Published online June 7, 2018

Journal of Environmental Quality TECHNICAL REPORTS

SURFACE WATER QUALITY

Controls of Chloride Loading and Impairment at the River Network Scale in New England

Shan Zuidema,* Wilfred M. Wollheim, Madeleine M. Mineau, Mark B. Green, and Robert J. Stewart

Abstract

Chloride contamination of rivers due to nonpoint sources is increasing throughout developed temperate regions due to road salt application in winter. We developed a river-network model of chloride loading to watersheds to estimate road salt application rates and investigated the meteorological factors that control riverine impairment by chloride at concentrations above thresholds protective of aquatic organisms. Chloride loading from road salt was simulated in the Merrimack River watershed in New Hampshire, which has gradients in development density. After calibration to a regional network of stream chloride data, the model captured the distribution of regional discharge and chloride observations with efficiencies of 93 and 75%, respectively. The estimate of road salt application is within uncertainties of inventoried estimates of road salt loading and is 122 to 214% greater than recommended targets. Model predictions of chloride showed seasonal variation in chloride concentrations despite a large groundwater storage pool. Interannual variation of mean summer chloride concentration near the outlet varied up to 18%, and the total river length exceeding impairment thresholds varied 12%. Annual snowfall, which drives road salt loading, correlated with chloride impairment only in headwater streams, whereas concentration variability at the outlet was driven primarily by dilution from clean runoff-draining undeveloped forested areas of the watershed. The role of summer meteorology complicates the protection of freshwater systems from chloride contamination.

Core Ideas

- A watershed-scale model of chloride (including road salt) transport was developed.
- Model road salt loading inferred from stream observations was similar to inventories.
- Seasonal chloride contamination in headwater streams covaried with annual snowfall.
- Chloride contamination in larger rivers was inversely related to summer precipitation.
- Comprehensive management of chloride requires controls on available dilution.

Increasing sodium chloride in watersheds adversely affects aquatic organisms at concentrations below current regulatory guidance (Findlay and Kelly, 2011; Cañedo-Argüelles et al., 2013, 2016). Both climate and development interact to control chloride contamination in temperate watersheds (Jackson and Jobbagy, 2005; Kaushal et al., 2005; Corsi et al., 2010, 2015). Aquatic biota are sensitive to salt content directly through biological maintenance of cellular osmotic balance (Cañedo-Argüelles et al., 2013), indirectly through mobilization of toxic metals (Findlay and Kelly, 2011), or correlatively through a host of chemical and habitat alterations (de Zwart et al., 2006). Widespread increases of freshwater salinization (Murray, 1977; Ghassemi et al., 1995; Kaushal et al., 2005; Anning and Flynn, 2014) and growing evidence of altered aquatic community structure at salt concentrations lower than regulatory recommendations (Findlay and Kelly, 2011; Morgan et al., 2012; Cañedo-Argüelles et al., 2013) motivate increased attention to regulating this ecological threat (Cañedo-Argüelles et al., 2016).

Globally (Ghassemi et al., 1995; Cañedo-Argüelles et al., 2013) and in the United States (Anning and Flynn, 2014), irrigation is the primary cause of freshwater salinization. However, in New England where irrigated agriculture is minimal, the USEPA rated 22.8% of streams as poor or fair for salt content (USEPA, 2013). Since the mid-20th century, winter roadway deicing has become a primary driver of increasing freshwater salinity throughout northern temperate regions (Jackson and Jobbagy, 2005). Concentrations of chloride in streams covary with sodium chloride (halite) purchased for deicing purposes in northeastern (Godwin et al., 2003; Jackson and Jobbagy, 2005; Kaushal et al., 2005; Kelly et al., 2008; Trowbridge et al., 2010) and mid-western (Sander et al., 2007; Corsi et al., 2010, 2015) watersheds. Most roadway deicers are chloride salts, with halite being by far the predominant source (Granato et al., 2015). We

S. Zuidema, Univ. of New Hampshire, Dep. of Earth Sciences, 56 College Rd., Durham, NH; S. Zuidema, W.M. Wollheim, M.M. Mineau, and R.J. Stewart, Univ. of New Hampshire, Earth Systems Research Center, 8 College Rd., Durham, NH; W.M. Wollheim, Univ. of New Hampshire, Dep. of Natural Resources and the Environment, 46 College Rd., Durham, NH; M.B. Green, Plymouth State Univ., Center for the Environment, 17 High St., Plymouth, NH; M.B. Green, US Forest Service, Northern Research Station, 11 Campus Blvd., Newton Square, PA. Assigned to Associate Editor Ray Anderson.

Abbreviations: C_{DEI}, the deicer loading parameter; FrAMES, Framework for Aquatic Modeling in the Earth Systems; IRD, impaired reach days; LoVoTECS, Lotic Volunteers Temperature, Electrical Conductivity, and Stage; LOWESS, locally weighted scatterplot smoothing; MCMC, Markov chain Monte Carlo; MRW, Merrimack River watershed; NACL, Nonpoint Anthropogenic Chloride Loading; NSE, Nash–Sutcliffe efficiency; OSC, outlet summer concentration; PONE, probability of non-exceedance; SUMP, summer precipitation.

J. Environ. Qual.
doi:10.2134/jeq2017.11.0418
Supplemental material is available online for this article.
Received 5 Feb. 2018.
Accepted 23 Apr. 2018.
*Corresponding author (shan.zuidema@unh.edu).

currently lack generalizable estimates of road salt application rates at regional scales.

Road salt application rates are largely controlled by the amount of snow and frozen precipitation received (Sander et al., 2007; Kelly et al., 2008; Perera et al., 2013; Kilgour et al., 2014). A significant fraction of applied deicer infiltrates to and accumulates in groundwater. As a result, streams maintain elevated chloride concentrations during summer when groundwater dominates streamflow (Godwin et al., 2003; Kelly et al., 2008, 2012; Kincaid and Findlay, 2009; Daley et al., 2009; Cooper et al., 2014). Therefore, when animal activity is often greatest (Demars et al., 2011), baseflow chloride concentrations can routinely exceed concentrations that biota can tolerate (>100 mg L^{-1}) for extended periods (Findlay and Kelly, 2011; Corsi et al., 2015) and can exceed the USEPA chronic threshold for chloride of 230 mg L^{-1} in urban areas.

Empirical studies of road-salt-driven salinization have previously focused on multiyear trends and less on interannual meteorological variability, although such variability is evident (e.g., Fig. 2 in Kaushal et al., 2005). In many temperate regions, such as New England, significant changes are expected in both winter and summer climate (Hayhoe et al., 2006; Campbell et al., 2010; Wake et al., 2014a, 2014b). Although expectations are for shorter and warmer winters, it is not clear that the form of precipitation will necessarily lead to a reduction in required road salt usage (Arvidsson et al., 2012). Previous models used for investigating anthropogenic chloride in the environment include catchment mass balance (Kelly et al., 2008; Shaw et al., 2012; Betts et al., 2014), statistical models (Anning and Flynn, 2014; Corsi et al., 2015), local- (Bester et al., 2006) to regional-scale (Boutt et al., 2001; Wayland et al., 2002) numerical groundwater transport models, and a spatially distributed catchment model (Jin et al., 2011). Presently, there have been few attempts to utilize macroscale models to investigate changes in road salt usage and chloride impairment associated with interannual dynamics of climate and human development.

In this study, we examined the ability of a macroscale model to represent the dynamics of chloride solute transport and characterize potential chloride impairment of a relatively large watershed across both space and time. We developed and applied the Nonpoint Anthropogenic Chloride Loading (NACL) and transport model within the Framework for Aquatic Modeling in the Earth System (FrAMES) (Vörösmarty et al., 1998; Wollheim et al., 2008; Wisser et al., 2010; Stewart et al., 2013). We focused on simulating chloride because this single anion is the primary driver of salinization throughout the study region and is largely conservative in the hydrologic system (Kirchner et al., 2010), making it ideal for process-based representation. However, we relate chloride to specific conductance because the latter was the primary metric measured, and it characterizes the total osmotic stress experienced by vulnerable aquatic species (Cañedo-Argüelles et al., 2013). Using data from an extensive network of electrical conductance sensors, we inferred a regional and spatially homogenous loading and transport function to parameterize FrAMES-NACL. We hypothesized that road salt application rates derived from inventory estimates at northern US locations (Godwin et al., 2003; Sander et al., 2007; Trowbridge et al., 2010) are the same as derived by calibration to stream chloride concentrations. Furthermore, we hypothesized that climate indices of summer dryness are as important to predict interannual variability in warm-season impairment as frozen precipitation the preceding winter in both small and large rivers. Understanding chloride response during meteorologically different years enhances our ability to manage chloride pollution of watersheds as annual precipitation regimes (Hayhoe et al., 2006) or land cover (Samal et al., 2017) shift.

Materials and Methods

Study Watershed

The Merrimack River watershed (MRW, 13,000 km^2) is representative of the northeastern US watersheds (Fig. 1) with increasing development toward the river outlet. Beginning in the White Mountain National Forest, the Merrimack flows 280 km south to the head of tide dam in Lawrence, MA. The watershed includes pristine and highly valued aquatic ecosystems that are important habitat for sport fishing (New Hampshire Fish and Game Department, 2015) and may be threatened by increasing salinity. Although we focus on the MRW because the watershed is illustrative of the processes relevant throughout the region, we use additional observational data from the neighboring Piscataqua River watershed to inform model behavior.

The population in the MRW has been increasing steadily at 5 to 15% per decade since 1940 (NHOEP, 2010; US Census Bureau, 2015) and is expected to double in the

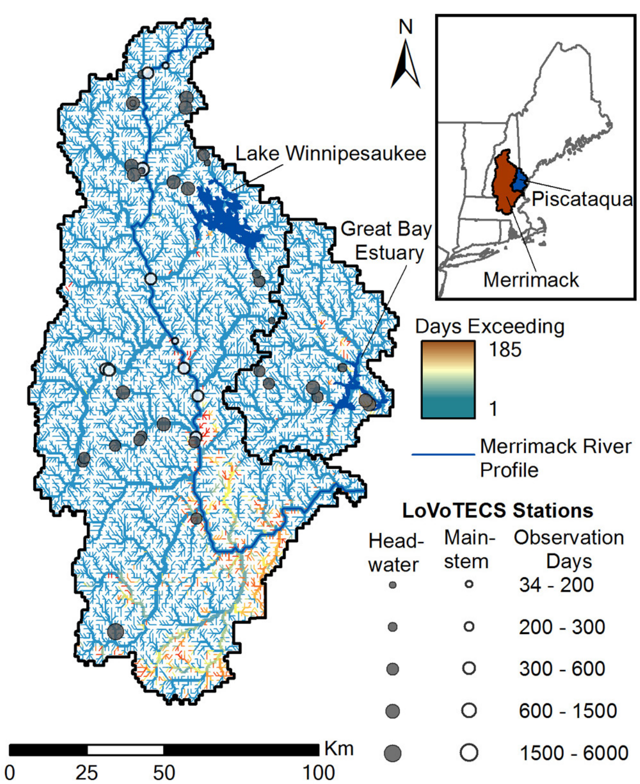

Fig. 1. Study domain in the Merrimack and Piscataqua River watersheds in New Hampshire and neighboring Maine and Massachusetts. The map indicated the median number of days exceeding the 600-µS cm^{-1} threshold between 1998 and 2014. Lotic Volunteers Temperature, Electrical Conductivity, and Stage (LoVoTECS) stations in headwater (less than order 6) and mainstem (order 6 and greater) are depicted in closed gray and open white circles, respectively, and sized is based on the number of days with qualified data. Lake Winnipesaukee and the Great Bay Estuary were excluded from analysis.

coming century (Bierwagen et al., 2010). The population residing in the MRW is ~1.7 million people. Impervious areas have increased from 4.6 to 5.1% between 2000 and 2010 (Xian et al., 2011; Thorn et al., 2017). For the MRW, annual precipitation averages 1100 mm, and precipitation during winter months averages 260 mm, with 220 mm of winter precipitation falling in frozen forms (Rienecker et al., 2011). Projections of future climate suggest the potential for warmer winters (Contosta et al., 2017) consistent with recent trends (Burakowski et al., 2008) that may counteract increasing salt loading concomitant with continued development.

Conductivity Sensor Network

A network of in situ, high-frequency sensors characterized specific conductance in streams, rivers, and storm drainage infrastructure in diverse land cover throughout New Hampshire, eastern Massachusetts, and western Maine (Contosta et al., 2017; Inserillo et al., 2017). The Lotic Volunteers Temperature, Electrical Conductivity, and Stage (LoVoTECS) network collected data throughout the study region from 2011 to 2016. The network used long-term in situ deployments of data-logging potentiometric electrical conductivity and pressure transducer sensors (HOBO U24 specific conductivity and HOBO U20 stage, respectively) at locations throughout the study region (Fig. 1). Sampled catchments exhibited 0 to 54% impervious cover (Xian et al., 2011) and ranged in size from 1.4 to 7300 km^2. Sensor data are distributed through the Data Discovery Center (http://ddc.unh.edu). Periodic chemical analysis of stream water throughout the network showed a strong linear correspondence (Supplemental Fig. S1) between specific conductance (k_0) and riverine chloride concentration (C_R) across the network following Eq. [1], similar to relationships reported by others (Novotny et al., 2008; Perera et al., 2009; Trowbridge et al., 2010):

$$k_0 = 3.96C_R + 31.2 \quad [1]$$

At low chloride concentrations, Eq. [1] is greater than observed chloride concentrations, evidenced by the separation between the linear best fit from locally weighted scatterplot smoothing (LOWESS) regression of the data ~20 mg Cl L^{-1} (Supplemental Fig. S1), which is attributed to the decreasing contribution of chloride to total electrolytic composition in pristine waters. The linear regression equation was used to convert between chloride and specific conductance in this study because it was consistent with the LOWESS at higher chloride concentrations that were the focus of the study. We found no significant differences from Eq. [1] according to stream size or subregion.

The LoVoTECS network included 47 stations with data in the Merrimack and Piscataqua River watersheds (Fig. 1). These stations recorded data at 1- to 3-min intervals, which were resampled to hourly averages for comparison with chemistry data and resampled to daily averages for model calibration and validation For model calibration, we used data from 39 stations that had between 170 and 1240 d of data between 2011 and 2015 (Fig. 1).

Model and Application

The Nonpoint Anthropogenic Chloride Loading Model

We developed a module for NACL within FrAMES, a fully distributed, rasterized modeling platform used for studies of hydrologic and aquatic biogeochemical processes across scales (Wollheim et al., 2008; Wisser et al., 2010; Stewart et al., 2011, 2013). The Framework for Aquatic Modeling in the Earth Systems controls vertical water transfer and terrestrial runoff generation (Supplemental Fig. S2a), which is routed through a one-dimensional simulated topological network river system (Vörösmarty et al., 1998; Wisser et al., 2010). The model uses a series of conceptual stores representing snowpack, soil storage, quick-flow storage, baseflow-generating groundwater storage, and river storage across each 45-s (~1.4-km^2) pixel of the study domain. Chloride moves through soils and groundwater conservatively according to the simulated hydrological partitioning (Supplemental Fig. S2b). Chloride from precipitation and road salt is applied to the watershed at the soil or impervious surface. Chloride from domestic and agricultural sources is loaded directly to shallow groundwater. We treat all domestic waste in a manner appropriate for septic release of chloride because the representation is accurate throughout most of the model domain, and because domestic loading is constant the flowpath through groundwater produces an equivalent chloride flux. The FrAMES-NACL model transports chloride mass through the topological river network using a linear reservoir routing scheme. Within each reach, chloride is converted to specific conductance (μS cm^{-1}) using Eq. [1]. Additional changes to FrAMES to account for the dynamics of chloride including long-term storage in groundwater and direct snowmelt on impervious surfaces are discussed in the supplemental material. We parameterized chloride loading from precipitation, domestic waste, agricultural runoff, and road salt application using data and assumptions defined in the supplemental material. Briefly, road salt was applied to a fraction of treated impervious areas based on the amount of received snowfall, at a spatially average homogenous rate specified by the deicer loading parameter (C_{DEI}, kg Cl mm^{-1} m^{-2}) that neglects known differences in salt application for different types of impervious surfaces. The FrAMES-NACL model was tested by comparing the relationship between chloride and impervious cover between simulations and observations (Kaushal et al., 2005; Daley et al., 2009). Supplemental Table S1 provides descriptions of 10 parameters of the model relevant to this study. Geographic and meteorological data used by FrAMES-NACL are described in the supplemental material.

Assessing Road Salt Loading

To address our first hypothesis, we use FrAMES-NACL to calibrate a deicer application rate (C_{DEI}) and compare it with empirical estimates from three studies (Godwin et al., 2003; Sander et al., 2007; Trowbridge et al., 2010) that inventoried road salt usage. Calibration used a Markov chain Monte Carlo (MCMC) approach (see the supplemental material) aimed to minimize model observation misfit for discharge (Q, mm d^{-1}) and chloride, after conversion to specific conductance (μS cm^{-1}). Observations represented daily mean discharge (Q) from USGS stream gages (n = 28) and specific conductance (n = 39 LoVoTECS network stations). We compared station-specific probabilities of non-exceedance (PONE) for both discharge and specific conductivity using the acceptance ratio (see the supplemental material), Nash–Sutcliffe efficiency (NSE), RMSE, and median residuals. We also assessed model performance using RMSE on daily and temporally aggregated time series for the suite of stations in our dataset.

Characterizing Road Salt Impairment

We used FrAMES-NACL to investigate the influence of climatic drivers interacting with present-day land use to generate riverine chloride impairment throughout the river network. We quantified the degree to which interannual climate variability explained variation in two metrics of impairment in time and space. We selected a threshold of 600 μS cm^{-1} (140 mg Cl L^{-1}) to define chloride impairment (see the supplemental material) during the biological active (productive) season of mid-April through October, which is typical of ecotoxicological assessments of aquatic species (Ejsmond et al., 2010; Ippolito et al., 2012; Kraus et al., 2014). Impaired reach days (IRD) was calculated by counting the number of productive season days that the riverine-specific conductance predicted for a grid cell exceeding 600 μS cm^{-1}, multiplying by the local river length in the grid cell, and summing for the entire river network. We also use the mean outlet summer conductivity (OSC) from August at USGS Gaging Station 01100000 on the Merrimack River at Lowell, MA, as a metric that integrates all upstream processes. The FrAMES-NACL predictions of stations that exhibited impairment were validated against LoVoTECS stations exhibiting impairment using the Peirce skill score. The Peirce skill score is the probability of detecting an exceedance (600 μS cm^{-1}) minus the probability of a false detection (Manzato, 2007). We controlled for stations with incomplete data records. Comparisons were limited to stations with at least 90 d of data during each productive season. To validate predictions of the OSC metric, predicted and observed August mean concentrations were compared at all fifth or greater order stations along the Merrimack River (n = 8 stations).

The importance of seasonality for stream impairment due to road salt was characterized by correlating interannual variance in a simulated impairment with a suite of watershed average meteorological indices. Indices tested for control of stream impairment included the total annual precipitation, total season precipitation (preceding winter [December–February], spring [March–May], summer [June–August], autumn [September–November]), preceding winter snowfall, annual number of dry days (days with <1 mm precipitation), annual number of days with heavy (>10 mm) precipitation, number of summer (average temperature $\geq$ 25°C) days, and the number of dry (<1 mm) summer (average temperature $\geq$ 25°C) days. We expected the number of dry days each year to be the most predictive of chloride impairment throughout the river network, as it should be the main driver of baseflow conditions when chloride levels are high. We standardized each year's impairment metrics and climatic indices for years between 1998 and 2014 (n =17) to z-scores after confirming normal distributions using a Shapiro–Wilks test at $\alpha = 0.05$. Using ordinary least squares, we regressed impairment metrics against climate indices, testing for significance at $\alpha = 0.05$.

Results and Discussion

Nonpoint Anthropogenic Chloride Loading Model Behavior

The time series of discharge indicates reasonable timing and magnitude of flows across sites (Supplemental Fig. S4). At the optimal parameter values found by the MCMC, the median station residual of mean summer runoff was +9.8% of observations and ranged from −79 to +55%. The PONE of discharge corresponded closely between observations and FrAMES-NACL (acceptance ratio [R_A] and NSE were 0.88 and 0.93 for calibration stations and 0.85 and 0.99 for validation stations, respectively; Supplemental Table S2, Supplemental Fig. S5a), with a very small negative bias of −0.04 m^3 s^{-1} (Supplemental Table S2), reflecting reliable representation of the distribution of storm magnitudes. The FrAMES-NACL model predicted flashier hydrology than observations at all watershed scales, and as time series were averaged over longer intervals, the RMSE of modeled runoff decreased from 3.3 to 2.3 m^3 s^{-1} (Supplemental Table S2).

The FrAMES-NACL model correctly identified stations that were observed to exceed the threshold of 600 μS cm^{-1} (Supplemental Fig. S5b), indicating that the model can be used to predict the spatial distribution of exceedance values despite using a spatially homogenous deicer application rate. The acceptance ratio (R_A) calculated on PONE was 0.53 for calibration stations and 0.38 for downstream stations reserved for validation (Supplemental Table S2). The calibrated NSE on specific conductivity for PONE was 0.75 and was lower for validation stations (Supplemental Table S2). Because low values of specific conductance are overpredicted by Eq. [1], specific conductivity at stations with low human development, including many of the stations on the largest river segments, is biased high, indicated by a positive median residual ($\hat{r}_{0.5}$, Supplemental Table S2) and decreasing the NSE for these stations. Despite the low NSE, absolute performance described by the RMSE (32 μS cm^{-1}, Supplemental Table S2) at downstream stations was much lower than for upstream stations (180 μS cm^{-1}), indicating that upstream errors canceled out.

The FrAMES-NACL model correctly captures (i) temporally stable baseflow chloride concentrations, (ii) small increases in baseflow concentration late in the summer for moderately to highly developed catchments, and (iii) wintertime peaks from deicer application only in highly developed catchments (Fig. 2). As with discharge times series, resampling the specific conductivity time series to 1-wk or longer timescales (most consistent with our analysis) improves the RMSE of model performance. Whereas annual-modeled specific conductivity exhibited a high bias (Supplemental Table S2), mean summer specific conductance was biased slightly low (median residual = −7.4%). During summer storms, the model's dilution response is often flashier than observed, consistent with the flashy response observed in discharge. Since we focused on summer periods when exceedance values were most biologically relevant, the low bias means our estimates of impairment were conservative.

Mean annual chloride concentration in rivers correlated with upstream development density (Nimiroski and Waldron, 2002; Kaushal et al., 2005; Novotny et al., 2008; Daley et al., 2009; Trowbridge et al., 2010; Kelting et al., 2012; Corsi et al., 2015). The FrAMES-NACL model predicted increases in mean annual chloride as a function of impervious surfaces, similar to Daley et al. (2009) for the study region (Fig. 3a). The FrAMES predictions were also similar to those reported by Kaushal et al. (2005) over the range of imperviousness in their study.

Road Salt Loading Parameterization

The FrAMES-NACL model predicted an average road salt loading rate of 6.5 g Cl mm^{-1} m^{-2} with a 95% credible interval

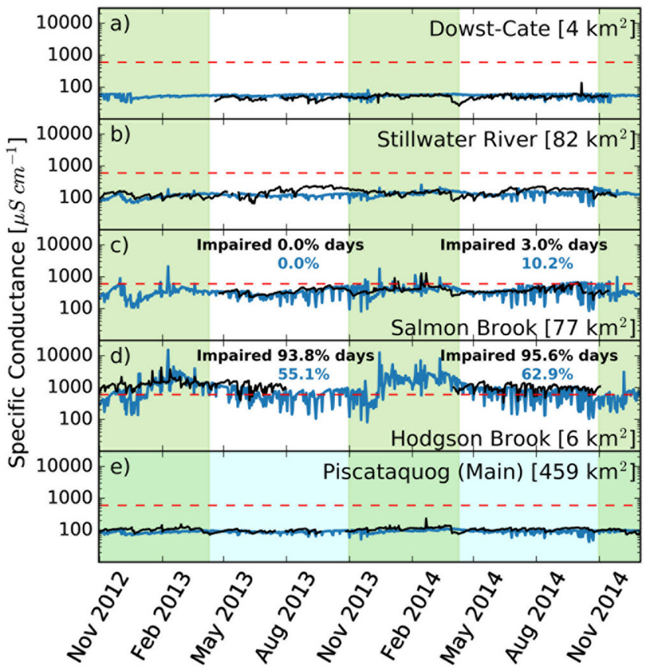

Fig. 2. Time series of specific conductivity at five stations comparing the Framework for Aquatic Modeling in the Earth Systems (FrAMES)-Nonpoint Anthropogenic Chloride Loading (NACL) data (blue) with observational data (black). Values in parentheses denote catchment area. Light bands indicate the productive season (mid-April through October). Dashed red lines depict the 600-μS cm^{-1} impairment threshold. The percentage of reporting days exceeding the impairment threshold is provided for each year where applicable.

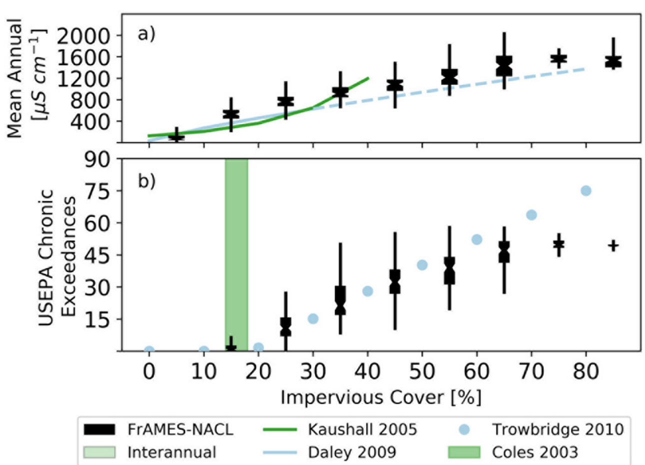

Fig. 3. Boxplots binned by imperviousness of the Framework for Aquatic Modeling in the Earth Systems (FrAMES)- Nonpoint Anthropogenic Chloride Loading (NACL) model for headwater (a) flow-weighted mean annual specific conductance, and (b) number of USEPA chronic threshold exceedances for chloride. Relationships between imperviousness and mean annual chloride concentrations (Kaushall et al., 2005; Daley et al., 2009) are given in terms of specific conductivity following Eq. [1]. USEPA chronic exceedances of the chloride standard from Trowbridge et al. (2010) uses mean annual concentration from Daley et al. (2009). The band of most biologic stress identified by Coles et al. (2004) is shown in (b).

(5.3–11 g Cl mm^{-1} m^{-2}, Supplemental Fig. S6). The majority (95%) of C_{DEI} posterior distribution was within the uncertainty of the local inventory estimate from Trowbridge et al. (2010) (T10) and completely bounded by the range of all three inventory studies. Moreover, the appropriateness of estimated road salt inputs (36 ± 24 Mg Cl km^{-2}) from FrAMES-NACL was further supported by the consistency in the ratio of road salt to total inputs of chloride between this study (89%) and estimates from southeastern New York (91%; Kelly et al., 2008). A lower ratio of road salt to total chloride in Minnesota (61%; (Novotny et al., 2009) reflected significantly lower agricultural input in the MRW. The similarity in ranges of model uncertainty and inventory uncertainty suggest that the model captured road salt loading to within expectations. Therefore, our hypothesis that deicer application rates inferred from stream chemistry and from inventories of applicators are equivalent was supported. The methodology presented here may be an appropriate supplement to inventorying deicer application rates and may identify areas that need further study. The estimated road salt application rate was greater than the 2.1 and 2.9 g Cl mm^{-1} m^{-2} recommended by Environment Canada (2004) (EC04), and the Salt Institute (2007) (SI07), respectively (Supplemental Fig. S6).

Despite the consistencies between FrAMES-NACL estimates of loading and the pool of inventory studies, loading in the Merrimack was distinct from any one inventory. The best estimates of loading rate from three inventories yielded 3.8, 11, and 12 g Cl mm^{-1} m^{-2} from Trowbridge et al. (2010) (T10), Sander et al. (2007) (S07), and Godwin et al. (2003) (G03), respectively. The deicer loading parameter therefore has a mode 73% higher than the local inventory of T10, and 40 to 45% lower than values from other inventories (G03 and S07).

Differences in loading may be attributed to location or to time varying application rates. Mean winter temperature in Twin Cities S07 was ~3°C cooler than the MRW, explaining a higher loading from that study (by reduced effectiveness of sodium chloride as a deicer); however, climatologic explanations do not explain the magnitude of the difference between the MRW and Twin Cities, nor greater loading in the Mohawk River G03 than the MRW because mean winter temperatures were similar. The study catchments of T10 are located within the MRW but are located toward the southern extent of the domain at lower elevations, making a climatological explanation possible since average winter temperatures averaged ~6°C warmer in southern portions of the watershed. Depending on the use of impervious areas for driving or walking, differing loading rates are common (Environment Canada, 2004; Salt Institute, 2007; Sander et al., 2007). At the resolution of our model, pixels represent many types of impervious areas, justifying our selection of a single average loading rate. However, both subcatchments within our model and differences in impervious use between each of the three inventory studies likely played a significant role in creating observed differences in application estimates. In addition, temporal variation in loading rates (Jackson and Jobbagy, 2005; Kilgour et al., 2014; Corsi et al., 2015) provide a realistic explanation for the greater estimated road salt loading between our study and that by T10. Stream concentrations used for calibration reflected average loading over the recent past integrated by the transit time distributions through the studied catchments. Road salt loading may be higher on average over that time period than the single winter of the study of T10.

Depending on the year, FrAMES-NACL retains up to 57% of deicer chloride within groundwater storage, or releases more chloride from storage than deicer applied (up to 17%). On average, FrAMES-NACL retains ~14% of applied deicer, slightly lower retention than the 22 to 37% reported by Jin et al. (2011)

and Shaw et al. (2012), but consistent with the long-term storage (17–20%) predicted for the Toronto metropolitan area (Perera et al., 2013).

After equilibration with current deicer application and the ratio of annual snowfall (220 mm snow water equivalent) to runoff (608 mm), river concentrations should approach a steady-state annual mean chloride concentration of 1.4 g Cl L^{-1} f_{imp}^{-1}, where f_{imp} is the fraction of catchment impervious area. Therefore, catchments with >16% impervious cover would have an annual mean chloride concentration exceeding the USEPA chronic threshold of 230 mg Cl L^{-1}.

Chloride Impairment in the Merrimack River Watershed

Validation of Chloride Impairment Metrics

The FrAMES-NACL model accurately identified stations in our observation network exceeding the impairment threshold (600 μS cm^{-1}). The Peirce skill score was a perfect 1.0 ± 0.02 for identifying stations with exceedances of either 1 or 30 d above the threshold for stations that have at least 90 d of data in a productive season. However, FrAMES-NACL underpredicted the number of days >600 μS cm^{-1} by ~55% for stations that did exhibit exceedances. Underprediction of exceedance duration was consistent with the more dynamic nature of conductivity in the model discussed above (Fig. 2, Supplemental Fig. S4b). Observations indicate that stations cluster near 0 and 100 d of impairment (for stations with complete data coverage through the productive season), whereas FrAMES-NACL predicted a more even distribution of intermediate days impaired. Thus, FrAMES-NACL provided an underestimate of the number of days impaired while accurately estimating locations of impairment, allowing us to make qualified inferences at the network scale.

The FrAMES-NACL model captured both the longitudinal trend in observed chloride between 2012 and 2014, and at the furthest downstream station (at Lowell) between 1999 and 2004 (Supplemental Fig. S7), which validated the OSC metric. All observational data on Supplemental Fig. S7 were not used in model calibration. For the basin profile stations, the relative absolute error was 15.4 ± 5.3% (Supplemental Fig. S7b). Moreover, the mean of summertime USGS grab samples from 1999 to 2004 at Lowell (195 ± 44 μS cm^{-1}, n = 23) was not significantly ($\alpha \leq 0.05$) different from simulated values on sampled days (213 ± 64 μS cm^{-1}) (Supplemental Fig. S7c).

Recent Chloride Impairment

The FrAMES-NACL model predicted that up to 11% of the Merrimack River network exceeded the 600-μS cm^{-1} chloride threshold on at least 1 d in the productive season (Fig. 1). Figure 1 shows that impaired reaches were most prevalent in the southern Merrimack watershed and consisted predominately of headwater (first-order) reaches elsewhere. The largest river exhibiting any impairment was fourth-order river draining (211 km^2); however, the largest stream with a median value of impaired days each year above zero over the 17-yr record was second-order draining (14 km^2). The period mean of IRD, the product of river length exceeding 600 μS cm^{-1} times the duration of impairment, was 1.3 × 10^5 ± 4.0 × 10^4 km d (± interannual variability). The period mean for OSC (summertime conductivity at basin mouth) was 216 ± 27 μS cm^{-1}, which is lower than the 600-μS cm^{-1} impairment criteria threshold but higher than pristine conditions.

The FrAMES-NACL model shows that a threshold of imperviousness leading to chloride impairment exists at <20% impervious cover. The annual number of exceedances of the USEPA chronic water quality threshold for chloride (230 mg Cl L^{-1} for 4 d) predicted by FrAMES-NACL was similar to that predicted from the relationship between chloride exceedances and mean annual chloride concentration identified by Trowbridge et al. (2010, Fig. 3b and 4), when using mean annual chloride from Daley et al. (2009) as the predictor (Fig. 3a). Both FrAMES-NACL and the function of Trowbridge et al. (2010) predicted negligible USEPA chronic exceedances below 20% impervious cover. Exceedances per year increase linearly through ~60% impervious cover (Fig. 3b). Previous findings for streams in New England found changing aquatic community structure at mean impervious cover ranging from 14 to 18% (Fig. 3b; Coles et al., 2004). Impairment of aquatic taxa observed at impervious cover <20% is consistent with stress from prolonged exposure to chloride at concentrations <230 mg Cl L^{-1} (Findlay and Kelly, 2011; Cañedo-Argüelles et al., 2013).

Interannual Variability in Riverine Chloride Impairment

Between 1998 and 2014, both metrics of chloride impairment (IRD, OSC) suggest that climate drives variability in impairment (Fig. 4). The two impairment metrics correlate with different individual meteorological indices. Even with the damping from groundwater storage, the predicted interannual SD of riverine impairment was 12% for IRD and 18% for OSC (Fig. 4). The IRD was positively correlated with snowfall (r^2 = 0.34, p = 0.015), and OSC inversely correlated with summer precipitation (SUMP) (r^2 = 0.20, p = 0.001) (Fig. 4b and 4d). We hypothesized that the number of dry days should correlate with increased impairment. Although more dry days led to greater impairment, the relationships were not statistically significant, (p = 0.075 and 0.068 for IRD and OSC, respectively), providing only weak support for our hypothesis (Fig. 4c and 4f). Inverse correlations of OSC with SUMP support summertime dryness as an important factor in controlling productive season salt impairment in larger rivers (Fig. 4d).

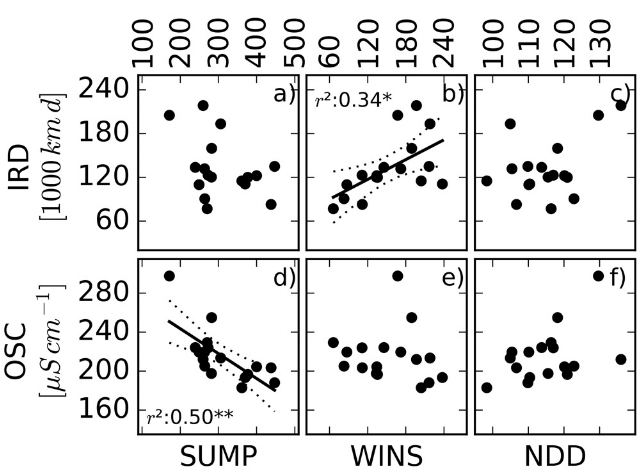

Fig. 4. Interannual correlations between impaired reach days (IRD) and outlet summer concentration (OSC) impairment metrics and select meteorological indices, including total summer precipitation (SUMP), winter frozen precipitation (WINS), and number of dry days (NDD). Bold lines represent best fit for relationships, with dotted lines representing 95% confidence intervals on the fit. *, Significant at the 0.05 and 0.01 probability levels, respectively.**

The positive correlation between IRD and snowfall (Fig. 4b) results from salt application being driven by frozen precipitation during winter. Most road salt infiltrates groundwater (the fraction of directly connected impervious area is low), and despite the large groundwater exchange pool, shallow groundwater is responsive enough to propagate the effects from the previous winter. Since small streams dominate total network length (Leopold, 1964), the IRD is driven by small stream responses, particularly in urban headwaters.

Greater snowfall has an inverse effect on OSC, a metric for large river, because it increases dilution from pristine catchments during snowmelt; however, the relationship is not statistically significant ($p = 0.66$, Fig. 4e). The weak correlation between snowfall (i.e., recent loading) and downstream concentrations (OSC) illustrates the importance of the scale-dependent processes of river network dilution on defining concentrations experienced by aquatic organisms.

As SUMP increases, IRD and OSC decline, although the response of OSC is much stronger (Fig. 4a and 4d). Snowfall and SUMP have similar effects on the OSC metric because both dilute chloride emanating from the relatively few headwater catchments that are chloride sources. Dilution from high SUMP has a limited effect on the IRD metric because higher than average precipitation cannot substantially alter chloride concentration in a large groundwater storage pool. Instead, SUMP can only increase the time that a contaminated headwater catchment is diluted by storm runoff, thereby lowering IRD in some catchments. Despite the overly dynamic response of FrAMES-NACL, this influence of SUMP on IRD was not significant (Fig. 4a).

Studies of riverine chloride contamination tend to focus on the trends of annual or seasonal chloride concentration (Anning and Flynn, 2014; Corsi et al., 2015). One study reported 20% interannual variability in mean annual chloride concentrations from subcatchments surrounding Baltimore, MD (Kaushal et al., 2005 Fig. 2), similar to this study (Fig. 4). After significant floods in southeastern New Hampshire during 2006 and 2007, observed chloride concentrations across a broad range of discharge were distinctly lower, suggesting flushing of legacy chloride from the fifth-order watershed (Daley et al., 2009). The mechanisms that control the dilution of road salt at affected reaches should be considered as an important secondary predictor of potential habitat degradation (Hale et al., 2014). Mechanisms that can influence dilution potential from clean headwaters include drinking and irrigation water abstractions in headwaters, and storage behind recreational dams. If climate patterns change (Hayhoe et al., 2006), reduced headwater dilution capacity from increasing forest evapotranspiration or drought would exacerbate the effects of chloride contamination.

Limitations of Model Structure

Our immobile zone parameterization for long-tail groundwater transport appears reasonable. Optimized values for the immobile zone exchange mechanism suggest a groundwater transit time >1 to 2 yr, consistent with typical catchment transit times (McDonnell et al., 2010), including catchments of the Merrimack River (Benettin et al., 2015) and shallow groundwater flow paths (Morgenstern et al., 2010). Some observations of groundwater transit time (Morgenstern et al., 2010; Stewart et al., 2010) are longer than calibrated here, and other immobile zones would be required to represent the broad range of groundwater transport timescales (Haggerty and Gorelick, 1995).

Greater dilution during rain events (Fig. 2) results in underestimates of specific conductance in developed catchments. The greater model responsiveness compared with observations follows primarily from assuming timescales of transport and hydrodynamic response to be equal in the soil and surface flow paths, although transport should lag hydrodynamic catchment response (Beven, 1982; Kirchner et al., 2000). In addition, we are not simulating impoundments and the influence of reservoirs, which provide additional storage for damping changes in concentration.

The FrAMES-NACL model neglects several processes that may account for the stronger dilution response than observations. Nonconservative chloride transport and processing including organochlorine formation, microbial processing, plant uptake, and storage in sediment micropores would dampen catchment chloride response (Bastviken et al., 2007; Kincaid and Findlay, 2009; Redon et al., 2011, 2012; Shaw et al., 2012; Öberg and Bastviken, 2012); however, these processes are most significant in pristine systems and diminish in importance as total loading (e.g., via road salt) increases (Svensson et al., 2010). Prolonged chloride storage on rough road surfaces is mobilized during precipitation through the summer, and first-flush-specific conductance can locally exceed 50 mg Cl L^{-1} (230 $\mu S\ cm^{-1}$) (Ostendorf et al., 2001), considerably greater than that represented by NACL (typically <1 mg Cl L^{-1}). Representing a reservoir for chloride storage and release from infrastructure (Ostendorf et al., 2006) is an appropriate improvement for future work. A final possibility is that storm events mobilize more groundwater with elevated chloride than represented by FrAMES-NACL (McDonnell, 1990, 2013; Kirchner et al., 2000). The shallow groundwater pool is represented with an exponential residence time distribution; a γ distribution (with $\alpha < 1$), characteristic of many environmental systems (Hrachowitz et al., 2010), may better represent rapid mobilization from groundwater with high chloride. Models accounting for these processes can be tested against observational data to evaluate evidence for these mechanisms.

Conclusions

We find road salt loading inferred from stream chloride concentrations at regional watershed scales to be consistent with inventoried estimates. A combination of inventory approaches and catchment-scale chloride mass balance modeling informed by stream chemistry data is likely to provide more realistic estimates of chloride balance through time. Loading estimates, derived here and from existing inventories, are considerably greater than recommended deicer application rates, offering an opportunity for improved management that can reduce potential chloride impairment. Given the sensitivity of FrAMES-NACL to interannual variability of winter snowfall, which drives loading via road salt applications, adoption of loading recommendations may reduce chloride impairment within several seasons throughout much of the moderately developed MRW. Reduced loading to the watershed is achieved using a combination of education, liability reduction (New Hampshire Revised Statutes, 2016), deicing fleet management technology, location-specific melt prediction (Trenouth et al., 2015), or stormwater management systems (Trenouth et al., 2018).

Using a combination of these strategies, Toronto achieved lower than recommended application rates (~1 g Cl mm^{-1} m^{-2}) (Perera et al., 2009; Kilgour et al., 2014). Models, like FrAMES-NACL, can be used in more specific settings to understand consequences of changing management practices, but they require more detailed deicer application parameterizations specific to management questions. The variability of the large river chloride is predominately controlled by dilution from water available from pristine catchments upstream, so management strategies on large rivers need to recognize the role of the entire river network.

Supplemental Material

Supplemental material describes methodology used is available in more detail, including more thorough descriptions of sensor data, mass balance calculations, parameterization, Markov-chain Monte Carlo experiments, and the definition of the impairment threshold. Two tables and six figures are included in the supplemental text.

Acknowledgments

We gratefully acknowledge the technical assistance of S. Glidden and A. Proussevitch, the support of all LoVoTECS volunteers and coordinators (E. Volitis and A. Inserillo), including partners with the Plum Island Estuary Long–Term Ecological Research site. We are also grateful for the instructive comments from four anonymous reviewers. This research was funded by the National Science Foundation Established Program to Stimulate Competitive Research (EPS 1101245). Partial funding was provided by the New Hampshire Agricultural Experiment Station. This is Scientific Contribution no. 2745. This work was completed in partial fulfillment of the requirements for a Ph.D. in Earth System Science at the University of New Hampshire.

References

Anning, D.W., and M.E. Flynn. 2014. Dissolved-solids sources, loads, yields, and concentrations in streams of the conterminous United States. USGS, Reston VA. doi:10.3133/sir20145012

Arvidsson, A., G. Blomqvist, and G. Öberg. 2012. Impact of climate change on use of anti-icing and deicing salt in Sweden. In: Winter maintenance and surface transportation weather: International Conference on Winter Maintenance and Surface Transportation Weather, Coralville, IA. 30 April–3 May 2012. Transport. Res. eCirc. E-C162. Transport. Res. Board, Washington, DC. p. 3–10.

Bastviken, D., F. Thomsen, T. Svensson, S. Karlsson, P. Sandén, G. Shaw, et al. 2007. Chloride retention in forest soil by microbial uptake and by natural chlorination of organic matter. Geochim. Cosmochim. Acta 71:3182–3192. doi:10.1016/j.gca.2007.04.028

Benettin, P., S.W. Bailey, J.L. Campbell, M.B. Green, A. Rinaldo, G.E. Likens, et al. 2015. Linking water age and solute dynamics in streamflow at the Hubbard Brook Experimental Forest, NH, USA. Water Resour. Res. 51:9256–9272. doi:10.1002/2015WR017552

Bester, M.L., E.O. Frind, J.W. Molson, and D.L. Rudolph. 2006. Numerical investigation of road salt impact on an urban wellfield. Ground Water 44:165–175. doi:10.1111/j.1745-6584.2005.00126.x

Betts, A.R., B. Gharabaghi, and E.A. McBean. 2014. Salt vulnerability assessment methodology for urban streams. J. Hydrol. 517:877–888. doi:10.1016/j.jhydrol.2014.06.005

Beven, K. 1982. On subsurface stormflow: Predictions with simple kinematic theory for saturated and unsaturated flows. Water Resour. Res. 18:1627–1633. doi:10.1029/WR018i006p01627

Bierwagen, B.G., D.M. Theobald, C.R. Pyke, A. Choate, P. Groth, J.V. Thomas, and P. Morefield. 2010. National housing and impervious surface scenarios for integrated climate impact assessments. Proc. Natl. Acad. Sci. USA 107:20887–20892. doi:10.1073/pnas.1002096107

Boutt, D.F., D.W. Hyndman, B.C. Pijanowski, and D.T. Long. 2001. Identifying potential land use-derived solute sources to stream baseflow using ground water models and GIS. Ground Water 39:24–34. doi:10.1111/j.1745-6584.2001.tb00348.x

Burakowski, E.A., C.P. Wake, B. Braswell, and D.P. Brown. 2008. Trends in wintertime climate in the northeastern United States: 1965–2005. J. Geophys. Res. 113:D20114. doi:10.1029/2008JD009870

Campbell, J.L., S.V. Ollinger, G.N. Flerchinger, H. Wicklein, K. Hayhoe, and A.S. Bailey. 2010. Past and projected future changes in snowpack and soil frost at the Hubbard Brook Experimental Forest, New Hampshire, USA. Hydrol. Processes 24:2465–2480. doi:10.1002/hyp.7666

Cañedo-Argüelles, M., C.P. Hawkins, B.J. Kefford, R.B. Schäfer, B.J. Dyack, S. Brucet, et al. 2016. Saving freshwater from salts. Science 351:914–916. doi:10.1126/science.aad3488

Cañedo-Argüelles, M., B.J. Kefford, C. Piscart, N. Prat, R.B. Schäfer, and C.-J. Schulz. 2013. Salinisation of rivers: An urgent ecological issue. Environ. Pollut. 173:157–167. doi:10.1016/j.envpol.2012.10.011

Coles, J.F., T.F. Cuffney, G. McMahon, and K.M. Beaulieu. 2004. The effects of urbanization on the biological, physical, and chemical characteristics of coastal New England streams. US Dep. Inter., USGS, Reston, VA.

Contosta, A.R., A. Adolph, D. Burchsted, E. Burakowski, M. Green, D. Guerra, et al. 2017. A longer vernal window: The role of winter coldness and snowpack in driving spring transitions and lags. Glob. Change Biol. 23:1610–1625. doi:10.1111/gcb.13517

Cooper, C.A., P.M. Mayer, and B.R. Faulkner. 2014. Effects of road salts on groundwater and surface water dynamics of sodium and chloride in an urban restored stream. Biogeochemistry 121:149–166. doi:10.1007/s10533-014-9968-z

Corsi, S.R., L.A. De Cicco, M.A. Lutz, and R.M. Hirsch. 2015. River chloride trends in snow-affected urban watersheds: Increasing concentrations outpace urban growth rate and are common among all seasons. Sci. Total Environ. 508:488–497. doi:10.1016/j.scitotenv.2014.12.012

Corsi, S.R., D.J. Graczyk, S.W. Geis, N.L. Booth, and K.D. Richards. 2010. A fresh look at road salt: Aquatic toxicity and water-quality impacts on local, regional, and national scales. Environ. Sci. Technol. 44:7376–7382. doi:10.1021/es101333u

Daley, M.L., J.D. Potter, and W.H. McDowell. 2009. Salinization of urbanizing New Hampshire streams and groundwater: Effects of road salt and hydrologic variability. J. North Am. Benthol. Soc. 28:929–940. doi:10.1899/09-052.1

de Zwart, D., S.D. Dyer, L. Posthuma, and C.P. Hawkins. 2006. Predictive models attribute effects on fish assemblages to toxicity and habitat alteration. Ecol. Appl. 16:1295–1310. doi:10.1890/1051-0761(2006)016[1295:PMAEOF]2.0.CO;2

Demars, B.O.L., J.R. Manson, J.S. Ólafsson, G.M. Gíslason, R. Gudmundsdóttir, G. Woodward, et al. 2011. Temperature and the metabolic balance of streams. Freshwater Biol. 56:1106–1121. doi:10.1111/j.1365-2427.2010.02554.x

Ejsmond, M.J., M. Czarnołęski, F. Kapustka, and J. Kozłowski. 2010. How to time growth and reproduction during the vegetative season: An evolutionary choice for indeterminate growers in seasonal environments. Am. Nat. 175:551–563. doi:10.1086/651589

Environment Canada. 2004. Priority substances list assessment report: Road salts. Environ. Canada and Health Canada, Gatineau, QC.

Findlay, S.E.G., and V.R. Kelly. 2011. Emerging indirect and long-term road salt effects on ecosystems. Ann. N. Y. Acad. Sci. 1223:58–68. doi:10.1111/j.1749-6632.2010.05942.x

Ghassemi, F., A.J. Jakeman, and H.A. Nix. 1995. Salinisation of land and water resources: Human causes, extent, management, and case studies. Univ. New South Wales, Sydney, NSW.

Godwin, K.S., S.D. Hafner, and M.F. Buff. 2003. Long-term trends in sodium and chloride in the Mohawk River, New York: The effect of fifty years of road-salt application. Environ. Pollut. 124:273–281. doi:10.1016/S0269-7491(02)00481-5

Granato, G.E., L.A. DeSimone, J.R. Barbaro, and L.C. Jeznach. 2015. Methods for evaluating potential sources of chloride in surface waters and groundwaters of the conterminous United States. USGS, Reston, VA. doi:10.3133/ofr20151080

Haggerty, R., and S.M. Gorelick. 1995. Multiple-rate mass transfer for modeling diffusion and surface reactions in media with pore-scale heterogeneity. Water Resour. Res. 31:2383–2400. doi:10.1029/95WR10583

Hale, I.L., W.M. Wollheim, R.G. Smith, H. Asbjornsen, A.F. Brito, K. Broders, et al. 2014. A scale-explicit framework for conceptualizing the environmental impacts of agricultural land use changes. Sustainability 6:8342–8451. doi:10.3390/su6128432

Hayhoe, K., C.P. Wake, T.G. Huntington, L. Luo, M.D. Schwartz, J. Sheffield, et al. 2006. Past and future changes in climate and hydrological indicators in the US Northeast. Clim. Dyn. 28:381–407. doi:10.1007/s00382-006-0187-8

Hrachowitz, M., C. Soulsby, D. Tetzlaff, I.A. Malcolm, and G. Schoups. 2010. Gamma distribution models for transit time estimation in catchments: Physical interpretation of parameters and implications for time-variant transit time assessment. Water Resour. Res. 46:W10536. doi:10.1029/2010WR009148

Inserillo, E.A., M.B. Green, J.B. Shanley, and J.N. Boyer. 2017. Comparing catchment hydrologic response to a regional storm using specific conductivity sensors. Hydrol. Processes 31:1074–1085. doi:10.1002/hyp.11091

Ippolito, A., M. Carolli, E. Varolo, S. Villa, and M. Vighi. 2012. Evaluating pesticide effects on freshwater invertebrate communities in alpine environment: A model ecosystem experiment. Ecotoxicology 21:2051–2067. doi:10.1007/s10646-012-0957-5

Jackson, R.B., and E.G. Jobbagy. 2005. From icy roads to salty streams. Proc. Natl. Acad. Sci. USA 102:14487–14488. doi:10.1073/pnas.0507389102

Jin, L., P. Whitehead, D.I. Siegel, and S. Findlay. 2011. Salting our landscape: An integrated catchment model using readily accessible data to assess emerging road salt contamination to streams. Environ. Pollut. 159:1257–1265. doi:10.1016/j.envpol.2011.01.029

Kaushal, S.S., P.M. Groffman, G.E. Likens, K.T. Belt, W.P. Stack, V.R. Kelly, et al. 2005. Increased salinization of fresh water in the northeastern United States. Proc. Natl. Acad. Sci. USA 102:13517–13520. doi:10.1073/pnas.0506414102

Kelly, V.R., G.M. Lovett, K.C. Weathers, S.E.G. Findlay, D.L. Strayer, D.J. Burns, and G.E. Likens. 2008. Long-term sodium chloride retention in a rural watershed: Legacy effects of road salt on streamwater concentration. Environ. Sci. Technol. 42:410–415. doi:10.1021/es071391l

Kelly, W.R., S.V. Panno, and K.C. Hackley. 2012. Impacts of road salt runoff on water quality of the Chicago, Illinois, region. Environ. Eng. Geosci. 18:65–81. doi:10.2113/gseegeosci.18.1.65

Kelting, D.L., C.L. Laxson, and E.C. Yerger. 2012. Regional analysis of the effect of paved roads on sodium and chloride in lakes. Water Res. 46:2749–2758. doi:10.1016/j.watres.2012.02.032

Kilgour, B.W., B. Gharabaghi, and N. Perera. 2014. Ecological benefit of the road salt code of practice. Water Qual. Res. J. 49:43–52. doi:10.2166/wqrjc.2013.129

Kincaid, D.W., and S.E.G. Findlay. 2009. Sources of elevated chloride in local streams: Groundwater and soils as potential reservoirs. Water Air Soil Pollut. 203:335–342. doi:10.1007/s11270-009-0016-x

Kirchner, J.W., X. Feng, and C. Neal. 2000. Fractal stream chemistry and its implications for contaminant transport in catchments. Nature 403:524–527. doi:10.1038/35000537

Kirchner, J.W., D. Tetzlaff, and C. Soulsby. 2010. Comparing chloride and water isotopes as hydrological tracers in two Scottish catchments. Hydrol. Processes 24:1631–1645. doi:10.1002/hyp.7676

Kraus, J.M., T.S. Schmidt, D.M. Walters, R.B. Wanty, R.E. Zuellig, and R.E. Wolf. 2014. Cross-ecosystem impacts of stream pollution reduce resource and contaminant flux to riparian food webs. Ecol. Appl. 24:235–243. doi:10.1890/13-0252.1

Leopold, L.B. 1964. Fluvial processes in geomorphology. W.H. Freeman, San Francisco, CA.

Manzato, A. 2007. A note on the maximum Peirce skill score. Weather Forecast. 22:1148–1154. doi:10.1175/WAF1041.1

McDonnell, J.J. 1990. A rationale for old water discharge through macropores in a steep, humid catchment. Water Resour. Res. 26:2821–2832. doi:10.1029/WR026i011p02821

McDonnell, J.J. 2013. Are all runoff processes the same? Hydrol. Processes 27:4103–4111. doi:10.1002/hyp.10076

McDonnell, J.J., K. McGuire, P. Aggarwal, K.J. Beven, D. Biondi, G. Destouni, et al. 2010. How old is streamwater? Open questions in catchment transit time conceptualization, modelling and analysis. Hydrol. Processes 24:1745–1754. doi:10.1002/hyp.7796

Morgan, R.P., K.M. Kline, M.J. Kline, S.F. Cushman, M.T. Sell, R.E. Weitzell, and J.B. Churchill. 2012. Stream conductivity: Relationships to land use, chloride, and fishes in Maryland streams. N. Am. J. Fish. Manage. 32:941–952. doi:10.1080/02755947.2012.703159

Morgenstern, U., M.K. Stewart, and R. Stenger. 2010. Dating of streamwater using tritium in a post nuclear bomb pulse world: Continuous variation of mean transit time with streamflow. Hydrol. Earth Syst. Sci. 14:2289–2301. doi:10.5194/hess-14-2289-2010

Murray, D.M. 1977. An economic analysis of the environmental impact of highway deicing salts. Environ. Prot. Technol. Ser. EPA-600/2-76-105. US Gov. Print. Office, Washington, DC.

New Hampshire Fish and Game Department. 2015. New Hampshire wildlife action plan 2015: Aquatic habitat. New Hampshire Fish Game Dep., Concord.

New Hampshire Revised Statutes. 2016. Chapt. 508: Limitations of Actions. Sect. 508:22. Liability limited for winter maintenance. New Hampshire Revis. Statutes, Concord.

NHOEP. 2010. 2010 census. New Hampshire Office Energy Planning. http://www.nh.gov/oep/data-center/census/ (accessed 24 June 2015).

Nimiroski, M.T., and M.C. Waldron. 2002. Sources of sodium and chloride in the Scituate Reservoir drainage basin, Rhode Island. US Dep. Inter., USGS, Reston, VA.

Novotny, E.V., D. Murphy, and H.G. Stefan. 2008. Increase of urban lake salinity by road deicing salt. Sci. Total Environ. 406:131–144. doi:10.1016/j.scitotenv.2008.07.037

Novotny, E.V., A.R. Sander, O. Mohseni, and H.G. Stefan. 2009. Chloride ion transport and mass balance in a metropolitan area using road salt. Water Resour. Res. 45:W12410. doi:10.1029/2009WR008141

Öberg, G., and D. Bastviken. 2012. Transformation of chloride to organic chlorine in terrestrial environments: Variability, extent, and implications. Crit. Rev. Environ. Sci. Technol. 42:2526–2545. doi:10.1080/10643389.2011.592753

Ostendorf, D.W., E.S. Hinlein, D.P. Ahlfeld, and J.T. DeJong. 2006. Calibrated models of deicing agent solids, pavement texture, and specific conductivity of highway runoff. J. Environ. Eng. 132:1562–1571. doi:10.1061/(ASCE)0733-9372(2006)132:12(1562)

Ostendorf, D.W., D.C. Peeling, T.J. Mitchell, and S.J. Pollock. 2001. Chloride persistence in a deiced access road drainage system. J. Environ. Qual. 30:1756–1770. doi:10.2134/jeq2001.3051756x

Perera, N., B. Gharabaghi, and K. Howard. 2013. Groundwater chloride response in the Highland Creek watershed due to road salt application: A re-assessment after 20 years. J. Hydrol. 479:159–168. doi:10.1016/j.jhydrol.2012.11.057

Perera, N., B. Gharabaghi, and P. Noehammer. 2009. Stream chloride monitoring program of City of Toronto: Implications of road salt application. Water Qual. Res. J. Canada 44:132–140.

Redon, P.-O., A. Abdelouas, D. Bastviken, S. Cecchini, M. Nicolas, and Y. Thiry. 2011. Chloride and organic chlorine in forest soils: Storage, residence times, and influence of ecological conditions. Environ. Sci. Technol. 45:7202–7208. doi:10.1021/es2011918

Redon, P.-O., C. Jolivet, N.P.A. Saby, A. Abdelouas, and Y. Thiry. 2012. Occurrence of natural organic chlorine in soils for different land uses. Biogeochemistry 114:413–419. doi:10.1007/s10533-012-9771-7

Rienecker, M.M., M.J. Suarez, R. Gelaro, R. Todling, J. Bacmeister, E. Liu, et al. 2011. MERRA: NASA's modern-era retrospective analysis for research and applications. J. Clim. 24:3624–3648. doi:10.1175/JCLI-D-11-00015.1

Salt Institute. 2007. The snowfighters handbook: 40th year edition, A practical guide for snow and ice control. Salt Inst., Alexandria, VA.

Samal, N., W.M. Wollheim, S. Zuidema, R.J. Stewart, Z. Zhou, M.M. Mineau, et al. 2017. Projections of coupled terrestrial and aquatic ecosystem change relevant to ecosystem service valuation at regional scales. Ecosyst. Soc. 22(4).

Sander, A., E. Novotny, O. Mohseni, and H. Stefan. 2007. Inventory of road salt use in the Minneapolis/St. Paul metropolitan area. St. Anthony Falls Lab. http://conservancy.umn.edu/handle/11299/115332 (accessed 27 May 2014).

Shaw, S.B., R.D. Marjerison, D.R. Bouldin, J.-Y. Parlange, and M.T. Walter. 2012. Simple model of changes in stream chloride levels attributable to road salt applications. J. Environ. Eng. 138:112–118. doi:10.1061/(ASCE)EE.1943-7870.0000458

Stewart, M.K., U. Morgenstern, and J.J. McDonnell. 2010. Truncation of stream residence time: How the use of stable isotopes has skewed our concept of streamwater age and origin. Hydrol. Processes 24:1646–1659. doi:10.1002/hyp.7576

Stewart, R.J., W.M. Wollheim, M.N. Gooseff, M.A. Briggs, J.M. Jacobs, B.J. Peterson, and C.S. Hopkinson. 2011. Separation of river network–scale nitrogen removal among the main channel and two transient storage compartments. Water Resour. Res. 47:W00J10. doi:10.1029/2010WR009896

Stewart, R.J., W.M. Wollheim, A. Miara, C.J. Vörösmarty, B. Fekete, R.B. Lammers, and B. Rosenzweig. 2013. Horizontal cooling towers: Riverine ecosystem services and the fate of thermoelectric heat in the contemporary Northeast US. Environ. Res. Lett. 8:025010. doi:10.1088/1748-9326/8/2/025010

Svensson, T., G.M. Lovett, and G.E. Likens. 2010. Is chloride a conservative ion in forest ecosystems? Biogeochemistry 107:125–134. doi:10.1007/s10533-010-9538-y

Thorn, A.M., C.P. Wake, C.D. Grimm, C.R. Mitchell, M.M. Mineau, and S.V. Ollinger. 2017. Development of scenarios for land cover, population density, impervious cover, and conservation in New Hampshire, 2010–2100. Ecol. Soc. 22:19. doi:10.5751/ES-09733-220419

Trenouth, W.R., B. Gharabaghi, and H. Farghaly. 2018. Enhanced roadside drainage system for environmentally sensitive areas. Sci. Total Environ. 610–611:613–622. doi:10.1016/j.scitotenv.2017.08.081

Trenouth, W.R., B. Gharabaghi, and N. Perera. 2015. Road salt application planning tool for winter de-icing operations. J. Hydrol. 524:401–410. doi:10.1016/j.jhydrol.2015.03.004

Trowbridge, P.R., J.S. Kahl, D.A. Sassan, D.L. Heath, and E.M. Walsh. 2010. Relating road salt to exceedances of the water quality standard for chloride in New Hampshire streams. Environ. Sci. Technol. 44:4903–4909. doi:10.1021/es100325j

US Census Bureau. 2015. County census statistics, Massachusetts. US Census Bureau, Suitland, MD.

USEPA. 2013. National rivers and streams assessment 2008–2009, A collaborative survey. USEPA, Washington, DC.

Vörösmarty, C.J., C.A. Federer, and A.L. Schloss. 1998. Potential evaporation functions compared on US watersheds: Possible implications for global-scale water balance and terrestrial ecosystem modeling. J. Hydrol. 207:147–169. doi:10.1016/S0022-1694(98)00109-7

Wake, C., E. Burakowski, P. Wilkinson, K. Hayhoe, A. Stoner, C. Keeley, and J. LaBranche. 2014a. Climate change in northern New Hampshire: Past, present, and future. Clim. Solutions New England, Durham, NH.

Wake, C., E. Burakowski, P. Wilkinson, K. Hayhoe, A. Stoner, C. Keeley, and J. LaBranche. 2014b. Climate change in southern New Hampshire: Past, present, and future. Clim. Solutions New England, Durham, NH.

Wayland, K.G., D.W. Hyndman, D. Boutt, B.C. Pijanowski, and D.T. Long. 2002. Modelling the impact of historical land uses on surface-water quality using groundwater flow and solute-transport models. Lakes Reservoirs: Res. Manage. 7:189–199. doi:10.1046/j.1440-1770.2002.00187.x

Wisser, D., B.M. Fekete, C.J. Vörösmarty, and A.H. Schumann. 2010. Reconstructing 20th century global hydrography: A contribution to the Global Terrestrial Network-Hydrology (GTN-H). Hydrol. Earth Syst. Sci. 14:1–24. doi:10.5194/hess-14-1-2010

Wollheim, W.M., C.J. Vörösmarty, A.F. Bouwman, P. Green, J. Harrison, E. Linder, et al. 2008. Global N removal by freshwater aquatic systems using a spatially distributed, within-basin approach. Global Biogeochem. Cycles 22:GB2026. doi:10.1029/2007GB002963

Xian, G., C. Homer, J. Dewitz, J. Fry, N. Hossain, and J. Wickham. 2011. Change of impervious surface area between 2001 and 2006 in the conterminous United States. Photogramm. Eng. Remote Sensing 77:758–762.