



Research article

Na/Cl molar ratio changes during a salting cycle and its application to the estimation of sodium retention in salted watersheds

Hongbing Sun^{*}, Maria Huffine, Jonathan Husch, Leeann Sinpatanasakul

Department of Geological, Environmental, and Marine Sciences, Rider University, Lawrenceville, NJ 08648, USA

ARTICLE INFO

Article history:

Received 20 July 2011

Received in revised form 13 May 2012

Accepted 25 May 2012

Available online 5 June 2012

Keywords:

Sodium retention

Cation exchange

Watershed

Road salt

ABSTRACT

Using soil column experiments and data from natural watersheds, this paper analyzes the changes in Na/Cl molar ratios during a salting cycle of aqueous-soil systems. The soil column experiments involved introducing NaCl salt at various initial concentrations into multiple soil columns. At the start of a salting cycle in the column experiments, sodium was adsorbed more than chloride due to cation exchange processes. As a result, the initial Na/Cl molar ratio in column effluent was lower than 1, but increased thereafter. One-dimensional PHREEQC geochemical transport simulations also were conducted to further quantify these trends under more diverse scenarios. The experimentally determined Na/Cl molar ratio pattern was compared to observations in the annual salting cycle of four natural watersheds where NaCl is the dominant applied road deicing salt. Typically, Na/Cl molar ratios were low from mid-winter to early spring and increased after the bulk of the salt was flushed out of the watersheds during the summer, fall and early winter. The established relationship between the Na/Cl molar ratios and the amount of sodium retention derived from the column experiments and computer simulations present an alternative approach to the traditional budget analysis method for estimating sodium retention when the experimental and natural watershed patterns of Na/Cl molar ratio change are similar. Findings from this study enhance the understanding of sodium retention and help improve the scientific basis for future environmental policies intended to suppress the increase of sodium concentrations in salted watersheds.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Sodium is commonly considered more reactive than chloride in an aqueous-soil system (Drever, 1997; Freeze and Cherry, 1979). If equal molar amounts of sodium and chloride are flushed through an aqueous-soil system, sodium tends to have greater adsorption onto soil colloids than chloride due to its readiness to exchange with other cations. As a result, the overall Na/Cl molar ratio in this type of soil solution is expected to be less than 1.0. The more sodium is adsorbed, the lower the Na/Cl molar ratio. Therefore, the Na/Cl molar ratio can be used as an indicator of the sodium retention in natural and experimental aqueous-soil systems.

For this study, we define a salted watershed as a watershed

where the amount of anthropogenic salt input, primarily the application of sodium chloride in the form of road deicing salt, is significantly larger than the amount of salt input from natural weathering. If a relationship model between the Na/Cl molar ratio in stream discharge and the amount of sodium retention for a salted watershed can be established, the actual sodium retention can be estimated based upon the measurement of Na/Cl molar ratios.

Traditional studies on the estimation of sodium retention have commonly used a simple budget analysis method, i.e. a direct estimation of the difference between salt input and output for a specific watershed (Kelly et al., 2008). In these studies, the input amount of road deicing salt, the main contributor to increased sodium chloride in a watershed, is estimated as the product of lane mileage and tons of salt per lane-mile reported by state departments of transportation (DOT). Although this method is workable for a small watershed

^{*} Corresponding author.

E-mail address: hsun@rider.edu (H. Sun).

(Howard and Haynes, 1993; Kelly et al., 2008), for large salted watersheds located across multiple states, this method can be laborious and difficult to apply. This is due to the highly variable amounts of salt applied on roads, parking lots and driveways owned by multiple state, township and private entities, and the variable amounts of salt released into streams from sewage and water softeners (Godwin et al., 2003; Kaushal et al., 2005).

Increases of sodium in streams have been reported for many regions in the northeastern United States (Fig. 1), Canada and Europe where road deicing salt applications are regular and significant (Howard and Beck, 1986, 1993; Kjensmo, 1997; Labadia and Buttle, 1996; Locat and Gelinis, 1989; Lofgren, 2001; Meriano et al., 2009; Shanley, 1994; Velbel and Price, 2007); these applications have been considered as the primary reason for the observed increases (Kelly et al., 2008). High concentrations of sodium in a watershed are not only detrimental to fluvial, lacustrine and riparian ecosystems, but represent a potential health threat to people (Ramakrishna and Viraraghavan, 2005).

There has been an increase in the number of incidences of sodium concentrations exceeding 20 mg/l limit (recommended by the United States Environmental Protection Agency and the American Heart Association) in rivers that supply more than one-half of the drinking water for riparian states in the United States where sodium is not treated (Godwin et al., 2003; Nimiroski and Waldron, 2002). An insufficient understanding of watershed sodium retention can hinder the effectiveness of an environmental policy that intends to reduce sodium loading. For example, the 1990 Rhode Island state-mandated application of road salt with a $\text{CaCl}_2/\text{NaCl}$ ratio of 6:4, specifically for the purpose of sodium reduction, has not produced any obvious sodium reduction since the policy's inception (Breault and Smith, 2010; Nimiroski and Waldron, 2002).

Through laboratory soil column experiments, computer simulations and analyses of field data, this study examines the change in molar ratio of sodium and chloride due to their differential adsorption onto soil colloids and establishes relationship models between the Na/Cl molar ratio and sodium retention. Four soil column experiments with variable ionic concentrations, along with multi-scenario computer simulations

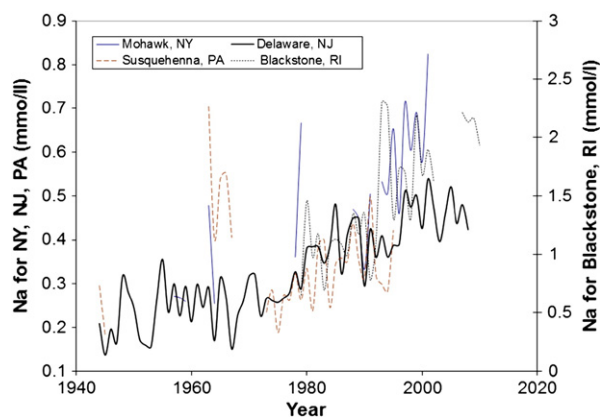


Fig. 1. Historical changes in sodium concentrations in water samples from four watersheds in the northeastern United States. Data were obtained from the United States Geological Survey (USGS) water quality online database.

of sodium and chloride transport and cation exchange, were conducted to establish the basis for this method. Sodium and chloride concentrations from four natural watersheds, Delaware River (DR), Mohawk River (MR), Susquehanna River (SR) and Blackstone River (BR) (Fig. 2), were examined to delineate the seasonal and long-term changes of Na/Cl molar ratios. These watersheds were selected because of their salting history, the availability of long-term records of sodium and chloride concentrations in their constituent streams and, in particular, the availability of long-term records from the pre-salting era prior to 1964. In comparison to the traditional budget analysis method, this new molar ratio approach can estimate sodium retention in situations where the traditional method has difficulty.

2. Ion-exchange soil-column experiments

The total adsorption of sodium or chloride onto soil colloids is a function of their physical, electrostatic and chemical adsorption processes. Due to chloride's conservative properties, its total adsorption is relatively insignificant, except for a small effect due to anion exchange (Freeze and Cherry, 1979). For sodium, its retention due to physical adsorption is relatively insignificant because of the weak van der Waals force involved. In addition, because of its chemical properties and the commonly low salt saturation in soil solutions, sodium deposition by chemical reaction can be ignored (Shanley, 1994). Therefore, the adsorption of sodium by electrostatic adsorption, i.e. cation exchange, is the only significant contributor to its retention and is the main adsorption mechanism evaluated in the soil column experiments and computer simulations discussed here.

Four two-inch (50.8 mm) diameter columns were filled with approximately 400 g of dried loamy soil collected from a site in the Delaware River Watershed (DRW) of New Jersey. Tap water was flushed through the soil columns using a constant head set-up, following Fetter (2000), for the initial 48 h so that the ions on the soil colloids and in the soil solutions were at equilibrium. Then 1.0, 0.5, 0.25 and 0.125 mol of sodium chloride solutions (1100 ml in volume) were flushed through each column, respectively, using a falling-head apparatus to avoid any overflow of the injected solutions. Tap water was added once or twice each day after the sodium chloride solution, with no overflow, to flush the salt through the soil column. The concentrations of sodium, potassium, calcium and magnesium in the discharge solutions were all measured by Inductively Coupled Plasma (ICP) Spectrometry. The concentration of chloride in the discharge solutions was measured by titration with silver nitrate and sodium chromate. The concentrations of sodium, calcium, magnesium, potassium and chloride in the tap water also were measured and subtracted from that of the discharge solution in the final calculations. The discharges from each soil column were collected for 10 to 14 days; the collection was stopped when a steady linear change of sodium and chloride concentration was observed. The measurement of non-sodium cation concentrations was performed to better delineate and understand the overall cation exchange process, as well as to provide the initial concentrations of major cations for the repeated salting simulations, which are discussed in a later section.

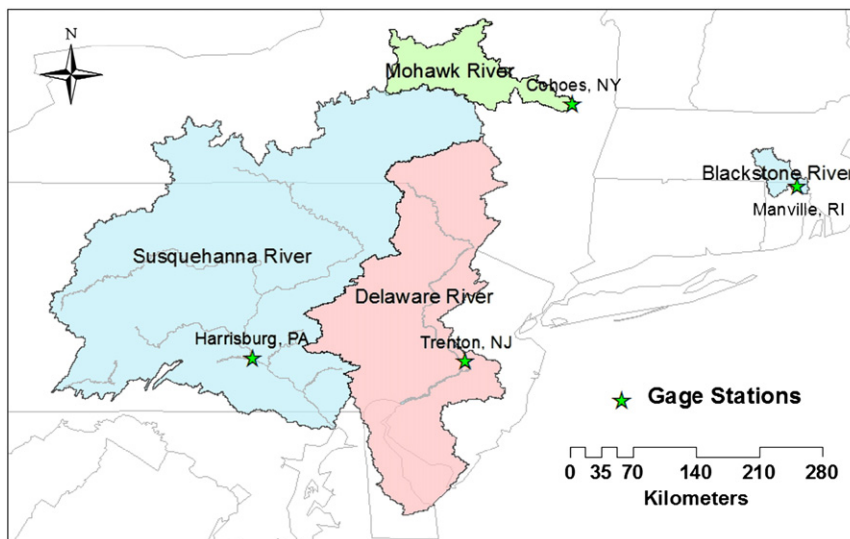


Fig. 2. Location map of gage stations and the four watersheds.

3. Determination of cation exchange capacity of experimental soil

Cation exchange exists in soil due to the negative surface charge created by isomorphous substitution and by the presence of hydroxyl and other functional groups in clay, non-clay minerals and organic matter. In moist soil, cations such as Mg^{2+} , Ca^{2+} , K^+ and Na^+ exist in a hydrated state and are held by electrostatic attraction. The concentration ratio of any of these two cations in soil solution equals their concentration ratio on the surface of soil colloids at equilibrium as described by Gaines and Thomas's (1953) ratio law. When a large amount of sodium in the form of dissolved deicing salt enters the soil solution, Na^+ will be adsorbed onto the negatively charged sites on the surface of soil colloids and will replace other cations in order to maintain this ratio balance. However, this cation exchange process is completely reversible. Once the relative concentrations of Mg^{2+} , Ca^{2+} , K^+ and Na^+ change, Mg^{2+} , Ca^{2+} and K^+ can replace Na^+ on the exchange sites, thus resupplying Na^+ back to the soil solution.

The cation exchange capacity (CEC) of a soil determines the maximum amount of sodium that can be retained due to electrostatic adsorption in that soil (Shanley, 1994); hence, CEC needs to be measured accurately. The CECs of two 25-gram soil samples used in the column experiment were measured by the "ammonia acetate at pH 7" method using a Hach DR/850 colorimeter (Chapman, 1965; Hendershot et al., 2008). The average CEC measurement for the two samples was 19.39 cmol/kg.

To further understand the mineral components of soil colloids that contribute to a soil's CEC and provide an alternative measurement of CEC by the "ammonia acetate at pH 7" method, quantitative X-ray powder diffraction analyses were conducted to obtain the modal abundance of clay minerals in two soil samples that were used in the soil column experiments. Full X-ray diffraction spectra were collected between 5° and 65° two-theta angle using Cu K-alpha radiation and a step-size of 0.02° . Mineral modal abundances were

calculated using the RockJock program based on the full spectrum intensities (Eberl, 2003). The amount of soil organic matter was measured using the loss on ignition (LOI) method in a furnace heated at $550^\circ C$ for 4 h and calculated after adjusting for structural water loss (Sun et al., 2009). The soil CEC was calculated as the summed product of the modal weight percent of all clay minerals, organic matter and their average corresponding CEC, as reported by Drever (1997). As only the CECs of clay minerals are significant, the modal weight percentages of non-clay minerals were not included (Table 1). However, the modal abundance of iron oxides determined by the quantitative X-ray diffraction analysis will be used for the surface complexation calculation in a later section. Overall, the separate methods used to determine the CEC are in good agreement (Table 1).

4. Modeling NaCl transport

Computer simulations of Na^+ and Cl^- transport utilized PHREEQC, a one-dimensional transport and ion-association

Table 1

Modal weight percent of clay minerals, organic matter and estimated CECs (cmol/kg).

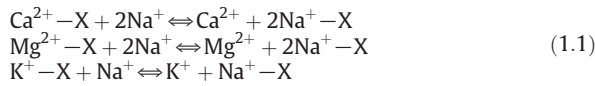
	Average CEC ^a	Sample 1		Sample 2	
		Weight %	CEC	Weight %	CEC
Kaolinite	5	5.67	0.284	2.1	0.10
Smectite	115	10.53	12.11	6.3	7.30
Illite	16.7	3.41	0.57	8.5	1.41
Biotite + vermiculite	80	4.65	3.72	3.6	2.92
Chlorite	2	7.05	0.141	4.8	0.10
Organic matter	200	2.11	4.22	2.8	5.49
Total CECs (cmol/kg)		21.04		17.32	
^a Average CECs from above clay minerals and organic matter	19.2 (cmol/kg)				
CEC from "ammonia acetate at pH 7" method	17.05, 21.72 (cmol/kg)			Average = 19.39 (cmol/kg)	

^a CEC estimates from mineral and organic matter contents were based upon average values reported by Drever (1997).

aqueous model (Parkhurst and Appelo, 1999). The purpose of the simulations was to further examine the relationship between the Na/Cl molar ratio in the discharge solution and the retention of sodium by soil colloids initially determined in the soil column experiments, as well as for additional scenarios of CEC and flow characteristics. The simulations used PHREEQC's exchange, reaction and transport modules.

4.1. Cation exchange reaction

The cation exchange reactions simulated by PHREEQC follow a ratio law: at equilibrium, the concentration ratio of two cations in solution equals the concentration ratio of the two cations adsorbed onto the solid. Based upon Gaines and Thomas (1953) theory, the cation exchange reaction and concentration changes of the ions due to these reactions can be established as the following (Appelo and Postma, 2005):



$$\beta_{\text{Na}^+}^2 \left(\frac{m_{\text{Ca}^{2+}}}{K_{\text{Na}^+\text{Ca}}^2 m_{\text{Na}^+}^2} + \frac{m_{\text{Mg}^{2+}}}{K_{\text{Na}^+\text{Mg}}^2 m_{\text{Na}^+}^2} \right) + \beta_{\text{Na}^+} \left(\frac{m_{\text{K}^+}}{K_{\text{Na}^+\text{K}} m_{\text{Na}^+}} \right) + \beta_{\text{Na}^+} = 1 \quad (1.2)$$

$$\begin{aligned} \text{meq}_{\text{Na}-x} &= \beta_{\text{Na}^+} * \text{CEC}, \text{meq}_{\text{Ca}-x} = \beta_{\text{Ca}^{2+}} * \text{CEC}, \\ \text{meq}_{\text{Mg}-x} &= \beta_{\text{Mg}^{2+}} * \text{CEC}, \text{meq}_{\text{K}-x} = \beta_{\text{K}^+} * \text{CEC} \end{aligned} \quad (1.3)$$

where m is the concentration (meq/l), $-X$ denotes the negatively charged organic or inorganic colloid particles, β is the equivalent fraction of the particular element as a fraction of CEC (cmol/kg or meq/l for porewater), K is the given exchange coefficient of the paired elements and $\text{meq}_{\text{Na}-x}$ and other meq_{-x} terms (cmol/kg) are the amounts of sodium and other cations that are adsorbed onto the soil colloids, respectively. Eq. (1.1) are the general exchange equations of the major cations; Eq. (1.2) is used for solving the equivalent fraction of the sodium as a fraction of CEC, β_{Na^+} ; and Eq. (1.3) is used to calculate the concentrations of cations adsorbed onto the soil colloids based upon β and CEC. Calcium, magnesium and potassium are the three common elements that are considered to have a significant effect on the cation exchange of sodium in soil solutions (Brady and Weil, 2008); as such, they are the only elements included here.

4.2. Transport process

For one-dimensional transport modeling, PHREEQC simulates the advection, reaction and dispersion of sodium and chloride transport by solving the following solute transport equation numerically (Parkhurst and Appelo, 1999):

$$\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} + D_L \frac{\partial^2 C}{\partial x^2} - \frac{\partial q}{\partial t} \quad (2)$$

where C is the concentration in water (mol/kgw, moles per kilogram of water), t is time (s), v is pore water flow velocity (m/s), x is distance (m), D_L is the hydrodynamic dispersion coefficient (m²/s, $D_L = D_e + \alpha_L v$, with D_e the effective diffusion coefficient, α_L the dispersivity (m)) and q

is concentration in the solid phase (expressed as mol/kgw in the pores).

For this study, each simulated soil column was divided into 40 cells. The average hydraulic conductivity was measured using the constant head permeameter method (Fetter, 2000). The soil porosity was calculated as "1 – soil bulk density/particle density," following Dingus (1998). The initial dispersivity was obtained by fitting the "one dimensional" dispersion equation (Brigham, 1974; Fetter, 1998) to data from the experimental soil columns. Simulation results for two CEC scenarios, 19.2 cmol/kg and 9.6 cmol/kg (the average and one-half average of the calculated CECs in Table 1), are presented. Each simulation was run for approximately ten days, at which time the daily sodium and chloride discharge concentrations became stable. Variable amounts of NaCl, ranging from 0.0625 to 1.25 mol in 1100 ml of double distilled water, were injected through the simulated soil columns. The columns were flushed using tap water with known cation concentrations to simulate soil flushing by subsequent watershed precipitation.

5. Comparison of experimental and simulation results

Experimental results provide the basic flow parameters and soil characteristics utilized in the PHREEQC simulations, as well as a basic understanding of how sodium chloride concentrations change after additional tap water is flushed through the soil columns. Among the five ions measured, the concentration peak for potassium reached the column outlet first, followed by the concentration peaks for magnesium, calcium, chloride and lastly sodium. It took approximately 200 cm of water (~3181 cm³), depending on the concentration of injected salt, to flush the bulk of the injected sodium chloride through the experimental soil columns (Fig. 3). The depth of water, calculated as the volume of water flushed through a unit cross-section area of the soil column, instead of the volume of water, is used in Fig. 3 to make it comparable to the amount of actual precipitation in a natural watershed in later discussions. Initially, the observed Na/Cl molar ratios were much less than 1.0 in all solutions (Fig. 4). The low Na/Cl molar ratios observed may reflect the initial active replacement of sodium by other cations on the soil colloids, following Gaines and Thomas' (1953) theory, while chloride

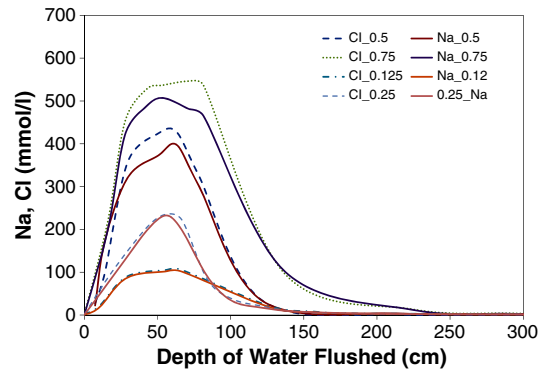


Fig. 3. Sodium and chloride concentrations versus amount of water flushed through the soil column. In the legend, the number after the element is the amount of moles of NaCl injected. The concentration data were measured from soil column discharge.

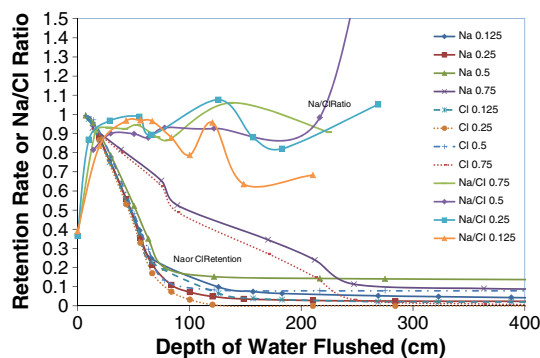


Fig. 4. Na/Cl molar ratios and amount of sodium and chloride retention measured in the soil column discharge solutions versus amount of water flushed through the soil columns. In the legend, the number after the element is the amount of moles of NaCl injected. Each soil column contained approximately 400 g of soil with an average CEC of 19.2 cmol/kg. Retention rate is calculated as the quotient of the total amount of sodium or chloride and amount of sodium or chloride retained.

was transported more conservatively through the soil column. The low molar ratios also may partially reflect the low Na/Cl ratios in tap water during initial salt and water mixing in the column. Once chloride was exhausted from the column, Na/Cl ratios increased again due to the depletion of chloride, whereas sodium was later supplied from the exchange sites. The Na/Cl ratios shown in Fig. 4 fluctuate at the later stages of the experimental runs mainly due to the inaccuracy of the titration method for measuring chloride at low concentrations. The observed Na/Cl molar ratio pattern for the soil columns is similar to the Na/Cl molar ratio patterns observed in the studied watersheds, which will be discussed in a later section. The retention of sodium at a specific flushing period is calculated as:

$$\text{Retention of Na} = \frac{\text{Injected Na} + \text{Na from Tap Water} - \text{Na in Effluent}}{\text{Injected Na} + \text{Na from Tap Water}} \quad (3)$$

The retention of chloride was calculated by replacing the Na in Eq. (3) with Cl. The average total sodium retention at the end of all experimental runs was 6.5%. Chloride retention was negligible (<1%) at the end of the experimental runs except for one column (Fig. 4). The measured sodium retention rate for the soil column experiments depended on the soil CEC, the amount of water flushed through the soil column and the initial amount of sodium injected.

PHREEQC simulated sodium concentrations were compared to the measured sodium concentrations in Fig. 5. Dispersivity coefficients were calibrated in the simulations according to the initial amount of Cl^- injected (Fetter, 1998). In addition to the cation exchange reactions modeled for the major cations, scenarios that included surface complexation reactions based upon the model by Dzombak and Morel (1990) were simulated as well. The model by Dzombak and Morel (1990) used a strong and a weak -OH site on ferrihydrite ($\text{Fe}(\text{OH})_3$) and the Gouy–Chapman double layer equation for defining the surface potential. Goethite was used in place of ferrihydrite and its corresponding specific surface area ($60 \text{ m}^2/\text{g}$) and weak and strong -OH sites (0.02 mol/mol Fe for weak -OH sites, $5 \times 10^{-4} \text{ mol/mol Fe}$ for strong

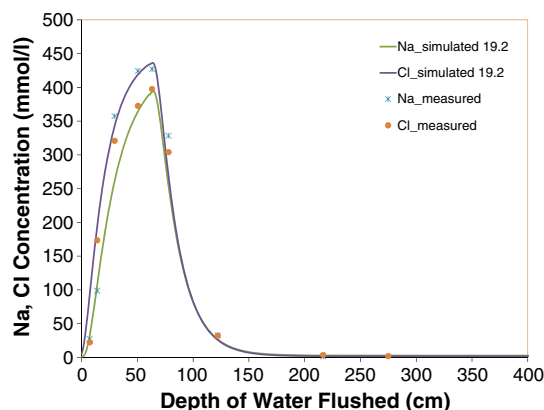


Fig. 5. PHREEQC simulations (curves) and experimental sodium and chloride concentrations (data points) for 0.5 mol of NaCl injected versus amount of water flushed through the soil column. For the PHREEQC simulated soil columns, conductivity = 0.52 m/day, CEC = 19.2 cmol/kg, dispersivity = 0.1037 m^2/s , porosity = 0.64, and mass = 400 g of soil.

-OH sites) were used in the PHREEQC simulation following Appelo and Postma (2005).

The simulated sodium and chloride concentrations are generally in agreement with the measured sodium and chloride concentrations (Fig. 5), except for column #1, which had an unusually high flow rate due to a relatively loose soil packing. Surface complexation reactions were not significant in affecting the concentrations of major cations in the simulated results. The retention rates were calculated using Eq. (3). Overall, sodium retention increases with a decreasing amount of NaCl injection, unless the injected sodium concentration is too low for sodium to effectively replace other cations on the exchange sites (Figs. 6 and 7).

The changing patterns of the Na/Cl ratio and amount of sodium and chloride retention were calculated from the results of the simulated sodium and chloride concentrations (Figs. 6 and 7; CEC = 19.2 and 9.6 cmol/kg, respectively). The initial low Na/Cl ratios in Figs. 6 and 7 were due to initial active retention of sodium by cation exchange on soil colloids and the low Na/Cl ratios in tap water, which is similar to the situation in the column experiments. Once a simulated injection commenced, a portion of the injected sodium was retained within the column due to cation exchange, while the remainder of the sodium and chloride was flushed through the column. As a result, Na/Cl ratios increase during this stage. The ratio's rate of increase slowed once the peaks of chloride and sodium concentration passed through the simulated outlet. After chloride was exhausted from the system, and while sodium was still being supplied from cation exchange sites in accordance with the ratio law, a later rapid increase in the Na/Cl ratio was observed (Figs. 6 and 7). Based upon the measured Na/Cl molar ratio at the discharge of a soil column and the amount of water flushed, the proportion of sodium retention can be obtained. If the CEC of the soil medium is different from Figs. 6 (19.2) and 7 (9.8), an interpolation method can be used.

The retention of sodium is due to cation exchange and its temporary entrapment during transport. The entrapment refers to the process of sodium or chloride being temporarily trapped in the soil column purely due to the limited supply of flushing water. The retention of chloride is due only to its temporary

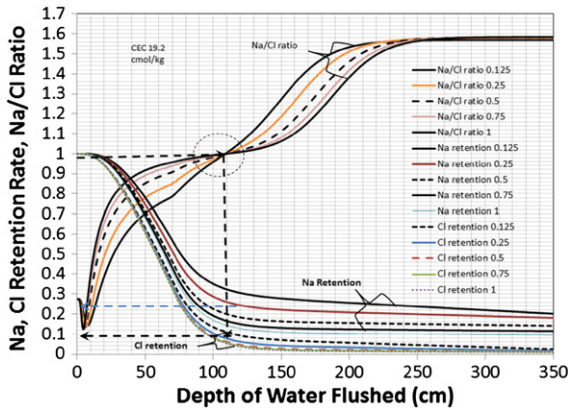


Fig. 6. Na/Cl molar ratio and amount of sodium and chloride retention versus the amount of water flushed through the PHREEQC simulated soil columns. All parameters used are the same as given in Fig. 5. The uppermost curves show Na/Cl ratios, the lower middle curves show Na retentions, and the lowest curves show chloride retentions. The dashed lines with arrows show how retention rates are obtained. To obtain the sodium or chloride retention rate, start with the Na/Cl ratio on the Y axis, proceed horizontally to the Na/Cl ratio curve, and then proceed vertically to the sodium or chloride retention curve. In the example shown, the 0.5 mol sodium and chloride retention curves were selected.

entrapment during transport; hence, no anion exchange is considered in the simulations. Given that the Na/Cl molar ratio can be calculated from the measured concentrations of sodium and chloride in most watersheds, the relationship established by Figs. 6 and 7 may be used to estimate sodium retention if the dominant sources of sodium in a watershed are from deicing road salt where NaCl is the main constituent.

Repeated salting and mixed salting scenarios also were investigated experimentally. In the repeated NaCl salting scenario, the cumulative retention of sodium in the soil columns increased only slightly after the second salting and then showed no apparent increase with additional salting. For the experiment involving the injection of 0.5 mol CaCl₂ and NaCl into the soil column with a 6:4 weight ratio solution, by the end of a prolonged flushing period with tap

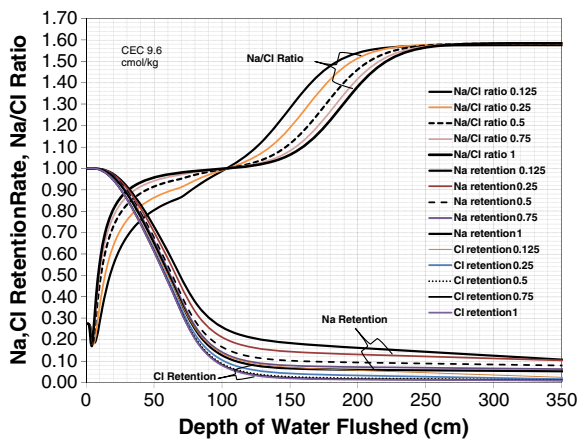


Fig. 7. Na/Cl molar ratio and amount of sodium and chloride retention versus the amount of water flushed through the PHREEQC simulated soil columns. All parameters are the same as in Figs. 5 and 6 except that the CEC used is 9.6 cmol/kg.

water, there was an insignificant amount of sodium retained in the column. This occurs because calcium has a higher affinity for adsorption than sodium. Hence, the cation exchange sites were preferentially filled by calcium. However, it needs to be remembered that in a watershed, annual precipitation typically is not sufficient to flush out all sodium, calcium and chloride, due to volumetric storage in natural soil profiles. In addition, except for areas immediately adjacent to the salted surface, soil colloid cation exchange sites rarely are saturated by the amount of salt typically applied. This is different from the experimental soil columns where all soil cation exchanged sites can be saturated at the salting stage when the concentration of injected salt is high.

6. Estimations of sodium and chloride retention in a watershed

6.1. Comparison of Na/Cl ratios of experimental/simulation results to field data

The experimental and simulation results in Figs. 4, 6 and 7 show a similar and consistent trend for the Na/Cl molar ratio from the start of the salt injection to the end of the measurement/simulation. During initial injection, the Na/Cl molar ratio in the effluent was less than 1.0 due to the active retention of sodium by cation exchange while chloride transport continued conservatively. Once the bulk of the Na⁺ and Cl⁻ was flushed through and most cation exchange sites were filled or partially filled, some sodium was supplied from the cation exchange sites back into solution and the Na/Cl molar ratio increased.

In comparison, and based upon the most recently available United States Geological Survey (USGS) data, the monthly change in Na/Cl molar ratios in the discharge of all four watersheds evaluated in this study (Delaware River, Mohawk River, Susquehanna River, and Blackstone River; Fig. 8), were similar to the Na/Cl molar ratio changes from the simulations and experiments. During the initial road deicing salt application and dissolution period, typically December through March, Na/Cl molar ratios in the discharge were generally low. This is likely due to the adsorption of sodium by soil cation

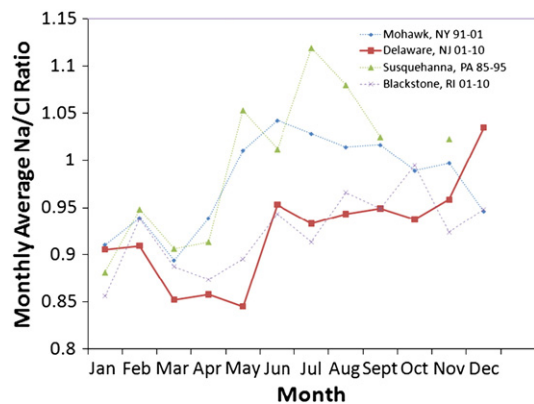


Fig. 8. Ten-year monthly average of the Na/Cl ratios for the four watersheds studied determined from the most recently available data for each watershed. In the legend, the numbers after the state name are the years over which the data were averaged, e.g. 1991 to 2001.

exchange sites. Na/Cl molar ratios increased once the late spring and early summer precipitation-induced flushings occurred and the soil cation exchange sites located adjacent to salted surfaces were partially saturated; hence, more sodium and chloride were flushed into the watershed. The Na/Cl molar ratio in the river discharge remained relatively stable during the summer and early fall periods and then declined in the late fall. However, in examining the Na/Cl molar ratios during an annual salting cycle from the four watersheds, it was noted that their Na/Cl molar ratios did not decrease to the low levels seen in the early salting stage of the experiments (Fig. 8). These relatively high initial Na/Cl molar ratios during the early stages of salting in natural watersheds might be a result of multi-stage salting and flushing in these watersheds. In addition, a portion of the salt being applied could have been removed directly from road surfaces and into storm drain systems and streams, avoiding contact with soil particles or being absorbed, thereby raising the measured Na/Cl molar ratios of these watersheds.

The observed decade-long decreasing trends of Na/Cl molar ratios (Fig. 9) for natural watershed reflect the overall retention of sodium in the studied basins where sodium input from anthropogenic salt sources has surpassed the amount of sodium released from the weathering of albite and other sodium-bearing minerals (Sun et al., 2010). This trend also has been reported for other watersheds in the northern US and Canada (Godwin et al., 2003; Kelly et al., 2008; Meriano et al., 2009). In the case of the Delaware River at Trenton, where sodium and chloride concentration data have been collected by the USGS since 1944, the Na/Cl molar ratio declined from an annual average of 1.56 in the 1940s to an annual average of 0.82 in 2009 (Fig. 9). A Na/Cl molar ratio of 1.56 indicates that sodium sources in the watershed are mainly from natural weathering, whereas a Na/Cl molar ratio of 0.82 indicates that sodium sources are predominantly anthropogenic sources, mainly road deicing salting because the increased supply of chloride that accompanies the sodium in the road deicing salts decreases the Na/Cl ratio in the watershed.

6.2. Estimation of sodium retention based upon Na/Cl molar ratios

The similarity of Na/Cl molar ratio patterns between an annual salting cycle of a natural watershed and the salt injection experiment cycle implies that if the input of sodium

from road deicing salt is the dominant input source, the annual retention of sodium in a watershed due to artificial salting may be comparable to the retention observed in the soil column experiments. Therefore, if a watershed has a similar CEC, a known amount of water flushed through annually, and salt input concentrations comparable to those for the soil column experiments, the relationship between the watershed's sodium and chloride retention and Na/Cl ratio is likely to be similar to those of the simulations in Figs. 6 and 7. For example, in the DRW, the current monthly average molar chloride concentration is more than three times that of the pre-salting 1944 to 1964 levels, which is an indication that the artificial salt input significantly exceeds natural release due to weathering. Sodium chloride is estimated to be between 94% and 96% of the total artificial salt input into the basin (approximately 75% deicing salt, 21% from other salt sources, including water softeners, and 5.5% from sewage based upon 2000–2007 data from PA DOT, NJ DOT and NY DOT and the method by Kelly et al., 2008).

The effective cation exchange capacity (ECEC) for the top 30 cm of soil in the basin, 10.94 cmol/kg, is calculated as the weighted average of all soil map units provided by the United States Department of Agriculture (USDA, see Appendix A). This ECEC value is close to the ECEC value (9.6 cmol/kg) used in the PHREEQC simulations that resulted in the relationships shown in Fig. 7. The sodium input solution concentrations from road runoff immediately adjacent to an interstate highway (I-95) in the DRW ranged from 12,473 ppm to 4276 ppm (on 30 March 2007, Sun et al., 2010). In the soil column experiments and PHREEQC simulations, 0.125 to 1.0 mol of NaCl in 1100 ml of solution gave sodium concentrations ranging from 2163 to 20,909 ppm. This range of input salt concentrations was comparable to the sodium concentration in the actual runoff water from I-95. Based upon the average annual Na/Cl ratios for the last ten years, the annual average retention rates of sodium and chloride were estimated for the DRW utilizing the relationship between Na/Cl molar ratios and retention of sodium and chloride shown in Fig. 7 (Table 2). A ten-year period average was used in these calculations to reduce the impact of annual fluctuations. This method of estimating retention is based on the concept that for a fixed Na/Cl molar ratio, sodium retention is mainly a function of the soil CEC, the amount of the water flushed through the system, which can be estimated from precipitation, and the initial amount of salt applied. If the artificial input of sodium is not

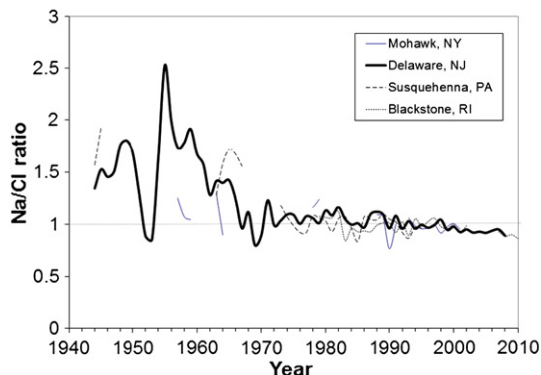


Fig. 9. Changes in Na/Cl ratios for the four watersheds studied.

Table 2

Average retention rate (in percent) of Na and Cl at the end of November and December and average annual retention in DRW above Trenton, NJ for 2001 to 2010.

Period	Na/Cl molar ratio	Na %	Cl %	Cl/Cl ₄₄₋₆₄	Sample size
<i>Retention based on the Nov. and Dec. average of Na/Cl ratios</i>					
2001–2010	0.96	30	20	3.03	10
<i>Retention based on the annual average of Na/Cl ratios (Jan.–Dec.)</i>					
2001–2010	0.94	41	31	3.21	67

Note. The retention percentages for Na and Cl were obtained from Fig. 7, using the 0.5 mol concentration (12,473 ppm) curve, based on the averaged Na/Cl ratios given in the second column. Cl/Cl₄₄₋₆₄ is the ratio of the averaged chloride concentration during the 2001–2010 (post-salting) period to the averaged chloride concentration during the 1944–1964 (pre-salting) period.

significantly larger than the weathering release, a correction factor can be considered when the retention rate is estimated from this relationship.

The estimated sodium retention rate is more reliable for the period between 2001 and 2010 than for prior years, largely because the release of sodium due to weathering in the watershed is proportionally more significant prior to 2001.

Use of this method to generate an initial estimate of sodium retention from road deicing salt also may be applicable when a relatively short period of sodium chloride data have been collected for a watershed, and the application of road deicing salt has occurred for a prolonged period. This is the case for the Mohawk River, where the ECEC estimate for the top 30 cm of soil is 7.45 cmol/kg, similar to the ECEC estimate for the DRW, based upon the soil ECEC GIS database of the USDA (see Appendix A for details). The Mohawk River sodium retention rates for the period from 1995 to 2001, as determined from Fig. 7 and after adjustment for the low watershed ECEC, are listed in Table 3. The 1995 to 2001 period is the most recent time for the MRW when both sodium and chloride concentrations were reported by the USGS.

7. Discussion

The amount of sodium retention in an aqueous-soil system is affected mainly by the CEC of the soil colloids, the amount of water flushed through the system and the concentration of the initial salt input. The application presented emphasizes that as long as these three factors are similar, the relationship between the Na/Cl molar ratio and sodium retention for a salted watershed and experimental soil columns is similar when deicing salt (NaCl) dominates the sodium input in a watershed. However, as discussed in Section 6.1, the Na/Cl molar ratio for an annual salting cycle in the watershed examples do not drop to the low initial levels seen in the experimental data. Therefore, a number of cautions are required if Figs. 6 or 7 are to be applied appropriately. The first caution is to examine the assumption that deicing road salt is the dominant source of sodium and that only a small portion of the deicing salt in the studied watershed is flushed directly through storm drains without interacting with watershed soils. For example, the application of this model to a heavily paved, urban watershed where storm drains are ubiquitous most likely would not be appropriate. The second caution is to examine the similarity of

the experimental relationship of the Na/Cl molar ratio and the amount of water flushed to those found in the studied watersheds. For the DRW, where road deicing salt is the dominant sodium source and the salt is washed off mainly onto adjacent soil (>67%), the ten-year average of a 0.96 Na/Cl molar ratio for 0.5 mol of injected salt concentration yields a total depth of flushed water of approximately 110 cm in Fig. 6, which is reasonable in comparison to the actual average yearly precipitation of 123 cm. It is likely that the reliability of the estimate based upon this method also will improve with further increases in the application of road salt, i.e. weathering release of sodium is minimized, and more accurate estimates of the ECEC for the entire watershed.

Traditional determinations of sodium retention require the accurate estimation of artificial input and weathering release. With multiple potential sources of anthropogenic salt from multiple agencies, private entities and residences, an accurate estimation of sodium input is difficult, particularly for a large watershed that crosses multiple state boundaries (Godwin et al., 2003). This study, in addition to exploring the change of the Na/Cl molar ratio in a salting cycle by using the relationship between Na/Cl molar ratio and sodium retention, provides an alternative method for examining sodium retention that overcomes some of these constraints.

The determined sodium and chloride annual retention rates of 30% to 40% presented in Section 6.2 are comparable to the retention rates reported in two previous studies. Kelly et al. (2008) estimated sodium retention to be 39% and chloride retention to be 33% for a small watershed in New York State, based upon available artificial salt input and output data. Howard and Haynes (1993) reported a retention rate of 45% for deicing salt in their study of a small watershed in the Toronto, Ontario area.

In the northeastern United States, there are approximately 120 cm of precipitation annually (Sun, 2004). This annual amount of water flushing in a watershed is unlikely to remove all sodium and chloride in soil produced by road salting, based upon the available field data, our simulations and experimental results and other studies (Kelly et al., 2008). Therefore, sodium and chloride retentions likely will elevate the sodium and chloride concentrations in the streams of most salted watersheds for years to come even if specific steps are taken to reduce anthropogenic salt inputs in the near future.

8. Conclusion

A high rate of soil sodium retention and the subsequent release is the underlying reason for observed increases in sodium concentrations for many watersheds in the northeastern United States, Canada and countries in Europe where winter deicing road salt is applied on a regular basis. This study examined the change of the Na/Cl molar ratio in a salting cycle and provided an alternate method of estimating the sodium retention based upon the different adsorption properties of sodium and chloride in soil during transport. This method uses the relationship between the Na/Cl molar ratio and the retention rate of sodium derived from the analysis of soil column experiments, computer simulations of sodium transport and field data. The annual sodium retention rate over the last two decades was determined to be between 30% and 40% in the MRW in New York as well as in the DRW

Table 3

Average retention rate (in percent) of Na and Cl at the end of November and December and average annual retention in Mohawk River above Cohoes Station.

Period	Na/Cl molar ratio	Na %	Cl %	Cl/Cl _{57,58}	Sample size
<i>Retention based on the Nov. and Dec. average of Na/Cl ratios</i>					
1995–2001	0.99	15	7	2.71	12
<i>Retention based on the annual average of Na/Cl ratios (Jan.–Dec.)</i>					
1995–2001	0.95	40.5	30.5	2.34	88

Note: the estimation given here utilized the 0.5 mol concentration curves of Fig. 7, with the retention values reduced by 1% due to the lower ECEC of the Mohawk River Watershed. Cl/Cl_{57,58} is the ratio of the averaged chloride concentration during the 1995–2001 (post salting) period to the averaged chloride concentration during the 1957–1958 (pre-salting) period.

in New York, Pennsylvania and New Jersey. This alternate method produced results comparable to previous determinations of sodium retention. The relatively high rate of sodium retention determined in this study indicates the difficulty of successfully instituting any environmental remediation policy that intends to quickly reduce sodium concentrations in a watershed.

Acknowledgments

The authors wish to thank Steve Peaslee from the US National Soil Survey Center for his help with the soil ECEC GIS maps. We thank Anthony Navoy and Zoltan Szabo from the USGS Trenton office, and Jorge Coppen from the Patuxent Wildlife Research Center, Maryland for their constructive discussions. We also thank the constructive suggestions from two anonymous reviewers and the editor. The authors recognize the many field and laboratory contributions of Daniel Carlson, Jessica Horton, Ashley Leighton, and other undergraduate students from the Department of Geological, Environmental, and Marine Sciences (GEMS) at Rider University. We acknowledge the financial support of Rider University and U.S. National Science Foundation grants MRI-0821172 and MRI-1126281. Gerri Hutner provided editorial assistance.

Appendix A. Estimation of effective cation exchange capacity of a watershed

The ECEC is the sum of the extractable base of the soil plus aluminum. ECEC determines the maximum amount of sodium that can be retained by electrostatic adsorption in soil. From the chemical property GIS map established by the US National Soil Survey Center for soil series at various depths, the statistics of the CEC for the depth of interest can be extracted (Fig. 10). For this project, ECECs for the DRW and MRW were calculated for the top 30 cm of soil from 234 soil mapping units, based upon the weighted percentage of the area of each mapping unit. For the DRW, the averaged ECEC is 10.94 cmol/kg; for the MRW, the averaged ECEC is 7.45 cmol/kg. The 30 cm depth was selected because it is the depth where most of the active cation exchange of applied sodium will take place (Brady and Weil, 2008; Essington, 2004).

References

- Appelo, C.A.J., Postma, D., 2005. *Geochemistry, Groundwater and Pollution*, second ed. CRC Press, Florida.
- Brady, N.C., Weil, R.R., 2008. *The Nature and Properties of Soils*. Prentice Hall, New Jersey.
- Breault, R.F., Smith, K.P., 2010. *Streamflow, Water Quality, and Constituent Loads and Yields, Scituate Reservoir Drainage Area, Rhode Island, Water Year 2009*. USGS Open-File Report 2010-1275.
- Brigham, E., 1974. *The Fast Fourier Transformation*. Prentice-Hall, New Jersey.
- Chapman, H.D., 1965. Cation-exchange capacity. In: Black, C.A. (Ed.), *Methods of Soil Analysis – Chemical and Microbiological Properties: Agronomy*, 9, pp. 891–901.
- Dingus, D.D., 1998. *Soil Science Laboratory Manual*. Prentice Hall, New Jersey.
- Drever, J.I., 1997. *The Geochemistry of Natural Waters*, third ed. Prentice Hall, New Jersey.
- Dzombak, D.A., Morel, F.M.M., 1990. *Surface Complexation Modeling: Hydrous Ferric Oxide*. Wiley and Sons, New York.
- Eberl, D.D., 2003. *User's guide to RockJock – a program for determining quantitative mineralogy from powder X-ray diffraction data*. US Geological Survey. Open-File Report 03-78.
- Essington, M.E., 2004. *Soil and Water Chemistry*. CRC Press, New York.
- Fetter, C.W., 1998. *Contaminant Hydrogeology*, second ed. Prentice Hall, New Jersey.
- Fetter, C.W., 2000. *Applied Hydrogeology*, fourth ed. Prentice Hall, New Jersey.
- Freeze, R.A., Cherry, J.A., 1979. *Groundwater*. Prentice Hall, New Jersey.
- Gaines Jr., G.L., Thomas, H.C., 1953. Adsorption studies on clay minerals. II. A formulation of the thermodynamics of exchange adsorption. *The Journal of Chemical Physics* 21, 714–717.
- Godwin, K.S., Hafner, S.D., Buff, M.F., 2003. Long-term trends in sodium and chloride in the Mohawk River, New York: the effect of 50 years of road-salt application. *Environmental Pollution* 124, 273–281.
- Hendershot, W.H., Lalonde, H., Duquette, M., 2008. Ion exchange and exchangeable cations. In: Carter, M.R., Gregorich, E.G. (Eds.), *Soil Sampling and Methods of Analysis*. Canadian Society of Soil Science. CRC Press, Florida.
- Howard, K.W.F., Beck, P., 1986. Hydrochemical interpretations of groundwater flow systems in Quaternary sediments of southern Ontario. *Canadian Journal of Earth Sciences* 23, 938–947.
- Howard, K.W.F., Beck, P.J., 1993. Hydrogeochemical implications of groundwater contamination by road de-icing chemicals. *Journal of Contaminant Hydrology* 12, 245–268.
- Howard, K.W.F., Haynes, J., 1993. *Urban geology 3. Groundwater contamination due to road de-icing chemicals – salt balance implications*. Geoscience Canada 20, 1–8.
- Kaushal, S.S., Groffman, P.M., Likens, G.E., Belt, K.T., Stack, W.P., Kelly, V.R., Band, L.E., Fisher, G.T., 2005. Increased salinization of fresh water in the Northeastern United States. *Proceedings of the National Academy of Sciences of the United States of America* 102, 13517–13520.
- Kelly, V.R., Lovett, G.M., Weathers, K.C., Findlay, S.E.G., Strayer, D.L., Burns, D.J., Likens, G.E., 2008. Long-term sodium chloride retention in a rural watershed: legacy effects of road salt on streamwater concentration. *Environmental Science and Technology* 42, 410–415.

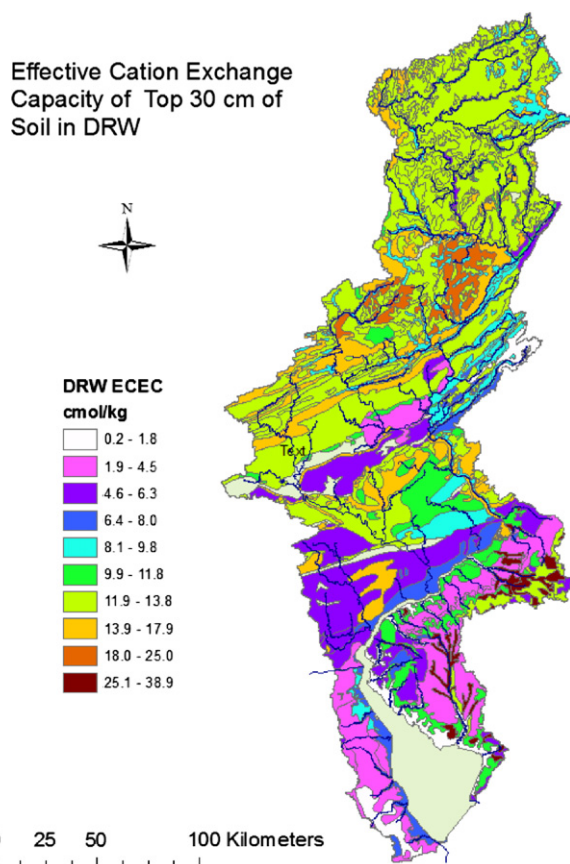


Fig. 10. Map of soil ECEC for the top 30 cm of soil in the Delaware River Watershed determined from soil geochemical data provided by the USDA.

- Kjensmo, J., 1997. The influence of road salts on the salinity and the meromictic stability of Lake Svinsjoen, southeastern Norway. *Hydrobiologia* 347, 151–158.
- Labadia, C.F., Buttle, J.M., 1996. Road salt accumulation in highway snow banks and transport through the unsaturated zone of the Oak Ridges Moraine, southern Ontario. *Hydrological Processes* 10, 1575–1589.
- Locat, J., Gelinis, P., 1989. Infiltration of de-icing road salts in aquifers: the Trois-Rivieres-Ouest case, Quebec, Canada. *Canadian Journal of Earth Sciences* 26, 2186–2193.
- Lofgren, S., 2001. The chemical effect of deicing salt on soil and stream water of five catchments in southeast Sweden. *Water, Air, and Soil Pollution* 130, 863–868.
- Meriano, M., Eyles, N., Howard, K.W.F., 2009. Hydrogeological impacts of road salt from Canada's busiest highway on a Lake Ontario watershed (Frenchman's Bay) and lagoon, City of Pickering. *Journal of Contaminant Hydrology* 107, 66–81.
- Nimiroski, M.T., Waldron, M.C., 2002. Sources of sodium and chloride in the Scituate Reservoir drainage basin, Rhode Island. USGS Water Resources Investigation Report 02-4149.
- Parkhurst, D.L., Appelo, C.A.J., 1999. PHREEQC, version 2 — a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. USGS Water Resources Investigations Report 99-4259.
- Ramakrishna, M.T., Viraraghavan, T., 2005. Environmental impact of chemical deicers. *Water, Air, and Soil Pollution* 166, 49–63.
- Shanley, J.B., 1994. Effects of ion exchange on stream solute fluxes in a basin receiving highway deicing salts. *Journal of Environmental Quality* 23, 977–986.
- Sun, H., 2004. Estimating the fate of precipitation from stream discharge: a case study in New Jersey. *The Bulletin — New Jersey Academy of Science* 49, 9–15.
- Sun, H., Nelson, M., Chen, F., Husch, J., 2009. Soil mineral structural water loss during LOI analyses. *Canadian Journal of Soil Science* 89, 603–610.
- Sun, H., Lucarino, K., Huffine, M., Husch, J.M., 2010. Retention of sodium in a watershed due to the application of winter deicing salt. *Proceeding Papers of the Joint Session of the 10th International Symposium on Stochastic Hydraulics and 5th International Conference on Water Resources and Environment Research, Canada*, pp. 1–10.
- Velbel, M.A., Price, J.R., 2007. Solute geochemical mass-balances and mineral weathering rates in small watersheds: methodology, recent advances, and future directions. *Applied Geochemistry* 22, 1682–1700.