



Mineralogical and anthropogenic controls of stream water chemistry in salted watersheds



Hongbing Sun*, John Alexander, Brita Gove, Eric Pezzi, Nicole Chakowski, Jonathan Husch

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

ARTICLE INFO

Article history:

Available online 11 July 2014

Editorial handling by M. Kersten

ABSTRACT

The relatively stable concentrations of calcium (42.2–122.3 mg/l) and magnesium (48.9–88.1 mg/l) between 2012 and 2013 and their possible weathering paths identified by mass balance models for both soil solutions and stream water from a small salted (regular applications of winter road deicing salt) watershed in New Jersey, USA indicate that the weathering of feldspars and dissolution of carbonates are the primary sources for these cations. However, the relatively stable and lower concentrations of sodium and chloride in soil solutions (19.6–46.1 mg/l for Na and 12.7–88.3 mg/l for Cl) and their fluctuating and higher concentrations in stream water (14.6–103.1 mg/l for Na and 15.2–260.4 mg/l) from the same watershed during the same period also indicate that road deicing salt is the primary source for sodium and chloride in stream water. Furthermore, positive correlations between calcium and sulfur concentrations (correlation coefficient $r = 0.77$) and magnesium and sulfur concentrations ($r = 0.73$) in stream water between 2009 and 2013, as well as positive correlations between sulfur and iron concentrations in soil compositions ($r = 0.27$), indicate that both the dissolution of gypsum and the oxidation of pyrite into hematite might be the primary sources of sulfate in the watershed. Analyses of water chemistry from the related and much larger Delaware River Watershed (DRW) show that sodium and chloride concentrations have increased steadily (2.7 times for Na and 4.56 times for Cl for 10-year average) due to the regular application of winter deicing salt from 1944 to 2011 for which data are available. The greater increase of stream water chloride concentrations compared with sodium concentrations also results in the steady decline of Na^+/Cl^- molar ratios from 1.51 to 0.92 for the 10-year average during that time in the DRW and approximately 78% of the chloride in the DRW now being anthropogenic. In addition, the decline of sulfate concentration from 22.08 to 14.59 mg/l (~34%) for the 10-year average from 1980 to 2011 in the DRW stream water may be attributed to the decline of sulfate levels in atmospheric deposition resulting from enhanced national and state environmental regulations and a shift in local economic activities. There also are more periods of low silica stream water concentrations in the DRW than in the past, perhaps as a result of recent increases in summer stream temperatures combined with an increase of impervious surface area in the region. Warmer stream water might cause the temporary bloom of biota requiring silica, particularly plankton, increasing its uptake from stream water, while an expanded impervious surface area increases the contribution of low-silica runoff water to total stream discharge, thereby lowering the silica concentration in stream water. The combined results of this study illustrate the possible changing anthropogenic factors that can control stream water chemistry in salted watersheds and that these factors need to be taken into account when future water quality regulations and policy are considered.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Total stream water chemistry typically results from the combination of ions derived from baseflow, surface runoff, precipitation, and bioactivity in a watershed. Traditionally, Ca^{2+} , Mg^{2+} , Na^+ , and K^+ are regarded as the major cations in stream water, while HCO_3^- ,

SO_4^{2-} , and Cl^- are regarded as the main anions (Drever, 1997; Kehew, 2001). Commonly, the most important source of calcium and magnesium in stream water is attributed to the dissolution of calcite and dolomite in soil, depending on the underlying watershed geology (Blum et al., 1998). High ratios of Mg/Ca usually indicate greater dissolution of magnesium-related minerals, whereas low Mg/Ca ratios indicate greater dissolution of calcite (Morala et al., 2008). Sodium is attributed to the dissolution of albite, anorthoclase, and Na-beidellite (a smectite group clay) in

* Corresponding author.

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

the absence of anthropogenic sources (Bowser and Jones, 2002). Sources of potassium are attributed to the dissolution and hydrolysis of K-feldspar and biotite (Bowser and Jones, 2002; Brady and Weil, 2008). Potassium also has a high solubility and is readily leached from organic matter, hence, its concentration in stream water is affected more by decaying of organic matter than other cations (Markewitz and Richter, 2000).

For anions in stream water, the concentration of HCO_3^- is related to the partial pressure of CO_2 of air, bio-respiration in the watershed, and the equilibrium balance of carbonate minerals in soil solutions (Langmuir, 1997; Mortattia and Probst, 2003; Kim et al., 2005). Sulfate has been attributed to atmospheric deposition in some regions, as well as to the dissolution of gypsum and the oxidation of pyrite in others (Rochelle et al., 1987; Katz, 1989; Rice and Bricker, 1995; Peters et al., 2006). Natural sources of chloride are usually attributed to evaporites and occasionally to silicate minerals (Peters, 1991; Mullaney et al., 2009).

More recently, the application of road deicing salt has significantly increased the anthropogenic input of sodium chloride to a level that surpasses natural sources in the northern United States, Canada, and parts of Europe (Godwin et al., 2003; Kelly et al., 2008, 2012; Novotny et al., 2009; Sun et al., 2012). This increase has resulted in many situations where both sodium and chloride concentrations in stream water exceeded the US Environmental Protection Agency's (USEPA) water quality criteria, with the increase being more apparent for chloride because of its relatively low soil retention rate due to its conservative property (Corsi et al., 2010; Dailey et al., 2014; Jackson and Jobbagy, 2005; Kaushal et al., 2010). For this study, a salted watershed is defined as one that has regular applications of winter deicing salt. Other anthropogenic factors, such as an increase in the partial pressure of atmospheric CO_2 and increased air/water temperatures, also affect the saturation ratios of other ions, such as bicarbonate and silica (Amiotte Suchet and Probst, 1995; Karim and Veizer, 2000; Mortattia and Probst, 2003). In particular, global warming and deforestation result in more intense exposures of ground and water surfaces to sunlight and this has been considered as the reason for increased stream water temperatures and the resulting changes in water quality (Isaak et al., 2012; Whitehead et al., 2009; Kaushal et al., 2010). In West Virginia, the blooming of benthic diatoms due to increased sunlight penetration caused by forest defoliation between 1988 and 2003 has been reported to result in declining concentrations of silica, a common weathering product in stream water (Grady et al., 2007; Schoelynck et al., 2014). On the other hand, many researchers also have attributed the recent decline of sulfate concentrations in stream water to the decline of sulfate deposition from the atmosphere as a result of enhanced environmental regulations (Skjelkvale et al., 2001; Majer et al., 2005; Jenkins, 1999). Competing claims on sources of major ions in stream water, shifting equilibrium of weathering reactions, and changed mineral stability patterns due to increasing anthropogenic impacts require that our traditional understanding of the sources of major ions in stream water from the surface and subsurface be re-examined in order to assess the geochemical transformations caused by recent anthropogenic activity in watersheds.

This study analyzed numerous factors that can control the concentrations of major cations, including Ca^{2+} , Mg^{2+} , Na^+ , and K^+ , and the anions HCO_3^- , SO_4^{2-} , and Cl^- , through comparison of stream water, soil solution, soil mineralogy, and soil chemical compositions in the Centennial Lake Watershed (CLW), New Jersey (Fig. 1). In addition, an analysis of the water chemistry data record (1944–2012) for the Delaware River Watershed (DRW), which encompasses parts of New Jersey, Pennsylvania, and New York, allowed for the relationships among the changing ion concentration trends and recent anthropogenic events to be identified and examined. Statistical methods, including correlation dendrogram

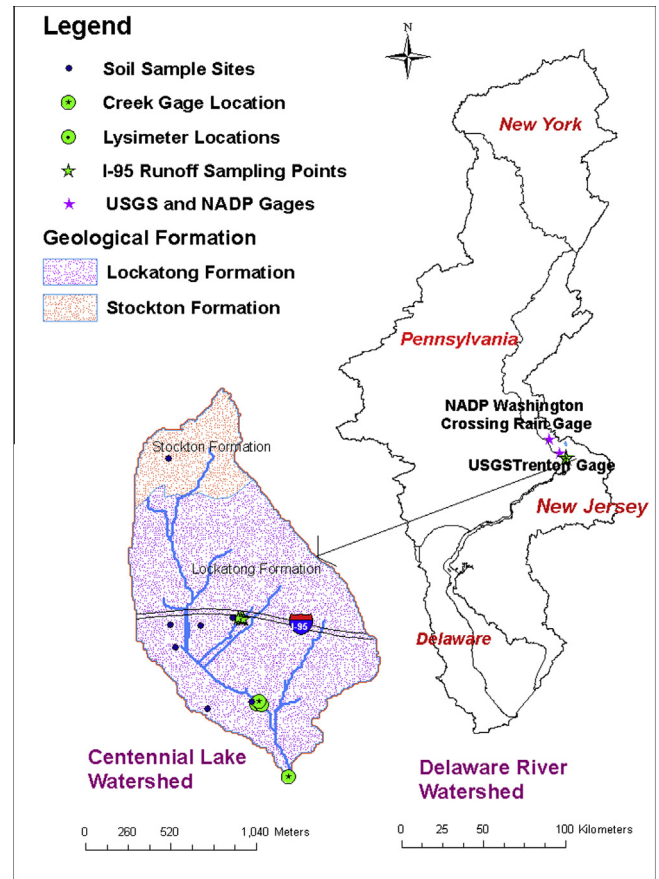


Fig. 1. Sample site location maps for the studied watersheds, including the underlying geological formations for the smaller watershed (CLW). NADP is the abbreviation for the US National Atmospheric Deposition Program. The right watershed is the DRW.

analyses, mass balance analyses of weathering reactions based on water chemistry, and mineral stability analyses, also were conducted.

The combined results of this study will increase our understanding of the shifting roles of both mineralogical and anthropogenic controls on water chemistry in an era of increased human influence. In addition, elucidating the factors that control stream water chemistry at a time when winter salting is common not only has significance for understanding aqueous geochemical processes, but also has implications for improving future water quality regulations and public policy.

2. Collection and analyses of water and soil samples in the CLW

2.1. Field and laboratory methods

Stream water samples were collected weekly between September and April from 2009 to 2013. The CLW has 1.02 square kilometers of catchment area for the upstream gage and 1.95 square kilometers for the downstream gage (Fig. 1). Soil solution samples from three locations in a wooded area, two near the stream bank and one slightly above the bank, were collected by lysimeters buried at approximately 110 cm depth near the upstream gage #1 location (Fig. 1). Soil samples from eight locations within the CLW were collected using a set of hand augers at 20 cm vertical intervals with total profile depths ranging from 60 to 180 cm, depending on the position of the C Horizon. Samples of road runoff water from three transects oriented perpendicular to the road surface, with three collection cups per transect buried just under the

surface at one meter horizontal intervals (total of nine cups), were collected before and after salting events in 2006–2009 and in 2012–2013 along Interstate 95 in Lawrence Township, New Jersey.

All stream water and soil solution major cation and anion elemental concentrations were measured by a Spectra Arcos Inductively Coupled Plasma (ICP) Spectrometer, which can simultaneously measure the emitted light spectrum from 165 to 770 nm with low ppb detection limits for all elements reported on in this study. In addition, total sulfate and nitrate concentrations were measured with either a HACH DR/850 or a DR/890 colorimeter with an estimated detection limit of 0.01 mg/l for nitrate and 4.9 mg/l for sulfate, following manufacturer recommended methods. The HCO_3^- concentrations of stream, soil solution, and road runoff water were measured by hydrochloride titration. The US National Atmospheric Depositional Program (NADP) provided precipitation compositions. The two DRW precipitation collection stations utilized for this study are located at Washington Crossing, New Jersey, and Milford, Pennsylvania (Fig. 1). However, because precipitation compositional data from the NADP did not include HCO_3^- concentrations, HCO_3^- concentrations in precipitation were estimated based upon the charge balance of their major cations and anions, following the approach of Dikaiakos et al. (1990).

Eight soil profiles were collected from the CLW (Fig. 1). Selection of the soil profile sites was based on the types of land cover and accessibility. All profile sites were in wooded areas except for the three profiles along I-95 that were 0.9, 1.8, and 2.7 meters behind the guardrail in a grassy area. Bedrock underlying the CLW consists of black shale and dark argillite of the Lockatong Formation and mudstone and sandstone lenses of the Stockton formation, both of Triassic age.

Mineral identifications and modes in selected watershed soil samples were determined by quantitative X-ray analysis utilizing a Rigaku X-ray powder diffraction spectrometer and USGS RockJock software (Srodon et al., 2001). Following the method recommended by Eberl (2003), 2 g of soil sample were mixed with 0.222 g of zincite (ZnO) in a ball mill and an X-ray diffraction spectrum for the sample was collected from 5° to 65° two-theta using Cu K-alpha radiation and a step-size of 0.02° . Mineral modal abundances then were calculated using the USGS RockJock software based on mineral spectra intensity relative to that of zincite, which is used as an internal reference standard. The purpose of obtaining modal abundances was to identify the minerals that might be responsible for the release of ions into soil solutions and stream water. Soil mineral modal abundances also provide the mineralogical basis for the mass balance analyses of weathering reactions and the mineral stability diagrams for soil solutions and stream water.

The chemical compositions of 18 soil samples from various depths above the riverbank in the CLW were analyzed by ICP, utilizing a lithium metaborate fusion and nitric acid dissolution method modified after Cremer and Schlocker (1976). One gram of lithium metaborate was mixed with 0.2 g of powdered sample in a graphite crucible. The prepared graphite crucible then was put in a muffle furnace at 1100°C for 15 min. The resulting molten bead was poured into 100 ml of 5% nitric acid solution immediately after removal from the furnace. The concentrations for 32 elements in the dissolved solution then were analyzed with the Spectra Arcos ICP. Elemental recovery from the soil samples was greater than 92 percent, based on the summation of the primary elements' oxide values.

2.2. Analytical and experimental results and explanations

Compared to sodium and chloride concentrations, calcium and magnesium concentrations in stream water are relatively constant over time (Fig. 2). On the other hand, both sodium and chloride concentrations in spring 2013 were about twice their peak

concentrations in fall of 2012 due to the application of road deicing salt. Overall, concentrations of calcium and magnesium are higher in soil solutions, whereas concentrations of sodium, chloride, and potassium are higher in stream water (Table 1). Also of note are the significant concentration spikes for sodium and chloride in runoff water along the Interstate 95 transects following road deicing salt applications compared to the Ca, Mg, K, and S concentrations.

Soil samples collected from wooded areas in the CLW are mainly silty loam. For soil samples collected near I-95, there are more pebbles in the loamy texture, perhaps due to disturbance when the highway was constructed. Quartz is the largest mineral component, followed by various feldspars containing calcium, sodium, and potassium in most soil profiles except the two sites near I-95 (Table 2). The two I-95 sites have less than 1% of combined Na and Ca feldspar. Clay minerals, including Ca, Na, and Fe-smectites, kaolinite, muscovite, and biotite occur in significant amounts. Their distributions in the wooded sample sites are fairly consistent within the CLW except the sites along I-95 which have a slightly high amount of smectite. The site near the upper boundary of the watershed underlain by Stockton Formation has a slightly lower amount of quartz near the surface (37.5%). Dolomite and calcite, significant mineralogical sources of magnesium and calcium in the soil solution, also are found in small amounts in all profiles. Small amounts of pyrite, which is a possible source of sulfate in soil solutions, also exist. Some minor amounts of the hematite and goethite, which are likely the oxidized products of pyrite, also are found.

For bulk soil mineral chemistry, SiO_2 and Al_2O_3 are the most abundant oxides found (Table 3). In addition, magnesium oxide concentrations are higher than those for calcium in the bulk soil minerals with a molar ratio average of 3.02. The magnesium and calcium molar ratios averaged 1.23, 0.62, and 0.57 in three lysimeters and 0.85 and 0.84 in upstream and downstream water samples. Also, note that both sulfur and chloride are measured in all soil samples shown in Table 3 and these samples are from a soil profile in a wooded area (~ 521 m from the highway) where road salt impact is relatively weak. Their measurement in this soil profile supports their occurrence being at least partially due to natural sources and not solely anthropogenic. In addition, there is about 3% of TiO_2 , which usually is abundant in sedimentary rocks and soil due to its resistance to weathering (Tables 2 and 3). Titanium exists in titanite, rutile or as a substitution in phyllosilicate minerals in soil (Young and Nesbitt, 1998; Ibhi and Nachit, 2000). The compositional similarities and variances of the common elements from soil samples, soil solution, and stream water are illustrated by the ternary diagrams and dendrograms in the following section.

2.3. Relationships among ion concentrations in stream water, soil solution, and soil minerals

A molar concentration ternary diagram for calcium, magnesium, and potassium plus sodium (Fig. 4) indicates that relative proportions of cation concentration for stream water are interme-

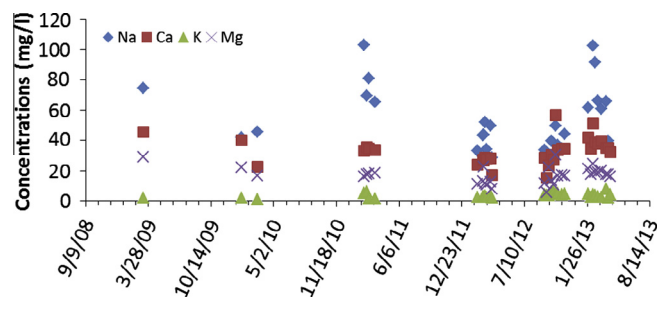


Fig. 2. Major cation concentrations for CWL upstream water from 2009 to 2013.

Table 1
Average major ion concentrations (mmol/l) in Centennial Lake watershed stream water and soil solutions from 2009 to 2013. Ion ratios in the left column are ratios of the average concentration of an ion in soil solution to the average concentration of the ion in downstream water.

	Na	Ca	K	Mg	Al	Fe	Si	S	Cl
Soil solutions	1.382	2.458	0.048	2.531	0.002	0.003	0.854	0.739	1.471
Upstream water	2.015	0.810	0.101	0.671	0.001	0.001	0.277	0.264	1.831
Downstream water	2.653	0.781	0.137	0.644	0.002	0.002	0.196	0.256	3.479
Ion ratios	0.521	3.147	0.350	3.930	1.000	1.500	4.357	2.887	0.423

Table 2
Mineral weight modal abundances of a soil profile located near lysimeter #3. Values in the depth row are the range of depths at which soil samples were collected in centimeters; F is feldspar.

Depth (cm)	0–15	15–30	30–45	45–60	65–80	80–95	95–110	110–150	150–180	Formula
Quartz	53.91	54.90	60.38	54.86	57.74	61.88	46.66	58.07	53.06	SiO ₂
K-feldspar	3.98	4.04	4.24	8.76	4.14	4.26	5.94	6.50	4.12	KAlSi ₃ O ₈
Anorthoclase F.	0.00	1.61	0.64	0.00	0.00	0.00	2.10	0.03	0.77	(Na, K)Si ₃ O ₈
Albite	3.52	5.04	5.27	6.11	6.39	6.28	3.19	4.88	6.06	NaAl ₃ Si ₃ O ₈
Oligoclase F.	1.00	7.00	3.20	0.00	0.24	1.02	1.60	0.47	4.84	CaAl ₂ Si ₂ O ₈
Andesine F.	2.89	4.81	0.01	1.68	4.80	1.12	0.00	0.07	0.00	(Ca, Na)(Al, Si) ₄ O ₈
Calcite	0.00	1.04	0.00	0.02	0.00	0.17	0.17	0.00	0.00	CaCO ₃
Dolomite	0.36	0.09	0.07	0.00	0.33	0.40	0.60	0.17	0.72	CaMg(CO ₃) ₂
Magnetite	0.54	0.24	0.67	0.44	0.91	0.23	0.00	0.40	0.00	Fe ₃ O ₄
Gypsum	0.00	0.00	0.00	0.00	0.00	0.00	0.60	0.04	0.26	CaSO ₄ * 2H ₂ O
Pyrite	0.01	0.04	0.00	0.27	0.00	0.08	0.11	0.16	0.00	FeS ₂
Hematite	0.70	0.63	0.52	0.79	0.43	0.60	0.93	0.78	0.53	Fe ₂ O ₃
Goethite	0.88	0.75	1.14	1.12	1.04	0.91	1.59	1.03	0.76	Fe ₂ O ₃ * nH ₂ O
Titanite	0.40	0.48	0.00	1.71	0.00	0.00	0.00	0.00	0.00	CaTiSiO ₅
Rutile	0.00	0.25	0.00	1.07	0.00	0.13	0.00	0.33	0.00	TiO ₂
Kaolinite	9.09	4.18	7.23	7.45	6.91	6.52	9.47	9.34	8.21	Al ₂ Si ₂ O ₅ (OH) ₄
Ca-smectite	0.93	0.00	2.48	1.13	1.38	2.35	2.75	1.61	3.60	Ca _{0.165} Al _{2.33} Si _{3.67} O ₁₀ (OH) ₂
Fe-smectite	4.78	3.63	2.47	3.05	2.15	4.26	5.44	4.51	4.73	Fe _{0.165} Al _{2.33} Si _{3.67} O ₁₀ (OH) ₂
Illite	4.83	3.06	3.00	0.71	2.90	1.81	3.03	2.64	1.03	(K,H ₃ O)(Al, Mg, Fe) ₂ (Si, Al) ₄ O ₁₀ [(OH) ₂ , (H ₂ O)]
Biotite	2.16	1.60	1.25	1.66	1.61	1.46	2.64	1.19	2.30	KMg ₃ AlSi ₃ O ₁₀ (OH) ₂
Chlorite(Mg, Ca)	0.77	0.00	0.00	0.71	0.32	0.00	2.45	0.00	1.61	(Ca, Mg) ₅ Al ₂ Si ₃ O ₁₀ (OH) ₈
Fe-chlorite	3.42	2.40	2.04	2.27	2.16	1.80	3.14	2.26	3.14	(Fe, Mg) ₅ Al ₂ Si ₃ O ₁₀ (OH) ₈
Muscovite	5.84	4.22	5.40	6.18	6.54	4.72	5.11	5.52	4.01	KAl ₂ (AlSi ₃ O ₁₀)(F, OH) ₂
Total %	100.00	100.00	100.00	100.00	100.00	100.00	97.51	100.00	100.00	

Table 3
Average weight percent of oxides for soil samples determined by ICP analysis after lithium metaborate fusion and HNO₃ dissolution. Depth column is the average depth at which soil samples were collected in centimeters.

Depth (cm)	Na ₂ O	CaO	K ₂ O	MgO	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	S	Cl	TiO ₂
7.5	1.450	1.597	1.986	1.95	8.514	4.627	69.441	0.121	0.626	3.104
22.5	1.857	1.001	2.395	1.24	10.016	4.642	68.462	0.075	0.526	3.016
37.5	1.974	0.526	2.751	0.99	11.127	4.654	68.566	0.088	0.543	3.103
52.5	1.815	0.533	2.466	0.93	11.458	4.404	69.148	0.048	0.551	3.189
72.5	1.685	0.445	2.039	0.92	11.711	4.523	69.028	0.194	0.532	3.350
87.5	1.856	0.453	2.304	0.95	12.020	4.500	68.216	0.249	0.568	3.393
102.5	1.788	0.423	2.185	0.90	12.421	4.235	68.923	0.163	0.552	3.150
130	1.855	0.421	2.343	0.89	12.526	4.521	68.505	0.018	0.515	3.106
165	1.843	0.425	2.261	0.88	12.795	4.236	68.798	0.015	0.528	2.946

diate between those for soil solutions and highway runoff water. The concentration proportions of calcium and magnesium in stream water are relatively higher than those in the runoff water, but lower than those in soil solutions. The observed higher concentration proportions of sodium and chloride in highway runoff water collected predominantly during the winter and spring are attributed to the dissolution of winter deicing salt (Fig. 3). Lysimeters are located away from the roadways in wooded areas (Fig. 1) where road salt impact on the chemical composition of soil solution is relatively weak, hence, high elemental concentration ratios of calcium, magnesium, aluminum, iron, silicon, and sulfur (Table 1) between soil solution and stream water indicate that natural weathering release is most likely the primary source of these elements in soil solution and stream water assuming the riparian soil solution chemistry from the lysimeters located near the bank

is similar to baseflow chemistry (Seibert et al., 2009). The low elemental concentration ratios for the sodium and chloride between soil solution and stream water indicates the more anthropogenic influence on these elements in stream water. However, the low elemental concentration ratio of potassium between soil solution and stream water might be an indication of more potassium being leached directly from organic matter into runoff water without infiltrating the soil due to its high solubility (Markewitz and Richter, 2000; Bowser and Jones, 2002).

Proportions of cation molar concentration in rainwater are similar to that of stream water except for a relatively low proportion of magnesium. In addition, the relative molar concentration proportions of sodium + potassium (indicated as Na + K in Fig. 4a) in precipitation are higher than those for calcium and magnesium as is evident from their plotted position towards the right corner of

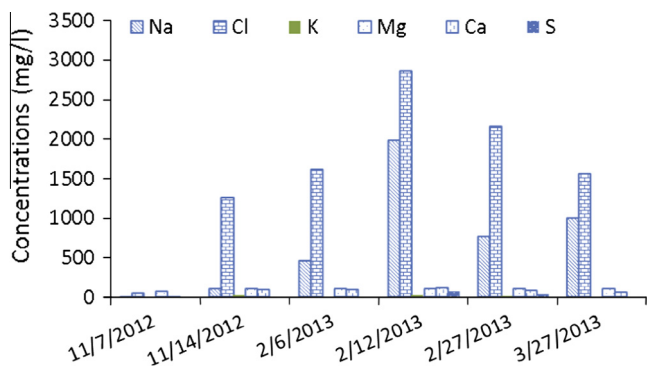


Fig. 3. Average ion concentrations showing differences between pre- and post-salting runoff water along three transects next to I-95. Data collected on 11/7/2012 is the pre-salting baseline data.

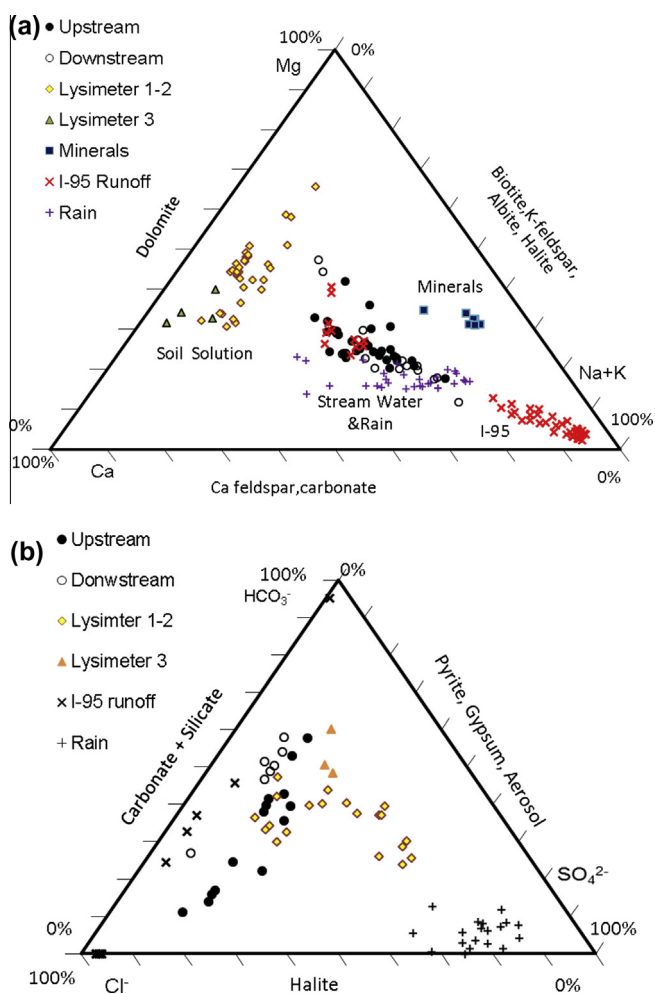


Fig. 4. Ternary diagrams of major cation (a) and anion concentrations (b) for the CLW stream water, soil solutions, leached solutions, soil mineral compositions, I-95 runoff, and precipitation at Washington Crossing. Concentration units used for calculation are milliequivalent. The minerals along the triangle borders are the main minerals that may be responsible for controlling the ion concentrations shown at the apices.

the ternary base. Precipitation (or wet) deposition of cations is less than 3% of cation discharge in stream water while dry deposition might be approximately 60–70% of the wet deposition (Rochelle et al., 1987; Likens et al., 1990). The proportions of wet and dry ion deposition into the CLW and the data used for deriving these percentages will be discussed in a later section.

For stream water, soil solutions, and precipitation anions, the relative proportions of molar HCO_3^- and Cl^- are larger than those for SO_4^{2-} (Fig. 4b). Also, the concentrations for HCO_3^- in soil solutions are higher than found in stream water.

On average, roughly 50% of annual stream water comes from direct runoff and another 50% comes from baseflow in the DRW region (Sun, 2004). This discharge partition was summarized by Sun (2004) based upon the work of Sloto (2004), the New Jersey Water Supply Authority (2000), and groundwater recharge calculations using the seasonal recession method, the recession curve displacement method, and the long-term stream discharge of the Delaware River at Trenton. The concentrations for calcium, magnesium, silica, and sulfate in stream water are only approximately 1/3 of that in soil solution (Table 1); hence, direct runoff into the stream dilutes the concentrations of these elements and compounds from soil solutions if we assume that riparian soil solution chemistry from the lysimeters located near the stream bank is similar to baseflow chemistry (Hendershot et al., 1992; Seibert et al., 2009). Therefore, baseflow is the primary source of these elements and compounds in stream water. On the other hand, average sodium and chloride concentrations in stream water are almost twice those observed in soil solutions, with higher concentrations for chloride than for sodium (Table 1). When baseflow is about 50% of the stream discharge and chloride concentrations of soil solution is roughly 42% of the chloride concentrations in stream water (Table 1), there is an implication that approximately 21% of the stream salt is from soil solution ($50\% \times 0.42 = 21\%$ by assuming a unit stream discharge). Selection of chloride over sodium in the calculation is because chloride is more conservative. Excluding the roughly 3–5% atmospheric salt deposition (see following discussions on the wet and dry deposition), about 75% ($100\% - 21\% - 4\% = 75\%$) of the chloride in the CLW stream water is anthropogenic. As 73% of the CLW is considered developed based on the U.S. National Agricultural Statistics Service (USNASS)’s 2013 land cover data (<http://nassgeodata.gmu.edu/CropScape>), the dominant source of this anthropogenic salt in the CLW will likely be road deicing salt at the present time. Historical changes in the proportions of sodium and chloride due to natural weathering release, as compared to anthropogenic sources, will be described when long-term compositional data for the DRW is discussed in a later section.

2.4. Mineral sources of ions in CLW stream water

As previously shown, calcium and magnesium in CLW stream water are primarily derived from soil solutions through baseflow (Table 1). Traditionally, sources of calcium and magnesium in soil solutions are attributed to the dissolution of carbonates, predominantly calcite and less so to dolomite due to the faster dissolution rate of calcite because of kinetic considerations (Drever, 1997; Langmuir, 1997; Kehew, 2001). Blum et al. (1998) argued that even when there is only a small amount in an aquifer, calcite is still the most likely primary source of calcium. However, for all CLW soil samples analyzed (Table 2), there is little identified calcite, although there are minor amounts of gypsum (Sun et al., 2009). On the other hand, there are relatively large amounts of Ca-feldspar (Oligoclase) and Ca-smectite identified in all CLW soil samples (Table 2). In addition, the relative high $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratios in the stream (upstream average 0.85, downstream average 0.84, Lysimeter #1 average 1.23, Lysimeter #2 average 0.63, Lysimeter #3 average 0.57) indicate that multiple sources of magnesium, including dolomite, biotite, chlorite, sepiolite, and brucite, might exist as well.

From dendrogram cluster analyses of ion concentrations for soil solution, there are strong correlations among calcium, magnesium, and potassium concentrations, as well as among sodium, chloride,

and sulfur concentrations (Fig. 5a). The strong correlations among calcium, magnesium, and potassium in soil solutions indicate that these elements are derived from a common source, whereas the strong correlations among sodium, chloride, and sulfur indicate these elements are derived from a second, different source. By examination of the mineral abundances and their chemical formulae in Table 2, the most likely sources for calcium, magnesium, and potassium are the various forms of feldspars and smectite clay minerals with a large inter-layer space that can hold many exchangeable cations, in addition to the traditional calcite and dolomite sources.

The stronger correlations between sodium and chloride concentrations in stream water compared to those in soil solutions indicate that sodium and chloride in stream water are mainly from a common anthropogenic source: the halite used in road deicing salt (Fig. 5b).

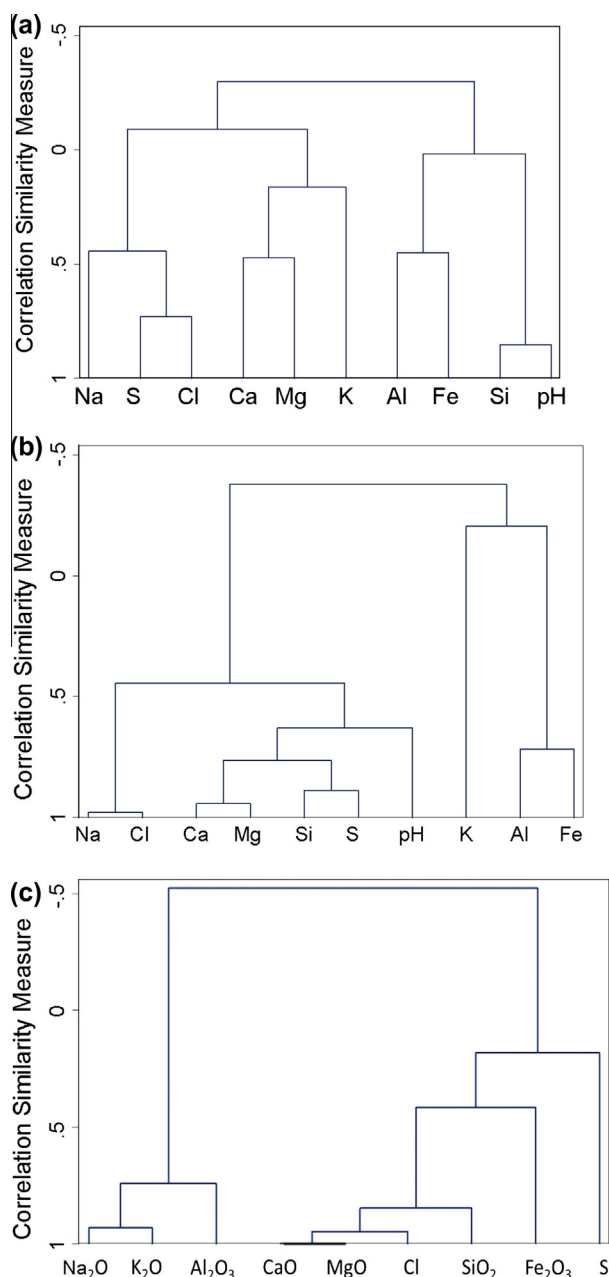
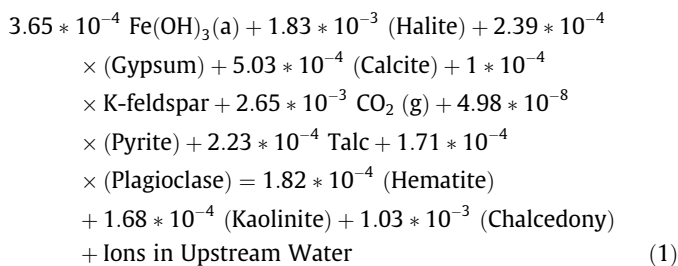


Fig. 5. Cluster analysis dendrograms for CLW ion concentration correlation coefficients from (a) lysimeter #1; (b) upstream creek; (c) soil mineral composition.

Strong correlations among CaO, MgO, Cl, and SiO₂ in bulk soil compositions (Fig. 5c) indicate that chloride might be present in the original soil as either chloride evaporites or in various Cl-bearing silicate minerals, as discussed by Mullaney et al. (2009) and Sandland et al. (2004). The positive correlations between sulfur (S) and hematite (Fe₂O₃) concentrations in bulk soil compositions (Fig. 5c) indicate that at least a portion of the soil Fe₂O₃ was derived from the oxidation of pyrite or other iron and sulfur-bearing minerals. Strong correlations among bulk soil N₂O, K₂O, and Al₂O₃ concentrations substantiate the mineral abundance data from X-ray powder diffraction (Table 2) and support the prior conclusion that various feldspars, such as anorthoclase and albite, are the major sources of sodium and potassium in soil solutions.

The mass-balance equation coefficients for likely weathering reactions that can produce the observed ion concentrations (Table 1) in CLW soil solutions and stream water collected by lysimeters are presented in Table 4. These coefficients are derived from the PHREEQC inverse modeling procedure (Parkhurst and Appelo, 1999; Appelo and Postma, 2005) and are based upon the average measured ion concentrations in soil solutions and stream water, after correction for any ion contributions from precipitation. The coefficients in Table 4 are the molar amounts of minerals that were involved in either dissolution (positive coefficient) or precipitation (negative coefficient) and they are not unique. The mineralogical results from the PHREEQC inverse modeling runs shown in Table 4 are in general agreement with the soil mineral modal abundances determined by X-ray diffraction (Table 2).

Using the coefficients shown in Table 4, the reaction equation that best reproduces the average ion concentrations of CLW upstream water is:



Eq. (1) states that for CLW stream water, dissolution of halite from road deicing salt along with the dissolution of plagioclase, are the primary and secondary sources of sodium, respectively; dissolution of calcite, gypsum, plagioclase, and talc are the primary sources of calcium and magnesium; K-feldspar dissolution is the primary source of potassium; and the dissolution of gypsum and pyrite are two of the apparent natural sources of sulfur. Talc in Eq. (1) as a minor source of magnesium is added because of its present in some soil samples in the CLW. Also note in Eq. (1) that an increase in the partial pressure of CO₂ in soil solutions and stream water favor the dissolution of all primary minerals, including the feldspars. Though the weathering reaction in Eq. (1) presents our optimal explanation for CLW stream water chemistry based on its ion concentration and available minerals, alternative explanations also exist. For example, another model, which involves the dissolution of various feldspars to produce both smectite and kaolinite as the end product of weathering, instead of only kaolinite as the end product, also reproduces the stream water ion concentrations satisfactorily and is supported by the mineral stability diagrams discussed in the following section. Fe(OH)₃(a) in Eq. (1) was solely to provide a source of iron for mass balance purpose. In addition, because of the limited mineral species used in the calculation, some minerals species and the cation exchange processes were omitted in the reaction models. The saturation indices of calcite varied significantly from spring to summer due to evaporation as pointed out by Sun et al. (2008). Therefore,

Table 4

Mass balance transfer coefficients for soil weathering reaction models based on the average ion concentrations of upstream water and soil solutions collected between 2012 and 2013 in the CLW. A positive coefficient indicates the dissolution of a mineral, while a negative coefficient indicates the precipitation of a mineral.

Phase	Upstream coefficient	Saturation index	Lysimeter 1, 2 coeff.	Saturation index	Formula
Fe(OH) ₃ (a)	3.65E-04				Fe(OH) ₃
Halite	1.83E-03	-7.09	1.34E-03	-7.36	NaCl
Gypsum	2.39E-04	-2.45	7.39E-04	-1.73	CaSO ₄ ·2H ₂ O
Pyrite	4.98E-08		1.66E-07		FeS ₂
Hematite	-1.82E-04	15.43	1.42E-06	14.96	Fe ₂ O ₃
Dolomite		-1.75	-1.62E-01	0.07	CaMg(CO ₃) ₂
K-feldspar	1.00E-04				KAlSi ₃ O ₈
Kaolinite	-1.68E-04		-1.16E+00		Al ₂ Si ₂ O ₅ (OH) ₄
Ca-montmorill.			9.93E-01		Ca _{0.165} Al _{2.33} Si _{3.67} O ₁₀ (OH) ₂
CO ₂ (g)	2.65E-03	-1.89	3.34E-01	-1.39	CO ₂
Calcite	5.03E-04	-0.83		0.03	CaCO ₃
Chalcedony	-1.03E-03	-0.01	-8.23E+00	0.6	SiO ₂
Sepiolite		-7.88	2.00E+01	-2.85	Mg ₂ Si ₃ O _{7.5} OH·3H ₂ O
Beidellite			4.37E-04		(NaKMg _{0.5}) _{0.11} Al _{2.33} Si _{3.67} O ₁₀ (OH) ₂
Talc	2.23E-04	-4.56	-1.33E+01	-0.14	Mg ₃ Si ₄ O ₁₀ (OH) ₂
Plagioclase	1.71E-04				Na _{0.62} Ca _{0.38} Al _{1.38} Si _{2.62} O ₈

coefficients of dissolution and precipitation of calcite and dolomite listed in Table 4 will vary from season to season. This variation is particularly apparent for soil solutions collected by lysimeter. For example, calcite and dolomite for soil solution from lysimeter #1 were both saturated in the October 2012 samples when the soil water temperature was high, but unsaturated in the March 2012 samples when the soil water temperature was low and pH was slightly high.

CLW stream water and soil solution mineral stability diagrams for the CaO–Na₂O–K₂O–AsI₂O₃–H₂O–SiO₂ system at 25 °C and 1 atmospheric pressure reveal that kaolinite and smectite should be the most stable soil minerals in the watershed (Fig. 6). Consistent with these results is the fact that smectite, muscovite, and kaolinite are the most abundant clay minerals in watershed soils, as determined by X-ray diffraction analysis (Table 2). The stability diagrams in Fig. 6 also illustrates possible weathering paths for parent minerals that can result in these stable minerals as end products. Boundary lines between the mineral phases were plotted based on the difference in Gibb's Free Energy between the paired minerals following conventional practice (Langmuir, 1997; Kehew, 2001; Güler and Thyne, 2004). The plot for the CaO–SiO₂–Al₂O₃ system shows that soil solutions are in equilibrium with kaolinite and Ca-beidellite (a Ca-smectite group mineral) while the Na₂O–SiO₂–Al₂O₃ and K₂O–SiO₂–Al₂O₃ system plots indicate that the solutions are in equilibrium only with kaolinite. The stability regions for both soil solutions and stream water indicate that the weathering of feldspars into Ca-beidellite (smectite group), muscovite, and kaolinite is one of the most likely processes for the release of calcium, magnesium, potassium, and sodium into the soil solutions, and supports the weathering models previously determined by mass balance analysis (Table 4).

For anions, average sulfate concentrations in CLW soil solutions are close to three times the average sulfate concentrations in CLW stream water (Table 1). Therefore, the natural release of sulfate from the oxidation of sulfide and the dissolution of gypsum may be the main source of the sulfate in this stream. However, the modal abundances of pyrite and gypsum in CLW soils are low for all eight of the soil profiles analyzed; this suggests that additional sulfate and sulfide minerals occur in the soil.

For chloride in soil solutions, some may be due to post-salting flooding and infiltration of stream water into surrounding soils. This is supported by the significant correlation between sodium and chloride in soil solutions (Fig. 5a), although the correlation is not as strong as for stream water where the salting process is the primary source of both ions. Since chloride also was found in soil samples where inundation from stream water is unlikely (Table 3),

other sources, such as evaporite and silicate minerals, are required, as discussed earlier.

Silica concentrations in soil solutions are higher than those in stream water (Table 1), which is typical in a natural water system (Langmuir, 1997). As indicated in the stability diagrams (Fig. 6), all water samples are saturated for quartz, although not for amorphous silica. Stream water appears to be undersaturated with respect to both calcite and dolomite since most of their data points plot below the CO₂ partial pressure lines in the CaO–SiO₂–Al₂O₃ stability diagram (Fig. 6).

In summary, the main source of calcium and magnesium in the CLW is from the weathering of feldspars, dolomite, and calcite. The main source of sodium and chloride in CLW stream water is from the dissolution of halite due to the frequent application of winter road deicing salt, whereas potassium is from the dissolution of K-feldspar, anorthoclase, bitotie, and muscovite. Bio-uptake and leaching from organic matter may accelerate the potassium release from soil due to the high solubility of potassium as discussed earlier. Major sources of sulfate in the CLW are the oxidation of pyrite and the dissolution of gypsum, in addition to the atmospheric wet and dry deposition, which will be discussed in a later section. Therefore, the combined weathering of feldspars, oxidation of pyrite, dissolution of gypsum, and dissolution of halite from road salt are the most likely set of processes that control the geochemical equilibrium in the various CLW aqueous systems.

3. Long-term DRW ion concentrations trends

In order to examine long-term anthropogenic influences, including the impacts of repeated road salt applications, environmental regulations on sulfate deposition, global climate change, and increasing atmospheric CO₂ partial pressure on stream water chemistry over time, an extensive data record of stream water chemistry is required. Water chemistry data for the Delaware River, collected about 1–3 times monthly since 1944 by the United States Geological Survey (USGS) from their Trenton, New Jersey, Station, was analyzed for this purpose. Since the CLW resides within, and is a small tributary basin to, the much larger DRW, (Fig. 1), general conclusions for anthropogenic impacts on DRW stream water chemistry also should be applicable to the CLW.

3.1. Concentration trends for major cations

For major cations, the dramatic change in sodium concentrations is its significant increase over the past 68 years in the DRW

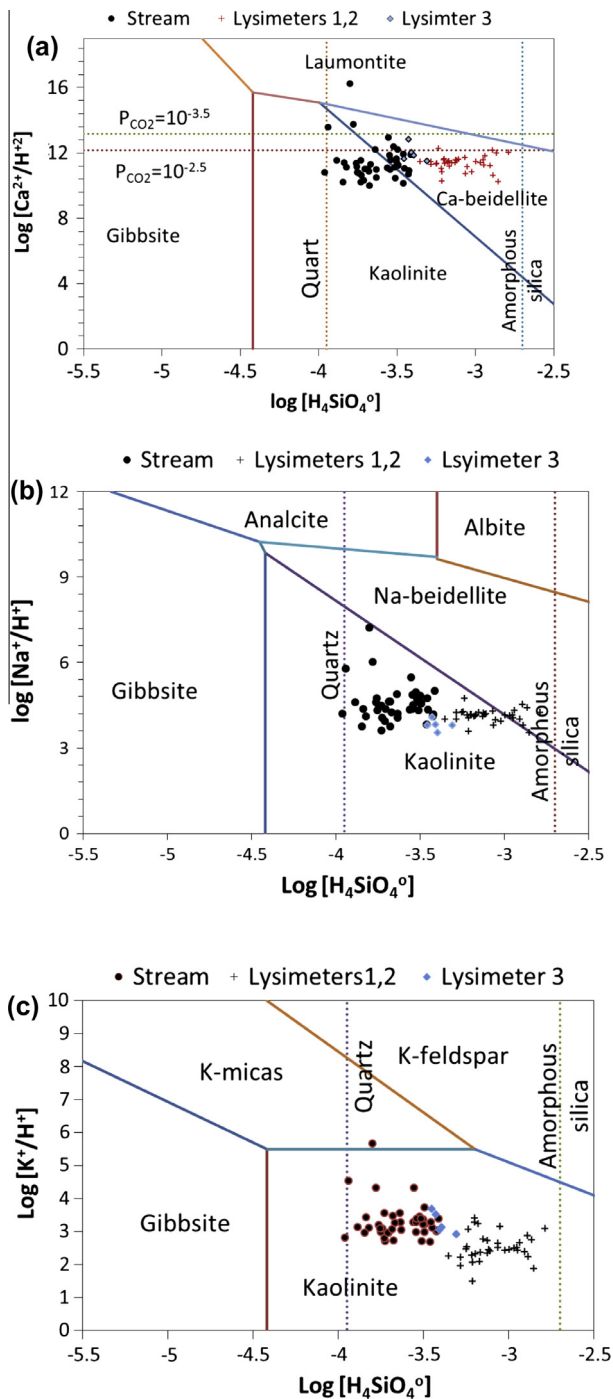


Fig. 6. Mineral stability diagrams in the CaO–Na₂O–K₂O–Al₂O₃–H₂O–SiO₂ system at 25 °C and 1 atmospheric pressure for CWL stream water and soil solutions. Symbols give sample type.

(Fig. 7a), with a t value of 25.61 for its regression slope (a Z value of 18.86 for the STATA non-parametric NPTREND test) based on 693 data points. The present normalized average annual sodium concentration is more than twice the average annual sodium concentration for the pre-salting period, prior to 1970 (Table 5). This trend of increasing sodium concentrations over the same general time period also has been reported for many other watersheds in the northern US, Canada, and Europe (Kelly et al., 2008; Labadia and Buttle, 1996; Lofgren, 2001).

The area normalized precipitation ion concentration shown in Table 5 is the product of the concentration (kg/L³) and the average

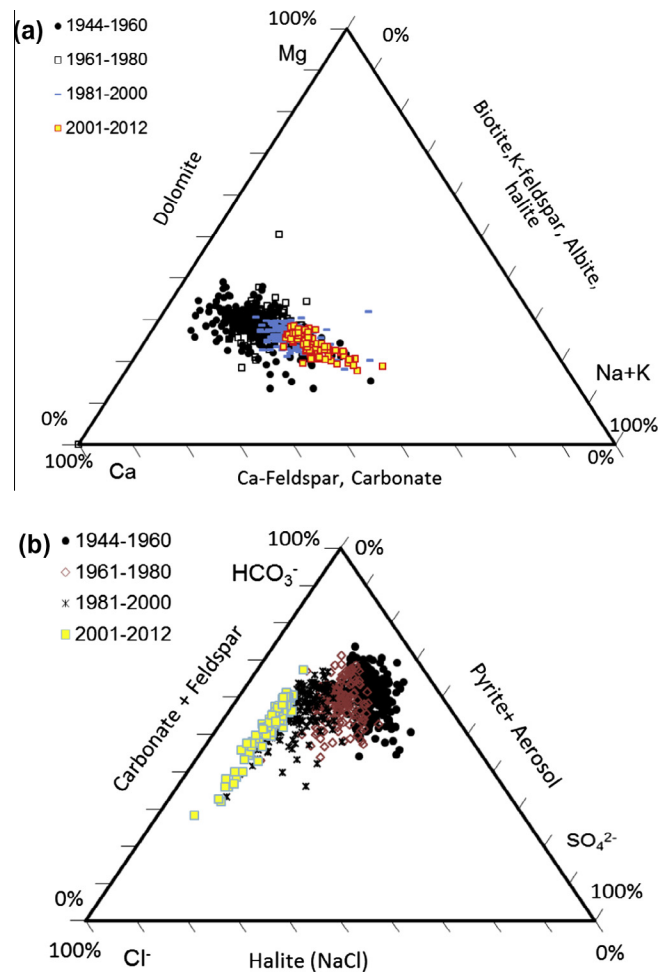


Fig. 7. Ternary diagrams of major cations (a) and major anions for four time periods of the Delaware River at Trenton, NJ. Concentration units used for calculation are milliequivalent. Notice the marked increase in the relative concentration of chloride over time. The minerals along the triangle borders are the main minerals that may be responsible for controlling the ion concentrations shown at the apices.

annual precipitation (L/year, L is the length unit here) for the listed period. The area normalized stream ion concentration was obtained by dividing the average product of regular concentration (kg/L³) and the instantaneous discharge of the stream (L³/time) by the catchment area (17,560 km²) of the DRW at Trenton. The “Annual precipitation ion input as a percentage of Delaware River ion discharge” in Table 5 was the quotient of the normalized ion concentrations from the Delaware River at Trenton and the average of normalized precipitation ion concentrations measured at the Milford and Washington Crossing precipitation measurement sites.

Different from the dramatic increase of sodium concentrations, calcium and magnesium concentrations exhibit a much smaller, though still statistically significant, long-term upward trends over the past 68 years based on regression analyses. Their long-term concentration increases might be attributed to the cation exchange release from soil colloids due to the increased loading of sodium chloride from anthropogenic sources. Their average concentrations (Table 5), excluding seasonal fluctuations, are consistent with fairly constant weathering release and discharge removal within the DRW (Sun et al., 2008). Seasonal fluctuations may come from changes in weathering rates due to discharge, temperature variations, and cation exchange with sodium from road salt applications. They are shown by the significant positive similarity correlation coefficients between concentrations of these elements and temperature and the significant negative correlation

Table 5

Normalized 10-year average annual concentrations and regression trend of major ions, pH, and charge ratios in precipitation at Milford, PA and Washington Crossing, NJ and Delaware River stream water at the Trenton, NJ USGS station^a. Units: kg/hectare/year except for pH.

	SiO ₂	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	NO ₃ ⁻	pH	Z ⁺ /Z ⁻
<i>Milford, PA (precipitation)</i>											
1981–1990	–	0.88	0.27	1.12	0.26	–	24.54	2.33	17.74	4.29	0.92
1991–2000	–	0.84	0.22	1.27	0.20	–	21.89	2.43	18.04	4.35	0.95
2001–2010	–	0.94	0.23	1.24	0.31	–	16.37	2.42	13.95	4.54	1.00
<i>Washington Crossing, NJ (precipitation)</i>											
1981–1990	–	1.25	0.47	2.09	0.29	–	25.43	4.12	15.79	4.33	0.93
1991–2000	–	0.83	0.37	2.26	0.24	–	21.25	4.28	15.60	4.38	0.95
2001–2010	–	1.01	0.34	2.13	0.24	–	18.59	4.12	13.50	4.50	0.99
<i>Delaware River at Trenton (n = 695, basin area, 17,560 square kilometers, downstream)</i>											
1944–1950	10.91	90.16	30.39	31.46	8.60	245.68	149.28	31.68	8.06	7.03	1.01
1951–1960	12.60	91.61	31.10	32.68	9.54	255.18	151.05	36.16	7.98	7.10	0.99
1961–1970	7.33	63.82	22.08	25.73	6.26	166.78	107.32	35.79	7.64	7.12	1.00
1971–1980	9.40	107.85	36.55	46.27	11.78	304.15	156.62	67.06	15.25	7.92	1.02
1981–1990	8.23	94.26	32.89	50.83	7.91	–	125.56	75.11	9.45	8.00	–
1991–2000	8.71	89.38	29.87	56.82	7.96	279.67	99.83	88.10	9.08	7.88	1.02
2001–2011	11.10	115.07	38.11	84.84	9.91	366.67	108.09	143.10	10.46	7.86	1.02
<i>Regression trends of ion concentrations in the Delaware River at Trenton between 1944 and 2012. For SO₄²⁻, between 1980–2012</i>											
Regression <i>t</i> -test	–7.29	4.09	3.73	25.61	–2.92	6.04	–12.55	34.30	4.57	18.34	–
Data number used	690	694	694	693	466	536	231	694	565	693	–
<i>Average annual ion precipitation as percentage of Delaware River ion discharge at Trenton</i>											
1981–1990	–	1.1%	1.1%	3.2%	3.5%	–	19.9%	4.3%	177.3%	53.9%	–
1990–2000	–	0.9%	1.0%	3.1%	2.8%	–	21.6%	3.8%	185.1%	55.5%	–
2001–2010	–	0.8%	0.7%	2.0%	2.8%	–	16.2%	2.3%	131.2%	57.6%	–

^a Precipitation data are from NADP and stream data are from the US Geological Survey. Z⁺/Z⁻ is the positive to negative charge ratio and *n* is the sample size. Regression *t*-test is for the regression slope of concentration vs. sample date. Any *t* value >1.97 or <–1.97 indicates a significant trend with 95% confidence. A positive *t* value indicates an increasing trend while a negative *t* value indicates a decreasing trend. The higher the *t* value is, the stronger the trend is.

coefficients between concentrations of these elements and river discharge in the dendrogram cluster analyses for DRW stream water chemistry (Fig. 8b).

There also is a slight decrease of potassium concentrations over the 68-year period in the DRW (Table 5). Potassium typically is a weathering product of k-feldspar, anorthoclase, muscovite, and/or biotite, as well as being leached from organic matter due to its high solubility (Markewitz and Richter, 2000; Brady and Weil, 2008). Leaching from organic matter accelerates the release of the potassium from soil in DRW stream water; hence, the continuing loss of forest and farm land in the DRW (Sun et al., 2006) might progressively decrease the release of potassium that was facilitated by the decay of organic matter over the past 68 years.

3.2. Concentrations trends for major anions

In contrast to the major cations, the anthropogenic effects on aqueous concentrations of the major anions, HCO₃⁻, SO₄²⁻, NO₃⁻ and Cl⁻, in the DRW are more evident (Fig. 7b). These four anions comprise approximately 95% of the total anions in DRW and during the pre-salting era weathering-related processes controlled their concentrations. From the ternary diagrams (Fig. 7b), the proportional increase of chloride concentrations over time is apparent. From Table 5, chloride's average concentration in the 2001–2011 period is more than four times the 1944–1950 pre-salting period, and has increased by 111.43 kg/hectare/year since that time (143–31.68 = 111.43, where 143.1 and 31.68 are the respective average chloride concentrations during the periods of 2000–2011 and 1944–1950 in Table 5). This increase of 111.43 kg/hectare/year is roughly 78% (111.43/143.1 = 78%) of the normalized annual chloride in the DRW stream between 2001 and 2011. That is to say that approximately 78% of the total chloride in the stream is anthropogenic, assuming the current weathering release and atmospheric deposition of chloride is the same as that for 1944–1950. This level of 78% anthropogenic chloride in DRW stream water is comparable with the 75% anthropogenic chloride in the stream water of the

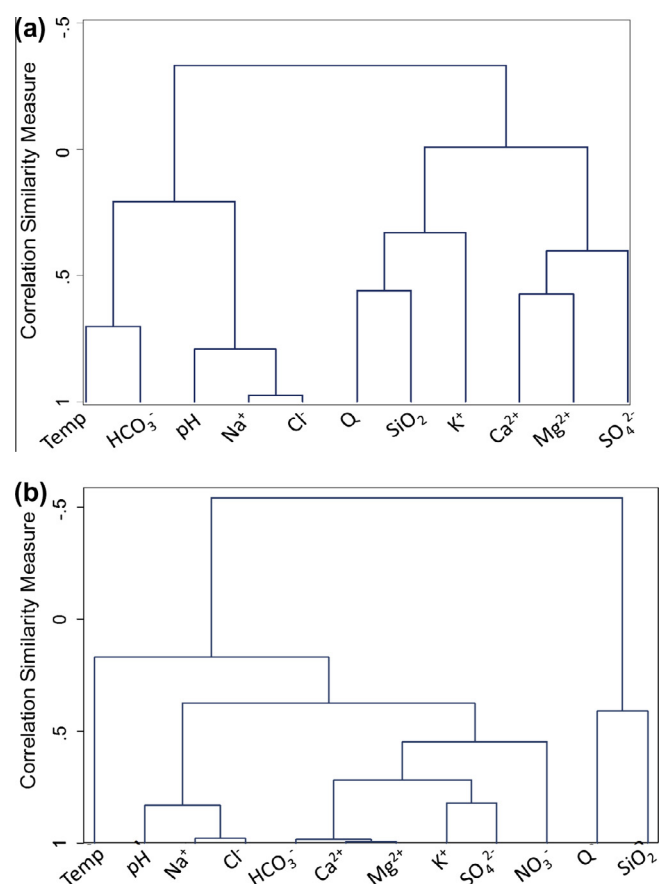


Fig. 8. Cluster analysis dendrograms for ion concentrations correlation coefficients from the Delaware River at Montague (a. upstream) and at Trenton (b. downstream). “Temp” in the X-axis is the abbreviation for temperature and “Q” is for discharge.

CLW obtained from the ratio of chloride concentration in soil solution/stream water discussed in the previous section.

The average annual chloride/bromide ratios for the DRW ranged from 629.4 to 1023.1 during 1999–2006, and averaged 911.3 for the most recent available data between 2003 and 2006 (Philadelphia Water Department, Baxter Water Treatment Plant Surface Water Intake, 2007). High chloride/bromide ratios corroborate that an anthropogenic source is the dominant contributor of chloride in the DRW at the present time (Mullaney et al., 2009; Panno et al., 2006). Currently, non-grass/pasture agricultural land compromises only 11.2% of the total land area in the DRW based on USNASS's 2013 land cover data (<http://nassgeodata.gmu.edu/CropScape>); hence, a non-agricultural anthropogenic source, mainly road deicing salt, is likely the main driver of the recent chloride increase in the DRW.

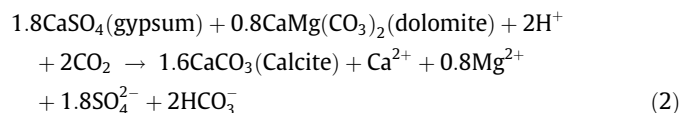
Furthermore, if it is assumed that sodium and chloride entered the watershed from anthropogenic sources in about the same molar amounts (1:1 from NaCl), and that their 1944–1950 concentrations were strictly the result of weathering and atmospheric deposition, the difference between the anthropogenic input and the actual change in DRW stream water concentrations between 1944–1950 and 2001–2011 from Table 5 would be a measure of the annual sodium retention during the 2001–2011 period. That is to say there was at least 26% of annual sodium retention during the 2001–2011 period, if we assume minimum chloride retention. If we assume a 30% chloride retention, as suggested by Sun et al. (2012), the same calculation would yield roughly 48.3% of annual sodium retention. If a large amount of chloride retention is assumed as suggested by Novotny et al. (2009), the percentage of sodium retention in the DRW could be significantly higher. The retention of sodium here is defined as its retainment by physical (adsorption to a solid surface due to relatively weak Van Der Waals forces), electrostatic (cation exchange), and chemical adsorptions, as well as transient entrapment during its transport in the DRW.

Another notable trend is the change of Na^+/Cl^- molar ratio over the past 68 years in the DRW (Fig. 9). Before the salting period (roughly before 1960), Na^+/Cl^- molar ratios were significantly greater than 1.0, largely due to the fact that weathering releases from albite and anorthoclase were the main sources of sodium (Blum et al., 1998). Since that time, the application of road salt has gradually overwhelmed the natural supply of sodium and chloride; Na^+/Cl^- molar ratios have decreased overtime because sodium is retained more than chloride when runoff water interacts with soil colloids (Shanley, 1994; Sun et al., 2012). In addition to the long-term decreasing trend in Na^+/Cl^- molar ratios, changes in this ratio's seasonal cycles are apparent. Generally, the average monthly Na^+/Cl^- molar ratios in February and March are significantly different from the average monthly Na^+/Cl^- molar ratios from August to November based on 95% confidence non-paired *t*-tests. There also is a changing pattern. Prior to 1960, Na^+/Cl^- molar ratios peaked at 2.1 in April and May when stream water contains the most dissolved ions. More recently, Na^+/Cl^- molar ratios peak at around 0.96 in the fall, typically October and November, when the effects of the prior winter's applied road salt have been diluted by subsequent precipitation events and the natural weathering release of sodium exceeds that of chloride. The annual hysteresis plots of monthly average Na/Cl molar ratio vs. discharge following Aubert et al. (2013) and Evans and Davies (1998) also show a progressive change of the hysteresis loops from a simple counter-clock-wise pattern to a mixture of clock- and counter-clock-wise pattern (Fig. 9b). These changes are very likely due to the increased supply of sodium and chloride from deicing road salt and the expanded impervious surface area in the DRW in more recent times (Sun et al., 2006).

A significant reduction in sulfate concentrations for DRW stream water only is apparent after 1980, with a *t* value of -12.55 for its

regression slope (a *Z* value of -10.66 for the nonparametric STATA NPTREND test). In addition, atmospheric wet deposition accounts for approximately 20% of the total DRW sulfate input from 1981 to 2011, based upon the wet deposition data collected by the US National Atmospheric Deposition Program (NADP; Table 5). During this same time, anthropogenic sulfate input has declined nationally, based on NADP wet deposition data, and it has been suggested that this is the result of recent environmental regulations, such as the Clean Air Act (Jenkins, 1999). Because sulfate reduction in DRW stream water coincided with, and is equivalent in magnitude to, the decline in atmospheric sulfate deposition, it is likely that the observed decline in sulfate concentrations for DRW stream water is at least partially related to the simultaneous decline in atmospheric sulfate deposition. This assumes that 60–70% of the total sulfate deposition is wet deposition, as suggested by Rochelle et al. (1987) and Likens et al. (1990).

Because atmospheric deposition only can account for roughly 20% of the sulfate in stream water, majority of the sulfate in DRW stream water likely comes from the dissolution of gypsum, as indicated by the correlation between sulfate, calcium, and magnesium (Fig. 8), and the oxidation of pyrite, similar to what has been shown to be the case for the CLW. The oxidation of pyrite to hematite and goethite will be similar to the reactions in (1). The dissolution equation for gypsum in a carbonate system is given below (Drever, 1997).



Both reaction Eqs. (1) and (2) imply that an increase in the partial pressure of CO_2 in soil solutions and stream water will favor the dissolution of dolomite, gypsum, and other primary minerals, as well as increasing bicarbonate concentrations in stream water, as suggested by Mortattia and Probst (2003). Therefore, the increasing trends over time for bicarbonate concentrations (or the total alkalinity) and pH in DRW stream water may be due to the combination of a decline in sulfate input from atmospheric deposition, increased average summer water temperature, and an increase in the atmospheric partial pressure of CO_2 . For concentrations of NO_3^- , even though there is a statistically significant increasing trend for the overall data from 1944 to 2012 (a slope *t* value of 4.57 and a *Z* value of 5.02 from STATA nonparametric NPTREND test), the increase actually occurred between 1944 and 1971, and a significant concentration decrease occurred between 1985 and 2012 (a slope *t* value of -4.56 and a *Z* value of -4.09 from nonparametric NPTREND test), which is similar to the trend in most other streams in the US (Goodale et al., 2005).

4. Discussion

Correlations requiring further study are between sulfate (or sulfur) and other major ions. In CLW upstream water, sulfur concentrations were most positively correlated with chloride concentrations, followed by sodium (Fig. 5a). These correlations are best explained by a strong anthropogenic influence on sulfate concentrations, since the main source of both sodium and chloride is road deicing salt. In addition, the observed decrease in sulfate concentrations as the collection distance increases away from the highway I-95 transects, supports an anthropogenic control mechanism, given the reduced influence of vehicle emissions with increasing distance from the highway.

For soil solution collected by lysimeters, sulfur concentrations were most highly correlated with silicon concentrations, followed by magnesium and calcium (Fig. 5 middle panel). These

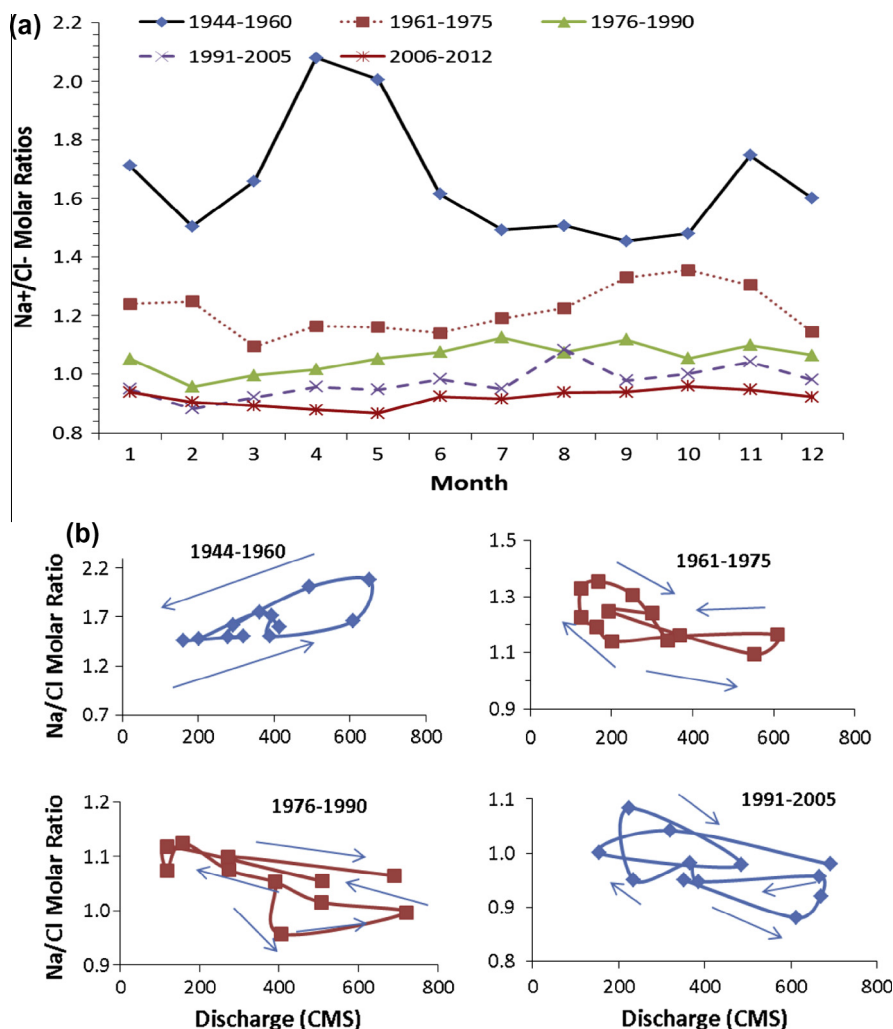


Fig. 9. (a) Progressive decline, (b) progressive change of the seasonal hysteresis loop, for the monthly average of Na/Cl molar ratio at an approximately 15-year interval from 1944 to 2012 for the Delaware River at Trenton, NJ. Discharge unit is cubic meter per second (CMS).

Table 6

Mass balance transfer coefficients for Delaware River (Trenton, NJ) weathering reactions during four periods of time. A positive coefficient indicates the dissolution of a mineral while a negative coefficient indicates the precipitation of a mineral.

	1944–1960	1961–1980	1981–2000	2001–2012	Formula
Halite	1.50E–04	2.43E–04	3.95E–04	4.98E–04	NaCl
Gypsum	2.64E–04	2.21E–04	1.82E–04	1.34E–04	CaSO ₄ * 2H ₂ O
Dolomite	1.71E–04	1.95E–04	1.93E–04	1.87E–04	CaMg(CO ₃) ₂
K-feldspar	4.00E–05	3.87E–05	3.38E–05	2.91E–05	KAlSi ₃ O ₈
Kaolinite	–5.55E+01	–2.02E–03	–8.55E–06	–1.56E–05	Al ₂ Si ₂ O ₅ (OH) ₄
Ca-montmorillon	–3.10E–03	–2.40E–03	–7.17E–06		Ca _{0.165} Al _{2.33} Si _{3.67} O ₁₀ (OH) ₂
CO ₂ (g)			3.92E–04	4.48E–04	CO ₂
Calcite	3.84E–04	3.43E–04	1.17E–05	5.45E–05	CaCO ₃
Plagioclase	1.13E–04	3.16E–05		1.45E–06	Na _{0.62} Ca _{0.38} Al _{1.38} Si _{2.62} O ₈

correlations are best explained by the weathering of gypsum since there are less anthropogenic influences on sulfate concentrations in soil solutions. Strong correlations between SO₄²⁻ and Ca²⁺ and Mg²⁺ concentrations for the upstream Delaware River water, as measured at Montague, New Jersey, confirm the relationship between sulfate concentrations and gypsum dissolution in the DRW (Fig. 8a). However, strong correlations between SO₄²⁻ and K⁺ concentrations, observed in downstream Delaware River water at Trenton, New Jersey (Fig. 8b), require further exploration and analyses to fully understand sulfate behavior.

The general mass balance models for Delaware River water chemistry at Trenton are similar to those for the CLW (Table 6). Even though many alternative models can be established to explain the concentration change, feldspar, carbonate, and evaporite dissolution generally are the most important mineralogical sources of cations; smectite and other clay minerals are intermediate weathering products; and kaolinite is the end product of mineral weathering. The apparent increase in average calcite saturation in the four periods in Table 6 (saturation indices, –1.70, –1.14, –0.79, and –0.84, at an average water temperature

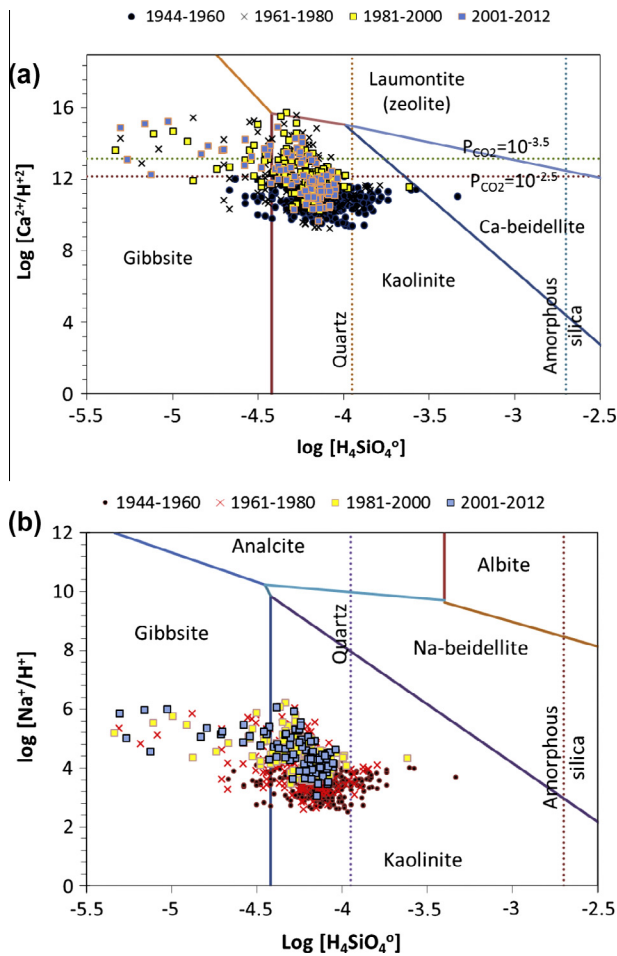


Fig. 10. Mineral stability diagrams in the MgO–Na₂O–H₂O–Al₂O₃–SiO₂ system at 25 °C and 1 atmospheric pressure at four time periods for the Delaware River at Trenton, NJ. (a) MgO-system and (b) Na₂O-system.

of 13.23 °C) and the resultant decreasing dissolution coefficients for calcite in the mass balance models of the DRW is supported by increased $\log [\text{Ca}^{2+}/\text{H}^{+2}]$ values in the CaO–SiO₂–Al₂O₃ stability diagram during the same periods (Fig. 10). In addition, changes in saturation indices of calcite from spring to summer in the DRW also is obvious, as shown by a previous study (Sun et al., 2008). The contemporaneous reduction in the dissolution of sodium plagioclase is indicated by the lower transfer coefficients in the weathering reaction models for recent years, most likely due to the increasing application of road salt (Table 6) during that time.

Even though the decreasing trend for silica (SiO₂) concentrations in the DRW is not as dramatic as the decrease of sulfate in recent decades (a negative slope with $t = -2.22$, $p = 0.027$), there are more numerous low silica concentrations in the post-1980 period, and mineral stabilities now are in equilibrium with gibbsite and kaolinite, instead of only kaolinite, as seen in the pre-1980 data (Fig. 10). These more recent and more frequent observations of low silica concentrations in the Delaware River might be a biogeochemical response to increased average summer stream water temperatures. Similar declines in silica concentrations have been reported for many streams in West Virginia between 1988 and 2003 (Grady et al., 2007). An increased silica uptake by blooming benthic diatoms and other biota, resulting from increased sunlight penetration after forest defoliation by gypsy moths, has been reported as the most likely cause for these declines in silica stream water concentrations (Grady et al., 2007; Schoelynck et al., 2014). The blooming of biota due to increased stream water temperatures

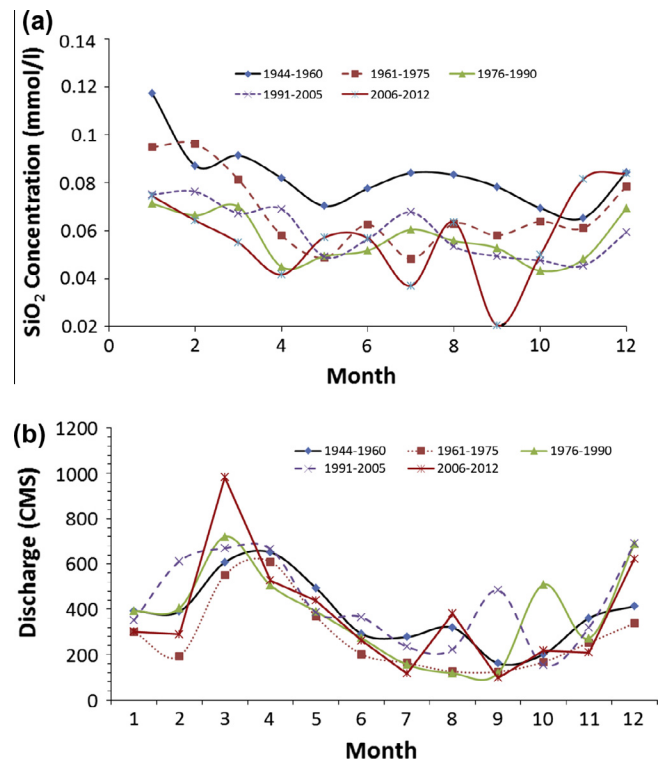


Fig. 11. (a) Monthly average silica concentration and (b) monthly average discharge (cubic meter per second, CMS) at an approximately 15-year interval between 1944 and 2012 for the Delaware River at Trenton, NJ. Notice the seasonal variation and slight decline of silica concentrations over the years.

related to global warming, as well as increased sunlight exposure due to deforestation, also has been reported in many regions (Kaushal et al., 2010; Isaak et al., 2012). The negative correlation between silica concentration and stream water temperature ($r = -0.26$, $t = 5.7$) and the low stream silica concentrations during the summer in the DRW is consistent with this biogeochemical uptake of silicon model (Fig. 11a), although the temperature effect on the growth of diatoms in stream water may be complicated (Wall et al., 1998). However, because silica concentrations are generally higher in groundwater and soil water than in runoff water (Langmuir, 1997; Drever, 1997), decreasing silica concentrations might also be due to the increased proportion of runoff water in total stream discharge resulting from the increased impervious surface area in the DRW over the past few decades, whereas total stream discharge remains relatively stable (Sun et al., 2006) (Fig. 11b).

5. Conclusions

Analyses of mineralogical and anthropogenic influences on water chemistry from two related watersheds indicate that calcium and magnesium concentrations increased slightly, from 14.48 to 15.42 mg/l and from 4.90 to 5.10 mg/l for the 10-year average between 1944 and 2011 in the DRW. The weathering of plagioclase feldspar and dissolution of dolomite and calcite are considered to be the main sources for these two elements. The weathering of albite and anorthoclase are considered to be the main mineralogical sources of sodium before around 1960, prior to the era of frequent road salt applications. For potassium in stream water, the dissolution of anorthoclase feldspar, potassium feldspar, muscovite, and biotite are its main sources and easy leaching from organic matter accelerates its release from soil solution. The weathering of various primary feldspars also produced the secondary stable clay minerals, smectite and kaolinite. For sulfate, the

dissolution of gypsum and oxidation of pyrite are the primary sources, though atmospheric deposition can make up to 20% of the total sulfate in stream water.

After the initiation of frequent road salt applications during the 1960s, sodium and chloride concentrations increased two to four times in the DRW. Chloride concentrations increased more than those for sodium, due to the preferential adsorption of sodium onto negatively charged soil colloids. Currently, about 75–78% of chloride in CLW and DRW stream water are estimated to be anthropogenic, based on the ratios of chloride concentrations in soil solution and stream water in the CLW, and the chloride concentration change from 1944 to 2012 in the DRW. On the other hand, 10-year average sulfate concentrations in stream have declined by almost 34% since the 1980s, most likely in response to decreasing atmospheric deposition resulting from stricter state and federal environmental regulations and shifting economic activities in the local region. Recent increases in bicarbonate concentrations and pH values in the DRW are attributed mainly to the reduction in sulfate concentrations and increase in summer stream temperatures.

In addition, more frequent low silica concentrations in the DRW during recent years may be related to increasing summer stream water temperatures caused by global climate change, although the increased proportion of runoff water in total stream discharge also might contribute to the more frequent low silica concentrations since silica concentrations tend to be lower in surface runoff than in baseflow. Mass balance analyses of the weathering reactions for the pre- and post-salting periods in the DRW also indicate a reduction in the dissolution of sodium plagioclase due to the increased loading of sodium chloride from winter deicing road salt.

Acknowledgments

The authors thank Nicholas Mazza, Kristian Feher, Kaitlyn Rose, Muhammad Sarwar, Leeann Sinpatanasakul, Maria Huffine, and many other undergraduate students from the Department of Geological, Environmental, and Marine Sciences (GEMS) at Rider University for their field and laboratory assistance during this project. Critical comments from two anonymous reviewers and associate editor Sarah Fortner improved the paper significantly. Editorial assistance of Gerri Hutner is appreciated as well. Finally, we acknowledge the ongoing financial support of Rider University and National Science Foundation Grants MRI-0821172 and MRI-112 6281.

References

- Amiotte Suchet, P., Probst, J.L., 1995. A global model for present day atmospheric CO₂ consumption by chemical erosion of continental rocks (GEM-CO₂). *Tellus* 47B, 273–280.
- Appelo, A.C.J., Postma, D., 2005. *Geochemistry, Groundwater and Pollution*, second ed. CRC Press, New York.
- Aubert, A.H., Gascuel-Oudou, C., Merot, P., 2013. Annual hysteresis of water quality: a method to analyse the effect of intra- and inter-annual climatic conditions. *J. Hydrol.* 478, 29–39.
- Blum, J.D., Gazis, C.A., Jacobson, D.A., Chamberlain, C.P., 1998. Carbonate versus silicate weathering in the Raikhot watershed within the high himalayan crystalline series. *Geology* 26, 411–414.
- Bowser, C.J., Jones, B.F., 2002. Mineralogical controls on the composition of natural waters dominated by silicate hydrolysis. *Am. J. Sci.* 302, 582–662.
- Brady, N.C., Weil, R.R., 2008. *The Nature and Properties of Soils*. Prentice Hall, New Jersey.
- Corsi, S.R., Graczyk, D.J., Geis, S.W., Booth, N.L., Richards, K.D., 2010. A fresh look at road salt: aquatic toxicity and water-quality impacts on local, regional, and national scales. *Environ. Sci. Technol.* 44, 7376–7382.
- Cremer, M., Schlocker, J., 1976. Lithium borate decomposition of rocks, minerals, and ores. *Am. Min.* 61, 318–3211.
- Dailey, K.R., Welch, K.A., Lyons, W.B., 2014. Evaluating the influence of road salt on water quality of Ohio rivers over time. *Appl. Geochem.* 47, 25–35.
- Dikaiakos, J.G., Tsiouris, C.G., Siskos, P.A., Melissos, D.A., Nastos, P., 1990. Rainwater composition in Athens, Greece. *Atmos. Environ., Part B* 24, 171–176.
- Drever, J.L., 1997. *The Geochemistry of Natural Waters*, 3rd Ed. Prentice Hall, New Jersey.
- Eberl, D.D., 2003. User's Guide To RockJock – a program for determining quantitative mineralogy from powder X-ray diffraction data. US Geol. Surv. Open-File Rep., 03–78.
- Evans, C., Davies, T.D., 1998. Causes of concentration/discharge hysteresis and its potential as a tool for analysis of episode hydrochemistry. *Water Res. Res.* 34, 129–137.
- 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. *Environ. Pollut.* 124, 273–281.
- Goodale, C.L., Aber, J.D., Vitousek, P.M., McDowell, W.H., 2005. Long-term decreases in stream nitrate: successional causes unlikely; possible links to DOC? *Ecosystems* 83, 1689–1700.
- Grady, A.E., Scanlon, T.M., Galloway, J.N., 2007. Declines in dissolved silica concentrations in western Virginia streams (1988–2003): gypsy moth defoliation stimulates diatoms? *J. Geophys. Res. – Biogeosci.* 112, G1.
- Güler, G., Thyne, G.D., 2004. Hydrologic and geologic factors controlling surface and groundwater chemistry in Indian Wells–Owens Valley area, southeastern California. *USA J. Hydrol.* 285, 177–198.
- Hendershot, W.H., Savoie, S., Courchesne, F., 1992. Simulation of stream-water chemistry with soil solution and groundwater flow contributions. *J. Hydrol.* 136, 237–252.
- Ibhi, A., Nacht, H., 2000. The substitution mechanism of Ba and Ti into phyllosilicate phases: the example of barium–titanium biotite. *Ann. Chim. Sci. Matér.* 25, 627–634.
- Isaak, D.J., Wollrab, S., Horan, D., Chandler, G., 2012. Climate change effects on stream and river temperatures across the northwest U.S. from 1980–2009 and implications for salmonid fishes. *Climatic Change* 113, 499–524.
- Jackson, R.B., Jobbagy, E.G., 2005. From icy roads to salty streams. *Proc. Natl. Acad. Sci. USA* 102, 11487–11488.
- Jenkins, A., 1999. Environmental chemistry, end of the acid reign? *Nature* 401, 537–538.
- Karim, A., Veizer, J., 2000. Weathering processes in the Indus River Basin, implications from riverine carbon, sulfur, oxygen, and strontium isotopes. *Chem. Geol.* 170, 153–177.
- Katz, B.G., 1989. Influence of mineral weathering reactions on the chemical composition of soil water, springs, and ground water, Catocin Mountains, Maryland. *Hydrol. Process.* 3, 185–202.
- Kaushal, S.S., Likens, G.E., Jaworski, N.A., Pace, M.L., Sides, A.M., Seekell, D., Belt, K.T., Secor, D.H., Wingate, R.L., 2010. Rising stream and river temperatures in the United States. *Front Ecol. Environ.*, 1–7. <http://dx.doi.org/10.1890/090037>.
- Kehew, A.E., 2001. *Applied Chemical Hydrogeology*. Prentice Hall, Upper Saddle River, New Jersey.
- 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 stream water concentration. *Environ. Sci. Technol.* 42, 410–415.
- Kelly, W.R., Panno, S.V., Hackley, K.C., 2012. Impacts of road salt runoff on water quality of the Chicago, Illinois, Region. *Environ. Eng. Geosci.* 18, 65–81.
- Kim, K., Rajmohan, N., Kim, H., Kim, S., Hwang, G., Yun, S., Gu, B., Cho, M.J., Lee, A.S., 2005. Evaluation of geochemical processes affecting groundwater chemistry based on mass balance approach, a case study in Namwon, Korea. *Geosci. J.* 39, 357–369.
- 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. *Hydrol. Process.* 10, 1575–1589.
- Langmuir, D., 1997. *Aqueous Environmental Geochemistry*. Prentice-Hall, New Jersey.
- Likens, G.E., Bormann, F.H., Hedin, L.O., Driscoll, C.T., Eaton, J.S., 1990. Dry deposition of sulfur, a 23-year record for the Hubbard Brook Forest ecosystem. *Tellus* 42, 319–329.
- Lofgren, S., 2001. The chemical effect of deicing salt on soil and stream water of five catchments in southeast Sweden. *Water Air Soil Pollut.* 130, 863–868.
- Majer, V., Krám, P., Shanley, J.B., 2005. Rapid regional recovery from sulfate and nitrate pollution in streams of the western Czech Republic – comparison to other recovering areas. *Environ. Pollut.* 135, 17–28.
- Markewitz, D., Richter, D.D., 2000. Long-term soil potassium availability from a Kanhapludult to an aggrading loblolly pine ecosystem. *For. Ecol. Manage.* 130, 109–129.
- Morala, F., Cruz-Sanjulián, J.J., Olías, M., 2008. Geochemical evolution of groundwater in the carbonate aquifers of Sierra de Segura (Betic Cordillera, southern Spain). *J. Hydrol.* 360, 281–296.
- Mortattia, J., Probst, J., 2003. Silicate rock weathering and atmospheric/soil CO₂ uptake in the Amazon basin estimated from river water geochemistry, seasonal and spatial variations. *Chem. Geol.* 197, 177–196.
- Mullaney, J.R., Lorenz, D.R., Arntson, A.D., 2009. Chloride in groundwater and surface water in areas underlain by the glacial aquifer system, Northern United States. *USGS Sci. Invest. Rep.*, 2009–5086.
- New Jersey Water Supply Authority, 2000. *Water Budget in the Raritan River Basin. Technical Report for the Raritan Basin Watershed Management Project*. Trenton, New Jersey.
- Novotny, E.V., Sander, A.R., Mohseni, O., Stefan, H.G., 2009. Chloride ion transport and mass balance in a metropolitan area using road salt. *Water Res. Res.* 45, W12410.
- Panno, S.V., Hackley, K.C., Hwang, H.H., Greenberg, S.E., Krapac, I.G., Landsberger, S., O'Kelly, D.J., 2006. Characterization and identification of Na–Cl sources in ground water. *Ground water* 44, 176–187.

- 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 Resour. Invest. Rep., 99–4259.
- Peters, N.E., 1991. Chloride cycling in two forested lake watersheds in the west-central Adirondack mountains, New York, USA. *Water Air Soil Pollut.* 59, 201–215.
- Peters, N.E., Shanley, J.B., Aulenbach, B.T., Webb, R.M., Campbell, D.H., Hunt, R., Larsen, M.C., Stallard, R.F., Troester, J., Walker, J.F., 2006. Water and solute mass balance of five small, relatively undisturbed watersheds in the US. *Sci. Total Environ.* 358, 221–242.
- Philadelphia Water Department, Baxter Water Treatment Plant Surface Water Intake, 2007. The Delaware River Watershed Source Water Protection Plan, Philadelphia, PA.
- Rice, K.C., Bricker, O.P., 1995. Seasonal cycles of dissolved constituents in stream water in two forested catchments in the mid-Atlantic region of the eastern USA. *J. Hydrol.* 170, 137–158.
- Rochelle, B.P., Church, M.R., David, M.R., 1987. Sulfur retention at intensively studied sites in the US and Canada. *Water Air Soil Pollut.* 33, 73–83.
- Sandland, T.O., Du, L., Stebbins, J.F., Webster, J.D., 2004. Structure of Cl-containing silicate and aluminosilicate glasses: A ³⁵Cl MAS-NMR study. *Geochim. Cosmochim. Acta* 68, 5059–5069.
- Schoelynck, J., Muller, F., Vandevenne, F., Bal, K., Barao, L., Smis, A., Opdekamp, W., Meire, P., Struyf, E., 2014. Silicon–vegetation interaction in multiple ecosystems: a review. *J. Veg. Sci.* 25, 301–313.
- Seibert, J., Grabs, T., Kohler, S.K., Laudon, H., Winterdahl, M., Bishop, K., 2009. Linking soil- and stream-water chemistry based on a riparian flow-concentration integration model. *Hydrol. Earth Syst. Sci.* 13, 2287–2297.
- Shanley, J.B., 1994. Effects of ion exchange on stream solute fluxes in a basin receiving highway deicing salts. *J. Environ. Qual.* 23, 977–986.
- Skjelkvale, B.L., Stoddard, J.L., Andersen, T., 2001. Trends in surface water acidification in Europe and North America (1989–1998). *Water Air Soil Pollut.* 130, 787–792.
- Sloto, R.A., 2004. Geohydrology of the French Creek basin and simulated effects of drought and ground-water withdrawals. Chester County, Pennsylvania. USGS Water-Resources Investigations Report 03-4263, New Cumberland, Pennsylvania.
- Srodon, J., Drits, V.A., McCarty, D.K., Hsieh, J.C.C., Eberl, D.D., 2001. Quantitative X-ray diffraction analysis of clay-bearing rocks from random preparations. *Clays Clay Miner.* 49, 514–528.
- Sun, H., 2004. Estimating the fate of precipitation from stream discharge, a case study in New Jersey. *Bull. N. J. Acad. Sci.* 49, 9–15.
- Sun, H., Hewins, D., Latini, D., Husch, J., 2006. Changes in impervious surface area, flood frequency, and water chemistry within the Delaware River basin during the past 50 years, initial results. In: Proceedings of the 7th Int. Conf. on Hydroscience and Engineering (ICHE-2006), Philadelphia.
- Sun, H., Natter, C. and Lacombe, P., 2008. Erosion and weathering processes in the Delaware River basin. In: Goring, M.L. (Ed.), Proceedings of GANJ XXV Environmental and Engineering Geology of Northeastern New Jersey, p. 27–38.
- Sun, H., Nelson, M., Chen, F., Husch, J., 2009. Soil mineral structural water loss during LOI analyses. *Can. J. Soil Sci.* 89, 603–610.
- Sun, H., Sinpatanasakul, L., Husch, J., Huffine, M., 2012. Na/Cl molar ratio changes during a salting cycle and its application to the estimation of sodium retention in salted watersheds. *J. Contam. Hydrol.* 136–137, 96–105.
- Wall, G.R., Phillips, P.J., Riva-Murray, K., 1998. Seasonal and spatial patterns of nitrate and silica concentrations in Canajoharie Creek, New York. *J. Environ. Qual.* 27, 381–389.
- Whitehead, P.G., Wilby, R.L., Battarbee, R.W., Kernan, M., Wade, A.J., 2009. A review of the potential impacts of climate change on surface water quality. *Hydrol. Sci. J.* 54, 101–123.
- Young, G.M., Nesbitt, H.W., 1998. Processes controlling the distribution of Ti and Al in weathering profiles, siliciclastic sediments and sedimentary rocks. *J. Sediment. Res.* 68, 448–455.