Determination of Deicing Ions (Na^+ and Cl^-) in the Kinnickinnic River

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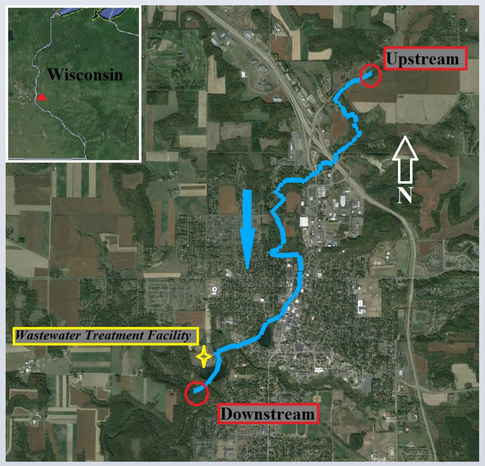
Abstract

Specific conductance and NaCl concentrations were monitored in the Kinnickinnic River at two sites near River Falls, WI during the spring of 2013. The purpose was to: determine the nature of dissolved NaCl in the river, compare the mass of NaCl municipally applied with an experimentally determined mass present in the river, identify a potential relationship between specific conductance and dissolved NaCl, and compare NaCl concentrations with biota toxicity limits. Analysis of ions in the river indicated a one-to-one stoichiometric ratio between sodium and chloride, suggesting an anthropogenic source. Baseflow surveys and USGS data were used to determine unique discharges downstream; mean monthly salt concentrations and cumulative discharge downstream were used to determine a salt load between the two sites. The City of River Falls applied 1,373 tonnes of deicer during the 2012/13 winter; private and commercial entities were not considered. It is estimated that a wastewater treatment facility contributed an additional 157 tonnes of NaCl to the river. Water sample analysis accounted for the presence of 780 tonnes NaCl in the river during the study. NaCl concentrations did not exceed the threshold required to dominate specific conductance. Downstream maximum and mean chloride were 93.4 mg L^{-1} and 35.5 mg L^{-1} respectively, which is below the toxicity threshold of most organisms. It is unlikely that NaCl loading poses a significant threat to the Kinnickinnic River.

Introduction

Deicer loading in freshwater ecosystems can have significant impact on organisms through disruption of cellular osmoregulatory function, causing mortality at high concentrations (1); salt loading has been documented in lacustrine (2), riverine (3), and subsurface environments (4) which poses a threat to a wide variety of biota. The Kinnickinnic River was chosen to study as it is a class I trout stream with many sensitive receptors. The region is characterized by carbonate, sandstone, shale, and glacial deposits, lacking any significant natural sources of halite (3).



City of River Falls and Kinnickinnic River (maps.google.com)

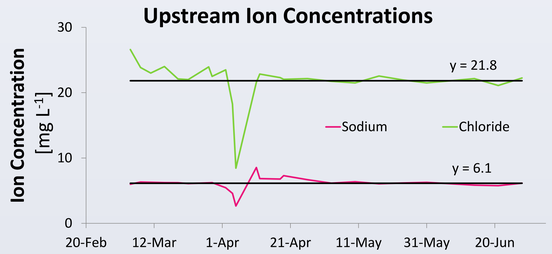
Objectives

1. Identify the presence and source of sodium and chloride ions in the Kinnickinnic River
2. Compare the mass of deicer present in the river, determined by laboratory analysis, with the mass of deicer applied by the City of River Falls during 2012-13 winter
3. Identify a potential relationship between deicer ion presence and specific conductance for easy estimation of deicer concentrations
4. Compare mean and maximum identified salt concentrations with acute and chronic toxicity levels associated with organisms indigenous to the river

Materials & Methods

Sample Collection

- Two sites were sampled
  - Biweekly in Mar & April and weekly in May & June
  - Forty-eight water samples taken in total
- A wastewater treatment facility discharged into sample area
  - Sampled effluent and obtained discharge data (5)
  - (WWTF discharge)*[NaCl] = (mass NaCl)
- Background Concentrations
  - Upstream ion concentrations considered background
  - The following plot illustrates minimal deviation from mean sodium and chloride concentrations upstream:



Discharge Data

- USGS gaging station 7.7 km southwest of the downstream sampling site
- Mean daily discharges were converted into monthly discharges (6)
- Local baseflow surveys used to correct discharges by creating a unique value at the downstream sample site (7)

Parameters Determinations

- Specific conductance
  - Measured onsite 1.5 m from bank
  - YSI PRO2030
- Chloride
  - EPA Method 9253 – titrimetric analysis
  - Silver nitrate; potassium chromate
    - $Ag^+ + Cl^- \rightarrow AgCl$
    - $2Ag^+ + CrO_4^{2-} \rightarrow Ag_2CrO_4$
- Sodium
  - Flame photometry
  - Sherwood 420 flame photometer
- Standard Recoveries:
  - Sodium concentrations were used in calculating total NaCl concentrations due to best standard recoveries:

	Standard	Calculated	Recovery
	mg L^{-1}		
Na^+	6.5	6.1	94%
	9.7	9.4	96%
	13.0	13.0	100%
Cl^-	35.0	40.4	115%
	77.1	85.6	111%

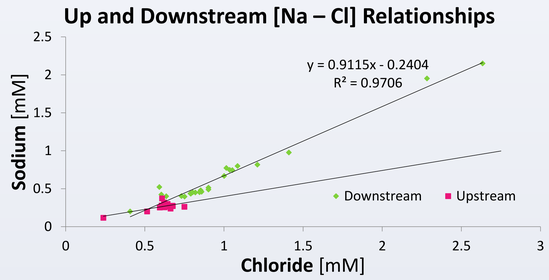
Toxicity

- Conducted literature review
- Most toxicity data were summarized by the Canadian Council of Ministers of the Environment (8)

Results

1. Nature of Dissolved Ions

- Unlike upstream (slope 0.34), downstream a nearly one-to-one stoichiometric ratio was observed between sodium and chloride ions:



2. Salt Recovery

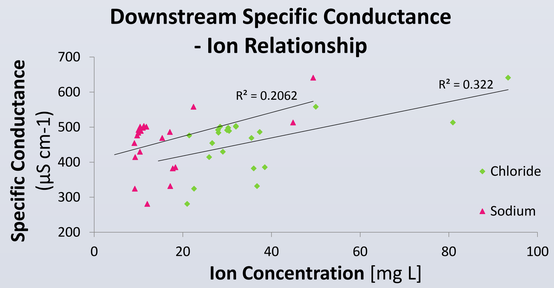
- Mean background concentration: **15.6 mg L^{-1} NaCl**
- Mass from wastewater treatment facility: **157.2 tonnes NaCl**
- Experimental salt mass calculated using the following equation:

$$=([\boldsymbol{Downstream}] - [\boldsymbol{Background}]) * (\boldsymbol{Discharge}) - (\boldsymbol{WWTF})$$

- = **780 tonnes** NaCl present in the Kinnickinnic River during study

3. Specific Conductance - Deicer Relationship

- Little correlation was observed between specific conductance and dissolved deicer concentrations:



4. Toxicity Evaluation

- Few toxicity data exist regarding species found in the Kinnickinnic River, so categories of species were considered
- Maximum and mean downstream [Cl^-]: **93.4** and **35.5 mg L^{-1}**
- Glochidium toxicity values were reported as LC_{50} rather than IC_{50}; inhibited organisms will not survive this parasitic stage of life (8).
- Rainbow trout used as proxy for brown and brook trout

Species	Acute LC_{50} [mg L^{-1} Cl^-]		Chronic LC_{50} [mg L^{-1} Cl^-]	
Brown Trout			607	8
Rainbow Trout	8,634	9		
Bullfrog	5,846	8		
Fish+	7,979	8, 9		
Frog+	3,335	8, 10	2,369	8
Waterflea+	2,467	8, 9, 11		
Bivalve+	1,369	8		
Glochidium+	434	8, 12		
+ indicates combination of multiple species				

Looking north near downstream sample site (Michael McCarty)

Conclusions

1. A one-to-one stoichiometric relationship between sodium and chloride typically indicates an anthropogenic source of NaCl (2, 3, 13).
   - The observed molar ratio between sodium and chloride in the Kinnickinnic River is nearly one-to-one, so it is likely that an anthropogenic source of NaCl is present.
2. The City of River Falls applied 1373 tonnes of deicer to city streets during 2012/13 (14, 15), and approximately 780 tonnes were accounted for in the Kinnickinnic River.
   - It is estimated that approximately 60 percent of NaCl applied to city streets will make its way to the Kinnickinnic River by July annually.
3. Typically a conductivity of 1,400 µS cm^{-1} (i.e. 200 mg L^{-1} Cl^-) is needed before deicing ions will dominate specific conductance (11).
   - A general positive relationship was observed between specific conductance and ions; however, it is not possible to accurately estimate NaCl concentrations in the Kinnickinnic River using specific conductance readings.
4. With respect to chloride, toxicity is typically not observed in macroscopic organisms at the levels present in the Kinnickinnic River.
   - It is unlikely winter deicing activities will have a significant impact on biota in the Kinnickinnic River.

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