



Soil as a reservoir for road salt retention leading to its gradual release to groundwater



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ABSTRACT

Road salt application elevates Na and Cl concentrations throughout the year in many surface water and groundwater systems. This study explores the role of soils in extending the lag time between road salt application and the delivery of Na and Cl to shallow groundwater in a temperate environment. Intact soil cores were collected near karst springs at both an urban and a rural site at distances of 1 m, 5 m, and 13 m from nearby roads that experience winter salting. Cores were manipulated in the lab to simulate various field conditions; treatments included irrigation with: 1) deionized (DI) water (DI group) as a control, 2) NaCl solution (salt group) to mimic prolonged exposure to road salt, or 3) NaCl followed by DI water (recovery group) to mimic winter road salting followed by dilute rainfall in spring. In the first NaCl irrigation of the salt and recovery groups, soils retained 62% of the applied Cl and 66% of the applied Na on average, which was largely stored in the porewater. Throughout the 5 week study, Ca, Mg, and K were elevated and the pH was depressed in leachate from salt group compared to DI group cores due to cation exchange. Likewise, cation exchange enhanced Na retention so that salt and recovery group cores retained half of the applied Na at the end of the experiment, compared to a quarter of the Cl. Na and Cl retention were greater for soils from the rural site, which is characterized by higher organic matter (OM) and sand content, faster infiltration, and lower bulk density than for the urban site, which has higher bulk density and more silt and clay. Furthermore, extractable Cl in untreated field soils was positively correlated with soil water content, OM, and sand content, suggesting that these properties may control retention. We assume Cl retention to be the result of porewater retention, microbial uptake, and chlorination of soil OM. After the addition of 2000 mg Cl to the salt group cores, non-conservative Cl behavior ceased because the retention capacity of the soils had been exhausted. Recovery rates during DI flushes of recovery group cores indicate that these soils slowly release Na and Cl for at least 2.5–5 months following salt application. This gradual release from soils helps to explain the year-round persistence of high salt concentrations in some surface waters and groundwaters.

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1. Introduction

Widespread road salt application began in the 1960s in the United States, and has led to the degradation of many aquatic systems. NaCl is the most common deicing agent due to its effectiveness, availability, and affordability (Ramakrishna and Viraraghavan, 2005). Following deicing applications, salt-laden meltwaters can be transported directly to streams or infiltrate soils and subsequently introduce Na and Cl to groundwater.

Contaminated groundwater can then contribute Na and Cl to surface waters via baseflow, thereby leading to high surface water concentrations year-round (Corsi et al., 2015; Kaushal et al., 2005; Ledford and Lautz, 2015; Meriano et al., 2009). Indeed, high road salt application can substantially shift the ionic composition of waters toward being Na–Cl dominated (Godwin et al., 2003).

Elevated Na and Cl concentrations are of concern because of their deleterious effects on aquatic ecosystems. Surface waters impacted by road salt show decreased biodiversity and a shift toward the dominance of salt-tolerant species (Fay and Shi, 2012; Panno et al., 1999). In particular, road salt harms wetland vegetation (Panno et al., 1999; Richberg et al., 2001), trees (Fay and Shi, 2012; Kelsey and Hootman, 1992), macroinvertebrates (Demers,

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1992), and amphibians (Karraker et al., 2008). Furthermore, salt application can create sodic conditions in roadside soils, causing colloidal dispersion, weakening soil structure, and accelerating adsorption-desorption reactions (McBride, 1994; Sun et al., 2015).

A number of studies have demonstrated long-term increases in both surface water and groundwater Cl concentrations over the past few decades as a result of road salt application (Corsi et al., 2015; Godwin et al., 2003; Kaushal et al., 2005; Kelly, 2008; Kelly et al., 2008). These increases suggest incomplete flushing of salt from watersheds between salting seasons, indicating the presence of some reservoir for Na and Cl storage. Temporary retention in soils or groundwater creates a lag time between road salt application and the delivery of Na and Cl to streams; if this lag time is great enough, baseline concentrations will increase.

Na retention in soils occurs mainly through cation exchange processes in which Na adsorbs to clays, replacing other cations such as Ca, Mg, and K (DeSimone et al., 1997). Because Na is generally retained to a greater extent than Cl, Na/Cl ratios in soil porewaters and nearby streams decrease following salt application, then increase as soils recover (Sun et al., 2012). Schweiger et al. (2015) found a trend of decreasing Ca, Mg, and K concentrations in 52 springs with increasing distance from a road because road salt enhanced cation exchange near the road; this was observed on both seasonal and long-term timescales. The extent of cation exchange depends on the soil type and the degree of contamination. Howard and Beck (1993) found that for some highly contaminated spring waters in metropolitan Toronto, Ontario, >30% of incoming Na had been adsorbed during recharge, while other soils that were already saturated with salt had porewater Na/Cl ratios of 1 and did not support any cation exchange.

Cl has traditionally been considered a conservative ion in soils, but recent lab and field studies have revealed significant soil Cl retention. Based on a soil column lab experiment, Kincaid and Findlay (2009) suggest that Cl retention and gradual release could explain a 2 month lag between salt application and complete flushing of Cl from soils, even though the precipitation volume in the first 4 weeks of the experiment was sufficient to replace the porewater 3–10 times. A field study near an Ontario highway revealed that 75% of the NaCl applied during the previous winter (November through April) was retained in the top 2.8 m of the soil in September (Labadia and Buttle, 1996). The transport of Cl dissolved in soil porewaters is limited by porewater velocities, which can include both rapid preferential flow through structures such as macropores and biopores, as well as slower flow through the soil matrix (Legout et al., 2009). Other Cl retention mechanisms include non-specific adsorption, uptake by plants (Lovett et al., 2005), microbial uptake, and microbial chlorination of soil organic matter (OM; Bastviken et al., 2007; 2009). In this paper, we distinguish between “conservative retention,” where Na and Cl move through soils at the same rate as the porewater, but are retained because soils hold the porewater, and “non-conservative retention,” where Na and Cl move slower than the porewater due to interaction with soil particles, plants, or microbes. The degree of Cl retention varies based on soil type, water residence time, and salt application rate (Labadia and Buttle, 1996; Bastviken et al., 2006; Kincaid and Findlay, 2009).

This study evaluates the Na and Cl retention capacity of soils collected from two sites with differing land use (i.e., urban and rural) to determine how long soils hold road salt contamination before releasing it to groundwater. At each site, ongoing water quality monitoring of karst spring water has revealed elevated Na and Cl concentrations in shallow groundwater which persist throughout the year (Robinson et al., 2015; Robinson and Hasenmueller, 2016). Moreover, a first flush of Cl has been observed at the onset of flooding events as late as September at the

karst springs (Robinson and Hasenmueller, 2016) as well as proximal streams (Hasenmueller and Robinson, 2016), providing evidence of soil Cl retention 6 months after road salt application. Thus, we conducted a lab experiment testing the extent to which soils collected at various distances from the road at the urban and rural sites can retain and release Na and Cl following road salt application. Additionally, we measured a suite of physical and chemical soil parameters to understand which soil properties and transport mechanisms control salt retention and lead to differences in retention between the urban and rural sites as well as determine the relative importance of soil properties compared to land use. We hypothesize that: 1) soils from both sites can retain Cl for up to 6 months due to both conservative porewater retention and non-conservative Cl behavior, 2) Na retention is greater than Cl retention due to cation exchange, leading to a slower release time for Na compared to Cl, 3) Na and Cl retention capacity can be depleted through sufficient salt application, and 4) retention capacity depends more on soil properties such as grain size and OM than on proximity to salted roads.

2. Methods

2.1. Soil collection sites

Soils were collected from two locations in east-central Missouri with differing land use (i.e., rural and urban), but similar lithology (i.e., limestone) and vegetation (i.e., deciduous forest). Both sites are characterized by a temperate climate, with 100 cm of average annual precipitation and an average annual temperature of 13.5 °C (NOAA, 2016). Soils at both sampling locations are located near groundwater-fed karst springs contaminated by road salt (i.e., average Cl concentrations are >10 mg/L; Kleeschulte and Sutley, 1995).

Our rural endmember, Rockwoods Spring, is located within Rockwoods Reservation, a 7.6 km² park in Wildwood, Missouri. The karst spring is hosted in the Upper Ordovician Plattin Formation with a discharge range of 0.015–0.3 m³/s and a water residence time of approximately one year (Frederickson and Criss, 1999). The average Cl concentration in spring water is 63 mg/L (Robinson et al., 2015). Soils within the basin consist of the rubbly Gasconade rock outcrop complex, silt loams ranging from normal to very gravelly, and an area of sand and gravel pits (USGS, 2014; USDA, 2016). We sampled the Horsecreek silt loam, which is dark brown (10 YR 3/3), well-drained, and of neutral pH (USDA, 2016).

Our urban endmember, Blackburn Spring, is located 27 km east of Rockwoods Spring in Blackburn Park in Webster Groves, Missouri. The site hosts a karst spring that issues from Upper Mississippian-Meramecian St. Louis Limestone (Harrison, 1997) in a low intensity residential setting 0.7 km from a major highway (USGS, 2014). The average Cl concentration in spring water at this site is 192 mg/L (Robinson et al., 2015). Soils within the urban basin include the Harvester, Winfield, and Iva urban land complexes and the upland urban land consociation. The soils we sampled are classified as urban land karst Harvester complex, which is a moderately well-drained brown (10 YR 4/3) and dark yellowish-brown (10 YR 4/4) silt loam with pockets of brown (7.5 YR 4/4) silty clay loam; the soil has neutral pH (USDA, 2016).

2.2. Field methods

To evaluate road salt retention in soils and subsequent release to the shallow groundwater at our sites, soil samples were collected near each spring, along a transect perpendicular to the nearest road. On July 17, 2015, 36 intact cores were obtained at distances of 1 m and 13 m from the road at each site (i.e., 9 cores at each site and

distance interval) because road salt contamination is often concentrated in soils within 15 m of roads (Labadia and Buttle, 1996; Lundmark and Olofsson, 2007). Intact cores were acquired by driving 7.6 cm-diameter PVC tubes to 15 cm depth, which coincides with the shallowest soil depth observed at the sites. Upon return to the lab, 12 cores (3 from each sampling location) were extruded in 5 cm segments for soil characterization (see Section 2.3.2), and the other 24 were randomly selected to undergo two types of flushing treatments as described in Section 2.3.1.

On September 12, 2015, a second suite of soil cores were collected for a flushing experiment that incorporated additional test parameters, including a third treatment group and leachate cation and pH levels. We collected 18 intact cores 5 m from the road at the urban and rural sites in the same manner as those collected in July. Additionally, a 7.6 cm-diameter auger was used to collect soils along a transect at 1 m, 2.5 m, 5 m, 8 m, 13 m, and 15.8 m or 20 m from the road (exposed bedrock at the rural site prevented sample collection at 20 m from the road) for characterization (see Section 2.3.2). Auger samples were collected in 5 cm depth intervals to 15 cm depth. We collected triplicate auger samples at 5 m from the road where the flushing experiment cores were collected.

Infiltration rates were measured in triplicate at distances of 1 m and 13 m from the road on July 29, 2015 and at 5 m from the road on September 12, 2015 using a 15.2 cm-diameter PVC ring infiltrometer driven to a depth of 5 cm. Measurements on July 29 are intended to characterize soil conditions of the core sampling date 12 d earlier. Although moisture conditions were not identical due to 3.2 cm of rain between July 17 and 29, a qualitative comparison of the sites is possible based on the July 29 data.

2.3. Lab methods

2.3.1. Core flushing experiment

July cores were randomly assigned to two treatment groups with a total of 11 irrigations: the “DI group” and the “recovery group.” The DI group was irrigated with deionized (DI) water throughout the experiment to serve as a control. The recovery group was flushed twice with the NaCl solution (2000 mg/L Cl, 1300 mg/L Na, with other cations below detection: Ca < 2 mg/L, Mg < 0.4 mg/L, and K < 0.2 mg/L), then with DI water for the remainder of the experiment to simulate retention of Na and Cl following the road salting season. The September cores included the DI and recovery treatments as well as a third treatment: the “salt group,” which was flushed with the NaCl solution throughout the experiment to test soil response to long-term salt exposure. All the September treatment groups underwent 10 irrigations. For both flushing experiments, cores were irrigated with 100 mL of the appropriate solution (corresponding to an average week of spring rainfall; NOAA, 2016) every 3 d, except for a 9–10 d drying out period between irrigations 4 and 5 to mimic field conditions during periods of low rainfall.

Approximately 3 h after each flush, the leachate volume from the bottom of each core was measured and subsamples were filtered (0.2 µm filter) for Cl analysis on a Metrohm Compact IC Pro Ion Chromatograph (IC; Herisau, Switzerland). Duplicates showed that instrument precision was ±2%. Leachate volume was not measured for the first flush for some of the July cores; this volume was estimated based on regression using the leachate volumes of the following two flushes (Fig. S1). For the September cores, we also measured the pH of the leachate using an EcoSense pH10A pen (Yellow Springs, Ohio) and filtered and acidified (1% HNO₃) subsamples for analysis of Na, Ca, Mg, and K by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES; Perkin-Elmer Optima 7300DV; Waltham, Massachusetts) in accordance with the EPA 200.7 Method (USEPA, 1994). Precision was ±8% and

accuracy was ±15% based on duplicates and Sigma Aldrich Trace-CERT standards. After the final irrigation, the cores were extruded in 5 cm depth segments and analyzed for bulk density, gravimetric water content, and Cl content. September post-experiment cores were also analyzed for Na, Ca, Mg, K, Al, and cation exchange capacity (CEC).

2.3.2. Soil physiochemical characterization

To understand the physical controls on salt retention, we analyzed untreated soil samples (the “characterization group”) in 5 cm depth segments for both the July and September sampling events. July characterization samples from 1 m to 13 m were analyzed for bulk density, water content, OM, and extractable Cl. September 5 m characterization and transect samples were analyzed for these same parameters, as well as total C, total N, particle size distribution, extractable Na, Ca, Mg, K, Al, and CEC.

Water content was determined by drying ~10 g of soil at 70 °C for 3 d, then passing the sample through a 2 mm-sieve and subtracting the mass of particles >2 mm (Gardner, 1986). All other analyses were performed on oven-dried soils passed through a 2 mm-sieve. OM was determined by loss on ignition; samples were oven-dried at 105 °C overnight, then placed in a muffle furnace at 550 °C for 4 h (Heiri et al., 2001). Total C and total N were measured on ground samples using an Elemental Combustion System (Costech Analytical Technologies, Valencia, California). Particle size was analyzed using a Beckman Coulter LS 13320 Laser Diffraction Particle Size Analyzer (Indianapolis, Indiana). Dried subsamples for particle size analysis were passed through a splitter to minimize sorting, suspended in DI water by vigorous stirring, and then dispersed by sonification once they were loaded in the instrument. Instrument precision was ±5%. The mass fraction of particles >2 mm was determined by wet sieving a dried, previously unsieved 50 g subsample, then oven-drying the large particles.

We also measured extractable Cl and cations in characterization, transect, and treated samples. For Cl, we added 25.0 mL of 0.01 M CaNO₃ to 10.0 g soil and shook the mixture for 15 min, then filtered the solution and measured Cl by IC (Keeney and Nelson, 1982). Major cations were extracted by adding 30 mL of 0.1 M BaCl₂-NH₄Cl (for Na, Ca, Mg, and K) or 30 mL of 1 M KCl (for Al) to 3 g soil, shaking for 30 min, allowing samples to settle overnight, then filtering and acidifying the supernatant for analysis by ICP-OES (Amacher et al., 1990; Barnhisel and Bertsch, 1982). We used major cation data to calculate CEC; we will use the term CEC here to describe the sum of Na, Ca, Mg, K, and Al displaced by either BaCl₂-NH₄Cl or KCl.

2.4. Statistical methods

Statistical analyses were performed in SPSS using a significance level of $\alpha = 0.05$. Repeated measures ANOVA was used to measure changes in the release of ions (Cl, Na, Ca, Mg, and K) as well as pH, leachate volume, and cumulative retention of Na and Cl with the factors time, treatment, and site for all analyses, as well as distance from the road for July cores. We analyzed the July and September cores separately. Cumulative element retention (Cl or Na) was calculated as the total amount of the element added minus total element release for all flushes up to the current irrigation. Mauchly's test was used to assess sphericity; when the assumption of sphericity was not met, the Greenhouse-Geisser adjustment was used because epsilon values were less than 0.75. The OM content, total C, total N, bulk density, and water content of characterization cores were analyzed using ANOVA to test for differences with site, distance (July cores), and depth. Post-hoc Bonferroni analyses were used to determine which levels of each factor were significantly different.

Pearson's R was used to test correlation between soil parameters including OM, CEC, water content, total C, total N, dry bulk density, particle size (percent sand, silt, and clay), extractable Cl and Na, and distance from the road. Soil properties were measured for each 5 cm depth segment within cores, then depth-averaged to produce a value for the entire core. The 16 transect and characterization cores collected in September were used in the analysis.

3. Results

3.1. Initial soil properties

Laser diffraction analysis on September transect samples shows that rural soils had particle sizes of 1–4% clay, 14–50% silt, and 47–84% sand, while the urban soils had 4–5% clay, 48–57% silt, and 38–48% sand (Fig. 1). At both sites, clay and silt generally increased with depth, while sand tended to decrease with depth. Particle size showed little variation with distance from the road, except that rural soils at 5 m and 15.8 m had higher sand content. Among cores taken 5 m from the road, rural cores had more sand and urban cores had more silt and clay content (Table 1; Fig. 1). The mass fraction

>2 mm was quite variable at both sites, ranging from 2–59% at the rural site and 2–25% at the urban site. Samples from 5 m to 15.8 m (at the base of a limestone outcrop) at the rural site had high gravel content, while samples at 5 m and 8 m at the urban site had high gravel content. There was no statistical difference between gravel content at the rural and urban sites.

Water content varied significantly by site for September cores, and with site, depth, and distance from the road for July cores (Tables 1 and 2); at corresponding sampling locations, water content was lower in September than July (Fig. 2). At the urban site, the road is elevated and our sampling sites therefore decrease in elevation with increasing distance from the road. Likewise, transect samples show that soil water content increased by 7.7% between 1 m and 20 m (Fig. 2). There was no trend in water content with distance from the road at the rural site. Water content generally decreased with depth in cores collected from the field (Fig. 2).

Results for total C, total N, OM, and CEC are also shown in Fig. 2, and all four parameters were higher at the rural site. Indeed, depth-averaged rural cores had 5–19% OM, with the highest values at 5 m and 15.8 m; urban cores had 4–7% OM (Fig. 2). OM, total C, and total N tended to decrease with soil depth, but the patterns were not

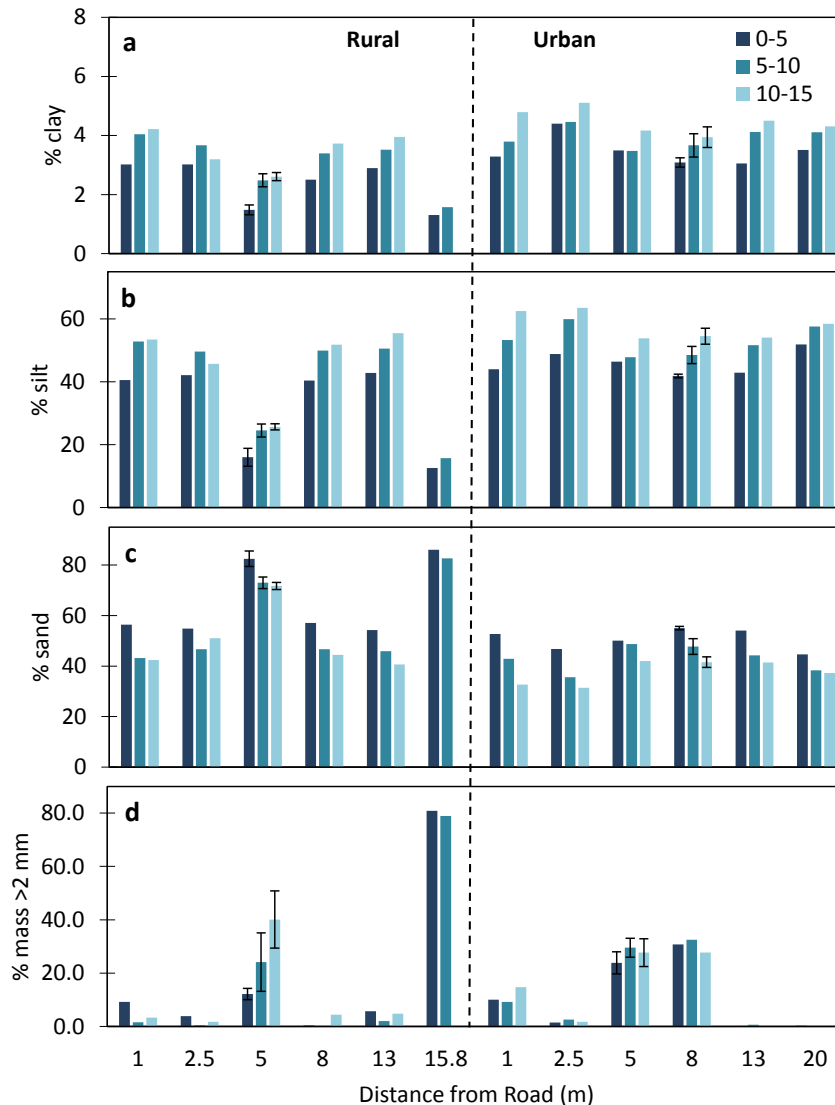


Fig. 1. Particle size for soil characterization samples collected in September. Samples were collected in triplicate at 5 m; standard error is shown. Volumetric percent clay (a), silt (b), and sand (c) are shown, as well as the mass percent greater than 2 mm (d).

Table 1

ANOVA results for main effects and significant interactions for soil properties of September characterization samples from 5 m. Significant p-values are presented in bold.

	num df	den df	F	p
Extractable Cl				
site	1	12	3.385	0.091
depth	2	12	0.262	0.774
Extractable Na				
site	1	12	1.330	0.271
depth	2	12	0.262	0.774
Water content				
site	1	9	8.799	0.016
depth	2	9	0.969	0.416
Bulk density				
site	1	12	108.765	<0.0005
depth	2	12	0.038	0.962
site*depth	2	12	7.222	0.009
OM				
site	1	12	0.074	0.790
depth	2	12	0.630	0.549
Total N				
site	1	12	12.624	0.004
depth	2	12	0.926	0.423
Total C				
site	1	12	25.642	<0.0005
depth	2	12	2.136	0.161
CEC				
site	1	12	12.259	0.004
depth	2	12	1.122	0.358
Extractable Ca				
site	1	12	14.072	0.003
depth	2	12	0.747	0.495
Extractable Mg				
site	1	12	7.496	0.018
depth	2	12	0.912	0.428
Extractable K				
site	1	12	3.645	0.080
depth	2	12	0.471	0.635
Clay				
site	1	12	35.297	<0.0005
depth	2	12	4.108	0.044
Silt				
site	1	12	160.941	<0.0005
depth	2	12	5.308	0.022
Sand				
site	1	12	146.210	<0.0005
depth	2	12	5.280	0.023
>2 mm				
site	1	12	0.049	0.829
depth	2	12	1.699	0.224
Infiltration				
site	1	12	8.018	0.015

statistically significant (Table 1). CEC ranged from 2800 to 10 400 mg/kg at the rural site and 2900–4700 mg/kg at the urban site; at 5 m from the road, CEC was significantly higher at the rural than urban site (Table 1; Fig. 2).

In July, depth-averaged soil extractable Cl concentrations ranged from 8.1–15.2 mg/kg at the rural site and 8.6–19.2 mg/kg at the urban site (Fig. 3). July extractable Cl showed a significant three-way interaction between site, distance, and depth (Table 2). Samples collected along a transect in September show extractable Cl concentrations of 14.2–74.0 mg/kg in rural soils and 10.1–20.4 mg/kg in urban soils; extractable Cl was higher in the rural soil compared to the urban soil at corresponding distances from the road. Depth-averaged extractable Cl was also higher in corresponding soil samples collected in September compared to July at both sites. At the rural site, the highest extractable Cl concentrations were 5 m from the road. Extractable Cl concentrations generally decreased with distance from the road at the urban site, particularly in the top 5 cm.

Table 2

ANOVA results for main effects and significant interactions for July characterization samples. Significant p-values are presented in bold.

	num df	den df	F	p
Extractable Cl				
site	1	22	0.447	0.497
depth	2	22	12.030	<0.0005
distance	1	22	13.046	0.002
site*depth	2	22	9.446	0.001
distance*depth	2	22	4.400	0.025
site*distance*depth	2	22	3.979	0.038
Water content				
site	1	22	5.037	0.035
depth	2	22	9.190	0.001
distance	1	22	4.480	0.046
Bulk density				
site	1	22	1.666	0.210
depth	2	22	1.097	0.351
distance	1	22	0.178	0.667
OM				
site	1	22	7.995	0.010
depth	2	22	7.113	0.004
distance	1	22	2.701	0.115
site*distance	1	22	6.544	0.018

Cation extractions performed for September samples showed that extractable Na was highest 1 m from the road at both sites (Fig. 3). At the rural site, soils had 63 mg/kg Na at 1 m and ranged from 0 to 37 mg/kg Na between 2.5 m and 15.8 m from the road. Soils at the urban site had 71 mg/kg Na at 1 m from the road; further from the road concentrations ranged from 6–30 mg/kg. Concentrations were higher at the urban site, except at 5 m from the road where the rural site had higher extractable Na, and at 13 m where extractable Na was below detection at certain depth intervals (Fig. 3). A two-way ANOVA (Table 1) showed no effect of site or depth on extractable Na or K for cores from 5 m, although K was higher at the urban site at each distance from the road. Extractable Ca and Mg both varied with site, with higher concentrations at the rural site; there was no significant effect of depth (Table 1). Extractable Al was below detection (<0.1 mg/L) for a subset of 15 samples representative of all sites and treatment groups. Therefore, Al was considered insignificant for our samples and was excluded from CEC calculations.

Pearson correlations (Table 3) were used to determine how soil properties influence Cl concentrations in field soils. Extractable Cl was positively correlated with OM, total C, total N, and water content, which were all strongly positively correlated with each other. Cl also correlated negatively with silt and positively with sand; there was a negative, but non-significant, correlation between Cl and clay. Extractable Na was not significantly correlated with any of the soil properties except Cl. CEC was negatively correlated with clay but positively correlated with OM. OM and water content both showed negative correlations with silt and clay and a positive association with sand.

Infiltration rates ranged from 4.6–53.7 mL/s (average = 23.4 mL/s) at the rural site and 1.5–9.5 mL/s (average = 4.9 mL/s) at the urban site. At corresponding distances from the road, infiltration was faster at the rural site (Table 1), likely due to the lower bulk density compared to the urban soils. In July, infiltration rates (average ± standard deviation) were 4.6 ± 0.8 mL/s and 1.5 ± 0.3 mL/s at 1 m from the road and 11.9 ± 3.2 mL/s and 3.8 ± 1.4 mL/s at 13 m at the rural and urban sites, respectively. The highest infiltrations rates at each site were measured at 5 m from the road in September: 53.7 ± 27.1 mL/s at the rural site and 9.5 ± 4.2 mL/s at the urban site.

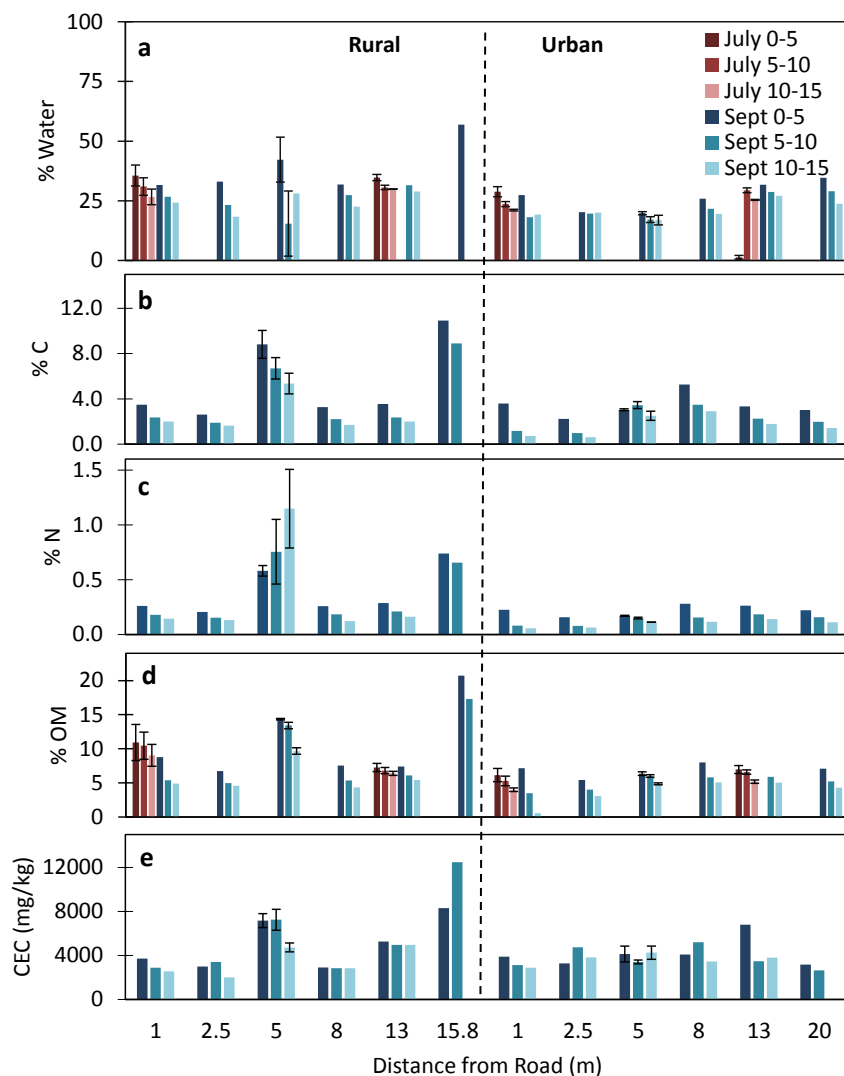


Fig. 2. Water content (a), total C (b), total N (c), OM (d), and CEC (e) in soils collected to characterize conditions prior to the flush experiment. July samples (red shades) and September 5 m samples (blue shades) were collected in triplicate; standard error is shown. For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.

3.2. Soil core flushing experiment

3.2.1. Cl behavior in July cores

The cores collected in July were subjected to either the DI or the recovery treatment. Over 11 flushes, the 1 m rural DI cores released 0.7 mg Cl, while the 13 m rural cores released only 0.3 mg Cl (Fig. 4a). Urban DI cores 1 m from the road released 1.1 mg, and urban cores taken 13 m from the road had a total Cl release of 0.9 mg (Fig. 4a).

The recovery group cores were flushed twice with 200 mg Cl; in the first irrigation, the leachate volumes for some cores were estimated through regression (Fig. S1). In the first flush, leachate Cl contained 24–153 mg Cl (Fig. 4b), except for two cores which released no leachate. In the second salt irrigation, cores released 37–181 mg Cl. The third flush consisted of DI water; Cl content in the leachate dropped 40.3% and 71.7% for rural cores and 91.0% and 98.9% for urban cores at distances of 1 m and 13 m from the road, respectively. During flushes 3–11 (all DI water), Cl released in the rural cores collected at 1 m and 13 m declined by 1.4 mg and 1.1 mg per cm of water added, leading to a total release of 225 mg and 156 mg, respectively. For urban cores at 1 m, leachate Cl decreased

by 0.3 mg per cm of DI water added during the DI flushes, with a total release of 69 mg Cl. The Cl in urban cores from 13 m did not decrease after flush 3 and only released 16 mg Cl during flushes 3–11 (Fig. 4b). At the end of the experiment, the recovery treatment rural cores retained 26% and 15% of the Cl applied during the first two flushes, and urban cores retained 26% and 27% at 1 m and 13 m from the road, respectively. Repeated measures ANOVAs for the dependent variables Cl release and Cl cumulative retention showed significant interactions between treatment and site as well as between treatment and distance from the road (Table 4). Cumulative retention was higher at the rural site due to the high retention in the first two flushes.

3.2.2. Na and Cl behavior in September cores

Cores collected in September underwent DI, salt, or recovery treatments. Leachate Cl was higher for the September DI group than for the July DI cores. Cumulative Cl release was 3.1 mg and 3.3 mg for September rural and urban DI cores, respectively (Fig. 4c). Total Na release was 1.0 mg and 1.3 mg over the course of the experiment for rural and urban DI cores, respectively (Fig. 5a). Differences in salt release between the July and September cores may be

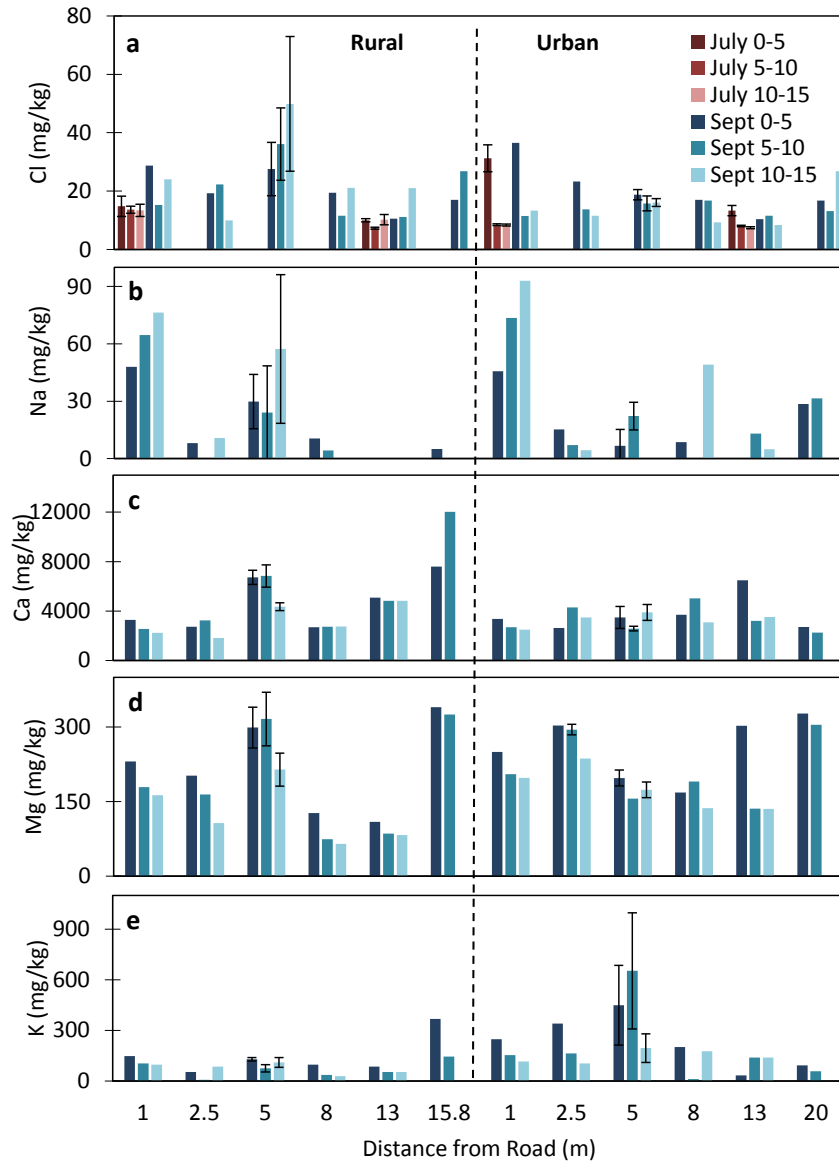


Fig. 3. Cl and cation concentrations in soils collected to characterize conditions prior to the flush experiment. July samples (red shades) and September 5 m samples (blue shades) were collected in triplicate; standard error is shown. Missing bars in b denote concentrations below detection. For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.

explained by variations in soil properties, differing moisture conditions, or a seasonal effect. There was no precipitation in the week prior to July sampling, whereas in the 4 d before September sampling, 0.3–3.4 cm rain fell per day, totaling 5.3 cm.

The salt group cores from both sites showed substantial retention. A total of 200 mg Cl was added during each flush, and in the first irrigation event, the rural cores retained 97 mg (49%) and the urban cores retained 125 mg Cl (63%). Leachate Cl content increased by 2.6 mg per cm solution added for the rural cores and by 3.5 mg per cm solution for the urban cores in subsequent flushes (Fig. 4d). After 10 flushes, leachate from the rural cores had Cl concentrations of 1997 mg/L, within error of the input concentration of the 2000 mg/L Cl irrigation solution. Final Cl concentrations in the urban leachate slightly exceeded the concentration of the irrigation solution at 2054 mg/L. However, cores from neither site released the input mass of Cl in the final flush: rural cores released 158 mg and urban cores released 170 mg Cl. At the end of the experiment, net retention for the rural cores was 578 mg (29% of applied Cl),

while the urban cores retained 507 mg Cl (25%).

Likewise, 130 mg Na was added during each flush. Rural salt group cores retained 60% of the Na during the first flush, then leachate Na increased by 1.3 mg per cm irrigation solution added in subsequent flushes for a final concentration of 964 mg/L in the leachate. Urban cores retained 72% of the Na in the initial flush, followed by an increase of 1.8 mg per cm of irrigation solution, with leachate concentration of 1038 mg/L in the final flush (Fig. 5a). After 10 flushes, both sites showed leachate Na concentrations below that of the 1300 mg/L Na flush solution, indicating potential for continued Na retention. In total, rural and urban cores retained 50% and 45% of Na applied over the course of the experiment, respectively.

The recovery group treatment was identical to the salt group for the first two flushes. In the third irrigation, the recovery cores were flushed with DI water, leading to an 82% and 88% decrease in leachate Cl and a 90% and 92% decrease in leachate Na for rural and urban cores, respectively (Figs. 4d and 5a). For the remainder of the

Table 3
Pearson correlations for soil properties in September auger samples (n = 16). Correlations are highlighted yellow for p < 0.05 and green for p < 0.01.

	Distance	OM	Water Content	Dry BD	CEC	Total N	Total C	Clay	Silt	Sand	>2 mm	Cl	Na
Distance	1	.239	.312	-.129	.307	.049	.186	-.158	-.071	.077	.157	-.150	-.304
OM	.239	1	.893	-.734	.930	.878	.981	-.904	-.946	.945	.658	.585	.162
Water Content	.312	.893	1	-.745	.803	.855	.869	-.734	-.783	.781	.287	.751	.405
Dry BD	-.129	-.734	-.745	1	-.579	-.733	-.661	.778	.771	-.773	-.178	-.430	-.092
CEC	.307	.930	.803	-.579	1	.787	.907	-.795	-.850	.848	.699	.418	.010
Total N	.049	.878	.855	-.733	.787	1	.875	-.807	-.883	.880	.389	.767	.352
Total C	.186	.981	.869	-.661	.907	.875	1	-.894	-.941	.940	.687	.637	.224
Clay	-.158	-.904	-.734	.778	-.795	-.807	-.894	1	.964	-.968	-.666	-.446	-.024
Silt	-.071	-.946	-.783	.771	-.850	-.883	-.941	.964	1	-1.000	-.663	-.530	-.103
Sand	.077	.945	.781	-.773	.848	.880	.940	-.968	-1.000	1	.665	.526	.099
>2 mm	.157	.658	.287	-.178	.699	.389	.687	-.666	-.663	.665	1	.009	-.275
Cl	-.150	.585	.751	-.430	.418	.767	.637	-.446	-.530	.526	.009	1	.750
Na	-.304	.162	.405	-.092	.010	.352	.224	-.024	-.103	.099	-.275	.750	1

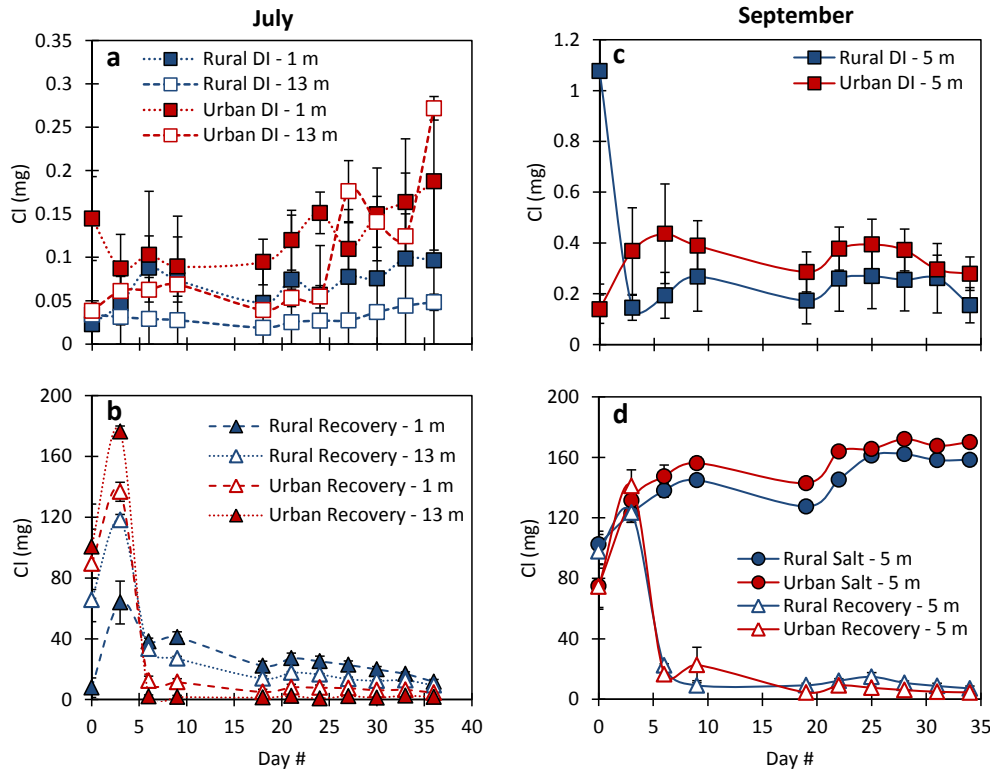


Fig. 4. Leachate Cl concentrations for July (a–b) and September (c–d) cores from the DI (a, c), recovery (b, d), or salt (d) treatment groups. July cores were collected 1 m and 13 m from the road and September cores were collected 5 m from the road at each site. Results are presented as mean ± standard error over time; n = 3.

experiment (i.e., flushes 3–10), rural leachate Cl dropped by an average of 0.5 mg and Na decreased by 0.2 mg per cm DI water added, for a total release of 94.9 mg Cl and 36.9 mg Na (Figs. 4d and 5a). Urban core leachate decreased by 0.9 mg Cl and 0.3 mg Na per cm DI water added (i.e., flushes 3–10), for a cumulative release of 71.9 mg Cl and 27.2 mg Na. At the end of the experiment, rural and urban cores still retained 21% and 27% of the Cl added during the two initial salt flushes, and 45% and 51% of Na, respectively. Percent net Cl retention was similar between July and September recovery

cores.

Repeated measures ANOVAs showed that Cl release, Na release, cumulative Cl retention, and cumulative Na retention varied significantly with treatment. Rural cores also had higher cumulative Na retention than urban cores, although there was no significant main effect of site on cumulative Cl retention. Both cumulative Na retention and cumulative Cl retention were affected by a significant interaction between site and treatment (Table 4): rural cores retained more Na and Cl in the salt treatment, but urban cores

Table 4

Repeated measures ANOVA results for main effects and significant interactions for July and September leachate Cl and cations. Time represents the repeated measure (10–11 flushes). Significant p-values are presented in bold. Degrees of freedom were calculated with a Greenhouse-Geisser adjustment.

	df	F	p
July Cl release			
time*site	1.395	15.272	<0.0005
time*treatment	1.395	74.780	<0.0005
time*distance	1.395	5.548	0.019
time*site*treatment	1.395	15.273	<0.0005
time*treatment*distance	1.395	5.546	0.019
July Cl retention			
time*site	1.114	55.786	<0.0005
time*treatment	1.114	133.478	<0.0005
time*distance	1.114	10.749	0.003
time*site*treatment	1.114	56.637	<0.0005
time*treatment*distance	1.114	10.565	0.004
Sept. Cl release			
time*site	2.142	2.779	0.078
time*treatment	4.284	73.845	<0.0005
Sept. Cl retention			
time*site	1.416	3.710	0.059
time*treatment	2.831	344.841	<0.0005
time*site*treatment	2.831	4.928	0.013
Sept. Na release			
time*site	1.531	2.969	0.087
time*treatment	3.061	47.276	<0.0005
Sept. Na retention			
time*site	1.238	4.849	0.037
time*treatment	2.476	776.133	<0.0005
time*site*treatment	2.476	6.193	0.008
Sept. Ca release			
time*site	1.765	0.646	0.516
time*treatment	3.530	8.654	<0.0005
Sept. Mg release			
time*site	2.185	0.417	0.681
time*treatment	4.370	8.227	<0.0005
Sept. K release			
time*site	1.157	1.372	0.268
time*treatment	2.315	15.367	<0.0005

retained more during the DI flushes in the recovery treatment.

3.2.3. Major element and pH behavior in September cores

Average leachate Ca release in the DI cores was 0.5 mg for the rural site and 0.7 mg for the urban site. Although the NaCl flush solution was free of Ca (<2 mg/L), the salt group cores produced leachate with significantly higher Ca than the DI group at 9.5 mg for rural cores and 5.7 mg for urban cores. Recovery group Ca behaved like the salt group for the first two flushes, then began to decrease once cores were irrigated with DI water. However, the Ca concentrations declined more rapidly for the urban cores compared to the rural cores. In the final flush, recovery group Ca was 4.7 times higher than DI group Ca for the rural cores and 1.5 times higher than DI group Ca for the urban cores (Fig. 5b). Similarly, average Mg release per flush was 0.04 mg in rural DI cores and 0.1 mg in urban DI cores, yet both the rural and the urban salt group cores released 0.9 mg on average per flush. Leachate Mg decreased faster for urban recovery cores compared to the rural recovery cores. Indeed, the final leachate Mg for the rural recovery cores was 6.3 times higher than for the rural DI group, and Mg for the urban recovery cores was 1.2 times higher than for the urban DI group in the final flush (Fig. 5c). Average K release was 0.09 mg and 0.6 mg in rural and urban DI core leachate, while the salt group cores released 1.4 mg and 4.2 mg for the rural and urban sites, respectively. K release from recovery group cores was similar to DI group cores. K concentrations peaked during the eighth flush for both the rural and urban salt groups (Fig. 5d). Repeated measures ANOVAs confirm that leachate Ca, Mg, and K varied significantly by treatment, with

higher concentrations for salt group than DI group cores (Table 4).

The pH of the leachate from the September cores remained between 6.5 and 7.6 for the duration of the experiment (Fig. S2) and varied significantly by treatment (Table 4). The average pH of the DI group was 7.19, while the salt treatment had the lowest pH values at an average of 6.95. The average pH of the recovery group was 6.80 during the first two salt flushes, and then increased to an average of 7.28 during the DI flushes.

3.3. Analysis of treated soils

Post-experiment water content, extractable Cl, and cation concentrations for the DI, salt, and recovery group cores (Tables 5 and 6) were compared with initial characterization cores (Figs. 2 and 3). As expected, water content was higher in the treated cores after the experiment (Tables 5 and 6) than in the untreated, characterization cores (Fig. 2). In particular, porewater volume in post-experiment samples was on average 59% higher than rural characterization cores and 22% higher than urban characterization cores. Extractable Cl for the July experiment was higher for recovery cores than for DI or characterization cores. For the September experiment, mean extractable Cl and Na in the salt group cores were significantly higher than in the recovery group cores, which in turn were higher than the DI group and characterization cores; DI and characterization cores were statistically equivalent. Extractable Ca and K were statistically indistinguishable between the three treatment groups, but were higher in all treatment groups than in the characterization cores (Table S1). Extractable Mg was highest in the salt group, followed by the DI and recovery groups (which were not statistically different), and the characterization group had the lowest Mg.

4. Discussion

4.1. Salt retention capacity and timeline for release

Soils from both the rural and urban sites demonstrated a strong capacity to retain Na and Cl. This was particularly clear in the first NaCl irrigation when salt and recovery cores retained 62% of Cl and 66% of Na, on average. This high salt retention in the initial irrigation was largely caused by conservative porewater retention: salt content was lower in the leachate than in the irrigation solution partly because the leachate volume was smaller than the irrigation volume. In the salt treatment, leachate concentrations increased in subsequent flushes, until the final flush, when leachate Cl matched or slightly exceeded the concentration of the incoming irrigation solution. This indicates that after the addition of 2000 mg Cl over the course of the 5 week experiment, the capacity of the soils to retain Cl by any non-conservative mechanism was exhausted. However, the salt group cores were still releasing a lower mass of Cl in their leachate than they received through irrigation during the final flush, meaning that retention was still occurring in the porewater. At the end of the experiment, Cl was moving conservatively through the soil profile, but some was still retained at the same rate as water. Conversely, leachate Na concentrations in the final flush were still lower than irrigation solution concentrations, meaning that in addition to conservative porewater retention, retention via non-conservative Na behavior continued to occur.

While the salt group cores demonstrate how much Na and Cl these soils are capable of retaining, the recovery group cores reveal how long it takes the soils to release Na and Cl following road salt application. At the end of the experiment, the recovery cores still maintained about a quarter of the Cl and about half of the Na they received in the first two flushes. Based on their recovery rates, we estimate that it would take 14.8 weeks, 16.3 weeks, and 13.8 weeks

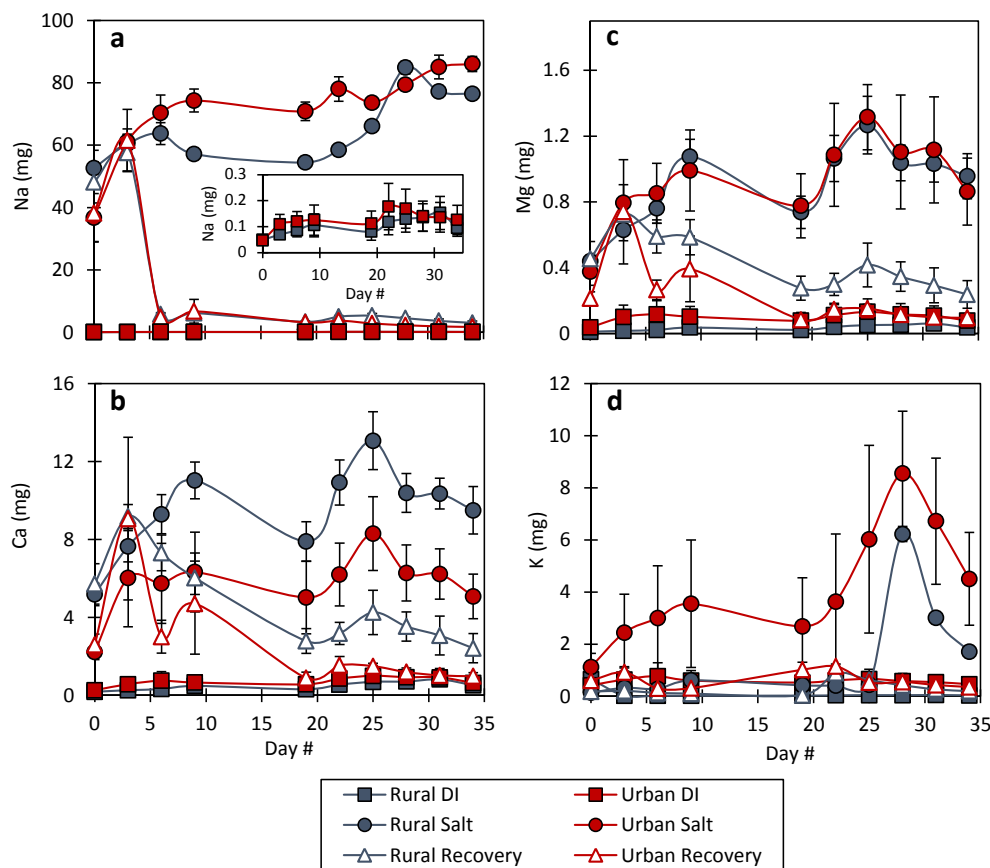


Fig. 5. Major cation concentrations in leachate from September cores. Na for all treatments is shown in a, with an inset showing the DI group cores. All treatments are plotted together for Ca (b), Mg (c), and K (d). Error bars show standard error among three replicate cores.

for the rural soils at 1 m, 5 m, and 13 m from the road, respectively, to release all added Cl. Urban soils require 17.5 weeks and 10.5 weeks to release all Cl at 1 m and 5 m, respectively. Urban cores from 13 m lost almost all the added Cl in the first DI flush indicating almost instantaneous Cl release. Our predicted 2.5–4 month soil retention timeline for Cl agrees reasonably with the findings of Kincaid and Findlay (2009), who estimated 2 months of Cl retention in New York soils (silt loams with similar OM content to our soils). Our experiment involved twice as many salt-free flushes as that of Kincaid and Findlay (2009), which may better capture the longer retention times observed in the field. Rural and urban cores from 5 m are predicted to release all Na in 20.7 weeks and 11.7 weeks, respectively; about 1–4 weeks longer than it takes for soils to release Cl because Na movement in soils is less conservative.

Our 2.5–5 month retention timeline for Na and Cl likely represents a minimum estimate for road salt storage in soils. In the field, these soils would likely retain salt longer than predicted by our experimental results due to drier and more variable moisture conditions, periodically higher road salt application rates, and more complicated water flowpaths than we simulated in the lab. Cores in our experiment received water more rapidly than they would in the field, with an average week of spring rainfall applied every 3 d except during the 9–10 d drying out period (between flushes 4 and 5), which slowed Na and Cl release. Conditions in the field would include more frequent and longer dry periods, slowing transport of salt-laden porewaters. Additionally, our intact cores only allowed vertical porewater transport through 15 cm of soil, whereas in the field, porewater can move both vertically through a soil profile of variable depth and horizontally along lateral flowpaths. Our

experiment showed that average Cl retention was significantly higher for rural soils than urban soils in July (there was no significant difference in Cl retention between the sites in September), and average Na retention was higher for rural soils than urban soils in September. However, total road salt application amounts are higher at the urban site due to a higher road density, increasing the timeline for salt release there. Salt application rates also vary from year to year depending on weather patterns, and the more salt that is applied, the longer it takes for soils to release the all applied Na and Cl from the previous winter. Therefore we expect soils to retain salt for more than 2.5–5 months in the field. In fact, monitoring of the shallow groundwater at both sites revealed evidence of Cl release from soils 6 months after salting had ceased (Robinson and Hasenmueller, 2016).

Both cumulative Na and Cl retention were controlled by an interaction between site and treatment. In the salt treatment, Na and Cl retention was higher for rural than urban cores; however, in the recovery treatment, urban cores retained more salt during the DI flushes. Therefore the rural soils can retain incoming salt more effectively, but they also release it more quickly. Leachate volumes were generally lower for our rural site in the first half of the July experiment (Fig. S1) and throughout the September experiment; lower leachate release corresponds to higher water retention and longer water residence, which could increase retention by providing more time for Cl to interact with soil particles and microbes. Bastviken et al. (2006) found that longer water residence times increased both Cl retention and release rates.

The DI cores released <4 mg Cl and <2 mg Na over the course of each flush experiment, showing that the salt released by the other

Table 5

Water content and extractable Cl for treated July cores by 5 cm depth segments. Standard deviation of three replicates is presented in parentheses.

	DI Treatment		Recovery Treatment	
	Water (%)	Cl (mg/kg)	Water (%)	Cl (mg/kg)
Rockwoods - 1 m				
0–5	41.52 (3.79)	13.2 (2.8)	66.73 (13.90)	223 (50)
5–10	36.61 (5.95)	10.1 (0.4)	45.53 (2.79)	144 (44)
10–15	36.94 (1.23)	16.4 (4.3)	39.98 (3.97)	203 (26)
Rockwoods - 13 m				
0–5	47.70 (6.24)	11.7 (2.6)	34.05 (2.34)	274 (95)
5–10	50.69 (4.08)	12.9 (3.1)	27.35 (8.55)	128 (25)
10–15	47.58 (1.00)	10.4 (0.9)	19.16 (8.54)	156 (66)
Blackburn - 1 m				
0–5	30.22 (0.28)	43.2 (19.1)	6.97 (4.34)	266 (43)
5–10	30.16 (0.78)	10.8 (2.1)	9.18 (6.48)	154 (80)
10–15			17.45 (17.02)	111 (37)
Blackburn - 13 m				
0–5	48.50 (12.86)	15.3 (1.7)	20.64 (4.41)	161 (23)
5–10	37.39 (1.81)	8.2 (0.6)	17.18 (1.64)	81.2 (18)
10–15	34.75 (1.55)	16.0 (5.9)	13.62 (3.37)	71.4 (10)

treatment groups came almost entirely from the added solution rather than from pre-existing salt contamination in the soil. We expected Cl in DI group leachate and in the characterization cores to decrease with distance from the road due to diminishing effects of road salt application. In July, leachate Cl was higher in DI cores from 1 m than 13 m; however, September cores from 5 m at each site produced higher leachate Cl than cores from either July location. Extractable Cl in untreated characterization cores from the rural site followed the same pattern, with concentrations 5 m from the road exceeding those at 1 m or 13 m, even among September transect samples. The unexpected pattern of extractable Cl concentrations peaking at 5 m from the road was likely driven by variation in soil properties with distance from the road. At the rural site, soils collected 5 m from the road had higher OM, total C, total N, CEC, and sand than soils at 1 m or 13 m. Furthermore, there was high variability in Cl among cores at 5 m. We suspect that soil properties at 5 m from the road at the rural site were different than at 1 m or 13 m because at 5 m the soils are located in a relatively low area that floods during heavy rain. This location also features

abundant trees.

4.2. Na retention via cation exchange

Higher percent retention and longer release timelines for Na compared with Cl can be explained by cation exchange processes. CEC was higher at the rural site, which also showed significantly higher Na retention. Evidence of cation exchange is seen through leachate concentrations of exchangeable cations. Salt group concentrations of Ca, Mg, and K were significantly higher than DI group concentrations because of replacement of these ions by Na on cation exchange sites. Ca and Mg release also varied with leachate volume: the DI and salt groups showed pronounced increases during the first four flushes and a decrease in the fifth flush after the drying out period. It is possible that some of the Ca and Mg we observed in the salt group leachate came from enhanced carbonate dissolution in the soils due to the ionic strength of the NaCl irrigation solution, but the magnitude with which the salt group Ca and Mg concentrations exceeded those of the DI group leads us to believe that cation exchange was the dominant control on the release of these ions.

A peak in salt group leachate K occurred in the eighth flush, while smaller peaks in Ca and Mg occurred in the seventh irrigation. Although we did not measure dissolved OM content in leachate, it is possible that the peak in divalent cations was associated with release of OM caused by sodic soil conditions. Amrhein et al. (1992) found that a peak in leachate Cu, Pb, Cr, Ni, and Fe was associated with a soluble OM peak in soil columns irrigated with NaCl. Although K is not strongly associated with OM (James et al., 2016), sodic conditions could also explain the K peak if colloid dispersion released interlayer K from 2:1 clay minerals (Norrström and Bergstedt, 2001). Indeed, the Na adsorption ratio (Na/(Ca + Mg)^{1/2} in mM/L) remained above 15 in salt group leachate throughout the experiment, indicating sodic conditions.

The release of exchangeable cations through the addition of road salt is important for two reasons. First, Ca, Mg, and K are important plant nutrients, so their release may influence primary productivity (Rendig and Taylor, 1989). Second, cation exchange is also a mechanism by which salt can induce the release of other, toxic metals from soils (Bäckström et al., 2004; Nelson et al., 2009), with

Table 6

Water content and extractable ions for treated September cores by 5 cm depth segments. Standard deviation of three replicates is presented in parentheses.

	Water (%)	Cl (mg/kg)	Na (mg/kg)	Ca (mg/kg)	Mg (mg/kg)	K (mg/kg)
Rockwoods - DI Treatment						
0–5	58.47 (2.42)	26.4 (4.8)	72.6 (20.3)	8260 (447)	358 (33)	125 (7)
5–10	58.25 (2.82)	16.9 (4.1)	65.9 (10.6)	6860 (398)	303 (33)	107 (9)
10–15	62.35 (4.39)	20.8 (5.9)	84.0 (13.5)	7570 (292)	374 (37)	119 (3)
Blackburn - DI Treatment						
0–5	33.48 (3.52)	33.4 (12.8)	65.2 (24.6)	3690 (543)	265 (11)	250 (26)
5–10	30.45 (2.40)	18.9 (4.5)	67.1 (50.6)	3330 (395)	235 (25)	195 (28)
10–15	33.68 (5.17)	16.7 (5.5)	83.6 (44.4)	3310 (161)	240 (33)	230 (64)
Rockwoods - Salt Treatment						
0–5	92.43 (24.85)	2900 (403)	1570 (540)	10 600 (567)	543 (16)	103 (37)
5–10	76.37 (6.48)	1400 (75)	991 (196)	9180 (357)	462 (16)	82.5 (34.4)
10–15	76.15 (0.60)	1320 (334)	1090 (228)	8520 (369)	448 (12)	81.1 (42.6)
Blackburn - Salt Treatment						
0–5	32.76 (5.07)	1050 (138)	856 (204)	2580 (355)	259 (69)	133 (51)
5–10	55.98 (21.77)	722 (24)	514 (136)	2320 (321)	271 (112)	225 (178)
10–15	37.98 (5.29)	829 (164)	604 (183)	2770 (781)	296 (112)	253 (194)
Rockwoods - Recovery Treatment						
0–5	59.81	388 (112)	339 (55)	9560 (2150)	472 (149)	117 (19)
5–10	77.63 (9.97)	190 (62)	288 (46)	8320 (1410)	404 (111)	105 (10)
10–15	79.92 (2.26)	216 (45)	300 (12)	8400 (877)	433 (36)	93.8 (7.8)
Blackburn - Recovery Treatment						
0–5	34.11 (2.90)	260 (50)	231 (20)	3370 (578)	201 (27)	213 (20)
5–10	31.55 (1.71)	89.0 (11.3)	189 (19)	3010 (422)	162 (25)	158 (21)
10–15	35.29 (0.56)	144 (14)	207 (16)	2760 (252)	145 (24)	137 (17)

deleterious effects on drinking water and aquatic life.

Leachate pH was significantly lower for salt group than DI group cores. Decreased pH in salt-impacted systems has been observed previously. Kim and Koretsky (2013) found that sediment cores incubated with NaCl had lower pH than control cores, which they attributed to enhanced microbial respiration or carbonate precipitation. Bäckström et al. (2004) found seasonally depressed pH in soil porewaters impacted by road salt due to proton displacement via cation exchange. Similarly, Schweiger et al. (2015) observed low pH in road salt impacted springs, and increasing pH with distance from a road among 52 German springs. They also cited cation exchange as the most likely mechanism for the pH reduction. In our cores, proton displacement was the most pronounced during the initial flush, when the leachate pH was the lowest for the salt and recovery groups.

Soil extraction results for Na and Cl in untreated, characterization and treated samples followed expected patterns due to salt retention: Na and Cl concentrations were highest in the salt treatment, followed by the recovery treatment, then the DI treatment (which had concentrations statistically equivalent to the characterization cores). However, results for Ca, Mg, and K were unexpectedly higher in all post-experiment treatments than in characterization cores, with the highest values observed in the salt treatment group. This is unusual because no Ca, Mg, or K was added to cores during the flush experiment, and salt group cores in particular released these ions in their leachate. These results may indicate that our method incompletely extracted exchangeable cations bound to clays or OM, so that soils in which these cations had been released to porewater appeared to have higher extractable cation concentrations.

4.3. Mechanisms for Cl retention

One mechanism for salt retention is the simple conservative retention of soil porewaters containing dissolved Na and Cl. As discussed in Section 4.1, water retention explains the large proportion of Na and Cl retained in all cores during first flush, when leachate volumes were small (some cores released no leachate until the second flush). Leachate volumes increased during subsequent irrigations, except between the fourth and fifth flush when cores were allowed to dry out for 9–10 d. This drying out period slowed release of Cl because the drier soils retained a larger proportion of the water applied in the following irrigation and therefore released less salt, even though evaporation had concentrated salt in the porewater. Further evidence for porewater retention over the course of the experiment is provided by the higher water content in treated cores compared to untreated, characterization cores. To distinguish between conservative Cl retention via porewater and non-conservative Cl retention mechanisms, we approximated the volume of porewater in recovery cores after the two salt irrigations and compared it to the volume of DI water subsequently added to the cores to test the extent to which the salt-laden porewater volume was replaced during the DI flushes. Porewater volume was calculated by multiplying initial water content (determined from the characterization cores) by the bulk sample mass, adding 200 mL of irrigation solution, and subtracting the leachate volume of the first two flushes; evaporative loss was excluded from the calculation. The porewater volume in each recovery treatment core was replaced 3.5–8.5 times during the DI flushes, depending on initial moisture conditions at the time and location of sampling, so in theory all the soil pores should have been flushed with DI. However, the salt retention we observed in the recovery treatment cores may be due to a variety of flow rates within the soil: some water may follow preferential flowpaths while other porewater clings to soil particles and is retained in the core. This means that although the

full volume of water was replaced multiple times in each core, some salt could nonetheless have been retained in porewaters conservatively.

In contrast, there are several potential Cl retention mechanisms constituting non-conservative Cl behavior. While this experiment quantifies salt retention, it does not allow us to distinguish between retention mechanisms. Nevertheless, Cl may be retained through chlorination of soil OM, uptake by microbes or plants, or non-specific adsorption. Formation of organochlorides is a relatively slow process: Bastviken et al. (2007) found that over 133 d, 4% of applied Cl was retained in Swedish forest soils through chlorination of OM, with most organochloride formation occurring after 35 d. If rates are similar for our soils (or slower due to 44% less OM in our soils), chlorination of OM is unlikely to have controlled Cl retention in our month-long lab experiment, but may be important over longer timescales in the field. Microbial Cl uptake is a faster process which caused 11–24% of Cl to be retained within a week in the Bastviken et al. (2007) experiment; this Cl was released again within a month. Rapid cycling of Cl by microbes is consistent with the timescale of retention and release we observed. Although we observed much higher Cl retention than Bastviken et al. (2007), some of this was attributable to physical retention in porewater: in the first flush, Cl retention was only 2–8% higher than water retention for September salt and recovery cores, and this extra Cl retention could be explained by microbial uptake. Vegetative Cl uptake and release has been observed on a multi-decadal, watershed scale (Lovett et al., 2005). Some intact cores in our experiment contained grass and other small plants which remained healthy throughout the experiment, and it is possible that these plants took up Cl from the soil porewater, although we cannot quantify the extent to which this occurred. However, it is unlikely that vegetative uptake controlled Cl retention because Cl was retained both in cores that contained vegetation and in those that did not. It is difficult to assess the importance of non-specific adsorption without detailed mineralogical information about our soils. Cl can adsorb to positively charged variable-charge mineral surfaces, and in addition to mineralogy, the extent of adsorption depends on surface area, OM, and soil pH (Black and Waring, 1979; McBride, 1994). Multiple mechanisms likely contributed to Cl retention via non-conservative behavior in our cores, but we hypothesize that microbial uptake was the most important.

Extractable Cl from field soils followed an unexpected pattern, with higher Cl in September than July at corresponding sampling locations, particularly at the rural site. Because no additional Cl was introduced by road salting between July and September, the increase in Cl must represent the release of some internal load, potentially through decomposition or dechlorination of OM or through microbial release. Internal Cl cycling could differ seasonally or could have been altered by changes in rainfall amounts. The forested rural site in particular may experience strong internal cycling of Cl through vegetative uptake followed by release during decomposition: high primary production would enhance uptake in July, but some of this OM would be decomposing and releasing Cl in September, although our sampling predated major autumn litter fall. Likewise, chlorination and subsequent dechlorination of OM could drive Cl cycling. Gustavsson et al. (2011) found higher rates of chlorination of OM in forested soils compared to agricultural or pasture soils, with 14–25% of added Cl undergoing chlorination over 138 d. Our urban soils are covered by a grassy lawn and contain less OM, so vegetative cycling and chlorination-dechlorination processes would be much less pronounced than at the rural site. Microbial Cl release could have been affected by changes in environmental conditions such as increased soil moisture due to the recent precipitation preceding September sampling (Bastviken et al., 2007), and microbially mediated changes could be greater

for the rural site compared to the urban site if the rural soils have a more diverse microbial community. The release of internal Cl in September was so substantial at the rural site that depth-averaged concentrations there exceeded urban concentrations at corresponding distances from the road—the opposite of the July pattern (Fig. 3a).

4.4. Soil parameters controlling retention

Soil characterization results reveal significant differences between the study sites, with higher OM, total C, total N, CEC, and sand at the rural site and higher bulk density, clay, and silt at the urban site. The forested setting contributes large amounts of OM in the form of leaf litter at the rural site, and total C and total N content correlate with OM. The urban site is a grassy lawn in an urban park, so lower OM and more compact soils are expected. Lower clay content and higher sand content at the rural site explain the faster infiltration rates observed there.

Our correlation analysis of soil properties provides preliminary insight into the parameters controlling Cl content in field soils. Sand, water content, OM, total C, and total N were strongly correlated with Cl and with each other. An association between Cl and OM could point to chlorination of OM as a mechanism for Cl retention; this mechanism can cause substantial retention on the timescale of years to decades (Bastviken et al., 2007). Alternatively, this relationship could indicate Cl retention via sorption to OM particles, although adsorption on mineral surfaces is more common (McBride, 1994). The correlation between Cl and water content indicates a link between Cl retention and porewater retention. However, water is negatively correlated with clay and silt and positively correlated with sand, suggesting that water content was higher in soils with larger pore spaces, not in soils with small particles that could more effectively retain water. It is possible that although the sandier soils facilitate faster infiltration, they also include more variability in flowpaths, with water draining rapidly through preferential pathways between sand grains. In this case, water in smaller pore spaces adjacent to clay particles could be retained longer because it interacts minimally with newer rainwater moving through preferential flowpaths. However, the correlation between Cl and water content may be driven by OM (which also correlates negatively with clay and positively with sand, water content, and Cl). OM may be responsible for holding water in the soils, which would cause retention of any dissolved Cl in the porewater. Because the parameters controlling Cl are also strongly correlated with each other, it is impossible to distinguish between their effects on Cl.

Surprisingly, CEC was negatively associated with clay but had a positive relationship with OM. This indicates that cation exchange sites on OM are more important than clay sites in these soils. A greater contribution of OM than clay to CEC has been observed in other soils, some with lower OM and higher clay content than ours (Drake and Motto, 1982; Hunt, 1981; Nwinyi, 1973; Turpault et al., 1996). Additionally, OM could block exchange sites on clays-size particles, rendering the clay fraction less important to CEC than OM particles and clay minerals in larger size fractions (Peinemann et al., 2000). Extractable Na was not correlated with any soil characteristics other than Cl; a larger sample size is likely required to resolve these relationships.

In addition to differences in soil characteristics, differing site history may explain the higher Na and Cl retention capacity observed at the rural site. Soils at the urban site have been exposed to higher road salt inputs for many years due to a higher road density. This means that more cation exchange sites are likely already occupied by Na from previous winters, lowering the soil's capacity to retain Na; the same is true for Cl and anion exchange

sites. Repeated exposure to road salt can dampen the dispersal effect caused by sodic conditions and reduce leaching of dissolved organic C and N when road salt is applied (Green et al., 2008). If most of the labile OM in the urban soils has already been leached during previous winters, this could reduce the ability of Cl to sorb to OM particles. Nevertheless, it appears that overall, soil type is more important than land use in controlling salt retention.

5. Conclusions

Retention in soils is an important factor in the delay between road salt application and the arrival of Na and Cl in shallow groundwater and streams. High summer Cl concentrations in streams are traditionally attributed to groundwater inputs, but we found that soils can also act as a reservoir for salt, explaining late-season first flush events whereby Na and Cl can increase temporarily at the onset of a flood. Soils gradually release salt to groundwater during spring and summer, and groundwater flow rates can subsequently control salt delivery to surface waters.

Our experiment examining Na and Cl retention in two soils of differing types and land uses shows that soils can take 2.5–5 months to release applied salt, with field conditions extending this timeline due to longer dry periods and deeper soils. We did not observe a clear pattern of decreasing Na and Cl with distance from the road; instead, we found that salt retention depended on soil type along our transects from roadways. Importantly, we observed that sandy soils high in OM retained more salt compared to denser, finer soils low in OM. Our results also highlight the importance of cation exchange in Na retention and in the displacement and subsequent release of other exchangeable cations including Ca, Mg, and K. Irrigation of soils with NaCl also depresses the porewater pH, likely as a result of cation exchange.

We found that conservative retention in soil porewaters is highly important in explaining Na and Cl dynamics. However, porewater movement alone cannot explain the retention we observed throughout this experiment; non-conservative retention mechanisms (via chlorination of soil OM, uptake by microbes or plants, or non-specific adsorption) also play a role in Cl retention. Nevertheless, highly impacted soils may receive enough salt to exhaust their ability to retain Cl non-conservatively by the end of winter, so that any further Cl retention is due to slow porewater movement. Future work should aim to isolate the effects of particular mechanisms explaining non-conservative Cl behavior.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://>

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