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Long-Term Sodium Chloride Retention in a Rural Watershed: Legacy Effects of Road Salt on Streamwater Concentration

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Sodium and chloride concentrations and export increased from 1986 to 2005 in a rural stream in southeastern New York. Concentrations increased 1.5 mg/L per year (chloride) and 0.9 mg/L per year (sodium), and export increased 33 000 kg/year (chloride) and 20 000 kg/year (sodium) during this period. We estimate that salt used for deicing accounted for 91% of the sodium chloride input to the watershed, while sewage and water softeners accounted for less than 10% of the input. Road salt use in the watershed did not increase during the study, but sodium and chloride from sewage and water softeners is likely to have increased slightly due to a small increase in population. Increased input from sewage and water softeners cannot account for the increase in concentration and export from the watershed. Model results suggest that the increase in streamwater concentration and export was likely due to a lag effect of long-term road salt use and subsurface build-up.

Introduction

Sodium chloride is widely used as a deicing agent in northern North America and Europe. The use of salt to deice roadways began around the 1940s (*1*, *2*) and increased rapidly until about 1970 and then again after 1990 (*2*). Continued increases are cause for concern, not only for humans because of the effects of increased sodium and chloride in drinking water (*2*) and the corrosive effects on cars, bridges, and other structures, but because of effects on ecosystems (*3*). Sources of sodium and chloride to ecosystems include road salt, oil field brine, water softeners, septic and sewage effluent, natural salt deposits, agriculture (fertilizer and livestock), rock weathering, and wet and dry deposition (*4–7*). In the snowbelt areas of North America, increases in surface water chloride over background levels are usually associated with increases in impervious surfaces and urbanization (*8–10*), road density (*11*), and human population density (*12*). Salt can enter a water body via overland flow as well as subsurface flow (*13*). Some recent work shows that chloride can be retained in soil (*9*, *14*). Long-term measurement (*6*, *15*) as well as modeling studies (*5*, *16*) show a lag effect of chloride entering streams suggesting that, even if salt input decreases or ceases, concentrations in surface waters may continue to increase, possibly for decades.

We used a 20-year record of sodium and chloride concentration and export in a rural stream together with estimates of sodium and chloride sources to the watershed to evaluate the importance of various sources, how they have changed over time, and how they relate to export from the watershed. To aid in interpreting these data, we used a simple mass balance model to estimate groundwater and streamwater chloride concentrations, export, and net retention over time.

Materials and Methods

The study site is the East Branch of Wappinger Creek and its watershed in Dutchess County, NY. The watershed area is 6243 ha, and the land use is 91% forested or open field and 9% residential and commercial. There are 136 km of road surface in the watershed (3.9 km of them are dirt roads) and 6 ha of parking surface. The village of Millbrook with a 2005 population of 1559 is the only municipality within this watershed. The Millbrook sewage treatment plant is approximately 3 km upstream from the sampling site for this project. Total population of the watershed in 2005 was 2539. Approximately 44% of the people in the watershed are served by private wells and septic systems, and the remainder use the Millbrook village public water supply and sewage system.

Sample Collection. Stream samples were collected at the end of every month at the Cary Arboretum, Institute of Ecosystem Studies (IES), in Millbrook, NY (N41.786 W073.741). Samples were collected when the stream was as near base flow as possible; however, base flow varied seasonally and was generally higher in winter than summer. Samples collected between 1985 and 1998 were not filtered and were stored in the light at room temperature before analyses were completed. Samples from January 1999 onward were filtered using glass fiber filters and stored in the dark at 4 °C until analyses were completed. Export estimates were made using measured concentrations and discharge, which was estimated using rating curves and stream height measurements.

Input Source Estimation. Sources of sodium and chloride in the watershed were estimated using a combination of data sources. Municipal road salt application in the watershed was estimated using road surface length (lane miles) in the watershed together with the application rate of anti-icing salt used by several local substations served by the New York State Department of Transportation (NYS DOT). The NYS DOT provided data on the amount of salt used for the winter of 1996–1997 through winter 2004–2005. We considered winter salt used as a source for the following calendar year (e.g., salt in winter 1996–1997 was a source for calendar year 1997). To estimate salt used per winter before 1997, we used a regression between yearly total snow depth at IES and total anti-icing salt used based on data from 1997 to 2005 ($n = 9$ years, $r^2 = 0.54$). We estimated commercial and residential anti-icing salt by estimating the area of parking areas in the village of Millbrook and assumed the same salt application rate used by the NYS DOT. We estimated the area of parking lots using the Dutchess County Online Parcel Access Map (http://geoaccess.co.dutchess.ny.us/parcelaccess/), which provided parking area size and date established. Note that a 16% solution of calcium chloride was used by the

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transportation department to control dust on dirt roads during summer, the mass of chloride from which was 0.1% of the total mass of sodium chloride used for winter anti-icing. We included the chloride from calcium chloride dust control as part of our road salt estimation.

We estimated water softener salt by assuming that all houses in the watershed outside of the village of Millbrook had water softeners. This is likely to be an overestimate. The village of Millbrook receives municipal water from a shallow well field, which yields water with a low mineral content making water softeners unnecessary. Houses outside of the Millbrook village receive water from individual wells, usually drilled deep into the bedrock, which often supply hard water. We determined the number of houses in the watershed and the year they were built using the Dutchess County Online Parcel Access Map. We used an estimate of 125 kg per year water softener salt used per house based on an average family size of 2.6 people (US Census Bureau), 380 L of water per person per day (*17*), an average hardness (mineral content) level for this area of 2.6 grains/L (*18*), and an average water softener removal rate of 7370 grains removed per kg sodium chloride used (*19*).

We calculated sewage (septic and sewage treatment plant) input to the watershed using an estimate of 3.3 kg chloride per person per year by excretion, 9.1 kg chloride per person per year from other household wastes, 0.73 kg per person per year from chlorination at the sewage treatment plant (*6*), and 4.95 kg sodium per person per year from $NaHCO_3$ used at the Millbrook sewage treatment facility to neutralize pH. We calculated sodium input from excretion and household wastes using an equivalent chloride to sodium ratio of 1.2 (molar ratio of seawater).

We estimated wet deposition of sodium and chloride using precipitation collected at IES. Samples were collected on an event basis using the wet side of an automatic wet–dry collector. We estimated dry deposition as net throughfall flux. Throughfall samples were collected from 1993 to 1999 in a forested area near the precipitation collection station. Twenty funnel/bottle throughfall collectors were placed randomly beneath the forest canopy, and the throughfall solution was collected weekly during the spring, summer, and fall. In the winter, these were replaced by 20 polyethylene buckets to collect ice and snow, which were collected biweekly. Two additional collectors were placed in the open for bulk deposition estimates. Dry deposition was throughfall flux (samples collected under canopy) minus bulk flux (samples collected in the open).

We estimated weathering using a chloride concentration measurement of 0.6 mg/L taken in 1905 from the East Branch of Wappinger Creek near Millbrook, NY (*20*). Because 1905 was prior to the use of deicing salt and water softeners, we assumed that all of the stream export in 1905 resulted from atmospheric deposition and rock weathering. Using an estimated flow of 1 m^3/s, which is the average discharge for our station, we estimated stream chloride export in kg per year. Using an equivalent chloride to sodium ratio of 1.2 (molar ratio of seawater), we estimated sodium associated with chloride. In addition to the sodium that is associated with chloride, we assumed that 22% of the sodium in the stream is not associated with chloride (*21*). We subtracted wet and dry deposition from the estimated stream export of sodium and chloride based on the 1905 concentration to estimate the rock weathering component.

All chemical analyses were completed at the IES Rachel Carson Analytical Facility. Chloride concentrations were determined using a Dionex 500 DX ion chromatograph, and sodium concentrations were determined using a Perkin-Elmer AAnalyst 300 atomic absorption spectrometer.

Model. To help interpret our data, we created a simple, spreadsheet-based model of chloride dynamics in the watershed (Figure 1). The model calculates a watershed mass balance for water and chloride with an annual time step. Water is input to the watershed by precipitation, and 50% of the precipitation is assumed to be lost to evapotranspiration on an annual basis (*22*). The remaining 50% is added to a groundwater pool, the capacity of which is fixed, so that an amount of water equal to 50% of the precipitation leaves the groundwater pool and becomes streamwater each year. Chloride is input to the watershed through all of the sources discussed above. A small fraction of the chloride (called the bypass fraction) flows directly to the stream through occasional overland flow or from impervious surfaces, and the remainder is transferred to the groundwater pool. (Here we use "groundwater" as an analogue for all subsurface chloride pools.) This input of chloride is used to calculate the concentration of chloride in the groundwater pool each year. The export of chloride from the groundwater pool into streamwater was calculated from the water drainage (50% of current year's precipitation) and the current concentration of chloride in the groundwater. Water exported in streamflow was assumed to have the same chloride concentration as the groundwater. Thus, the amount and concentration of chloride in the groundwater and surface water pools were controlled by the balance of inputs and outputs to the watershed. The model was parametrized with measured precipitation and chloride input data from 1986 to 2005. Prior to 1986, precipitation was assumed to be equal to the 1986–2005 mean, and annual road salt chloride input was increased linearly over 30 years from an assumed value of 0 in 1956 to 767 603 kg (the mean of the 1986–2005 input) in 1985. The bypass fraction was assumed to be 10% and the groundwater pool was assumed to be equivalent to 5 m of water.

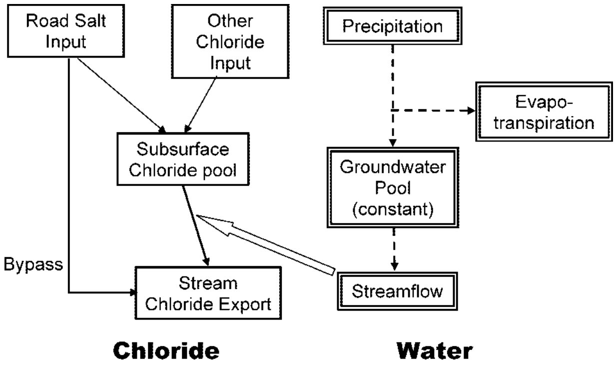

FIGURE 1. Watershed chloride model. Left hand side represents chloride pools and fluxes (single lines), and right-hand side represents water pools and fluxes (dashed lines). Block arrow indicates that streamflow is used in the calculation of chloride export.

Results

Concentration. Sodium and chloride concentrations in the East Branch of Wappinger Creek increased steadily between 1986 and 2005 ($r^2 = 0.86$ for chloride and $r^2 = 0.88$ for sodium) at a rate of 1.5 mg/L per year (chloride) and 0.9 mg/L per year (sodium) (Figure 2A). Concentrations of sodium and chloride were about three times higher in 2005 than they were in 1986. Sodium and chloride concentrations have increased steadily in summer as well as winter (Figure 2B). Molar equivalent sodium and chloride were strongly correlated in streamwater (slope = 1.08, $r^2 = 0.99$).

Export. There was no trend in mean annual water yield; sodium and chloride export also increased steadily between 1986 and 2005 ($r^2 = 0.45$ for chloride and $r^2 = 0.50$ for sodium) at a rate of 33 000 kg/year and 20 000 kg/year for chloride and sodium, respectively, with 2.8 times more sodium and 2.5 times more chloride exported in 2005 than in 1986 (Figure

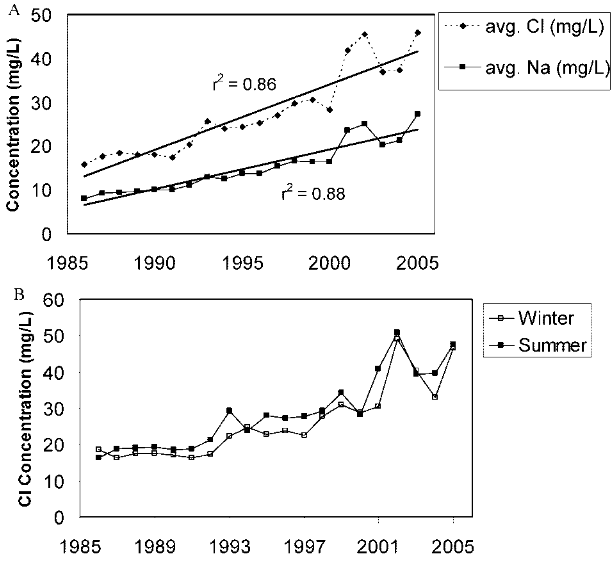

FIGURE 2. (A) Yearly average sodium and chloride concentration (mg/L) and (B) summer (May−September) and winter (October−April, October−December are from previous year) chloride concentrations (mg/L) for the East Branch of the Wappinger Creek at the Cary Arboretum (Institute of Ecosystem Studies), Millbrook, NY (1986–2005). Straight lines are regression lines through the annual mean data. Slopes for regression lines are 1.5 mg/L/year (Cl$^-$) and 0.9 mg/L/year (Na$^+$).

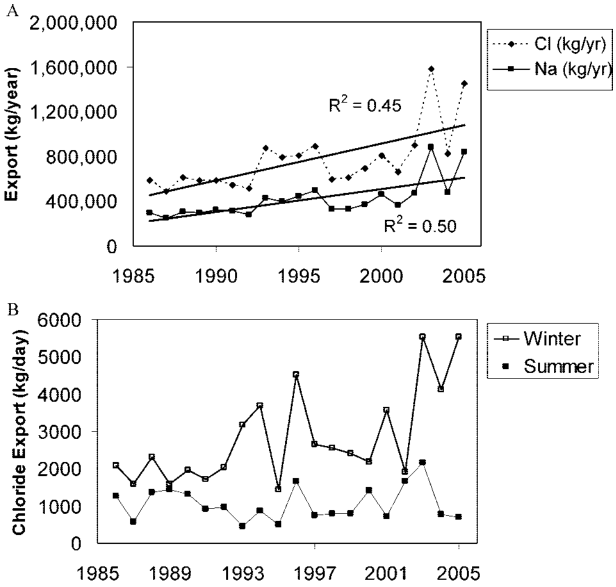

FIGURE 3. (A) Yearly total export (kg/year) in East Branch of the Wappinger Creek at the Cary Arboretum (Institute of Ecosystem Studies), Millbrook, NY (1986–2005). Slopes for regression lines are 32 757 kg of Cl$^-$/year and 20 140 kg ofNa$^+$/year. (B) Summer (May−September) and winter (October−April, October−December are from previous year) average chloride export (kg/day).

3A). An increase in chloride export over time is evident only during winter months, and most chloride export occurred during winter months (Figure 3B). The volume of water exported from the system was higher in winter than summer, and the greater export of chloride during winter probably reflected this difference. Since 2000, there has been considerable year-to-year variation in both concentration and export of sodium and chloride.

Input. Based on our estimates and calculations, over the 20-year measurement period municipal roadway anti-icing salt contributed 83% and parking area anti-icing salt contributed 8% of the total input of sodium chloride to the watershed (Table 1). Thus, 91% of the sodium chloride input to the watershed was from salt used for anti-icing. Sewage contributed 4% and water softeners contributed 3% of the total sodium chloride to the watershed. Only 2% of sodium and chloride was from atmospheric deposition and rock weathering. Thus 98% of the sodium and chloride input to this rural watershed was anthropogenic.

TABLE 1. Estimated Average Input from Different Sources of NaCl (kg/year) to the East Branch of Wappinger Creek at the Cary Arboretum (Institute of Ecosystem Studies), Millbrook, NY (1986–2005 except Dry Deposition, which is 1993–1999)

source	input (kg/year)
road salt	1 180 231 (83%)
parking area salt	113 094 (8%)
sewage	52 414 (4%)
water softeners	43 594 (3%)
wet deposition	18 319 (1%)
rock weathering	13 717 (1%)
dry deposition	442 (<1%)
total input	1 421 811

Input of sodium and chloride to the watershed varied widely on a yearly basis largely because of variability in road salt use (Figure 4), which, in our estimate, is coupled with snowfall each year. Estimated net retention or release, which is the sum of all input sources less export, also varied yearly. In some years, especially in the early years of the study, there was net retention in the watershed, while in other years, especially later years, there was net release of sodium and chloride. Input of sodium chloride from sewage and water softeners increased during the study (86 952 kg in 1986 to 105 006 kg in 2005), but this increase only accounted for about 1% of the increase in export over the same period (878 781 kg in 1986 to 2 283 053 kg in 2005).

Model Results. Our model suggests that, when a steady supply of chloride is released to the stream, concentration and flux of chloride from the watershed can increase steadily in ground and streamwater, but will eventually level off (Figure 5A). Although the simple mass balance model predicted stream chloride concentration in the correct range, it underestimated the rate of increase of chloride concentration that was actually observed in the stream (Figure 5A). Also, recent high stream chloride concentrations measured in 2001, 2002, and 2005 do not indicate a plateau of chloride concentration as predicted by the model. Thus, to date, we have not seen the leveling off of chloride that was predicted by the model. The combination of very low water volumes and large amounts of road salt used in 2001 could explain the spike for that year. Subsurface build-up of chloride in the watershed during 2001 could have been flushed from the system during the wetter 2002. One sample in March 2005 that had a very high concentration of sodium and chloride could explain the spike in average concentration for that year. In general, the model fits the observed stream chloride export and retention data well, except during 2003 and 2005 when export spiked and retention fell below model-predicted values (Figure 5B). A combination of high precipitation and large mass of salt use during 2003 and 2005 could explain the spike in export for those years.

Discussion

Increasing Trends in Streamwater Salt. Increases in stream sodium and chloride are to be expected where there has been an increase in road salt application (*2*). Chloride increases in surface waters are usually attributed to human activities, such as urbanization (*23, 24*), increases in imper-

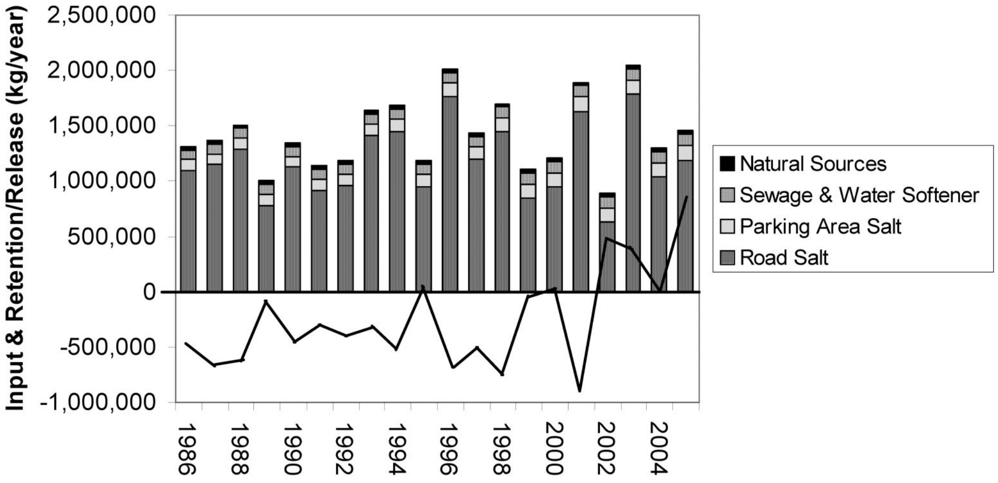

FIGURE 4. Yearly input of sodium and chloride (kg/year) to the East Branch of Wappinger Creek at the Cary Arboretum (Institute of Ecosystem Studies), Millbrook, NY (1986–2005). Net retention/release (solid line) is equal to the sum of all input sources minus the stream export.

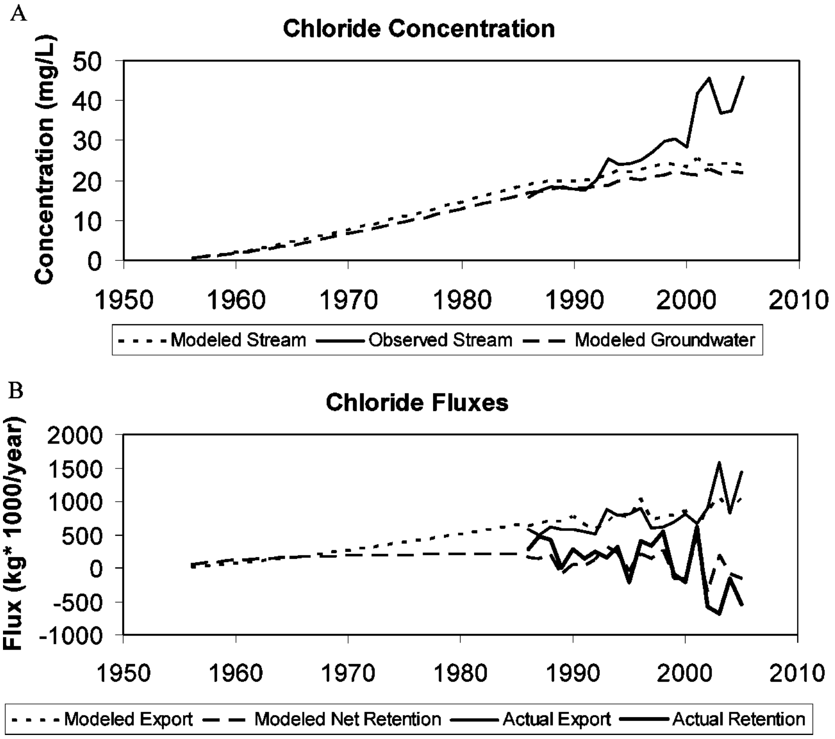

FIGURE 5. Model results: (A) chloride concentrations (mg/L) and (B) chloride fluxes (1000 kg/year).

vious surfaces (*8, 9*), or other human effects (*12, 25*). In our local watershed, stream salt concentrations and export increased, yet these increases were not explained by increases in urbanization or road salt use. Although there was an increase in population in our watershed with concomitant increases in sodium and chloride from sewage effluent and water softener use, these increases were far too small to explain the increase in sodium and chloride export. Instead, we attribute the increase to a storage effect of long-term road salt use and subsurface build-up of salt. This explanation is consistent with other long-term studies of sodium and chloride in fresh waters (*4, 15*).

Retention. Increases in summer concentrations indicate that chloride was retained in the groundwater or soils. There is ample evidence that sodium and chloride can be retained in watersheds for significant lengths of time. Howard and Haynes (*26*) reported that only 45% of salt applied in an urban Toronto catchment was released annually and subsurface buildup continued even though application rates did not increase. Demers and Sage (*27*) also reported that high chloride concentrations were not restricted to the salt application period in the Adirondack Mountains, New York. Nimiroski and Waldron (*4*) reported no measurable reduction in sodium 10 years after reduction in use in a Rhode Island watershed. Godwin et al. (*15*) found that, even though the population declined over a 47-year period in the mostly rural Mohawk River, NY, watershed, sodium and chloride still increased. Chloride has also been demonstrated to be retained in a mostly paved drainage system in Massachusetts (*28*). Several mechanisms may retain sodium or chloride in a watershed. While small amounts of chloride can be retained in vegetation resulting in net ecosystem retention (*29*), larger amounts of chloride may be retained in soil micropores or groundwater, or by incorporation into soil organic matter as organic chlorine compounds (*9, 14, 30*). The formation and remineralization of organic chlorine compounds can cause the soil to act either as a sink or a source of chloride; however, little is known about the conditions that control the opposing processes (*31–33*). Although it is clear that sodium and chlorine or chloride may be retained in the subsurface (soil and groundwater), there is a need for additional research on mechanisms for their retention and release.

Summer and winter comparisons in our study indicate that, while most export occurs in winter, summertime concentrations were high and increasing, suggesting a slow release of sodium and chloride from groundwater or other subsurface storage. Yearly budgets of input and output of sodium chloride revealed retention of these elements in our watershed during some years, especially early years of the study. As with other models (*5, 16*), our model suggests that the chloride concentration and export increases we have observed are due to subsurface buildup, but that concentrations and export should stabilize if road salt use were not to increase. Because of the high interannual variation in concentration and export in the stream, especially in later years of the study, it may be difficult to determine if stabilization has occurred.

Potential Effects. Increasing sodium concentrations in drinking water reservoirs pose a serious human health concern (*4*). Additionally, ecosystem effects of rising sodium chloride can be significant but many environmental questions remain unanswered. High concentrations of sodium and chloride are often found in surface and groundwater close to roads (*34*), and in urban areas concentrations can exceed 3000 mg/L (*8, 35*), which can exceed tolerance for freshwater life (*36*). Ecosystem functions can be altered at lower concentrations than lethal levels (*3, 34*). For example, accumulation of dense salt water in lakes or reservoirs can prevent or prolong spring mixing (*1*). Chloride addition to a forested stream changed net nitrogen mineralization in a debris dam from consumption to production of inorganic nitrogen, although chloride additions had no effect on net nitrogen mineralization in material from a stream that had a history of exposure to chloride (*37*). Increased sodium or chloride levels can influence invasive species' ability to colonize an area (*34*), potentially reducing the viability of endangered species (*38*). Other ecosystem effects include soil cation exchange of sodium for calcium and magnesium and increased mobility of hydrogen ions (*13, 30, 39, 40*). The lethal effect of salt on some organisms has been documented (*36*), however, we know much less about the salt concentrations and ecological conditions that are necessary to affect ecosystem function. Increased salt concentrations may combine with sublethal effects from other sources, such as other pollutants or change in water level or temperatures, to inhibit ecosystem function, such as primary production. Determination of critical levels of sodium or chloride perhaps should not only include consideration of lethal levels, but also effects on biodiversity and ecosystem function, especially when endangered species are affected or invasiveness of unwanted species is enhanced. Salinity is increasing in rivers and lakes nationwide (*8, 12*), and continued monitoring will be important to understand its effects.

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