

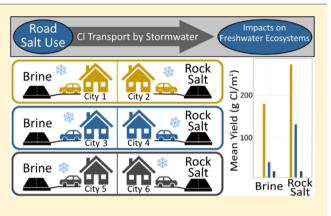
Comparison of Contributions to Chloride in Urban Stormwater from Winter Brine and Rock Salt Application

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Supporting Information

ABSTRACT: The use of road salt to increase roadway safety during winter storms releases high concentrations of chloride into urban and suburban stormwater. This stormwater flows into nearby streams, resulting in concentrations of chloride that can exceed water quality standards intended to protect aquatic life. As chloride pollution is not readily filtered by soil or plants, mitigation will require reductions in the amount of salt used. In this study, cities in St. Louis County, Missouri, U.S., were used as a test case for brining as a best management practice (BMP) to reduce salt use relative to the standard practice of spreading solid rock salt. The practice of brining involves the dissolution of road salt in water and the application of the resulting brine solution to roadways in advance of a forecasted winter storm. During the winters of 2016-2017 and 2017-2018, stormwater runoff from



residential areas was monitored in paired cities to determine if the availability of brining as a BMP for salt application on residential roads would result in a decrease in chloride in stormwater and, therefore, a decrease in chloride reaching urban streams. The use of brining by city governments resulted in a 45% average reduction of chloride loads conveyed to streams, demonstrating that brining is a highly viable BMP for local municipal operations.

■ INTRODUCTION

Since the 1940s, road salt has been applied to pavement to facilitate the melting of snow and ice across the United States (U.S.), with these applications reaching a current rate of over 20 million tons per year.¹ This practice is now common in countries throughout the world where winter temperatures fall below freezing. While salt application has become a common practice for public safety, several compelling reasons to reduce the use of road salts have been identified. Salt is highly corrosive to transportation infrastructures (roads and bridges) and motor vehicles.^{2,3} Accumulation of salt in groundwater is causing concerns regarding the sodium content and potability of drinking water supplies,^{4,5} and high chloride concentrations in source water may contribute to costly damage to drinking water infrastructures.⁶ Additionally, road salt is toxic to species in terrestrial⁷⁻¹⁰ and aquatic¹¹⁻¹⁴ ecosystems that receive chloride-laden stormwater.

Increases in stream chloride concentrations caused by road salt have resulted in violations of water quality standards that are intended to protect aquatic life in the U.S. and Canada.^{15,16} In the U.S., such violations may result in the inclusion of waterbodies on the state list of impaired waters,¹⁷ which has consequences for stormwater permits issued to stormwater managing authorities (e.g., state departments of transportation and local departments of public works). Under Phase II stormwater permitting associated with the U.S. National Pollutant Discharge Elimination System (NPDES) program,

regulatory agencies may require permit holders to enact a set of minimum control measures, including increased stormwater monitoring and the implementation of pollution prevention measures and best management practices.

Several best management practices (BMPs) have been developed and implemented to reduce the amount of salt needed for winter snow and ice removal. BMPs utilizing geothermal heat, incidental heat from wastewater, solar heat, or electrically generated heat are used on a small scale to reduce icing on bridges, sidewalks, and runways.¹⁹ Prewetting of solid rock salt is a BMP that accelerates the onset of snowmelt and increases the adherence of salt to the pavement; this practice is most effective at reducing total salt use with dry snow, after plowing, and when a high rate of salt application is needed.²⁰ A variety of technological BMPs may be incorporated into salt spreaders (e.g., GPS systems and temperature sensors) to improve the accuracy and efficiency of anti-icing (ice prevention) and deicing (ice removal) activities.²¹ The antiicing BMP of brining involves the application of dissolved salt (\sim 23% solution by weight) to pavement in advance of winter storms. Brining has been shown to prevent bonding of snow and ice to the pavement and decrease the time it takes to clear

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the pavement while at the same time decreasing costs and reducing the frequency of accidents.²¹ Brining has also been demonstrated to provide a greater proportion of residual salt on the pavement than rock salt, preventing salt from being dislodged by traffic in the hours following application and increasing the duration of the beneficial melting period.²² Michael Fitch et al.²³ modeled the environmental life cycle costs of three types of winter road treatments (rock salt, brine, and calcium magnesium acetate) and found that brine application had the lowest overall environmental burden for energy use, greenhouse gas emissions, water use, and biological oxygen demand and a 36% reduction in chloride use compared to solid rock salt.

Several prior studies have examined the use of brine on highway systems^{22,24,25} or on parking lots and sidewalks.²⁶ To date, there has been no quantification of the ability of these practices to reduce salt use on urban roadways maintained by local communities, despite the greater density of salted roadways in urban landscapes and the resulting threats to infrastructures and large networks of aquatic habitats.

The objective of this study is to investigate whether the use of salt brine on urban roads results in a reduction of chloride transported to streams via stormwater systems. This is accomplished by examining loads of chloride in stormwater in three pairs of cities within St. Louis County, Missouri, U.S.; in each pair, one city uses brining technology, while the other relies on solid rock salt. We hypothesize that cities using brine will contribute less chloride to stormwater systems during winter storm events.

METHODS

Study Sites. The transport of chloride in stormwater was studied in six cities in St. Louis County, Missouri, U.S. (Figure 1). The St. Louis area has a moist temperate climate and receives approximately 116 cm of precipitation annually; winter precipitation averaging 38 cm may fall in the form of rain, freezing rain, sleet, snow, or a combination.²⁷ Few winter storms result in snow and ice remaining on the landscape for

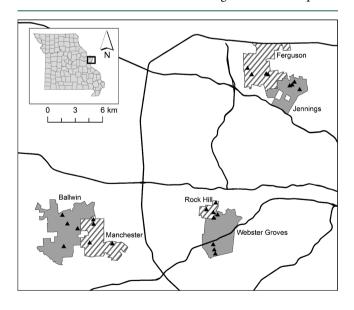


Figure 1. Sampling locations (triangles) in study cities in Missouri, U.S., that use brine (gray) and those without brining technology (striped diagonally). Interstate highways are represented by black lines.

more than 3 days. There is no season-long snow cover, development of winter snowpack, or associated spring melting period that is typical in colder or mountainous regions.

Three cities in this study (Ballwin, Jennings, and Webster Groves) have adopted the use of brine anti-icing pretreatment practices to prepare roadways for winter storms and then follow-up as needed with rock salt application and/or plowing. Three other cities (Manchester, Ferguson, and Rock Hill) located adjacent to the brining cities were selected for comparison as these municipalities rely solely on rock salt application and/or plowing to treat roads for winter precipitation. Thus, this study implements a matched pairs design with three replicates. Residential areas of each city were studied to exclude the influence of salt application in commercial and industrial zones with large areas of heavily used sidewalks and parking lots.

We recognize that adjacent cities are not necessarily similar in land use and socioeconomic characteristics, which can influence the rate of application and transport of salt across the landscape. To address this issue, pairing of adjacent cities was based on local variation in land use and socioeconomic variables (e.g., city revenue, per capita income, and density of development) that might impact salt use within city limits (e.g., city salt budget, resident expectations for road conditions, and likelihood of residents to use salt on private driveways and sidewalks). To confirm the similarity of the neighboring paired cities, a principal component analysis (PCA) was conducted on 13 demographic, economic, and land use metrics (Tables S1 and S2). The PCA includes the six study cities and three non-study cities of comparable size in St. Louis County as an outgroup.

Within each of the six cities, sampling was conducted at four locations within the stormwater system for two winters (December to April): 2016-2017 and 2017-2018. The same sampling locations were used in both winters except for one location in Webster Groves in 2016-2017, which was determined to have a contributing drainage area (hereafter termed pipeshed) an order of magnitude smaller than the other locations in the study. Data from this site were excluded and the site was replaced with one of appropriate size in 2017-2018. Pipeshed drainage area for each site was defined as the land area contributing to each stormwater inlet feeding into the stormwater system up-gradient of the monitoring location. ArcGIS (ESRI, Redlands, CA, U.S.; version 10.4.1) was used to delineate pipesheds using LiDAR topographic data (1.4 m resolution) from the Missouri Spatial Data Information Service (MSDIS). Stormwater inlet and pipe locations were provided by the Metropolitan St. Louis Sewer District. Pipesheds were field-verified to allow adjustments for inaccuracies in the LiDAR data and recent changes in the built environment. Pipesheds ranged in size from 1.84 to 17.1 hectares (Table 1).

Road salt application data for the two winters of the study were provided by the six study cities as part of their annual stormwater permit reporting and include date of salt application, temperature, amount and type of precipitation, estimated salt application rate, lane-miles of pavement salted, and total salt used. This format was selected to allow public works departments to work with familiar documentation for the purpose of improving consistency in reporting among cities.

Data Collection and Analysis. In each stormwater sampling location (Figure 1), electrical conductivity (μ S/cm), temperature (°C), and pressure (kPa) were recorded in

Table 1. Ranges of Pipeshed Characteristics in Each City^a

city	pipeshed (hectares)	impervious area (%)	road area (%)	roadway (lane-miles)
Manchester	5.2-14.6	23.3-36.7	6.8-11.9	0.52-1.50
Ballwin*	5.2-13.0	32.0-38.2	8.0-13.0	0.75-1.74
Ferguson	7.0-12.5	29.9-35.5	7.9-13.8	1.61-2.51
Jennings*	1.8-16.7	29.8-37.6	3.9-12.3	0.32-2.86
Rock Hill	3.6-17.1	30.8-37.1	7.7-12.1	0.71-1.97
Webster Groves*	8.9-13.9	31.4-33.4	9.5-12.6	1.79-2.60
a (*) .	1			

^{*a*}Asterisk (*) indicates cities where brine is used.

each stormwater pipe at 5 min intervals using data loggers (HOBO Freshwater Conductivity Data Logger U24-001 and HOBO Freshwater Level Data Logger U20-001-04, Onset, Bourne, MA, U.S.). Loggers were secured using wire rope and held in place with the assistance of sandbags. Pressure readings were used to calculate water depth within each pipe. Measurements of barometric pressure were made in each pair of cities using a data logger installed in the stormwater access pipe above the conveyance pipe to enable air pressure compensation in water depth calculations within the HOBOware Pro software (Onset, Bourne, MA, U.S.). HOBOware Pro was also used to convert conductivity readings to specific conductance (conductivity normalized to 25 °C) and to calibrate conductivity based on specific conductance measurements from monthly grab samples. Manning's equation was used to estimate continuous flow using water levels, a roughness coefficient of 0.015 for concrete pipes, pipe diameter, and slope (Table S3). Flow and specific conductance data were uploaded to the Water Quality Portal (https://www. waterqualitydata.us/) and are publicly available for download.

In piped stormwater systems, blockages may cause water to pool at the sensors or groundwater may infiltrate pipes, causing baseflow-type water level data that are not the result of storms. The baseflow separation function R package EcoHydRology²⁸ was used with parameters at default settings to perform a recursive digital filter hydrograph separation on the flow dataset to remove such baseflow data.

Chloride concentrations were determined in monthly stormwater grab samples using the silver nitrate method (Hach method 8207; range: 10 to 10,000 mg Cl⁻/L). Quality assurance for chloride measurements included field blanks, field duplicates, laboratory duplicates, and laboratory standards. Paired specific conductance and chloride measurements from the grab samples were plotted following the work of Granato and Smith.²⁹ When chloride is present at low concentrations, the contribution of other ions to specific conductance can confound a simple linear regression. As a result, piecewise linear regression was used to account for interference from other ions found in urban stormwater. The breakpoint in the data was identified by finding the split point in the transition zone that resulted in the lowest mean squared error for the two resulting linear models. The linear equations were then used to convert measured specific conductance into estimated chloride concentrations (hereafter termed chloride data).

Flow and chloride data were multiplied for each 5 min interval and then summed to determine chloride loads for each pipeshed during each winter as a whole and during specific storm events. Chloride loads were standardized by roadway area to determine the yield as the mass of chloride conveyed per square meter of road (g Cl^-/m^2). For this study, winter was defined as the period beginning 2 days prior to the first precipitation event that resulted in salt application in study cities and ending 20 days following the last precipitation event for which salt use was reported by the cities. This resulted in winter study periods of December 14, 2016 to March 30, 2017 and December 4, 2017 to April 26, 2018. Chloride yields were averaged across the pipesheds within a city and summed separately for each winter.

In addition to season-long chloride yields, yields for individual storm events were calculated to exclude low-flow periods. Site-to-site differences in non-storm conveyance were substantial and included inputs from groundwater intrusion, residential sump systems, and construction activities. It is well documented that chloride loads attributable to groundwater intrusion are delivered via stormwater pipes outside of winter storm periods.^{30,31} The chloride in urban groundwater is primarily accumulated residual salt, including salt applied in prior years, and, in our study area, this likely includes salt dating from before the recent adoption of brining in two cities.³¹ As these loads of accumulated chloride are reflective of land use history and may mask differences generated by current BMP use, we restrict the interval to storm periods.

Storm events were identified based on a combination of local weather data and storm flow data. Precipitation data were downloaded from NOAA Climate Data Online (https://www. ncdc.noaa.gov/cdo-web/) for 10 active weather stations located within or near the study area (Table S4). Precipitation and flow data were summarized on a daily basis and evaluated to identify dates in which precipitation was reported at multiple weather stations and flow was noted in all paired cities. Storms were excluded if they were not present in all three pairs. Chloride data were evaluated over the first 48 h of each storm. Based on visual inspection of the data, event flow rarely lasted more than 12 h, coinciding with the short duration of the storms and rapid snowmelt. In the rare instances when the storm and/or runoff persisted for a longer period, the 48 h period was considered appropriate in order to meet our stated objective of evaluating the effectiveness of brine as an anti-icing BMP. Individual storms that last more than 48 h would result in solid rock salt application to maintain clear roads, and thus further chloride measurements would not be evaluative of the BMP.

Severe cold weather in early January 2018 caused over 1300 water main breaks in St. Louis County, including at least six recorded within the study pipesheds. Such breaks resulted in artificially increased flow and often required rock salt applications for public safety. As these non-storm deposits of salt are not informative to our goal of evaluating brining as a BMP and the application of salt was uneven among pipesheds, storms in January 2018 were not evaluated due to the likelihood of spurious results.

Nine storm events were identified in the study period (Table 2). Data from each sampling site and storm period were evaluated to eliminate records that suggested inaccuracies. In particular, individual sites that did not register flow during a storm were excluded for that storm event. Data were excluded from Jennings/Ferguson on December 16, 2016 and Ballwin/ Manchester on February 17, 2018 due to a lack of flow in one city of the pair, which suggested that the storm did not encompass both cities. Data were also missing from individual sites during two storms due to equipment failure. This resulted

Table 2. Mean Chloride Yield (g Cl^-/m^2 road) Conveyed through the Stormwater System during Each 48 h Storm Event and the Differences in Yield between the Paired Cities^{*a*}

City	12/16/	12/22/	1/13/	1/18/	2/7/	3/9/	12/22/	2/17/	3/5/	Total
	2016	2016	2017	2017	2017	2017	2017	2018	2018	mean
										yield
Manchester	107;	333;	1675;	35.0;	26.8;	8.7;	0.4;	-	0.02;	2186
	88.7	250	2199	38.6	40.7	10.8	0.5 (4)		0.03	
	(4)	(4)	(4)	(4)	(4)	(4)			(4)	
Ballwin	85.8;	328;	904;	27.7;	72.3;	0.01;	2.9;	-	0.3;	1421
	78.8	200	445	31.9	67.0	0.02	4.1 (4)		0.5	
	(4) *	(4) *	(4) *	(4)	(4)	(3) *			(4)	
Difference	21.2	5.5	771	7.3	-45.5	8.7	-2.6		-0.3	
Ferguson	-	41.0;	93.2;	4.6;	5.8;	2.6;	3.7;	2.5;	0.1;	154
		48.0	69.0	6.3	9.6	4.3	4.9 (4)	3.4	0.1	
		(4)	(4)	(3)	(3)	(3)		(2)	(4)	
Jennings	-	88.3;	47.9;	2.4;	1.7;	0.9;	2.9;	11.6;	1.5;	157
		51.1	60.1	4.1	3.3	1.9	4.4 (4)	13.2	2.6	
		(4)	(3)	(3)	(4)	(4)		(2)	(3)	
Difference		-47.4	45.4	2.3	4.1	1.6	0.7	-9.1	-1.4	
Rock Hill	131;	182;	816;	7.4;	7.0;	2.9;	6.8;	12.1;	2.4;	1168
	218	171	1067	7.4	2.5	5.7	10.0	8.1	4.2	
	(4)	(4)	(4)	(4)	(4)	(4)	(4)	(2)	(3)	
Webster	99.9;	64.1;	184;	0.9;	1.5;	0.4;	0.7;	0.7;	0.3;	353
Groves	136	52.0	175	1.2	1.3	0.7	1.3 (4)	1.1	0.4	
	(2)	(3)	(3)	(2)	(3)	(3)		(3)	(4)	
Difference	30.7	118	631.9	6.5	5.4	2.4	6.1	11.5	2.2	

"Standard deviation is reported in italics, and the number of stormwater sites contributing to the mean is reported in parenthesis. Gray shading of positive differences indicates storms in which stormwater from the brining city conveyed less chloride per square meter of roadway than the paired non-brining city. Asterisks indicate instances when the city of Ballwin reported using brine as part of the treatment for the storm.

in a dataset of calculated chloride yields from 177 site-by-storm combinations (Table 2).

The mean chloride yields for each storm event within each city were compared among paired cities using a linear regression with a 95% confidence interval (n = 25 city pair by storm combinations). While the linear regression was used to identify the significance of the correlation between chloride yields from paired cities, this approach does not identify if the relationship included a tendency for the brining city to deliver a significantly lower yield than the non-brining city. Therefore, a Wilcoxon signed-rank test (one-tailed) was applied to the paired values for each storm to determine if the difference between mean chloride yields from brining and non-brining cities was greater than zero. Any resulting differences were quantified as a percent difference: 1 - (sum total mean yield for non-brining cities). All statistical analyses were performed in R.³²

RESULTS AND DISCUSSION

Community Similarity. The results of the PCA support the city pairings in our experimental design. In particular, economic, demographic, and land use metrics indicate that the pairs of neighboring cities selected for this study were more similar to each other than to other cities in St. Louis County (Figure 2). The first two PCA axes accounted for 76.5% of the variance among cities. The first PCA axis, accounting for 48.8% of the variation, had strong associations with demographic (median age and percent white [as defined by the U.S. Census Bureau]), educational (percent with bachelor's degree), and economic metrics (percent unemployed, median household income, per capita income, and percent owner-occupied residences); all of these metrics had a positive association

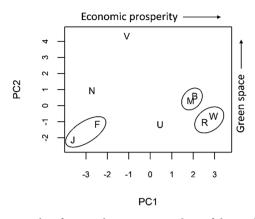


Figure 2. Results of principal component analysis of the similarity of nine cities in Missouri, U.S. The three pairs of cities used in the study are circled. PC1 is dominated by economic and demographic variables and accounts for 48.8% of the variance, while PC2 is dominated by population density and land use variables and accounts for 27.6% of the variance (B = Ballwin, M = Manchester, F = Ferguson, J = Jennings, R = Rock Hill, W = Webster Groves, V = Valley Park, N = Bellefontaine Neighbors, and U = University City).

except percent unemployment (Table S5). The second PCA axis accounted for 27.6% of the variation and had strong associations with population density (population per km^2) and land use metrics (percent low density development, percent forest, and percent impervious surfaces); these metrics had a negative association with the exception of percent forest (Table S5).

The similarity of the paired cities and their residents with regard to socioeconomic and demographic characteristics suggests that the average behavior of individuals in one city may be more similar to the average behavior of individuals in the adjacent paired city than to the average behavior of individuals in a non-paired city. It is well documented that the behavior of individuals in a community and the community expectations for individual behavior have a reciprocal impact on each other, such that individuals will tend to conform to social norms (for example, whether to shovel or salt sidewalks).^{33,34} This is not intended to suggest that individual differences in behavior are unimportant, but rather that, by our pairing of cities with similar characteristics, we expect that differences in individual behavior should be minimized.

Regression of Specific Conductance and Chloride. Specific conductance readings from grab samples ranged from 0.23 to 19.91 mS/cm. Associated chloride measurements ranged from 7 to 7150 mg Cl⁻/L). Specific conductance readings from the data loggers ranged from 0 to 37.955 mS/ cm. Less than 1.9% of the dataset had a specific conductance of >19.91 mS/cm. The relationship between specific conductance and chloride in stormwater grab samples was well described by the piecewise linear model (Figure S1). The model determined that the breakpoint between the two linear regressions occurred at 2.44 mS/cm. Equation 1 (adjusted $R^2 = 0.79$; n = 198) was applied when the specific conductance is <2.44 mS/cm; otherwise, eq 2 (adjusted $R^2 = 0.996$; n = 24) was applied

$$Cl^{-} = 195 \times \kappa - 77.4 \tag{1}$$

$$CI^{-} = 382 \times \kappa - 427 \tag{2}$$

where κ is the specific conductance (mS/cm).

Stormwater Chloride Yields. Chloride yields delivered during the nine identified storms in the winters of 2016–2017 and 2017–2018 are shown in Table 2. Of the nine storm events studied, the storm that began on January 13, 2017 resulted in the greatest stormwater chloride yield in five of the cities. The chloride conveyed for this storm accounted for over 60% of the chloride measured across all nine storms for four of the cities.

The storms that coincided with known brine applications are noted in Table 2; this information was not available from Jennings or Webster Groves. Yields measured in the cities of Manchester and Ballwin were the highest overall. In five of the eight storms recorded in this pair, the brining city, Ballwin, conveyed smaller yields than Manchester. The three instances when stormwater runoff from Ballwin had higher chloride yields coincide with storm events for which they did not report using brine as a pretreatment.

In Webster Groves, which uses brine, less chloride was delivered per square meter of road than in the neighboring Rock Hill for all nine storms. For many storms, the yield in Webster Groves was less than a quarter of that in Rock Hill.

Jennings and Ferguson had similar yields of chloride for this 2 year period. The lack of difference between the chloride yields in Jennings and Ferguson may be explained by several factors. First, the microclimate in this pair may have substantial differences relative to the other pairs. The intensity of winter storms in this area of St. Louis County tends to be decreased, possibly due to the proximity of these cities to the confluence of the Missouri River and Mississippi River. It is possible that these large waterways serve to thermally buffer the air in the vicinity and thereby lead to a decrease in frozen precipitation. Second, while these cities were similar to the other two pairs with regards to population density and land use (Figure 2, PC2), they were at the opposite end of the PCA with regard to economic and demographic characteristics (Figure 2, PC1). In addition, the brining member of the pair, Jennings, was at the furthest end of PC1, suggesting that it was the least economically wealthy of the nine cities evaluated. This suggests that economic factors may play a role in the effectiveness of brining as a BMP. It is unknown whether this is due to the level of road-clearing service expected by city residents, the capacity of these cities to provide services due to budgetary restrictions, or some other factor.

Linear regression models for chloride yield in the three pairs of cities for each storm revealed a strong correlation between chloride transport in cities that use brine and those that do not (Figure 3; p < 0.0001; adjusted $R^2 = 0.887$), with brining cities conveying 45% less chloride in the first 2 days of a winter storm event. The 95% confidence interval for this regression indicates that the relationship is well above the 1:1 line for storms requiring more than minimal salt use. The potential for undue influence of the data point in the upper right of Figure 3 was evaluated by the removal of this point and reanalysis of the data. Removal of this data point resulted in no qualitative change to the results and the confidence interval remained above the 1:1 line (Figure S2).

The Wilcoxon signed-rank test was used to evaluate the difference between non-brining cities and brining cities on a per-storm basis. The significant difference (p = 0.027) verified that stormwater runoff from the brining cities contains less chloride per unit of road area than stormwater from cities that do not utilize brining as a BMP.

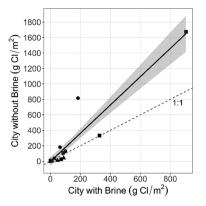


Figure 3. Linear regression with 95% confidence interval of chloride yields in cities that use brine versus those without brine. Each point represents the chloride yield from a pair of cities during an individual storm event (triangles: Ferguson/Jennings; squares: Manchester/Ballwin; circles: Rock Hill/Webster Groves). The dashed 1:1 line represents equal chloride transport from paired cities. Points falling above the dashed line represent instances when cities with access to brine conveyed less chloride than those that only use solid rock salt.

Evaluation of season-long chloride yields for paired cities results in the generation of six data points. This dataset is too small to evaluate for significant differences, but the trend was similar to the regression shown in Figure 3 for two of the three city pairs (Figure S3).

City Salt Use. Prior studies of chloride associated with stormwater have been conducted using models with no field testing,²³ at the parking lot scale under highly controlled conditions, 20,35 at the highway scale in non-urban settings, 22,24,25,36 or within a single watershed. 37,38 While such studies are informative during the development and initial deployment of a new technology or BMP, brining as a BMP has moved beyond this phase and requires full-scale field tests of its implementation. The aim of this study was to evaluate the use of brining across multiple municipalities within a region. Data collected from stormwater pipes in cities across St. Louis County indicate that the availability of brining as a BMP for city public works departments results in a decrease in the amount of chloride conveyed through the stormwater system. This finding is noteworthy, particularly given the importance of accurate forecasting of weather and road conditions. Surveys of winter maintenance practitioners and consultants in 2005 and 2014 found that adoption of brining and other anti-icing practices has been slowed by concerns about the accuracy of forecasting and the importance of these forecasts in selecting the best material to apply to roads for the anticipated conditions.³⁹ In climatic regions like St. Louis where winter temperatures often hover near 0 °C, the successful use of appropriate BMPs depends heavily on the ability to accurately forecast the timing and form (rain vs sleet or snow) of precipitation events. Our results support the efficacy of brining as a BMP, even in a region where it may be difficult to predict the form that winter precipitation will take.

Detailed records of municipal salt application in cities that apply brine can be used to demonstrate differences in salt use. McCullouch²⁵ used rock salt and brine application records to develop estimates of cost effectiveness for this BMP for the Indiana Department of Transportation. In four of the six highway districts studied, brine application resulted in a decrease in salt use; use for the salting methods was approximately equal in the other two highway districts.²⁵

Table 3. Total Chloride Yields during the Nine Winter Storms Included in the Study and Total Salt Application Reported	by
the Cities through the Two Winters of the Study Period ^a	

city	road area (km² pavement)	stormwater chloride (g Cl ⁻ /m ² road)	reported rock salt use (tons)	reported salt for brine use (tons)	reported application (tons/km² road)
Manchester	1.2	1143	690		576
Ballwin	1.8	736	1461*	145	873
Ferguson	1.2	73	739		605
Jennings	0.85	85	43	**	50**
Rock Hill	0.27	617	144		541
Webster Groves	1.5	173	681	29	489

"Single asterisk (*) indicates the exclusion of 365 tons of rock salt applied in association with water main breaks in 2018; other cities did not report salt applied for this purpose. Double asterisks (**) indicates that, while records include the use of brine, the amount applied was not reported and therefore cannot be factored into the total.

These results are similar to our findings that the use of brine either displayed a positive effect or no effect on salt use/ chloride yield. However, our study does not attempt to develop a chloride budget based on the salt use reported by each city or the collected stormwater data (Table 3) because, despite the use of standard forms, the cities each reported salt use differently. For example, Ballwin was the only city to report salt use in association with water main breaks and Jennings reported instances when brine was applied during one winter, but not the amount of material used. Development of budgets on a pipeshed basis would also be complicated by the fact that reported salt use is for the city as a whole and does not detail how many passes were made on any given street.

Creation of city-wide chloride budgets is also challenging because a portion of the roadways in each city are operated and maintained by external municipalities, including the Missouri Department of Transportation and St. Louis County Department of Transportation (note that these areas were excluded in our selection of the monitored pipesheds). Application of salt to commercial and residential parking areas and walkways is difficult to predict and is expected to be highly variable among cities. In addition, discharges from uncovered salt piles in commercial areas can contribute greatly to chloride loads. The importance of such discharges was demonstrated in February 2018 when in-stream chloride concentrations of over 20,000 mg/L in a St. Louis County stream were traced to an uncovered salt pile (Haake, unpublished data). Finally, salt use in cities is not necessarily limited to storm events, as witnessed in January 2018 when water main breaks throughout the region led to extensive nonstorm salt use. Of the six cities in this study, only Ballwin reported salt used for this purpose. The high degree of uncertainty associated with the above sources makes developing an accurate chloride budget in these cities not possible.

Prior studies have used salt application data to generate a chloride budget across urban landscapes and found chloride retention on the landscape of over 50%.^{37,40,41} This retention is attributed to chloride that is held in lakes and wetlands, moves into groundwater, or is retained in soils. Within the residential areas included in this study, there were no lakes, wetlands, or stormwater basins that would receive runoff from the roadways. Chloride retention is lower and conveyed loads are higher in areas with curb-and-gutter drainage relative to areas with open drainage channels.³⁷ This may have had a minor influence on the results for two non-brining cities (Manchester and Ferguson), as one pipeshed in each city included some roads with roadside swales leading to

stormwater inlets rather than curb-and-gutter configurations, potentially increasing infiltration and reducing the stormwater chloride yield. However, as these are both non-brining cities, this underestimation of chloride yield would cause the 45% reduction in transported chloride yield with the use of brine to be a more conservative estimate of chloride reduction.

The cities participating in this study are independent political units representing populations with different socioeconomic status, resources, and culture. Care was taken to minimize such differences between paired cities. Meanwhile, differences remained among the three pairs, both in terms of metrics used in the distance matrix (Figure 2) and the measured chloride loads (Table 3), with greater chloride loads in more economically prosperous cities. The differences among the cities are demonstrated in part by the investment in brining technology. Jennings purchased their system in 2009 for \$16,517, an investment that paid for itself in the first winter of use.⁴² Webster Groves purchased a brining system in 2013 for approximately \$115,000 with the expectation that it would reduce employee overtime costs and cut salt use by 20-40%.⁴³ Ballwin spent approximately \$161,000 for a brining system in 2015 and reduced overtime wages by approximately \$20,000 per year.⁴⁴ Reductions in overtime wages are attributable to the ability of road crews to apply brine during normal work days, while winter storms do not conform to conventional business hours.

Water quality standards for chloride have been developed, but exceedances of those standards are common in urban areas during the winter. In St. Louis County, 16 segments of 14 streams consistently fail to meet state water quality standards for the protection of aquatic life due to excessive chloride from road salt, representing 3.4% of all impaired waters listings for the state.⁴⁵ Such listings often have consequences for stormwater permitting, particularly in the form of minimum control measures that set guidelines for measures expected of permit holders. For example, the current permit for the primary stormwater authority in St. Louis County requires that municipal salt applicators report their salt use and any utilization of alternative deicing strategies to reduce the amount of salt applied.⁴⁶ However, improvements to water quality will require action beyond monitoring of salt use. Based on the present study, the use of salt brine is an effective BMP that allows cities to reduce the load of chloride delivered to streams by stormwater systems.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b02864. Data used for analyses in this study are archived at DOI: 10.5281/zenodo.3458258.

Regression of specific conductance with chloride, municipal characteristics evaluated via PCA, individual stormwater site characteristics, and sources of local weather data (PDF)

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Notes

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