Environmental Science & Technology

Article

Cite This: Environ. Sci. Technol. XXXX, XXX, XXX−XXX

pubs.acs.org/est

Long-Term Climatic and Anthropogenic Impacts on Streamwater Salinity in New York State: INCA Simulations Offer Cautious Optimism

Kristina Gutchess,*[,†] Li Jin,[‡] José L. J. Ledesma,[§] Jill Crossman,[‖] Christa Kelleher,[†,⊥] Laura Lautz,[†] and Zunli Lu[†,#]

[†]Department of Earth Sciences, Syracuse University, 204 Heroy Geology Laboratory, Syracuse, New York 13244, United States

[‡]Geology Department, State University of New York College at Cortland, Cortland, New York 13045, United States

[§]Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences (SLU), P.O. Box 7050, 750 07 Uppsala, Sweden

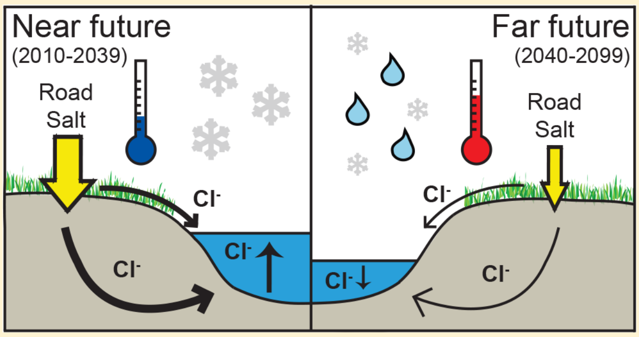
[‖]Department of Earth and Environmental Sciences, University of Windsor, Memorial Hall, 401 Sunset Avenue, Windsor, Ontario N98 3P4, Canada

[⊥]Department of Civil and Environmental Engineering, Syracuse University, 151 Link Hall, Syracuse, New York 13244, United States

[#]State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen 361102, China

Supporting Information

ABSTRACT: The long-term application of road salts has led to a rise in surface water chloride (Cl^-) concentrations. While models have been used to assess the potential future impacts of continued deicing practices, prior approaches have not incorporated changes in climate that are projected to impact hydrogeology in the 21st century. We use an INtegrated CAtchment (INCA) model to simulate Cl^- concentrations in the Tioughnioga River watershed. The model was run over a baseline period (1961−1990) and climate simulations from a range of GCMs run over three 30-year intervals (2010−2039; 2040−2069; 2070−2099). Model projections suggest that Cl^- concentrations in the two river branches will continue to rise for several decades, before beginning to decline around 2040−2069, with all GCM scenarios indicating reductions in snowfall and associated salt applications over the 21st century. The delay in stream response is most likely attributed to climate change and continued contribution of Cl^- from aquifers. By 2100, surface water Cl^- concentrations will decrease to below 1960s values. Catchments dominated by urban lands will experience a decrease in average surface water Cl^-, although moderate compared to more rural catchments.



INTRODUCTION

Concentrations of chloride (Cl^-) in surface water have risen at unprecedented rates since the application of deicing salts to roads began in the 1950s.[1−5] In New York State, 90−450 lbs. of road salt per lane mile of road are applied to highways during a given event.[6] Only approximately 10% of this salt is attached to vehicle traffic and transported away without entering local streams.[7] The rest enters adjacent catchments as nonpoint source pollution through surface runoff annually, contributing to a rise in baseline concentrations of Cl^- over time.[8,9] Elevated concentrations of Cl^- in surface water may threaten sensitive biota,[1,3,4,10] increase corrosivity,[11,12] and jeopardize the quality of drinking water resources.[11−15]

Anthropogenic stressors on a catchment (such as urbanization and deicing practices) can have long-term effects on the potability of drinking water resources and terrestrial ecosystems.[1,2,16] Even more profound impacts on water chemistry are possible due to potential future changes to climate.[17,18] Many studies have employed basic mass balance or mixing models to understand the extent to which future changes in road salt usage might impact water quality.[7,8,19,20] To date, few studies have provided predictions of water quality changes incorporating both future changes in climate and anthropogenic effects related to road salt usage. The integrated catchment (INCA) family of models was initially developed for the assessment of nitrogen sources within mixed land-use catchments,[21,22] but has since been expanded to simulate fluxes in phosphorus, carbon, mercury, and sediments in a variety of settings.[23−29] The INCA model framework employs process-based, reaction kinetic

Received: August 28, 2017
Revised: November 19, 2017
Accepted: December 27, 2017
Published: December 27, 2017

DOI: 10.1021/acs.est.7b04385
Environ. Sci. Technol. XXXX, XXX, XXX−XXX

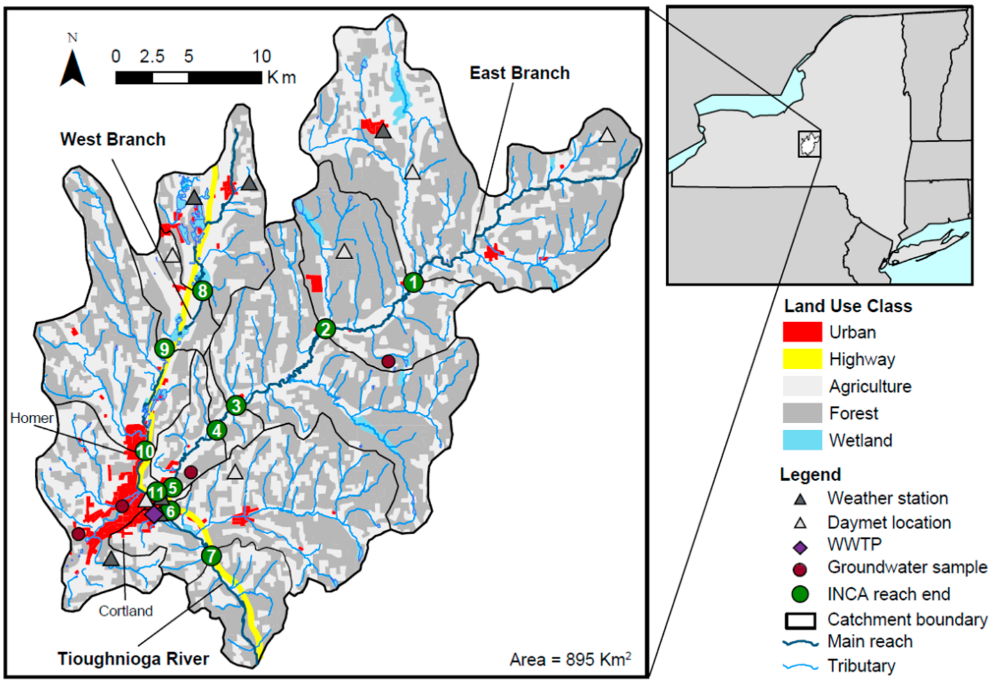


Figure 1. INCA reach structure and land use classification.[32,33,41] Land use classification of the Tioughnioga river watershed is based on classification scheme developed by Anderson.[33,41] USGS flow station (USGS Station Number: 01509000) is located at the end of Reach 6. Daymet locations indicate geographic coordinate position of single-pixel extraction of daily temperature and precipitation outputs. Inset denotes location of study area relative to New York State.[63] Map generated using ArcGIS software version 10.4 by Esri.

equations to simulate principle hydrologic and biogeochemical processes. The model is dynamic and features a mass-balance approach to track temporal and spatial variations across both land and stream components at daily time steps at the catchment scale.

Here we provide a present-day calibration and the first future simulation of stream Cl^- under a variety of climatic conditions, changes in land use, and snow management practices throughout the twenty-first century. We modify the INCA-N modeling framework to simulate daily fluxes in stream Cl^- (hereby INCA-Cl) featuring a new multibranched structure under 16 different future scenarios.[27,30] We apply the INCA-Cl model to a mixed land-use headwater stream network in New York State (Figure 1).

■ MATERIALS AND METHODS

Site Description. The Tioughnioga River in central New York is a main headwater catchment to the Upper Susquehanna River Basin and Chesapeake Bay. Two main tributaries (East and West Branches of the Tioughnioga River) converge in Cortland County in central New York to form the Tioughnioga River. This study focuses on an approximately 900 km^2 (266 km^2 West Branch and 496 km^2 East Branch) segment of the upstream reach[32] (Figure 1). Land use in the Tioughnioga River watershed is dominated by forest and agriculture.[33] Urban land accounts for a greater proportion of area in the West Branch and is concentrated toward the catchment outlet. The West Branch flows adjacent to Interstate 81 for the entirety of its reach. Mean annual temperature and average annual precipitation in the City of Cortland are 8.1 °C and 99 cm, respectively (NOAA CDC GHCND: USC00301799). Snowfall typically occurs from October to April and accounts for a significant proportion of annual precipitation, with an average of 189 cm from 1900−2000 (NOAA CDC GHCND: USC00301799).

The river is underlain by a two-aquifer valley-fill system comprised of a surficial unconfined sand and gravel aquifer and a confined basal sand and gravel aquifer separated by a glaciolacustrine confining unit.[34−37] The aquifer system overlies organic rich shale interbedded with siltstone, sandstone, and limestone of Upper to Middle Devonian age.[34−37] The aquifer provides drinking water to inhabitants of the cities of Cortland, Homer, and surrounding communities. It has been designated as a primary aquifer by the New York State Department of Environmental Conservation (NYS DEC) and as a sole source aquifer by the U.S. Environmental Protection Agency under the Safe Drinking Water Act.[37] Primary aquifers are recognized by the NYS DEC as highly productive aquifers utilized as municipal water supply sources. A sole source aquifer designation indicates that reasonable alternative drinking water sources do not exist.

INCA-Cl Model Setup. INCA is a dynamic, semi-distributed, process-based solute transport model originally developed to assess sources of nitrogen in catchments.[21,22] The INCA Model was previously used to simulate stream Cl^- concentrations in a single stem main river that treats the tributaries as aggregated inputs.[12] In this study, we modified an existing INCA-N model and incorporated the new multi-branched structure to simulate daily estimates of in-stream concentrations of Cl^- in the Tioughnioga River watershed. Within the model, Cl^- is transferred through the catchment by individual processes operating across five land use classes and a multireach river network. Inputs to INCA include daily time series of precipitation, temperature, hydrologically effective rainfall (HER) and soil moisture deficit (SMD). HER reflects the proportion of precipitation that eventually becomes surface runoff (i.e., after accounting for evapotranspiration and

DOI: 10.1021/acs.est.7b04385
Environ. Sci. Technol. XXXX, XXX, XXX−XXX

Table 1. Watershed characteristics for Tioughnioga River. Reaches 1 through 5 correspond to East Branch Tioughnioga River, whereas reaches 6-7 and 8-11 are located within the Main Branch of the Tioughnioga River, and the West Branch, respectively

river name	reach number	reach area (km^2)	reach length (m)	land use class (%)				
				urban	highway	agriculture	forest	wetland
East Branch Tioughnioga River	1	219.22	26 634	1.21	0.00	42.87	53.90	2.01
East Branch Tioughnioga River	2	93.66	10 578	1.51	0.00	24.65	71.62	2.22
East Branch Tioughnioga River	3	147.84	13 847	0.31	0.00	30.51	67.72	1.45
East Branch Tioughnioga River	4	10.74	2847	0.00	0.00	47.99	51.60	0.41
East Branch Tioughnioga River	5	24.32	7190	3.16	0.00	52.77	44.07	0.00
Tioughnioga River	6	3.17	947	25.96	6.71	2.02	65.31	0.00
Tioughnioga River	7	130.17	4956	3.72	0.87	37.44	57.70	0.28
West Branch Tioughnioga River	8	65.36	12 166	2.61	3.33	42.27	45.80	5.98
West Branch Tioughnioga River	9	25.83	3293	1.07	4.42	42.41	46.01	6.09
West Branch Tioughnioga River	10	100.93	6274	2.79	1.79	42.02	51.83	1.56
West Branch Tioughnioga River	11	73.40	4918	17.45	1.58	52.11	28.86	0.00

interception), whereas SMD is defined as the depth of water required to return soil water content to field capacity (maximum). HER and SMD were estimated using the Precipitation, Evapotranspiration and Runoff Simulator for Solute Transport (PERSiST) model by the processes outlined by Futter et al.[38] Daily precipitation and temperature estimates were calculated for 7 weather stations (NOAA Climatic Data Center) located within the catchment area using the Theissen-polygon area-weighted approach.[39] Missing data were supplemented with area-weighted mean daily temperature and precipitation data generated by the Daymet single-pixel extraction tool.[40]

The study area was divided into 11 reaches and associated subcatchments. Reach boundaries were selected based on locations of measured water chemistry and U.S. Geological Survey (USGS) flow stations (Figure 1). Two main branches were simulated individually by splitting into multiple reaches to reflect the heterogeneity of the catchment with different land uses. Reaches 5 and 11 represent the mouth of the East and West branches, respectively (Figure 1). Subcatchment delineation was derived using a digital elevation model in ArcGIS version 10.4. The percentage of each of five land use classes (urban, highway, agriculture, wetland, and forest), total area, and reach length were also calculated for each subcatchment (Table 1) in ArcGIS.

Cl^- inputs to the model included (1) atmospheric deposition of Cl^-, (2) road salt application, and (3) water softener usage (Supporting Information (SI) Table S1). Daily loads of road salt application and water softener usage were determined based on area, 2000 U.S. census data, water usage, state road salt purchase records, and meteorological conditions. Natural atmospheric deposition rates of Cl^- were measured at the Aurora Research Farm in adjacent Cayuga County, New York (NY08) (National Atmospheric Deposition Program (NTN)). Based on the 2012−2015 average annual Cl^- deposition at this site, we calculated annual wet deposition of Cl^- to be 0.59 kg/ha/yr. This value was used as the deposition rate in the model. Dry deposition was calculated to be 0.20 kg/ha/yr, which represents the same proportion of total atmospheric Cl^- deposition as was observed in Cornwall NY, approximately 292 km from the southwest study area.[42]

The new multibranched INCA-Cl model setup allows for variable road salt application rates to reflect different salting practices for highway and local roads in each individual subcatchment. Daily road salt application rates were derived from relationships between state road salt purchase records, land cover, and meteorological conditions. State road salt purchase records indicate that from 2012 through 2015 an average of 23 000 and 9000 tons of road salt were purchased annually for application to urban areas and Interstate-81 in Cortland County, respectively.[43] We used 60−68% of the purchased amounts as model input to reflect the proportion of Cortland County and Interstate-81 within the model area while accounting for an additional 10% loss via direct wash off.[17] In New York State, road salts are commonly applied when precipitation occurs at subzero (Celsius) temperature to prevent traffic accidents.[44] Thus, road salt applications were calculated to be 76 days per year (on average) during the calibration period, using weather data. Daily Cl^- application rates were, then, estimated for both highway and urban land use classes of 38.7 and 21.4 kg Cl^-/ha/d, respectively, based on the total number of subzero days, the total area of highway and urban land use classes.

Water softeners have been used in the Tioughnioga River watershed to combat water hardness issues for decades.[35,45−47] Daily Cl^- inputs from water softener for each subcatchment were estimated based on per capita water and water softener use. We simplified estimates by assuming that all households in the study area use water softeners, as in previous studies,[2,15] which likely results in an overestimation. Based on U.S. Environmental Protection Agency estimates, we assumed average water consumption and water softener usage of 400 L/person/day and 125 kg/year, respectively.[2,48] The amount of water softener used per subcatchment was derived by multiplying the per capita-softener consumption by the population (SI Table S1).

Calculated inputs estimated that road salt accounts for approximately 87% of the total Cl^- inputs into the Tioughnioga River catchment from 2012 to 2015 (SI, Table 1). Prior studies suggested in addition to a dominant source of salinity from road salt, the natural migration of deeper, more saline groundwater could potentially contribute to streamwater salinity especially at the summer baseline. However, given the insignificant volume (typically <0.1%)[20,45−47] from the deep groundwater, it was not included in this modeling study.

Model Calibration and Sensitivity Analysis. Daily simulations for the INCA-Cl model were performed for the Tioughnioga River watershed from January 1st, 2012 through December 31st, 2015 (n = 1461 days). The INCA model was calibrated manually to discharge data and stream Cl^- concentrations across spatial and temporal scales. Manual calibration has been proved as a robust method for obtaining

DOI: 10.1021/acs.est.7b04385
Environ. Sci. Technol. XXXX, XXX, XXX−XXX

acceptable simulations with the INCA family of models.[49] Modeled streamflow was calibrated to mean daily discharge (USGS Station Number: 01509000). The model was calibrated to weekly/biweekly surface water Cl^- concentrations measured at reach 5 and reach 11 (sampling and analysis details in ref 20) and daily Cl^- concentrations from a specific conductance probe installed at the bottom of reach 11 from 2012 to 2014. The probe recorded surface water conductivity at 30 min increments from November 2013 to July 2014 and October 2014 to January 2015. Daily specific conductance values were then converted to daily concentrations of Cl^- based on a laboratory standard curve for model calibration. Bimonthly surface water samples were collected at several downstream locations along the East and West Branches of the Tioughnioga River in 2014. Sample sites were selected based on accessibility and confluences of major tributaries. Subcatchment boundaries were delineated to these downstream points. Cl^- data collected in 2014 at reach 2, 3, 4, and 7 were also used to assist calibration. Groundwater samples were collected from four locations from 2012 to 2014 ($n = 19$) (Figure 1). Samples were analyzed for concentrations of Cl^- via ion chromatography (Dionex-ICS 2100) calibrated with five internal laboratory standards for anions. The average Cl^- concentrations in groundwater samples (35 and 70 mg/L, for East and West Branch respectively) were used as the groundwater Cl^- input for the model. INCA model fit was assessed based on values of R^2 coefficients and Nash-Sutcliffe (N−S) coefficients.

A simple "one-at-a-time" sensitivity analysis of INCA-Cl flow and Cl^- related parameters was performed to assess the effects of hydrological, catchment, and in-stream variability of concentrations of Cl^- in surface water. We adopted a previously employed approach in which selected parameter values from the parameter set with the highest model efficiency coefficients (Nash-Sutcliffe (N−S) coefficients) were varied by 2× and 0.5×.[50] The sensitivity of parameters was then defined as

$$N - S_{Best} - 0.5 \times (N - S_{2\times} + N - S_{0.5\times}) \quad (1)$$

Future Scenarios. Monthly mean values for average daily temperature and daily precipitation for two Global Climate Models (GCMs) (HADCM3 and CGCM2) and two Intergovernmental Panel on Climate Change (IPCC) emissions scenarios (A2 and B2) were obtained from the Canadian Climate Data and Scenarios (CCDS). Scenarios were selected to represent a range of emissions scenarios (moderate to extreme, with A2 representing higher CO_2 emissions). GCMs were selected because of their differences in projections for future precipitation, with CGCM2 producing more conservative outputs. We note that HADCM3 and CGCM2 perform well in northern catchments.[51] Monthly mean future temperature and precipitation series were bias corrected with local meteorological stations (NOAA CDC Station ID: GHCND: USC00301799) using the Δchange method (SI).

Future daily INCA inputs were generated using the PERSiST model by simulating scenarios spanning 1961−1990 and 2010−2039, 2040−2069, and 2070−2099 (SI Figure S1).

Using the application rates determined for the calibration period, daily road salt application was generated based on future meteorological projections for scenarios A2 and B2 for each GCM. During moderate to heavy snowfall rates of greater than 1.27 cm/h characteristic of lake effect snow (LES), deicing salt is often applied at higher rates.[44] To account for potential increases in increased winter precipitation in the form of LES into the mid-21st century due to declining Great Lakes ice cover,[52,53] additional scenarios were run with daily application rates of 2× present day values.

Population in the U.S. is projected to increase rapidly[31] and the associated changes in effluent discharge rates were calculated assuming population in Cortland County continues to increase at a rate equal to 1900−2010 increase.[54] We determined potential future urban land use percentages in each subcatchment from extrapolated future population data and current land use proportions, assuming that population density in urban areas in the Tioughnioga River watershed remains constant. Increases in urban land cover were accommodated by decreases in forest cover.

RESULTS AND DISCUSSION

Model Calibration. To simulate concentrations of Cl^- in surface water, the INCA model was first calibrated to daily streamflow. Simulated values fit daily observations of flow at the main branch well with an R^2 of 0.72 and a N−S of 0.68 (Figure 2a). Maximum streamflow typically occurs following spring snowmelt during the month of April, whereas minimum streamflow occurs in summer months following prolonged dry periods. Modeled flow captured the seasonal variations and the timing of the rising and falling limbs. Peak flows were aligned and of similar magnitude with some overestimation. This may be due to the spatial variation of heavy rainfall events in the study area.

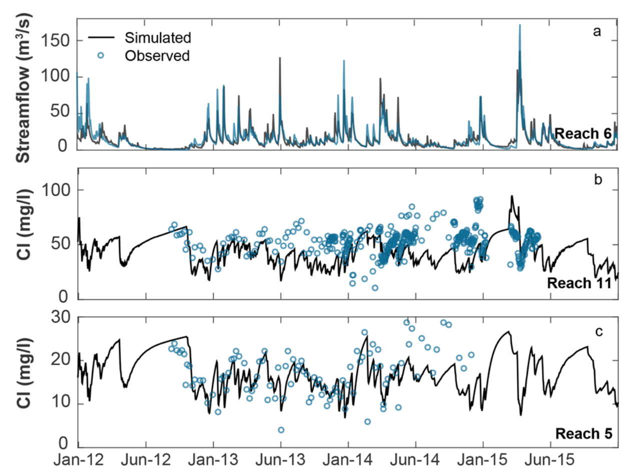


Figure 2. INCA calibration results from 2012 to 2015. (a) simulated and observed daily streamflow at reach 6 (Main Branch Tioughnioga River at Cortland, USGS Gauging Station ID 01509000). (b) simulated and observed Cl^- for reach 11 (West Branch). c) simulated and observed Cl^- for reach 5 (East Branch).

The INCA-Cl model simulations fit the observations well (Figure 2). While the model closely represented the mean conditions of the catchment, we found that the model often underestimated stream Cl^- during extremely low flow (flows less than approximately 5 m^3/s). These conditions tended to occur during late summer to early fall when streamflow was likely sustained by groundwater discharge. An overestimation of streamflow, and subsequent dilution, at the same time intervals may account for some of the differences between modeled and observed stream Cl^- concentrations (Figure 2). Simulated average daily Cl^- fluxes were approximately 13 000 kg/day and 19 000 kg/day at the mouths of East Branch and West Branch, respectively. There was generally a satisfactory fit of observed and simulated daily Cl- fluxes throughout the catchments, with

DOI: 10.1021/acs.est.7b04385
Environ. Sci. Technol. XXXX, XXX, XXX−XXX

R^2 ranging from 0.70 to 0.90 and N−S values ranging from 0.12 to 0.77 (SI Table S5).

Uncertainty and Sensitivity. Uncertainty within the INCA family of models can generally be attributed to uncertainty in parametrization, structural uncertainty within the modeling framework, and the understanding of physical and chemical processes including model inputs.[15,17,24,55]

The most sensitive parameters for modeling streamflow were consistent with findings in previous studies in which a variation of the INCA model was used.[29,56] Flow velocity modifiers "a," and "b," along with the base flow index parameter were the most sensitive to perturbations (Table 2). These parameters are dimensionless and used to define flow velocity (as $V = a \times Q^b$, where V is equal to streamflow velocity, and Q is stream discharge). Flow velocity modifiers impact the simulated residence time of surface water and therefore shape flow flashiness. The base flow index parameter represents the fraction of water that is transferred from upper to lower model storage and alters the response time of subsurface water, contributing to streamflow from precipitation and snowmelt. Best-fit parameter values were determined from model calibration and are in similar ranges established in prior modeling exercises.[24,27,35,56,57]

Table 2. Results of Sensitivity Analysis Obtained with Best-Fit Model Calibration[a]

parameter	reach 6	reach 5	reach 11
baseflow index	0.08	3.76	0.55
degree day melt-factor for snowmelt	0.00	0.00	0.00
direct runoff residence time	0.01	0.00	0.00
dry deposition Cl	0.00	0.00	0.00
flow parameter 'a'	0.13	0.24	0.06
flow parameter 'b'	1.02	0.11	0.22
groundwater residence time	0.00	0.55	0.00
initial concentration Cl^- in groundwater	0.00	7.43	2.41
initial concentration Cl^- in soil water, highway	0.00	0.00	0.00
initial concentration Cl^- in soil water, urban	0.00	0.00	0.00
soil water residence time	0.04	0.02	0.01
threshold soil zone flow	0.03	0.06	0.06
snow-water equivalent factor	0.00	0.00	0.00
wet deposition Cl	0.00	0.00	0.00

[a]Results are shown as the average difference in N−S statistics of the perturbed simulations (2×−0.5×) and the best-fit model run. Higher values represent parameters more sensitive to changes. A value of zero signifies that the parameter exhibited no sensitivity to changes.

Model sensitivity to Cl^- varied across subcatchments, likely due to differences in land use distribution and magnitude of in-stream concentrations of Cl^-. Parameters relating to snowmelt and atmospheric deposition were insensitive. The initial concentration of Cl^- in groundwater was the most sensitive parameter in terms of in-stream concentrations of Cl^-, followed by flow parameters (Table 2). In the model calibration, average measured Cl^- values were used as groundwater input (70 mg/L and 35 mg/L for West Branch and East Branch, respectively; see Materials and Methods). However, groundwater Cl^- concentrations varied across the catchment depending on location, depth and time of measurement.[20,35,45,46] For example, during dry periods, the amount of recharge to shallow aquifer decreases. Thus, the system may be more likely to exhibit influence from deeper, more saline groundwater. The complex groundwater sources could introduce the uncertainties that result in the underestimated Cl^- during extremely low flow condition.

Considering the high level of agreement between observed and modeled Cl^- for the INCA-Cl model of the Tioughnioga River catchment and the incorporation of observed data (e.g., streamflow, temperature, precipitation, surface water Cl^-, groundwater Cl^-), we believe our model to have reproduced the main processes operating at the catchment scale with relative accuracy. Thus, the calibrated model has potential for long-term and future scenario analysis.

System Response to Future Changes. *Baseline Simulation.* Under the 30-year baseline period (1961−1990), mean daily streamflow ranged, respectively, from 0.2 to 211.6 m^3/s, with an average of 10.6 m^3/s. Similar to the calibration

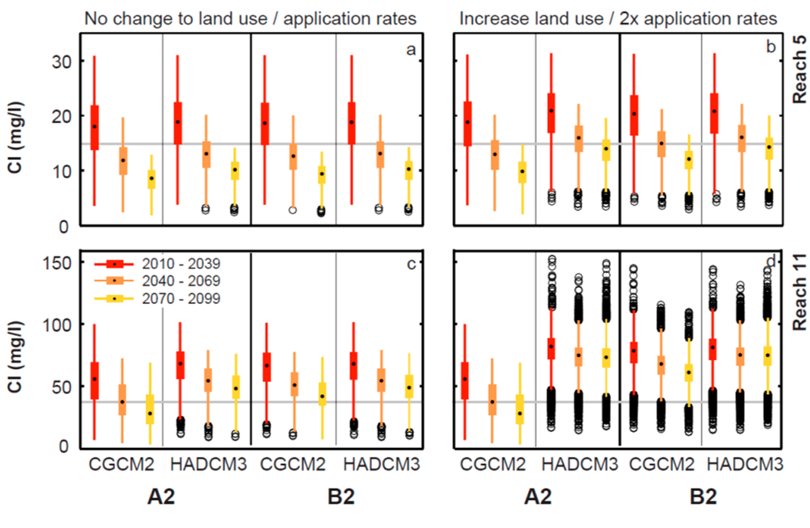


Figure 3. INCA-Cl model results for reaches 5 and 11. Simulated Cl^- in (a) reach 5 assuming no change in land use or salting practices. (b) reach 5 assuming 2× increase application rate of road salts and increased urbanization, (c) reach 11 under current conditions, and (d) reach 11 subjected to increased (2× current rate) deicing salt application and urbanization. Gray line signifies mean daily Cl^- during baseline period. Open circles represent outliers. IPCC scenarios A2 (economics focused−higher CO_2 emissions translating to greater future temperature increases) and B2 (more environmentally focused−resulting in lesser increases in future temperature) were considered for this analysis.

DOI: 10.1021/acs.est.7b04385
Environ. Sci. Technol. XXXX, XXX, XXX−XXX

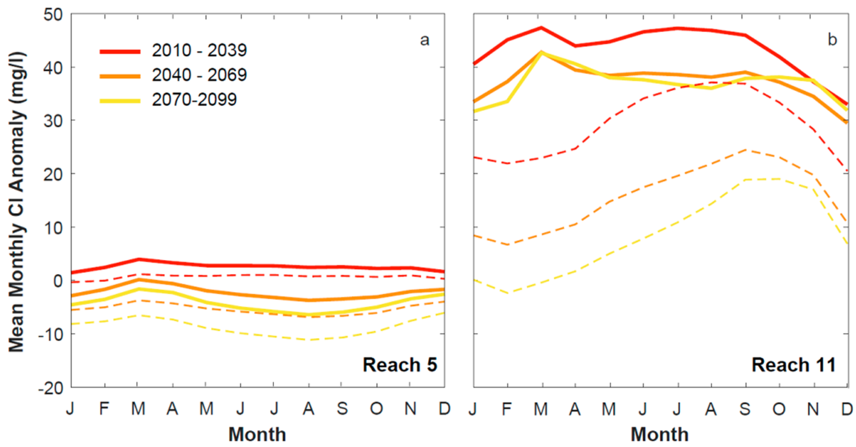


Figure 4. Mean monthly anomaly in surface water concentrations of Cl^- for reaches 5 and 11 (a and b, respectively) during future simulations. The lower limit of each future period is shown as a dashed line and represents the mean monthly anomaly in-stream Cl^- for the simulation period resulting from constant application rates and no change in land use, GCM CGCM2 and IPCC scenario A2. The upper bound is plotted as a solid line and represents surface water Cl^- concentrations under an increase in urbanization, 2× application rates, GCM HADCM3, and IPCC scenario B2.

period, maximum flows occur following spring snowmelt and high intensity rainfall events. Summer months are characterized by extended periods of low flow.

From 1961 to 1990 daily concentrations of stream Cl^- in reaches 5 and 11 ranged from 4.10 to 30.5 mg/L and 8.4 to 81.7 mg/L, respectively. Average Cl^- concentrations in reaches 5 and 11 during the baseline period were 17.9 and 35.7 mg/L, respectively. Annual maximum stream Cl^- for downstream reaches typically occurred during low flow periods as stream Cl^- concentrations approached that of groundwater. Peaks in stream Cl^- also accompanied spring snowmelt. For descriptive statistics of baseline and calibration periods refer to SI Table S2c.

Future Climate-Induced Changes to Stream Cl^- Concentrations. Mean daily concentrations of Cl^- are projected to increase between the baseline period (1961−1990) and future simulation period 2010−2039 (Figure 3). Mean daily concentrations of Cl^- in all subcatchments are highest for 2010−2039 in all 16 scenarios, followed by markedly lower mean daily Cl^- concentrations into the latter half of the 21st century (Figure 3). Descriptive statistics for daily Cl^- for baseline and future simulation periods can be found in SI Table S2.

In the latter half of the future simulation period (post 2040s), all GCM-IPCC combinations predicted a decrease in the frequency and occurrence of snowfall as winter temperatures crossed the freezing threshold of water. An increasing proportion of winter precipitation was projected to be rain (SI Table S3, Figure S2). Although rates will continue to be highly variable, all model scenarios consistently predicted declines in average annual snowfall totals through the end of the twenty-first century. HADCM3 scenarios (A2, B2) predicted more winter precipitation for the catchment into the twenty-first century than CGCM2 scenarios (SI Table S3). This is based on the GCM's projections for future precipitation.[58,59] Higher precipitation rates yielded increased snowfall totals, and greater associated annual road salt loads, producing wider ranges in surface water Cl^- for HADCM3 scenarios compared to CGCM2 (Figure 3). Furthermore, A2 scenarios generally projected more elevated warming trends than B2 scenarios; which results in less road salt applied in the model (SI Table S3, Figure S2). The variability of future climate dynamics was included intentionally to account for uncertainty within GCMs and to provide land use managers with a range of possible outcomes (SI Figure S2).

As a result of projected reductions in snowfall, the model applied less road salt across the reach network in 2040−2099 than in preceding decades (2010−2039 and baseline period) across all simulations (SI Table S4). As winter snowfall transitions to rain, Cl^- stored in shallow groundwater from previous decades may serve as a continual source of stream Cl^-, until reservoirs are depleted, leading to an overall net loss of Cl^-. Without perturbations to daily road salt application rates, an overall decline in mean daily stream Cl^- concentrations by as much as to prebaseline levels by the end of the current century is likely (Figure 3a−c), but not before reaching peak concentrations in decades preceding the 2040s.

Our findings are comparable to those observed in earlier investigations, while offering a dynamic approach to simulating future changes in surface water Cl^- as we incorporate variability in climate, land use, and snow management practices to our future estimates. Estimates vary from that of a previous study in the catchment in which a simplified mixing model was used to simulate future stream Cl^- concentrations.[20] The 2016 study calculated ranges of roughly 40−60 mg/L flow-weighted mean Cl^- in the West Branch (reach 11) given a variable increasing rate of road salt application from 2010 through 2050, while INCA-Cl outputs suggest more appropriate mean ranges of 55−66 mg/L Cl^- and 39−54 mg/L Cl^- from 2010 to 2039 and 2040−2069, respectively (SI Table S2). In this study, INCA model results reveal that an average of approximately 4700−7100 tons of Cl is exported annually from the East and West Branches of the Tioughnioga River, respectively. The 2016 study[20] estimated an overall annual export of 14 500−24 500 tons Cl^-. Jin et al. (2011)[14] predicted that under a 100% increase in application rate, stream Cl^- concentrations in a suburban Hudson River tributary could increase by up to 13%. Novotony and Stefan[60] estimated that with no change to annual Cl^- loading surface water, Cl^- would continue to rise steadily for several decades in the Twin Cities Metropolitan Area of Minneapolis, Minnesota. Perera et al.[9] projected an increase in baseflow Cl^- concentrations in the Highland Creek Watershed (Toronto) using a simplified mass balance approach. In general, our results are similar to simplified

DOI: 10.1021/acs.est.7b04385
Environ. Sci. Technol. XXXX, XXX, XXX−XXX

approaches into the early twenty-first century. However, the coupling of mass transfer with dynamic climate and hydrology inputs in our analysis leads to an overall decline in mean daily concentrations of Cl^- into the latter half of the twenty-first century (Figure 3), which is a novel finding compared to previous studies.

Future Anthropogenic Impacts on Surface Water Cl^-. Coupled with urbanization, the impacts of deicing practices are prolonged into the latter half of the century, with mean monthly concentrations of Cl^- in surface water of urbanized catchments upward of 40 mg/L above baseline concentrations (Figure 4).

Our model simulations suggest that future concentrations of Cl^- in surface water are sensitive to anthropogenic-induced changes alongside climatic factors. The greatest positive anomalies in concentrations of Cl^- occurred in simulations subjected to urbanization, elevated application rates, or both (SI Table S2).

The variation in response times between reaches 11 and 5 required for surface water Cl^- to return to baseline concentrations (Figure 3) may be explained by the difference in groundwater Cl^- concentrations. Higher groundwater Cl^- measured in the West Branch, attributed to long-term road salt application,[30,35,46] may act as a high-Cl^- source for surface water Cl^-. This subsequently enriches dilute rainfall and snowmelt relative to low-Cl^- groundwater in the East Branch, thereby moderating the overall decrease in stream Cl^- over time. Cl^- attenuation in groundwater has been observed extensively in mixed-land use and urban catchments and suggested as a buffer for stream Cl^-.[8,15,61,62]

The presence of the Interstate Highway in the West Branch may also contribute to the slow recovery of salinity despite future declines in salt application (Figure 3, 4), as it serves as a continual source of road salt that is absent in all reaches of the East Branch (Figure 1). Heisig[8] noted a strong positive relationship between log Cl^- concentrations and annual application rate of deicing salt in a small mixed land use catchment in southeastern NY, consistent with the elevated application rates of interstate highways. In Central Massachusetts, the greatest Cl^- concentrations observed in the Mill River Watershed coincided with runoff from interstate and state highways.[15]

We attribute the increase in surface water Cl^- from baseline concentrations projected for 2010–2039 to be predominantly controlled by greater annual Cl^- inputs to the system. Under all simulations mean daily streamflow underwent a steady decline throughout the twenty-first century. Thus, elevated concentrations of Cl^- cannot be explained by dilution processes (SI Figure S3). Furthermore, land-use changes were assumed proportional to current land cover distributions. Although the same percent-increase was applied across all subcatchments, those with higher urban land-cover at the beginning of the simulation period were subjected to greater urbanization, and thus higher road salt loads (see Materials and Methods).

In general, subcatchments in the West Branch were more sensitive to changes in land use and climate, likely due to the greater proportion of urban lands in the reach. In contrast, the East Branch did not respond as drastically to anthropogenic forcings, experiencing only minor changes in mean daily surface water Cl^- concentrations and with Cl^- concentrations falling below baseline conditions into the end of the century regardless of urbanization and salt application characteristics (Figure 3a,b). Rural catchments were projected to approach baseline levels of salinity by approximately midcentury despite anthropogenic factors (Figure 3a,b). Whereas, simulations in the West Branch only declined to baseline levels of Cl^- by the end of the 21st century for one climate scenario (CGCM2, Scenario A2), with mean concentrations approaching, but continuing to exceed, baseline concentrations in all but one of the most extreme salting scenarios (Figure 3d). This suggests that densely paved catchments may not recover as readily as those that are more sparsely populated.

Implications and Future Work. The wide range of results projected by INCA-Cl simulations reflect inherent uncertainty in climate and population change studies. It is suggested that while simplified mass balance approaches do provide a suitable first-approximation for addressing water quality concerns, they are inherently unable to incorporate the intricacies of dynamic changes in climate and land cover components that may be imminent. The INCA-Cl process-based model generates a more realistic range of responses to plausible future changes, and provides a useful tool in future management planning.

Increased urbanization may lead to a ubiquitous upward trend in surface water salinity from 2010 to 2039 as a direct result of deicing practices. This continuation of present-day trends has the potential to further stress already-impaired water resources and aquatic ecosystems. However, our simulations suggest that these effects may be reversible over the next century as climate drivers shift winter precipitation type, thus lessening the need for deicing measures and allowing concentrations of Cl^- to naturally return to baseline values. Catchments in regions where climate models predict an increase in snowfall may experience different changes, thus modeling approaches considering regional climate changes are necessary in order to accurately assess the response of these systems. Our simulations predict a cautiously optimistic outcome for drinking water resources contaminated by deicing practices during the latter half of the 1900s.

Although the main goal of this study was to demonstrate the importance of long-term climate variability to salinity management, additional uncertainty (e.g., groundwater Cl^- concentrations) may require attention in future research to improve the accuracy of model predictions. Spatial and temporal groundwater heterogeneity is a common phenomenon and our catchment is no exception.[20,35,45,46] Our model underestimates streamwater Cl^- concentration during some summer intervals at low flow conditions, which may be due to changes in groundwater Cl^- concentration. Available shallow groundwater data[20,45] do not indicate temporal variations that may contradict our conclusion about the role of climate change. However, long-term groundwater monitoring data with improved spatial coverage may provide more insight into the role of groundwater in future studies.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b04385.

Detailed description of delta change method Figures S1–S2 Tables S1–S5 (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: kmgutche@syr.edu.

DOI: 10.1021/acs.est.7b04385
Environ. Sci. Technol. XXXX, XXX, XXX–XXX

ORCID
Kristina Gutchess: 0000-0002-9745-5049
José L. J. Ledesma: 0000-0002-4181-5498

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank Bruce Adams of the Cortland Waste Water Treatment Facility for access to weather station data for the City of Cortland and Patrick Reidy of Cortland County Soil and Water Conservation District whom aided with field sampling, historic water quality data, and information regarding snow management practices. K.G. was supported financially by the Syracuse University Water Fellowship and NRT: Education Model Program on Water-Energy Research (EMPOWER) at Syracuse University (DGE-1449617). The SUNY Cortland faculty research program 2012−2013, the Syracuse University Campus as a Laboratory for Sustainability Program (2017−2018), and the Geological Society of America Graduate Student Research Grant (Grant No. 11575−17, supported by National Science Foundation Grant No. 1712071), provided partial funding for this work. J.L.J.L. was funded by NordForsk (60501) and Formas (2015−1518).

REFERENCES

(1) Kaushal, S. S.; Groffman, P. M.; Likens, G. E.; Belt, K. T.; Stack, W. P.; Kelly, V. R.; Fisher, G. T. Increased salinization of fresh water in the northeastern United States. *Proc. Natl. Acad. Sci. U. S. A.* **2005**, *102* (38), 13517−13520.

(2) Kelly, V. R.; Lovett, G. M.; Weathers, K. C.; Findlay, S. E. G.; Strayer, D. L.; Burns, D. J. Long-term sodium chloride retention in a rural watershed: Legacy effects of Road Salt on Stream water concentration. *Environ. Sci. Technol.* **2008**, *42* (2), 410−415.

(3) Kelly, W. R.; Panno, S. V.; Hackley, K. C.; Hwang, H. H.; Marinsek, A. T.; Markus, M. Using chloride and other ions to trace sewage and road salt in the Illinois Waterway. *Appl. Geochem.* **2010**, *25* (5), 661−673.

(4) Kelly, V. R.; Findlay, S. E. G.; Schlesinger, W. H.; Chatrchyan, A. M.; Menking, K. Road salt: moving toward the solution. *Cary Institute of Ecosystem Studies*, **2010**.

(5) Corsi, S. R.; Cicco, L. A.; Lutz, M. A.; Hirsch, R. M. River chloride trends in snow-affected urban watersheds: increasing concentrations outpace urban growth rate and are common among all seasons. *Sci. Total Environ.* **2015**, *508*, 488−497.

(6) New York State Department of Transportation (NYS DOT). Chapter 5 Snow and ice control. In *Highway Maintenance Guidelines*; Operations Division, Office of Transportation Management: New York, 2012; pp 80.

(7) Shaw, S. B.; Marjerison, R. D.; Bouldin, D. R.; Parlange, J.; Walter, M. T. Simple model of changes in stream chloride levels attributable to road salt applications. *J. Environ. Eng.* **2012**, *138* (1), 112−118.

(8) Heisig, P. M. *Effects of residential and agricultural land uses on the chemical quality of baseflow of small streams in the Croton watershed, Southeastern New York*; U.S. Geological Survey Water-Resour. Invest. Report 99−4173, 200015p

(9) Perera, N.; Gharabaghi, B.; Howard, K. Groundwater chloride response in the Highland Creek watershed due to road salt application: A re-assessment after 20 years. *J. Hydrol.* **2013**, *479*, 159−168.

(10) Jackson, R. B.; Jobbágy, E. G. From icy roads to salty streams. *Proc. Natl. Acad. Sci. U. S. A.* **2005**, *102* (41), 14487−14499.

(11) Kaushal, S. S. Increased salinization decreases safe drinking water. *Environ. Sci. Technol.* **2016**, *50* (6), 2765−2766.

(12) Kaushal, S. J.; Duan, S.; Doody, T. R.; Haq, S.; Smith, R. S.; Newcomer Johnson, T. A.; Newcomb, K. D.; Gorman, J.; Bowman, N.; Mayer, P. M.; Wood, K. L.; Belt, K. T.; Stack, W. P. Human-accelerated weathering increases salinization, major ions, and alkalinization in fresh water across land use. *Appl. Geochem.* **2017**, *83*, 121−135.

(13) Ramakrishna, D. M.; Viraraghavan, T. Environmental impacts of chemical deicers − a review. *Water, Air, Soil Pollut.* **2005**, *155*, 49−63.

(14) Mullaney, J. R.; Lorenz, D. L.; Arntson, A. D. *Chloride in groundwater and surface water in areas underlain by the Glacial Aquifer System, Northern United States*; U. S. Geological Survey Water Resour. Invest. Open-File Report 2009−5086, **2009**.

(15) Jin, L.; Whitehead, P.; Siegel, D. I.; Findlay, S. Salting our landscape: An integrated catchment model using readily accessible data to assess emerging road salt contamination to streams. *Environ. Pollut. (Oxford, U. K.)* **2011**, *159* (5), 1257−1265.

(16) Rhodes, A. M. Y. L.; Newton, R. M.; Pufall, A. N. Influences of Land Use on Water Quality of a Diverse New England Watershed. *Environ. Sci. Technol.* **2001**, *35* (18), 3640−3645.

(17) Crossman, J.; Whitehead, P. G.; Futter, M. N.l; Jin, L.; Shahgedanova, M.; Castellazzi, M.; Wade, A. J. The interactive responses of water quality and hydrology to changes in multiple stressors, and implications for the long-term effective management of phosphorus. *Sci. Total Environ.* **2013**, *454−455*, 230−244.

(18) Whitehead, P. G.; Sarkar, S.; Futter, M. N.; Caesar, J.; Barbour, E.; Butterfield, D.; Sinha, R.; Nicholls, R.; Hutton, C.; Leckie, H. D. Dynamic modeling of the Ganga river system: impacts of future climate and socio-economic change on flows and nitrogen fluxes in India and Bangladesh. *Environ. Sci. Processes Impacts.* **2015**, *17* (6), 1082−1097.

(19) Novotony, E. V.; Sander, A. R.; Mohseni, O.; Stefan, H. G. Chloride ion transport and mass balance in a metropolitan area using road salt. *Water Resour. Res.* **2009**, *45* (12), W12410.

(20) Gutchess, K.; Jin, L.; Lautz, L.; Shaw, S. B.; Zhou, X.; Lu, Z. Science of the Total Environment Chloride sources in urban and rural headwater catchments, central New York. *Sci. Total Environ.* **2016**, *565*, 462−472.

(21) Whitehead, P. G.; Wilson, E. J.; Butterfield, D. A semi-distributed Integrated Nitrogen model for multiple source assessment in Catchments (INCA): Part I - model structure and process equations. *Sci. Total Environ.* **1998**, *210−211*, 547−558.

(22) Whitehead, P. G.; Wilson, E. J.; Butterfield, D.; Seed, K. A semi-distributed integrated flow and nitrogen model for multiple source assessment in catchments (INCA): Part II - application to large river basins in south Wales and eastern England. *Sci. Total Environ.* **1998**, *210−211*, 559−583.

(23) Rankinen, K.; Lepistö, A.; Granlund, K. Hydrological application of the INCA model with varying spatial resolution and nitrogen dynamics in a northern river basin. *Hydrol. Earth Syst. Sci.* **2002**, *6* (3), 339−350.

(24) Wade, A. J.; Whitehead, P. G.; Butterfield, D. The integrated catchments model of phosphorus dynamics (INCA-P), a new approach for multiple source assessment in heterogeneous river systems: model structure and equations. *Hydrol. Earth Syst. Sci.* **2002**, *6* (3), 583−606.

(25) Futter, M. N.; Butterfield, D.; Cosby, B. J.; Dillon, P. J.; Wade, A. J.; Whitehead, P. G. Modeling the mechanisms that control in-stream dissolved organic carbon dynamics in upland and forested catchments. *Water Resour. Res.* **2007**, *43* (2), 116.

(26) Lazar, A. N.; Butterfield, D.; Futter, M. N.; Rankinen, K.; Thouvenot-Korppoo, M.; Jarritt, N.; Lawrence, D. S. L.; Wade, A. J.; Whitehead, P. G. An assessment of the fine sediment dynamics in an upland river system: INCA-Sed modifications and implications for fisheries. *Sci. Total Environ.* **2010**, *408* (12), 2555−2566.

(27) Whitehead, P. G.; Jin, L.; Baulch, H. M.; Butter, D. A.; Oni, S. K.; Dillon, P. J.; Jarvie, H. P. Modelling phosphorus dynamics in multi-branch river systems: A study of the Black River, Lake Simcoe, Ontario, Canada. *Sci. Total Environ.* **2011**, *412−413*, 315−323.

(28) Futter, M. N.; Poste, A. E.; Butterfield, D.; Dillon, P. J.; Whitehead, P. G.; Dastoor, A. P.; Lean, D. R. S. Using the INCA-Hg model of mercury cycling to simulate total and methyl mercury

DOI: 10.1021/acs.est.7b04385
Environ. Sci. Technol. XXXX, XXX, XXX−XXX

concentrations in forest streams and catchments. *Sci. Total Environ.* **2012**, *424*, 219−231.
(29) Jin, L.; Whitehead, P. G.; Futter, M. N.; Lu, Z. Modelling the impacts of climate change on flow and nitrate in the River Thames: assessing potential adaptation strategies. *Nord. Hydrol.* **2012**, *43* (6), 902−916.
(30) Jin, L.; Whitehead, P. G.; Heppell, C. M.; Lansdown, K.; Purdie, D. A.; Trimmer, M. Modelling flow and inorganic nitrogen dynamics on the Hampshire Avon: Linking upstream processes to downstream water quality. *Sci. Total Environ.* **2016**, *572*, 1496−1506.
(31) Colby, S. L.; Ortman, J. M.*Projections of the Size and Composition of the U.S. Population: 2014 to 2060: Population Estimates and Projections. Current Population Reports, P25-1143*; U.S. Census Bureau: Washington, DC, 2014.
(32) U.S. Geological Survey. 1:2,000,000-scale Digital Line Graph, NYS Hydrography (1980). U.S. Geological Survey: Reston, VA, 1980.
(33) U.S. Geological Survey. 1:250,000 Scale Land Use and Land Cover, Binghamton Quadrangle (ARC Export: 1990). U.S. Geological Survey: Reston, VA, 2001.
(34) Reynolds, R. Hydrogeology of the Surficial Outwash Aquifer at Cortland, Cortland County, New York. *U. S. Geol. Surv. Water Resour. Invest. Open-File Report 85-4090* **1987**.
(35) Miller, T. S.; Sherwood, D. A.; Jeffers, P. M.; Mueller, N. Hydrology, Water-Quality and Simulation of Ground-Water Flow in a Glacial Aquifer System, Cortland County, New York. *Water Resour. Invest. Open-File Report 96−4255* **1998**.
(36) Kappel, W.; Miller, T. Hydrogeology of the Tully Trough in Southern Onondaga County and Northern Cortland County, New York. U. S. Geological Survey Water-Resources Investigations Report 03−4112 2003.
(37) Miller, T. S. Hydrogeology and Simulation of Ground- Water Flow in a Glacial-Aquifer System at Cortland County, New York. *U. S. Geological Survey Fact Sheet FS 054−03* **2004**.
(38) Futter, M. N.; Erlandsson, M. A.; Butterfield, D.; Whitehead, P. G.; Oni, S. K.; Wade, A. J. PERSiST: a flexible rainfall-runoff modelling toolkit for use with the INCA family of models. *Hydrol. Earth Syst. Sci.* **2014**, *18*, 855−873.
(39) Thiessen, A. H. Precipitation for large areas. *Mon. Weather Rev.* **1911**, *39*, 1082−1084.
(40) Thornton, P. E.; Thornton, M. M.; Mayer, B. W.; Wei, Y.; Devarakonda, R.; Vose, R. S.; Cook, R. B. Daymet: Daily Surface Weather Data on a 1-km Grid for North America, Version 3. Oak Ridge National Laboratory Distributed Active Archive Center for Biogeochemical Dynamics, Oak Ridge, Tennessee, USA, 2017. DOI 10.3334/ORNLDAAC/1328.
(41) Anderson, J. R.; Hardy, E. E.; Roach, J. T.; Witmer, R. E. A land use and land cover classification system for use with remote sensor data. *Geol. Surv. Prof. Paper 864* **1976**.
(42) Nichols, J. Dry deposition estimates of nitrate, sulfate and chloride based on throughfall measurements at Black Rock Forest. *Lamont-Doherty Earth Observatory of Columbia University* **1999**, unpublished manuscript.
(43) New York State Office of General Services (NY GSA). (2007). State contract award notices—Commodities: Road salt delivery schedules, 2002−2016. http://www.ogs.state.ny.us/purchase/spg/awards/01800DS00.HTM (accessed April 4, 2017).
(44) New York State Department of Transportation (NYSDOT). Chapter 5 Snow and Ice Control. In Highway Maintenance Guidelines, 2006.
(45) Buller, W. Hydrologic Appraisal of the Water Resources of the Homer-Preble Valley, New York. *U. S. Geol. Surv. Water-Resour. Invest. Open-File Report 78−94* **1978**.
(46) Buller, W.; Nichols, W.; Harsh, J. F. Quality and Movement of Ground Water in Otter Creek-Dry Creek Basin, Cortland County, New York. *U. S. Geol. Surv. Water-Resour. Invest. Open-File Report 78−3* **1978**.
(47) Waller, R. M.; Finch, A. J. Atlas of eleven selected aquifers in New York. *U. S. Geol. Surv. Water Resour. Invest. Open-File Report* **1982**, 82−553.
(48) United States Environmental Protection Agency. Indoor water use in the United States. U. S. Environ. *Protection Agency Water Sense*, EPA832-F-06-004.
(49) Ledesma, J. L. J.; Köhler, S. J.; Futter, M. N. Long-term dynamics of dissolved organic carbon: Implications for drinking water supply. *Sci. Total Environ.* **2012**, *432*, 1−11.
(50) Futter, A. M. N.; Löfgren, S.; Köhler, S. J.; Lundin, L.; Moldan, F.; Bringmark, L. Simulating Dissolved Organic Carbon Dynamics at the Swedish Integrated Monitoring Sites with the Integrated Catchments Model for Carbon, INCA-C. *Ambio* **2011**, *40* (8), 906−919.
(51) Walsh, J. E.; Chapman, W. L.; Romansovsky, V.; Christensen, J. H.; Stendel, M. Global climate model performance over Alaska and Greenland. *J. Clim.* **2008**, *21*, 6156−6174.
(52) Wright, D. M.; Posselt, D. J.; Steiner, A. L. Sensitivity of lake-effect snowfall to lake ice cover and temperature in the Great Lakes Region. *Mon. Weather Rev.* **2013**, *141*, 670−689.
(53) Notaro, M.; Bennington, V.; Vavrus, S. Dynamically downscaled projections of lake-effect snow in the Great Lakes Basin. *J. Clim.* **2015**, *28*, 1661−1684.
(54) Forstall, R. L. *Population of States and Counties of the United States: 1790 to 1990*; U.S. Bureau of the Census: Washington, DC, 1996.
(55) Rankinen, K.; Karvonen, T.; Butterfield, D. An application of the GLU methodology for estimating the parameters of the INCA-N model. *Sci. Total Environ.* **2006**, *365*, 123−139.
(56) McIntyre, N.; Jackson, B.; Wade, A. J.; Butterfield, D.; Wheater, H. S. Sensitivity analysis of a catchment-scale nitrogen model. *J. Hydrol.* **2005**, *315* (1−4), 71−92.
(57) Jackson-Blake, L. A.; Wade, A. J.; Futter, M. N.; Butterfield, D.; Couture, R. M.; Cox, B. A.; Crossman, J.; Ekholm, P.; Halliday, S. J.; Jin, L.; Lawrence, D. S. L.; Lepistö, A.; Lin, Y.; Rankinen, K.; Whitehead, P. G. The Integrated Catchment model of phosphorus dynamics (INCA-P): Description and demonstration of new model structure and equations. *Environ. Modell. Software* **2016**, *83*, 356−386.
(58) Wilby, R. L.; Whitehead, P. G.; Wade, A. J.; Butterfield, D.; Davis, R. J.; Watts, G. Integrated modelling of climate change impacts on water resources and quality in a lowland catchment: River Kennet, UK. *J. Hydrol.* **2006**, *330* (1−2), 204−220.
(59) Crossman, J.; Futter, M. N.; Palmer, M.; Whitehead, P. G.; Baulch, H. M.; Woods, D.; Dillon, P. J. The effectiveness and resilience of phosphorus management practices in the Lake Simcoe watershed, Ontario, Canada. *J. Geophys. Res.: Biogeosci.* **2016**, *121*, 2390−2409.
(60) Novotny, E. V.; Stefan, H. G. Projections of chloride concentrations in urban lakes receiving road de-icing salt. *Water, Air, Soil Pollut.* **2010**, *211* (1−4), 261−271.
(61) Kincaid, D.; Findlay, S. Sources of elevated chloride in local streams: groundwater and soils as potential reservoirs. *Water, Air, Soil Pollut.* **2009**, *203*, 335−342.
(62) Ledford, S. H.; Lautz, L. K.; Stella, J. C. Hydrogeologic processes impacting storage, fate, and transport of chloride from road salt in urban riparian aquifers. *Environ. Sci. Technol.* **2016**, *50* (10), 4979−4988.
(63) U.S. Census Bureau. 1:500,000-scale Cartographic Boundary Shapefiles − States. U.S. Census Bureau MAF/TIGER geographic database, 2016.