Transport of road salt contamination in karst aquifers and soils over multiple timescales

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HIGHLIGHTS

• Continuous karst spring data elucidated salt transport over multiple timescales.
• Conduit flow rapidly transported some salt while the rest moved via diffuse flow.
• An urban spring had more conduit flow while a rural spring had more diffuse flow.
• Salt stored in soil was released year-round by first flush events during flooding.
• Cl− increased at a rural spring over 20 years due to inter-annual salt retention.

GRAPHICAL ABSTRACT

ABSTRACT

Road deicing has caused widespread environmental Na+ and Cl− release for decades, yet the transport and retention of these contaminants in karst aquifers and soils are poorly understood. We examined the transport dynamics of Na+ and Cl− from road salt in shallow groundwater during flooding and over seasonal timescales by intensively monitoring an urban and a rural karst spring over approximately 2 years. Furthermore, we used a 20-year dataset for the rural spring to determine how salt retention affected long-term geochemical trends in the shallow groundwater. Salt transport was governed by hydrologic pathways through karst aquifers: during winter and early spring floods, flow through preferential pathways rapidly transported salty meltwater or stormwater over hours to days, while the remaining salt-contaminated water moved diffusely through the rock matrix on timescales of months to years. Flood hydrograph separations revealed that event water constituted 61.2% of stormflow on average at the urban spring, leading to more extreme variability in salt concentrations during flooding and throughout the year. This variability indicates that baseflow contributions to urban streams overlying karst aquifers with preferential flowpaths are likely less effective at buffering salt concentrations. In contrast, salt concentrations were less variable in the baseflow-dominated rural spring (28.7% event water). Furthermore, salt was episodically released from soils to shallow groundwater throughout the year during first flush events. A Cl− mass balance indicates that Cl− applied during previous winters persists within the springs’ recharge basins for more than a year, raising baseline concentrations as road salt is introduced faster than it can be flushed from the basin. Inter-annual salt retention by soils or slow groundwater movement likely caused significant Cl− and specific conductivity (SpC) increases at the rural spring from 1996 to 2016. Accumulation of salt in shallow groundwater can elevate baseflow concentrations in surface waters, where it threatens aquatic organisms.

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1. Introduction

Road salting improves winter travel safety but also releases Na\(^+\) and Cl\(^-\) into the environment, altering the chemistry of nearby soil, groundwater, and streams. Following road salt application, Na\(^+\) and Cl\(^-\) enter soils and then are delivered to shallow groundwater, which feeds local surface water features via baseflow. Surface water Na\(^+\) and Cl\(^-\) concentrations increase with impervious surface area and can remain elevated throughout the year due to temporary salt retention within watersheds (Corsi et al., 2010, 2015; Dailey et al., 2009; Kaushal et al., 2005; Ledford et al., 2016; Mason et al., 1999; Novotny et al., 2008a).

Catchment-scale salt retention is important because if Na\(^+\) and Cl\(^-\) cannot be flushed completely from watersheds between road salting seasons, these ions build up and increase background concentrations in streams. Long-term Na\(^+\) and Cl\(^-\) increases have been observed in several lakes and streams in North America (Bowen and Hinton, 1998; Corsi et al., 2015; Dailey et al., 2014; Dailey et al., 2009; Godwin et al., 2003; Kaushal et al., 2005; Kelly et al., 2008; Novotny et al., 2008a; Perera et al., 2013; Sun et al., 2014) and Europe (Müller and Gächter, 2012; Thunqvist, 2004). Groundwater salt concentrations are increasing as well; in the Chicago, Illinois metropolitan area, Kelly (2008) found that groundwater Cl\(^-\) concentrations increased from 6 mg/L prior to 1950 to a median value of 20 mg/L from 1990 to 2005. In Connecticut, average groundwater Cl\(^-\) increased from 2 mg/L in 1894 to 29 mg/L in 2002–2007 (Cassanelli and Robbins, 2013).

Mass balance studies quantify the annual salt retention that is responsible for these long-term increases. Howard and Haynes (1993) found that 45% of Cl\(^-\) applied as road salt left an urban Canadian watershed as stream runoff each year from 1988 to 1991, with the rest being temporarily stored in groundwater. Perera et al. (2013) performed a new mass balance for the same Canadian watershed from 2004 to 2008, this time accounting for dual porosity in the aquifer due to “urban karst” (i.e., a dual porosity aquifer in which the secondary porosity is created by adding permeable fill material around pipes and drains; this secondary porosity is superimposed upon the primary porosity of the rock matrix). They found that about 60% of the applied Cl\(^-\) was released from the watershed as runoff or as groundwater flow through preferential flowpaths, with the other 40% entering the aquifer where it flowed diffusely through the rock matrix (Perera et al., 2013). Most mass balance studies show annual Cl\(^-\) retention in watersheds ranging from 40 to 78% (Meriano et al., 2009; Novotny et al., 2008b; Ruth, 2003). However, a multi-year mass balance study (1985–2007) of a rural New York stream showed net Cl\(^-\) retention within the watershed some years and net Cl\(^-\) release other years (Kelly et al., 2008). In these mass balance studies, Cl\(^-\) retention is usually attributed to slow groundwater movement, although soils contribute to Cl\(^-\) retention as well (Labadia and Buttle, 1996; Lax and Peterson, 2009).

Movement through soils slows Na\(^+\) and Cl\(^-\) transport partly because the conveyance of these ions depends on the residence time of porewaters and partly because they are retained through interactions with the soil. Na\(^+\) is retained through adsorption to negatively charged sites on clays or organic matter, replacing other major cations or metals and releasing them to the soil porewater (Backstrom et al., 2004; Meriano et al., 2009; Nelson et al., 2009; Robinson et al., 2017; Schweiger et al., 2015). Cl\(^-\) has traditionally been considered a conservative ion, but recent evidence has shown that it can be retained in soils (Robinson et al., 2017) through plant or microbial uptake, non-specific adsorption, and chlorination of soil organic matter (Bastviken et al., 2007, 2009; Lovett et al., 2005; McBride, 1994). Soil retention delays the release of Na\(^+\) and Cl\(^-\) to shallow groundwater, and then groundwater flow rates control the timing of its delivery to surface waters.

Elevated Na\(^+\) and Cl\(^-\) concentrations from road salt contamination have a wide range of ecological impacts for plants and aquatic organisms. Individual species have varying salt tolerances, and road salt contamination causes ecosystems to shift toward dominance by salt-tolerant species, reducing biodiversity among macroinvertebrates (Demers, 1992; Williams et al., 1997), amphibians (Collins and Russell, 2009), and wetland plants (Panno et al., 1999; Richberg et al., 2001). The USEPA designates a Cl\(^-\) chronic exposure limit for aquatic life at 230 mg/L and an acute exposure limit at 860 mg/L (USEPA, 2017). Indeed, acute exposure can cause mortality for amphibians and macroinvertebrates at Cl\(^-\) concentrations on the order of 1000 mg/L (Blasius and Merritt, 2002; Collins and Russell, 2009; Sanzo and Heecan, 2006; Williams et al., 1999).

Springs provide a window into conditions in the shallow subsurface, and they have previously been examined to elucidate spatial patterns in shallow groundwater salt contamination (Foos, 2003; Howard and Beck, 1993; Schweiger et al., 2015). Karst springs are of particular interest because of their dual porosity aquifers, where karst conduits can facilitate rapid and unpredictable transport of some contaminated water, while the rest is retained in the aquifer longer as it travels slowly through the rock matrix. Although carbonate karst lithology is widespread, the transport of road salt contamination in karst aquifers is understudied. Temporal Na\(^+\) and Cl\(^-\) variations in karst-hosted shallow groundwater have rarely been investigated over multiple timescales, and the mechanisms driving these variations are not well understood. Toran et al. (2009) credited epikarst storage for year-round elevated Cl\(^-\) in three karst springs, as well as for controlling specific conductivity (SpC) patterns during floods. Reisch and Toran (2014) continuously monitored a karst spring during snowmelt and found that the proportion of diffuse versus conduit flow (which have differing transport timescales for road salt contamination) depended on melting rates. However, high temporal resolution sampling of shallow groundwater impacted by road salt has not to our knowledge been combined with long-term data. Consequently, the connection between short-term variability in shallow groundwater salt concentrations and long-term geochemical trends remains unexplored. Additional work is needed to explain how salt transport and retention in shallow karst aquifers affects the timing of Na\(^+\) and Cl\(^-\) delivery to surface waters.

In this study, karst springs were monitored to examine the geochemical effects of road salt contamination on shallow groundwater over multiple timescales including flood, seasonal, and inter-annual responses. We used 2 years of intensive water quality monitoring data from an urban and a rural karst spring to evaluate flooding behavior and salt transport pathways, assess seasonal Na\(^+\) and Cl\(^-\) variations, and perform a Cl\(^-\) mass balance. We also examined geochemical trends for the past 20 years at the rural spring. Our main objectives were to determine: 1) how geology and land use influence road salt transport through partitioning of flow into baseflow and event water, 2) how retention and release of salt in soils affect shallow groundwater Na\(^+\) and Cl\(^-\) concentrations, 3) what transport mechanisms govern seasonal Na\(^+\) and Cl\(^-\) variations and annual salt retention in karst aquifers, and 4) whether long-term increases in salt concentrations occur in shallow karst aquifers that can feature rapid transport of contaminants through preferential flowpaths. Understanding the mechanisms by which Na\(^+\) and Cl\(^-\) are transported and retained in the shallow subsurface helps explain temporal patterns of salt contamination in surface waters, where elevated concentrations are ecologically damaging.

2. Methods

2.1. Study sites

We monitored two karst springs in areas of differing land use in east-central Missouri (Fig. 1). The regional climate is temperate, with an average temperature of 13.5 °C and about 100 cm of precipitation annually (NOAA, 2017a). Snow and ice are common in the winter, with an average of 45.2 cm of snowfall per year (NWS, 2017). The regional lithology is dominated by Paleozoic carbonate rocks (USGS, 2014a) and karst features are common in this area.

We selected Blackburn Spring as our urban land use site in this study. It is located 0.7 km from a major highway in an area of mostly low intensity development (USGS, 2014b) in Webster Groves, Missouri,
within Blackburn Park (Fig. 1a). It issues from the Late Mississippian-Meramecian St. Louis Limestone (USGS, 2014a), and several sinkholes occur near the spring (USGS, 2014c). We compared urban Blackburn Spring with Rockwoods Spring, our rural land use site, to assess the impact of land use differences on road salt transport and retention in karst systems. However, it should be noted that even watersheds in rural areas have shown elevated stream Cl\(^-\) levels from road salt contamination (Kaushal et al., 2005; Kelly et al., 2008). Rockwoods Spring is located in a deciduous forest (USGS, 2014b) in the Rockwoods Reservation, a 7.6 km\(^2\) park in Wildwood, Missouri that is surrounded by low density development (Fig. 1b). Rockwoods Spring issues from the Upper Ordovician Plattin Formation (Frederickson and Criss, 1999). Frederickson and Criss (1999) estimated its water residence time at approximately 1 year and its discharge range at 15–300 L/s. Discharge at Blackburn Spring was not measured prior to our study, but it is lower than that of Rockwoods Spring. The recharge areas had not been delineated for either of the springs prior to this study, but both springs are located in areas with separate sanitary and storm sewer systems. We were unable to obtain sewer maps for the areas around the springs, and it is possible that some stormwater is directed out of the recharge areas via storm sewers, particularly at the more urbanized Blackburn Spring site. See Section 3.1 for the basin characterization results of this study, which include discharge, recharge basin area, and land use.

2.2. Field methods

To characterize the transport of road salt contamination over various timescales, we combined field grab sampling, high frequency sampling during floods, and continuous in situ monitoring at both springs over an approximately 2-year period (2014–2016). We collected weekly field grab samples for major ion and isotopic analyses at both springs. Untreated grab samples (i.e., samples that were not filtered or acidified) were collected for Cl\(^-\) analysis in high density polyethylene bottles, while subsamples for major cation analysis were field-filtered (0.2 \(\mu\)m filter) into polypropylene centrifuge tubes and acidified (1% HNO\(_3\)); both sample types were stored at 4 \(^\circ\)C until analysis. Untreated subsamples for isotopic analysis were collected with no head space in air-tight glass bottles and stored at room temperature until analysis. We also...
conducted four field measurements of water quality parameters including Cl⁻ (± 5 mg/L or 15% accuracy), SpC (± 0.001 mS/cm or 0.5% accuracy), and pH (± 0.2 accuracy) using a YSI Professional Plus with Quatro Cable. During flood events, more frequent sampling was conducted with an ISCO 3700 autosampler at Rockwoods Spring and by hand at Blackburn Spring. Precipitation samples were collected for isotopic analysis from a rain gage in nearby (11.3–37.7 km from the springs) Saint Louis, Missouri, concurrently with high-frequency spring sampling during flood events. For more detailed information on precipitation amounts, we used hourly data from Saint Louis Lambert Airport (NOAA, 2017b) which is located 19 km and 33 km from Blackburn Spring and Rockwoods Spring, respectively.

We continuously monitored (i.e., 5-minute data intervals) both karst springs for a suite of parameters, including Cl⁻, SpC, and pH with in situ water quality sensors (YSI 6600 sondes; instrument accuracy is identical to the YSI Professional Plus). The continuous monitoring period at Rockwoods Spring was from July 11, 2014 to November 1, 2016. At Blackburn Spring, monitoring began on July 25, 2014, but the sondes were removed on April 23, 2016 due to site vandalism. The instruments were calibrated biweekly, and these calibrations were used to correct the data for any instrument drift (Hasenmueller, 2011). Stage was measured at 5-minute intervals using a Solinst LT Levelogger Edge or LT Levelogger Junior Edge, and the data were compensated for barometric pressure using a Solinst Barologger. Stage measurements began on August 12, 2014 at both springs, but at Blackburn Spring, stage data are only available until February 13, 2016 because of data loss due to the theft of our instrument. We used an acoustic Doppler velocimeter (SonTek FlowTracker) to calculate discharge at known stages using the discharge-area method (e.g., 0.6-depth method), which enabled us to produce site-specific rating curves for discharge (Fig. S1), and subsequently make dissolved load determinations. In addition to 2 years of intensive monitoring at the two karst springs, a long-term dataset was collected at Rockwoods Spring. Approximately biweekly SpC data was collected from 1996 to 2011 (with less frequent sampling in later years), along with an archive of grab samples that were stored at room temperature in glass bottles until 2015. Samples from 1996 to 1998 in this archive are described by Frederickson and Criss (1999). A subset of the sample archive was previously analyzed for major elements by ion chromatography (IC) at the time of collection (Winston and Criss, 2004).

2.3. Lab methods

Spring grab samples were analyzed for Cl⁻ by titration using Hg(NO₃)₂ (Hach, 2012). Titration data were used to confirm the accuracy of our continuous monitoring data. Additionally, spring samples from the long-term archive were filtered and analyzed by IC (Metrohm Compact IC Pro Ion Chromatograph) because limited volumes were available. Titration precision was ± 13% and IC instrument precision was ± 2% based on duplicate samples. Major cations (Na⁺, Ca²⁺, Mg²⁺, and K⁺) in water samples were analyzed using a Perkin-Elmer Optima 7300DV Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) in accordance with the USEPA 200.7 Method (USEPA, 1994). Duplicates and Sigma Aldrich TraceCERT standards indicated a precision of ± 8% and an accuracy of ± 15% for the ICP-OES. H and O isotopes were measured with a Picarro L2130-i cavity ring-down spectrometer; instrument precision was ± 0.23‰ for δ¹⁸O and ± 0.04‰ for δD. The values are reported in the conventional manner, as δ¹⁸O and δD values that represent ‰ deviations from standard mean ocean water (V-SMOW; Craig, 1961).

2.4. Data analysis methods

2.4.1. GIS analysis

We estimated the recharge areas of Rockwoods Spring and Blackburn Spring using a 3-m resolution DEM (USGS, 2014c) in ArcMap 10.1. This approach is based on the assumption that the water table mimics the general shape of local topography, so that groundwater drainage divides approximately coincide with topographic highs (Eakin, 1966; Richardson et al., 2016). Although this assumption is not universally applicable and karst aquifers are particularly prone to recharge from unexpected sources, this method provides the best estimate of the spring recharge areas without undertaking an extensive dye tracing study. We also used a recharge area-discharge relationship for springs in Missouri (Criss, 2010) to guide the size of the recharge basins.

To estimate road salt application amounts, we calculated the lane-length of roads in each recharge basin (US Census Bureau, 2014). We obtained road salt application data (mass per lane-length per storm) for applications by the Missouri Department of Transportation, City of Wildwood, City of Webster Groves, and Rockwoods Reservation for 2008–2016. Local application data were not well correlated with national salt application (Table S1), so we were unable to use national data to estimate local application prior to 2008. The area of parking lots, private streets, sidewalks, and driveways within the springs’ recharge basins was determined by tracing these features using 15.3-cm resolution orthophotos (East-West Gateway, 2016). Private salt application data are difficult to obtain, so we assumed that these applications occurred at the same rate per area as municipal road applications. We also established upper and lower bounds for our salt application estimates by setting private application at half or double the rate of municipal applications (Howard and Haynes, 1993; Kelly et al., 2008; City of Madison, 2006; Meriano et al., 2009; Perera et al., 2013; Sassan and Kahl, 2007). Finally, we performed a supervised classification in ENVI 5.3 to evaluate land cover within each basin, including the proportion of impervious surfaces.

2.4.2. Hydrograph analyses

The hydrograph separation technique allows us to distinguish between sources of water during flooding. Spring discharge during flooding events is a combination of baseflow (“older” water in the basin) and event water (water recently added by the precipitation event; Lakey and Krothe, 1996; Toran and Reisch, 2013; Winston and Criss, 2004). During flooding, baseflow represents groundwater transported primarily via diffuse flow, while event water is rapidly transmitted through karst conduits. The fractional contribution of the baseflow to spring discharge (Xbaseflow) can be calculated using the concentration of a conservative tracer (C) as follows (Pinder and Jones, 1969):

\[
X_{\text{baseflow}} = \frac{C_{\text{spring}} - C_{\text{event}}}{C_{\text{baseflow}} - C_{\text{event}}} \tag{1}
\]

where \(C_{\text{spring}}, C_{\text{event}}, \) and \(C_{\text{baseflow}}\) are the tracer concentrations in spring water, event water, and baseflow, respectively. Tracers for hydrograph separations must be conservative and can only be used when there is a significant difference between the tracer concentrations in the precipitation and baseflow.

H and O isotopes are ideal tracers for hydrograph separations because the isotopic composition is an intrinsic property of the water molecule. However, other tracers such as SpC are also acceptable, as long as dissolved ions can be definitively attributed to baseflow or rainwater (Pellerin et al., 2008). Thus, SpC cannot be used for hydrograph separations during winter or early spring flood events because road salt increases the SpC of event water along its path to the spring. However, SpC-based separations can be used for summer and fall events when surface salt concentrations are lower, although flushing of salts from soils may reduce the accuracy of the calculation during the beginning of the flood.

We used both isotopic- and SpC-based hydrograph separations to assess the relative contributions of baseflow and event water to our springs. For isotope separations, a grab sample collected prior to the
start of rain event provided the isotopic composition of baseflow. The event water concentration was determined by isotopic analysis of precipitation samples for the event of interest. For SpC separations based on our continuous monitoring dataset, the SpC value 2 h prior to the start of rain was taken to be the baseflow value. A value of 0.054 mS/cm was used for the event water SpC based on analysis of local rainfall samples by Hasenmueller and Criss (2013). Given the relative difficulties of collecting physical isotope samples during every flooding response to rainfall (especially at Blackburn Spring where we did not have an autosampler) and that we had a continuous record of SpC for the springs, we used isotopic hydrograph separations to verify the accuracy of SpC-based separations for our study sites (Klaus and McDonnell, 2013). We then used our continuous SpC data to evaluate floods more extensively. Based on 59 samples from the two springs across six flood events, we found that the results of SpC-based separations were within 12% of the H and O isotope-based results. We did not perform hydrograph separations for winter and early spring floods due to the interference of road salt with the event water signature.

Lag times were also used to compare the hydrograph responses of the springs. We defined the lag time as the difference between the time of peak rain and the time of the first discharge peak during flood events. Longer lag times indicate a slower hydrologic response, while shorter lag times signify a flashier response.

### 2.4.3. First flush analysis

A first flush event occurs when salts stored in soil or on pavement are dissolved in early storm runoff and flushed into receiving waters, creating a transient increase in dissolved constituents at the start of a flood event. First flush events are quantified by comparing the normalized cumulative mass (the mass of Cl− transported up to the period of interest in the flood event divided by the total mass of Cl− transported during the flood event) to the normalized cumulative discharge volume (the volume discharged up to the period of interest in the flood event divided by the total flood volume) as the flood progresses (Bertrand-Krajewski et al., 1998; Kim et al., 2005; Lee et al., 2002; Saget et al., 1996; Sansalone and Buchberger, 1997; Stenstrom and Kayhanian, 2005). If the normalized cumulative mass exceeds the normalized cumulative volume, this means a disproportionately large amount of Cl− has been discharged early in the flood, which signals a first flush event. Therefore, when the normalized cumulative mass and volume are plotted against one another, deviations above the 1:1 line indicate first flush behavior. In addition to visually assessing deviations above the 1:1 line, we quantified first flush events by calculating the proportion of Cl− discharged in the first 20% of flood flow. We reported a first flush event if the cumulative mass ratio was >20% during that period. Although there is no physical significance to the first 20% of flow, this criterion has commonly been used to define the period in which a first flush occurs (Deletic, 1998; Kim et al., 2005; Stenstrom and Kayhanian, 2005).

### 2.4.4. Load calculations

Cl− loads were calculated by multiplying the discharge and Cl− concentration for each 5-minute interval and then summing these values over the season or year. There were some gaps in our Cl− and discharge datasets due to instrument failure and site vandalism, and it was necessary to account for these in our annual load calculations. For data gaps less than two days in length, we used a linear interpolation to fill in the Cl− or discharge values. For longer data gaps, we assigned the average discharge or seasonal average Cl− value to the missing time range instead. We defined a road salt year from November 1 to October 31 because local road salt application began in November of each year we examined. Thus, by defining the road salt year this way we were able to keep deicing activities for each winter together and group road salt applications with the subsequent recovery of shallow groundwater Cl− concentrations before the start of the next winter. Annual loads were calculated for the 2014–2015 and 2015–2016 road salt years at both springs, but only a rough estimate is possible for 2014–2015 at Blackburn Spring because of data loss due to site vandalism in 2016. Despite an incomplete dataset, we performed a coarse estimate for 2015–2016 Blackburn Spring Cl− export. In detail, after the discharge dataset ended in February 2016, discharge for February–October 2016 was estimated by scaling the average discharge from February–October 2015 to the amount of precipitation in February–October 2016 (compared to 2015 precipitation amounts). The continuous Cl− dataset ended in April at Blackburn Spring, and after this period we interpolated between lab measurements of Cl− from grab samples through July. For the period when no 2016 Cl− data was available (mid-July–October), we substituted the average Cl− value for this period in 2014 and 2015.

For our seasonal load comparisons, we defined the seasons as follows: winter as November 1–January 31, spring as February 1–April 30, summer as May 1–July 31, and fall as August 1–October 31. These seasonal definitions were selected so that winter coincides with the start of road salt season, but as a consequence, the early spring season contains some road salting activities as well. In particular, road salt applications continued through March in our study area during both 2014 and 2015. Despite road salting occurring during two “seasons,” we chose to define four seasons so that we could characterize intermediate salt transport timescales and the effects of seasonal changes in rainfall on salt transport.

### 2.4.5. Long-term dataset

The archive of grab samples (stored at room temperature in glass bottles until 2015) from Rockwoods Spring was tested to determine whether Na+ and Cl− in the samples had remained stable over time. To make this determination, we re-ran a subset of the spring sample archive which had already been analyzed for Na+ and Cl− at the time of collection (Winston and Criss, 2004). By comparing our new Na+ (ICP-OES) and Cl− (IC) results with the original geochemical data archive, we determined that Cl− in the samples had remained stable (±8%; Fig. S2a). This allowed us to obtain Cl− data for the entire archive of Rockwoods Spring samples from 1996 to 2011. Unfortunately, Na+ had not remained stable in the samples (±52%; Fig. S2b), likely due to leaching from the soda glass bottles, so we were unable to examine long-term Na+ trends. In addition to the long-term Cl− dataset, we had a record of SpC measurements that were taken at the time of sample collection (1996–2011).

In order to combine our continuous monitoring dataset (5-min intervals) with the archive dataset (approximately bi-weekly sampling) to assess long-term trends, we resampled the continuous monitoring data at a bi-weekly interval. In other words, instead of using the full continuous monitoring dataset, we selected a data point every two weeks so the temporal frequency of samples would be comparable with the rest of the long-term dataset. Furthermore, since different methods for Cl− analysis were used for the archive samples (IC) and the continuous Cl− data (YSI 6600 sonde), we developed a regression equation to compare Cl− measurements by IC and the continuous monitoring device ($R^2 = 0.92$; Fig. S3) and applied this to our resampled continuous monitoring dataset. We were then able to combine the datasets to assess Cl− and SpC trends from 1996 to 2016.

### 3. Results

#### 3.1. Basin characterization

Median discharge at Blackburn Spring was 12 L/s, with high flows of up to 680 L/s during our monitoring period (Fig. 2a). We used topographic analysis along with the average discharge to delineate an estimated recharge basin area for Blackburn Spring of 1.6 km² (Fig. 1) using a recharge-area-discharge relationship for springs in Missouri (Criss, 2010). Our classification indicates that the basin area consists of 36% impervious surfaces and 59% vegetative coverage, with the rest consisting of bare earth or open water (Fig. S4). The basin mostly
includes smaller roads, but also features a 2.8 km stretch of a major interstate (I-44). Roads account for 11% of the basin area, driveways and parking lots account for 7.8%, and sidewalks cover an estimated 2.1%.

The recharge area for Rockwoods Spring is estimated at 3.6 km² (Fig. 1) based on topographic analysis and the median discharge of 30 L/s (peak flows were as high as 310 L/s; Fig. 2a). Based on our classification, land cover within the basin is 96% vegetative coverage, 3% impervious, and 1% bare earth or open water (Fig. S4). Roads cover 1.4% of the basin area and 0.8% of the area is covered by other paved surfaces like driveways, parking lots, and sidewalks.

Because our basin delineations represent a best estimate of area (which we were unable to confirm for the scope of this study), our land cover results are vulnerable to local variability. To assess the impact of this vulnerability, we compared land cover within our estimated basin boundaries to that within square boundaries topographically up-gradient from each spring with an area predicted by the Criss (2010) recharge area-discharge relationship. Land cover results were within 1% for our estimated basins compared to the squares, confirming that the local land cover was well characterized despite uncertainties in the basin boundaries.

### 3.2. Continuous monitoring dataset

Hydrologic and geochemical monitoring results are shown in Fig. 2, including discharge (Fig. 2a), Cl⁻ applied through road deicing within the springs' estimated recharge basins (b), and SpC (c), Cl⁻ (d), and Na⁺ (e) values measured at the springs. An inset in d shows variability in Cl⁻ concentrations below 600 mg/L for Blackburn Spring. The USEPA chronic (230 mg/L; solid line) and acute (860 mg/L; dashed line) criteria for aquatic life are also included in d. Continuous monitoring results are shown in gray; circles indicate lab results and triangles denote field point measurements. Note that the scales for the various parameters are not always the same for the springs.

![Figure 2](image-url)

**Fig. 2.** Water quality monitoring results for Blackburn Spring (left panel) and Rockwoods Spring (right panel), including precipitation (NOAA, 2017b) and discharge (Q; a), Cl⁻ applied through road deicing within the springs' estimated recharge basins (b), and SpC (c), Cl⁻ (d), and Na⁺ (e) values measured at the springs. An inset in d shows variability in Cl⁻ concentrations below 600 mg/L for Blackburn Spring. The USEPA chronic (230 mg/L; solid line) and acute (860 mg/L; dashed line) criteria for aquatic life are also included in d. Continuous monitoring results are shown in gray; circles indicate lab results and triangles denote field point measurements. Note that the scales for the various parameters are not always the same for the springs.
between 3.1 and 70 mg/L over the course of the study (Fig. 2e). SpC was between 0.007 and 1.16 mS/cm and the median value was 0.67 mS/cm (Fig. 2c). Expectedly, Cl⁻ and Na⁺ were positively correlated with SpC for both springs (Fig. S5).

3.3. Flood response

3.3.1. Hydrologic response

We investigated the flood response for 68 events at Blackburn Spring and 31 events at Rockwoods Spring between August 2014 and January 2016. Fewer events were analyzed for Rockwoods Spring because its discharge responses were more attenuated, and therefore events causing multiple hydrograph responses at Blackburn Spring caused only a single (sometimes multi-peak) hydrograph response at Rockwoods Spring. The more gradual hydrograph response at Rockwoods Spring can be quantified by comparing the lag times for the springs. The lag time for Blackburn Spring is 3.6 h on average, while the average lag time for Rockwoods Spring is 15.9 h.

During the same period, SpC-based hydrograph separations were performed for 45 flood events at Blackburn Spring and 17 flood events at Rockwoods Spring, where floods from the first road salt event of the season through the end of March were excluded from separation analyses. By April, SpC-based hydrograph separations could be used because road salting had ended and no more Cl⁻ spikes occurred at Blackburn Spring. The average baseflow (weighted for discharge) was 38.8% of flood discharge at Blackburn Spring during the study period, compared to 71.3% at Rockwoods Spring.

3.3.2. Geochemical response

A typical flood response at both springs consisted of an overall decrease in Cl⁻ concentration and SpC due to dilution by event water, followed by a slower recovery to pre-storm levels. These dilution responses were observed during all summer and fall flood events, and during some winter and spring floods as well. The degree of dilution during flooding differed greatly between Rockwoods Spring and Blackburn Spring (Fig. 2c–e). In summer and fall, Cl⁻ dropped 128 mg/L on average during flood events at Blackburn Spring, with a maximum decrease of 346 mg/L in October 2015. At Rockwoods Spring, however, the average Cl⁻ dilution during summer and fall floods was only 33 mg/L, and the greatest dilution (85 mg/L decrease) was observed in August 2014. During many flood events at both sites, small increases in Cl⁻ loads occurred briefly at the beginning of the flood before the general dilution trend due to the first flush phenomenon (as Cl⁻ was flushed from soils; see Section 3.3.3). Loads subsequently decreased due to dilution by event water.

Following road salt application, the typical dilution effect observed during flooding was often reversed at Blackburn Spring because event water was saltier than baseflow. Thus, in some winter and early spring floods, increases rather than decreases in Cl⁻ and Na⁺ concentrations and SpC were observed at Blackburn Spring because of the dominance of event water at that site (Fig. S6). These events account for the large Cl⁻, Na⁺, and SpC maxima in January and March (Fig. 2c–e). Four such events were observed at Blackburn Spring between January and March 2015, with resulting Cl⁻ maxima ranging from 546 to 1342 mg/L. Although similar Cl⁻ and SpC maxima in early 2016 (up to 3881 mg/L Cl⁻) signal the same phenomenon, we are unable to verify the correspondence of these maxima with flood responses because our discharge data were lost due to the theft of our stage sensor. Nonetheless, precipitation records corroborate this explanation and point to six flood events between January and March 2016 in which Cl⁻ concentrations increased with discharge. The Cl⁻ load response was different for events in which Cl⁻ concentrations rose with flow: a sustained Cl⁻ load peak (rather than a brief Cl⁻ spike during the first flush) occurred during these winter and early spring events. No such extreme Cl⁻ spikes were observed at Rockwoods Spring during flood events in the winter and spring.

Flood response plays a major role in the transport of Cl⁻ in these springs, with 15.0% of the annual Cl⁻ load transported during flooding at Blackburn Spring and 32.4% at Rockwoods Spring during the 2014–2015 road salt year. Indeed, Cl⁻ is transported at a 20.8% and 56.1% greater rate during flood response than during baseflow at Blackburn Spring and Rockwoods Spring, respectively. Enhanced Cl⁻ transport during floods is largely a winter phenomenon: Cl⁻ transport during floods between January and March 2015 constituted 34.5% of annual stormflow Cl⁻ transport at Blackburn Spring and 27.0% at Rockwoods Spring.

Interestingly, the relationship between Na⁺ and Cl⁻ was different during flooding than during baseflow (Fig. 3). The molar Na⁺:Cl⁻ ratio is 1:1 in road salt, and yet during baseflow conditions, the slope of the Na⁺:Cl⁻ line was 0.71 for Blackburn Spring and 0.78 for Rockwoods Spring. During floods, the slope of the Na⁺:Cl⁻ line was 1.58 for Blackburn Spring, and for Rockwoods Spring, it was close to 1 at 0.96.

As with Cl⁻, more extreme variability in flood and seasonal pH response was observed at Blackburn Spring compared with Rockwoods Spring (Fig. S7). Indeed, the pH range of 5.6–9.1 at Blackburn Spring was much broader than at Rockwoods Spring (pH = 6.9–7.5). Although pH at Blackburn Spring showed some seasonal variability, with lower pH during times of higher biological productivity mainly in the summer months, most variation occurred during flood response. The pH decreased during flood responses, but this decrease was sometimes preceded by a transient pH increase at the start of the flood. These transient pH increases were common at Blackburn Spring but only occurred occasionally at Rockwoods Spring.

3.3.3. First flush events

In many flood events, the dilution effect was preceded by a transient increase in dissolved solids at the beginning of the flood response that represents a “first flush” of salt from soils (Lee et al., 2002). Fig. 4 shows the normalized cumulative Cl⁻ mass plotted against the normalized cumulative volume for all measured flood events at each site. Both sites show evidence of first flush behavior, with some curves plotting above the 1:1 line due to greater transport of Cl⁻ early in the flood response. However, this behavior is more pronounced at Blackburn Spring, where a majority of floods show a strong deviation above the 1:1 line. For Blackburn Spring, these large deviations above the 1:1 line occurred in all seasons, whereas for Rockwoods Spring, the strongest first flush events occurred during winter and spring (when road salt could have been flushed directly from pavement). Weaker first flush events at Rockwoods Spring were observed during summer and fall. Some deviations below the 1:1 line were also observed at both springs, indicating rapid dilution early in the flood response. Among the 62 Blackburn Spring flood events examined in this study (six were excluded from the flood dataset due to missing Cl⁻ data), 56 events included a first flush. The proportion of total flood-response Cl⁻ discharged in the first 20% of flow volume ranged from 8.6–68.6% for the 62 events examined. Over the study period, 30.5% of the total Cl⁻ transported during stormflow was transported in the first 20% of flow during the floods at Blackburn Spring in which a first flush occurred. Among 25 flood events at Rockwoods Spring (six were excluded due to incomplete data), 12.0–52.8% of Cl⁻ was transported in the first 20% of flow, and 22 events included a first flush. At Rockwoods Spring, 26.4% of total stormflow Cl⁻ was transported in the first 20% of flow during the floods in which a first flush occurred. No seasonal pattern was observed among the floods lacking a first flush response.

3.3.4. November 2015 flood event response

Of our many flood events, we selected one example in November 2015 that exemplifies typical flood behavior at each spring (Fig. 5). This event is the final flooding response observed in 2015 before road salting resumed for the winter. The flood occurred in response to 7.4 cm of rainfall between 08:00 on November 16 and 03:00 on
The most intense rainfall occurred at the end of the storm, with 3.0 cm falling between 17:00 on November 17 and 03:00 on November 18 (Fig. 5a).

The discharge response at Blackburn Spring included three major discharge peaks occurring 6.4 h, 21.0 h, and 36.2 h after the rain began in response to pulses of heavier rain. The first two peaks were each 54 L/s above baseflow discharge, and the third peak represented a 91 L/s increase from pre-storm flow conditions. Between these major peaks and after the third peak, the discharge recession was punctuated by a few minor increases in flow volume as the spring responded to increments of heavier rainfall (Fig. 5a). In contrast, the hydrograph response at Rockwoods Spring was much broader and only included one discharge maximum, which was 102 L/s higher than the pre-storm discharge and occurred 64.8 h after the rain started. The peak was followed by a gradual decline in discharge that lasted for 31.0 h (Fig. 5a).

Hydrograph separations show that baseflow accounted for 29.9% of the discharge over the course of the flood response at Blackburn Spring and 63.6% at Rockwoods Spring (Fig. 5a). At both springs, the baseflow appears to dominate the flow initially on the rising limb, but this is likely an artifact of the first flush effect, which complicates the use of SpC as a tracer.

Our normalized cumulative Cl$^-$ mass to volume calculations confirm the presence of a first flush during this flood, with 44.8% and 52.9% of Cl$^-$ delivered in the first 20% of flow at Blackburn Spring and Rockwoods Spring, respectively. At Blackburn Spring, the first flush manifested as transient spikes in Cl$^-$ during the sharp initial recession of this parameter due to dilution (Fig. 5b). At Rockwoods Spring, a slight increase in Cl$^-$ occurred during the first part of the rising limb of the hydrograph before Cl$^-$ concentrations decreased (Fig. 5b). At both springs, the impact of the first flush can be seen as peaks in the Cl$^-$ loads that occurred early in the flood (Fig. 5c). Both springs also showed a first flush of SpC (Fig. 5d), which mirrored the Cl$^-$ response (Fig. 5b), and major cations, with a peak in Na$^+$, Ca$^{2+}$, and Mg$^{2+}$ during the rising limb of the hydrograph (Fig. 5e).

This event also exemplifies the differences in the geochemical variability during flood response between the two springs. At Blackburn Spring, Cl$^-$ decreased by 137 mg/L to an initial minimum of 2.9 mg/L after 12.8 h, and then returned to this concentration in a second minimum after 42.2 h (Fig. 5b). The rate of Cl$^-$ dilution was rapid at the onset of flooding, with a decrease of 132 mg/L occurring over just 3 h. At Rockwoods Spring, the maximum Cl$^-$ dilution was only 45 mg/L. Cl$^-$ concentrations at Rockwoods Spring decreased more gradually, reaching a minimum of 4.4 mg/L after 50 h (Fig. 5b). The same dilution trends were seen in SpC and in the major cations. SpC decreased by 1.14 mS/cm at Blackburn Spring, but only by 0.33 mS/cm at Rockwoods Spring over the course of the flood response (Fig. 5d). Cations reached an initial minimum 13.1 h after the start of the Blackburn Spring response; Na$^+$ decreased by 74.2 mg/L, Ca$^{2+}$ decreased by 120 mg/L, and Mg$^{2+}$ decreased by 19.4 mg/L. Cations at Blackburn Spring reached a second minimum after 42.5 h, with concentrations within 1.3 mg/L of...
the first minimum (Fig. 5e). In contrast, it took 50.6–62.6 h for cations to reach their minimum values during the Rockwoods Spring flood response, with a total dilution of 32.9 mg/L for Na\(^+\), 20.3 mg/L for Ca\(^{2+}\), and 8.5 mg/L for Mg\(^{2+}\) (Fig. 5e).

### 3.4. Seasonal trends

When flood response periods are excluded, baseflow Cl\(^-\) concentrations at Blackburn Spring peaked in March (March average = 390 mg/L Cl\(^-\)) following the road salting season, but otherwise did not show any seasonal trend, with an average of 188 mg/L during the remaining months. Cl\(^-\) loads at Blackburn Spring varied seasonally (Fig. 6a), with only 213 kg/d exported in winter (November 2014–February 2015), followed by higher loads during spring (February–April 2015; 374 kg/d), and then declining Cl\(^-\) transport through summer (May–July 2015; 205 kg/d) and fall (August–October 2015; 107 kg/d). Note that road salt application occurred from November through March, and application was actually higher in spring than in winter (Fig. 6b). Patterns of Na\(^+\) concentrations were similar to those of Cl\(^-\), with maxima in the early spring and similar baseflow concentrations during the rest of the year. As with Na\(^+\) and Cl\(^-\), most variability in SpC occurred in response to floods, and baseflow values were relatively stable except immediately following salting season (Fig. 2).

At Rockwoods Spring, seasonal patterns in Cl\(^-\) concentrations were less dominated by spring flushing of road salt. Although Cl\(^-\) concentrations peaked in February and early March following road salting season, seasonal maxima also occurred during periods of low flow in the summer or fall (Fig. 2d). In fact, the months with the highest average baseflow Cl\(^-\) concentrations were October 2015 and July 2016, when discharge was low. Cl\(^-\) loads followed the same seasonal pattern as at Blackburn Spring for the 2014–2015 road salt year (Fig. 6a). In detail, during the 2014–2015 salting year, 118 kg/d was exported during winter, and Cl\(^-\) transport was highest in the spring at 180 kg/d, then loads declined in the summer (130 kg/d) and fall (56 kg/d). However, in 2015–2016, Cl\(^-\) loads at Rockwoods Spring were lowest in the winter (36 kg/d), and then comparable in spring (110 kg/d) and summer (124 kg/d), with only a small decline in the fall (87 kg/d; Fig. 6a). As at Blackburn Spring, Na\(^+\) (Fig. 2e) and SpC (Fig. 2c) at Rockwoods Spring varied with Cl\(^-\) (Fig. 2d), with maxima occurring both in March and during the summer or fall.

### 3.5. Inter-annual trends

#### 3.5.1. Annual mass balance using continuous monitoring data

Annual application and export of Cl\(^-\) was calculated for the 2014–2015 and 2015–2016 road salt years at both springs (Fig. 7), although the 2015–2016 export value for Blackburn Spring is only a rough estimate due to data loss. Our calculations show that the Blackburn Spring recharge basin received 66.2 t of Cl\(^-\) from deicing in 2014–2015, assuming that parking lots, driveways, and sidewalks were salted at the municipal application rate. If we assume private salt applications at half or double the municipal rate, this produces lower and upper bounds of 41.8 t and 115.0 t of Cl\(^-\) (Fig. 7). In 2014–2015, Blackburn Spring released 79.1 t of Cl\(^-\) (Fig. 7). Thus, unless private applications occur at a higher rate than municipal applications, our calculations show that Cl\(^-\) export from Blackburn Spring actually exceeded application for 2014–2015. Similarly, Blackburn Spring received 50.3 t of Cl\(^-\) (34.4–82.2 t with varying private application rates) in the 2015–2016 road salt year. Due to theft and vandalism at the Blackburn Spring site, our 2015–2016 Cl\(^-\) and discharge records are incomplete. However, we estimate that Blackburn Spring transported 59 ± 18 t of Cl\(^-\), based on 3.5 months of continuous discharge data and eight months of Cl\(^-\) data (with only biweekly grab samples for the last two months).

Export from Rockwoods Spring also exceeded applications for the 2 years we continuously monitored the spring. We estimate Cl\(^-\) application of 28.6 t (range for variable private application rates: 24.4–36.9 t) in 2014–2015 and 13.9 t (range for variable private application rates: 11.2–19.3 t) in 2015–2016 (Fig. 7). Rockwoods Spring released 42.5 t of Cl\(^-\) in 2014–2015, while in 2015–2016, Rockwoods Spring released 33.2 t of Cl\(^-\) (Fig. 7). Comparing the 2014–2015 data for the two springs, Cl\(^-\) release normalized to recharge basin area was 4.1 times higher for Blackburn Spring compared to Rockwoods Spring.

#### 3.5.2. Long term inter-annual trends at Rockwoods Spring

We combined historic SpC measurements and analysis of a sample archive for Cl\(^-\) with our 2014–2016 dataset to test for long-term geochemical trends at Rockwoods Spring. We found a small but significant increase in Cl\(^-\) (\(p = 0.028, n = 254\)) of 1.1 mg/L per year between 1996 and 2016 (Fig. 8a). Similarly, SpC increased 5.6 μS/cm per year over the 20-year period (\(p = 0.00097, n = 290\); Fig. 8b).

### 4. Discussion

#### 4.1. Hydrologic transport pathways control salt loads

The hydrologic pathways of shallow groundwater regulate the transport of dissolved salts and thereby determine temporal variations in Na\(^+\) and Cl\(^-\) concentrations during short-term flooding, seasonal, and inter-annual responses in karst spring systems. Shorter lag times and a higher proportion of event water at urban Blackburn Spring than rural Rockwoods Spring indicate important differences in hydrologic transport mechanisms. Here, we examine how hydrologic pathways control Na\(^+\) and Cl\(^-\) transport.

Longer lag times are characteristic of the larger recharge basin for Rockwoods Spring, and they also suggest a higher proportion of diffuse flow (Toran et al., 2009; Winston and Criss, 2004), as confirmed by our hydrograph separations. The higher proportion of event water at
Blackburn Spring is likely caused by both natural and anthropogenic factors. In karst settings, event water can be rapidly transmitted through conduits, bypassing slower, diffuse flowpaths through the aquifer. Although karst springs by their nature imply some extent of conduit flow, we believe that conduits are more prevalent in Blackburn Spring’s recharge basin compared to that of Rockwoods Spring. This hypothesis is supported by the presence of multiple sinkholes visible in topographic maps of the Blackburn Spring basin, indicating a high degree of karstification. These sinkholes can provide entry points for event water transmission to conduits, a process that may be exacerbated by high impervious surface area in urban settings. The high proportion of impervious surfaces in the Blackburn Spring basin may decrease in-hyder requiring infiltration and increase overland flow (Leopold, 1968) so that higher volumes of event water can be routed into sinkholes and conduits (Toran and Reisch, 2013), although Wiles and Sharp (2008) showed that joints and fractures in pavement substantially increase their permeability. In addition to the effects of natural karst features, urban areas are subject to anthropogenically-derived preferential flowpaths via “urban karst” where extensive installation of subsurface piping creates secondary porosity in the aquifer (Sharp et al., 2003). These pipes can also leak, increasing releases of stormwater to shallow groundwater during flooding (or drinking water or sewage releases during any flow condition; Christian et al., 2011). In the case of Blackburn Spring, abundant natural karst conduits, large areas of impervious surfaces, and subsurface piping likely increase the transmission of event water to the spring during flood events.

Because event water is rapidly delivered to Blackburn Spring through preferential flowpaths, this spring experiences extreme dilution of Cl⁻, major cations, and SpC during all summer and fall floods, as well as some winter and spring floods (Figs. 2 and 5). Conversely, the prevalence of event water also causes extreme increases in Cl⁻, Na⁺, and SpC during some winter and spring floods (Fig. 2). We found that the Cl⁻ concentration was only 0.2 mg/L in a Saint Louis, Missouri, rain sample during the November 2015 flood event discussed in Section 3.3.4, similar to the average Cl⁻ concentration of 0.6 mg/L in local rainfall (Hasenmueller and Criss, 2013). These results indicate minimal contributions of Cl⁻ from atmospheric deposition. Instead, high Cl⁻ concentrations in event water during winter and spring floods come from road salt dissolved along the flowpath. These post-salting flood responses in which Cl⁻ concentrations increase rather than decrease are important in transporting large amounts of Cl⁻ at Blackburn Spring (Fig. S6). These events are also ecologically significant as they are responsible for sudden exceedances of the USEPA acute exposure criterion for aquatic life (Fig. 2). Our findings at Blackburn Spring show that
for urban streams overlying aquifers with developed karst conduits or urban karst pathways, groundwater contributions will do little to buffer the geochemical variability of runoff during flooding the way they do in streams overlying single-porosity aquifers (Hasenmueller et al., 2016; Hasenmueller and Robinson, 2016).

At Rockwoods Spring, the dominance of diffuse flow buffers variations in salt concentrations during flood events. A higher proportion of diffuse flow also means that a higher proportion of road salt contamination is retained in the aquifer by slow transport. Frederickson and Criss (1999) estimated an overall water residence time on the order of 1 year for Rockwoods Spring based on isotopic analyses, but the residence time for water moving only by diffuse flow is likely longer. Therefore, Na⁺ and Cl⁻ can be retained for at least a year as they travel diffusely through the aquifer. Although the proportion of water transported by diffuse flow is smaller for Blackburn Spring than for Rockwoods Spring, it represents a significant mechanism for salt retention at both springs. Slow

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**Fig. 6.** Cl⁻ loads in spring water (a) and Cl⁻ applied through road deicing within the springs’ estimated recharge basins (b) by season at Blackburn Spring (dark gray) and Rockwoods Spring (light gray). Load results were determined from continuous in situ measurements of Cl⁻ and are reported as average rates in kg/day rather than t/season because some seasons contained data gaps.

**Fig. 7.** Annual Cl⁻ application (solid bars) and export (striped bars) for Blackburn Spring (dark gray) and Rockwoods Spring (light gray) for the 2014–2015 and 2015–2016 road salt years. The Blackburn Spring 2015–2016 Cl⁻ export value is depicted with a dashed outline because it represents a rough estimate due to limited data. Salt application data before our monitoring period (i.e., from 2008 to 2014) are shown for reference. Error bars demonstrate uncertainty in private application amounts: negative and positive error bars show Cl⁻ application estimates if private applications occur at half or double the municipal rate, respectively.
groundwater movement plays a large role in explaining elevated baseflow concentrations of Cl\(^-\), Na\(^+\), and SpC during the summer and fall (Fig. 2).

4.2. Retention in soils

Soils act as a temporary storage reservoir for salt before it is delivered to groundwater, and the mobilization of this salt manifests as a first flush event at the springs. At both sites, Cl\(^-\) first flush events occur year-round and represent an important mechanism for the transport of road salt contamination. A previous lab study showed that soils proximal to Rockwoods Spring and Blackburn Spring could retain Na\(^+\) and Cl\(^-\) for at least 2.5–5 months after road salt application (Robinson et al., 2017). Robinson et al. (2017) predicted that this timeline would be extended in the field due to more variable precipitation patterns and deeper soil profiles. Indeed, we observed first flush events indicating that salt was retained in recharge area soils for the entire non-salting portion of the year (mid-March to mid-November; Fig. 4). The fact that a first flush event occurred during the last pre-salting flood event in November 2015 (Fig. 5) highlights the year-round importance of soils as a reservoir for road salt contamination.

Robinson et al. (2017) also found that soils near Rockwoods Spring both initially retained salt more effectively and subsequently released it more quickly than soils near Blackburn Spring. The soils at urban Blackburn Spring are denser, finer-grained, and lower in organic matter (Robinson et al., 2017), likely because the topsoil has been disturbed through landscaping and construction of adjacent roads. Our field results are consistent with faster salt release rates from Rockwoods Spring soils, as first flush events at that site were less pronounced in the summer and fall than immediately following road salting season compared to Blackburn Spring (Fig. 4). We also observed more extreme first flush events at Blackburn Spring (demonstrated by deviations above the 1:1 line in Fig. 4a) compared to Rockwoods Spring. This is likely explained by higher road salt application rates at Blackburn Spring as well as physical differences between the basins: event water (containing salt flushed from soils or pavement) reaches Blackburn Spring more rapidly because 1) the smaller basin means a shorter travel distance and 2) preferential flowpaths are more prevalent. The delayed delivery of salt to groundwater due to retention in soils, coupled with the subsequent slow groundwater transport, explains the elevation of Cl\(^-\) and Na\(^+\) concentrations in shallow groundwater throughout the year.

We found that the Na\(^+\):Cl\(^-\) relationship differed based on first flush and flood response at both springs (Fig. 3), pointing to different soil retention processes depending on flow. During baseflow, the Na\(^+\):Cl\(^-\) slope was <1 for both springs because some Na\(^+\) was retained in soils on cation exchange sites, while Cl\(^-\) reached the spring more quickly because its movement in soils is more conservative (Dailey et al., 2014; Schweiger et al., 2015; Sun et al., 2012). During floods at Rockwoods Spring, the Na\(^+\):Cl\(^-\) slope was close to 1, indicating that Na\(^+\) was not retained as efficiently in soils and road salt contamination was more directly flushed to the spring. Unexpectedly, the Na\(^+\):Cl\(^-\) slope was >1 during floods at Blackburn Spring. The reason for this is unclear, but we hypothesize that H\(^+\) from acidic rainwater may have displaced Na\(^+\) from cation exchange sites during floods, releasing Na\(^+\) that had previously been retained in soils. Enhanced release of base cations has been observed in acid rain-impacted soils (Singh and Agrawal, 2008). However, since rainwater is equally acidic at our study sites, any difference in H\(^+\)-induced cation exchange would result from differences in soil properties such as the higher clay content near Blackburn Spring (Robinson et al., 2017). Alternatively, the dilute nature of rainwater may cause Na\(^+\) desorption from exchange sites at Blackburn Spring where Na\(^+\) content is higher in soils (Robinson et al., 2017). In either case, the release of base cations such as Na\(^+\) at the start of a flood response could explain the transient pH increases in the spring water, which were common at Blackburn Spring. More research is needed to explore Na\(^+\):Cl\(^-\) dynamics during flooding.

4.3. Annual retention and release

At both Rockwoods Spring and Blackburn Spring, our calculations showed Cl\(^-\) export exceeding application in the seasons (Fig. 6) and years examined (Fig. 7) examined. Although this is unusual among Cl\(^-\) mass balance studies, it is not unprecedented. From 1985 to 2005, Kelly et al. (2008) found that Cl\(^-\) discharged in a New York stream exceeded Cl\(^-\) inputs to its watershed in 14 of the 20 years studied, particularly at the beginning of the study period. It is unlikely that we found higher export than application because of overestimated Cl\(^-\) loads since these values were determined by continuous monitoring. In fact, it is likely that Cl\(^-\) loads were underestimated in the urban Blackburn Spring basin because some salty stormwater was likely diverted into the sewer system (Toran et al., 2009).

There are several potential explanations for our unusual finding of higher Cl\(^-\) export than application. One possibility is that we underestimated road salt application because our basin delineations underestimated the total area and/or impervious surface area of the recharge basins. This is plausible since groundwater divides do not necessarily coincide with topographic divides, and karst aquifers in particular are subject to recharge from unexpected sources. However, we are confident that the recharge basins are approximately the correct size based on the recharge area-discharge relationship established for proximal springs in Missouri by Criss (2010). Our recharge basin delineations may have also underestimated the impervious area due to variable densities of impervious surfaces. However, when we selected a square with the same total area as our estimated recharge basins, land use metrics did not vary >1%. Another potential problem could arise if our estimates of private road salt application were too low. Information about the salting of parking lots is notoriously difficult to obtain and it would be...
nearly impossible to gather data on individual residential applications. Therefore, private applications create significant uncertainty, particularly in highly urbanized areas. For this study, we follow the lead of past researchers by assuming application rates half to double the municipal rates (Howard and Haynes, 1993; Kelly et al., 2008; City of Madison, 2006; Meriano et al., 2009; Perera et al., 2013; Sassan and Kahl, 2007).

Alternatively, it is possible that Cl<sup>-</sup> export truly is higher than Cl<sup>-</sup> application for the years we studied. Although it would be impossible for outputs to exceed inputs on a long-term basis, it is entirely possible that the Cl<sup>-</sup> residence time in these basins is > 1 year and that the extra Cl<sup>-</sup> export we see in our study years is leftover from previous years. The winter of 2013–2014 (just before our monitoring dataset began) had below average winter temperatures (NOAA, 2017a) and application of deicing salts was ~32–193% higher than during our study years (Fig. 7). If the 2013–2014 salt was not completely flushed from the basins before the start of winter 2014–2015—which is supported by the year-round elevation of Cl<sup>-</sup> concentrations and occurrence of first flush events—then this salt would be expected to arrive at the springs during 2015 and possibly 2016 as well. We also observed delays in Cl<sup>-</sup> release between seasons (Fig. 6), further supporting this idea. If this is the case, then our finding of higher Cl<sup>-</sup> export than application underscores the importance of Cl<sup>-</sup> retention within these karstified basins. Cl<sup>-</sup> transport is limited first by infiltration rates and any non-conservative Cl<sup>-</sup> retention in soils (Robinson et al., 2017), then by groundwater flow rates. Additionally, episodic release from soils during flood response continues to supply salt to the shallow groundwater throughout the year.

Although Cl<sup>-</sup> residence times exceed 1 year in these karst basins, a higher proportion of applied Cl<sup>-</sup> may be flushed from karst aquifers compared to single porosity aquifers because a higher proportion of applied Cl<sup>-</sup> can be released through karst conduits. Since a Cl<sup>-</sup> mass balance for a shallow groundwater basin has not been performed before, we compare our results to Cl<sup>-</sup> loads in streams. Novotny et al. (2009) found that the watersheds of 10 streams in the Minneapolis-Saint Paul, Minnesota, metropolitan area received 8–80 t Cl<sup>-</sup>/km<sup>2</sup> (compared to Blackburn basin’s 40.2 t Cl<sup>-</sup>/km<sup>2</sup>), but only 3–32 t Cl<sup>-</sup>/km<sup>2</sup> were exported annually (Blackburn Spring’s export was substantially higher at 48.0 t Cl<sup>-</sup>/km<sup>2</sup>). Although it appears that karst conduits accelerated some Cl<sup>-</sup> release from the Blackburn Spring basin compared to non-karst urban watersheds, storage of Cl<sup>-</sup> in soils and diffuse groundwater flow still prevented fullflushing of the aquifer between road salting seasons. Therefore, karst aquifers are still subject to increasing baseline salt levels despite the presence of rapid flowpaths.

### 4.4. Increases in baseline Cl<sup>-</sup>

Cl<sup>-</sup> concentrations and SpC at Rockwoods Spring are highly variable due to seasonal variations and variable flow conditions, but a significant increase in these parameters is nonetheless apparent from 1996 to 2016 (Fig. 8). Our observed Cl<sup>-</sup> increase of 1.1 mg/L per year in shallow groundwater is comparable to the 1.5 mg/L annual Cl<sup>-</sup> increase observed by Kelly et al. (2008) in a rural New York stream from 1985 to 2005. In another New York stream, Godwin et al. (2003) observed a Cl<sup>-</sup> increase of about 1.7 mg/L per year from the 1950s to the 1990s, but the rate slowed to 1.0 mg/L per year from 1990 to 1998. However, the rate of Cl<sup>-</sup> increase at Rockwoods Spring is much lower than that found by Perera et al. (2013), who estimated a baseline Cl<sup>-</sup> increase of 6 mg/L per year in a Toronto area catchment. Overall, we found that despite enhanced flushing of salt through karst conduits, Cl<sup>-</sup> accumulated in our rural karst basin at a rate similar to or slightly lower than rates observed for other aquifer types.

The increase in SpC is driven by the increase in Cl<sup>-</sup> (and presumably also Na<sup>+</sup>); which is caused by 1) increased road salt application and/or 2) partial retention of Cl<sup>-</sup> from road salt within the basin. Local road salt application data are not available before 2008, so we cannot confirm whether an increase in application rate has occurred. However, based on qualitative comparison of aerial photos from the past 20 years, there have been no substantial changes in paved area within the Rockwoods Spring basin. The lack of new development, combined with the fact that temperatures during salting season (November–March; snowfall data was not available) have actually increased during this period, leads us to believe that an increase in road salt application over this period is unlikely.

The second explanation for the Cl<sup>-</sup> increase is more compelling. We assert that Cl<sup>-</sup> concentrations at Rockwoods Spring increased over time, despite similar road salt application rates, because the Cl<sup>-</sup> contamination from the previous winter’s road salt was not fully flushed from the recharge basin before road salting resumed in the next winter. This created a buildup of “legacy” Cl<sup>-</sup> in the shallow groundwater and soils which prevented the spring from returning to normal baseline Cl<sup>-</sup> concentrations during the non-salting season, even in years when road salting was minor. This explanation is consistent with the elevation of Cl<sup>-</sup> at Rockwoods Spring above unimpacted Missouri spring levels through the summer and fall (Kleeschulte and Sutley, 1995) and with the presumed year-round storage of Cl<sup>-</sup> in soils based on first flush events. It also supports our assertion that the excess Cl<sup>-</sup> exported in 2014–2015 and 2015–2016 represents “legacy” Cl<sup>-</sup> from an earlier salting season in 2013–2014.

To our knowledge, a long-term salt increase has never before been documented in a karst aquifer. The ability of karst conduits to rapidly transmit contamination might be expected to facilitate efficient enough flushing to exempt karst aquifers from the long-term salt increases observed in other groundwater settings (Cassanelli and Robbins, 2013; Kelly, 2008). However, our results indicate that even in an aquifer with significant preferential flowpaths, Cl<sup>-</sup> retention in soil and via diffuse groundwater flow extends the impact of road salt from a winter phenomenon to a year-round threat to ecosystems which will continue to grow in the future.

### 5. Conclusions

Short-term flooding, seasonal, and long-term hydrologic and geochemical responses in springs elucidate several fundamental findings about the mechanisms and multiple transport timescales governing road salt contamination in karst aquifers. Preferential flow through the aquifer delivers salt to springs within hours or days, while slower diffuse flow through the rock matrix delays salt delivery over timescales of months to years. Additionally, release of salt retained in soils episodically supplies additional salt to the shallow groundwater during flood responses throughout the year. Long-term salt increases in shallow groundwater result from retention and consequential buildup of salt within recharge basins.

Cl<sup>-</sup> retention in soils is indicated by first flush events, which we observed at both springs throughout the year. Cl<sup>-</sup> is not completely flushed from soils in either basin between road salting seasons; instead, soils episodically release salt to the shallow groundwater during floods. Event water (delivered via preferential flowpaths) dominated flood responses at Blackburn Spring, where baseflow (delivered via diffuse flow) only accounted for 38.8% of total stormflow, compared to 71.3% at Rockwoods Spring. The high proportion of event water at Blackburn Spring is explained by rapid delivery through karst conduits, reduced infiltration due to impervious surfaces, and potentially the urban karst phenomenon. Prevalence of event water creates more variability in Na<sup>+</sup>, Cl<sup>-</sup>, and SpC during flood response, with extreme dilution during summer and fall floods, and rapid salt increases during some winter and spring floods. Consequently, shallow groundwater contributions from highly karstified aquifers (or those dominated by anthropogenic preferential flow) are less effective at buffering salt concentrations in urban streams. The large chemical variations in the days following a flood event are superimposed on seasonally-varying baseline concentrations supplied by diffuse flow.

A Cl<sup>-</sup> mass balance showed that Cl<sup>-</sup> export from both springs actually exceeded road salt application within their recharge basins annually from
2014 to 2016. The excess exported Cl− is interpreted to be residual salt retained in the basin from previous winters. Incomplete flushing of “legacy” Cl− from catchments between salting seasons leads to long-term Cl− increases over time. Indeed, Cl− at Rockwoods Spring has increased by 1.1 mg/L per year over the past 20 years. Salt buildup in the subsurface is significant because this salt can be transported via baseflow to lakes and streams, where elevated Cl− concentrations have deleterious ecosystem impacts.

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Appendix A. Supplementary data

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References


