Environmental Earth Sciences (2019) 78:500
https://doi.org/10.1007/s12665-019-8500-0

ORIGINAL ARTICLE

Impact of road deicing salts on the Upper Passaic River Basin, New Jersey: a geochemical analysis of the major ions in groundwater

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Received: 13 March 2019 / Accepted: 23 July 2019 / Published online: 6 August 2019

Abstract

Road deicing salts, primarily sodium chloride, has been used widely to remove snow and ice from roadways in New Jersey and the northern United States since the 1950s. Currently, New Jersey stores up to 141 million kg of rock salt and 2401 m^3 of liquid calcium chloride in the winter season for road deicing. Road deicing helps to reduce accident rates, road delays, and to improve road accessibility. While it is known that the use of road deicers is beneficial, road salts have also been shown to affect surface water and groundwater quality. In this study, an analysis of major ion concentration of groundwater collected by the United States Geological Survey (USGS) for the Upper Passaic River Basin (UPRB) was carried out. The UPRB has a large area of urban land use and a number of significant roads that are regularly deiced during the winter. The results of the study have shown that the contribution of Cl^- to the TDS of groundwater increased significantly by the 2000s. Decadal bivariate plots of Na^+ vs Cl^- and Cl^- vs TDS showed a strong increase in the correlations between these ions from the 1960s to the 2000s. Bivariate plots of Na^+ vs Cl^- and Ca^{2+} vs Mg^{2+} display a strong correlation, while those of Na^+ vs Ca^{2+} and Cl^- vs Ca^{2+} display a poor correlation. These observations suggest a link between Na^+, Cl^- and TDS, a link between Ca^{2+} and Mg^{2+}, and no link between Ca^{2+} and Cl^-, and between Ca^{2+} and Na^+. Plots of Piper diagrams show that the groundwater facies have changed through time, starting as a single $Ca(HCO_3)_2$ species and shifting gradually towards a NaCl-dominated species. Plots of individual ion concentrations versus specific conductance show an increase in Na^+ and Cl^- over time and point towards an external influx of these ions. In general, groundwater in the UPRB is fresh with total dissolved solids less than 500 mg/L. Against the natural groundwater evolutionary trend, chloride is found to dominate over other chemical species in this freshwater system. These results provide evidence of a link between groundwater chlorides and road deicing salts in the UPRB.

Keywords Groundwater · Deicing · Salts · Contamination · New Jersey

Introduction

Road salt application reduces accident rates and road delays while improving road accessibility in regions that have frequent snow in the winter months. However, deicing also has negative repercussions on human health and the environment (Kuemmel and Hanbali 1992). Excess amounts of sodium chloride consumption are linked directly with hypertension, which can lead to minor or severe heart complications in patients on sodium-strict diets (Howard and Haynes 1993). In terms of ecological degradation, elevated levels of chloride and total dissolved solids due to deicing salt runoff are linked with adverse effects on many avian and aquatic species, mainly due to misidentification of food sources and hydrochemical toxicity (Corsi et al. 2010; Hopkins et al. 2013; Erickson et al. 2014; Sun et al. 2015; MPCA 2016a, b; Herb 2017).

Since the beginning of the twentieth century, road salt has been used as a deicing agent on motorways throughout the northeastern United States (Kelly et al. 2010). Primarily, sodium chloride (NaCl) brine has been the central deicing agent utilized, while in some cases, liquid calcium chloride ($CaCl_2$) has been used as a substitute (New Jersey Department of Transport (NJDOT 2018).

In the 1960s, approximately 32 billion kg of deicing material was used on roadways throughout the United States (Kelly and Matos 2014). This rate increased by 67% to 53

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billion kg of deicing material application in the 2000s. In 2017, New Jersey alone used 375, 3.1 and 4.5 million kg of NaCl deicing salt, $CaCl_2$ and brine, respectively (NJDOT 2018). NJDOT showed that New Jersey consumed 9700 kg of NaCl, 0.05 m^3 of $CaCl_2$ and 0.07 m^3 of brine per lane km in 2017 (NJDOT 2018).

The relationship between increased rates of deicing salt application and groundwater composition has been researched through numerous groundwater composition studies in the last 4 decades (Hutchinson 1970; Huling and Hollocher 1972; Howard and Haynes 1993; Howard and Beck 1993; Pilon and Howard 1997; Williams et al. 2000; Kelly 2008). Hutchinson (1970) first identified that increased chloride concentrations were associated with road salting in 100 wells along major highways in Maine and found 20% of these wells with chloride concentrations in excess of 250 mg/L. Pollock and Tolar (1973) found that the salinity of well water close to salted roads in Massachusetts was unacceptably high, and that it steadily increased during the period 1965–1971. Peters and Turk (1981) studied groundwater composition trends in the Mohawk River, New York from the 1950s to 1970s in relation to deicing application. Results of the study showed that there was a 72% increase in Na^+ concentration and a 145% increase in Cl^- concentration over a 20-year span. A second study of the Mohawk River Basin for the period 1952–1998 showed that Na^+ and Cl^- levels increased by 130 and 243%, respectively, while other major ions remained constant (Godwin et al. 2003). The study concluded that despite population decline and environmental regulations, Na^+ and Cl^- levels continued to rise, matching the rates of increased deicing application over the study time frame. USEPA (1992) reported that groundwater close to road salt application and storage areas had higher concentrations of chloride that in many cases exceeded secondary maximum concentration level of 250 mg/L for drinking water. Researchers have documented excessively high concentrations of chloride, in some cases exceeding 1400 mg/L, in shallow groundwater impacted by road salts in the Greater Toronto Area in Canada (Pilon and Howard 1997; Williams et al. 2000; Labadia and Butte 1996).

Foos (2003) determined the spatial distribution of road salt contamination in the groundwater of Gorge Metro Park, Cuyahoga Falls, Ohio. Using bivariate analysis, the composition of the groundwater in the region showed a near perfect correlation between Na^+ and Cl^- ($r^2 = 0.995$) and Cl^- and TDS ($r^2 = 0.997$) (Foos 2003). The strong correlations indicated that halite was the major dissolved solid in the groundwater system. The magnitude of the road salt application was found to be directly proportional to the groundwater contamination levels (Foos 2003).

Various historical studies have investigated groundwater composition in the Passaic River Basin (PRB) through well sampling and chemical analysis. One such study conducted by Anderson and Faust (1973) focused on water quality and streamflow dynamics to characterize the PRB by splitting the river basin into isochemical regions. The results indicated that in the northwestern section of the Upper Passaic River Basin (UPRB), a region dominated by igneous and metamorphic bedrock, TDS was generally less than 200 mg/L. The predominant cations were found to be Mg^{2+} and Ca^{2+}, ranging in total composition from 50 to 80%. The predominant anion was HCO_3^-, comprising a total of 50–80% of total anions (Anderson and Faust 1973). The southeastern region, which consists mainly of sedimentary bedrock, was found to have a higher TDS concentration, usually exceeding 100 mg/L and often 400 mg/L. Calcium and Mg^{2+} were found to make up 50% of total cations. This region possesses the highest amounts of Na^+ and K^+ in the entire basin at roughly 30–60% of total cations. The predominant anions were found, specifically, to be Cl^-, SO_4^{2-} and F^-. The study also notes that during both observation periods, 1923–1925 and 1962–1970, Na^+, K^+, HCO_3^-, and Cl^- all increased with time. Second, it is of relative importance to note that because the UPRB is a heavily industrialized setting, anthropogenic wastewater discharge can have a significant effect on measured TDS (Anderson and Faust 1973).

Czarnik and Kozinski (1994) noted groundwater quality variations against time in the central region of the PRB, which covers a significant percentage of the UPRB. Seventy-one water samples throughout the southeastern portion of the UPRB were collected from 1959 to 1988 to analyze regional groundwater quality. The results indicated that the predominant ions in the sedimentary part of the basin were Ca^{2+} and HCO_3^-, followed by Mg^{2+} and Na^+. In the igneous and metamorphic part of the basin, the predominant cation and anion were Ca^{2+} and HCO_3^-, respectively. The analysis concluded that major ions such as Mg^{2+}, Ca^{2+}, Na^+ and SO_4^{2-} had higher concentrations in the sedimentary part of the basin (Czarnik and Kozinski 1994). The above studies suggest that the assessment of groundwater contamination in relation to deicing road salts is essential in understanding the quality of groundwater resources in areas of use, such as the UPRB.

The objective of this study was to determine whether road deicing application has had a significant effect on the groundwater composition of the UPRB. This goal was accomplished by conducting an analysis of geostatistical and hydrochemical trends of groundwater samples covering a 50-year timeframe, 1960–2010, to (a) determine correlations in ion to ion relationships using simple linear regression, (b) identify trends in major ionic concentrations over time, specifically Na^+, Cl^-, Mg^{2+}, Ca^{2+}, and $SO4^{2-}$, and (c) evaluate the hydrochemical composition of groundwater facies in decadal segments.

Study area

The UPRB, also known as Water Management Area 06, is located in northern New Jersey, between latitudes 40°40″ and 41°10″ North and longitudes 74°15″ and 74°40″ West (Fig. 1). The UPRB covers an area of 936 km^2 in Morris County, which is a region of significant population increase, from 261,620 in 1960–492,276 in 2010 (U.S. Census Bureau 2015). In terms of land use, it is an urban development region with high-density population and roads for residential and commercial uses. There are approximately 4878 km of roads spread evenly throughout the area (Fig. 1) (New Jersey Geological Survey (NJGS) 2010). Using data from NJDOT and New Jersey Bureau of GIS (NJGIS), an estimate of the amount of road salt used in 2017 in the UPRB is found to be approximately 30 million kg (NJGIS 2018; NJDOT 2018).

The UPRB has a unique bedrock geology caused by its division into two halves by the Ramapo Fault which runs through the middle. To the southeast is the Newark Basin, which is dominated by hard sedimentary rocks, primarily sandstone of the Towaco Formation (Olsen 1980; Dalton et al. 1999). The Newark Basin also consists of igneous lava flows dominated by basalt, comprised of plagioclase, clinopyroxene, magnetite and ilmenite. In contrast, the New Jersey Highlands to the northwest is dominated by a large variety of metamorphic rocks including, but not limited to gneiss and granitic rocks, comprised of quartz, biotite and feldspars (Drake et al. 1996; Owens et al. 1998; Dalton et al. 1999; Tollo 2004). The differences in bedrock geology play a key role in determining groundwater system dynamics, specifically in terms of hydraulic conductivity, storage capacity, and contact time. Consequently, geologic variations can potentially influence ionic composition in groundwater. Sedimentary basins have a higher porosity (typically between 10 and 30%) than igneous and metamorphic basins (typically less than 10%) (Earle 2015). Similarly, hydraulic conductivity is lower in igneous and metaphoric environments (10^{-12}–10^{-8} m/s) than in sedimentary basins (10^{-8}–10^{-4} m/s) (Earle 2015). The porosities and hydraulic conductivities of the rocks in the UPRB fall within these ranges.

The UPRB includes the upper branches and the headwaters of the Passaic River along with the Whippany and Rockaway rivers (NJDEP 2007, 2012). The UPRB lies within a humid continental climatic region, varying between temperate and warm (Ludlum 1983). The average annual temperature is roughly 12 °C with average annual highs of 16 °C and lows of 4 °C (U.S. Climate Data 2018). The region has, on average, 1270–1524 mm of rain annually. Average snowfall from 1981 to 2010 was calculated to be 726 mm annually (National Climatic Data Center 2018).

Methodology

Data collection

To achieve the goals of this study, a large amount of quantifiable data spanning a substantial period of time is necessary. The USGS database stores a significant amount of groundwater quality data (U.S. Geological Survey 2016, 2018). Starting in the early twentieth century, the USGS began measuring and recording notable ion concentrations mainly in groundwater wells and open water sources. These measurements included, but are not limited to Na^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, $K^{+,}$ Cl^-, HCO_3^-, CO_3^{2-} and TDS. The field data used in this analysis consists of 573 different measurements from 1960 to 2010 within the UPRB (Table 1). The data set was compiled using Microsoft Excel (Version 14.4). The data were collected through various programs by the USGS—National Water Quality Assessment, USEPA, and NJDEP. Historical groundwater quality data are digitally stored in the National Water Information System web interface program. All recorded U.S. water quality data can be accessed at http://www.waterdata.usgs.gov/ by entering the location identifiers of the study site and indicating the data parameters. The data were collected from wells of various depths, screen locations, and aquifer types. The wells were not evenly sampled in all the decades considered in this study. Possible variations from these factors are not analyzed in this study.

The data used herein were selected to represent composite samples collected continuously throughout the study period. For the decadal analysis, the data were filtered to be satisfactorily representative of the entire decade. The selected samples were from monitoring wells that had chemical analyses for all the parameters of interest in the study. Due to the small scale of the UPRB which in underlain by a range of igneous, sedimentary and metamorphic rocks, the study area was considered to be regionally homogeneous. Thus, aquifers, well locations, and well depths were not segregated. This assumption is being made as a preliminary assessment technique that would be tested in a future study.

Data analysis

Linear regression analysis

The regression analysis of the water quality samples in the UPRB was done using a variety of methods aimed at ascertaining a clear understanding of whether, how, and why the groundwater composition has changed over time. The initial analysis approach was to compare the ion relationships of Na^+ vs. Cl^-, Mg^{2+} vs. Ca^{2+}, Na^+ vs. Ca^{2+}, Cl^- vs. Ca^{2+}, and Cl^- vs. TDS, using simple linear

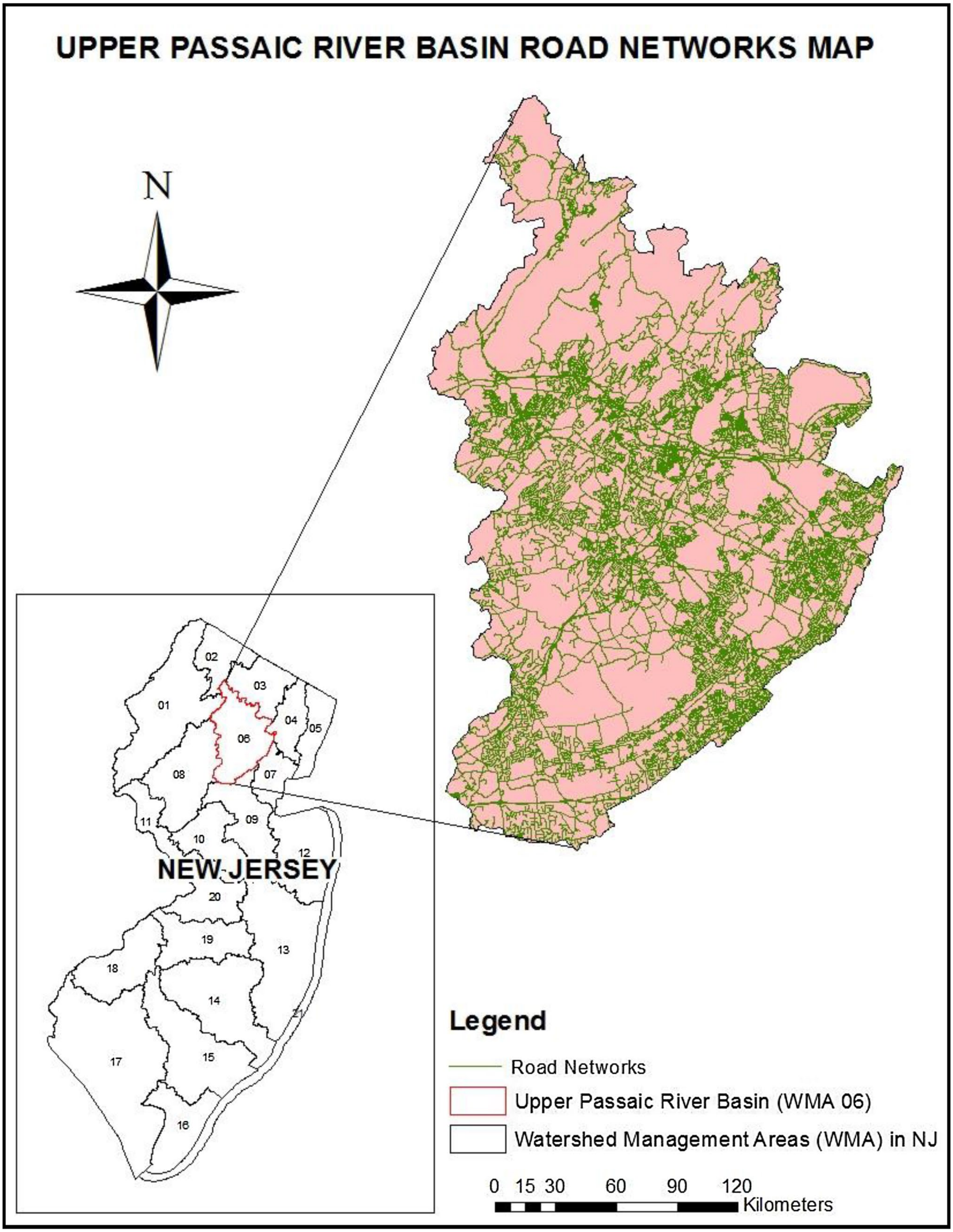


Fig. 1 Location and spatial distribution of roads of the Upper Passaic River Basin, New Jersey [modified from: NJDEP (2007) and NJGIN (2017)]

Table 1 Mean, standard deviation, and range for major ion concentration and TDS in the Upper Passaic River Basin (concentration in mg/L)

Ion	Collection period	Mean	Standard deviation	Max	Min	Data count
Na^+	1960–1969	15.77	16.57	84	3.60	35
	1980–1989	39.56	31.22	180	1.70	398
	1990–1999	37.26	34.03	190	1.83	108
	2000–2010	63.65	119.15	463	2.49	31
Mg^{2+}	1960–1969	13.27	4.87	34	6.30	35
	1980–1989	12.49	9.81	99	0.14	399
	1990–1999	11.78	7.57	28	0.24	108
	2000–2010	19.91	14.27	67	1.69	31
Ca^{2+}	1960–1969	39.69	19.27	134	18	35
	1980–1989	36.77	25.47	280	1.10	399
	1990–1999	33.57	19.51	87	1.40	108
	2000–2010	56.94	40.76	183	6.69	31
Cl^-	1960–1969	10.76	5.87	28	3.20	35
	1980–1989	60.71	49.88	300	0.80	399
	1990–1999	62.59	61.05	410	1.20	108
	2000–2010	139.62	250.18	960	2.01	31
$SO_4{}^{2-}$	1960–1969	52.86	81.34	505	17	35
	1980–1989	38.26	71.44	850	1.60	399
	1990–1999	25.67	14.93	93	2.99	108
	2000–2010	32.30	24.46	113	7.62	31
K^+	1960–1969	0.85	0.41	2	0.30	35
	1980–1989	1.98	1.88	27	0.30	398
	1990–1999	1.50	1.10	6	0.18	108
	2000–2010	1.75	1.50	6	0.33	31
$HCO_3{}^+CO_3$	1960–1969	138.43	24.53	213	84	35
	1980–1989	142.42	52.36	257	38	65
	1990–1999	208.42	148.32	573	67	12
	2000–2010	210.11	122.48	341	66	9
TDS	1960–1969	238.92	134.29	934.05	132.38	35
	1980–1989	361.06	162.49	1507.71	66.19	397
	1990–1999	261.06	133.87	897.27	51.48	105
	2000–2010	451.33	508.13	2066.67	58.84	30

regression analysis. This was carried out using the Microsoft Excel graph feature.

Decade-averaged statistical analysis

Complementary to the bivariate plots, decade average statistics were calculated for TDS, Na^+, Ca^{2+}, Mg^{2+}, K^+, Cl^-, $HCO_3{}^-$+ $CO_3{}^{2-}$, and SO_4^{2-}. This was done to observe how the average concentrations of these ions have varied throughout the study period. A Schoeller diagram (Schoeller 1955) was also developed to observe the magnitude of change of each ion on a logarithmic basis. All observations can be seen in Table 1, which includes data statistics such as standard deviation, maximum and minimum values, and data count.

Groundwater species

A Piper diagram (Piper 1944) was created to represent each decade within the study timeframe, resulting in four plots that show decadal variations of the data. Piper diagrams allow for the evaluation of the changing ionic composition of the groundwater species.

Prediction interval analysis

Using a 95% prediction interval plot, a statistically predicted increase was juxtaposed by the actual recorded increase. Prediction interval plots were carried out for Mg^{2+}, Na^+, Cl^-, Ca^{2+} and $SO_4$2$^-$ based on Eq. 1 (Kutner et al. 2005):

$$\hat{y}_{\mathrm{h}} \pm t_{(\alpha/2,n-2)} = \sqrt{\mathrm{MSE}\left(1+\frac{1}{n}+\frac{(x_h-\bar{x})^2}{\sum(x_i-\bar{x})^2}\right)} \qquad (1)$$

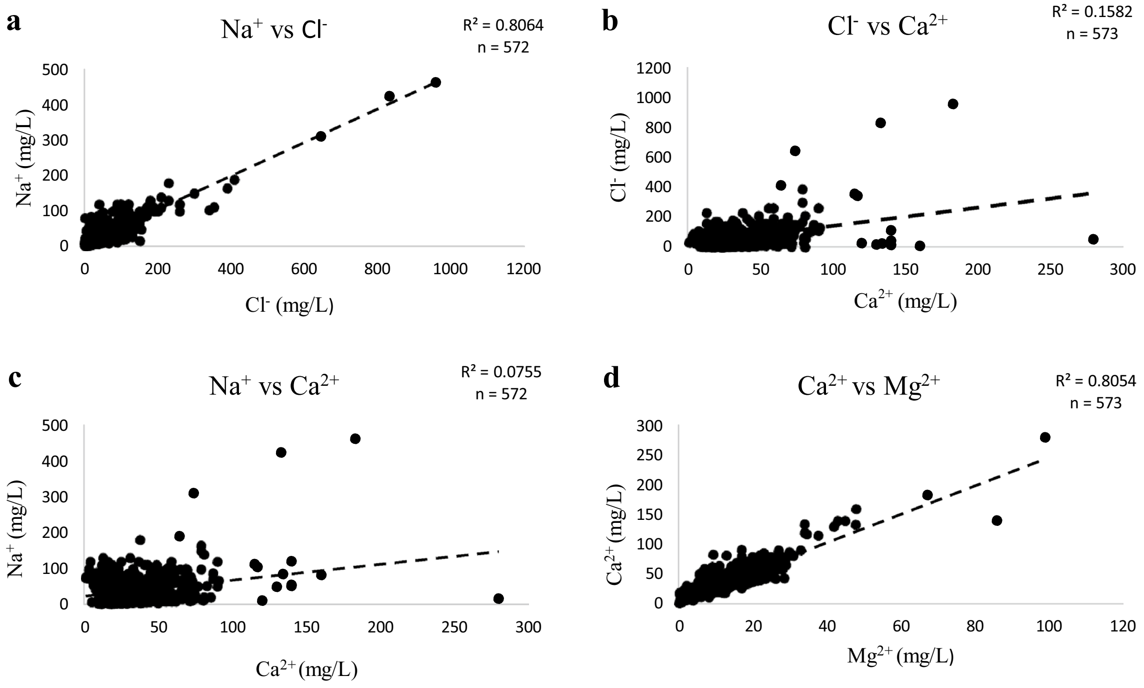


Fig. 2 Regression relationships between major ions in the Upper Passaic River Basin: **a** sodium and chloride, **b** chloride and calcium, **c** sodium and calcium, **d** calcium and magnesium

where $\hat{y}_h$ is the predicted value of the response, x_h is the predictor, $t(\alpha/2, n-2)$ = student t (statistic for applicable degrees of freedom), and $\sqrt{\mathrm{MSE}\left(1+\frac{1}{n}+\frac{(x_h-\bar{x})^2}{\sum(x_i-\bar{x})^2}\right)}$ is the standard error of the prediction

These 95% confidence intervals were derived for the ion concentrations to specific conductance relationships of the 1960–1969 data. Specific conductance is an index variable that is easily measurable in the field. It is a measure of water's capacity to conduct an electric charge and is controlled by the type and concentration of ions dissolved in the water. Specific conductance can be related to the concentrations of individual ions and used to calculate average concentrations and average yields of the ions (Steel 1976). The intricate relationship between ion concentrations and specific conductance and its use in prediction analysis is described in the papers by Steel and Matalas (1974) and Peters and Turk (1981). Their approach is used in this paper, because a substantial record of specific conductance is available in the USGS database. The intervals and the regression equations for both 1960–1969 and 2000–2010 records were plotted on the same graph for comparison as described in Peters and Turk (1981). Details of the analysis are presented in the report by Firor (2019).

Results

Linear regression analysis

Regression analysis for Na^+ vs Cl^- ($r^2=0.81$, $n=572$) indicates an overall strong correlation (Fig. 2a). The strong correlation suggests that both Na^+ and Cl^- are derived from the same source. The relationship between Cl^- vs Ca^{2+} ($r^2=0.16$, $n=573$), Na^+ vs Ca^{2+} ($r^2=0.08$, $n=572$), and Ca^{2+} vs Mg^{2+} ($r^2=0.81$, $n=573$) is shown in Fig. 2b–d. The low correlations (Fig. 2b, c) suggest that the presence of Ca^{2+} is generally not associated with the same source as Na^+ and Cl^-. Due to the fact that there is a significant presence of Ca^{2+}-rich rocks in the region, it seems that the majority of Na^+ and Cl^- in the groundwater system are from an outside source, unrelated to the geology. The high correlation in Ca^{2+} and Mg^{2+} (Fig. 2d, Table 2), suggests a natural geological source. Previous studies of groundwater composition have noted that Ca^{2+} and Mg^{2+} are ubiquitous in groundwater due to geologic weathering (Ismail Chenini and Abdallah 2010). While Cl^- vs Ca^{2+} shows little or no correlation from 1960 to 2000, a good correlation is seen in the 2000–2010 data ($r^2=0.75$, $n=31$) (Table 2). The strong correlation is likely to be associated with the increased usage of $CaCl_2$ deicing material during the period of 2000–2010.

A decadal breakup of the Na^+ vs Cl^- data shows a correlation that is increasing over time (Fig. 3a–d). The 1960–1969 data show no correlation ($r^2=0.02$, $n=35$),

Table 2 Regression analysis correlations for major ion to ion relationship in the Upper Passaic River Basin

Y dependent (mg/L)	*X* independent (mg/L)	Sample period (year)	Correlation coefficient (R^2)	Sample size (*n*)
Na^+	Cl^-	1960–1969	0.02	35
		1980–1989	0.68	398
		1990–1999	0.66	108
		2000–2010	0.98	31
		Cumulative*	**0.81**	**572**
Mg^{2+}	Ca^{2+}	1960–1969	0.81	35
		1980–1989	0.81	399
		1990–1999	0.70	108
		2000–2010	0.89	31
		Cumulative*	**0.81**	**573**
Na^+	Ca^{2+}	1960–1969	0.38	35
		1980–1989	0.01	398
		1990–1999	0	108
		2000–2010	0.57	31
		Cumulative*	**0.08**	**572**
Cl^-	Ca^{2+}	1960–1969	0.14	35
		1980–1989	0.22	399
		1990–1999	0.4	108
		2000–2010	0.75	31
		Cumulative*	**0.16**	**573**
Cl^-	TDS	1960–1969	0.17	35
		1980–1989	0.36	397
		1990–1999	0.78	105
		2000–2010	0.97	30
		Cumulative*	**0.62**	**567**

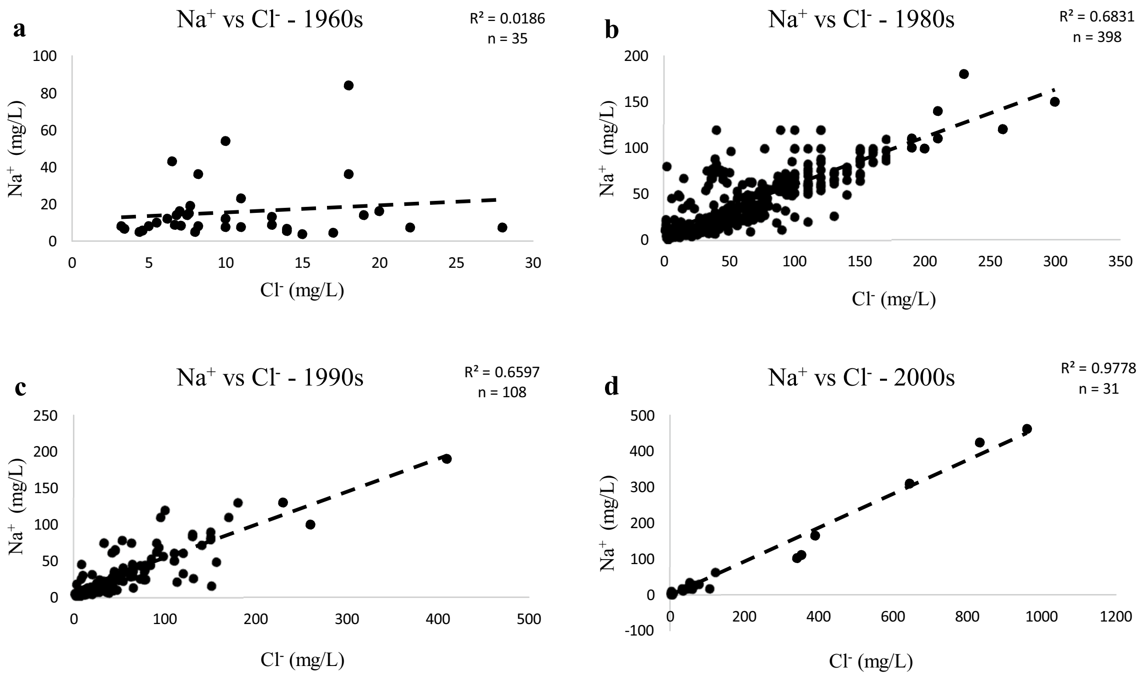


Fig. 3 Relationship between sodium and chloride concentrations for samples collected in the 1960s, 1980s, 1990s and 2000s in the Upper Passaic River Basin

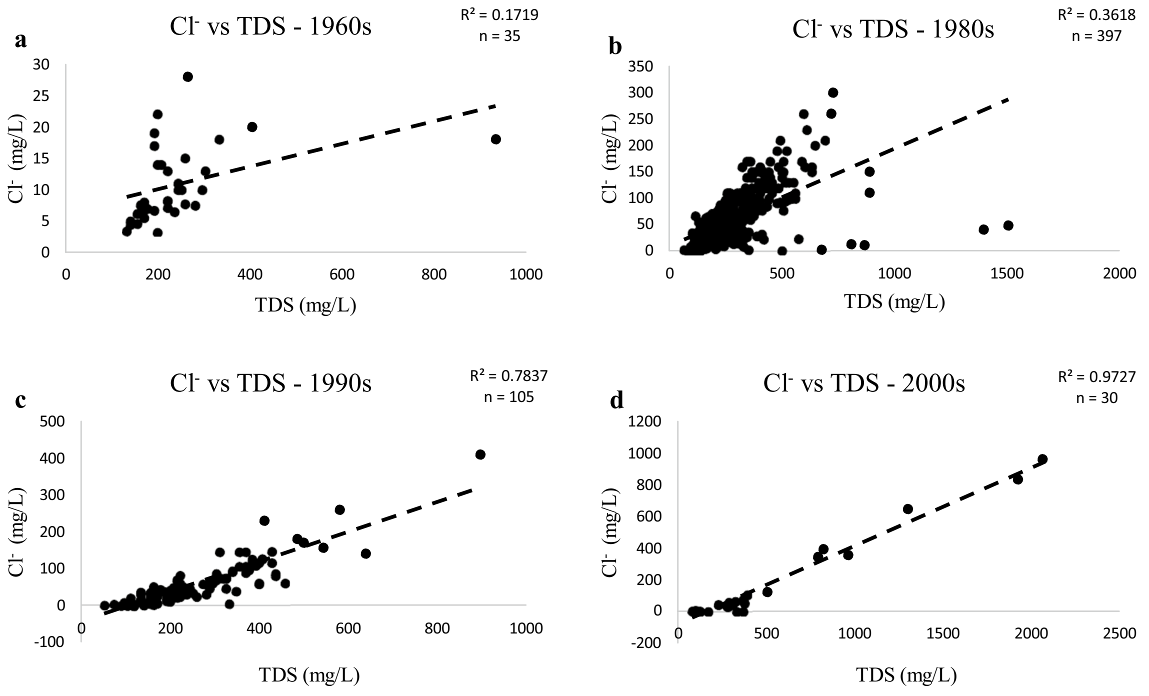


Fig. 4 Relationship between chloride and total dissolved solids concentrations for samples collected in the 1960s, 1980s, 1990s and 2000s in the Upper Passaic River Basin

while the most recent 2000–2010 data set has a near perfect correlation ($r^2=0.98$, $n=31$). The increasing trend in correlation over time is directly relates to the increase in NaCl deicing application for New Jersey (Kelly and Matos 2014).

An analysis of Cl^{-} concentration with respect to TDS gives insight into how the anionic composition of groundwater can be influenced from an external source. Plots of decade data of Cl^{-} vs TDS (Fig. 4a–d) clearly establish a trend of increasing correlation over time. Chloride vs TDS has essentially no correlation ($r^2=0.17$, $n=35$) in 1960–1969. The correlation evolves gradually with the 1980–1989 ($r^2=0.36$, $n=397$), 1990–1999 ($r^2=0.78$, $n=105$) to nearly perfect in 2000–2010 ($r^2=0.97$, $n=30$). This relationship (Table 2) and the earlier observations (see Table 1) establish that Cl^{-} is continually becoming the most abundant ion in the groundwater, in addition to increasing at a faster rate than the other major ions. This is presumed to result from a steady influx of Cl^{-} into the groundwater system from an external source. Additionally, substantial amounts of Cl^{-} often occur with high levels of TDS in groundwater on geologic timescales of thousands to millions of years. A drastic increase in TDS concentrations in previously identified freshwater species implicates an external source of contamination in the groundwater system (Chebotarev 1955; Freeze and Cherry 1979). The rapid increase of Cl^{-} in the generally fresh groundwater (TDS < 1000 mg/L) of the UPRB within 50 years would indicate an external, rather than a natural geologic source. Furthermore, the increasing nature of Cl^{-} contribution to TDS corresponds with the increased rates of NaCl deicing application in the UPRB.

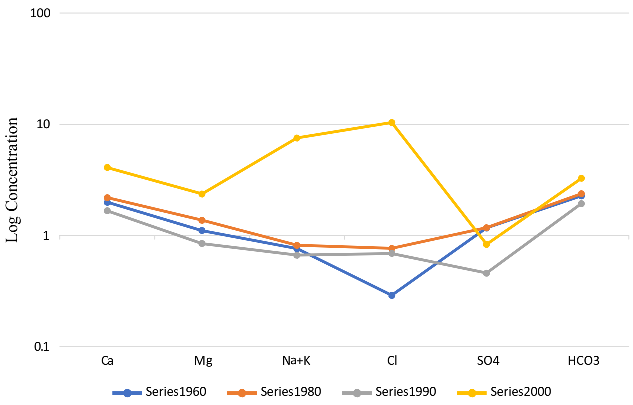
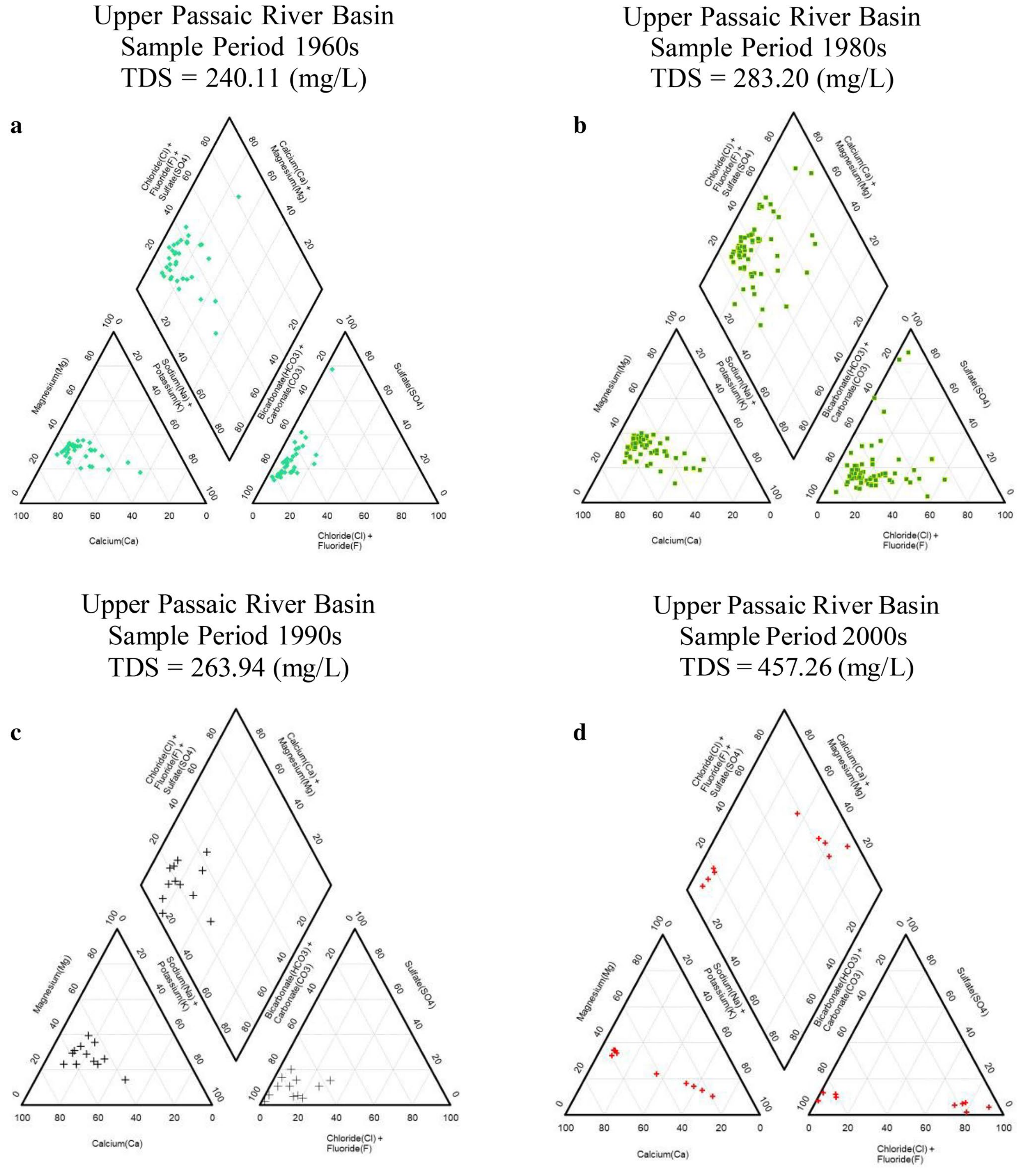


Fig. 5 A Schoellar diagram depicting log concentrations of major ions for the 1960s, 1980s, 1990s and 2000s in the Upper Passaic River Basin

Decade-averaged concentration patterns of major ions

A Schoeller diagram (Fig. 5) was constructed to evaluate the distribution pattern of the ions further. The figure confirms that concentrations of Na^{+} and Cl^{-} are much higher than the other major ions, Ca^{2+}, Mg^{2+}, and SO$_4^{2-}$, and are increasing at a greater rate than the other major ions.


Upper Passaic River Basin
Sample Period 1960s
TDS = 240.11 (mg/L)

Upper Passaic River Basin
Sample Period 1980s
TDS = 283.20 (mg/L)

Upper Passaic River Basin
Sample Period 1990s
TDS = 263.94 (mg/L)

Upper Passaic River Basin
Sample Period 2000s
TDS = 457.26 (mg/L)

Fig. 6 Piper diagrams showing groundwater facies in the Upper Passaic River Basin (F is assumed equal to zero in the plot)

Sulfate (SO_4^{2-}) is the only ion that showed a decrease in concentration over time during the study period. This points to the likelihood that Na^+ and Cl^- concentrations are being influenced from an outside source.

Groundwater species

Figure 6a shows the ionic composition of the UPRB groundwater samples from 1960 to 1969, and indicates that most

Table 3 Calculated mean of major ion concentration for the Upper Passaic River Basin (concentrations in mg/L)

Constituent	1960s	2000s	Difference	Percent increase
Sodium (Na)	15.77	63.65	47.88	303.60
Magnesium (Mg)	13.28	19.09	5.81	43.71
Calcium (Ca)	39.57	53.98	14.41	36.42
Chloride (Cl)	10.26	134.87	124.61	1214.90
Sulfate (SO_4)	50.69	30.98	− 19.70	− 38.87

groundwater would be classified as being fresh during this period. The diamond plot in the Piper diagram shows that the composition of groundwater during this period was dominated by $Ca(HCO_3)_2$, representative of the upper zone of the early natural groundwater evolution process. Figure 6b shows how the chemical composition of groundwater changed in the 1980–1989 period. Influenced by an increased flux of Cl^-, a transition from a $Ca(HCO_3)_2$-dominated composition to a composition dominated by $Ca(HCO_3)_2 + Cl^-$ species is seen during the period 1980–1989. The change in the chemical composition observed during this period is consistent with trends seen in groundwater that has undergone some degree of evolution, but the corresponding TDS continues to indicate freshwater.

The piper diagram for 1990–1999 shows the water composition again dominated by $Ca(HCO_3)_2$ (Fig. 6c), although this is likely to be a sampling artifact as a larger proportion of groundwater samples came from the metamorphic region of the UPRB during this period. Figure 6d, which covers 2000–2010, indicates that the chemical composition of groundwater in the region is dominated by both $Ca(HCO_3)_2$ and NaCl. It can be deduced from these observations that the NaCl water species is an external component to the natural $Ca(HCO_3)_2$-dominated groundwater. The presence of the two varying dominant species could also be due to variations in the geology of the bedrock in the UPRB. Specifically, the $Ca(HCO_3)_2$ species could be representative of the metamorphic region of low permeability rocks. Contrastingly, the NaCl species in the sedimentary bedrock may reflect an external influx of deicing NaCl due to high porosity and permeability of the rocks. Throughout the study period, the average TDS remained that of freshwater (< 1000 mg/L), which under uncontaminated natural evolution should contain little or no chloride.

Prediction interval analysis

Table 3 shows the averages for the 1960–1969 and 2000–2010 data sets, along with their difference and percent changes. Chloride has the most notable change over time, with an overall increase of 1215%. Similarly, Na^+ increases at a substantial rate, with a percent increase of 304%. $Mg2^+$ and Ca^{2+} also show overall increases of 44 and 36%, respectively. $SO_4{}^{2-}$ is the only ion that records a decrease of 39% rather than an increase over time.

A comparison of the ion concentration and specific conductance relationships of the recent (2000–2010) data with those of the historic (1960–1969) data shows significant differences in every case (Fig. 7). The regression lines of the recent record do not overlap the 95% confidence band of concentration estimates based on the 1960–1969 data, suggesting nonuniform loading in the rock weathering regimen of the UPRB. The Na^+ and Cl^- regression lines show larger increase in Na^+ and Cl^- concentrations at higher specific conductances with the 2000–2010 data than the 1960–1969 data (Fig. 7a, b), as opposed to lower concentrations of Mg^{2+}, Ca^{2+}, and $SO_4{}^{2-}$ (Fig. 7c–e). This tends to show that availability of Na^+ and Cl^- has increased, indicating an external influx of Na^+ and Cl^-.

Limitations

It is important to mention that the results in this study were obtained from a spatially variable dataset of wells. While a total of 573 well samples were used throughout the study period, the same wells were not continually sampled for each decade. Thus, the decadal analysis does not use all 573 wells for every decade. As a result, the spatial distribution of the data set varies slightly over some decades. Consequently, a degree of caution must be applied when directly comparing results from different decades. Furthermore, some inconsistencies may also arise when comparing the number of samples for each decade. The 1980s and 1990s sample periods had considerably more samples than the 1960s and 2000s. Nonetheless, it is considered that the conclusions of this study will not be significantly affected by these limitations.

In general, it is recommended that the following should be considered in a future study to improve the analysis: (1) the number of times each well is sampled in each decade, (2) sorting of well depth, screen location and aquifer type for possible contribution from the geologic source, and (3) possible reactions of certain ions in the environment, such as ion exchange.

Conclusion

Increases in population, road mileage density and urban development over the past 50 years in the Upper Passaic River Basin have led to increase in road salt application rates. This application of NaCl for road deicing has had a significant impact on the groundwater composition over

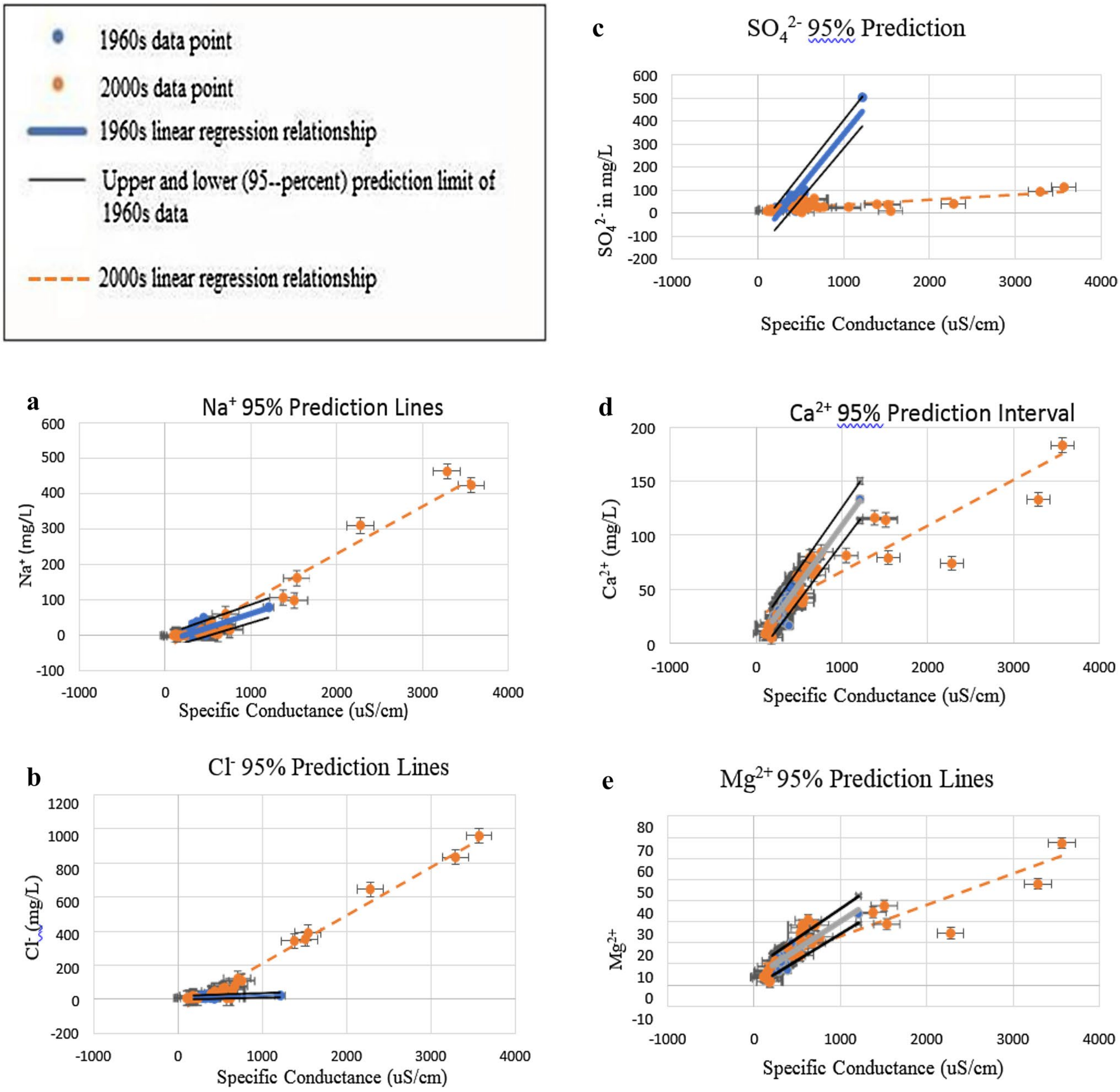


Fig. 7 Relationships between major ions and specific conductance for 1960s and 2000s data: **a** sodium, **b** chloride, **c** sulfate, **d** calcium, **e** magnesium

time. Chloride concentration shows increasingly significant contribution to TDS over time and has increased at a rate that would suggest that the chemical composition of groundwater in the region has been affected by anthropogenic factors.

Plots of sodium vs chloride concentrations correlate strongly, suggesting a common source for both ions. The correlations increased in strength over time from 1960 to 2010, and correspond with increased rates of NaCl deicing application.

Sodium and chloride concentrations increased at a faster rate than the other major ions during this period, and regression analysis indicates that Ca^{2+} has no significant association with Na^+ and Cl^-, indicating a separate origin for Na^+ and Cl^- on one hand, and the other major ions on the other. Furthermore, statistically significant increase occured in Na^+ and Cl^- concentrations over a 50-year period, which is shorter than would be expected in a natural evolution of groundwater chemistry which normally takes place on a geologic timescale. Therefore, the high levels of Na^+ and

Cl^- appear to be directly related to deicing salt application, while the other ions are following the natural evolution process in the system. The groundwater in the UPRB has low TDS (< 1000 mg/L), and plots of piper diagrams show that the water was fresh and had a chemical composition dominated by $Ca(HCO_3)_2$ in the 1960s. By 2000–2010, the groundwater had a mixed composition dominated by both $Ca(HCO_3)_2$ and NaCl. This compositional change may be attributable to both deicing salts and the geologic variation in the bedrock of the UPRB. The $Ca(HCO_3)_2$ composition is likely to be the natural background composition of groundwater in the metamorphic region and this is likely to have persisted in this region due to the low hydraulic conductivity of the aquifer and soil and the slow rate of infiltration of road salts into groundwater. In contrast, the chemical composition of groundwater in areas underlain by sedimentary rocks has rapidly changed to NaCl dominance, due to the higher hydraulic conductivity of soil and aquifer materials which has allowed road salts to rapidly infiltrate into groundwater.

This analysis of road deicing salt application is of significance for better understanding of the anthropogenic influence on regional groundwater quality in the UPRB. Such analyses can help not only for identifying regions that are prone to anthropogenic contamination, but also in designing better environment management techniques.

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