

Retention of Sodium in a Watershed due to the Application of Winter Deicing Salt

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Abstract

This study attempts to couple a laboratory experiment, where the input and output sodium can be measured directly, with data from a large river basin, where the application of deicing salt is regular and long-term concentrations of sodium are monitored, to examine the issue of sodium retention in a watershed. In an artificial laboratory setting, 0.5 and 1.0 molar solutions of sodium chloride were separately injected into four constructed soil columns packed with approximately 400 grams of air-dried, loamy soil. After the soil columns were flushed for two to three weeks, the retention rates of sodium in the columns were measured. The rates increase with the decreasing sodium chloride input and reduced water flow. Measured retention rates for chloride are smaller on average than those for sodium by about 20%. The estimated cation exchange capacity (CEC) of the soil used for the columns can not account for the total sodium retention. The fact that the amount of sodium retention is larger than the soil CEC suggests that other retention processes, in addition to cation exchange, are occurring as well. These other processes include physical adsorption due to weak van der Waals forces and transient entrapment of sodium during the transport process. Examination of historical data for sodium and chloride concentrations in the Delaware River Basin (DRB) obtained from two USGS gage stations reveals that the concentration of both ions has increased over the past 50-60 years. The DRB includes parts of Delaware, New Jersey, New York, and Pennsylvania (USA) and supplies a significant portion of the potable water used in this region. The historical data also reveals that the average molar ratio of Na/Cl in the DRB has declined from an average of 1.45 in the 1940s to 0.83 in 2008. The best explanation for this decline is the increasing applications of deicing salt over time, which masks the release of sodium due to weathering, and the fact that more sodium from deicing salt is retained in DRB soils than chloride. This natural unequal adsorption of sodium and chloride is consistent with the results from the soil column experiments. In addition, total sodium input from deicing salt, as estimated from road lane mileage and salt input per lane mile data, is significantly larger than sodium output by Delaware River discharge, at least for the past 20 years, which, again, indicates overall sodium retention in the DRB. The hydraulic conditions and soil characters in soil column experiment, in many ways being comparable to the hydraulic and soil conditions in a natural watershed, suggests that sodium retention in most watersheds may vary from year to year depending on the amount of salt applied, runoff and soil conditions.

Keywords- road salt, sodium retention, column experiment, cation exchange, watershed

1. Introduction

Increased sodium concentrations in river water due to the retention of sodium from the long-term application of road salt (mainly sodium chloride) have been widely reported for many watersheds in the northeastern United States and Canada. Howard and Haynes (1993) reported that only 45% of the deicing salt applied in a Toronto area watershed was released annually through local streams. Nimiroski and Waldron (2002) reported no measurable reduction in sodium concentration in the Scituate Reservoir Basin of Rhode Island 10 years after the state mandated replacement of pure sodium chloride with a 6:4 mixture of magnesium chloride and sodium chloride deicing salt in 1990. Kelly et al. (2008) reported a long-term increase of sodium due to its retention in a rural watershed in New York State. There are many other similar reports of sodium retention within watersheds from the United States, Canada and other countries (Howard and Beck, 1986 and 1993, Kjensmo, 1997, Labadia and Buttle, 1996, Locat and Gelinis, 1989, Lofgren, 2001, and Shanely, 1994).

The high concentration of sodium in a watershed is not only potentially detrimental to fluvial, lacustrine, and riparian ecosystems, but also is a health threat to people (Ramakrishna and Viraraghavan, 2005). For example,



Figure 1. Setup of a soil column used for the sodium injection experiments.

there are increased incidences of sodium concentrations exceeding the 20 mg/l level recommended by the United States Environmental Protection Agency (USEPA) and the American Heart Association (AHA) in rivers that supply more than half of the drinking water for US riparian states (Godwin et al., 2003, Nimiroski and Waldron, 2002, Sun et al., 2006, 2008). Fully understanding and quantifying the retention of the sodium is the prime scientific basis for any meaningful environmental policy that intends to ameliorate sodium concentrations in a watershed (Kelly et al., 2008).

The retention of the sodium in a watershed is generally regarded as the mass difference between the sodium input and output of that watershed (Kelly et al., 2008). Though the estimation of sodium output of a watershed from river discharge is relatively straight forward, estimating the amount of sodium input from multiple possible sources is more difficult. Potential input sources include deicing salt from state, municipal, and private entities, rock weathering, sewage water treatment plants, and home, municipal, and industrial water softeners (Kelly et al., 2008). In addition, the retention rate of sodium also varies from basin to basin due to different soil characteristics, including their variable cation exchange capacity. Therefore, experiments with an artificial watershed in a laboratory setting, where the mass of sodium input and output can be directly measured, would enable the quantification of sodium retention. Results from the laboratory study can then be applied to an actual watershed once the basic mechanism of sodium retention is better understood. Because both sodium and chloride are applied together in deicing salt, chloride concentrations will be discussed as well, although sodium retention is the main focus of this paper.

2. Methods

2.1 Soil Column Experiment

A constructed soil column can be visualized as an artificial mini-watershed, where a fixed mass of sodium is introduced into the column. The amount of sodium output through the discharge of the column can be calculated as the product of the measured volume and concentration of sodium in the discharge. The sodium retention will be the difference between the amount of sodium input and output.

In this study, four two-inch diameter columns were filled with approximately 400 grams of dried loamy soil typical in the Delaware River Basin (DRB). Both falling-head and constant-head flow apparatus were set up in the lab (Figure 1).

For the two soil columns with the falling-head setup, tap water was added, with no allowed overflow, once or twice each day, depending on head level. The flow rate of one soil column was purposely faster than the other, and was achieved by varying the water heads and soil packing of the two columns. One-mole aqueous solution of sodium chloride was injected into the each column. The concentrations of the sodium, calcium, magnesium, potassium and chloride of tap water were measured and subtracted from that of discharge solution in the final calculation. The other two soil columns had a constant-head setup, achieved by allowing for continuous overflow once a certain hydraulic head was reached. 0.5-mole aqueous solution of sodium chloride was injected into each

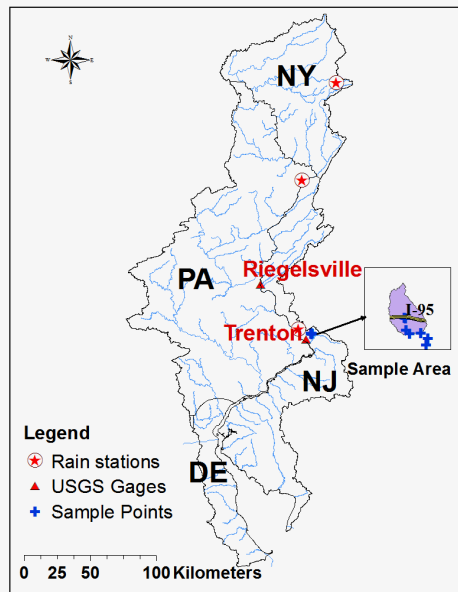


Figure 2. Locations of field samples, rain stations, and USGS river gages in the Delaware River Basin (DRB). Catchment area of the DRB above the Trenton Station is 6780 square miles.

column. Discharge solutions were collected from the outlets of the columns at varied time intervals, ranging from once every hour to once every day, with the interval increasing with time since salt solution injection.

The concentrations of sodium, potassium, calcium, magnesium, aluminum, and silicon in the discharge solutions were measured by Inductively Coupled Plasma (ICP) Spectrometry. The concentration of chloride in the discharge solutions was analyzed by the titration with silver nitrate and sodium chromate. The discharge collection of each injection lasted for two to three weeks, at which time a low, but steady linear change in cation concentration was observed. The determination of non-sodium cation concentrations was done in order to determine the total cation exchange capacity (CEC) of the soils.

For the mineral characterization of the soils used in the column experiments, X-Ray powder diffraction data were collected from 5-65° two-theta using Cu K-alpha radiation and a step-size of 0.02 degrees. Mineral modal abundances (in weight percent) were calculated using the RockJack Program (Eberl, 2003), and were based on the mineral spectra density determined by the X-ray diffraction analyses. More details about this method of soil mineral modal analysis are given by Sun et al. (2009).

The amount of soil organic matter was measured using the loss on ignition (LOI) method in a furnace heated at 550°C for four hours. The mineral modes and organic matter content are also needed in order to determine the CEC of the soils used in the column experiments.

2.2 Field Data Collection

Long-term sodium and chloride concentration data in the Delaware River at the Trenton and Riegelsville Stations (Figure 2) were taken from the United States Geological Survey (USGS) database in order to examine their historical change. The amount of road salt (sodium chloride) applied within the DRB from 1981 to 2008, in tons per lane mile, was obtained from the New Jersey, New York, and Pennsylvania Departments of Transportation (NJDOT, NYDOT, and PADOT, respectively). In addition, actual salt application data was available for a few regions of the DRB managed by PADOT. Finally, the change in total lane mileage within the DRB from 1993 to 2008 was also obtained in order to calculate total salt usage to corroborate the data provided by the DOT of various states.

Surface runoff water samples were obtained since 2006 along three transects from a localized area of the DRB in 25 PVC cups and two lysimeters. The three transects were located close to Interstate 95 (Figure 2), a large highway where deicing salt was applied regularly every winter. The goal of this collection was to examine changes in pre- and post-salt application concentrations for sodium, potassium, calcium, and magnesium in highway runoff water.

Table 1. % of Retention after 3 weeks of flushing with varied amount of sodium input

	1 mole injection		0.5 mole injection	
	Column 1	Column 2	Column 3	Column 4
sodium input (gram)	23	23	11.5	11.5
sodium retained (gram)	6.06	12.03	4.383	7.66
% of sodium retention	36	52.3	41.8	66.7
Average flow rate (ml/hr)	150	30	190	40
Amount of H ₂ O flushed through** (cm)	210	241	1132	416

* Indicates the uncorrected retention rate for the repeated run. **Amount of H₂O flushed through is calculated as the total volume of water collected at the end of collection divided by the cross-section area of the soil column.

3. Results and Discussions

3.1 Retention Rates of Sodium and Chloride in Soil Columns

For the falling-head columns (1 and 2) with 1 mole injection of sodium chloride, column 1 had a faster flow rate. For the constant-head columns (3 and 4) with the 0.5 mole injection of sodium chloride, column 3 had a faster flow rate (Table 1). Following a quick discharge of sodium and chloride initially after the injection, slightly decreasing, but not constant, linear retention rates for both sodium and chloride were observed, usually by the third day after injection.

Overall, in the slow flow runs of columns 2 and 4, the retention rates of sodium, which is the percentage of sodium retained, are higher than those in the fast runs of columns 1 and 3. In addition, the retention rates of sodium in columns with 0.5 moles of sodium chloride injection are higher than those with 1 mole of sodium chloride injection. The average amount of sodium retention also is higher than that of chloride, except for the fast-flow column 1.

For columns 3 and 4, a 10% correction to the amount of sodium input was made to account for the initial spillage of sodium chloride solution from the overflow due to the sodium chloride upward dispersion right after the injection. The overflow was maintained to preserve the constant-head setup.

3.2 Cation Exchange Capacity of Column Soils.

The estimated cation exchange capacity (CEC) of two column soil samples was calculated as the summary

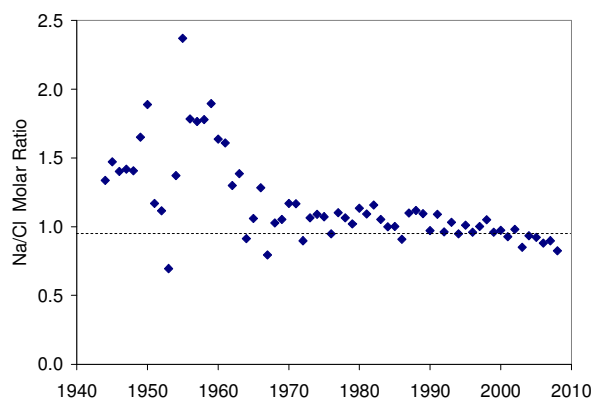


Figure 3. Concentrations of sodium and chloride of the Delaware River at Trenton station from 1944 to 2008.

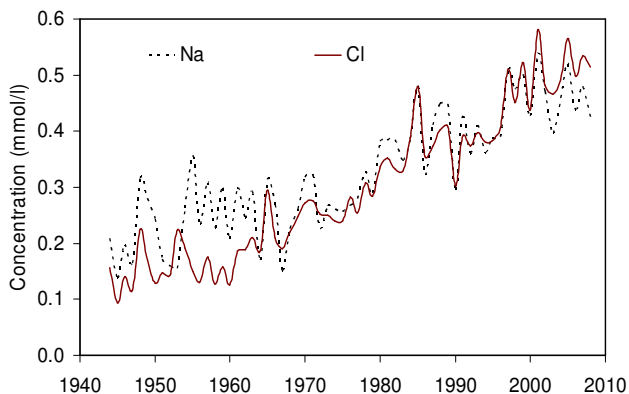


Figure 4. Delaware River sodium/chloride molar ratios at the Trenton Station from 1944 to 2008.

product of the modal weight percent of all clay minerals, organic matter and the average cation exchange capacity for each, as reported by Drever (1997). Because only the CECs of clay minerals are significant, the modal weight percentages for non-clay minerals are not listed. In addition, because of the difficulty in individually determining the modal amounts of biotite and vermiculite, the two minerals were treated as a 50:50 mixture in the calculation (Table 2).

Table 2. Modal weight percentage of clay minerals, measured organic matter and estimated CEC. CEC estimation was based on the average CEC* of individual minerals, as given by Drever (1997).

	average CEC* (cmol/kg)	Sample 1		Sample 2	
		Weight%	CEC	Weight%	CEC
Kaolinite	5	6.1	0.305	5.67	0.284
Smectite	115	7.5	8.620	10.53	12.11
Illite	16.7	6.3	1.052	3.41	0.57
biotite+vermiculite (50:50) mixture	80	1.5	1.2	4.65	3.72
Chlorite	2	3.6	0.072	7.05	0.141
Organic Matter	200	3.05	6.1	2.11	4.22
Total CEC(cmol/kg)		17.35		21.04	
Average CEC (cmol/kg)	19.2				
Average of Ca+Mg+K in solution for columns 2 and 4 (cmol/kg)			5.06		

Based on the estimated CEC of soil samples, the average maximum amount of sodium that can be retained by CEC in the 400-gram soil samples is 1.77 gram, which is less than 50% of the sodium retained for all the columns (Based on Table 1). As an alternative, the total amount of calcium, magnesium and potassium in the discharge solution in cmol/kg can also be used to approximate CEC of the soil. The total equivalent molar percentage of calcium, magnesium and potassium in the discharge solution over the total moles of sodium retained is also less than 50% of the sodium retained from these four sets of soil columns.

3.3 Change of Sodium Concentration and Sources of Sodium in the Delaware River Basin (DRB)

Long-term change of sodium and chloride concentrations in the DRB

Based on the data collected from USGS, annual average sodium concentration for the Delaware River increased from 3.2 mg/liter in 1945 to 12.46 mg/liter in 2008 based on the best-fit linear trend line for data recorded at the Trenton Station, an increase of roughly 4 times (Figure 3). Annual average chloride concentrations for the Delaware River changed from approximately 3.3 to 20.7 mg/liter between 1945 and 2008 at the Trenton Station, based on the best-fit linear trend line, an increase of more than 6 times (Figure 3). Concentrations of both sodium and chloride at the Riegelsville Station, located upstream from the Trenton Station, also increased, but by a lesser amount.

Overall, the concentrations of both sodium and chloride are at their highest from the end of January to March when snow and ice are removed from local roads. Another interesting trend observed was that the average annual sodium/chloride ratio at the Trenton Station fell from around 1.45 in the 1940s to 0.83 in 2008 (Figure 4). This will be discussed further (see below).

Sources of sodium in the DRB

The first apparent natural source of sodium is precipitation. The average concentrations of sodium measured within the DRB between 1983 and 2008 at three different precipitation stations, all maintained by the National Atmospheric Deposition Program (Figure 2), were 2.27 (Milford, PA), 4.34 (Washington Crossing, NJ), and 1.61 ueq/liter (Biscuit Brook, NY). These precipitation amounts of sodium are insignificant compared to the amount of sodium measured in the Delaware River at Trenton, which averages 9.3 mg/l between 1983 and 2008. The sodium concentrations of precipitation also exhibited no meaningful long-term increasing trend. Therefore, the

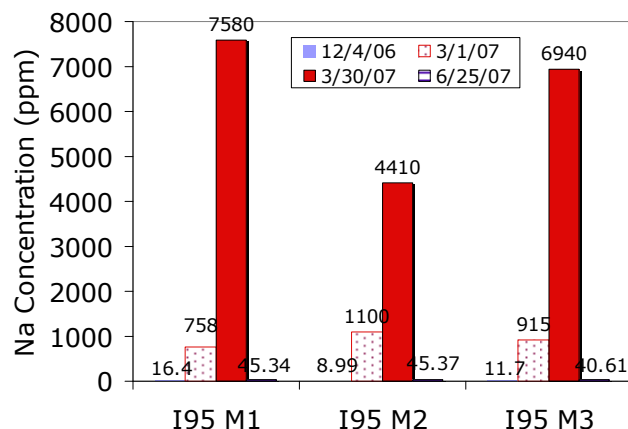


Figure 5. Average pre- and post-salting sodium concentration from three transect along I-95 in the DRB, NJ. Pre-salting data was collected on 12/4/06.

main source for the observed increase of sodium (and presumably chloride as well) in the Delaware River is unlikely to be precipitation.

A second potential source of sodium is salt released from agricultural areas. However, due to a nearly 50% decline in farmland within the DRB from 1950 to 2004 (Sun et al., 2006), agricultural areas also are not a likely source for the increased sodium observed in the river water. The relative constant amounts of sodium and chloride measured in the Delaware River at the Trenton Station prior to 1965 and their steady increase since 1965, based on Figure 3, coincides with development and increase of the local road network within the DRB. This correlation of salt increase and the development of road network in DRB corroborates the conclusion that farmland cannot be the major source of sodium chloride increase in the DRB.

The third potential source of sodium is the chemical weathering of albite feldspar, a common Na-bearing silicate mineral. Prior to 1965, the source of sodium appears to be mainly from weathering, as indicated by the sodium/chloride average ratio being 1.45 during the 1940s (Figure 4). This ratio drops to ~1 between 1970 and 1990 and is less than 1 now based on the sodium/chloride ratios of Delaware River at Trenton Station. Because chloride is generally regarded as a conservative ion and sodium an active ion, if sodium chloride is injected into a soil column, there will be more sodium absorbed in the soil column (Drever, 1997). This unequal adsorption was also substantiated by our experiment results of #2 and #4 columns when sufficient exchange time was allowed. A value of less than 1 for the sodium/chloride ratio indicates that sodium and chloride were unequally absorbed in the basin and a large quantity of sodium chloride is coming from an outside source. An analysis of geochemical mass balance of water chemistry of 2005 in the Delaware River at Trenton, NJ by USGS NETPATH, which models the weathering sources of minerals in the river solution (see Appendix for details), also indicates a large outside source of sodium chloride.

The fourth potential source of sodium, and which is the most likely source of the observed increase, is the artificial introduction of sodium chloride into the DRB. Among the artificial sources, deicing road salt is the main contributor based on the data we collected and reported by other people (Kelly, 2008). After roughly projecting the total road lane mileage (data from NJDOT, NYDOT, and PADOT) within the DRB, the total molar input of sodium chloride from all state roads is approximately 1.1 times the molar output of sodium chloride of the Delaware River from 1981 to 2004 above the Trenton Station. If the release of sodium chloride from sewage, local roads, residential pavements, and other sources are included, as done by Kelly et al., (2008), it may add an additional ~17% of sodium chloride into the river. Therefore, there appears to be more annual input of sodium into the basin from artificial sources than output via the river.

3.4 Fluctuation of Sodium Concentration in Runoff Water in DRB

From 2006 to 2009, surface runoff water from seven transects in a localized area of the DRB was collected and analyzed (Figure 2). Three transects were located next to Interstate 95, where deicing salt is regularly applied during each winter season. For runoff data collected near the I-95 highway, a large surge in sodium concentration was observed each time salt was applied (Figure 5). The post-salting sodium concentration in the highway runoff water is greater than 400 times the pre-salting level for the 2006-2007 data, although the sodium level dropped to near pre-salting levels during the following summer (Lucarino and Sun, 2007). There also is a subtle decreasing

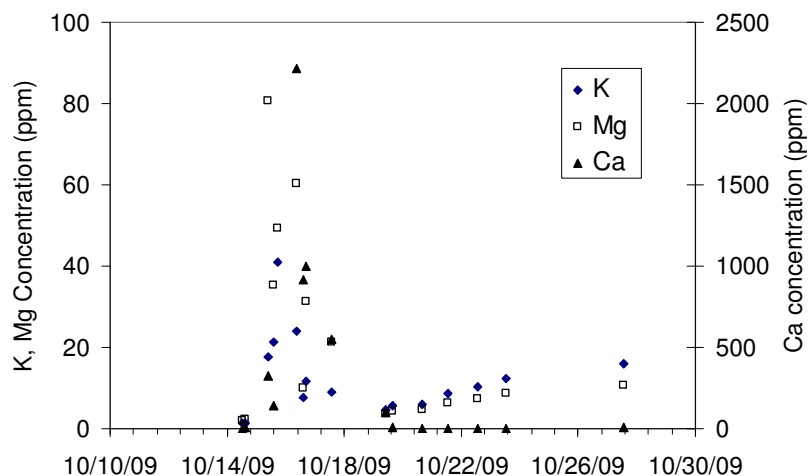


Figure 6. Calcium, magnesium and potassium concentrations in column 4 after the injection of sodium chloride.

trend in sodium/chloride ratios as the collection point moves away from I-95. In addition, the sodium/chloride ratio is higher in the pre-salting runoff (December 4, 2006) than the post-salting runoff.

3.5 Sodium Adsorption

The retention of sodium in soil can be caused by physical, electrostatic (cation exchange) and chemical adsorptions, as well as transient entrapment during transport. In the soil column experiments, after the initial injection of sodium chloride, sodium will replace most of the other cations at soil exchangeable sites. These replacements are documented by the increasing amount of calcium, magnesium and potassium observed in the soil column discharge solutions over time (Figure 7).

The maximum (or full) amount of sodium retained through cation exchange (electrostatic adsorption) will be the cation exchange capacity (CEC) of the soil samples. From the measured concentrations of calcium, magnesium and potassium in the column experiments, and the estimated average CEC as the full amount of sodium that the soil can hold at the end of the three-week run, the retention of sodium due to CEC only accounts for <50% of the total sodium retained in these four sets of soil column experiment. The chemical adsorption of sodium as precipitates due to chemical bonding is less significant because it is unlikely sodium is being saturated in soil waters for a prolonged period of time. Therefore, most of the sodium is likely to be retained by the transient entrapment of transport and physical adsorption. The transport entrapment of sodium is the temporary entrapment of sodium in a soil pore due to the non-connectivity of some soil pores and the nonlinear flow paths for soil pores that have no-outlets, and the transport rate becoming infinitely slow.

Physical adsorptions of cations and anions are due to weak van der Waals forces through complexation near surfaces (Drever, 1997). The amount of entrapped and adsorbed sodium is the difference between the total sodium retained and the sodium being retained by cation exchange at a particular time period. In the soil column experiments, after about three weeks, the amount sodium that is not retained by cation exchange accounts for more than 50% of the sodium retained. A more dynamic model of cation exchange, surface absorption, and transport processes will be modeled with the PHREEQC program (Parkhurst and Appelo, 1999) in our later study.

3.6 Retention Rate of Sodium in DRB

Based on the experiment result, the retention rate, which is the percentage of sodium being retained, depends on the amount of salt input, flow rate, and soil conditions in the soil columns. Given the same soil conditions and the same duration of the experiment, the larger the flow rate and the total amount of salt input, the lesser the percentage of sodium retention. The average precipitation within the DRB is about 119 cm each year. Approximately 52.3%, i.e., 62 cm of the precipitation will, eventually, goes to the Delaware River through runoff and baseflow (Sun, 2004). In comparison, the amount of water flushed through the four constructed soil columns (Table 1), ranging from 210 to 1132 cm, are larger than three times the amount of average annual precipitation that goes into the Delaware River. The average gradient of the Delaware River (~0.01) also is much smaller than the

flow gradient (~0.1 to 0.5) attained in these soil columns. Thus, the normalized flow rate (discharge/unit area) in the columns is larger than the flow rate in the Delaware River. For the two fast-flow columns (#1 and 3), some preferential micro-flow paths were observed in the columns. The process that the solution runs through these preferential flow paths is similar to a direct water runoff into a stream in a watershed. The process that water runs through the soil pore spaces and discharges through the outlet of the column is similar to the process of the baseflow. The amount of sodium applied via deicing salt by the states over the entire 6780 square miles of the DRB, averaging at approximately 0.004 g/inch²/year based on our initial estimation between 1981 and 2005, is much smaller than the 23 and 11.5 grams of sodium applied through a ~15.46 inch² of cross section area in the soil columns. Therefore, the amount of sodium annually retained in the DRB can be estimated based on the experimental data from further study. This sodium retention within the DRB is the underlying basis for the continuing sodium increase in the DRB. The sodium retention also explains the non-reduction of sodium observed in Rhode Island 10 years after the state mandated replacement of sodium chloride by a 6:4 mixture of MgCl₂ and sodium chloride (Nimroshi and Wladron, 2002).

4. Conclusions

A high rate of sodium retention in soils is the underlying reason for the increase of sodium concentration in many watersheds in the northeastern United States and Canada where winter deicing road salt is applied on a regular basis. The sodium retention rate after two to three weeks of leaching in four experimental soil columns produced a range of retention values depending on the amount of salt applied, flow rate, and column flush times given the identical soil conditions. Slow flow rates and small amounts of salt application usually resulted in a higher retention rate. We believe the retention rate of the sodium in most watersheds can be approximated based on further experimental data. The apparent high retention rate of sodium speaks to the difficulty of successfully instituting any environmental policy that intends to quickly reduce the amount of sodium concentration in a watershed.

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Appendix

Geochemical Mass Balance of Solutes in the Delaware River

In order to determine sodium input from a natural source, the weathering of the common rock-forming mineral, albite, needs to be evaluated. The albite weathering rate is related to the mass balance (including the charge balance) of the dissolution and precipitation of minerals and deicing salt in the watershed. The widely applied thermodynamic reaction USGS NETPATH program (Plummer et al., 1994, Velbel and Price, 2007) was used for these mass balance analyses. Initial studies of two representative geochemical mass balance models for 1945 and 2005 in the DRB are presented below. In both models, the mineral species on the left side of the equation are the dissolution species and the mineral species on the right side of the equation are the precipitation species.

The model for 1945 is:

0.093 sodium chloride + 0.044 Albeit +12.133 Ca-Montmorillinite+ 1.92 Biotite + 0.205 Gypsum = +1.934 Dolomite +11.493 Kaolinite +3.15 Illite + 16.336 SiO₂+ Balanced ions in the river.

The model for 2005 is:

0.52 sodium chloride +0.022 MgCl₂ +7.316 Ca-Montmorillinite+ 0.236 Chlorite +0.168 Gypsum = +0.961 Dolomite +8.778 Kaolinite +10.053 SiO₂+ Balanced ions in the river.

The year 1945 represents a period of insignificant deicing salt application due to fewer paved roads within the DRB at that time. Significant deicing salt application in the DRB is represented by the year 2005. The above two equations revealed some significant changes of dissolution and precipitation of mineral species from 1945 to 2005 in the DRB. The first change is the significant increase of sodium chloride dissolution in the 2005 model, as indicated by its larger mass transfer coefficient in the model. This change reflects the reality of elevated sodium chloride concentrations in the DRB in 2005 due to the increased application of deicing salt. The second change is the addition of MgCl₂ dissolution and lack of albite dissolution in the 2005 model. One possible explanation for the addition of MgCl₂ in the 2005 model is the increased use of CaCl₂ as an alternative deicing salt. The lack of albite

dissolution in the 2005 model may be due to the significant retention of sodium in the basin which masks the release of sodium from albite weathering in recent years.