Modeling the effects of road salt on soil, aquifer, and stream chemistry

Joel Moore1,2, Steven M. Lev1,2, Ryan E. Casey2,3
1Dept. of Physics, Astronomy, & Geosciences, Towson University, moore@towson.edu, slev@towson.edu, Towson, MD, USA
2Urban Environmental Biogeochemistry Laboratory, Towson University, Towson, MD, USA
3Dept. of Chemistry, Towson University, racasey@towson.edu, Towson, MD, USA

ABSTRACT

Millions of tons of de-icing compounds, primarily the road salt NaCl, are added annually to roads and other impervious surfaces across the northern regions of North America and Europe. In the last decade, scientists and regulators have become increasingly aware that runoff containing high concentrations of NaCl from road salt negatively impacts roadside soils, shallow groundwater, and freshwater streams. A concurrent development has been the growing use of stormwater management basins (SMBs) to redirect surface runoff from impervious surfaces into shallow groundwater. An unanticipated consequence has been the loading of NaCl into those SMBs and subsequently into shallow groundwater. As water containing NaCl flows through shallow groundwater, high Na concentrations will “push” important plant micronutrients like Ca, K, and Mg off the cation exchange complex in shallow aquifers and soils. This chemical alteration will likely have negative effects on the plant communities overlying the shallow groundwater and perhaps also for the freshwater streams into which the groundwater discharges. We use a year-long geochemical dataset from a SMB and adjacent shallow groundwater aquifer in Maryland along with the USGS program PHREEQC, to model changes in aqueous chemistry and the composition of the cation exchange complex.

INTRODUCTION

The use of de-icing compounds, primarily the road salt NaCl, has increased over the last several decades across the northern regions of North America and Europe. Application rates in the US tripled from 1975 to 2005, reaching nearly 25 million tons per year (Mullaney et al., 2009). It has become increasingly clear that runoff containing road salt is negatively impacting the chemistry of roadside soils, shallow groundwater, and freshwater streams (e.g., Kaushal et al., 2005; Ramakrishna and Viraraghavan, 2005). This impact has been particularly apparent in the steadily increasing concentrations of sodium (Na) and chloride (Cl) in freshwater streams across northern Europe and North America (Löfgren, 2001; Kaushal et al., 2005; Casey et al., 2013). In many urban and suburban areas, concentrations of Cl in streams episodically, or even seasonally, exceed the chronic or the acute thresholds set by the US EPA for the protection of aquatic ecosystems (Kaushal et al., 2005; Kelly et al., 2008). High Na and Cl concentrations in streams have negative implications for human health and for ecosystem function (e.g., Kaushal et al., 2005; Ramakrishna and Viraraghavan, 2005; Findlay and Kelly, 2011).

Research to date has focused on stream chemistry. However, increasing attention is being devoted to the surface and subsurface pathways by which road salt moves from the site of application to the streams (e.g., Ostendorf et al., 2009; Casey et al., 2013). Characterizing these pathways is critical to being able to predictively model road salt runoff to assess future impacts of road salt runoff or of any regulations proposed to reduce the impact of road salt. The pathways taken will depend on the age of development within a watershed. In watersheds where development occurred before the 1970s or 1980s, runoff from roads and other impervious surfaces often flows into storm sewers and then directly into streams. However, in newer development, surface runoff is directed into engineered stormwater management basins (SMBs). SMBs are added as a best-practice solution to mitigate the impact of runoff from impervious surfaces to surface water by creating infiltration basins that reconnect runoff with groundwater in an attempt to restore pre-development hydrology. SMBs also act as a sink for runoff containing sediments and metal-rich debris produced by automobiles, e.g., Zn from tires and Cu from brake pads and prevent those materials from moving into streams. An unintended consequence of SMBs is the
transfer of road salt to shallow groundwater and eventually low-order streams (Casey et al., 2013). Some of the salt is retained in the SMB-groundwater system. In fact the SMBs seem to act as a “capacitor” for road salt where some portion of road salt is retained and then slowly released to shallow groundwater and surface waters (Casey et al., 2013).

The goal of this study is to model the effects of NaCl addition on soil, aquifer, and stream chemistry. In particular, we are interested in modeling how the addition of NaCl affects the composition of the cation exchange complex (CEC) in soils and aquifers. The cation pool most readily available for plant growth and nutrition – Ca, K, and Mg – is contained in the CEC. We will show that the addition of solutions with high concentrations of Na changes soil and aquifer chemistry and by altering groundwater chemistry affects stream chemistry. We will use PHREEQC to model the effects of Na addition.

FIELD SITE DESCRIPTION & METHODS

The study site is located in Baltimore County, Maryland within the Piedmont physiographic province. Bedrock at the field site is late Proterozoic schist containing biotite, plagioclase feldspar (oligoclase), muscovite, and quartz. The bedrock has weathered to form the Baile soil series. Baile soils are acidic (pH ≤ 5.3) and poorly drained (Soil Survey Staff). Given the parent material and soil acidity, the CEC is likely to be primarily found on secondary kaolinite and soil organic matter. The site contains two stormwater management basins (SMBs) on the south side of a small floodplain. SMB P5 (to the east) collects runoff from a medium-sized condominium complex and secondary and tertiary roads; SMB P6 (to the west) collects runoff from a small condominium complex. The SMBs are designed to allow runoff from a moderate precipitation event (e.g., a 5 year storm event) to completely infiltrate in 24-48 hours. Infiltrated runoff flows ~200 meters to the northeast across the floodplain through a shallow groundwater aquifer where it discharges to three first-order streams, which drain into an unnamed second-order tributary (Unnamed Stream) of Red Run, or discharges directly into Unnamed Stream. Red Run is a tributary of the Gwynns Falls, which drains into the Chesapeake Bay via the Patapsco River.

Fifty-five stainless steel wells were installed at the site in 2009 with 13 wells within the SMBs and 42 for sampling of the shallow groundwater along the flow pathway between the SMBs and Unnamed Stream. Groundwater was collected from the wells in June and Nov. of 2009 and Feb. and May of 2010. The conductivity of water samples was measured in the

Figure 1. Groundwater Cl concentrations in floodplain wells (adapted from Flora, 2012)
field using a YSI-30 conductivity meter. Samples were syringe filtered (0.45 μm) before analysis. Cations (Ca, K, Mg, and Na) and anions (Br, Cl, F, NO₂, NO₃, PO₄, and SO₄) were analyzed using a Dionex ICS-5000 ion chromatograph. Geochemical modeling is performed using PHREEQC (Parkhurst and Appelo, 1999) with the PHREEQC database. Model parameters are a combination of measured (groundwater) and literature (CEC) values. The model cation exchange complex (CEC) is 100 meq kg⁻¹ based on the weighted average for the site (Soil Survey Staff). The soil bulk density is 1.44 g cm⁻³ (Soil Survey Staff). Porosity is calculated to be 0.45 based on the bulk density and an assumed mineral density of 2.7 g cm⁻³. Using the bulk density and porosity, the CEC is converted to a solution basis (320 meq L⁻¹).

RESULTS & DISCUSSION

Groundwater Geochemistry

The geochemistry of the floodplain aquifer falls into two categories: 1) undisturbed groundwater that is relatively dilute (Ca > Mg > Na > K) and 2) groundwater enriched in NaCl from road salts that is found below the SMBs and in plumes extending out from the SMBs (Table 1, Fig. 1). Undisturbed groundwater is primarily found on the west and north sides of the shallow groundwater aquifer (Fig. 1). NaCl enriched water appears within two persistent Na and Cl shallow groundwater plumes, the eastern plume from SMB P5 and the western plume from SMB P6 (Fig. 1). The subsequent results and discussion will focus on the P5 plume. Solute concentrations in the SMBs and plumes are 10²–10³ higher than undisturbed groundwater; relative cation concentrations are Na >> Ca > Mg > K (Table 1). Though the plumes are persistent, Cl (Fig. 1 and Fig. 2) and Na (Fig. 2) concentrations fluctuate seasonally as water containing road salt flows through the system. Plume Cl concentrations were relatively low in June 2009 (5000 – 20,000 μmol L⁻¹ or 5 – 20 meq L⁻¹), in part because the 2007 – 2008 and 2008 – 2009 winters had below average snowfall. The plumes expanded and concentrations increased up to a maximum of 100,000 μmol L⁻¹ in Feb. and May 2010 following the application of road salt.

Cl is assumed to be a conservative tracer, i.e., to flow through the groundwater at the same rate as the water because it is negatively charged and thus will react minimally with negatively-charged sites in the CEC. In contrast, positively charged Na has the potential to sorb to CEC sites. When present in equal concentrations, major cations preferentially sorb to the CEC in the following order Ca > Mg > K > Na. However, when Na concentrations are high, Na can replace Ca and Mg on the CEC. The groundwater has the Na:Cl molar ratio ~1 in the SMBs and along a transect of the SMB P5 plume flowpath in May of 2009 (Fig. 2). In contrast, Na concentrations are much lower than Cl with Na:Cl ratios ranging from 0.04 – 0.43 along the transect in Feb. and May 2010 (Fig. 2). In fact, in May 2010, a relatively clear chromatographic pattern where Cl concentrations are roughly constant but Na concentrations decrease along the transect (Fig. 2). This pattern occurs as cation exchange removes Na and reduces the Na:Cl ratio along the flow path.

<table>
<thead>
<tr>
<th>Concentration (meq L⁻¹)</th>
<th>Percent concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ca</td>
</tr>
<tr>
<td>Groundwater</td>
<td></td>
</tr>
<tr>
<td>Undisturbed</td>
<td>0.69</td>
</tr>
<tr>
<td>Avg. SMB P5</td>
<td>8.83</td>
</tr>
<tr>
<td>Avg. SMB P5 low conc.</td>
<td>2.66</td>
</tr>
<tr>
<td>Avg. SMB P5 high conc.</td>
<td>16.0</td>
</tr>
<tr>
<td>Avg. P5 plume</td>
<td>0.91</td>
</tr>
<tr>
<td>Cation exchange complex</td>
<td></td>
</tr>
<tr>
<td>Undisturbed</td>
<td>227</td>
</tr>
<tr>
<td>Equilib. with P5 low conc.</td>
<td>195</td>
</tr>
<tr>
<td>Equilib. with P5 high conc.</td>
<td>109</td>
</tr>
<tr>
<td>After 5 years of flow from P5</td>
<td>177</td>
</tr>
<tr>
<td>After 10 years of flow from P5</td>
<td>155</td>
</tr>
</tbody>
</table>

Table 1. Geochemistry of the groundwater (measured) and CEC (calculated or modeled)
Modeling of groundwater and CEC geochemistry

The CEC composition in equilibrium with the various groundwater chemistries was modeled using PHREEQC. The undisturbed CEC is dominated by Ca and Mg (~99% of cations, Table 1). The size of the CEC pool (320 meq L\(^{-1}\)) greatly exceeds undisturbed groundwater cation pool (1.48 meq L\(^{-1}\)). The significantly different composition of NaCl enriched water entering the groundwater from the SMBs, both in terms of concentrations (49 – 350 meq L\(^{-1}\)) and elemental ratios, is predicted to impact the CEC composition. When the CEC pool is equilibrated with the low concentration end member from SMB P5, Na replaces ~60% of the Mg and 15% of the Ca; when equilibrated with the high end member, Na replaces nearly 90% of the Mg and >50% of the Ca in the CEC (Table 1).

Of course, the groundwater is not stagnant but is continually flowing, and the chemical composition oscillates between the low and high concentration end members from P5. We used the reactive transport capability of PHREEQC to model solution and CEC chemistry changes for the P5 transect over a 10-year time period. We modeled the ~200 m distance from P5 to Unnamed Stream as a 200 grid cell system. The residence time of water in each grid cell was 1.67 days, based on an estimated flow rate of 0.6 m per day (Flora, 2012). The input chemistry oscillated between high concentration water (20 days) and low concentration water (345 days) from SMB P5. Dispersivity was set at 5 m.

Modeling results for geochemistry are shown in Fig. 3. Na concentrations at the northeast end of the plume flow path increased from 0.33 to 36 meq L\(^{-1}\) over the first two years of salt input and then more gradually increased with time (Fig. 3). Ca concentrations increased from 0.69 to 34 meq L\(^{-1}\) over the first year, remained high

![Figure 2. Na and Cl concentrations along transect of P5 plume. Dashed line is secondary EPA limit (7.04 mmol L\(^{-1}\)) for drinking water.](image1)

![Figure 3. Model results for solution chemistry at northeast end of transect along P5 plume.](image2)
through year 2, and then decreased toward the weighted average of the input Ca concentration. Note that predicted groundwater Ca concentrations entering the stream are higher than those in the undisturbed system. The pattern for Cl (not shown) looks similar to Na although the values oscillate around a constant concentration after year 1. Modeled Na and Cl peaks arrive at the end of the flow path at the same time with no lag for Na. The synchronicity of peak arrival indicates that something is missing in the model. The two most likely factors missing in the model are 1) a kinetic component for sorption and 2) a hydrological regime that is more complex than plug flow and is perhaps changing in response to Na loading, which is known to reduce permeability in soils. Future modeling work will address those factors.

Modeled CEC compositions are reported in Table 1. The CEC changed most rapidly in the first 5 years with Na increasing from <1% up to >26% of the CEC. In contrast, Ca concentrations decreased by 22% and K and Mg decreasing by ~35% compared to undisturbed CEC concentrations. Na concentrations continued to increase and Ca, K, and Mg concentrations continued to decrease from years 5 – 10. After 10 years of reaction with road salt-enriched water, Na increased from 0.60% to 37.4% of the CEC while Ca and Mg dropped by 38% and 50%, respectively.

**SUMMARY**

Our results, both analytical and modeling, show that road salt loading into a soil, shallow aquifer, and stream system significantly impacts the geochemistry. Waters containing road salt have significantly higher concentrations of solutes than undisturbed water. Additionally, the cation ratio is substantially altered, and Na, which has little value as a nutrient to flora or fauna, becomes the dominant cation in the system. Future work will involve collection and analysis of the CEC to compare to model results, more frequent collection of groundwater samples, and addition of more complexity to the modeling effort.

**ACKNOWLEDGMENTS**

We acknowledge the hard work by Rob Flora as part of his M.S. thesis work, Funding was provided by the USGS–Maryland Water Resources Research Center and a USGS National Competitive Grant through the Water Resources Research institute at the University of Maryland (Project ID: 2007MD160G).

**REFERENCES**


