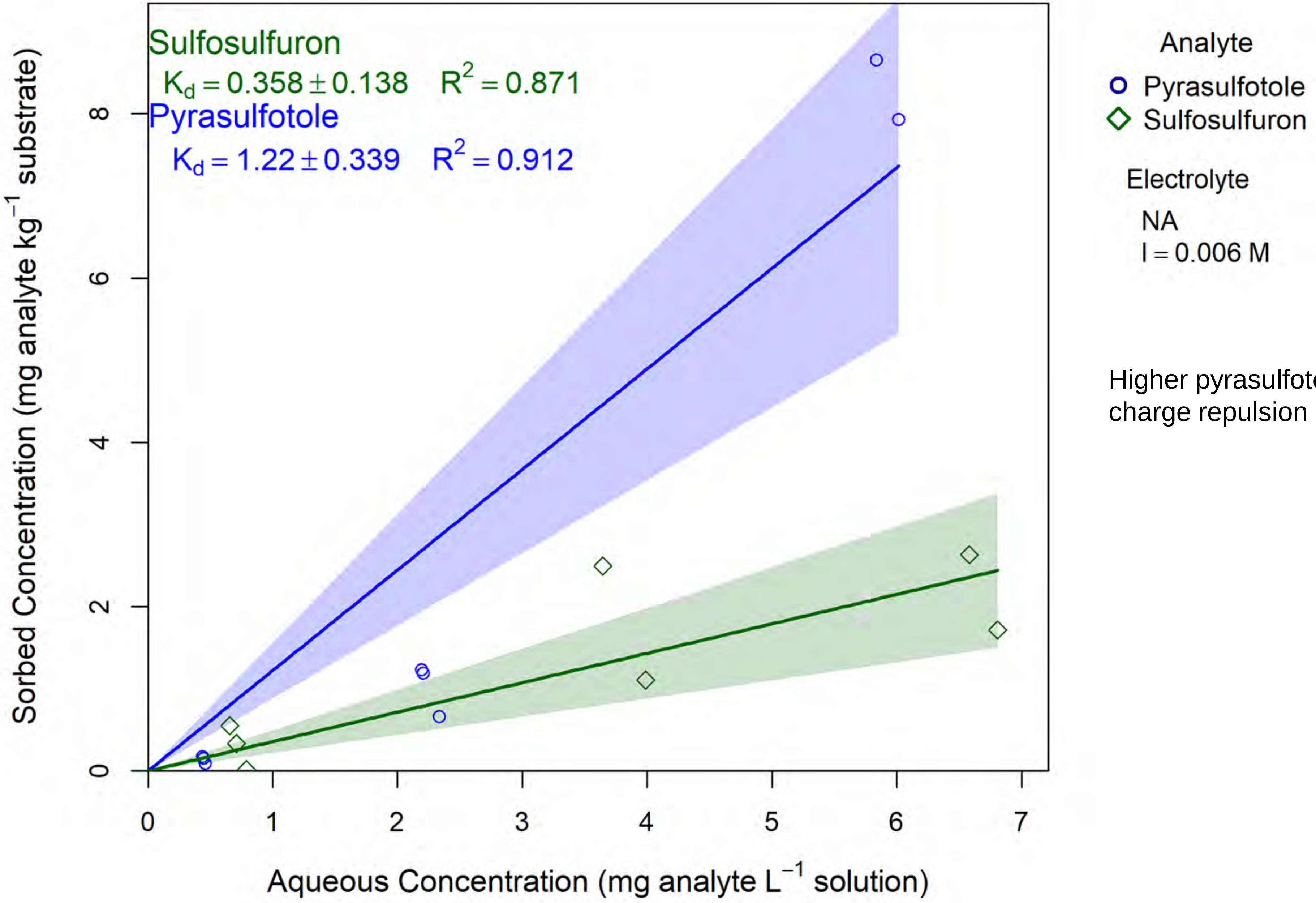
Sorption to iron oxides under pH influence



Higher sulfosulfuron sorption, influence of pH

No pyrasulfotole pH influence, uncertainty, pKa, site competition

Agricultural soil pH ~ 8 : inferred soil organic matter sorption



Beaverton (loam) batch equilibrium results, end over end shaking

Higher pyrasulfotole sorption, pKa, negative charge repulsion

Conclusions

- Overall, batch equilibrium studies demonstrate low sorption potential of sulfosulfuron and pyrasulfotole for iron oxides and soil organic matter
- Lag times of 5-15 years likely influenced by sorption, application proximity and patterns
- Soil transport is important: Preliminary HYDRUS 1D modeling of transport in thin soils (< 50cm) suggests transit times to shallow aquifers of ~1-3 years

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Questions?