

Origins of stream salinization in an upland New England watershed

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Abstract Salinity levels are above historical levels in many New England watersheds. We investigated potential sources of salinity in the Pemigewasset River, a relatively undeveloped watershed in northern New England. We utilized a synoptic sampling approach on six occasions between April and September 2011 paired with a novel land use analysis that incorporated traditional watershed and riparian zones as well as a local contributing area. We established background specific conductivity (SC) and found that SC was above established background levels in both the mainstem of the river (peak of $172 \mu\text{S cm}^{-1}$) and multiple tributaries. Specific conductivity was highest during low flow conditions (June) indicating potential groundwater storage and release of de-icing salts applied during winter months. Development in the watershed and riparian zone was found to be more strongly associated with elevated SC, compared to roads. The local contributing area was not found to be strongly associated with SC; however, there was evidence that the local contributing area may contribute to SC under low flow conditions.

Keywords Conductivity · Land use · Pollution transport · Pollution storage · Freshwater

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Introduction

Anthropogenic salinization of freshwater streams and rivers is increasing globally through activities such as mining, agriculture, discharge of saline wastewater (Williams 2001), and application of de-icing salts (Kaushal et al. 2005; Ramakrishna and Viraraghavan 2005; Kaushal et al. 2018). In dryland agricultural systems, irrigation and the subsequent evaporation, concentration, and leaching of salts and minerals in irrigation and soil water are the primary cause of freshwater salinization (Williams 1987). Mining contributes to the salinization of freshwaters by fragmenting and exposing geologic materials that then oxidize and release salts and ions such as SO_4^{2-} , HCO_3^- , Ca^{2+} , and Mg^{2+} into streams (Griffith 2014; Evans et al. 2014). In cold regions of North America and Europe, application of de-icing salts, such as NaCl, can lead to salt runoff and leaching and subsequent increases in Cl^- and total dissolved solids (TDS) in freshwater streams and rivers (Godwin et al. 2003; Kaushal et al. 2005; Gardner and Royer 2010; Kelting et al. 2012).

The negative impacts of freshwater salinization are extensive, including salinized water being less suitable for industry, agriculture, freshwater biota, and drinking water (Williams 1987). In the USA, Cl^- and total dissolved solids (TDS) are not regulated as primary water pollutants, but they are listed as nuisance pollutants. The United States Environmental Protection Agency (USEPA 2018) recommends a limit of 250 mg L^{-1} for Cl^- and 500 mg L^{-1} for TDS in human drinking water (USEPA 2018) and suggests a chronic impact threshold

of 230 mg Cl L⁻¹ and an acute impact threshold of 860 mg Cl L⁻¹ to maintain freshwater aquatic ecosystem health (USEPA 2006).

Salinity levels are above historical levels in many watersheds of NH, USA (Rosenberry et al. 1997; Daley et al. 2009), a state with greater than 80% forest cover, relatively little current agriculture, industry, or mining and few large urban centers compared to other Northeastern states. Efforts to understand and manage regional stream salinity levels have often focused on more urban areas where salinity is highest and anthropogenic sources of salinity can be more varied and concentrated. However, investigating background and anthropogenic salinity in headwaters is also critical for understanding the full breadth of salinity sources and for developing cost-effective management efforts to reduce salt loading across greater watershed areas. In cold regions, as paved areas expand and negative impacts on water quality increase with them, maintaining high-quality headwaters will become increasingly important because of their capacity to dilute downstream inputs and provide refugia for susceptible biota.

We investigated the temporal and spatial pattern of salinity in the Pemigewasset River (PEMI) watershed in central New Hampshire, a relatively rural watershed dominated by national forest, private forest lands, rural residential housing, and small villages and towns. The PEMI merges with the Winnepesaukee River to form the Merrimack River, where water quality is increasingly influenced by larger towns and small cities, often exceeding USEPA-suggested guidelines for Cl⁻ in its lower reaches (Daley et al. 2009). This watershed is well suited to address the origins of freshwater salinity because of its relatively simple land use pattern and prevalence of sub-watersheds with few anthropogenic impacts.

This research utilized a monthly synoptic water quality sampling on the mainstem of the PEMI River and across sub-watersheds with no to low anthropogenic sources of salinity, as well as watersheds with some minor development and roads. We show the spatial and temporal patterns of specific conductivity (SC, a measure of salinity) for one ice-free season. In order to evaluate potential sources or pathways that contribute to salinization in this upland watershed, we conducted a spatial analysis of land use parameters associated with potential anthropogenic salinity. We quantified primary and secondary roads where de-icing salts are utilized within the PEMI watershed and quantified the

developed areas within the watershed where both de-icing salts and other land management activities, such as housing development, can lead to salinization. We used multivariate analysis to test for relationships between SC and development and roads across three zones of influence: (1) the riparian management area (RMA), (2) the local contributing area (LCA), and (3) the watershed (WSH) on a monthly time step. Our primary hypothesis was that SC would have stronger relationships with land use in the LCA compared to the WSH and RMA due to de-icing salt application adjacent to these areas that creates small pollution plumes in adjacent soil and groundwater that are diluted as they enter streams and travel downstream.

Methods

Site description

The PEMI River at Plymouth, NH, drains 1613 km² and contains the smaller Baker, Mad, Lost, Beebe, and East Branch PEMI Rivers. The PEMI basin has an elevation range of 1600 to 140 m at Plymouth, NH, the lowest sample point in this study. The basin is predominantly forested with scattered rural residential development and small towns and minor agricultural operations in the basin valleys. Much of the upper area of the PEMI basin is part of the White Mountain National Forest, managed by the U.S. Forest Service and private forest landholders. The total population of the basin upstream of Plymouth is approximately 19,000 in 2015, distributed among the towns of Plymouth, Rumney, Orange, Bethlehem, Sandwich, Benton, Orford, Dorchester, Piermont, Wentworth, Groton, Warren, Ellsworth, Thornton, Holderness, Lincoln, Campton, Waterville Valley, Franconia, and Woodstock. The PEMI basin contains a four-lane interstate and a two-lane parkway that is generally parallel the river in the basin valley and numerous paved state and county roads. Outdoor tourism drives much of the local economy with three ski resorts, popular scenic auto tour routes, and extensive snowmobile corridors. The Hubbard Brook Experimental Forest (HBEF), located in the center of the basin, receives a mean annual precipitation of 1400 mm, with a snow pack generally persisting from December to mid-April (Campbell et al. 2010), a period when de-icing salts are commonly used on primary and secondary roads, as well as sidewalks and parking lots. The mean

annual temperature at the HBEF is 6 °C (Bailey et al. 2003). Stream discharge is generally highest during spring snowmelt and lowest in mid-summer when ground water contributions to flow dominate (Campbell et al. 2011).

The geology in the PEMI basin above Plymouth includes many bedrock outcrops, exposed by the Wisconsin glaciation approximately 12,000 YBP, and valleys filled with fluvial deposits (Cotton and Olimpio 1996). Soils of the basin are dominated by spodosols; however, variations of typical spodosols occur in response to hydrologic conditions (Bailey et al. 2014). The geologic production of solutes in the HBEF are very low, approaching precipitation concentrations of major ions and decreasing as evidenced in Likens and Buso (2012). The similar geologic environment of the PEMI basin to the HBEF suggests that the background weathering potential of geologic materials is similarly low.

Field and lab methods

We measured in situ SC and collected water samples at 13 sampling sites along the mainstem of the PEMI River and 35 sites on tributaries (Table 1). The sampling locations were selected to cover the length of the PEMI River and as many of its major tributaries as possible (Fig. 1). In order to ensure that field sampling could occur using synoptic methods (< 36 h), sampling locations were constrained to sites that could be safely accessed near public roads that did not require long hikes or traversing larger waters. We conducted field measurements monthly for one growing season (April–September 2011) (Fig. 2). Specific conductivity was measured in situ using a Yellow Springs Instruments, Inc. multimeter. Water samples were collected in borosilicate glass bottles and stored at room temperature before analysis. Samples from May, July, and September were analyzed for Cl^- using ion chromatography (Metrohm 761) with an inline cellulose membrane filter (0.15- μm pore size). Daily runoff data for the PEMI at Plymouth, NH (station 01076500), was acquired through the US Geological Survey website (USGS 2016).

GIS analysis

To evaluate the potential contribution of land use on SC at each of the 48 sample locations, we quantified

the density of winter maintained roads (hereafter, roads) and percent development in each of the watersheds and contributing areas. We defined RMA as land within 100 m of a stream or river and defined LCA as 0.4 km upslope from the sample location (Fig. 3). For each sample location, we delineated the watershed area (km^2) using a 10-m digital elevation model (USGS 2009). We calculated road density (km km^{-2}) for the three influence zones using a New Hampshire Department of Transportation dataset that identifies primary and secondary roads that are classified as maintained in winter months (NH DOT 2013). Roads that are noted as not maintained, unassigned, or private were excluded since we could not confirm winter maintenance for these roads. We calculated the developed land (%) in each watershed using the National Land Cover Dataset (Homer et al. 2015). We considered all lands classified as medium and high development in the dataset to be developed for our analysis, which generally includes dense suburban areas, but not rural residential housing or low-density suburban areas. Both the road and land cover data sets were utilized without field verification.

This GIS analysis provides six combinations of scales and land uses (Fig. 3) for multivariate analysis. We conducted all spatial analyses in ArcMap 10.3 (ESRI, Middleton, MA, USA) and, where needed given the overlapping nature of the sub-watersheds, developed iterative models using ArcMap Model Builder.

Statistical analysis

We tested the relationship between SC and Cl^- across all of our sites using simple linear regression. We utilized principle component analysis (PCA) to test for associations between two land use variables (roads and development) at three spatial levels (RMA, LCA, and watershed) (Fig. 3) and monthly SC to allow for groupings of multicollinear variables to be included in the analysis. Pearson correlations were used to test for associations between PCA loadings and PEMI River runoff (mm day^{-1}) at Plymouth, NH, during each monthly sampling. This analysis was intended to identify the site attributes that were most strongly associated with SC levels to develop new hypotheses about the basin's water quality and hydrology.

Table 1 Watershed attributes for the Pemigewasset River above Plymouth, NH

Watershed	Number of sample locations	Area (km ²)	Lowest sample elevation (m)
Paradise Brook	1	1.4	417.1
Clay Brook	4	11.0	146.1
Hubbard Brook	2	33.6	181.9
Lost River	4	77.1	215.2
Mad River	6	150.3	187.5
East Branch PEMI	3	297.6	240.2
Baker River	15	549.7	141.2
PEMI above Baker	12	1012.6	157.5
PEMI at Plymouth	1	1612.6	140.6

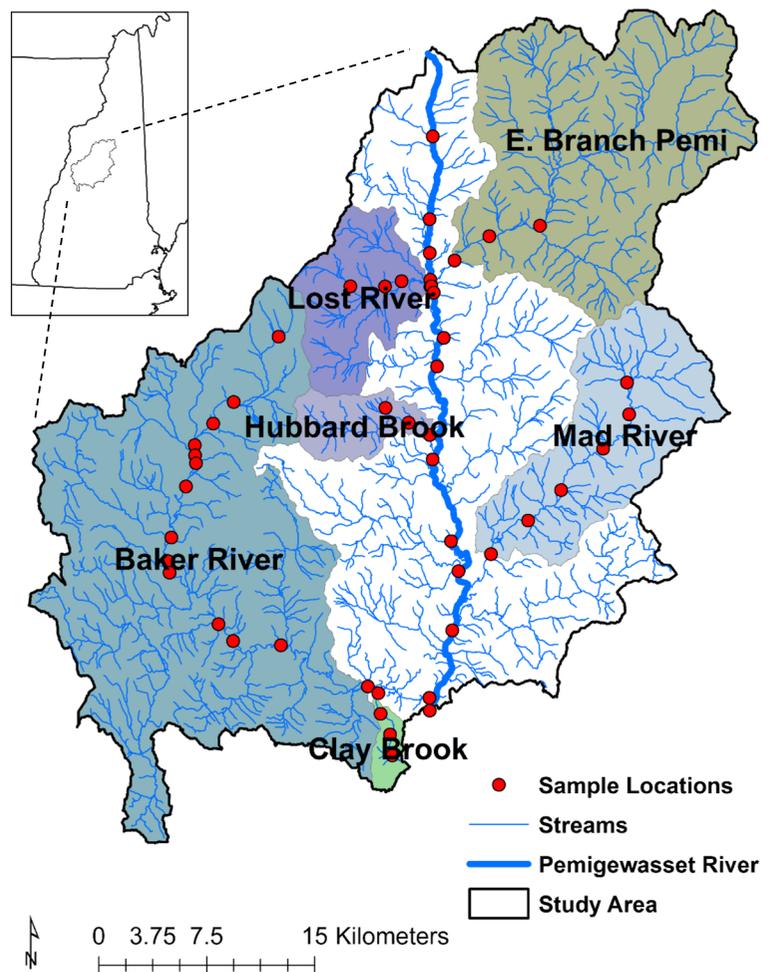
PEMI Pemigewasset River

Results

Land use

The land use analysis revealed that 3 of 48 sample sites had no roads at the LCA, including two sites on Clay Brook and the most downstream site on the East Branch of the PEMI (Table 2). Four additional sites had low road densities with less than 1 km km⁻² at the LCA scale. There were no sites without roads at the RMA and WSH scale. We found the highest road densities for all contributing areas in the lower reaches of the PEMI and Baker watersheds. As was expected due to a highway interchange, the most downstream site on the Baker River had the maximum road density (14.51 km km⁻²) for the study at the LCA level. There were unexpectedly high road densities in the

Fig. 1 Sample locations along the Pemigewasset River and tributaries



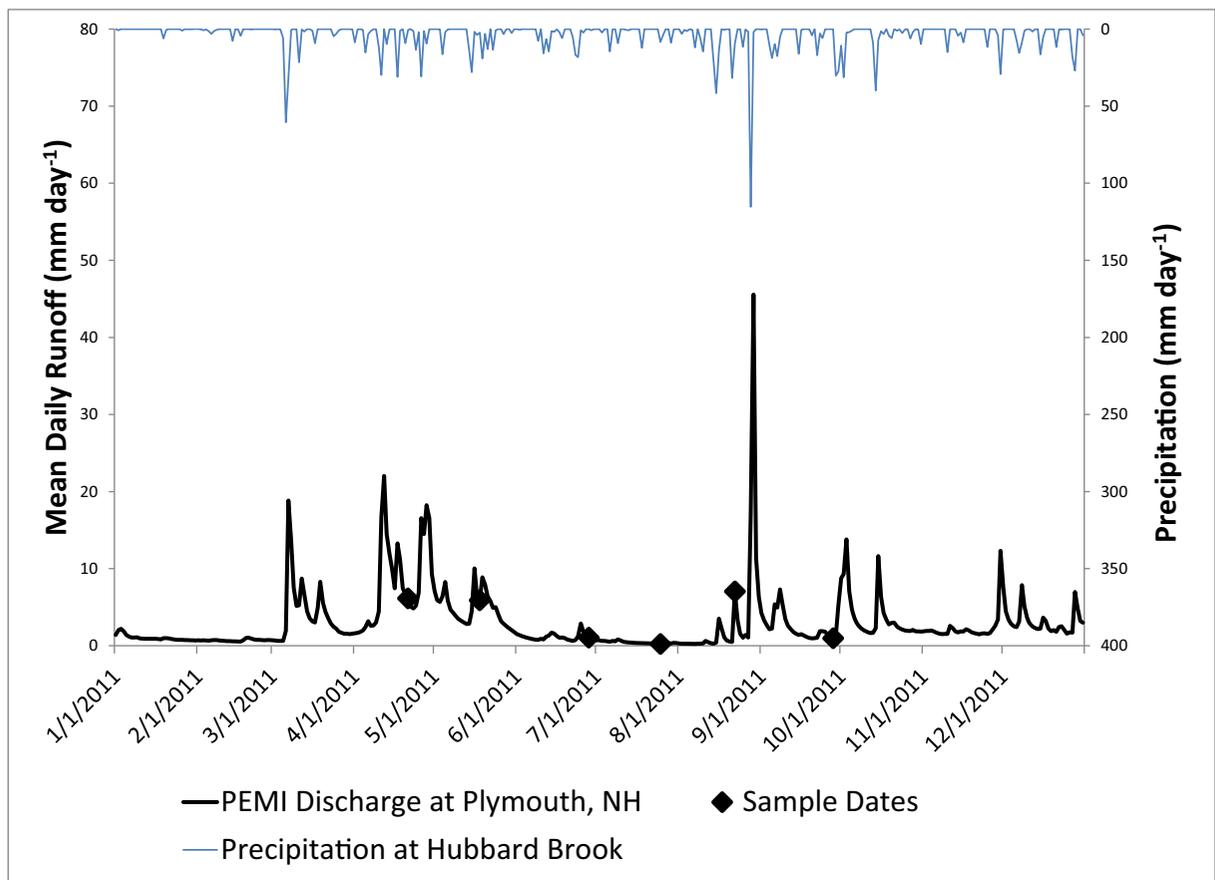


Fig. 2 Sample dates in relation to precipitation and runoff on the Pemigewasset River watershed at Plymouth, NH

LCA at more headwater locations such as the Hubbard Brook and Lost River (Table 2), caused by small clusters of roads being contained within the LCA.

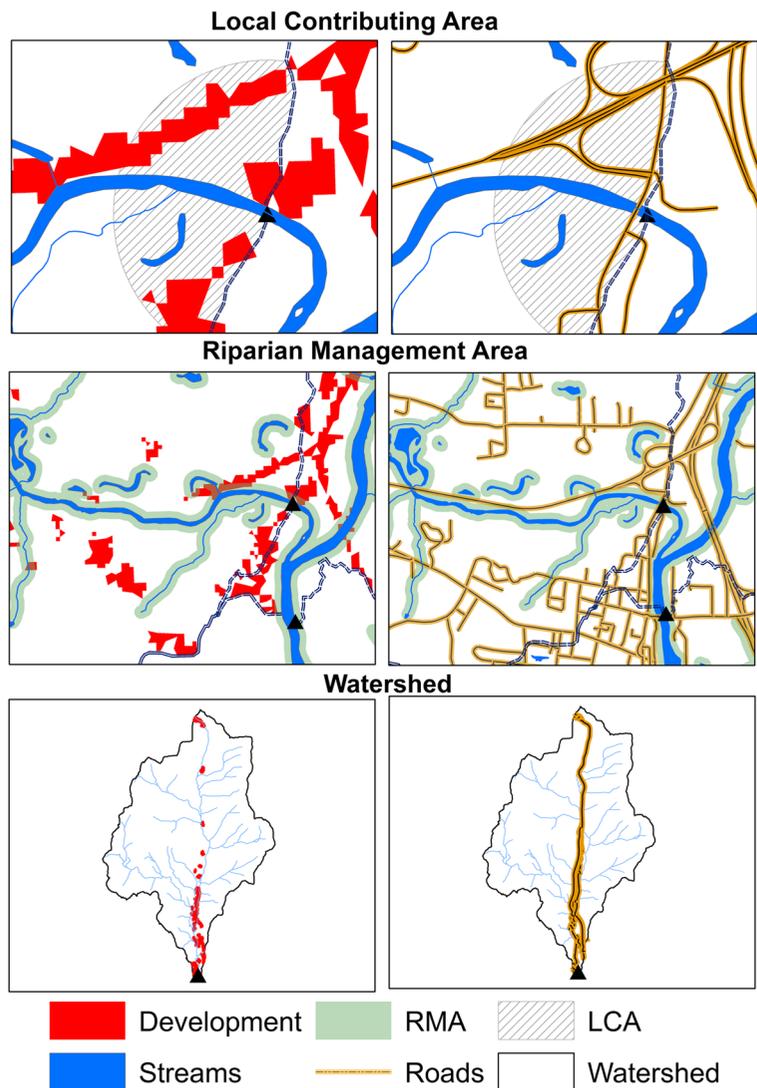
Development and road density were lowest at the WSH level and were highest at the LCA level (Table 2), which was presumably caused by small confined areas of development adjacent to and upstream from the sample location. As with road density, development was highest in the lower sites along the PEMI and Baker Rivers with a maximum in the LCA of 36.8%. Conversely, 19 sample locations had no development in the LCA, indicating that the LCA is effectively representing a wide range of land use near the sample points. Development in the RMA and WSH was an order of magnitude lower than the LCA at most sites, indicating that the LCA is quantifying land use that is not represented by the more conventionally studied RMA and WSH.

Specific conductivity

Specific conductivity was a strong predictor of Cl^- . In May, the R^2 for the simple linear regression was 0.73 ($SC = 2.9 \times Cl^- + 6.8$), while in July, the R^2 was 0.91 ($SC = 3.5 \times Cl^- + 19.7$) and in September, the R^2 was 0.87 ($SC = 3.1 \times Cl^- + 14.6$). During our study period, the mean SC was lowest during the May and August sample when runoff was relatively high and highest during the June and July sample when runoff was relatively low (Table 3). Across all sample locations, SC was highest in the PEMI and Baker Rivers (Fig. 4). Specific conductivity increased as watershed size increased in all months except April (Table 4); however, these relationships were strongest during June, July, and September sample periods with relatively low discharge (Figs. 3 and 4).

Specific conductivity of our least impacted headwater stream, Paradise Brook, was low with a mean

Fig. 3 Land use analysis for development (left cells) and roads (right cells) at influence zones including local contributing area (top two cells), riparian management area (middle two cells), and the watershed scale (bottom two cells)



of $9 \mu\text{S cm}^{-1}$ (± 3.1 SD). However, there were notable spikes in SC up to $18 \mu\text{S cm}^{-1}$, particularly during the July sampling date when runoff was low. These results demonstrate the variability in SC in a headwater stream, likely associated with relative contribution of groundwater, and show that background spikes and seasonal trends in SC can occur in an undeveloped northern New England headwater watershed.

The mean SC at the lowest elevation sample point in the study on the PEMI River in Plymouth, NH, was $58 \mu\text{S cm}^{-1}$ (± 46.8). At this location, SC was lowest during the high-runoff May and August sample periods (18 and $20 \mu\text{S cm}^{-1}$ respectively) and highest during the lowest runoff in July

($148 \mu\text{S cm}^{-1}$). However, higher SC was recorded at more upstream locations on the PEMI River. During the low-runoff July sample, the highest SC for all sample locations ($172 \mu\text{S cm}^{-1}$) and dates was recorded at a site 15 km upstream of the outlet on the mainstem of the PEMI River. Additional sample locations upstream of Plymouth on the PEMI River had relatively high SC during the July and April samples (Fig. 4).

Land use associations with specific conductivity

Specific conductivity strongly loaded on the first principle component for each of the monthly principle component analyses. Eigenvalues for these first

Table 2 Land use and specific conductivity in major watersheds of the Pemigewasset River

Focus watershed	Percentage developed			Road density (km km ⁻²)			Mean SC (μS cm ⁻¹)	SD	Range
	RMA	LCA	WSH	RMA	LCA	WSH			
<i>Paradise Brook</i>	0.0	0.0	0.0	0.13	0.34	0.05	9.3	3.1	5–14
<i>Clay Brook</i>	0.0	0.0	0.0	0.76	0.00	1.09	28	10.0	14–43
<i>Hubbard Brook</i>	0.2	0.0	0.1	1.04	6.52	0.52	27	18.1	14–63
<i>Lost River</i>	0.2	1.4	0.1	0.62	1.71	0.34	38	27.1	16–88
<i>Mad River</i>	0.3	12.9	0.3	1.26	0.42	0.72	38	14.3	24–63
<i>East Branch PEMI</i>	0.4	12.6	0.2	0.17	0.00	0.07	21	8.1	10–31
<i>Baker River</i>	0.4	26.0	0.2	1.29	14.51	0.82	51	33.5	22–112
PEMI above Baker	0.6	12.8	0.4	0.86	6.21	0.53	47	30.0	21–99
PEMI at Plymouth	0.5	13.0	0.3	1.05	8.67	0.66	58	46.8	25–148
Mean of 48 Sites	0.3	5.1	0.2	0.70	2.95	0.39			
Max of 48 Sites	2.2	36.8	0.8	2.92	14.51	1.09			
# of Sites = Zero	9	19	9	0	3	0			

Italicized types denote independent watersheds. *RMA* riparian management area, *LCA* local contributing area, *WSH* watershed, *SC* specific conductivity is from lowest sample point on watershed, *PEMI* Pemigewasset River

components ranged from 3.29 to 3.60, indicating that the first components represented much of the variability in the data. Therefore, we elected to only present the first principle component due to SC being the dependent variable of interest (Table 5). For each month, development in the RMA and the WSH were strongly loaded with SC. In July, road density at the LCA level was loaded with SC, and in August, road density at the RMA level was loaded with SC. Development at the LCA level did not load strongly with SC during any month. However, during periods of low flow, loadings were higher for the land use variables at the LCA scale, particularly for road density (Table 5). Across the monthly samplings, runoff was also negatively correlated ($a < 0.05$) with loadings for road density and development and LCA scales (Table 6).

Discussion

Background specific conductivity

Understanding how anthropogenic activities affect stream water SC requires establishing a benchmark or background range of SC that can be expected in a region. We expected that our most headwater stream with no development or roads could be used to establish this benchmark for our study and the region. At our most undeveloped headwater stream in the HBEF, Paradise Brook, we observed highest SC during lower runoff sample periods. However, these increases in SC were minor relative to other streams in this study and were below 20 μS cm⁻¹ for all sample dates. Long-term monitoring in the HBEF by Likens and Buso (2012) revealed that SC in precipitation and water in a reference

Table 3 Temporal summary of specific conductivity and discharge at the Pemigewasset River

	April	May	June	July	August	September
Mean SC	24	18	41	65	21	38
Median SC	24	20	41	70	21	40
SD	11.8	6.7	17.2	33.6	6.0	13.8
Max	70	32	82	172	35	66
Discharge (mm day ⁻¹)	6.2	5.9	1.1	0.2	7.1	1.0

Maximum SC values occurred at three sample points on the Pemigewasset River upstream of Plymouth, NH. $N = 48$. Summary statistics include sites that are nested

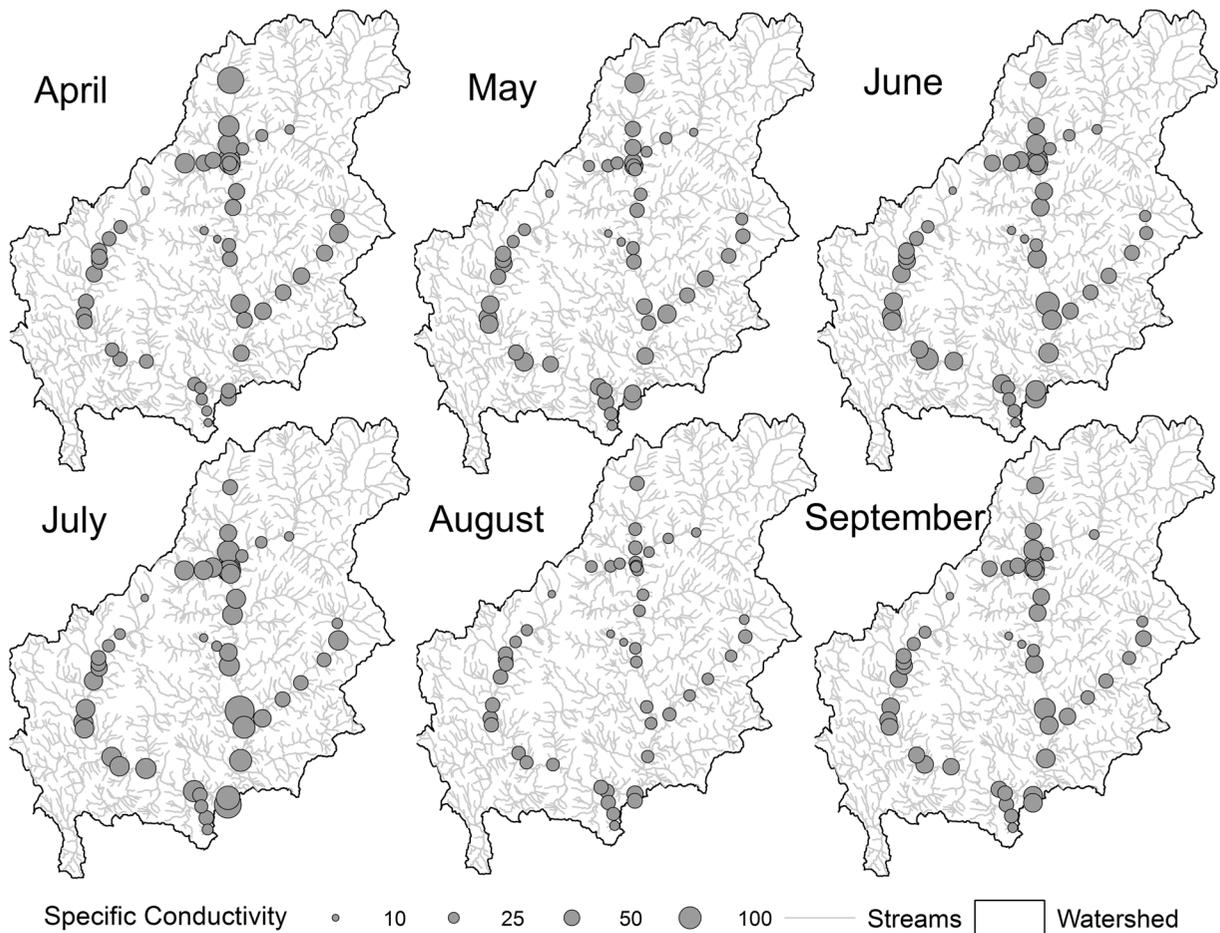


Fig. 4 Specific conductivity across the Pemigewasset River Watershed and tributaries for one ice-free season

stream adjacent to Paradise Brook had mean annual averages below $10 \mu\text{S cm}^{-1}$ and had a trend of decreasing electrical conductivity (EC) since the 1970s. These authors suggest the EC will continue to stay at these levels and may even decrease in non-impacted streams. Through analysis of 40+-year datasets from the HBEF,

Table 4 Pearson correlations between specific conductivity and watershed area

	<i>r</i> (<i>p</i> value)
April	0.057 (0.732)
May	0.320 (0.027)
June	0.568 (<0.001)
July	0.682 (<0.001)
August	0.238 (0.102)
September	0.535 (<0.001)

n = 48

they project that the mean annual precipitation EC will approach $3 \mu\text{S cm}^{-1}$ in this region and the mean annual stream water EC will approach $5 \mu\text{S cm}^{-1}$ over the next one to two decades in the HBEF due to recovery from historic acid deposition. Specific conductivity values and trends in streams at the HBEF are likely at the low range of a potential regional background benchmark for SC. The watersheds in the HBEF may have different land use histories and geologic weathering rates compared to other regional watersheds, which may result in lower SC relative to the region (Kaushal et al. 2018).

Griffith (2014) developed regional reference conditions for SC based on 25th percentiles of first- through fourth-order streams in third-order ecoregions using an extensive list of national datasets. Much of New Hampshire and our study area is classed as Northeastern highlands ecoregion which had a 25th percentile for SC of $<46 \mu\text{S cm}^{-1}$ in Griffith (2014). The 25th percentile of all measured streams in the ecoregion includes

Table 5 Eigenvalues and eigenvectors for principle component analysis addressing potential land use factors that associate with specific conductance in the Pemigewasset River watershed, New Hampshire

	April	May	June	July	August	September
Eigenvalue	3.57	3.40	3.50	3.40	3.29	3.60
Percentage variability explained	51.0	48.6	49.95	48.64	46.94	51.30
Road density (RMA)	0.346	0.398	0.320	0.303	<i>0.408</i>	0.316
Road density (LCA)	0.335	0.363	0.390	<i>0.411</i>	0.379	0.380
Road density (watershed)	0.133	0.250	0.160	0.146	0.283	0.163
Development (RMA)	<i>0.475</i>	<i>0.424</i>	<i>0.454</i>	<i>0.458</i>	<i>0.415</i>	<i>0.449</i>
Development (LCA)	0.327	0.328	0.349	0.356	0.338	0.350
Development (watershed)	<i>0.455</i>	<i>0.417</i>	<i>0.443</i>	<i>0.452</i>	<i>0.400</i>	<i>0.438</i>
Specific conductance	<i>0.459</i>	<i>0.431</i>	<i>0.442</i>	<i>0.421</i>	<i>0.405</i>	<i>0.461</i>

Italicized eigenvectors indicate significance at 0.40 threshold. *RMA* riparian management area, *LCA* local contributing area. Only first principle component is presented because specific conductance loaded on first component during each month

some streams with paved roads and development in their watersheds; hence, SC for the 25th percentile is likely higher than a truly undisturbed reference. Our sites generally fall below this benchmark, with only seven of our sample locations having a mean SC above this threshold, all of which were on are the mainstem of the PEMI and the Baker Rivers. The uppermost sample sites on our independent tributaries had mean SC values generally well below this threshold with the upper sample points on the Mad River, Clay Brook, Hubbard Brook, Baker River, and the East Branch of the PEMI all having a mean SC below 20 $\mu\text{S cm}^{-1}$. This suggests that much of our study area can still be considered a SC reference for the greater ecoregion. However, at downstream river sites, we see temporary increases of SC up to four times this background threshold. This could reduce the capacity of this headwater watershed to dilute higher salinity levels that are found in more urban downstream locations.

Land use signature

Our land use analysis selected development as a stronger predictive variable for SC when compared to roads. Similar results were also reported by Daley et al. (2009) for southeastern New Hampshire streams. They found that percent impervious surface was more strongly associated with Na^+ and Cl^- compared to roads. This association of stream water SC with metrics describing the total development in a watershed can potentially be caused by de-icing salt application on parking lots and at private residences (e.g., driveway, walkways) that would not be represented by road density metrics. In a rural stream in New York State, Kelly et al. (2008) estimated 83% of Cl^- was from road salt and 8% was from parking areas suggesting that contributions from parking lots can be important. However, in New Hampshire and elsewhere in the Northeast, there is little accounting of the amount of salt that is applied by

Table 6 Unrotated loadings for first principle components and correlation with runoff

	April	May	June	July	August	September	The Pearson <i>r</i>	<i>p</i> value
Road density (RMA)	0.654	0.735	0.598	0.560	0.739	0.599	0.92	<i>0.0094</i>
Road density (LCA)	0.633	0.670	0.730	0.758	0.687	0.720	-0.87	<i>0.0258</i>
Road density (watershed)	0.252	0.461	0.299	0.269	0.512	0.309	0.63	0.1754
Development (RMA)	0.898	0.782	0.850	0.844	0.753	0.851	-0.43	0.3906
Development (LCA)	0.617	0.606	0.652	0.657	0.613	0.664	-0.96	<i>0.0022</i>
Development (watershed)	0.859	0.769	0.829	0.834	0.724	0.830	-0.57	0.2381
Specific conductance	0.868	0.795	0.826	0.776	0.734	0.874	-0.28	0.5823
Runoff (mm d^{-1})	6.15	5.89	1.05	0.23	7.05	0.96		

Italicized *p* values indicate significance at alpha = 0.05. *RMA* riparian management area, *LCA* local contributing area

homeowners, business owners, and small companies offering plowing and de-icing services. In New Hampshire, there is currently a general education campaign to reduce the overuse of de-icing salts on roads at the government agency level through programs such as voluntary state applicator certifications. However, it is unknown if education campaigns are reaching citizens and small de-icing operators who manage residential and commercial driveways, sidewalks, and parking lots. Nevertheless, the use of de-icing salts by these groups undoubtedly contributes to the total loads in some areas in, which may help explain the strong relationship we found between SC and development.

Specific conductivity flowpaths

Our hypothesis that there would be a relationship between SC and land use at the LCA level was not supported by our data. We expected that application of de-icing salts in areas just upstream of our sample locations would drive this relationship. In contrast, we found that the strongest and most consistent associations between SC and land use were at the RMA level and the WSH level. This may be due to the sporadic timing of spring thaws which drive timing of spring flushes of de-icing salt into local waterways. Localized contributions of de-icing salts may have previously runoff or entered groundwater before our monthly sampling could safely occur. We also identified a negative relationship between runoff and PCA loadings for both road density and development at the LCA scale (Table 4), suggesting there may be a seasonal or runoff-based factor that is controlling the relationship between land use and SC.

We found the highest SC in summer months during baseflow conditions, many months after de-icing salts were washed off treated surfaces. This suggests that salinity sources such as de-icing salts are entering subsurface pathways or groundwater and are returning to surface waters at downstream locations through return flow, springs, or groundwater meeting a gaining stream. These potential pollutant pathways have been reported by other authors in northern regions. In an early study, Kunkle (1972) found that EC in one Vermont stream peaked in summer during baseflow and suggested that Cl^- entered groundwater and was released during baseflow. In a study using a mass balance approach, Howard and Haynes (1993) found that only 55% of road salt was being exported annually from a stream in the Toronto, Canada area, while the remainder was being

stored in shallow subsurface waters. In the aforementioned study of a rural stream in New York State, Kelly et al. (2008) found increases in summer Cl^- concentrations and reported a lag effect, with mass balances indicating that the salt being released was from previous build-up and storage. In a study that investigated Cl^- above and below road salt applications in the Adirondack Mountains of New York, Demers and Sage (1990) found elevated Cl^- levels in tributary streams for 4–6 months after the last salt application. In a southern New Hampshire stream, Harte and Trowbridge (2010) found that EC was highest during baseflow and suggested it was due to advective flow of high EC groundwater entering surface waters. Kaushal et al. (2005) also found elevated Cl^- throughout the year in more urban and suburban streams and suggested that this was due to gradual accumulations of Cl^- in groundwater. Understanding how these potential pollutant flowpaths, storage, and release mechanisms function in a headwater watershed is critical for developing de-icing salt management strategies that can be used to reduce salinity in these upland watersheds.

Conclusions

Specific conductivity in the majority of our mainstem and tributary sites was below regional background levels for the Northeastern highlands ecoregion. However, individual sample SC was above background levels at some sites in the mainstem of the PEMI and Baker Rivers and even some smaller tributaries had individual samples above background. If these increases in SC are persistently above background in these headwater watersheds, it means they have little capacity to dilute higher SC levels at more downstream locations. The goal of this study was to begin the process of understanding the sources of salinity and the pollutant transport pathways in this headwater system. We hypothesized that development and roads in LCAs would be associated with SC because of de-icing salt being applied in localized areas near streams and river crossings. Conversely, our study found that development and roads in the LCA were not strongly associated with SC. Higher loadings for the LCA during low runoff provides some evidence that the LCA could be functioning as a source of SC during low-runoff periods. It is also possible that our sampling intensity could have missed flushes of salt from LCAs into surface waters. High

SC levels in the drier summer months also indicate the potential subsurface transport and storage of salts in this system. Future research should address this potential for both temporary flushes of road salt into surface waters and for salts to percolate into groundwater. Identifying these local hydrologic pollutant pathways that explain the patterns that we have observed will aid in developing de-icing management plans that can reduce impacts on freshwater biota during low summer flows when surface water temperatures tend to be high and during spring emergence when many biota are beginning to increase metabolism but their movement may be constrained by ice.

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