

Effect of Road Salt Application on Seasonal Chloride Concentrations and Toxicity in South-Central Indiana Streams

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Contemporary information on road salt runoff is needed for management of water resources in regions experiencing urbanization and increased road density. We investigated seasonal Cl^- concentrations among five streams in south-central Indiana that drained watersheds varying in degree of urbanization and ranging in size from 9.3 to 27 km^2 . We also conducted acute toxicity tests with *Daphnia pulex* to assess the potential effects of the observed Cl^- concentrations on aquatic life. Periods of elevated Cl^- concentrations were observed during the winters of 2007–08 and 2008–09 at all sites except the reference site. The highest Cl^- concentration observed during the study was 2100 mg L^{-1} and occurred at the most urbanized site. The Cl^- concentration at the reference site never exceeded 22 mg L^{-1} . The application of road salt caused large increases in stream Cl^- concentrations, but the elevated Cl^- levels did not appear to be a significant threat to aquatic life based on our toxicity testing. Only the most urbanized site showed evidence of salt retention within the watershed, whereas the other sites exported the road salt relatively quickly after its application, suggesting storm drains and impervious surfaces minimized interaction between soils and salt-laden runoff. During winter at these sites, the response in stream Cl^- concentrations appeared to be controlled by the timing and intensity of road salt application, the magnitude of precipitation, and the occurrence of air temperatures that caused snowmelt and generated runoff.

NATURAL AND ANTHROPOGENIC SOURCES contribute Cl^- to aquatic systems (Feth, 1981; Kelly et al., 2008). Atmospheric deposition and rock weathering are natural sources of Cl^- , and the magnitude of these sources is dependent on geographic location and geologic setting (Kelly et al., 2008). In agricultural areas, the application of potassium fertilizer in the form of KCl can elevate background Cl^- concentrations in groundwater (e.g., Böhlke, 2002). Wastewater treatment plants and septic systems can be significant Cl^- sources in highly urbanized areas (Novotny et al., 2009), but in many temperate locations the application of deicers provides the majority of Cl^- inputs (Kelly et al., 2008; Peters and Turk, 1981). During winter months in northern latitudes, deicers are often applied to impervious surfaces such as roads, walkways, and parking lots to keep these areas clear of snow and ice. Deicers typically are composed mainly of a chloride salt, such as potassium, magnesium, calcium, or sodium chloride. Due to the low cost and ease of use and storage, NaCl, or rock salt, is the most commonly used deicer (Ramakrishna and Viraraghavan, 2005). Since it was first adopted in the 1950s, road salt use has increased dramatically, with current sales in the United States exceeding 15 million metric tons annually (The Salt Institute, 2008).

Urbanization increases the amount of impervious surfaces within a watershed, which in turn reduces infiltration and accelerates storm water runoff (Booth and Jackson, 1997; Paul and Meyer, 2001). Air temperatures above freezing after salt application can facilitate salt transport to streams, particularly through storm drains (Scott, 1980). Urbanization thus increases the amount of area that requires deicer application and also increases the potential for the deicer to be transported to surface waters. In the upper midwestern United States, it is projected that population and developed lands will increase 80 and 20%, respectively, by 2025 (Alig et al., 2004). This projected increase in urbanization could result in salinization of surface waters and groundwater in the midwestern United States, as has been reported in the northeastern United States (e.g., Godwin et al., 2003; Kaushal et al., 2005; Kelly et al., 2008). There are few published reports of Cl^- concentrations from midwestern streams despite widespread use of road salt. To our knowledge, the only published data on road salt runoff in Indiana are from a wetland adjacent to a major highway (Wilcox, 1986). Contemporary information on road salt

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Abbreviations: LC_{50} , median lethal concentration.

runoff is needed for improved management of water resources in the face of increasing urbanization.

Chloride can detrimentally affect aquatic life, but the concentration that elicits an effect varies widely among taxa and life stages. For example, 870 mg Cl⁻ L⁻¹ was lethal to fathead minnow embryos (Evans and Frick, 2001), whereas for several aquatic invertebrates the 96-h median lethal concentration (LC₅₀) values were between 5000 and 10,000 mg Cl⁻ L⁻¹ (Benbow and Merritt, 2004). It is estimated that about 10% of aquatic species would be negatively affected by long-term exposure to a Cl⁻ concentration of 240 mg L⁻¹ (Evans and Frick, 2001). The USEPA reports that “freshwater aquatic organisms and their uses should not be affected unacceptably if the 4-d average concentration of dissolved Cl⁻, when associated with Na⁺, does not exceed 230 mg L⁻¹ more than once every 3 yr on the average and if the 1-h average concentration does not exceed 860 mg L⁻¹ more than once every 3 yr on the average” (USEPA, 1988). The USEPA recommendations are not enforceable standards, and the state of Indiana does not regulate Cl⁻ as a water pollutant. Overall, daphnids (water fleas) appear to be among the most sensitive groups to high Cl⁻ concentrations; therefore, we used a daphnid to examine toxicity of Cl⁻ in the present study. Our rationale for this approach was that a concentration that is not harmful to daphnids would be unlikely to affect other aquatic taxa.

Many studies have focused on the fate of chloride ions originating from deicers, but less is known about the fate of the sodium ions (Jackson and Jobágy, 2005). If Na⁺ and Cl⁻ enter streams through surface run-off, the ions should be present in a molar ratio of 1:1, whereas a subsurface flow path would allow interaction with soil where Na⁺ could displace other cations and result in an in-stream molar ratio of less than 1:1. Sodium thus offers a means to identify the flow path of Cl⁻ as it moves from the landscape to surface waters. The goals of our study were to compare seasonal Cl⁻ concentrations among a group of streams that vary in degree of urbanization and to determine if the measured Cl⁻ concentrations were potentially toxic to aquatic life based on acute toxicity tests. We expected Cl⁻ concentrations to peak in the winter months as a result of road salt application and that storm drains and overland flow would be the dominant flow paths.

Materials and Methods

Site Descriptions

Research was conducted at five sites in south-central Indiana. Watershed boundaries at each sampling site were determined using the Owl-Hymaps online watershed delineation tool (Choi et al., 2005). Shapefiles of each watershed were imported into ArcGIS (ESRI, Redlands, CA), and watershed areas were determined. Land cover information from the 2001 National Land Cover Database (USGS, 2001) was clipped to each watershed boundary. Individual land cover polygons were summed

according to the land cover class, and the percentage of each type of land cover in the watersheds was calculated by dividing the total area of a land cover class by the watershed area. Road density (km km⁻²) in each watershed was determined with GIS as described above using a road density data layer (IGS, 2005).

The sites were located within 20 km of each other and represent a gradient in urbanization. The sites are labeled in order of increasing development as Site 1 through Site 5 (Table 1). Site 1 was a reference site on a small ephemeral stream in a sparsely populated, rural watershed northwest of Ellettsville, Indiana. Site 2 was located on Turtleback Creek, also near Ellettsville, in a rural/suburban watershed that contains residential developments but no commercial or industrial areas. Sites 3 and 4 were located on Jack's Defeat Creek in a developing suburban area with a population of approximately 6000 and a population density of 390 per km² (U.S. Census Bureau, 2009). Site 5 was located on Clear Creek in Bloomington, Indiana, which has a population of approximately 72,000 and a population density of 2150 per km² (U.S. Census Bureau, 2009). Discussions with municipal managers indicated the dominant deicer used on public roadways in the study region was NaCl, either as rock salt or as the main ingredient in commercial deicers. Other forms of deicers could have been used on private drives and parking lots.

Hydrological Monitoring

Discharge was measured continuously at Site 4 using a stilling well, HOBO pressure sensors (Onset Computer, Inc., Bourne, MA), and a rating curve developed during the study. Precipitation was monitored with tipping bucket rain gauges installed at locations throughout the study area. Two to five rain gauges were in operation throughout the study, and precipitation data presented here are averaged values across all available rain gauges. The rain gauges were not heated; therefore, precipitation in the form of snow and ice was not recorded until air temperatures were above freezing, which usually occurred within 24 to 48 h of winter storms. Air temperature was obtained from the Indiana State Climate Office.

Table 1. Watershed and land cover characteristics for each of the study sites.

	Site 1	Site 2	Site 3	Site 4	Site 5
Watershed characteristic					
Latitude, °N	39.25155	39.22881	39.22869	39.23833	39.12171
Longitude, °W	86.67486	86.61865	86.61797	86.62219	86.53723
Watershed size, km ²	9.3	4.8	17.5	27.0	20.8
Road density, km km ⁻²	2.1	5.0	4.3	4.8	10.9
Land cover, % of total watershed area					
Developed, open space	4.6	12.9	9.7	11.7	28.5
Developed, low intensity	0.3	1.7	4.0	3.7	27.9
Developed, medium intensity	0	0	2.0	1.6	17.1
Developed, high intensity	0.2	0	0.4	0.3	5.0
Total developed area	5.1	14.6	16.1	17.3	78.5
Forest	26.3	42.4	39.8	40.7	13.8
Shrub and grassland	2.0	0.5	2.9	3.0	1.3
Pasture	25.9	30.1	32.8	30.5	6.3
Crop	40.7	12.4	8.3	8.4	0.1

Water Chemistry Sampling

Water sampling began in September 2007 at Sites 2, 3, and 4; sampling at Sites 1 and 5 began in January 2008. Site 1, the reference site, was ephemeral and did not flow from August to November 2008. Samples of stream water were collected through a combination of grab sampling and automated sampling using ISCO portable samplers (Teledyne Technologies, Inc., Lincoln, NE). Grab samples were generally collected weekly during the winter and at least monthly during other seasons. Automated samples were collected every 2 to 6 h over a period of several days during winter storm events. All samples were filtered through Whatman GF/F filters (nominal pore size = 0.7 μm) in the field or at the laboratory after first rinsing the filter with sample water. Filtered samples were refrigerated and processed within a month. Chloride concentrations were determined on a Lachat QuikChem 8500 Flow Injection Analyzer (Hach, Loveland, CO) using the USEPA-approved Lachat method 10-117-07-1-A. The detection limit for Cl^- was 0.6 mg L^{-1} . Samples with Cl^- concentrations above the method range (300 mg L^{-1}) were diluted with deionized water and reanalyzed. Blank samples (deionized water) and commercial standards with known chloride concentrations of 10 and 100 mg L^{-1} were analyzed approximately every 10 samples as part of quality assurance protocol. In addition, field blanks and field duplicates were routinely collected and analyzed.

To investigate the relationship between Cl^- and Na^+ , we collected samples at Site 4 from a storm that occurred during 18 and 19 Dec. 2008. Samples were collected every 2 h using an automated sampler, and Cl^- concentrations were determined as described above. We focused on two cations, Na^+ and Ca^{2+} , and expected the concentration of Ca^{2+} to be unaffected by the application of road salt (NaCl). Cation samples were filtered (as for Cl^-) and acidified using one drop of 16.8 mol L^{-1} nitric acid. The concentrations of Na^+ and Ca^{2+} were determined on a Leeman Labs PS950 ICP-AES with a CETAC U5000AT+ Ultrasonic Nebulizer (Teledyne Leeman Labs, Hudson, NH) at the Indiana University-Purdue University Indianapolis Biogeochemistry Laboratory. Samples were diluted until the measurements were within the range of the calibration curve for each cation.

Chloride Toxicity Testing

Acute, 48-h tests were conducted to determine the LC_{50} value of NaCl on *Daphnia pulex*. This organism was selected due to its susceptibility to pollutants (e.g., Shaw et al., 2006). Daphnids used in this study were obtained from a laboratory culture that originated from an ephemeral pond in Oregon (Shaw, 2006). Daphnids were maintained in an artificial freshwater medium, termed COMBO (detailed by Kilham et al., 1998), with moderate hardness and a pH of 7.6. Culture and test organisms were held inside an incubator at 20°C with a photoperiod of 16 h of light and 8 h of dark.

Acute tests were conducted using two different test solutions, COMBO and filtered Site 4 stream water. Stream water was filtered through Whatman GF/F and 0.45- μm filters and aerated during storage. Daphnids used in the stream water toxicity tests were acclimated to filtered stream water from Site 4. Acclimation involved rearing at least three clutches in the

filtered stream water before the toxicity tests. Test solutions were prepared no more than 24 h before the test using reagent grade NaCl. Ten neonates were added to 30-mL borosilicate vials containing test solution. Three replicates per concentration or control were included in each test. Calculated test concentrations included 1.0, 1.5, 2.0, 2.5, and 3.0 $\text{g Cl}^- \text{L}^{-1}$ in COMBO and 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 5.5, and 10.0 $\text{g Cl}^- \text{L}^{-1}$ in stream water. Actual Cl^- concentrations were determined as described above. Test concentrations varied from the calculated Cl^- concentrations by an average of less than $\pm 1\%$. Acute tests with COMBO were conducted on 19 Aug. and 6 Nov. 2008. Acute tests with stream water were conducted on 6 Nov. and 9 Dec. 2008 and 29 Jan. 2009. Mortality in the control groups was <10% in all tests.

Acute (48-h) testing was conducted with filtered stream water from Sites 4 and 5 to determine if stream water with high Cl^- concentrations after road salt application would elicit mortality in *D. pulex*. The test was conducted on 5 Feb. 2009 using stream water collected during a storm event earlier that week. The water samples were collected at the time of peak Cl^- concentrations for that storm event; COMBO laboratory water was used as a control. Stream water samples and the control were analyzed in triplicate as described above.

Data Analysis

The Cl^- data were divided into two seasons: winter (1 December through 15 March of the following year) and nonwinter (16 March through 30 November of the following year). The delineation of seasons was based on air temperature and the application of road salt (all road salt applications occurred in the winter season). Differences among sites were examined with one-way ANOVA after \log_{10} transformation of the Cl^- concentrations using SPSS Version 17 (SPSS, Chicago, IL). Tukey's HSD was used for post hoc pairwise comparisons.

To obtain a robust LC_{50} for reagent grade NaCl in COMBO laboratory water and Site 4 filtered stream water, data from the various tests were pooled for analysis. All median lethal concentrations were determined using USEPA Probit Version 1.5 (USEPA, Washington, DC).

Results

Urbanization and Seasonal Cl^- Concentrations

Watershed sizes of the study sites ranged from 9.3 to 27 km^2 . Total developed area within the watershed of each site ranged from 5.1% at the reference site (Site 1) to 78.5% at Site 5 (Table 1). Road density tended to increase with increasing percentage of developed area, with a minimum road density of 2.1 km km^{-2} at Site 1 to a maximum at Site 5 of 10.9 km km^{-2} (Table 1).

Distinct spikes in Cl^- concentrations were observed during the winters of 2007–2008 and 2008–2009 at all sites except Site 1 (Fig. 1). Descriptive statistics for the winter and nonwinter samples are summarized in Table 2. The highest Cl^- concentration observed during the study was 2100 mg L^{-1} and occurred at Site 5, the most urbanized site (Table 2). Peak Cl^- concentrations at Sites 3 through 5 routinely exceeded 100 mg L^{-1} during winter storms, whereas Site 2 did not exceed 77 mg L^{-1} (Fig. 1). At Site 1, the reference site, Cl^- concentrations did

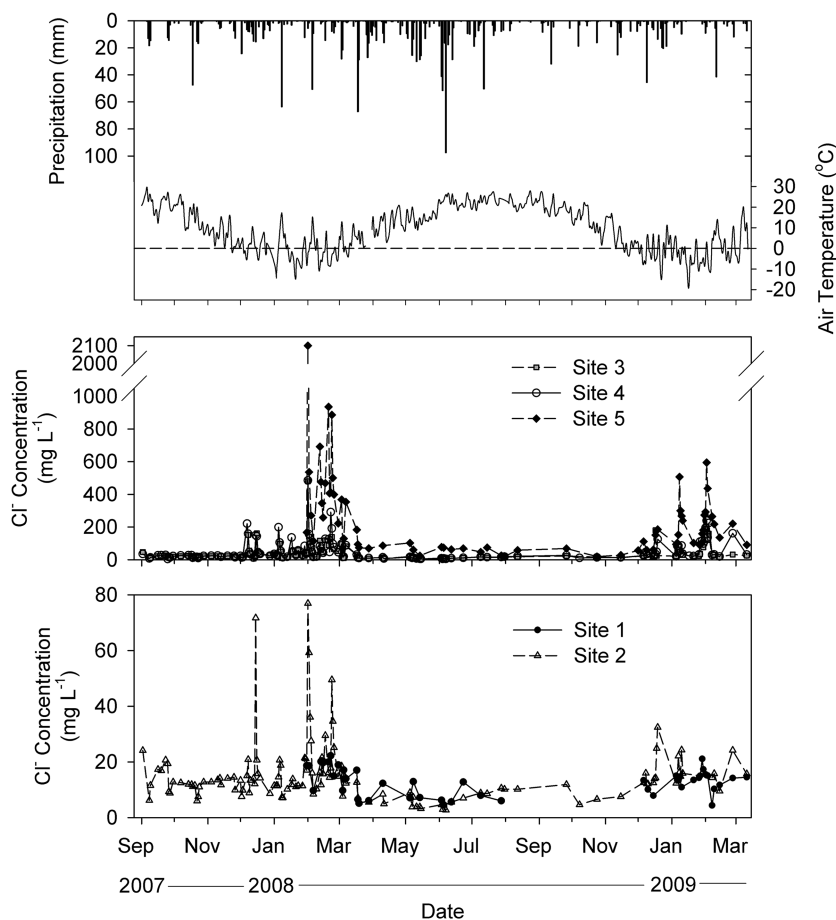


Fig. 1. Precipitation, air temperature, and in-stream Cl^- concentrations at the study sites from September 2007 through March 2009. Note the difference in scale for Cl^- concentration between the center and lower graphs.

not exceed 22 mg L^{-1} . Peak Cl^- concentrations were always associated with winter storms and the application of road salt (K. Gardner, personal observation). Large precipitation events during the summer did not affect Cl^- concentrations (Fig. 1). Across sites, there was a two- to threefold increase in median Cl^- concentrations between the nonwinter and winter samples. The minimum Cl^- concentration during winter was $<15 \text{ mg L}^{-1}$ in all sites but Site 5, which had a winter minimum of 56 mg L^{-1} (Table 2). Chloride concentrations varied significantly among sites during the winter periods based on ANOVA ($F_{4,180} = 39.88$; $P < 0.005$) (Fig. 2). Post hoc comparisons indicated that Sites 1 and 2 were significantly lower in Cl^- than the other sites and that Cl^- in Site 5 was significantly greater than all other sites (Tukey's HSD, $P < 0.05$).

The load of Cl^- in Jack's Defeat Creek (Site 4) approached or exceeded $10,000 \text{ kg d}^{-1}$ on several occasions during the study period (Fig. 3). During winter, increased Cl^- concentrations contributed to the high Cl^- loads, whereas high loads during the summer (e.g., June 2008 in Fig. 3) were the result of increased water volume with little change in Cl^- concentration. Because the Cl^- load in the stream was not proportional to discharge, we could not interpolate between dates on which Cl^- concentration was measured to determine a total Cl^- export from the watershed. However, during the winter of 2007–2008 our sampling captured nearly all of the road salt application and run-off events. Summing the calculated

loads gives a Cl^- export of 263,500 kg, which equates to an export of at least 670,000 kg of NaCl from the Site 4 watershed during the 2007–08 winter.

Na⁺ and Cl⁻ Flow Path

Road salt was applied on 18 Dec. 2008 in anticipation of an ice storm that did not occur. The precipitation occurred as rain on 19 December. Intensive sampling at Site 4 during this event indicated that Na^+ and Cl^- in the stream remained in a 1:1 molar ratio throughout the period of runoff and increased discharge (Fig. 4, inset). Concentrations of Na^+ and Cl^- peaked shortly after precipitation began and several hours before the peak in discharge (Fig. 4). This pattern suggests a first-flush phenomenon and indicates that overland flow was the likely pathway by which road salt entered the stream. Dissolved Ca^{2+} , conversely, remained steady as Na^+ and Cl^- increased, but as discharge increased due to runoff the background, Ca^{2+} concentration in the stream was diluted (Fig. 4).

Acute Cl⁻ Toxicity

A Cl^- concentration of 2500 mg L^{-1} or greater in COMBO laboratory water or filtered stream water resulted in 100% mortality of *D. pulex*. The 48-h LC_{50} for Cl^- in COMBO water was 2042 mg L^{-1} (95% confidence interval [CI], 1866–2194 mg L^{-1}). In filtered stream water from Site 4, the 48-h LC_{50} for Cl^- was 1812 mg L^{-1} (95% CI, 1596–2018 mg L^{-1}). *Daphnia pulex* maintained for 48 h in filtered stream water collected from Sites 4 and 5 during a winter storm in February 2009 experienced no mortality. The Cl^- concentrations in the water from Site 4 and 5 were 526 mg L^{-1} and 657 mg L^{-1} , respectively.

Table 2. Chloride concentrations for nonwinter and winter seasons in the study sites. If a site had more than one chloride sample for a date, the concentrations were averaged before calculating the descriptive statistics.

	Site 1	Site 2	Site 3	Site 4	Site 5
Nonwinter					
No. of samples	12	52	51	51	18
	mg $\text{Cl}^- \text{ L}^{-1}$				
Mean	8	10	15	15	57
Median	7	9	14	15	66
Max.	13	24	47	34	102
Min.	5	3	4	4	19
Winter					
No. of samples	36	77	78	88	52
	mg $\text{Cl}^- \text{ L}^{-1}$				
Mean	15	18	62	76	310
Median	15	15	35	46	221
Max.	22	77	481	485	2100
Min.	4	7	7	12	56

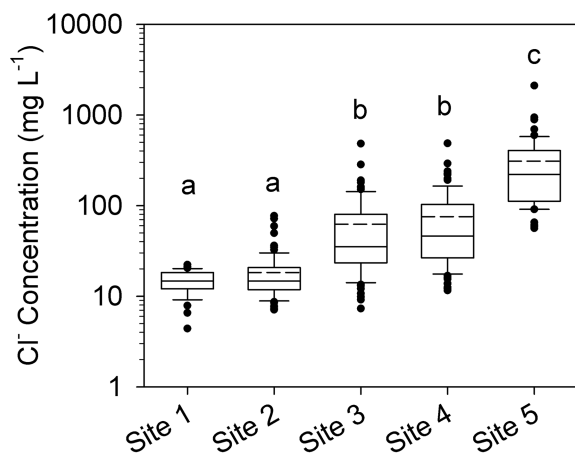


Fig. 2. Box plots of Cl^- concentrations for each site during the winter portions (1 December through 15 March) of the study period. The box indicates the 25th, 50th, and 75th percentiles; the whiskers indicate the 10th and 90th percentiles; filled circles are samples outside the 10th or 90th percentiles; the dashed line is the mean. Sites with the same lowercase letter were not statistically different (see text for details).

Discussion

The application of road salt had a demonstrable effect on Cl^- concentrations at all of the sites except Site 1, the reference site. The highest Cl^- concentration measured during our study was 2100 mg L^{-1} and occurred at Site 5, the most urbanized of the sites. This peak value exceeded the peak Cl^- concentrations of approximately 1400 to 1700 mg L^{-1} reported for urban streams in Toronto, Ontario (Crowther and Hynes, 1977; Williams et al., 1999) but was much less than the peak concentrations of 4600 to $11,000 \text{ mg L}^{-1}$ reported for streams in Baltimore, Maryland (Kaushal et al., 2005). The highest Cl^- concentrations occurred during winter but not always in association with increased discharge. Relatively small amounts of precipitation could elicit application of road salt if the precipitation was in the form of snow or ice. As a result, there was no correlation between discharge and Cl^- concentration at any site. Indeed, stream Cl^- concentrations often peaked well before discharge (see Fig. 4), suggesting the salt was mobilized early in the runoff period. Overall, patterns in stream Cl^- concentrations appeared to be a response to the unique combination of factors associated with each winter storm. The most important factors appeared to be timing and intensity of road salt application; the form, timing, and magnitude of precipitation; and patterns in air temperature. Scott (1981) reported the same factors were controlling the winter Cl^- concentrations in streams in Ontario, Canada.

During the nonwinter period, we observed Cl^- concentrations that were consistently $<20 \text{ mg L}^{-1}$ at all sites except Site 5, the most urbanized site. At Site 5, Cl^- concentration often exceeded 60 mg L^{-1} after precipitation in late spring or summer, which suggests that stored Cl^- was being mobilized months after the road salt was applied. This phenomenon has been reported in other areas (e.g., Demers and Sage, 1990; Kelly et al., 2008) and suggests the potential for salinization of groundwater (Kaushal et al., 2005). The low Cl^- concentrations at baseflow indicate that groundwater salinization had not occurred at the reference site or at Sites 2 through 4,

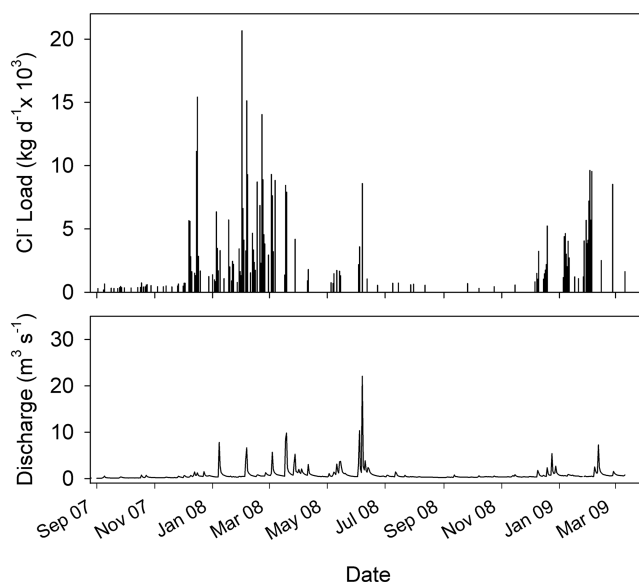


Fig. 3. Discharge (lower graph) and Cl^- load (upper graph) at Site 4 through the course of the study period.

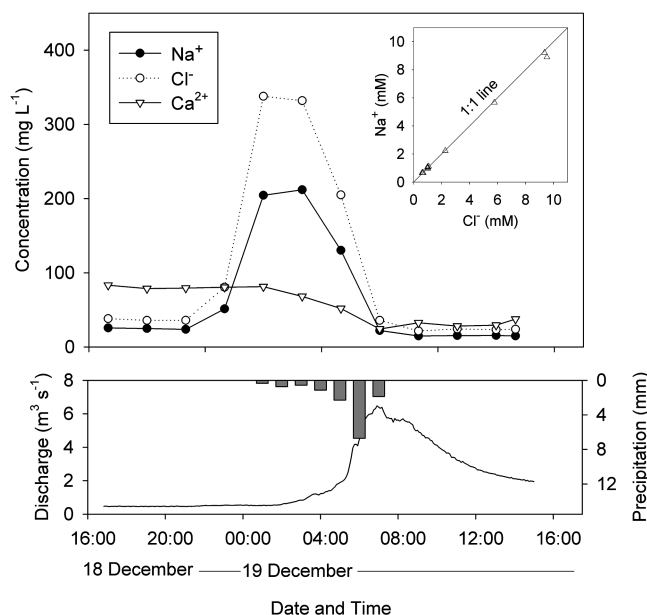


Fig. 4. Precipitation and discharge (lower graph) at Site 4 during a winter storm in December 2008. Upper graph shows the corresponding concentrations of Na^+ , Cl^- , and Ca^{2+} . Inset shows the molar concentrations of Na^+ and Cl^- in Site 4 during the storm event.

all of which are located in the Jack's Defeat Creek watershed. There is a growing evidence that impervious surfaces and storm drains decrease nitrogen retention within suburban and urban watersheds (Wollheim et al., 2005; Kaushal et al., 2008), and we expect an even larger impact on a conservative solute such as Cl^- . Based on the Cl^- loads from Site 4 (see Fig. 3), it appears that most of the applied road salt is exported quickly after application. We suggest this is because the primary flow paths for road salt in this watershed are storm drains and overland flow across impervious surfaces or frozen soil, none of which would allow for significant infiltration to groundwater. Because applied salt is quickly transported to streams, peak Cl^- concentrations are expected to increase in

agricultural and forested watersheds undergoing urban and suburban development.

We have data on Na⁺ concentrations from only a single winter storm event, but these data also support the notion that road salt was quickly exported from the Jack's Defeat Creek watershed. The molar ratio of Na⁺:Cl⁻ remained near 1 throughout the storm event indicating that there was little opportunity for Na⁺ to be preferentially retained within soil. This conclusion may not apply to storms that occur under different conditions, such as unfrozen soils or a slower melting and runoff period; more data on this process are clearly needed from a range of systems and hydrologic conditions. Alternatively, the long-term application of road salt could saturate soils with Na⁺ and allow Na⁺ to move conservatively through the soil (Mason et al., 1999). We believe Na⁺ saturation of soils in the Jack's Defeat watershed is unlikely because the presence of storm drains and impervious surfaces adjacent to roadways minimizes interaction between soils and salt-laden runoff. The rapid transport of runoff and solutes to streams, particularly through storm drains, is a common feature of urban streams (Paul and Meyer, 2001). We observed an increase in winter Cl⁻ concentrations with increasing urbanization and road density (see Fig. 2), which probably resulted from higher road salt input and more efficient infrastructure for drainage.

Using the road density for the Site 4 watershed and a salt application rate of 70 kg km⁻¹ of lane (Indiana Department of Transportation, personal communication), we estimate that at least 20,000 kg of NaCl are applied to roads in the watershed during a winter storm. If salt was applied 10 to 15 times during the winter of 2007–08, the total input of road salt was in the range of 200,000 to 300,000 kg. This does not include salt application to parking lots, sidewalks, or private drive ways. It also does not account for multiple applications to roadways during a storm, which is common during heavy snowfall. The export of NaCl from the Site 4 watershed during the winter of 2007–08 was 670,000 kg, and we believe this export accounts for the total input of road salt to the watershed. Increased development within the Jack's Defeat Creek watershed could lead to retention of Cl⁻ within soil or groundwater, but at present we cannot determine the road density or impervious coverage that would result in salinization of soils or groundwater.

Although the application of road salt caused large increases in stream Cl⁻ concentrations, the elevated Cl⁻ levels did not appear to be a significant threat to aquatic life based on our acute toxicity testing with *D. pulex*. The 48-h LC₅₀ determined in filtered stream water was approximately 1800 mg Cl⁻ L⁻¹, a concentration that was exceeded only in Site 5, the most urbanized site. The other sites had peak Cl⁻ concentrations that were <30% of the 48-h LC₅₀ (see Table 2). At Site 5, the peak Cl⁻ concentration of 2100 mg L⁻¹ was close to the concentration of 2500 mg L⁻¹ that caused 100% mortality in *D. pulex* during a 48-h assay. Overall, however, the Cl⁻ concentration measured during our study would not result in acute toxicity for aquatic organisms. Blasius and Merritt (2002) reached a similar conclusion in a study of road salt runoff effects on stream macroinvertebrates. Karraker et al. (2008) reported that susceptibility to Cl⁻ toxicity in amphibians varied between taxa and life stages, and that other factors, such as larval density dependence, strongly influenced the effect of Cl⁻ exposure.

We did not investigate the possibility of chronic sublethal or indirect effects, which could occur at lower Cl⁻ concentrations than do acute effects. However, the elevated Cl⁻ concentrations at all sites but Site 5 occurred in discrete pulses of 24 to 48 h and would therefore be unlikely to have chronic effects. At Site 5, however, we documented five periods during the study in which the 4-d average Cl⁻ concentration was >230 mg L⁻¹, suggesting the potential for chronic effects based on the USEPA recommendation that the 4-d average Cl⁻ concentration not exceed 230 mg L⁻¹ more than once every 3 yr.

Conclusions

We investigated road salt runoff in five streams in south-central Indiana that varied in degree of urbanization. The winter Cl⁻ concentrations increased with increasing development and road density. Several lines of evidence indicate that road salt entered the streams through storm drains and overland flow without interacting with soils or groundwater. Only the most urbanized site had elevated Cl⁻ concentrations after precipitation in spring and summer, suggesting some retention of road salt within the watershed. Patterns in Cl⁻ concentrations appear to be the result of factors that vary among winter storms, such as timing and magnitude of precipitation, salt application rates and timing, and patterns in air temperature. Acute toxicity testing indicated that the elevated Cl⁻ concentrations that occurred during winter were unlikely to cause direct mortality to aquatic organisms. Increased development at the study sites would most likely lead to greater salt application, more rapid runoff of precipitation, and greater in-stream Cl⁻ concentrations, but at present we cannot predict the amount or form of development that might cause acute toxicity during winter storms.

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