

Long-term trends in sodium and chloride in the Mohawk River, New York: the effect of fifty years of road-salt application

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“Capsule”: *Sodium and chloride have increased in the last 50 years in this river ecosystem.*

Abstract

Ecological studies have demonstrated the adverse effects of road-salt, primarily NaCl, on water quality, flora, and fauna. In this study, we quantified changes in ionic composition and solute flux of water draining the Mohawk River Basin (9103 km²) in New York State, from 1952 to 1998. Using various statistical, graphical, and modeling techniques, we showed that concentrations of Na⁺ and Cl⁻ have increased by 130 and 243%, respectively, while other constituents have decreased or remained constant. The use of de-icing salt on roads within the watershed, which we estimate at 39 kg km⁻² day⁻¹, appears to be the primary mechanism responsible for reported increases, accounting for the increase in NaCl export from 16 to 46 kg km⁻² day⁻¹ over the 47-year period. Moreover, despite population decline within this rural upstate watershed, increased environmental stewardship, and The Clean Water Act, concentrations of Na⁺ and Cl⁻ still increased during the 1990s.

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1. Introduction

Road-salt, primarily sodium chloride (NaCl), has been used widely to aid in snow and ice removal in the United States since the 1950s (Transportation Research Board [TRB], 1974). Currently, New York State applies approximately 9.36 Mg lane⁻¹ km⁻¹ day⁻¹ (second only to Massachusetts), resulting in an annual average of roughly 454 thousand Mg of road-salt (TRB, 1991). The benefits of de-icing roadways are usually measured in terms of reduced accident rates, reduced delays, and improved accessibility. For example, a study of vehicle accident rates in four states (i.e. New York, Illinois, Minnesota, and Wisconsin), reported that the use of de-icing salts reduced the accident rate on highways by 88% (Keummel, 1992). While road-salt application has clear benefits, anthropogenic loading of NaCl has been shown to affect groundwater and surface water quality detrimentally (Hoffman et al., 1981; Wilcox, 1986a; New York State Department of Transportation [NYS-

DOT], 1993; Forman and Alexander, 1998; Panno et al., 1999), and chronic inputs over the last 50 years are thought to negatively impact human health (Calabrese and Tuthill, 1980; Foster, 2000), native flora (Hutchinson, 1970; Wilcox, 1986b; Bogemans et al., 1989; Panno et al., 1999; Richburg et al., 2001), and fauna (Fraser and Thomas, 1982; Bollinger et al., 1999).

The application of road-salt appears to have been responsible for the observed increase in Na⁺ and Cl⁻ concentrations in the Mohawk River, New York from the 1950s to the 1970s (Peters and Turk, 1981). Through thorough statistical and geochemical analyses, Peters and Turk concluded that the increase in the concentrations of sodium and chloride, during two discrete time periods (1951–1953 and 1970–1974), was caused by road-salt application.

A conceptual model of road-salt contamination of surface water discharge must acknowledge both direct surface water runoff, resulting in immediate NaCl inputs, and longer term NaCl groundwater infiltration. Substantial evidence exists for both mechanisms (Wilcox, 1986a, 1986b; Panno et al., 1999; Richburg et al., 2000; Panno et al., 2002).

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Here, building on Peters and Turk (1981), we quantify changes in ionic composition and solute flux of water draining the Mohawk River Basin. We identify potential sources of observed hydrochemical changes by quantifying the chemical, physical, and biological landscape properties thought to influence water chemistry. The objectives of our study are to:

1. Determine the change in the ionic composition of river water discharge and the flux of ions from the two periods studied by Peters and Turk to 1990–1998;
2. Quantify the trend of change in each ionic constituent over the period from 1990 to 1998; and
3. Identify potential sources of an observed increase in NaCl by comparing a pre-impact reference condition to the current state of the watershed.

2. Methods

2.1. Hydrogeologic environment

The Mohawk River Basin occupies 9103 km² of 14 central NY counties (Fig. 1) and has a gauged discharge at Cohoes Dam (lat 42°47'07" N, long 73°42'29" W). In our analysis, this basin was delineated by combining the Mohawk and Schoharie Environmental Protection Agency (EPA) watersheds (watershed 02020004 and 02020005, respectively). While similar in geographic extent, this basin differs slightly from that defined by Peters and Turk in terms of total area, which they reported as 8951 km². The climate is best defined as temperate, with annual precipitation ranging from 900 to 1500 mm/year. Variation in precipitation within the watershed is influenced by Lake Ontario and the increased elevation of the Adirondacks and Catskill Mountains to the west, north, and south, respectively.

Surface water features totaling 8322 km in length exist within the basin, encompassing perennial and intermittent streams and shorelines of lakes and reservoirs. Topography of the basin is variable, exhibiting a range of elevation from 1 to 1234 m above sea level. Basin geology is dominated by Paleozoic shales and limestones, with minor deposits of sandstone, gypsum, and halite. In sum, over 40 distinct geologic formations exist within the watershed. Deep, often calcareous, glacial/alluvial deposits occur in the lowlands proximate to the Mohawk River. Description, lineage, and accuracy of data are presented in Table 1.

Objective 1. Determine the change in the ionic composition of river water discharge and the mean daily yield of ions from the two periods studied by Peters and Turk to 1990–1998.

Water chemistry data, from 1990–1998, consisting of concentrations of Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, and SO₄²⁻ at the USGS gauging station located at Cohoes, NY (lat 42°47'07" N, long 73°42'29" W) were acquired digitally from USGS Water Quality Samples for New York (2002). It is important to note that while these data reflect daily samples, significant gaps occur over the course of record. Following Peters and Turk (1981), we calculated mean solute concentrations and determined minima and maxima. Changes in water chemistry over time were examined by comparing these values to those from Peters and Turk (1981). Mean concentrations from the 1990s were compared to means from the 1950s and 1970s using a one sample *t*-test by calculating a 95% confidence interval for the data from the 1990s (Zar, 1999) using PROC MEANS in SAS (SAS Institute, 1990). Schoeller plots and bivariate plots were employed to assess relationships within and among solute data.

To compare the current flux of ions out of the Mohawk River basin to the fluxes of the 1950s and 1970s reported by Peters and Turk, we estimated mean daily yield of ions over the period from 1990 to 1998 using monthly mean concentrations and monthly mean discharge. Concentrations were averaged within each month because data were not available for most days. Peters and Turk overcame this shortcoming by using daily specific conductance measurements and linear regressions between conductance and ion concentration to model daily ion concentrations on a daily time step. However, specific conductance measurements were scarcer than ions concentrations for the 1990–1998 period. Where no data were available for a given month, we modeled monthly mean concentration by correcting the yearly mean concentration for discharge. The correction factor used was the slope of the line of a regression of ion concentration on discharge, obtained from an analysis of covariance with concentration predicted by discharge and year. This approach corrects predictions for the dilution effect of high discharge on ion concentrations and was justified considering that the relationship between discharge and ion concentration significant at $\alpha=0.05$ for all ions, excepting Ca²⁺ and Cl⁻ (Table 2). To estimate the mean monthly yield, measured or modeled monthly mean ion concentrations were multiplied by monthly mean discharge, and these were summed and standardized to mean daily yields (in units of kg km⁻² day⁻¹). Before comparing our ion fluxes to those calculated by Peters and Turk, we adjusted the latter for the different area used in this analysis.

Objective 2. Quantify the trend of change in each ionic constituent over the period from 1990 to 1998.

To determine whether concentrations of any ions have continued to change through the period from 1990 to 1998, we used multiple regression to fit a trend to

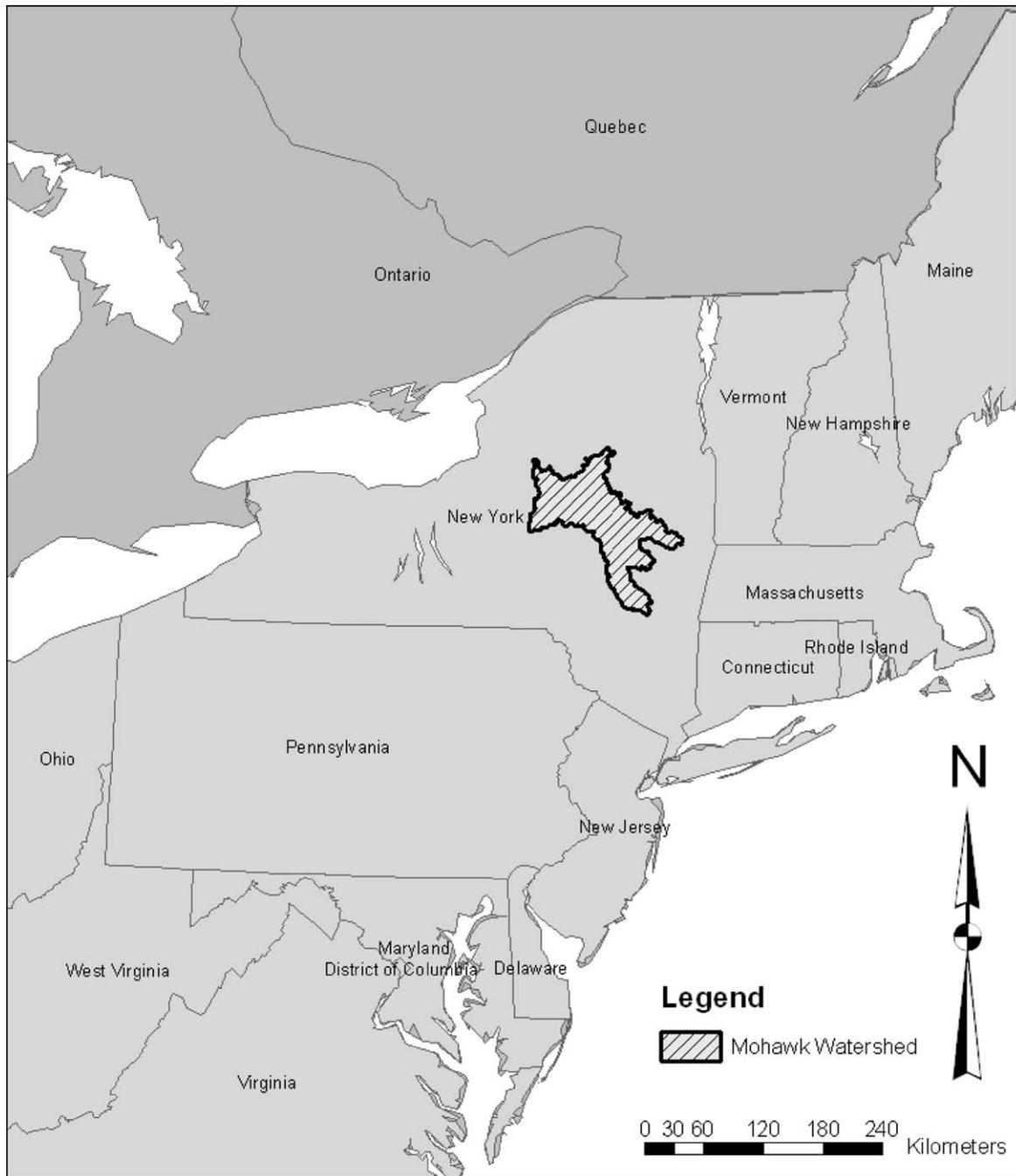


Fig. 1. Location of the Mohawk River Basin within New York State.

Table 1
GIS data layers, source and scale/resolution used in the landscape analysis of the Mohawk River Basin

Layer	Source	Scale/resolution
Topography	US Geological Survey (USGS) Digital Elevation Model (DEM)	Horizontal: 10 m, Vertical: 1 m
Land Use/Land Cover	USGS New York Land Cover Data Set (NLCD)	Horizontal: 30 m
Watershed Boundary	US Environmental Protection Agency National Hydrography Dataset (NHD)	1:100,000
Bedrock Geology	NY State Museum/NY State Geological Survey	1:250,000
Surficial Geology	NY State Museum/NY State Geological Survey	1:250,000
Hydrography	US Census Bureau, Census 2000 TIGER/Line Files	1:100,000
Roads	US Census Bureau, Census 2000 TIGER/Line Files	1:100,000

Table 2
Results of the analysis of covariance for solute concentration as a function of year and discharge^a

Ion	Total DF	Independent variable	Slope	Type III SS	MS	F-value	Probability
Na ⁺	76	Year	–	192.711	38.542	3.35	0.0091
		Discharge	–3.17E-03	52.418	52.418	4.55	0.0364
K ⁺	76	Year	–	0.608	0.121647	1.08	0.3769
		Discharge	3.34E-04	0.582	0.582	5.18	0.0259
Mg ²⁺	76	Year	–	7.469	1.494	1.66	0.1549
		Discharge	–1.01E-03	5.295	5.295	5.9	0.0177
Ca ²⁺	76	Year	–	121.062	24.212	1.69	0.1478
		Discharge	–2.61E-03	35.632	35.632	2.49	0.119
Cl [–]	80	Year	–	685.720	97.960	2.95	0.0090
		Discharge	–4.33E-03	98.098	98.098	2.95	0.0902
SO ₄ ^{2–}	80	Year	–	292.592	41.799	2.23	0.0415
		Discharge	–4.49E-03	105.254	105.254	5.61	0.0205

^a Slope refers to the estimated response of concentration to discharge ($\text{mg s l}^{-1} \text{m}^{-3}$).

concentrations over the time period using date and discharge as independent variables (Zar, 1999) in PROC REG in SAS (SAS Institute, 1990). Ion concentrations appeared to be related negatively to discharge, and thus, discharge was included to increase the power of the analysis and minimize any confounding effects of a change in discharge over the period of study. For this analysis, a significance level of $\alpha = 0.05$ was used.

Objective 3. Identify potential sources of an observed increase in NaCl by comparing a pre-impact reference condition to the current watershed HGS.

To confirm that water chemistry collected during the early period of record (i.e. 1950s) represents a “pre-impact” condition (sensu Peters and Turk), water/mineral interactions were simulated using a reaction path model [i.e. PCWATEQ, an IBM-PC version of WATEQ water chemistry and equilibrium model (Rollins, 1988)] to speciate water samples (USGS, 1952) into potential equilibrium phases according to saturation indices.

To evaluate potential anthropogenic impacts, landscape data including road distribution by class, human population, and current land use/land cover were acquired. Population time series were available only by county (US Department of Commerce, Bureau of Census, 1995, 2002). Therefore, to estimate the population of the watershed, the population density of each county was multiplied by its area in the watershed, and these values were summed for all counties.

We estimated an annual loading rate of NaCl as road-salt and through human excreta and household waste to the watershed. Using ArcView 3.2a GIS (ESRI, Inc., 2000), we calculated the length of road within the watershed (US Department of Commerce, Bureau of the Census, 1995 TIGER/Line data). We used a rate of $9.36 \text{ Mg lane}^{-1} \text{ km}^{-1} \text{ year}^{-1}$, which is a guideline for

the entire state (NYSDOT, 1999), and multiplied this application rate by the length and number of lanes in each of three general road classes: primary (interstate highway), secondary (intrastate highway), and local (urban/rural). To estimate the NaCl addition through human excreta and household waste, we used a high value of $12.4 \text{ kg Cl}^{-1} \text{ person}^{-1} \text{ year}^{-1}$ (Struzeski, 1971) and assumed that an equivalent amount of Na⁺ was released.

Assumptions: Throughout this research, we relied on several simplifying assumptions: specifically, that no significant introduction of geologic materials has occurred during the period of record and that reported ionic concentrations are free of sampling bias. Additionally, the following assumptions were employed in the ANCOVA analysis: errors are independent and normally distributed, the covariate (discharge) is not affected by the categorical variable (year), the response between concentration and discharge can be approximated by a linear function, and this relationship is the same for all years (Kuehl, 2000). Since this ANCOVA was used to calibrate a model and not test hypotheses, violation of these assumptions is probably insignificant, especially because of the relatively small effect that discharge had on the modeled concentrations. In the multiple regression analysis, the following assumptions were made: water samples were randomly selected, concentrations are normally distributed at each particular combination of independent variables, and the error in the independent variables is small compared to the error in concentration (Zar, 1999).

3. Results

Objective 1. Determine the change in the ionic composition of river water discharge and the mean daily yield of ions from the two periods studied by Peters and Turk to 1990–1998.

The mean, minimum, and maximum concentrations of Na^+ and Cl^- from the 1990s were all greater than their counterparts from both the 1950s and 1970s (Table 3). The 95% confidence intervals for these ions in the 1990s did not include either the 1950s or 1970s means. By comparison, mean SO_4^{2-} and Ca^{2+} concentrations were slightly lower than those from both earlier time periods, and the mean K^+ concentration was close to the 1950s and 1970s means. The mean concentration of Mg^{2+} in the 1990s was slightly greater than means from both earlier periods. As shown in Table 3, the magnitude of the change in Na^+ and Cl^- concentrations was much greater than that of any other changes.

The estimated mean daily yields of Ca^{2+} , Mg^{2+} , and K^+ for the 1990s are very similar to the estimates from the 1950s, all showing a change of less than 10% (Table 4). At the other extreme, Na^+ and Cl^- increased dramatically, by 130 and 243%, respectively. The estimated yield of SO_4^{2-} showed a decrease of 23%. Compared to the estimates from the 1970s, all ion yields from the 1990s showed a decrease in mean daily yield, except Na^+ and Cl^- , which showed an increase of 34 and 40%, respectively. The total estimated daily loss of Na^+ and Cl^- in the 1990s was $46 \text{ kg NaCl km}^{-2} \text{ day}^{-1}$.

Objective 2. Quantify the trend of change in each ionic constituent over the period from 1990 to 1998.

Table 3
Ionic composition of water in relation to collection period.^a

Ion	Collection period	Mean (standard deviation)	Maximum	Minimum	Lower bound of 95% CI	Upper bound of 95% CI
Na^+	52–53	6.4 (2.9)	12	2.9	12.325	14.085
	71–74	9.3 (3.6)	17	3.6		
	90–98	13.21 (3.9)	27	6.2		
K^+	52–53	1.3 (0.6)	2.2	0.3	1.282	1.435
	71–74	1.3 (0.4)	2.5	0.5		
	90–98	1.4 (0.34)	2.5	0.7		
Mg^{2+}	52–53	4.8 (1.2)	8.8	2	5.399	5.893
	71–74	5.3 (1.0)	7.6	3.4		
	90–98	5.6 (1.1)	7.3	2.8		
Ca^{2+}	52–53	31.8 (6.1)	40	14	30.626	32.513
	71–74	33.0 (5.1)	45	21		
	90–98	31.6 (4.2)	39	21		
Cl^-	52–53	7.7 (4.0)	16	1.1	18.949	21.813
	71–74	13.5 (4.9)	28	5.1		
	90–98	20.4 (6.5)	47	8.6		
SO_4^{2-}	52–53	26.0 (6.5)	39	15	18.650	20.917
	71–74	25.6 (5.7)	46	15		
	90–98	19.8 (5.1)	32	11		
Discharge	52–53	177.7 (200.9)	1540	7		
	71–74	210.9 (205.8)	1555	12		
	90–98	164.9 (209.8)	2622	9		

^a Concentration is in units of mg l^{-1} , and discharge in $\text{m}^3 \text{ s}^{-1}$. Values from the 1950s and 1970s are from Peter and Turks (1981). Values from the 1990s were calculated from USGS data (2002).

Table 4
Estimated mean yields of ions from the Mohawk River watershed in units of $\text{kg km}^{-2} \text{ day}^{-1}$ ^a

Ion	Mean yields			Change from the 1950s to 1990s		Change from the 1970s to 1990s	
	1952–1953	1971–1974	1990–1998	mg l^{-1}	%	mg l^{-1}	%
Na^+	7.768	13.334	17.863	10.095	129.959	4.530	33.973
K^+	2.330	2.763	2.172	-0.158	-6.780	-0.591	-21.376
Mg^{2+}	8.014	9.322	8.149	0.135	1.689	-1.172	-12.578
Ca^{2+}	46.205	58.497	47.009	0.804	1.740	-11.488	-19.638
Cl^-	8.201	20.079	28.130	19.929	243.015	8.051	40.095
SO_4^{2-}	36.343	44.042	28.068	-8.275	-22.769	-15.974	-36.270

^a Estimates for the 1950s and 1970s are from Peters and Turk (1981). Estimates for the 1990s were made by multiplying mean monthly concentrations by mean monthly discharge. See text for more detail.

The results of the multiple regression analysis of ion concentrations vs. date and discharge suggest that most ion concentrations have not increased from 1990 to 1998 (Table 5). However, both Na^+ and Cl^- showed a statistically significant trend of increase over this period, at rates of 0.0017 and 0.0027 $\text{mg l}^{-1} \text{ day}^{-1}$, translating into an increase of approximately 5 and 8 mg l^{-1} over the entire period, respectively. A bivariate plot of Na^+ and Cl^- concentrations suggests that a halite source is responsible for the increase in Na^+ and Cl^- , as seen in the nearness of the observed relationship to a 1:1 line (Fig. 2).

Objective 3. Identify potential sources of an observed increase in NaCl by comparing a pre-impact reference condition to the current watershed HGS.

Using the reaction-path model PCWATEQ and mean ionic concentrations for 1950s surface water, we determined that the Mohawk River Basin is undersaturated with respect to calcite (CaCO_3), calcite's polymorph

Table 5
Results of the multiple regression analysis of solute concentration over time, corrected for discharge^a

Ion	Slope	Standard error	<i>t</i> -value	Probability	Model adjusted <i>r</i> ²
Na^+	0.0017	0.000804	2.13	0.0367	0.1503
K^+	0.0000	7.65E-05	0.09	0.9313	-0.0016
Mg^{2+}	0.0000	0.000219	-0.04	0.9685	0.1903
Ca^{2+}	-0.0004	0.000879	-0.42	0.677	0.12
Cl^-	0.0027	0.00136	2.00	0.0493	0.1051
SO_4^{2-}	0.0002	0.00101	0.20	0.8422	0.1927

^a Slope refers to the least-squares estimate of the change in concentration over time ($\text{mg l}^{-1} \text{ day}^{-1}$).

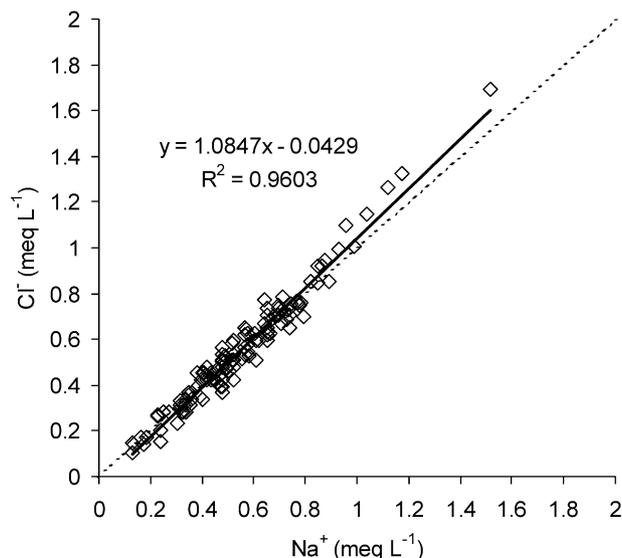


Fig. 2. Na^+ vs. Cl^- concentration for all samples from 1990–1998.

aragonite (CaCO_3), and dolomite ($\text{CaMg}(\text{CO}_3)_2$). Additionally, there is evidence that the evaporite minerals gypsum ($\text{CaSO}_4 \cdot n\text{H}_2\text{O}$), anhydrite (CaSO_4), and halite (NaCl) also serve to modify the surface waters. This is substantiated by the classic carbonate/gypsum co-dominated signature of 1950s waters seen in the Schoeller plot (Fig. 3) and qualitative assessment of watershed geology.

Analysis of TIGER/Line files shows that, within the Mohawk River Basin, there are 14,008 km of road that we distributed across three general road classes, primary (i.e. multiple lane interstate highway; 331 km), secondary (i.e. multiple lane intrastate highway; 1,752 km), and local (i.e. urban and rural two lane improved surface; 11,925 km) roads. Of the 20 recognized land-use/land-cover classes reported within the watershed, two classes, mixed forest and cropland/pasture accounted for 83% of the total watershed area, or 49.61 and 33.75%, respectively. Urban classes contributed less than 6% of the total area. Population density and estimated watershed population had reached its highest levels during the 1970s with five of 14 counties showing population declines during the 1990s, resulting in an estimated population reduction of 13,778 (Table 6).

We estimated the mean annual loading rate of road-salt as 14 metric tons $\text{NaCl km}^{-2} \text{ year}^{-1}$, or 39 $\text{kg NaCl km}^{-2} \text{ day}^{-1}$. Anthropogenic loading through excretia and household waste was estimated at 2.0 $\text{kg NaCl km}^{-2} \text{ day}^{-1}$.

4. Discussion

The results of this study suggest that the ionic composition of river water did significantly change from our reference condition through the 1990s. The most striking change is that of Na^+ and Cl^- , the mean concentrations of which both increased by more than 2-fold from the 1950s. That the 95% confidence intervals, which we calculated with the 1990s data, do not include the means from the 1950s or 1970s demonstrates that this increase is statistically significant; assuming that sampling bias was insignificant, this is likely a real difference. The increase in Na^+ and Cl^- concentrations from the 1970s to the 1990s was somewhat greater than the increase reported by Peters and Turk (1981) from the 1950s to 1970s, suggesting that the increase has not been constant.

These dramatic increases are in contrast with changes in other ionic constituents. It is possible that the observed change in Mg^{2+} from the 1950s to the 1990s is a result of differing methodologies; with the 1950s data determined by difference (Peters and Turk, 1981) rather than measured directly, as in the 1970s and 1990s. Sulfate had a slight decrease from the 1950s to 1970s, followed by a more pronounced decrease to the 1990s.

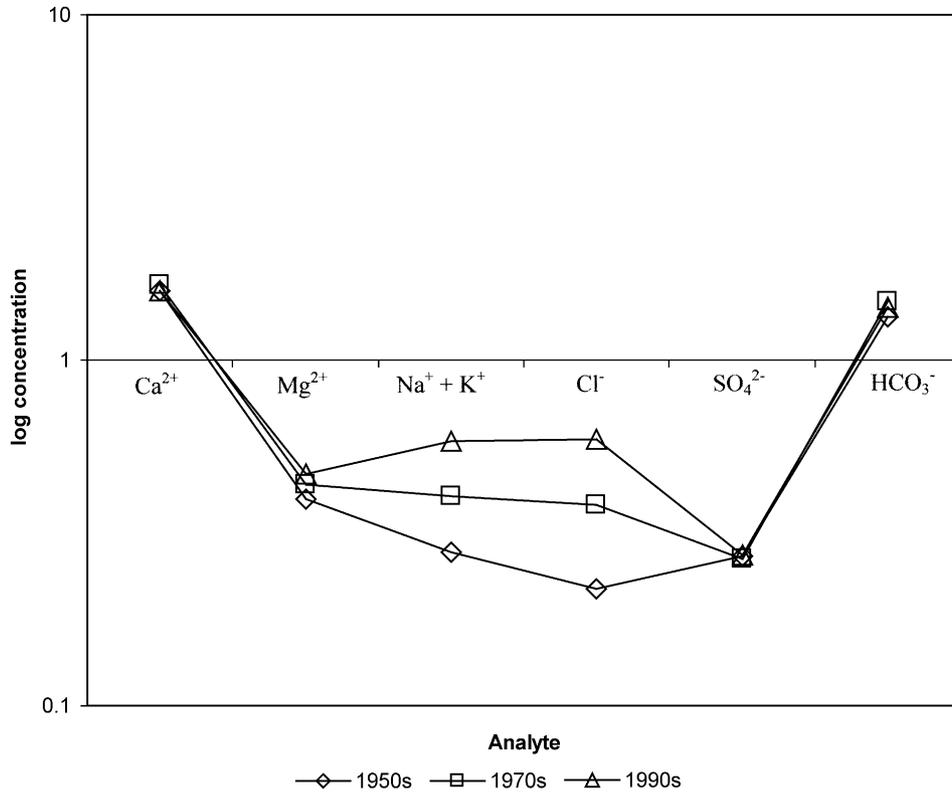


Fig. 3. A Schoeller depicting log (concentration) of major ions for the 1950s, 1970s, and 1990s.

Table 6

Population dynamics in the Mohawk River watershed. The population contributed by each county in the watershed was estimated by multiplying the population density for the whole county by the county area in the watershed. (Source: U.S. Census)

County	Area in watershed		Population density (people ha ⁻¹)			Calculated population in watershed		
	(ha)	(%)	1950	1970	1999	1950	1970	1999
Albany	29795	22	1.73	2.08	2.11	51680	61904	62960
Delaware	6635	2	0.12	0.12	0.12	776	781	799
Fulton	91897	67	0.37	0.38	0.38	33997	35073	35027
Greene	61478	36	0.17	0.19	0.28	10374	11959	17320
Hamilton	60405	13	0.01	0.01	0.01	530	609	669
Herkimer	177864	47	0.16	0.18	0.17	28940	31874	29845
Lewis	4400	1	0.07	0.07	0.08	297	312	362
Madison	6022	4	0.27	0.37	0.42	1625	2211	2499
Montgomery	106194	100	0.56	0.53	0.47	59594	55883	50363
Oneida	153907	47	0.68	0.84	0.70	105425	129165	107712
Otsego	7377	3	0.19	0.21	0.23	1425	1578	1702
Saratoga	23501	11	0.34	0.56	0.91	8057	13103	21417
Schenectady	42270	78	2.63	2.97	2.67	111017	125493	112711
Schoharie	138522	85	0.14	0.15	0.20	19400	21150	27597
Total	729475					302721	344451	330673

This decline is likely a result of decreases in atmospheric deposition of sulfur in the Northeast (Driscoll et al., 1998). For example, the mean concentration of SO₄²⁻ in precipitation decreased from 4.74 in 1980 to 1.81mg l⁻¹ at a site just outside of the Mohawk River Watershed (National Atmospheric Deposition Program/National Trends Network, 2002; site NY52).

The only plausible source of NaCl that can account for the large mean daily yields estimated in this study is de-icing salt. Treating the 1950s data as a pre-impact reference condition, road-salt is responsible for an export of approximately 30 kg NaCl km⁻² day⁻¹. This value is comparable to our estimate of NaCl additions to the watershed as road-salt (i.e. 39 kg NaCl km⁻²

day⁻¹). Of these two values, the first is likely a slightly conservative estimate, since we are assuming that the 1950s data represent pre-impact conditions. However, some NaCl contamination via road-salt may have been occurring in the 1950s. Our estimate of NaCl added to the watershed as road-salt is based on an extrapolation of a NYSDOT guideline and should be taken only as a rough estimate. For example, this guideline does not take into account that portions of this watershed receive some of the largest snowfalls in the state, and local municipalities are likely to apply road-salt at different rates. For example, Heisig (2000) reported that NaCl application rates in three southeastern New York watersheds (Croton, Catskill, and Delaware) ranged from 21 to 170 Mg ln⁻¹ km⁻¹ year⁻¹. Despite the potential shortcoming of our general estimate, the closeness of these two values further supports the idea that road-salt is the source of the observed increase in NaCl export, especially if one considers that some portion of road-salt enters ground water and does not immediately exit the watershed via surface water pathways. Additionally, ion exchange reactions in the soil involving Na⁺ and Cl⁻ likely play a role in this difference (Sparks, 1995; Rhodes et al., 2001).

High concentrations of road-salt have been shown to detrimentally impact ecosystem structure and function (Wilcox, 1986a; Panno et al., 1999; Richburg et al., 2001). These concentrations are higher than the surface water values we report here. However, values reported here represent the cumulative flux of road-salt within the watershed. Road-salt is not evenly distributed across the landscape, and areas within the watershed likely exceed critical ecological thresholds (e.g. surface water near to highways). Quantifying the relationship between local ionic concentration and flux and total discharge would provide a means of assessing ecological response to changes measured at the watershed scale.

Remediation of NaCl contamination has been estimated at 10 million dollars (US) annually in the Northeast and Northern Midwest (TRB, 1991). A recent government publication (NYSDOT, 1999) has identified alarming groundwater concentrations within the counties that comprise the Mohawk River Basin; chloride concentrations found in wells and springs of six of the 14 contributing counties range from 0.2 to 10800 mg/l, with a mean value of 62.12 mg/l ($n=288$). This same report suggests that persons on low sodium diets should not ingest water with sodium concentrations greater than 20 mg l⁻¹. Besides suggesting an additional impact of road-salt application, these results help to explain the disparity between mean daily yields and road-salt application.

Although it appears that road-salt application has had a substantial impact on the ionic composition of surface and ground water in this watershed, it is interesting to note that the Mohawk River Watershed is

ranked by the EPA as having “better water quality, [and] low vulnerability.” (EPA, 2002). Considering that less than 6% of the watershed is urban, it is likely that other New York State watersheds are even more impacted by the application of road-salt.

The substantial increases in Na⁺ and Cl⁻ concentrations from earlier periods to the 1990s do not indicate whether concentrations are continuing to change or have stabilized. One might expect them to have stabilized, in light of estimated population decline from the 1970s, the passage of the Clean Water Act in 1977, and a greater public awareness of environmental issues. However, the results of our multiple regression analysis indicate that concentrations of these two ions continued to increase in the 1990s.

Our research provides insight into the general patterns of long-term ionic concentration and flux in the Mohawk River Basin and the landscape properties potentially responsible for the measured changes. Subsequent research should focus on (a) identifying how temporal variability in local hydrologic features, e.g. lakes and wetlands, affects watershed discharge, both within and among watersheds; (b) the relative contribution of short and long term sources to surface water discharge within and among watersheds; and (c) the integration of landscape (i.e. watershed) and local (i.e. wetland, contributing source area) properties into a classification scheme capable of evaluating ionic concentration and flux, and ecological response at disparate scales.

5. Conclusion

“In every respect, the valley rules the stream” (Hynes, 1975). In this study, we quantified the changes in the ionic composition and solute flux of the Mohawk River Basin over a 47-year period, evaluating landscape properties potentially responsible for the observed hydrochemical changes. Based on these analyses, we draw several conclusions.

1. Concentrations of Na⁺ and Cl⁻ in the Mohawk River have increased substantially from the 1950s to the 1990s, while other constituents have decreased or remained the same.
2. Despite population decline within the watershed and the Clean Water Act of 1977, concentrations of Na⁺ and Cl⁻ have continued to increase in the 1990s. Further, while concentration and flux does show characteristic seasonal variation minimum concentrations, during the 1990s, are still substantially higher than pre-impact conditions.
3. The use of de-icing salt on roads, an estimated 39 kg km⁻² day⁻¹ addition, appears to be the primary

mechanism responsible for the increase in concentration, accounting for the increase in NaCl export from 16 to 46 kg km⁻² day⁻¹ from the 1950s to the 1990s.

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References

- Bogemans, J., Nierinck, L., Stassart, J.M., 1989. Effect of deicing chloride salts on ion accumulation in spruce (*Picea abies* (L.) sp.). *Plant and Soil* 113, 3–11.
- Bollinger, T. K., Mineau, P., Brownlee, L.L., Wickstrom, M.L., 1999. Toxicity of road-salt to House Sparrows. Poster presentation. Society of Toxicology and Chemistry.
- Calabrese, E.J., Tuthill, R.W., 1980. The influence of elevated levels of sodium in drinking water on elementary and high school students in Massachusetts. *Journal of Environmental Pathology and Toxicology* 4, 151–165.
- Driscoll, C.T., Likens, G.E., Church, M.R., 1998. Recovery of surface waters in the northeastern US from decreases in atmospheric deposition of sulfur. *Water, Air Soil Pollution* 105, 319–329.
- ESRI, Inc. 2000. ArcView 3.2a. Redlands, California, USA.
- Forman, R.T.T., Alexander, L.E., 1998. Roads and their major ecological effects. *Annual Review of Ecology and Systematics* 29, 207–231.
- Foster 2000. In “Reducing Cancer Mortality: A Geographical Perspective” Available online: (<http://www.elements.nb.ca/theme/transportation/salt/salt.htm>).
- Fraser, D., Thomas, E.R., 1982. Moose-vehicle accidents in Ontario: relation to highway salt. *Wildlife Society Bulletin* 10, 261–265.
- Heisig, P.M., 2000. Effects of residential and agricultural land uses on the chemical quality of baseflow of small streams in the Croton Watershed, Southeastern New York. New York Department of Environmental Protection. U.S. Geologic Survey, Troy, NY.
- Hoffman, R.W., Goldman, C.R., Paulson, S., Winters, G.R., 1981. Aquatic impacts of deicing salts in the central Sierra Nevada Mountains, California. *Water Resources Bulletin* 17, 280–285.
- Hutchinson, F.E., 1970. Environmental pollution from highway de-icing compounds. *Journal of Soil and Water Conservation* 25, 144–146.
- Hynes, H.B., 1975. The stream and its valley. IN Johnson and Gage. 1997. A landscape approach to analyzing aquatic ecosystems. *Freshwater Biology* 37, 113–132.
- Kuehl, R.O., 2000. Design of Experiments Statistical Principles of Research Design and Analysis, 2nd ed. Duxbury Thomson Learning, New York.
- Keummel, D. A. 1992. The public’s right to wintertime traffic safety. Transportation Research Board, 3rd annual International Symposium on Snow Removal and Ice Control Technology. Minneapolis, MN. summary of data Available online: (<http://www.saltinstitute.org>).
- National Atmospheric Deposition Program/NTN. 2002. <http://nadp.sws.uiuc.edu/New York State Department of Transportation>. 1993. Highway maintenance guidelines; snow and ice control.
- New York State Department of Transportation. 1999. NYSDOT guidance—road-salt contamination: procedures to evaluate and resolve road-salt contamination complaints.
- Panno, S.V., Hackley, K.C., Hwang, H.H., Greenberg, S., Krapac, I.G., Landsberger, S., O’Kelly, D.J. 2002 Source identification of sodium chloride contamination in natural waters: Preliminary results. In Proceedings of the 12th Annual Conference of the Illinois Groundwater Consortium. Available online <http://www.siu.edu/ordea/igc/index.html>.
- Panno, S.V., Nuzzo, V.A., Cartwright, K., Hensel, B.R., Krapac, I.G., 1999. Impact of urban development on the chemical composition of ground water in a fen-wetland complex. *Wetlands* 19, 236–245.
- Peters, N.E., Turk, J.T., 1981. Increases in sodium and chloride in the Mohawk River, New York, from the 1950’s to the 1970’s attributed to road-salt. *Water Resources Bulletin* 17, 586–597.
- Rhodes, A.M., Newton, R.M., Pufall, A., 2001. Influences of land use on water quality of a diverse New England watershed. *Environmental Science and Technology* 35, 3640–3645.
- Richburg, J.A., Patterson, W.A. III, Lowenstein, F. Effects of road-salt and *Phragmites australis* on the vegetation of a western Massachusetts calcareous lake-basin fen. *Wetlands* 21, 247–255.
- Rollins, L. 1988. PCWATEQ: A simple, interactive PC version of the water chemistry analysis program WATEQ-F.
- SAS Institute Inc. 1990. SAS/STAT release 7.0 edition. Cary, North Carolina, USA.
- Sparks, D.L., 1995. Environmental Soil Chemistry. Academic Press, San Diego, CA.
- Struzeski, Ed1971. Environmental impact of Highway Deicing. US Environmental Protection Agency, Edison, New Jersey, Water Quality Lab., 11040-GKKK, 120 pp.
- Transportation Research Board. 1974. NCHRP Synthesis of Highway Practice 24.
- Transportation Research Board. 1991. Highway Deicing: Comparing Salt and Calcium Magnesium Acetate. Special Report 235. Available online: (www.nas.edu/frb/publications/sr235.html).
- US Department of Commerce, Bureau of the Census.1995. New York State population by county.
- US Department of Commerce, Bureau of the Census.2002. New York State population by county.
- US Geologic Survey. 1952. Surface Water Supply, North Atlantic Slope Basins, New York to York River. US Geologic Survey water-supply paper 1250 (water quality).
- US Geologic Survey Water Quality Samples for New York 2002. Available online: (<http://waterdata.usgs.gov/ny/nwis/qwdata>).
- Wilcox, D.A., 1986a. The effects of deicing salts on water chemistry in Pinhook Bog, Indiana. *Water Resources Bulletin* 22, 57–65.
- Wilcox, D.A., 1986b. The effects of deicing salts on vegetation in Pinhook Bog, Indiana. *Canadian Journal of Botany* 64, 865–874.
- Zar, J.H., 1999. Biostatistical Analysis Fourth Edition. Prentice Hall, Upper Saddle River, NJ, USA.