

Cover Page

**Title:** Spatial and temporal modeling of road salts in a watershed with urban and agricultural land use

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**Abstract:**

Within the Chicago Metropolitan area (CMA), streams have chloride ( $\text{Cl}^-$ ) concentrations that are temporally variable and elevated in response to deicing applications. Gradual increase in both winter and summer baseline stream  $\text{Cl}^-$  concentrations is associated with steady buildup of  $\text{Cl}^-$  in the system. No model currently exists to understand how  $\text{Cl}^-$  varies temporally or spatially. The proposed project will develop a GIS model and fluid and solute model to determine the transport and fate of  $\text{Cl}^-$  in a system by addressing three objectives: 1) Does road salt applications elevate  $\text{Cl}^-$  concentrations in a stream throughout the year?; 2) Under what conditions will a watershed reach equilibrium between  $\text{Cl}^-$  inputs and outputs; 3) What is the time interval required for a system to return to background levels of  $\text{Cl}^-$  once inputs are decreased or ceased? Model development will focus on a smaller watershed, Little Kickapoo Creek (LKC), in central Illinois rather than the CMA. LKC watershed exhibits similar temporal  $\text{Cl}^-$  patterns as observed in the CMA, but has not witnessed a sustained elevation of  $\text{Cl}^-$ . LKC is also more accessible and provides simpler, fewer external variables, system to examine than CMA. LKC originates in an urban area and then transitions into an agricultural dominated area. Seven locations along LKC will be sampled every two weeks, with the water analyzed for major ions. The water chemistry data will be incorporated into a GIS to analyze for temporal and spatial trends related to deicing events. Additionally, a groundwater flow model coupled with a solute model will be developed to simulate  $\text{Cl}^-$  transport and fate in response to various recharge and application conditions. The project will serve as a pilot for deployment to larger areas, i.e. CMA or Illinois River. The project will directly involve two graduate students from the Illinois State University Hydrogeology M.S. program and two undergraduate students with course experience in GIS. All students will be involved in the water sampling and analyses. The GIS models will be developed primarily by the undergraduate students, and the graduate students will focus on the flow and solute models.

## **NARRATIVE - Spatial and temporal modeling of road salts in a watershed with mixed, urban and agricultural, land use**

### **I. Introduction**

Chloride ( $\text{Cl}^-$ ) is highly soluble and does not biodegrade, volatilize, precipitate, or absorb onto mineral surfaces [1, 2]. Thus,  $\text{Cl}^-$  is extremely mobile, easily transported within surface water or infiltrated into the subsurface. Natural sources of  $\text{Cl}^-$  include atmospheric deposition, rock weathering, and basin brines [3-5]. During winter months in northern latitudes, deicers, typically composed of a  $\text{Cl}^-$  salt, are applied to impervious surfaces, roads, walkways, and parking lots, to keep these areas clear of snow and ice [2, 6, 7]. In watersheds where deicers have been employed, natural  $\text{Cl}^-$  inputs contribute less than 1% of the  $\text{Cl}^-$  [1, 8], and inputs from agricultural and septic sewer systems only contribute an additional 1% to 3% to the total  $\text{Cl}^-$  load [8]. The remaining load is attributed to deicers, which serve as a nonpoint source of  $\text{Cl}^-$  [1, 4, 8]. Annual  $\text{Cl}^-$  use for road deicing in the US increased from 163,000 tons in 1940 to over 23 million tons in 2005 [9]; six states apply three quarters of the total mass of salt: New York, Ohio, Michigan, Illinois, Pennsylvania, and Wisconsin [10]. In the Chicago area, multiple entities apply over 270,000 tons of road salt, primarily as  $\text{NaCl}$ , to roads during an average winter [11, 12].

Between 35 to 55% of the applied salt will be transported away via overland flow, with  $\text{Cl}^-$  concentrations in excess of 1000 mg/L [13], to surface water bodies [14]. Following runoff, streams exhibit acute changes, 20- to 30-fold increases, in  $\text{Cl}^-$  concentrations [15-20]. The long-term use of deicers has had a chronic impact on streams [21, 22], with reported concentrations increasing 1.5 mg/L per year ( $\text{Cl}^-$ ). Rural watersheds with low density of roadways have seen increases in  $\text{Cl}^-$  concentrations as a result of deicing applications in urban areas [23, 24].  $\text{Cl}^-$  concentrations in the rural streams did not return to baseline levels in summer, even when no salt was being applied. Salt concentrations build up over many years and remain high in the soil and groundwater. Elevated concentrations within the groundwater contribute to elevated baseflow concentrations in streams during the spring and summer [3, 18, 25] and to chronic impacts on groundwater and surface water systems [1, 26, 27].

Between 45% to 65% of applied deicers accumulate in the shallow subsurface waters [2, 15, 28]. Infiltration of runoff from salted roads elevates  $\text{Cl}^-$  concentrations in roadside soils up to distances of 50 m [29-31], with  $\text{Cl}^-$  concentrations as high as 13,700 mg/L [20].  $\text{Cl}^-$  accumulation in soils and in groundwater subsequently raises the baseflow  $\text{Cl}^-$  concentrations in surface water bodies during the summer and leads to increases in the baseline salinity of surface waters [32, 33]. In select cases,  $\text{Cl}^-$  concentrations have increased by 243% over a 47-year period [17], and in other cases,  $\text{Cl}^-$  concentrations are up to 100 times greater than non-impacted streams [23]. Although acute concentration spikes associated with winter runoff can exceed 1000 mg/L [34], sustained, chronic, concentrations have been rising in streams. For example, the baseflow  $\text{Cl}^-$  concentration in Highland Creek (Toronto) has increased from 150 mg/L in 1972 to about 250 mg/L in 1995 [21]. Once in ground water,  $\text{Cl}^-$  can persist for many years [35], and even if deicing applications stopped, it would be decades before the  $\text{Cl}^-$  concentrations returned to pre-1960 levels in shallow ground water [4, 20].

Although  $\text{Cl}^-$  has typically been viewed as a benign ion in the environment, exposure to acute ( $> 1000$  mg/L) and chronic ( $>210$  mg/L)  $\text{Cl}^-$  concentrations can have deleterious effects on aquatic flora [2, 29, 36-49] and fauna [31, 50-52]. As a result of delayed (lagged)  $\text{Cl}^-$  concentrations in streams, sensitive life stages can be exposed to concentrations long after the winter period of application has occurred [53].

### **II. Research Objectives**

Aquifer salt loading can be quite variable due to diversity of road types, application rates, land use, soil characteristics, and subsurface geology.  $\text{Cl}^-$  concentrations in the recharging waters can also change with time due to variation in precipitation and application rates. Scarcity of accurate data (i.e. salt application rates) and complexities associated with characterizing the urban hydrologic system lead to difficulties in linking spatial variability with potential impact of this nonpoint source contaminant.

This project seeks to develop models to understand the transport and fate of  $\text{Cl}^-$  in a watershed. The overall purpose of this study is to focus on the presence of  $\text{Cl}^-$  in watershed, both the surface

water and the groundwater. Three objectives are established to examine spatial and temporal variations in  $\text{Cl}^-$  concentrations:

1. Does road salt applications elevate  $\text{Cl}^-$  concentrations in a stream throughout the year?
2. Under what conditions will a watershed reach equilibrium between  $\text{Cl}^-$  inputs and outputs?
3. What is the time interval required for a system to return to background levels of  $\text{Cl}^-$  once inputs are decreased or ceased?

The Illinois State Geological Survey and the Illinois State Water Survey have examined the issue of road salts in the Chicago metropolitan area and the subsequent effects on the Illinois River watershed [5, 13, 36, 54-58]. A pilot GIS model developed to evaluate the transport and fate of  $\text{Cl}^-$  within Illinois indicated that data are spatially and temporally too variable to accurately assess the problem [59]. Consistent temporal water quality data are needed to develop more adequate GIS and flow models. A smaller system, Little Kickapoo Creek (LKC) will be examined to establish prototype models that can be applied to larger systems. While the project will focus on a small watershed in central Illinois, the developed techniques and gained knowledge will be transferable to other watersheds, both within, i.e. the Illinois River and Chicago area watersheds, and outside of the state.

### III. Site Description

The study focuses on LKC, a low gradient, low order, perennial stream that occupies a glacial outwash valley (Figure 1). LKC headwaters in southeast Bloomington, Illinois; Bloomington's total population is 78,902 and is growing at an annual rate of 3.0% [60]. Upon leaving the urbanized area of Bloomington, LKC flows through a low density suburban setting and then into an agricultural area. The LKC watershed covers a total area of approximately 56  $\text{km}^2$ , from which 1.7  $\text{km}^2$  is road surface. The land use is 17% urban, 73% agricultural, and 10% forested/ wetland/ surface water areas; classifying the watershed as mixed urban and agricultural. The average annual precipitation for the area (1971-2000) is 95 cm of rain and 56 cm of snowfall [61]. Previous studies have examined and reported the geology, hydrology, and hydrogeology of the area [62-68].

### IV. Methodology

#### a. Stream $\text{Cl}^-$ concentrations

Waters will be sampled every two weeks from seven locations (LKC1-7) along LKC (Figure 1) and analyzed for major anions ( $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3\text{-N}$ ) and major cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$ ) in the water chemistry lab within the ISU Department of Geography-Geology. Quality assurance (QA) and quality control (QC) will be maintained during analysis of each sampling event by running blank, duplicate, and replicate samples. In-situ measurements of pH, specific conductance, and temperature will be recorded at each sampling event. Additionally, stage and discharge measurements will be recorded from an established fixed-datum at each location. Discharges will be calculated using the velocity-area method [69], where velocity will be measured using an electromagnetic flowmeter. Using the discharge and the concentration data, mass fluxes for the ions will be calculated. Sampling has already begun, starting in August 2015.

#### b. Numerical Modeling

The field data will be incorporated into a GIS to examine the spatial and temporal  $\text{Cl}^-$  signatures within the watershed following the work by Eggert *et al.* [59]. The chemistry and GIS data will serve as input and calibration data for the groundwater flow and solute models developed in MODFLOW and

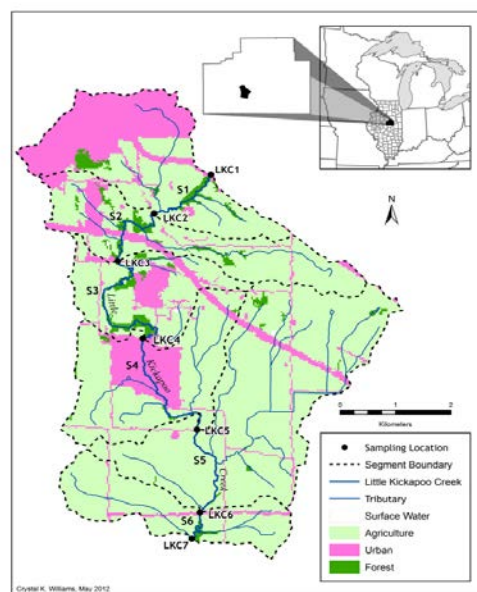


Figure 1: Little Kickapoo Creek watershed showing the proposed sampling sites and the land use for the area.

MT3D, respectively, to simulate the transport and fate analysis of the Cl<sup>-</sup> in the system. Once developed and calibrated, the MODFLOW and MT3D models will be subjected to various conditions, representing different application scenarios, to discern the storage potential of the watershed and the transport of Cl<sup>-</sup> in the system. As with the water sampling, model development was initiated in August 2015.

## **V. Expected Outcomes**

Outcomes from these activities detailed under this research project represent spatial and temporal data for Cl<sup>-</sup> within a watershed impacted by deicing agents. Results will: (1) quantify seasonal and controls on concentration and flux of Cl<sup>-</sup> in both the surface and subsurface waters, (2) identify the time for the system to reach equilibrium between Cl<sup>-</sup> input from deicers and the transport of Cl<sup>-</sup> out of the system, and (3) quantify the response of the system to changes in application rates of deicers to determine how the system can be remediated. Using a forward modeling approach to change Cl<sup>-</sup> inputs and hydrologic signals, it is possible to investigate other potential scenarios. These results represent baseline data necessary to support all future research activities and develop appropriate BMPs for Cl<sup>-</sup> applications.

## **VI. Training, Management Plan, and Timetable**

PI Peterson will oversee the project and will actively participate in the field sampling, model development, and student supervision. The project will run from March 1, 2016 to February 28, 2017. Stream sampling, initiated in August 2015, will continue to occur every two weeks over the entire course of the study. Graduate and undergraduate students will collect, analyze, and interpret the water chemistry data. Undergraduate student Kyagaba David Lwanga, a senior graduating in May 2017, is involved in water sampling and GIS development; upon his graduation, a rising senior, yet unidentified, will transition into Mr. Lwanga's role during the summer 2016. Groundwater flow and solute modeling will be conducted by two Hydrogeology MS students, advised by PI Peterson. Jessica Ludwikowski has begun MODFLOW and MT3D development, but will graduate in May 2016. Lucas Chabela has been involved in the water sampling and has started integrating into the model development with Ms. Ludwikowski. Mr. Chabela will serve as the lead student on the project, coordinating the water sample and modeling components. Research meetings will occur weekly during the academic year to bring the students up to speed on the literature and to assess project completion. The entire research team will conduct field experiments, generate research papers, and be involved in presentations at meetings. Students will present findings at the Illinois Water 2016 conference, an Illinois Groundwater Association meeting, and the annual Geological Society of America meeting. Data generated from the research will be integrated into exercises and projects for three courses, Groundwater Geology, Hydrology, Groundwater Modeling, that serve graduate students and upper level undergraduate students.

Graduate Students: Lucas Chabelas & Jessica Ludwikowski

Undergraduate Students: Kyagaba David Lwanga & a rising senior in 2016-2017

## **VII. Importance to Illinois**

Cl<sup>-</sup> concentrations along the Illinois River have ranged from 70 to 488 mg/L, with the highest concentrations nearer the Chicago area [55]. Temporally, concentrations are highest in the winter and early spring months and have been increasing at rates greater than 4.0 mg/L per year since 1990. Shallow groundwater in much of the Chicago region has elevated Cl<sup>-</sup> due to road salt [54], with about 43% experiencing rate increases greater than 1 mg/L/year and 15% having increases greater than 4 mg/L/year. Continual increases in Cl<sup>-</sup> concentrations in shallow groundwater in Chicago [54] illustrate that the system still has storage capacity for Cl<sup>-</sup>. The increases have resulted in public supply wells in the Chicago area having Cl<sup>-</sup> concentrations greater than 100 mg/L (35% in the western and southern counties); median values were less than 10 mg/L before 1960 [54]. Additionally, waters from these aquifers discharge to tributaries of the Illinois River, providing a sustained source of Cl<sup>-</sup> throughout the year. The concepts developed within the LKC watershed should be transferable to the Chicago metropolitan area and allow for the monitoring of Cl<sup>-</sup> in the Illinois River Watershed.

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