Laboratory evaluation of materials to treat chloride in stormwater

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Laboratory Evaluation of Materials to Treat Chloride in Stormwater

FINAL REPORT

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Introduction/Research Objective

Road salt application rates have increased steadily since the 1940s, with dramatic increases in the last 30 years. State departments of transportation as well as municipal public works departments are primarily concerned with public safety during winter events. Deicing salts such as sodium chloride or magnesium chloride lower the freezing point of water. Once dissolved, the sodium and chloride ions dissociate in solution. If this meltwater runs into the stormwater system, in many cases it is discharged directly into a local stream or river. If the meltwater runs onto a pervious area, it enters the soil and percolates through the unsaturated zone and travels readily through the soil, due to its negative charge and the negative charge on most soil surfaces. Practices have been implemented in many states to reduce salt loss from storage areas (Fitch, et al., 2005), however these methods are not practical on the expansive network of roads where deicing salts are applied. The ecological impacts of road salting are becoming clear (Brady, 2012; Findlay & Kelly, 2011).

Chloride concentrations in ground and surface waters in northern climates have been increasing for decades (Cassanelli & Robbins, 2013; Corsi, et al., 2015; Kaushal, et al., 2005; Mullaney, et al., 2009), with the most drastic increases found in urban watersheds, where deicing salt loading is highest. Although some mechanisms for chloride retention in soils exist (Bastviken, et al., 2006; Öberg, 2000), to date, no technique has been identified to prevent chlorides from getting into ground or surface waters. Reducing the mass of salt applied by using more efficient application methods seems to be the only practice to date aimed at minimizing the ecological impact of deicing salts.

Although a low percentage of drinking water wells have had chloride concentrations above the maximum contaminant level of 250 mg/L set by the U.S. EPA (Mullaney et al., 2009), much higher concentrations of chloride have been found in shallow groundwater and small streams (Kaushal, et al., 2005). High chloride levels in these ecosystems have negative effects on aquatic life (Brady, 2012; Findlay & Kelly, 2011). Connecticut is particularly vulnerable to the effects of road salt applications due to the large amount of urban land in our state. Clearly, this problem is going to get worse before it gets better, as no reasonably cost-effective alternative to road salt exists that can be used on a broad scale.

This project was a laboratory experiment designed to test the potential of two materials to reduce chloride concentrations in water. The objectives of the project were to determine the effect of an anion exchange resin and bioretention media on Cl retention. The broader goal was to build on the results of this laboratory research to reduce the impacts of road salt on aquatic systems in areas where salt is heavily applied. If successful, the results of this research could lead to a material and method to reduce chloride concentrations in stormwater runoff. This would benefit the aquatic life in Connecticut's streams (or potentially waters in other cold regions), and could reduce the potential for contamination of drinking water supplies as well.

Materials/Procedures/Progress

This project was performed in the Hydrology Laboratory in the Klinck Building at the University of Connecticut. A completely randomized factorial design was used. The factors included road salt concentration (zero, low and high), and ratio of resin:bioretention media (three levels from 0 to 10% resin by weight). There were three replicates of each factor, for a total of 27 treatments (3 salt levels X 3 anion resin percentages X 3 replicates = 27).

The anion exchange resin (A464, purchased from Evoqua Water Technologies LLC) was mixed with bioretention media (approximately 60% coarse sand, 20% leaf compost, and 20% topsoil) and installed in pvc soil columns (10.2 cm diameter x 30.5 cm long). Two layers of fiberglass window screen were installed on the bottom of the columns to contain the media. Column location on the bench was chosen at random (Figure 1).

Figure 1. Experimental setup in laboratory.

Road salt (95-99% sodium chloride, obtained from the facilities department at the University of Connecticut) was dissolved in deionized water to levels approximating those expected in melt water from winter deicing. Approximately once per week a measured quantity of salt solution (500 mL, or 2.7 cm, which is roughly equivalent to weekly precipitation in Connecticut) was applied to the top of the column, and collected after it passed through the media/resin blend. Three different influent chloride concentrations were applied: zero, low

(average 1,074 mg/L Cl), and high (4,645 mg/L). The columns were allowed to drain freely in between leachings, to simulate unsaturated soil conditions. The chloride concentration in leachate was measured with an ion-specific probe using method 9212 (US EPA 1996), and pH was also measured using an Orion pH meter. Although not part of the original proposal, the color of the leachate was also measured using method 2120 (APHA 2012), as distinct color differences were noted for different treatments. The experiments were conducted from June through November 2015. A total of 22 leaching events were performed.

Results/Significance

In the preliminary laboratory investigation that led to this project, conductivity measurements were used to get an estimate of how well the resin and the resin combined with bioretention media would reduce salt levels. Initial findings showed lower conductivity measurements from bioretention media combined with resin, whereas the resin alone did not change the conductivity in influent water.

Chloride

The current laboratory experiment measured chloride concentrations in influent and effluent water. The bioretention media alone with no resin added reduced influent chloride concentrations slightly, however by the fourth leaching (both high and low salt), effluent chloride concentrations were at or above influent levels (Figure 2). These findings indicate some storage of chloride in the media, presumably in the organic matter present (compost is a component of the media). Interestingly, the media with no resin and no salt showed measurable concentrations of chloride for the first two leachings, but concentrations dropped to near zero after that (Figure 2). It is not clear where this chloride came from.

In the treatments with resin included, the 10% resin/bioretention media blend was able to completely remove low concentrations of chloride, however breakthrough occurred after 5 leachings in the high salt application (Figure 3). The 100% resin treatment removed all of the chloride applied, even in the high salt application. This finding was in contrast to our preliminary investigation on the resin alone, where conductivity was measured instead of chloride. The likely explanation for this finding is due to the retention mechanism in the resin: the resin has hydroxyl (OH^-) anions on exchange sites that are displaced by chloride (Cl^-) anions. Therefore, when Cl is removed from water in contact with the resin, OH concentrations in that water increase proportionally. This is likely why the conductivity remained essentially the same in preliminary findings. When only Cl is examined, it is clear that the resin retains it quite readily, even at high concentrations. Interestingly, some white crystals began to form around the base of the columns with resin present after several leachings (Figure 4). It is presumed that this is sodium hydroxide, formed when dissociated sodium (Na) in influent water combined with free OH to from NaOH.
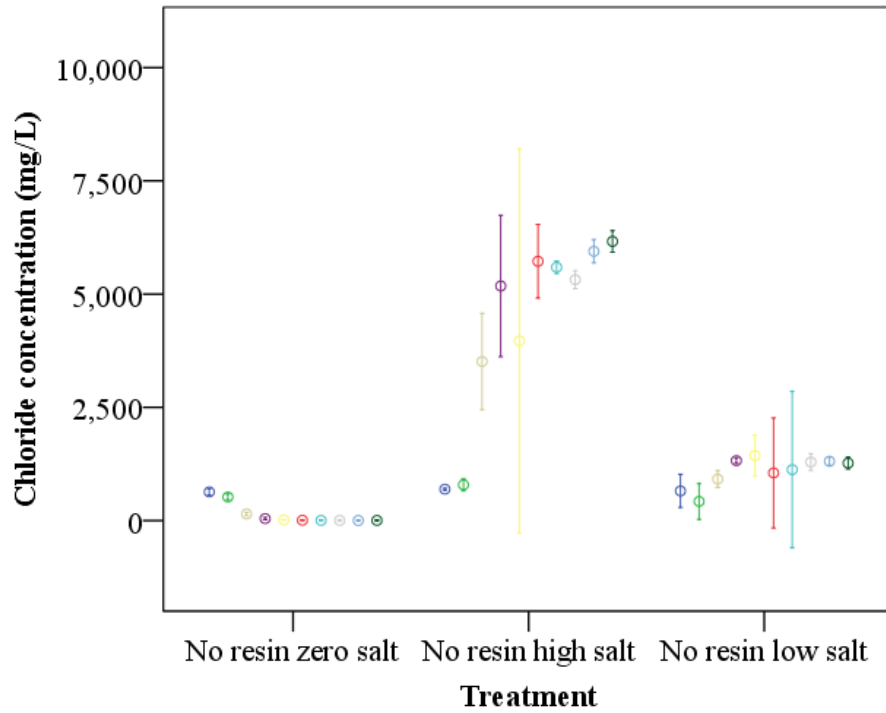
Figure 2. Chloride concentrations for ten successive leachings for different salt treatments with no resin. Error bars represent 95% confidence intervals.
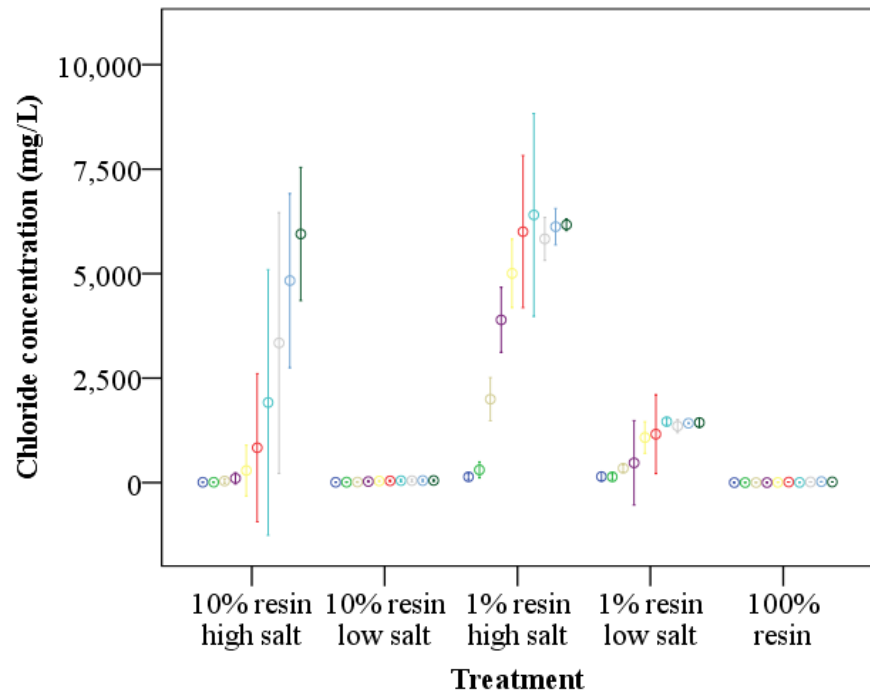

Figure 3. Chloride concentrations for 10 successive leachings for different salt and resin treatments. Error bars represent 95% confidence intervals.

Figure 4. Crystals forming around base of columns with resin present, presumed to be NaOH.

Due to the finding that the 1% resin treatment did not appear to have much impact, it was dropped from further analysis. Additional leachings were performed on the 10% resin until breakthrough occurred (Figure 5). After a number of leachings, an "extreme" salt solution (average 6,746 mg/L Cl) was applied to the 100% resin (Figure 6). The 100% resin retained all of the applied Cl through the duration of the study; additional leachings were performed with very high (~15,000 mg/L Cl) to force breakthrough. The total mass of Cl applied to the 100% resin treatments was 68.9 g Cl; the mass of the resin was 1,150 which results in roughly 6% retention by weight. However, breakthrough was observed in the 10% resin treatments after 4 leachings. In the 10% resin treatments, 205 g of resin was included in the mixture, and 9.2 g of
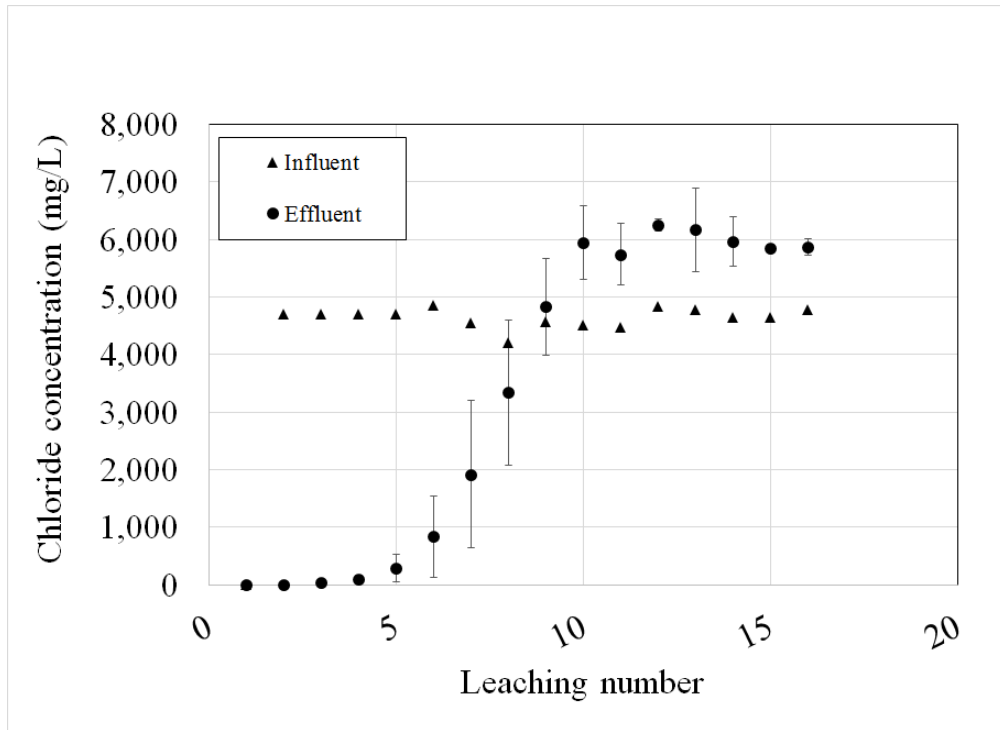
Figure 5. Influent and effluent chloride concentrations for the 10% resin/bioretention media blend. Error bars represent ± 1 standard deviation.
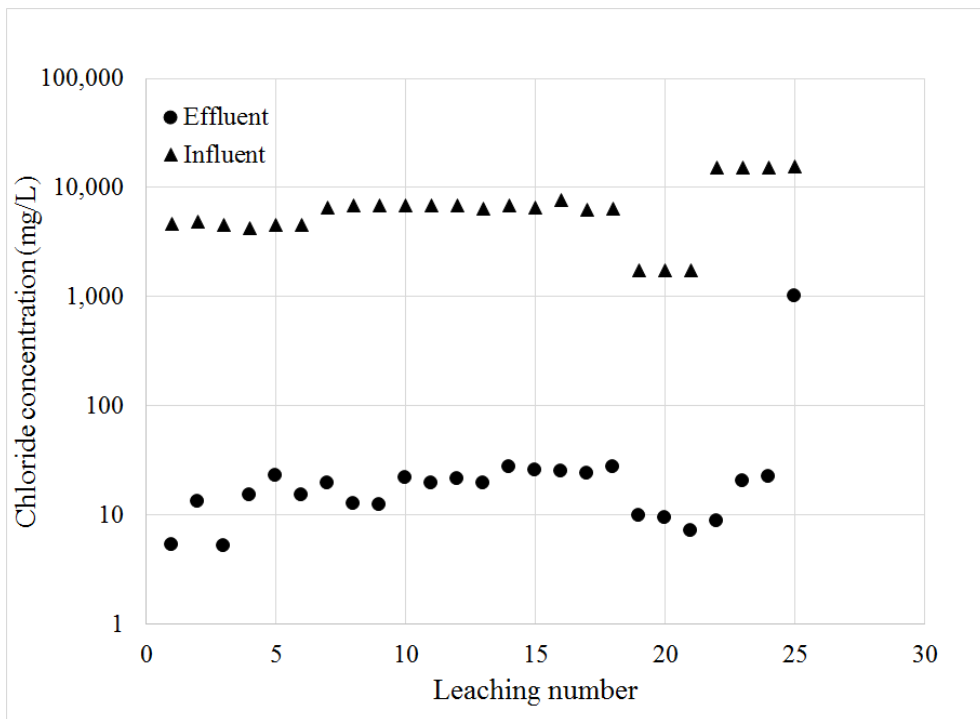

Figure 6. Influent and effluent chloride concentrations for 100% resin.

Cl was fully retained. Therefore, 9.2 g of Cl was retained per 205 g of resin, or roughly 4.4%. It is not clear why breakthrough in the 100% resin was 6% instead of 4.4%; perhaps there is some confounding effect from the bioretention media.

pH
pH of leachate from columns with zero resin/zero salt treatments averaged between $7 - 8$, whereas treatments with resin and salt application were much higher (Figure 7). Leachate from the zero resin control was significantly lower than the 10% resin high salt ($p<0.01$) and the 10% resin low salt ($p<0.05$) treatments. As discussed earlier, the excess OH anions displaced from the resin would raise the pH of the leachate, so these findings are not surprising. Leachate from the 100% resin treatment (not shown on graph) was consistently above pH 12, and was significantly higher ($p<0.001$) than any other treatment.
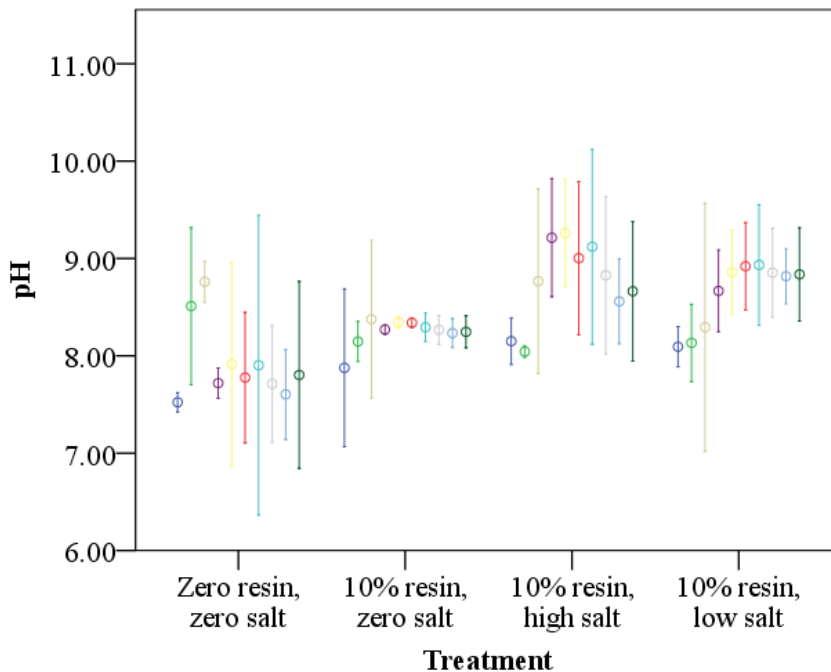

Figure 7. Leachate pH in 10 successive leachings. Error bars represent 95% confidence intervals.

Color
During the experiment, substantial differences in the color of the leachate were noted (Figure 8). As noted in the methods, color analysis was not part of the original proposal, however when the extreme color differences in leachate were noted, color analysis was performed. Some coloration was noted in the columns with no salt applied (both no resin and 10% resin treatments) initially, however color lightened over the course six analyses (Figure 9). Very dark color was noted on the 10% resin/high salt columns, and moderately dark color was noted on the

10% resin/low salt columns (Figure 9). It is suspected that the high pH generated by the OH anions caused leaching of humic molecules from organic matter in the media. Leaching of humic and fulvic acids has been noted in waters with high pH (Christman & Ghassemi, 1966). The effect moderated after six leachings, presumably after the organic matter pool became exhausted.
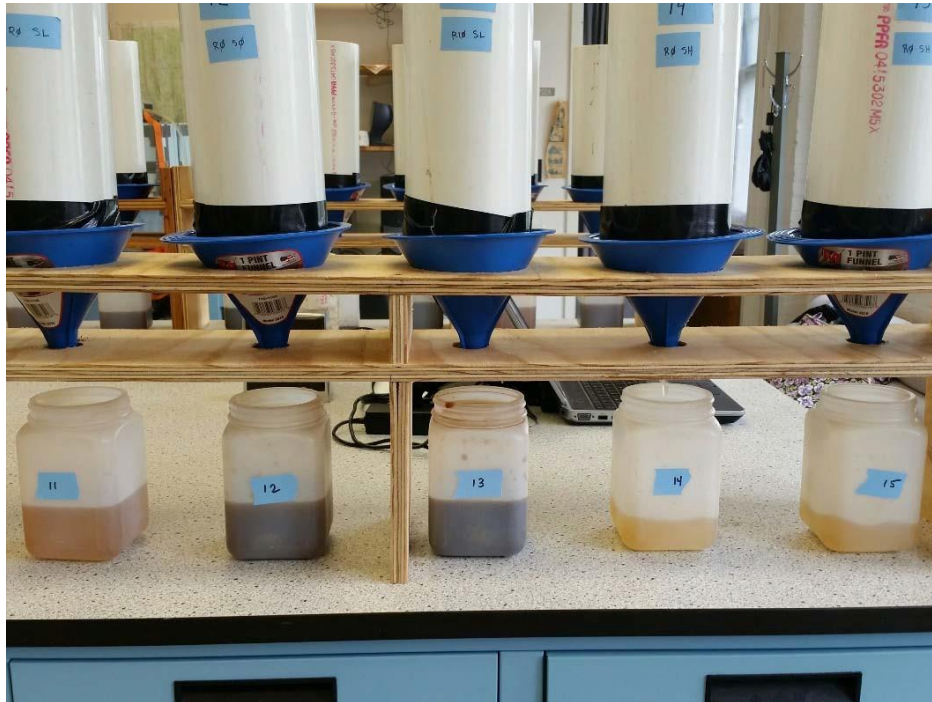

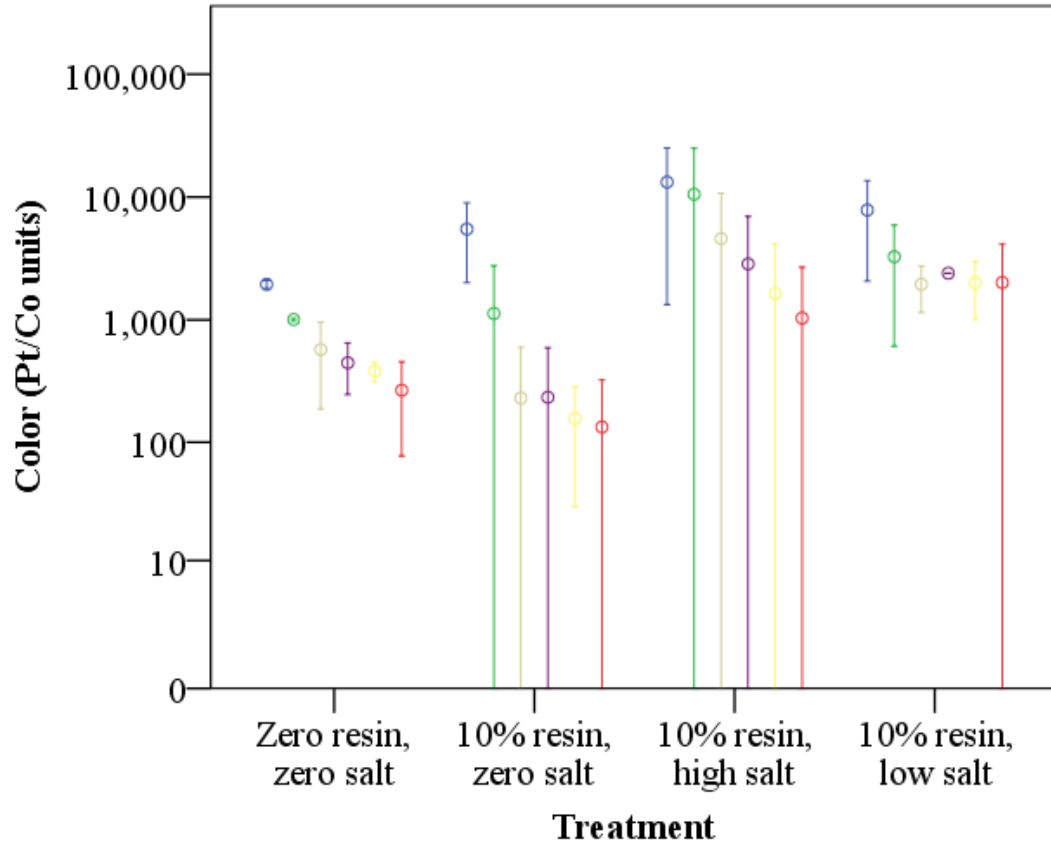**Figure 8. Color differences in leachate from different treatments.**

Figure 9. Leachate color of selected treatments.

Conclusions

Bioretention media and an anion exchange resin were leached with different concentrations of road salt. Although preliminary investigations prior to this study indicated an interaction effect between the resin and the bioretention media, the laboratory research associated with this study has indicated that the resin is the dominant chloride capture mechanism. The resin alone was able to retain very high (up to ~15,000 mg/L) concentrations of chloride, and 6% of applied chloride was retained before breakthrough occurred. The pH of water passing through the resin treatments was increased due to the release of OH ions from the resin. Unexpected changes in the color of leachate among treatments was also documented; it is surmised that the high pH increased the loss of humic and fulvic acids from the organic matter in the treatments which had bioretention media.

The anion exchange resin investigated in this study performed unexpectedly well in retaining high concentrations of chloride. The resin could be a promising tool in addressing the ongoing issue of excess road salt loading to surface and ground waters. Testing of the resin in a field application is the next step in determining if this is a viable solution.

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