Salt Fate and Transport on the Root River:
Investigating the potential sources and pathways of chloride to surface waters

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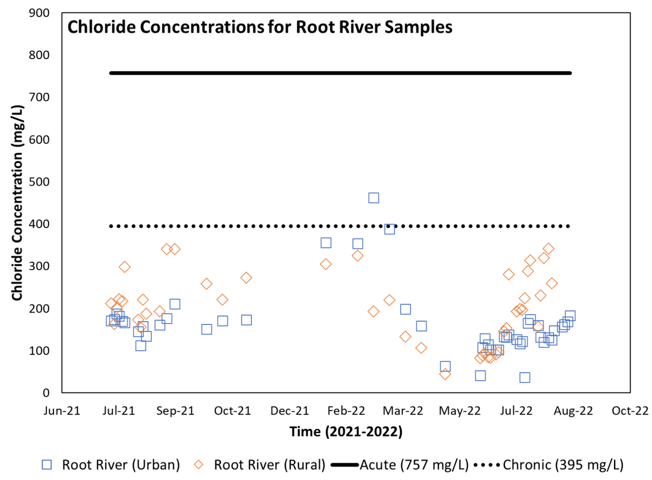


FIG 1

Displays discrete chloride concentrations (mg/L) of surface water samples from both study sites (urban and rural) on the Root River compared to the Wisconsin Department of Natural Resources (WiDNR) acute (757 mg/L) and chronic (395 mg/L) levels for chloride, based on aquatic life toxicity [1]. **Data shows that chloride levels on the Root River reach and exceed the chronic WiDNR levels for chloride.**

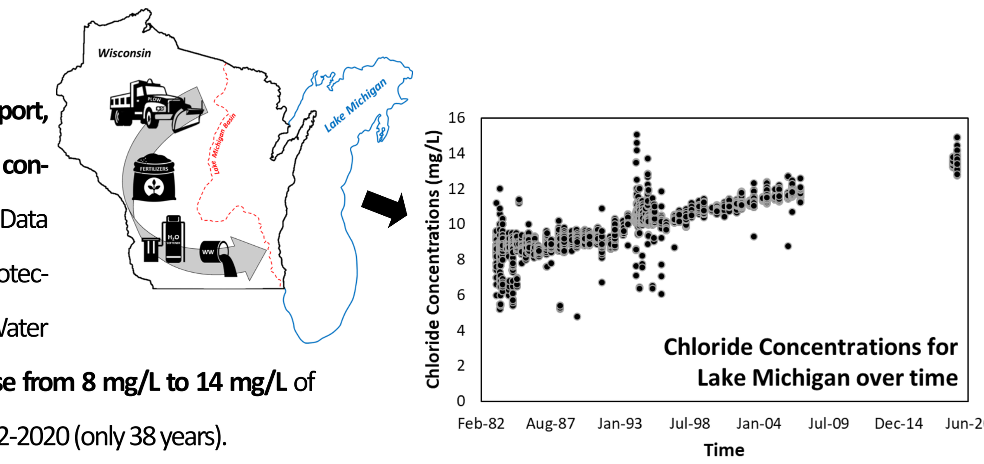
INTRODUCTION

WHAT? The preliminary understanding and observation of **high chloride (Cl^-) levels year-round** on the Root River in Racine County, WI (Fig 1) suggests the **idea that chloride persists in one or more hydrologic compartments** and is **subsequently transported to the surface water.** Additionally, chloride is present in numerous anthropogenic products (i.e., road salt ,NaCl, $CaCl_2$, $MgCl_2$; potash fertilizers, KCl; water softeners, commonly NaCl; and waste water effluent, Cl^-). Generating the questions of where does the chloride come from (source) and what hydrologic compartments transport the chloride to surface waters (pathway)?

WHY? It is hypothesized that these **four main sources of chloride are likely present within the study sites** (urban and rural) in addition to unlikely sources (i.e., precipitation, landfill leachate, basin brines, and sea water) and **account for the high chloride levels (salinization) observed** (Fig 1). Salinization of freshwaters can **redefine the biological and ecological windows within a 'freshwater' system** and has the ability to **affect anthropogenic uses** like **drinking water.** Salinization of the Root River is **occurring** and is **one of many catalysts** in the **salinization of Lake Michigan** due to **tributary loading of chloride** [2] (Fig 2). As over 10 million people are supplied drinking water by Lake Michigan, this research and similar studies are critical to understanding chloride transport.

FIG 2

Visual of the likely **sources, transport,** and **resultant increase in chloride concentrations** within Lake Michigan. Data collected by U.S. Environmental Protection Agency (EPA) from the U.S. Water Quality Portal [3]. Notice the **increase from 8 mg/L to 14 mg/L** of chloride for Lake Michigan from 1982-2020 (only 38 years).



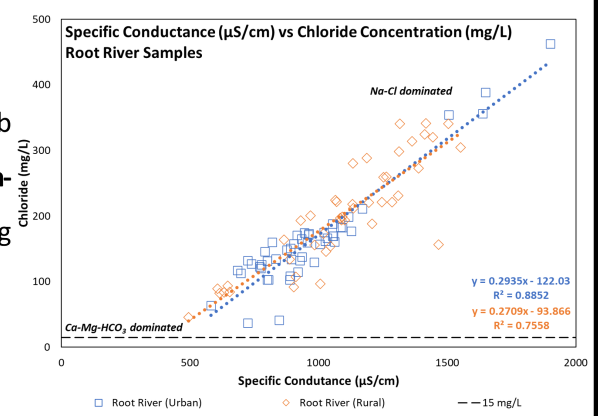
INVESTIGATING ROOT RIVER WATER

FIG 4

Regression for discrete specific conductance (CTD) vs discrete chloride concentration for **52** separate grab samples. This relationship is **essential** to accurately **quantify continuous chloride concentrations** and **continuous mass discharge (Md) of chloride.** Md of chloride is defined as the total mass of a solute (Cl^-) moving through a point at a specific time (Eq 1).

$$Md = C \times Q$$

*Where: **Md** = Mass Discharge (M/T), **C** = Concentration (M/L³), **Q** = Stream Discharge (L³/T)*



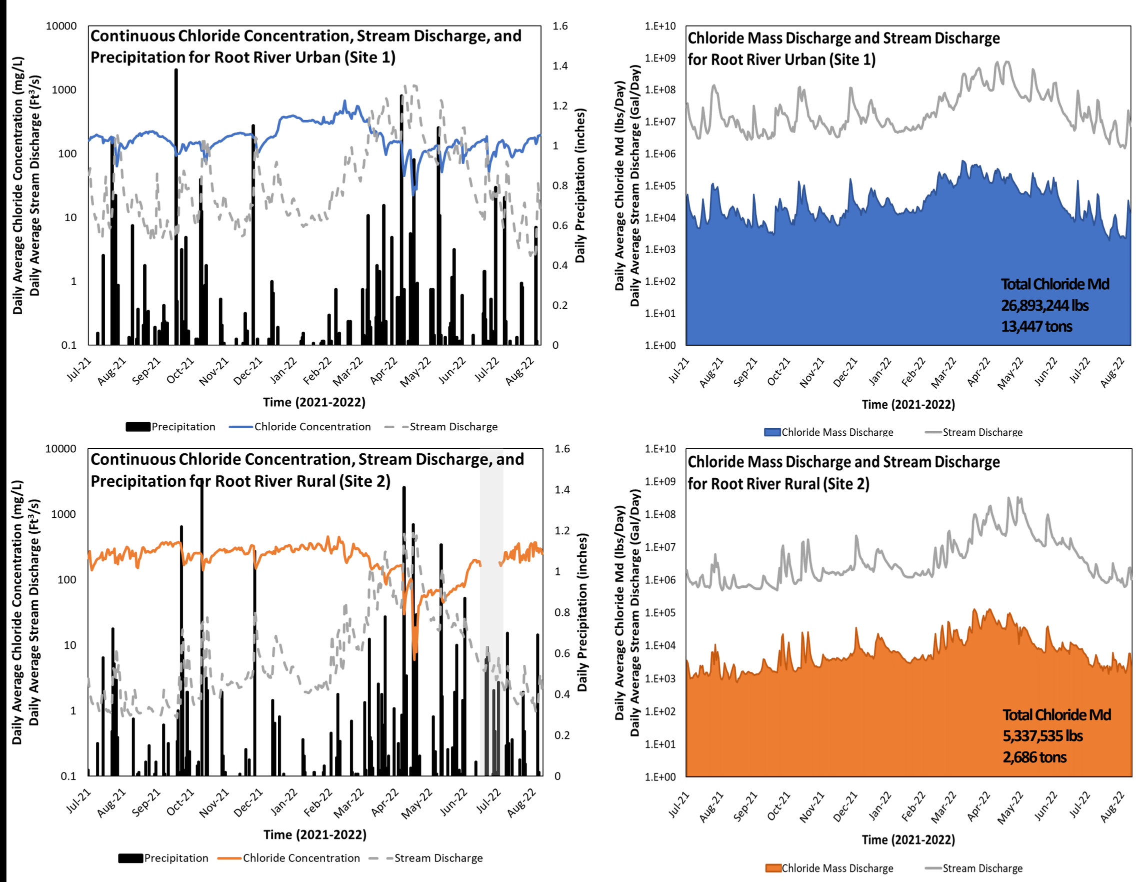
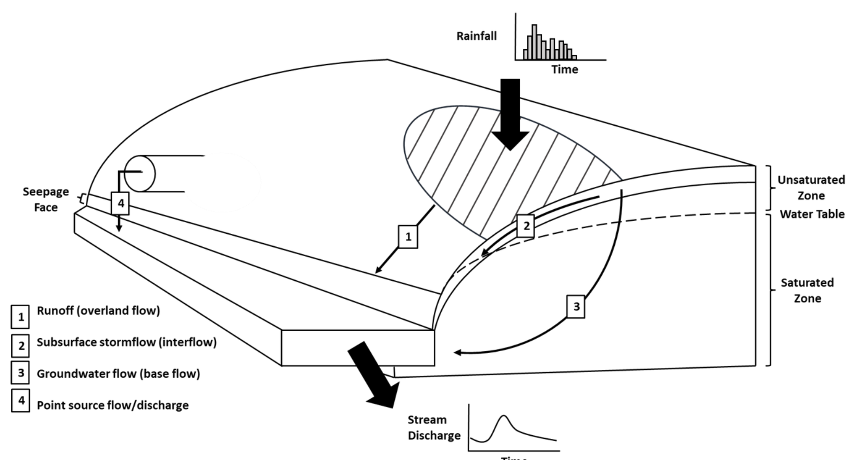


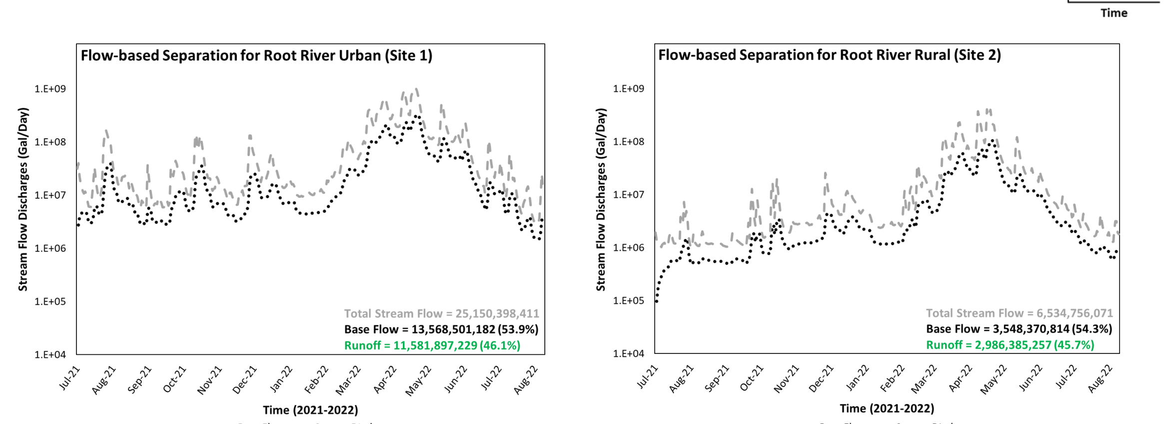
FIG 5

- Continuous precipitation, chloride concentration, and stream discharge for both study sites (left).
- **Total Md of chloride** was calculated by integration under the Md curve, this is compared to **stream discharge** to show that it **drives** the Md of chloride (right).
- Estimates show that **33,000 tons** of NaCl (**19,800 tons Cl^-**) was applied in 2020-21 but only **16,133 tons of Cl^-** was discharged from 2021-22. The mass of chloride into the Root River system ≠ the mass of chloride discharged out of the system, so **where is it going**?
- What are the **potential compartments** (pathways) that generate stream discharge on the Root River and their **influence**?

FIG 6

- Concept model of **potential pathways** water can take to **enter a stream** and contribute to **stream discharge** [4] (right).
- **Flow-based separation** for both study sites using WHAT analysis tool [5] (below). Separating total stream discharge into pathways of **base flow** and **runoff. Base flow** was the **dominate pathway** at both study sites.





LOOKING INTO THE WORK

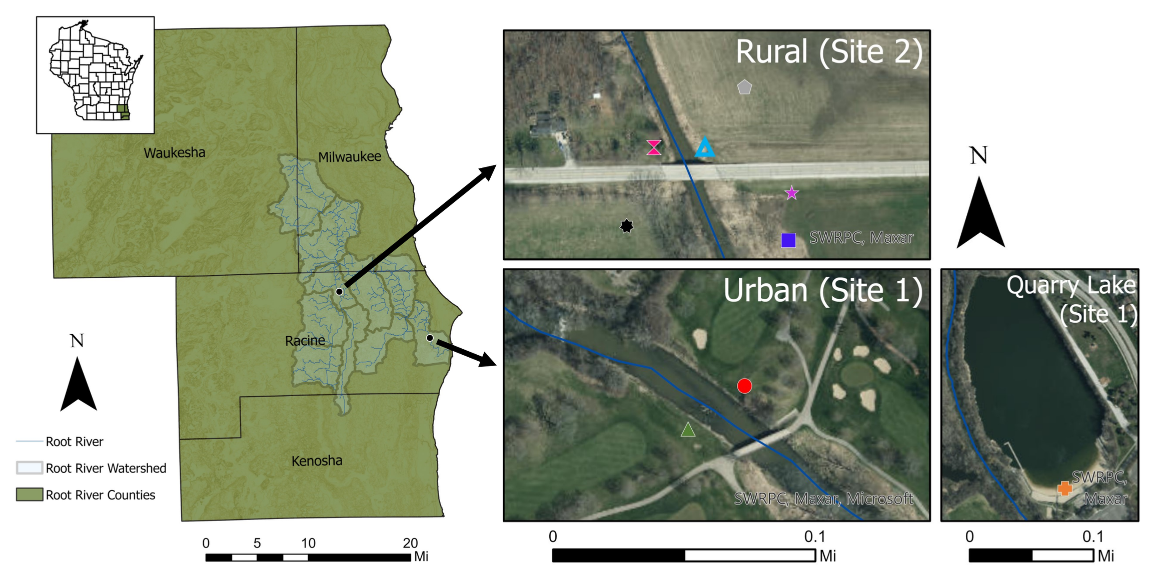
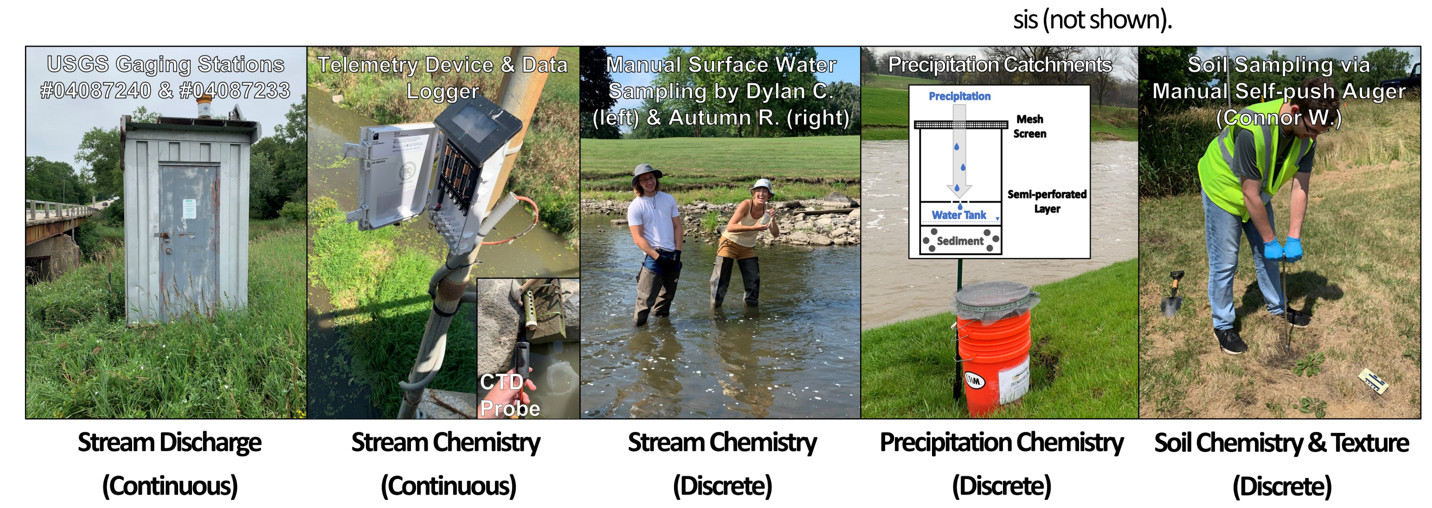


FIG 3

- Root River watershed, counties, and river channel (far left). **Study sites** (urban and rural) with soil sampling locations marked (left). **Urban land coverage** accounts for **74.38%** and **11.45%** for urban and rural sites, respectively.
- Root River is comprised of **117 Mi** of streams and drains approximately **193 Mi²**.
- **Each sampling technique** used at both study sites (below). Water samples were analyzed at the School of Freshwater Sciences and soil samples were split between UW Soil and Forage Analysis Lab and Paradis Lab for analysis (not shown).



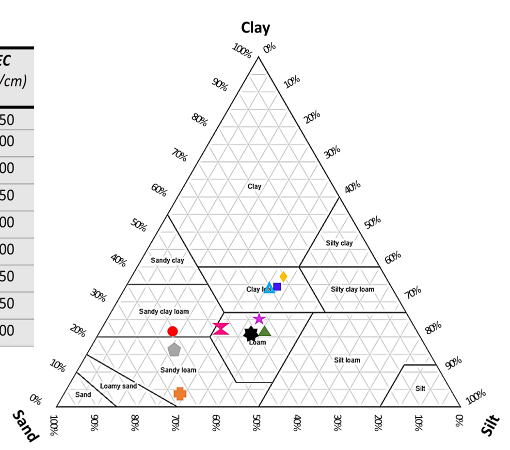
Stream Discharge (Continuous) | Stream Chemistry (Continuous) | Stream Chemistry (Discrete) | Precipitation Chemistry (Discrete) | Soil Chemistry & Texture (Discrete)

INVESTIGATING ROOT RIVER SOIL

FIG 8

Table for soil sample's **chemical** and **physical** properties (right) and ternary plot for **soil name** using **United States Department of Agriculture (USDA)** classification (far right). Data presented for soil samples collected on **8/24/22,** processed by UW Soil and Forage Analysis Lab.

Sample ID	Symbol	pH	OM (%)	P (mg/kg)	K (mg/kg)	Ca (mg/kg)	Mg (mg/kg)	Na (mg/kg)	Cl (mg/kg)	EC (µS/cm)
1	●	7.6	5.0	19.4	128.4	1922.0	483.1	2.6	10.5	150
2	▲	7.5	7.2	21.9	232.4	2101.0	557.9	1.5	12.0	200
3	◆	7.4	0.2	7.2	11.2	937.2	72.4	2.9	17.5	100
4	■	7.5	6.5	18.9	104.1	2691.7	730.6	20.3	24.0	350
5	★	7.6	6.6	17.4	53.3	3089.4	711.7	3.1	6.0	200
6	●	7.6	2.7	20.9	53.4	3017.1	291.5	17.5	97.0	600
7	△	7.9	4.1	41.8	73.3	3488.1	399.4	15.8	25.0	150
8	⧗	8.1	3.5	40.5	87.9	2487.7	280.3	28.6	26.5	250
9	●	7.7	8.4	13.4	120.9	2708.8	499.7	26.7	54.0	300



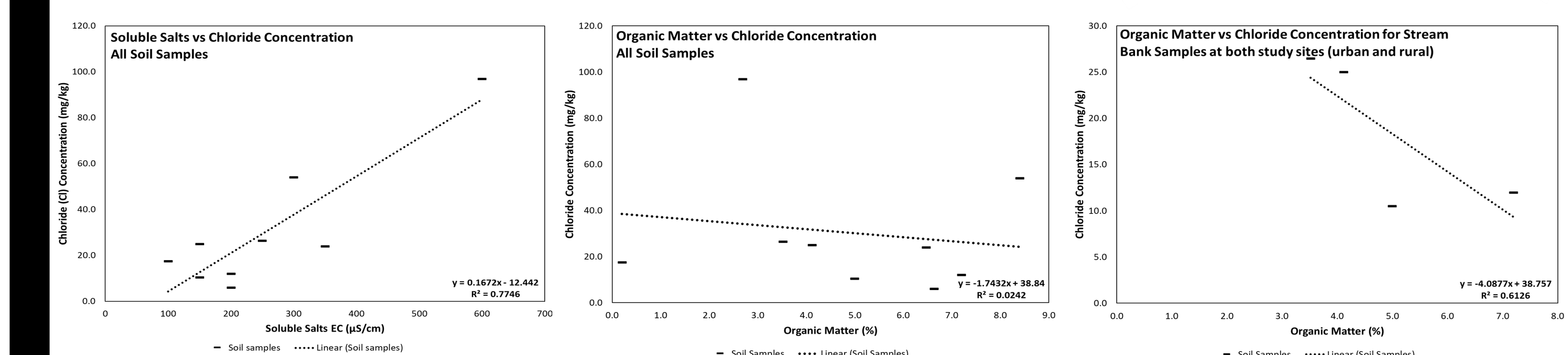
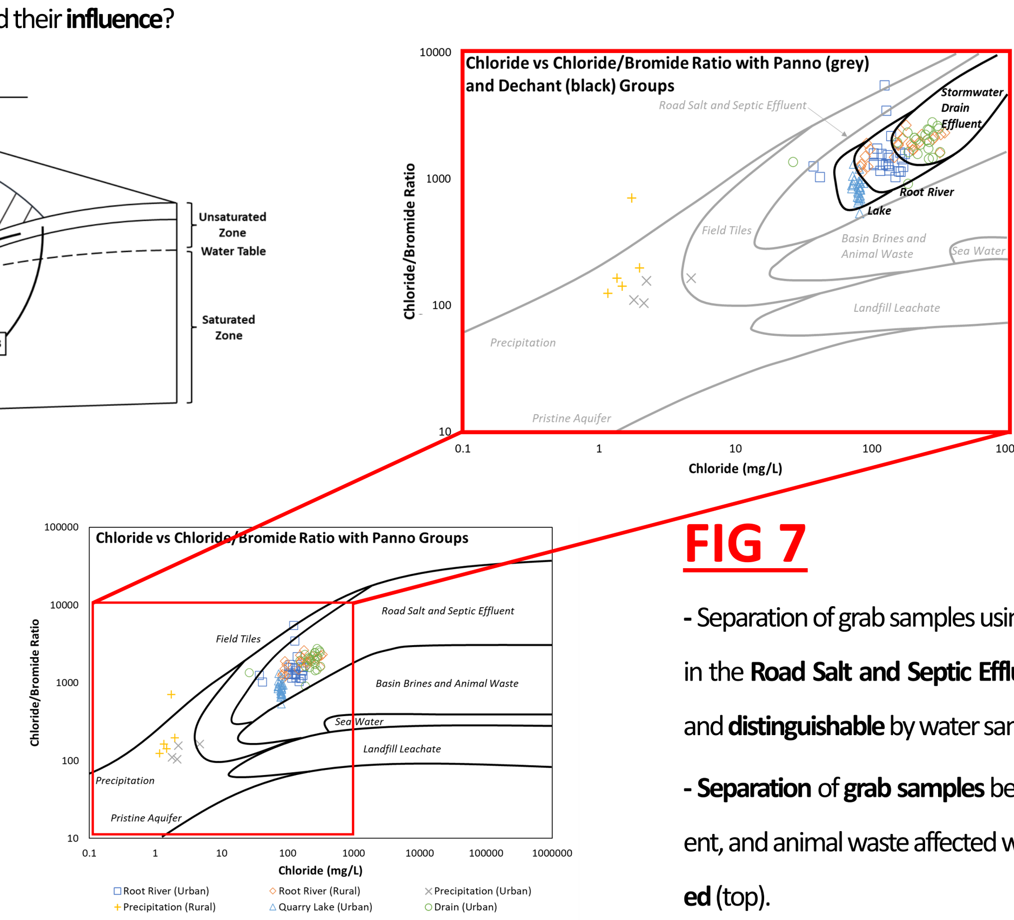
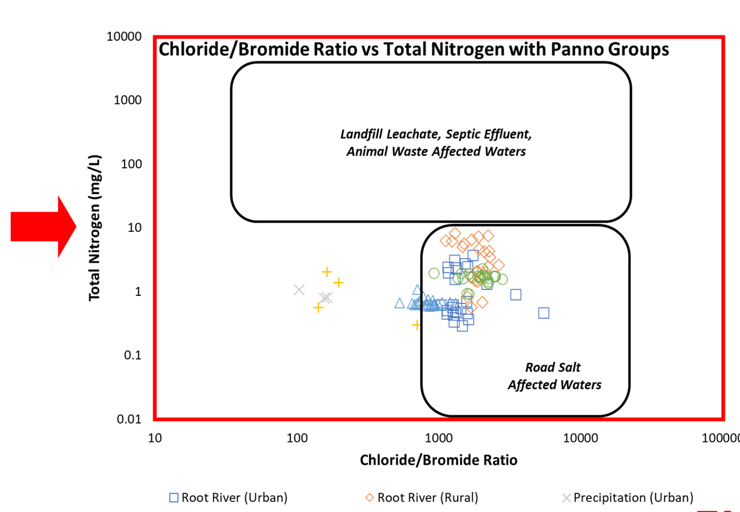


FIG 9

- Regression of soluble salts (µS/cm) from soil leachate vs chloride concentration (mg/kg) in the soil (left). **Soils** that **store more chloride** have **higher soil leachate conductance**. Do soil leachate conductance values fluctuate temporally?
- Regression of soluble salts (µS/cm) from soil leachate vs organic matter (%) in the soil (middle). This regression was plotted to **recreate previous work by Kincaid & Findlay (2009)** [7]. Where it was found that soil chloride retention (concentration) was associated with higher soil organic matter. However, **our results do not show this relationship**. This could be due to the range of our samples (i.e., stream bank, lake, ditch, woodlands, agriculture, and animal pasture) and the hydrological processes that control each type. When stream bank samples were isolated (right) we see a correlation but it is opposite of what Kincaid & Findlay (2009) observed. This leads to **new questions on how organic matter influences chloride retention in soil and if these influences are universal**?

KEY FINDINGS





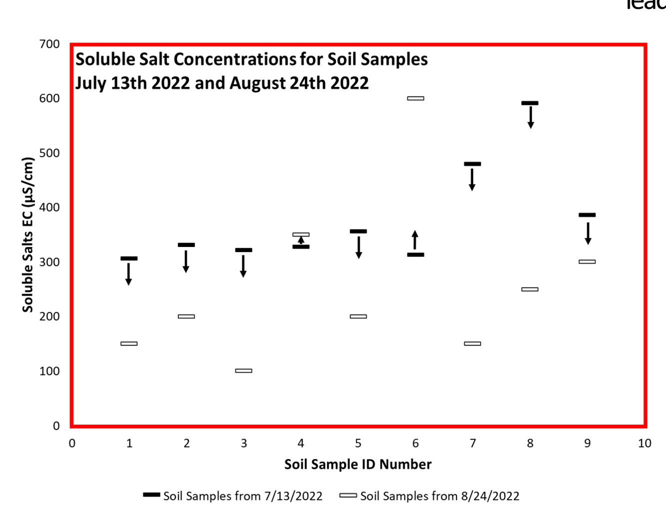


FIG 7

- Separation of grab samples using end-member **sources** [6]. Majority of grab samples plot within the **Road Salt and Septic Effluent group.** Within this group our grab samples are **consistent** and **distinguishable** by water sample type (i.e., lake, river, drain, and precipitation) (left).
- **Separation** of **grab samples** between **road salt** affected waters vs landfill leachate, septic effluent, and animal waste affected waters. **All** samples (except precipitation) **plot as road salt affected** (top).

FIG 11

- Comparison of soil sample leachate conductance **temporally**. Majority of soil samples **decreased in leachate conductance over the summer,** expected with the **lack of road salt use**. Interestingly, we see a **drastic increase for soil sample 6**, which can be **attributed to application of fertilizer** as that sample represents **agricultural fields** (sample ID 6 in Fig 3 & Fig 8).
- Therefore, **soil can act** as both a **pathway** and **secondary source** of chloride.

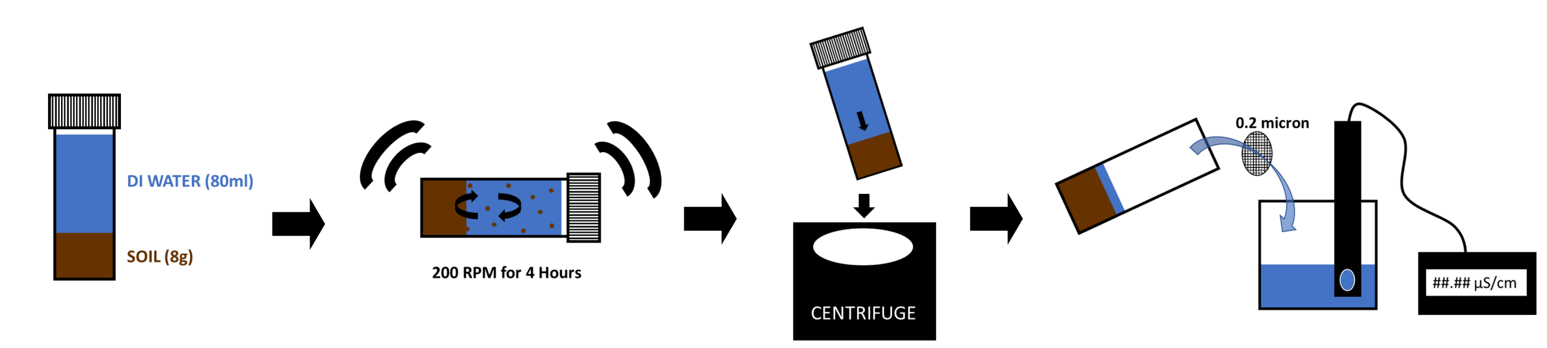


FIG 10

- Method for the **soil leaching experiments** conducted on the secondary set of soil samples collected on **7/13/2022** following UW Soil and Forage Analysis Lab's method as a guide [8].
- The goal was to generate **soil leachate conductance values** for soil samples **collected at different times** but at the same **location**. Here we **compare mid-summer (7/13/22) to late-summer/early-fall (8/24/22) soil samples** to understand **soil leaching overtime in the environment.** Kincaid & Findlay (2009) conducted soil leaching experiments in a lab while our experiments were not. It is important to note that we did not have control over the amount of precipitation or potential additions of chloride between the sampling dates. This experiment will uncover the **realistic soil leaching behavior** for the soil samples at the study sites (urban and rural).

FUTURE WORK

- Incorporate advanced hydrographic separation techniques to further separate the mass discharge of chloride and elucidate the relationship of hydrologic compartments and isotopic signatures temporally. Allowing us to further understand the age of the water and insight into when/if pathways for chloride sources dominate or have temporal patterns.
- Compare high-level analysis with low-level analysis for water and soil samples to see if simple, low-cost analyses yield similar results.
- Question how this data can be used to understand the effect of Waukesha's Water Diversion Plan on the Root River?
- Submit data as open source on SWIMS (Surface Water Integrated Monitoring System) via Water Quality Exchange Network.

ACKNOWLEDGMENTS

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