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A COMPARATIVE STUDY OF THE EFFECTS OF ROAD DEICING SALTS ON GROUNDWATER IN TWO WATER MANAGEMENT AREAS, NORTHERN NEW JERSEY

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Regression analyses of major ion concentration, and specific conductance were compared on a decadal basis from field data of the 1960s, 1980s, 1990s, 2000s, and 2010s to find if there is a statistically significant increase in calcium, chloride, and sodium compared to other major ions in groundwater in two Water Management Areas (WMAs) in northern New Jersey. The two WMAs, 03 and 04, correspond to the Middle Passaic River Basin (MPRB) and the Lower Passaic River Basin (LPRB), respectively. Time series graphical analyses, bivariate correlation relationships, statistical prediction interval evaluations, and multivariate analyses were used to determine the significance of the individual ion concentration trends. Time series analyses for the MPRBindicated that sodium and chloride levels are increasing at different rates throughout the study period. Bivariate plots showed no significant correlation between chloride and sodium, nor between chloride and total dissolved solids. Piper diagrams indicate that the groundwater facies in this WMA showed little to no change through time. Sodium and chloride showed only slight to moderate increases from the 1960s to 2010s in the groundwater of the MPRB. The combination of low deicing application, and low-porosity and low-permeability bedrock of basalt, gneiss, and granite are likely responsible for the low level of deicing contamination in the New Jersey WMA 03. Comparatively, concentrations of sodium, chloride, as well as calcium (a component of the less common deicing liquid: calcium chloride) increased at substantially greater rates in the LPRB. Bivariate plots of sodium vs chloride and calcium vs chloride showed strong correlations. This suggests that there is an observable relationship between these two pairs of ions individually produced by the deicing agents; NaCl and $CaCl_2$*. Additionally, calcium vs sodium showed no correlation, suggesting no intermolecular relationship between the two deicing agents. Groundwater facies analysis displayed a shift in groundwater composition from fresh to salt water in the LPRB within the relatively short evolutionary timeframe of the study. These observations indicate that deicing salt application has contaminated the groundwater in the New Jersey WMA 04. The high deicing application, high urbanization, high road density, and porous and permeable bedrock are considered to be responsible for the contamination.*

INTRODUCTION

Background

The urbanization of the Passaic River Basin in northern New Jersey has been accompanied by an increasing rate of application of road deicing materials, potentially influencing groundwater composition. The national annual weighted average of road salt (NaCl) application has increased by approximately 67 percent from 32 billion kg in the 1960s to 53 billion kg in the 2000s (Kelly and Matos, 2014). In the State of New Jersey, an estimated 6,000 kg of NaCl are applied annually for each lane-km of road (New Jersey Department of Transportation (NJDOT), 2018a). In the winter season of 2017-2018, the NJDOT applied 375 million kg of salt (NaCl) on New Jersey roads (NJDOT, 2018a). That same season, to supplement the effects of road salt, the NJDOT utilized an additional 4,512 m^3 of brine and 3,155 m^3 of liquid calcium chloride on NJ roads (NJDOT, 2018b). It is therefore imperative to assess how the introduction of road salts has been impacting regional groundwater composition.

In the past, various methodologies have been applied to evaluate the effects of road salts in aquifers (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) found that 20% of 100 groundwater wells along major highways in the State of Maine possessed chloride concentrations in excess of 250 mg/L. He associated these high chloride concentrations with road salting. Pollock and Tolar (1973) reported that well water close to salted roads in Massachusetts was unacceptably high, and to be steadily increasing from 1965 to 1971. Peters and Turks (1981) utilized linear regression analysis of major ion concentrations versus specific conductance in the Mohawk River, New York to determine the effects of sodium and chloride in the region's groundwater. They found that between the two study periods, 1951-53 and 1970-74, all the major ions, except sodium and chloride, showed insignificant increases. Sodium and chloride displayed a 20 percent increase in yield during the two decades. Through molar ratio and atomic weight analysis of the region's bedrock, the study found that the metasedimentary foundation contributed less than 6 percent of the basin's net dissolved yield of any particular ion.

Czarnik and Kosinski (1994) noted groundwater quality variations against time in the central region of the Passaic River Basin (PRB) in New Jersey. Seventy-one water samples throughout the southeastern portion of the PRB were collected from 1959-1988 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 Kosinski, 1994).

A later paper by Godwin et al. (2003), also analyzed long-term trends of NaCl in the Mohawk River. The study employed a Schoeller plot to visualize increases in major ion concentration from the 1950s to the 1990s. It was found that Na^+ and Cl^- ion concentrations had increased by 130 and 243 percent within that time frame, while other ion concentrations remained relatively steady (Godwin et al., 2003).

A separate study by Foos (2003), on the spatial distribution of road salt contamination in the Cuyahoga Falls, Ohio used multivariate analysis to assess the area's groundwater. The study found that most of the samples were alkali-chloride-rich on piper diagrams, and the total dissolved solids (TDS) concentrations ranged from 250 to 4733 mg/L (Foos, 2003). Through the strong correlations found by bivariate analysis between Na^+ and Cl^- as well as Cl^- and TDS, the study determined that halite was the major dissolved solid in the target region's water (Foos, 2003).

Problem Statement

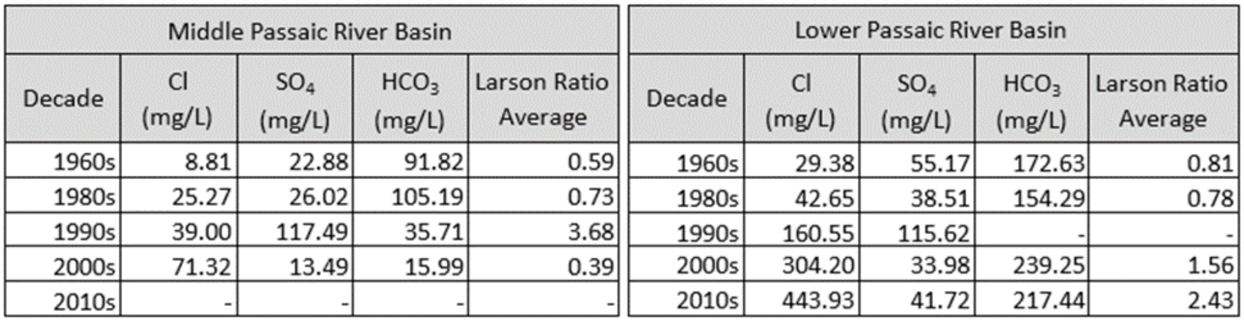
Sodium chloride, brine, and liquid calcium chloride are deicing agents that have been applied primarily for snow and ice removal from roadways in New Jersey since the early 1960s (NJDOT, 2018a). It has been reported from studies of vehicle accident rates in four states in the United States that deicing salts reduced accident rates on highways by 88 percent (Kuemmel and Hanbali, 1992). Though beneficial, the use of road salts has been shown to affect surface water and groundwater quality, and also has been correlated with loss of plant and macro-invertebrate life, loss of biodiversity, nutrient depletion of soils, release of toxins, infrastructure damage, and aquifer stratification and stagnation (Howard and Beck, 1993).

Chloride contamination in the groundwater could be a costly and dangerous problem which can result in lead (Pb) and copper (Cu) corrosion of public utilities (Stets et al., 2018). Understanding the chloride concentrations in the MPRB and LPRBis essential for effective damage control and the prevention of potential lead and copper poisoning risks. The Larson Ratio (LR): (2 $[SO_4^{2-}]$ + $[Cl^-]$) / $[HCO_3^-]$ is an ionic ratio commonly used to express the potential corrosivity of water (Stets et al., 2018). Ratios under 0.5 would indicate low to slight probability of corrosion, between 0.5 and 1 indicates moderate corrosion probability, and ratios greater than 1 indicate a clear risk of corrosion (Stets et al., 2018). An inventory analysis from the United States Geological Survey (USGS, 2018) showed that from the 1960s to the 2010s, LR averages in the MPRB had no obvious trend while the LR averages for the LPRB demonstrated an increasing trend that corresponds with Cl^- concentrations (Table 1). In the 1990s, a spike was observed in the LR of the MPRB, which however, was not related to the Cl^- trend, but could be linked to the drastic increase in SO_4^{2-} concentration within that decade. On the other hand, the LR of the LPRB showed an increasing trend that was directly related to the increasing Cl^- concentrations. This increasing corrosive potential of the groundwater in the LPRB is of concern, and herein shall be compared with the trend in the MPRB in order to determine a potential cause.

Study Objectives

This project utilizes statistical analyses aimed at evaluating deicer road salts as a source of groundwater contamination, using the historical water quality inventory collected from the 1960s to the 2010s by the USGS. Groundwater samples from the MPRB and LPRB, having significant variations in land use, road density, geology, and hydrology were analyzed in order to develop insight into the compounding effects of these variables on road salt contamination in groundwater.

In particular, the study aims at determining if road deicing materials are contaminating the groundwater of these two contrasting WMAs at different rates.



Middle Passaic River Basin				
Decade	Cl (mg/L)	SO_4 (mg/L)	HCO_3 (mg/L)	Larson Ratio Average
1960s	8.81	22.88	91.82	0.59
1980s	25.27	26.02	105.19	0.73
1990s	39.00	117.49	35.71	3.68
2000s	71.32	13.49	15.99	0.39
2010s	-	-	-	-

Lower Passaic River Basin				
Decade	Cl (mg/L)	SO_4 (mg/L)	HCO_3 (mg/L)	Larson Ratio Average
1960s	29.38	55.17	172.63	0.81
1980s	42.65	38.51	154.29	0.78
1990s	160.55	115.62	-	-
2000s	304.20	33.98	239.25	1.56
2010s	443.93	41.72	217.44	2.43

Table 1. Cl^-, SO_4^{2-}, and HCO_3^- ionic concentration averages and corresponding Larson Ratio Averages of the Middle and Lower Passaic River Basin groundwater from the 1960s to the 2010s (USGS, 2018)

STUDY AREA

Location and Setting

The MPRB and LPRB are situated on the northern section of the Atlantic Seaboard Fall Line, a 1,448-km escarpment on the eastern coast of the United States, where the Piedmont Plateau and Atlantic Coastal Plain meet (Naeser et al., 2016). This fall line marks the boundary between the hard, metamorphosed, and elevated terrain of the plateau and the sandy, sedimentary, and flat coastal plain (Naeser et al., 2016). The MPRB and LPRB are identified by the New Jersey Department of Environmental Protection, respectively, as Watershed Management Area 03 and Watershed Management Area 04 (Figure 1).

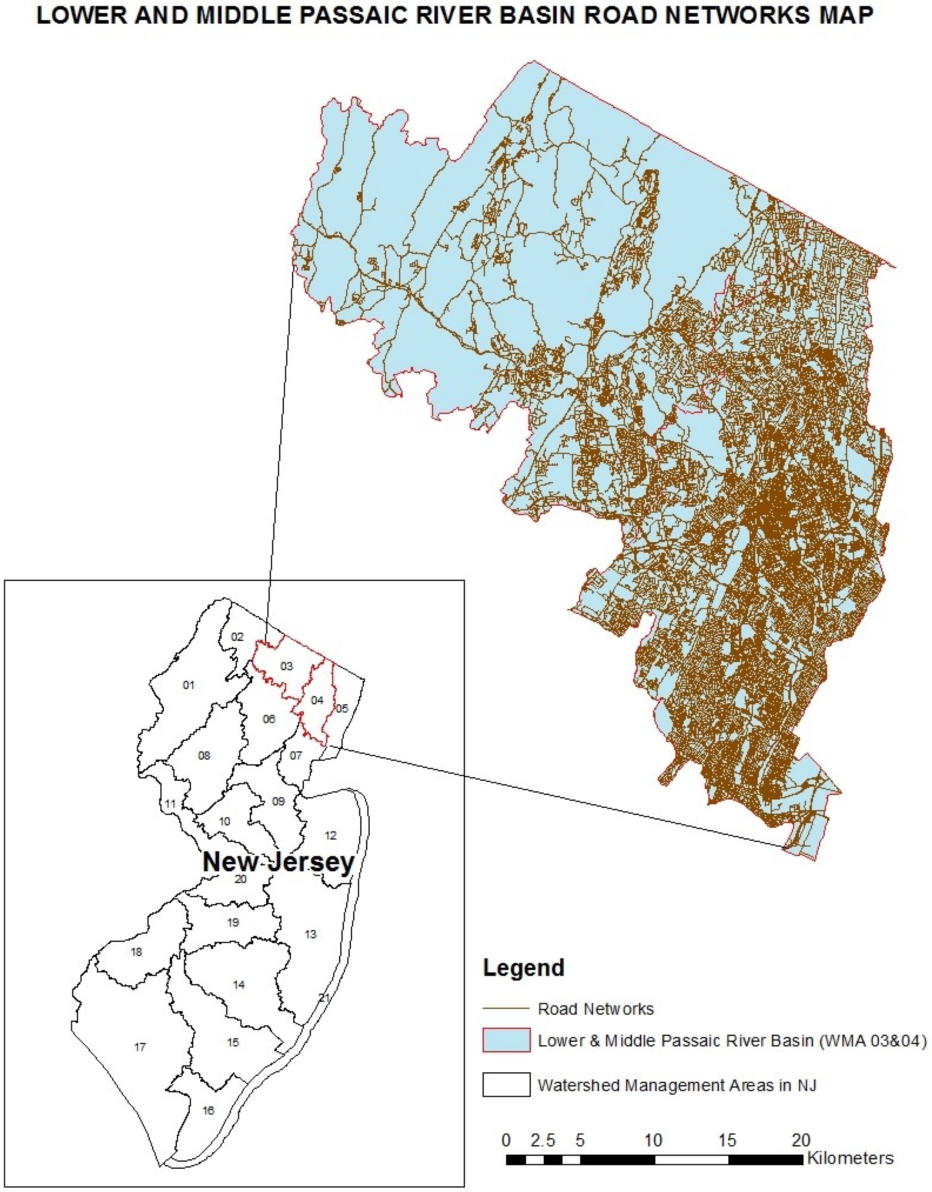
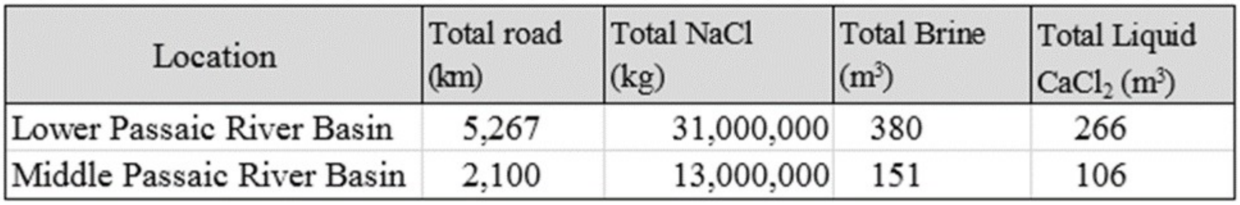


Figure 1. Location and Spatial Distribution of Roads of the Lower and Middle Passaic River Basins, New Jersey (modified from NJDEP, 2009)

The MPRB lies on the Piedmont Plateau, and consists of mostly suburban townships, lying in Passaic County and including smaller sections of Bergen, Morris, and Sussex Counties. The MPRB is overlain by 2,100 km of roads (Figure 1) (NJ Bureau of GIS, 2018), which amounted to a total use of 13 million kg of road salt in the year 2017 (Table 2).

Table 2. Deicing statistics for Lower and Middle Passaic River Basins for the year 2017 (Calculated from NJDOT and USGS data)



Location	Total road (km)	Total NaCl (kg)	Total Brine (m^3)	Total Liquid $CaCl_2$ (m^3)
Lower Passaic River Basin	5,267	31,000,000	380	266
Middle Passaic River Basin	2,100	13,000,000	151	106

The LPRB lies on the Atlantic Coastal Plain to the east of the Atlantic Seaboard Fall Line. The Atlantic Coastal Plain is an area of low relief extending 3,540 km from New York to Florida (Anderson, 1986). The coastal plain's average elevation is less than 900 meters above sea level and is mostly comprised of sedimentary bedrock (Anderson, 1986). The LPRB consists of major urbanized and industrial cities such as Newark, Paterson, Clifton, and East Orange. The LPRB is densely crowded by 5,267 km of roads (Figure 1) (NJ Bureau of GIS, 2018). The density of roads in the LPRB (10.8 lane-km per sq. km), an urban and industrial land use area, is over 300 percent greater than the road density of the MPRB (3.5 lane-km per sq. km), a rural and suburban land use area. This equates to 31 million kg of road salt being used in the LPRB in the year 2017 (Table 2).

Geology

The bedrock of the MPRB consists of mostly igneous and metamorphic rocks such as basalt, gneissand granite. These rock types are not adequate sources of Ca^{2+}, Mg^{2+}, Na^+, Cl^-, or SO_4^{2-} (Ries,1901). There are also small portions of sandstone in the MPRB. Sandstone is a sedimentary rock with high erosion rates and is considered a potential source for Ca^{2+} and Mg^{2+} due to its binding elements consisting of calcites and shales (NJ Bureau of GIS, 2018). However, the influence of denudation on Ca^{2+} and Mg^{2+} ion yield is likely insignificant because the total surface area of the sedimentary contributors is less than 10 percent of the total basin area.

The LPRB bedrock largely originates from the Brunswick Formation of Triassic age (Olsen, 1980). It consists of a heterogeneous mix of basalt, shale, sandstone, and conglomerate, which are known potential sources of Ca^{2+} and Mg^{2+}. The geology of the LPRB therefore suggests a significant natural source of Ca^{2+} and Mg^{2+}. Additionally, the LPRB's high storage capacity and heterogeneity permits the natural evolution of major groundwater ions Ca^{2+}, Mg^{2+}, Na^+, Cl^-, HCO_3^-, and SO_4^{2-}.

Natural Groundwater Evolution

According to the Chebotarev Sequence, Ca^{2+} and Mg^{2+} ions occur naturally through bedrock erosion in young and active groundwater stages, commonly found in upper (shallow) zones (Chebotarev, 1955). HCO_3^- and SO_4^{2-} are abundant in the intermediate zone, where water is less active. Cl^- anions are naturally allocated in aged and stagnant groundwater, in the lower (deep) zone. It is important to note that the natural occurrence of Cl^- in groundwater takes hundreds of thousands to millions of years (Freeze and Cherry, 1979).

TDS measurements assist in recognizing ion sources and the natural hydrochemical makeup of groundwater. A TDS concentration under 1,000 mg/L is indicative of freshwater. Freshwater bodies should have ion compositions largely consistent of Ca^{2+} and HCO_3^- (Fetter, 2014). On the other hand, a TDS concentration of 10,000-100,000 mg/L is indicative of saline

water. Aged and stagnant groundwater bodies tend to become saline and should contain higher levels of Na^+ and Cl^- (Freeze and Cherry, 1979). Considering it takes thousands to millions of years for saline bodies to naturally occur, a sudden increase in Na^+, Cl^-, and TDS between the 1960s and 2010s would suggest that the anthropogenic application of deicing materials is indeed contaminating regional groundwater (Fetter, 2014). Significant increases of Ca^{2+} concentration within the study timeframe may also be indicative of $CaCl_2$ liquid application. In contrast, a uniform increase in all major ions would suggest a natural domestic source such as bedrock weathering.

METHODOLOGY

Data Collection

The field parameters were collected from the USGS, which stores accumulated sample data from groundwater wells nationwide. One hundred and thirty-eight sample data for the MPRB and 83 for the LPRB were collected from the USGS database and analyzed in decadal portions from the 1960s, 1980s, 1990s, 2000s, and 2010s. A lack of data representative of the 1970s led to the omission of analysis for that decade. The data were collected from various agencies such as the USGS National Water-Quality Assessment (NAWQA), US Environmental Protection Agency (USEPA), and the NJ Department of Environmental Protection (NJDEP). The data are stored in the USGS online catalogue and can be retrieved by accessing https://nwis.waterdata.usgs.gov/nwis/gwlevels?

Field parameters used for this research consisted of specific conductance (uS/cm), TDS (mg/L), and ion mass concentration (mg/L) for major ions Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^-, HCO_3^-, SO_4^{2-}, CO_3^{2-}, and F^-. The data were from monitoring wells, and were filtered to be satisfactorily representative of the decades. The data were imported to Excel version 14.4 for statistical analyses, and then into ArcGIS to create ion concentration patterns. The shapefiles for the watershed basemaps (including boundaries, elevation, bedrock, and roads) were downloaded from the NJDEP Bureau of GIS (NJ Bureau of GIS, 2018).

Data Analysis

Time series and Schoeller Graphical Analysis

The mean values of the parameters Ca^{2+}, Mg^{2+}, Na^+, Cl^-, and TDS were plotted against time, in decades, for organized visualization of concentration trends. Additionally, Schoeller plots were created to display magnitudes of ion concentrations on a decadal basis. Time plots offer insight into ionic concentration trends through time and offer some general understanding to ion-ion relationships as well as their sources of origin.

Prediction Intervals

To examine the influence of deicing materials on groundwater, individual regression analysis of each major ion, Ca^{2+}, Mg^{2+}, Na^+, and Cl^-, was conducted as a function of the independent variable, specific conductance (Peters and Turk, 1981). Specific conductance is an index variable that is easily measure 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 Steele 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 linear trends between individual ions and specific conductance were compared between two sets of time: 1960s and 1990s for MPRB, and 1960s and 2000s for LPRB. These sample dates were chosen for comparison as they provided a sufficient data count for regression analysis and are representative of both incipient and recent stages of road salt application. Ninety-five percent prediction intervals were assigned to the 1960s dataset to determine whether the actual future observations fell within statistical estimates. The prediction interval for the dependent variable (y) was calculated from the independent variable (x), using equations described by Snedecor (1946) and Dixon (1975).

Bivariate Analysis

Bivariate regression analysis was used to examine individual ion to ion relationships. Comparison of major ions, Ca^{2+}, Mg^{2+}, Na^{+}, and Cl^{-}, as well as TDS allows for insight into the correlations between pairs of ion concentrations. Pearson's correlation coefficient, r, is indicative of the relationship between two data variables. Ions with correlation coefficients near or equal to a value of 1 have a positive, or unison, relationship and possibly originate from an analogous source (Hocking et al., 2018). Conversely, correlation coefficients closer to -1 have a negative relation with one another. Correlation coefficients close to 0 are of no relation with each other and, in this study, would be indicative of separate ion origins (Hocking et al., 2018).

The coefficient of determination, r^2, shows the percentage of variation in a bivariate regression analysis. The r^2 is simply the squared value of the correlation coefficient, r, and since squared values are always positive, the r^2 value always ranges from 0 to 1 with values closer to 1 signifying stronger correlation. The coefficient of determination is more useful in identifying bivariate correlations in regression analyses (Boyte et al., 2017).

Groundwater Species

Piper diagrams allowed for multivariate graphical representations of the water composition in the study areas. The piper diagrams were created through an excel program from "USGS Nevada Excel for Hydrology" (2018). For a proper representation of groundwater composition on the diagram, well samples must have provided ion concentration measurements for the following:

Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, SO_4^{2-} and Cl^{-}. Since a large portion of the dataset did not contain all the necessitated parameters, the sample set for this multivariate analysis was reduced to 41 samples for MPRB and 33 samples for LPRB.

In a piper diagram, cations and anions are segregated into individual Gibbs triangles, which are then projected onto a diamond plot in the center. The center diamond therefore provides a multivariate depiction of the sample dataset's ionic composition. Piper diagrams were composited for each decade to distinguish the groundwater ionic composition changes through time.

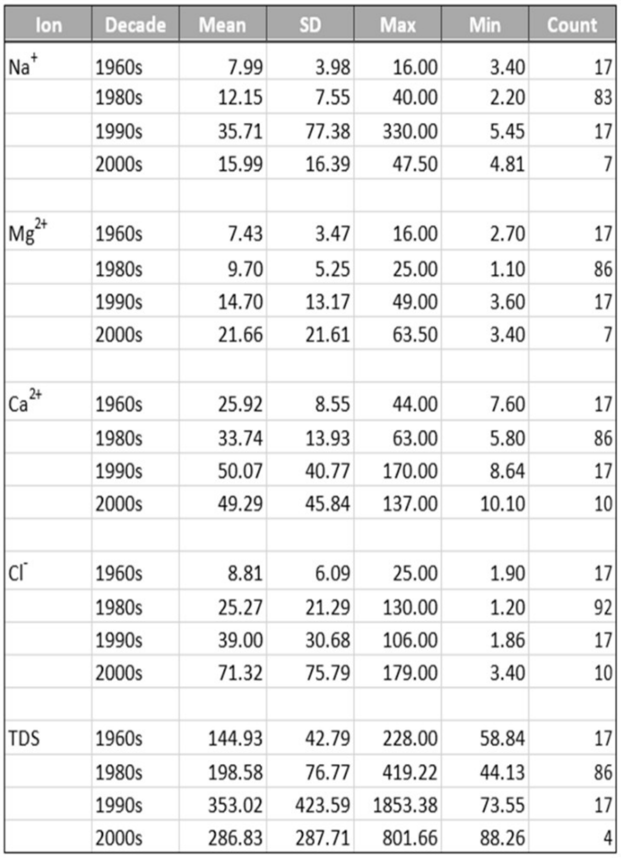
RESULTS

Time Series of Concentration Patterns

Table 3a depicts mean concentration increases over time for Cl^{-}, Ca^{2+}, Mg^{2+}, and TDS in the MPRB. There is no significant increasing trend in Na^{+}. There is indication that Na^{+} and Cl^{-} levels are increasing at different rates, suggesting a possible lack of relation between these two ions, and presenting no evidence of NaCl contamination. It is also observed that Ca^{2+} and Mg^{2+} ions are increasing at different rates, suggesting that there may be an outside source for Ca^{2+} such as $CaCl_2$.

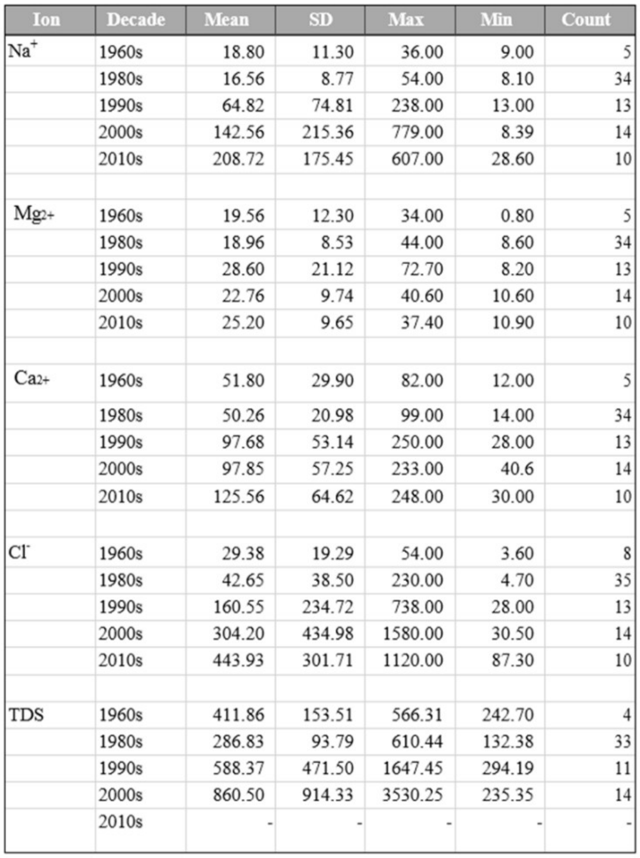
Table 3. Mean, standard deviation, range, and data count of major ion concentration and total dissolved solids, a) MPRB, b) LPRB (conc. in mg/L)

a)



Ion	Decade	Mean	SD	Max	Min	Count
Na^+	1960s	7.99	3.98	16.00	3.40	17
	1980s	12.15	7.55	40.00	2.20	83
	1990s	35.71	77.38	330.00	5.45	17
	2000s	15.99	16.39	47.50	4.81	7
Mg^{2+}	1960s	7.43	3.47	16.00	2.70	17
	1980s	9.70	5.25	25.00	1.10	86
	1990s	14.70	13.17	49.00	3.60	17
	2000s	21.66	21.61	63.50	3.40	7
Ca^{2+}	1960s	25.92	8.55	44.00	7.60	17
	1980s	33.74	13.93	63.00	5.80	86
	1990s	50.07	40.77	170.00	8.64	17
	2000s	49.29	45.84	137.00	10.10	10
Cl^-	1960s	8.81	6.09	25.00	1.90	17
	1980s	25.27	21.29	130.00	1.20	92
	1990s	39.00	30.68	106.00	1.86	17
	2000s	71.32	75.79	179.00	3.40	10
TDS	1960s	144.93	42.79	228.00	58.84	17
	1980s	198.58	76.77	419.22	44.13	86
	1990s	353.02	423.59	1853.38	73.55	17
	2000s	286.83	287.71	801.66	88.26	4

b)



Ion	Decade	Mean	SD	Max	Min	Count
Na^+	1960s	18.80	11.30	36.00	9.00	5
	1980s	16.56	8.77	54.00	8.10	34
	1990s	64.82	74.81	238.00	13.00	13
	2000s	142.56	215.36	779.00	8.39	14
	2010s	208.72	175.45	607.00	28.60	10
Mg^{2+}	1960s	19.56	12.30	34.00	0.80	5
	1980s	18.96	8.53	44.00	8.60	34
	1990s	28.60	21.12	72.70	8.20	13
	2000s	22.76	9.74	40.60	10.60	14
	2010s	25.20	9.65	37.40	10.90	10
Ca^{2+}	1960s	51.80	29.90	82.00	12.00	5
	1980s	50.26	20.98	99.00	14.00	34
	1990s	97.68	53.14	250.00	28.00	13
	2000s	97.85	57.25	233.00	40.6	14
	2010s	125.56	64.62	248.00	30.00	10
Cl^-	1960s	29.38	19.29	54.00	3.60	8
	1980s	42.65	38.50	230.00	4.70	35
	1990s	160.55	234.72	738.00	28.00	13
	2000s	304.20	434.98	1580.00	30.50	14
	2010s	443.93	301.71	1120.00	87.30	10
TDS	1960s	411.86	153.51	566.31	242.70	4
	1980s	286.83	93.79	610.44	132.38	33
	1990s	588.37	471.50	1647.45	294.19	11
	2000s	860.50	914.33	3530.25	235.35	14
	2010s	-	-	-	-	-

However, the overall increasing concentration trend observed in most of the major ions demonstrates that there is no noticeable contamination of NaCl and $CaCl_2$ on the MPRB groundwater. This lack of significant NaCl and $CaCl_2$ influence on the groundwater could be due to their relatively low application amounts (20.34 tons/sq. km) in the area.

Significant mean concentration increases over time can be seen for Cl^-, Na^+, Ca^{2+}, and TDS (Table 3b) in the LPRB. There is no significant increasing trend for Mg^{2+}. The observable increasing trend for Ca^{2+}, Na^+, and Cl^- is significant enough to support a hypothesis that there is an anthropogenic source for these ions. The increasing TDS trend is also likely related to the road salt contamination of the groundwater. Had the major ion sources been solely caused by domestic rock weathering, Mg^{2+} and Ca^{2+} ion concentrations would have increased at similar rates over time. The drastically different rates of increases in Mg^{2+} and Ca^{2+} is presumably introduced into the groundwater from various sources (Soriano, 2019).

The Schoeller plot for the MPRB indicates a consistent increase in all ion concentrations through time, except for Na^+ and SO_4^{2-} which decreased in the 2000s (Figure 2a). That Na^+ and Cl^- are increasing at different rates, suggests that they may have been introduced from different sources. Figure 2b shows significant magnitudes of increases for the three ion concentrations: $Cl \approx 15$, $Na \approx 11$, and $Ca \approx 3$ in the LPRB. It is postulated that the anthropogenic application of NaCl and, to a lesser extent, $CaCl_2$ are the causes for the observable ion increases in the LPRB.

Prediction Intervals Analysis

The averages for the historic (1960s) and recent (1990s for MPRB) and (2000s for LPRB) data sets are presented in Table 4, along with the differences and percent increases. Sodium and chloride have the most notable changes of 361% and 331% over time in the MPRB (Table 4a). These changes, Na^+ (722%) and Cl^- (1063%), are much larger in the LPRB relative to the other ions (Table 4b).

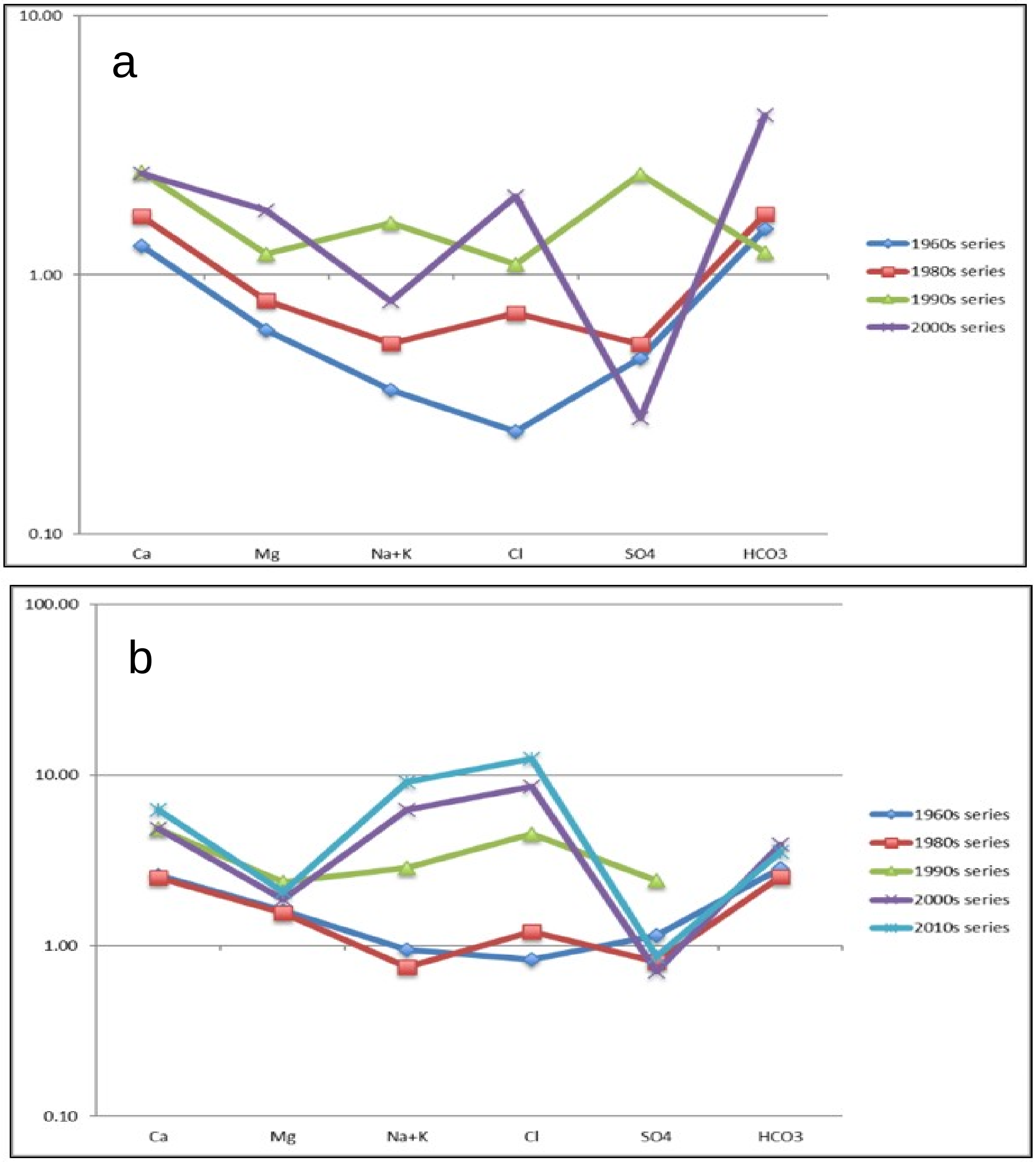
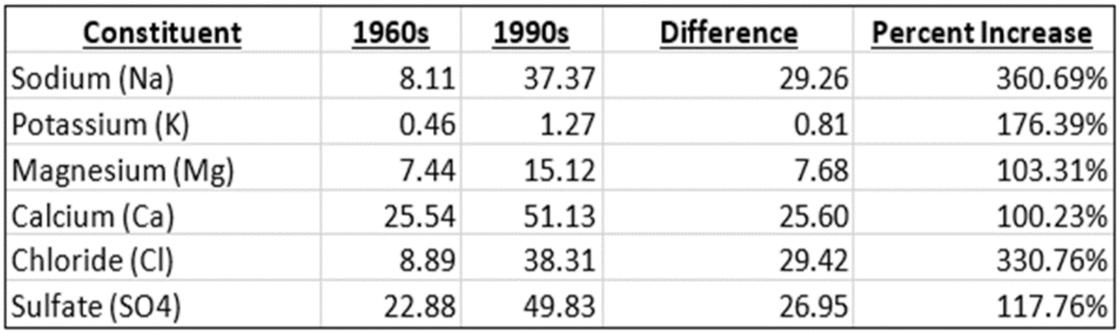


Figure 2. Schoeller plots depicting log (concentration) of major ions for the 1960s, 1980s, 1990s, and 2000s in the: a) MPRB, b) LPRB

The ion concentration and specific conductance relationships of the recent and historic data also show significant differences (Figures 3 and 4). Most of the regression lines of the recent record in the MPRB nearly overlap the 95 percent confidence band of the concentration estimates based on the 1960s data, except for Cl^- (Figure 3a), which shows a larger increase in Cl^- concentration at higher specific conductances with the 1990s data than with the 1960s data. Whereas most ion concentrations appear to follow the rock weathering regimen of the MPRB, the above average concentration of the Cl^- could be assumed to be the result of an additive effect of the use of both NaCl and $CaCl_2$ road deicing salts in the MPRB.

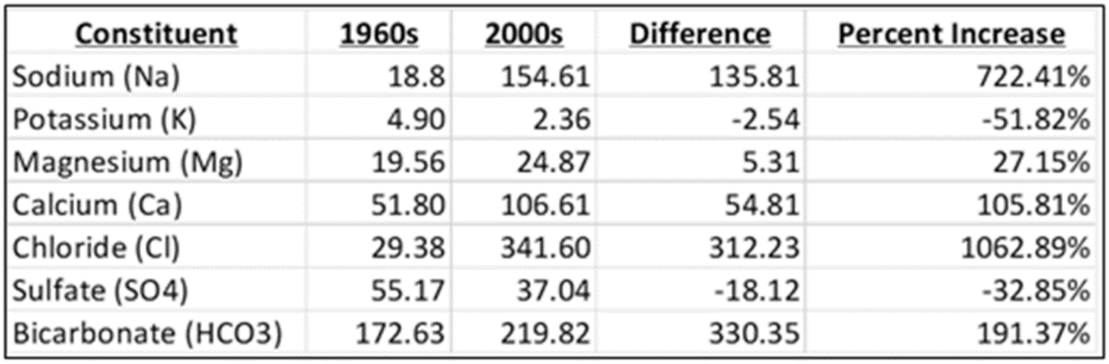
Table 4. Calculated mean yield of major ion concentrations from: a) MPRB, b) LPRB (yields in mg/L)

a



Constituent	1960s	1990s	Difference	Percent Increase
Sodium (Na)	8.11	37.37	29.26	360.69%
Potassium (K)	0.46	1.27	0.81	176.39%
Magnesium (Mg)	7.44	15.12	7.68	103.31%
Calcium (Ca)	25.54	51.13	25.60	100.23%
Chloride (Cl)	8.89	38.31	29.42	330.76%
Sulfate (SO4)	22.88	49.83	26.95	117.76%

b



Constituent	1960s	2000s	Difference	Percent Increase
Sodium (Na)	18.8	154.61	135.81	722.41%
Potassium (K)	4.90	2.36	-2.54	-51.82%
Magnesium (Mg)	19.56	24.87	5.31	27.15%
Calcium (Ca)	51.80	106.61	54.81	105.81%
Chloride (Cl)	29.38	341.60	312.23	1062.89%
Sulfate (SO4)	55.17	37.04	-18.12	-32.85%
Bicarbonate (HCO3)	172.63	219.82	330.35	191.37%

The Cl^- and Na^+ regression lines of the LPRB show larger increases in Cl^- and Na^+ concentrations at higher specific conductances with the 2000s data than the 1960s data (Figures 4a and 4b). The regression line with the 2000s data approximately overlaps the 95 percent confidence band of the 1990s data for Ca^{2+} (Figure 4c), while that of Mg^{2+} (Figure 4d) falls below the predicition band. These results of the regression analyses for LPRB support the hypothesis that Na^+ and Cl^- concentrations in groundwater are presently increasing at a higher rate in comparison to other major ions. This is an indication that the heavy application of road deicing NaCl is affecting the groundwater quality in the LPRB.

Bivariate Analysis

Table 5 shows ion correlation coefficients, r, and coefficients of determination, r2, for each decade and for the cumulative dataset. An increasing trend in correlation can be seen for Ca2+ vs Mg2+ as well as Na+ vs Cl- in the MPRB (Table 5a). Ca^{2+} and Mg^{2+} ($r^2 = 0.82$, n = 127) have strong correlation, assumed to be caused by transportation of eroded calcite by major rivers such as the Pompton River in the study area. Na+ vs Ca2+ (r2 = 0.40, n = 124) and Cl- vs Ca2+ (r2 = 0.47, n = 130) have weak correlations, indicating minimal link between Na+ and Ca2+ on one hand, and Cl- and Ca2+ on the other. Na+ vs Cl- (r2 = 0.03, n = 124) and Cl- vs TDS (r2 = 0.10, n = 124) show no significant correlation, signifying a weak link between the road salt ions, Na+ and Cl-, and that Cl- has no significant influence on TDS in the MPRB.

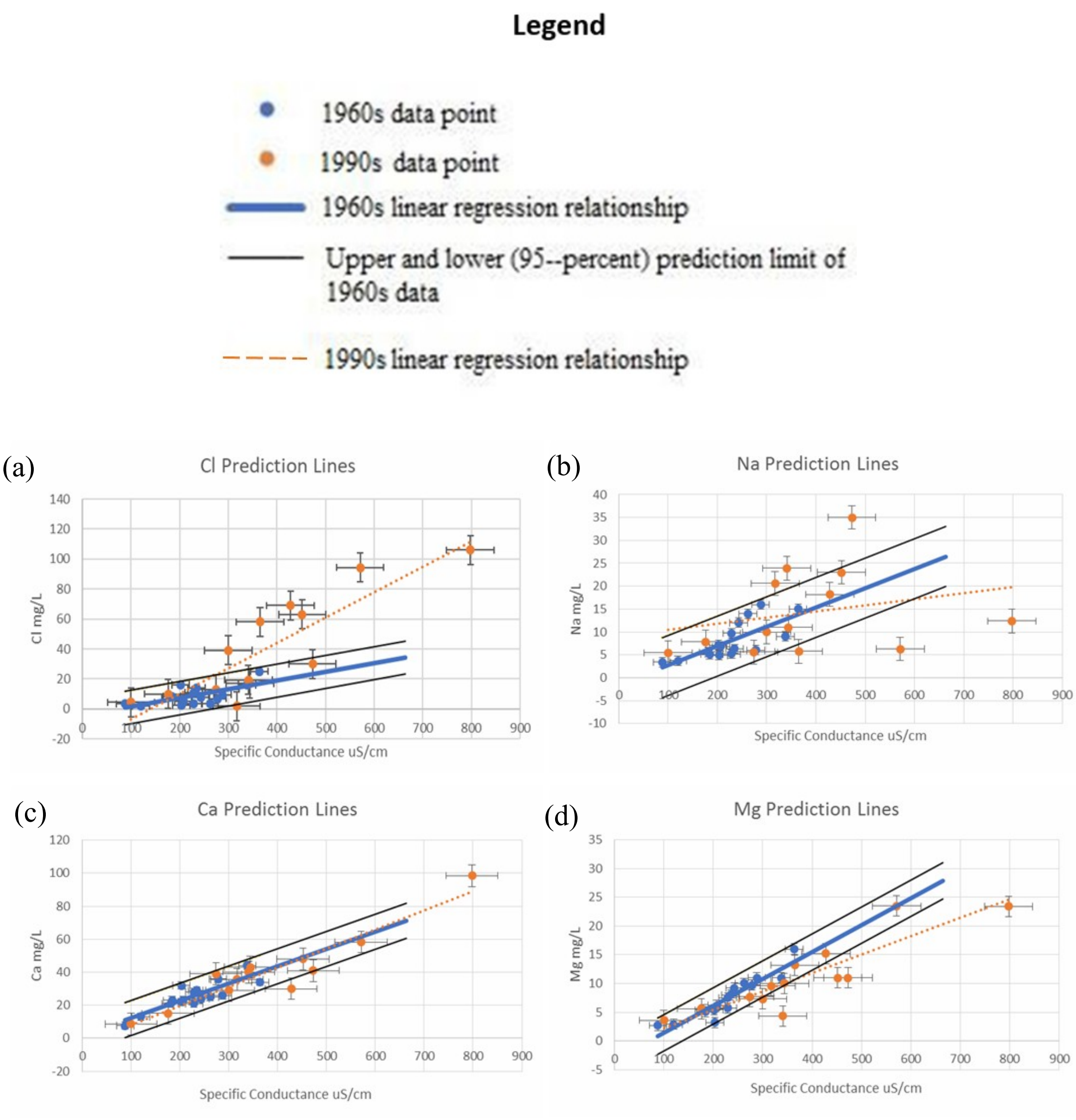


Figure 3. Relationships between major ions concentration and specific conductance, 1960s and 1990s in the MPRB.

Table 5b shows that the correlation between Ca^{2+} and Mg^{2+} decreases slightly through the study period. In the young sedimentary rock environment like the LPRB, $Ca(HCO_3)_2$ groundwater species should be dominant and a Ca^{2+} - Mg^{2+} relationship should remain consistent (Fetter, 2014). Therefore, this decreasing correlation between the ions implies an external Ca^{2+} contaminant ion, likely caused by the deicing liquid $CaCl_2$ application. Inspite of the decrease in correlation, the overall cumulative correlation for Ca^{2+} vs Mg^{2+} ($r^2 = 0.79$, n = 76) is strong, indicating a geological source for these two ions.

Contrary to the ion trends in the MPRB, the results from the LPRB show that Na^+ vs Cl^- ($r^2 = 0.78$, n = 76) has a strong correlation, indicating a common source for both ions (Table 5b). The relatively strong correlation of the Cl^- vs Ca^{2+} ($r^2 = 0.62$, n = 76) suggests some link between Cl^- and Ca^{2+}, probably from deicing $CaCl_2$, while the very weak Na^+ vs Ca^{2+} ($r^2 = 0.23$, n = 76) points toward

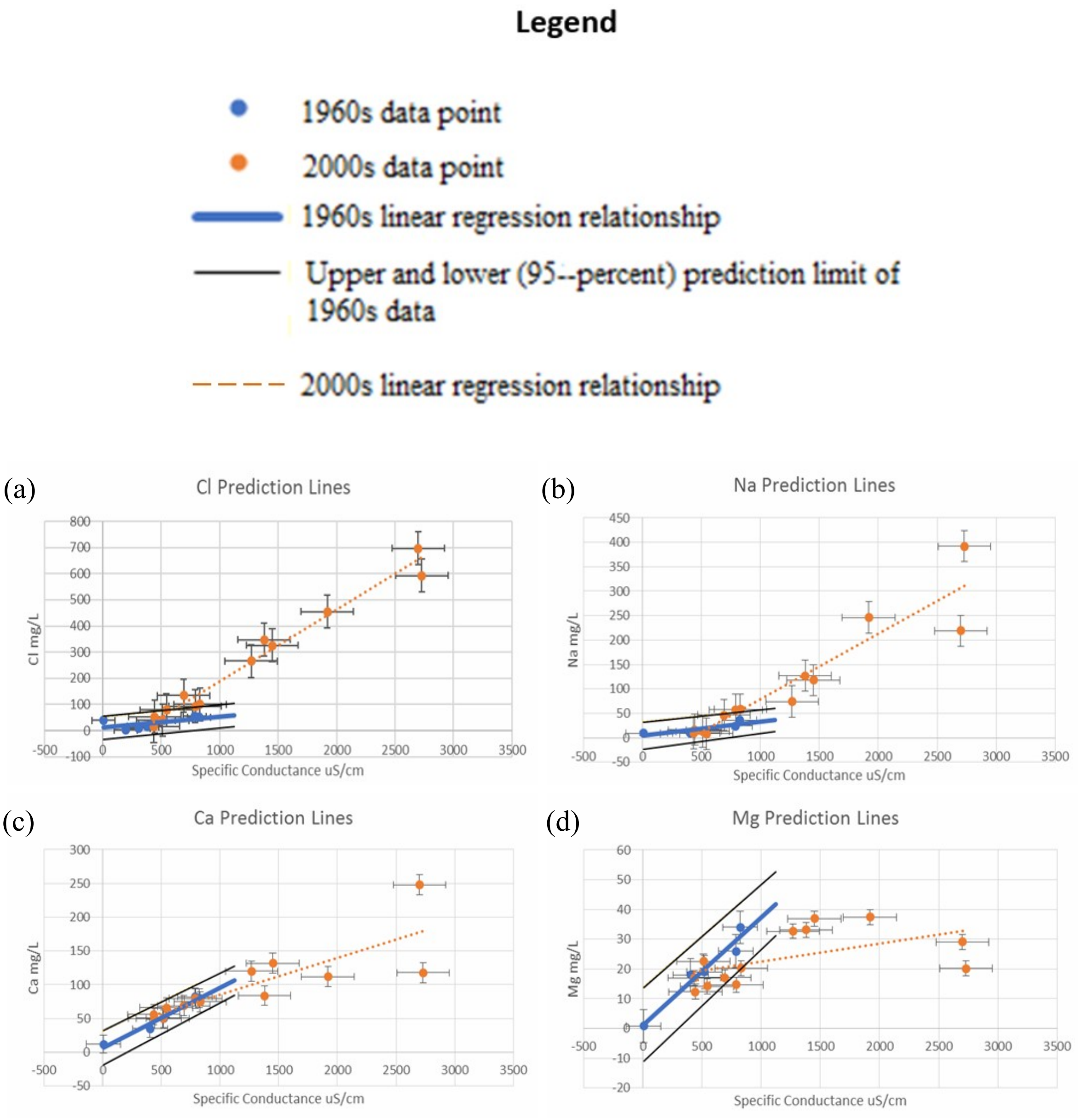


Figure 4. Relationships between Major ions concentration and specific conductance, 1960s and 1990s in the LPRB.

different origins. These bivariate analyses from the LPRB strongly support the hypothesis that the heavy application of deicing NaCl and $CaCl_2$ is contaminating the groundwater in this highly urbanized and industrialized WMA.

Groundwater Facies

The piper diagrams depict $Ca(HCO_3)_2$ groundwater facies in the MPRB throughout the study period (Figures 5). The $Ca(HCO_3)_2$ composition, along with a TDS concentration below 1000 mg/L suggests fresh water in the area (Freeze and Cherry, 1979). These results imply that the low rate of deicing NaCl and $CaCl_2$ application in this suburban WMA has had little or no influence on the groundwater.

Table 5: Regression analysis correlation relationships for major ions in the: a) MPRB, b) LPRB (in mg/L).

Y-dependant variable	X-independant variable	Decades	Pearson's r	r^2	n
Ca	Mg	60s	0.94	0.88	5
		80s	0.28	0.08	34
		90s	0.67	0.45	13
		00s	0.79	0.62	14
		10s	0.55	0.30	10
		Cumulative*	0.89	0.79	76
Na	Cl	60s	0.76	0.58	5
		80s	0.84	0.71	34
		90s	0.93	0.86	13
		00s	0.99	0.98	14
		10s	0.93	0.86	10
		Cumulative*	0.88	0.78	76
Cl	Ca	60s	0.72	0.52	5
		80s	0.62	0.38	34
		90s	0.20	0.04	13
		00s	0.93	0.86	14
		10s	0.61	0.37	10
		Cumulative*	0.79	0.62	76
Na	Ca	60s	0.88	0.77	5
		80s	0.41	0.17	34
		90s	0.48	0.23	13
		00s	0.93	0.86	14
		10s	0.32	0.10	10
		Cumulative*	0.48	0.23	76
Cl	TDS	60s	0.92	0.85	4
		80s	0.89	0.79	33
		90s	0.50	0.25	11
		00s	0.99	0.98	14
		10s	-	-	-
		Cumulative*	0.44	0.19	62

The groundwater facies in the LPRB in the 1960s and 1980s was $Ca(HCO_3)_2$ (Figure 6a and b). By the 2000s, there is an observable shift to both $Ca(HCO_3)_2$ and NaCl facies (Figure 6c). In the 2010s, the groundwater is almost completely NaCl facies (Figure 6d). The fact that this shift in groundwater facies occurred within the short time span of 50 years, while the TDS still indicates freshwater, suggests an influx of Cl^- from an external source beyond natural groundwater evolution processes.

CONCLUSION

The New Jersey WMA 03 (MPRB) lies on the North Eastern Piedmont, which is underlain by low-porosity and low-permeability metamorphic and igneous bedrocks. It is a suburban land use region with a low density of major roads (NJDOT, 2018b). Only minimal road salt deicing is necessitated due to the scarcity of major roads. Time series and Schoeller graphical analyses show no significantly pronounced increasing trends in the concentrations of Ca^{2+} or Na^+. Bivariate plots of ion concentrations showed insignificant correlations: Cl^- vs Ca^{2+} ($r^2 = 0.47$, n = 130), Na^+ vs Ca^{2+} ($r^2 = 0.40$, n = 124), Na^+ vs Cl^- ($r^2 = 0.03$, n = 124) between the deicing salt ions of Ca^{2+}, Cl^-, and Na^+. The area has been underlain by a fresh groundwater facies of $Ca(HCO_3)_2$ throughout the study period, showing no significant statistical concentration increase in deicing ions: Cl^- and Na^+. These results indicate that NaCl and $CaCl_2$ from road deicing are not major sources of contamination in the MPRB. The low-porosity and low-permeability igneous and metamorphic bedrocks of the region result in minimal seepage rates of deicing materials into the groundwater. The relatively low application of deicing materials in the MPRB (20.34 ton/sq. km) may also be insufficient to effectively influence the groundwater quality.

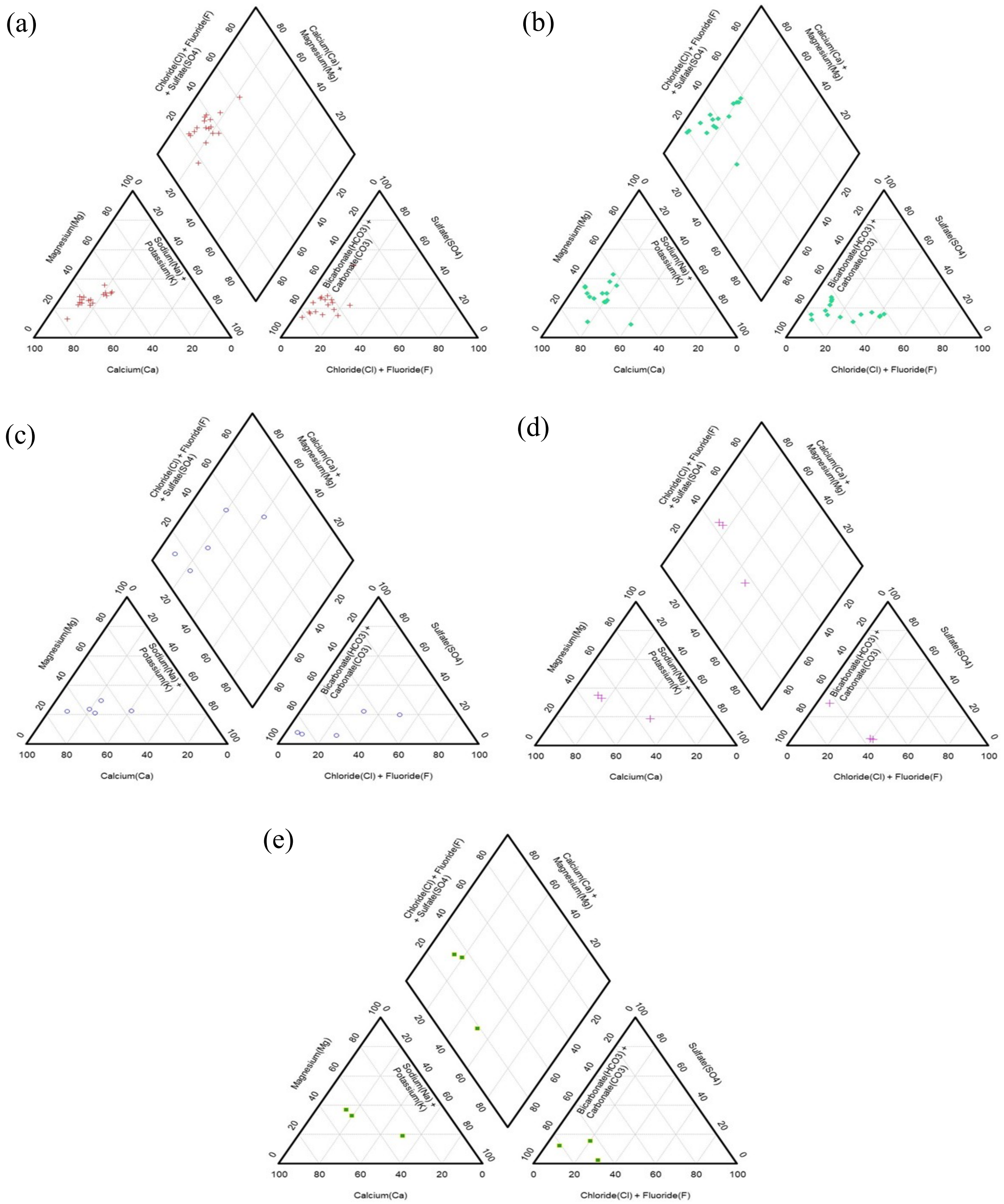


Figure 5. Piper diagrams showing the groundwater facies of the MPRB in the a)1960s, b)1980s, c) 1990s, d) 2000s, e) 2010s

Cl^- uniquely showed a much reduced concentration increase through time, and prediction interval analyses suggest minimal evidence of contamination from an external source. Nevertheless, the lack of bivariate correlation between all three deicing ions does not support a hypothesis of deicing salt contamination.

The WMA 04 (LPRB) is a densely populated urban and industrial area in which anthropogenic activities usually result in substantial contamination of soil and groundwater. This area is underlain by

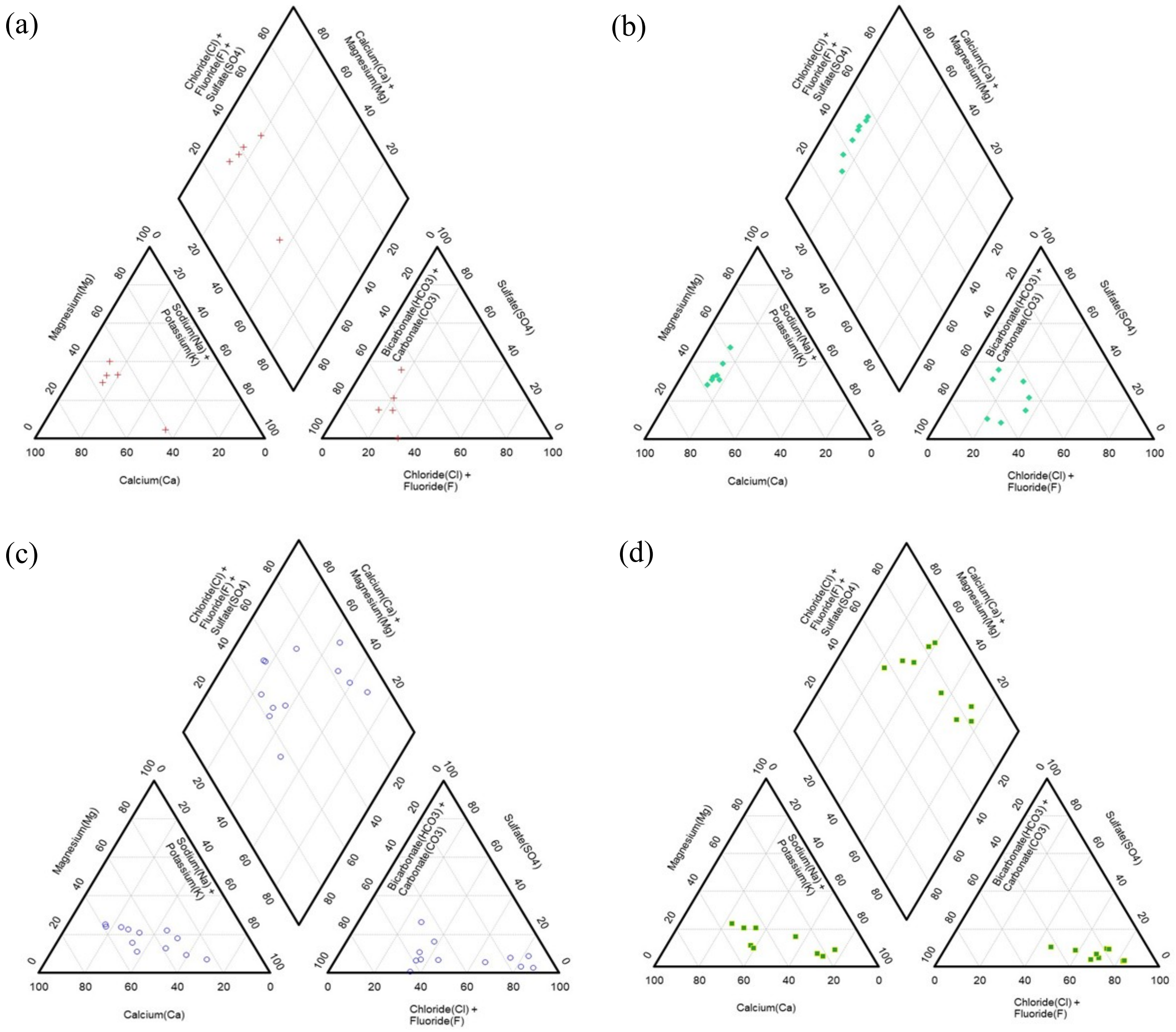


Figure 6. Piper diagrams showing the groundwater facies of the LPRB in the a)1960s, b)1980s, c) 2000s, d) 2010s.

shale and sandstone of relatively high porosity and permeability. A dense network of roads covers the area which requires a relatively heavy use of road deicing salts (64.38 tons/sq. km) in the winter season. The time series analysis of Cl^-, Na^+, and Ca^{2+} deicing ion concentrations showed sharp increasing trends throughout the study period, but Mg^{2+} did not increase at the same rate. Bivariate analyses indicated strong correlation between the deicing salt ions of Na^+ and Cl^- ($r^2 = 0.78$, n = 76) and moderate correlation between Cl^- and Ca^{2+} ($r^2 = 0.62$, n = 76), but very weak correlation between Na^+ and Ca^{2+} ($r^2 = 0.23$, n = 76). These results of the bivariate analyses suggest that there is an observable positive relationship between ions of each of the two major deicing materials, NaCl and $CaCl_2$. However, the results also suggest that there is no intermolecular relationship between the Na^+ from NaCl and Ca^{2+} from $CaCl_2$. The ion concentration and specific conductance relationships in the LPRB show larger increases in Cl^- and Na^+ concentrations at higher specific conductances with the 2000s data than the 1960s data.

Ion concentrations of Cl^-, Na^+, and Ca^{2+} appear to have increased at rates that are related to the total mass application of road salts, NaCl and $CaCl_2$. Cl^- shows the largest concentration increase, as it has a total atomic percentage of 60 between both deicing salts (NaCl and $CaCl_2$), making it the most abundant ion. Na^+ has the second largest increase as it has an atomic ratio of 1:1 in NaCl, which is by far the most extensively applied deicing salt. Ca^{2+} exhibits the smallest increase as it has an atomic ratio of 1:2 in liquid $CaCl_2$, the least commonly used deicing material. This study shows significant evidence that the groundwater in the LPRB is being contaminated by road deicing salts

This study clearly outlines the differences in groundwater chemistry between N.J. WMAs 03 (MPRB) and 04 (LPRB). In the LPRB, high concentration increases in Na^+, Cl^-, and to a lesser degree, Ca^{2+}, is indicative of the anthropogenic use of road salt, brine, and liquid calcium chloride for road deicing in the winter seasons. The relatively high rate of road deicing salt application in the dense road network of this urban region, and the high porosity and permeability of the sedimentary rocks allow for the penetration of the ions to the groundwater. That the increases in these ions are less pronounced to none existent in the MPRB is likely due to the combination of its suburban land use and low-porosity and low-porosity bedrock that reduce the seepage rate of contaminants to the groundwater. The low road density in this suburban area results in a lower amount of road deicing salt application during the winter season.

The results of this study can be used to identify the environmental characteristics of problematic regions such as the N.J. WMA 04 (LPRB) for utilization by winter maintenance management agencies to help in determining whether alternate deicing methods should be practiced in such areas. On the other hand, the identification of low problematic areas such as the WMA 03 (MPRB) is useful in minimizing time and monetary burden on the agency, and in increasing efficiency of mineral and material allocation.

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