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Hydrogeologic Processes Impacting Storage, Fate, and Transport of Chloride from Road Salt in Urban Riparian Aquifers

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Supporting Information

ABSTRACT: Detrimental effects of road salt runoff on urban streams are compounded by its facilitated routing via storm drains, ditches, and flood channels. Elevated in-stream salinity may also result from seasonal storage and discharge of chloride in groundwater, and previous work has hypothesized that groundwater discharge to streams may have the effect of diluting stream chloride concentrations in winter and enriching them in summer. However, the hydrogeological processes controlling these patterns have not been thoroughly investigated. Our research focuses on an urban stream and floodplain system in Syracuse, NY, to understand how groundwater and surface water exchange impacts chloride storage, fate, and transport. We created a 3D groundwater flow and solute transport model of the floodplain, calibrated to the distributions of floodplain hydraulic heads and groundwater fluxes to the stream throughout the reach. We used a sensitivity analysis to calibrate and evaluate the influence of model parameters, and compared model outputs to field observations. The main source mechanism of chloride to the floodplain aquifer was high-concentration, overbank flood events in winter that directly recharged groundwater. The modeled residence time and storage capacity of the aquifer indicate that restoration projects designed to promote floodplain reconnection and the frequency of overbank flooding in winter have the potential to temporarily store chloride in groundwater, buffer surface water concentrations, and reduce stream concentrations following periods of road salting.

INTRODUCTION

Urbanization has a clear impact on surface water quality. Alteration of stream corridors in urban areas, including cement bank armoring, channelization, floodplain development, and degradation of the riparian zone, collectively disconnect surface waters from riparian areas and groundwater.[1] Disconnection from groundwater, along with other hydrologic impacts of urbanization, results in decreased ecological function and ecosystem services provided by urban streams.[1−3] Stream restoration increasingly emphasizes restoration of those ecosystem functions and services, by improving riparian habitat and modifying channel hydromorphology to promote floodplain reconnection.[4] However, the effects of restoring hydrologic connectivity of streams and floodplains (i.e., the exchange of water between a stream and its riparian zone and floodplain aquifer) on chloride transport in areas impacted by road salt use are not well studied.[5]

In 2005 alone, 18 million megagrams of road salt were applied to U.S. roads for driver safety,[6] along with unquantified amounts applied to private parking lots and sidewalks. Even low levels of impervious surface cover result in increases of chloride concentrations in surface waters.[7−9] Baseflow chloride concentrations are increasing in urban streams, including during nonwinter months,[10−12] and this increase is due to chloride retention within watersheds.[13] There is a need to understand chloride dynamics in urban systems given the negative effects on aquatic and terrestrial organisms at high concentrations.[14,15] The U.S. EPA has established acute and chronic ambient water quality limits for chloride of 860 mg/L and 230 mg/L, respectively.[16] Groundwater storage is a major component of chloride fate and transport in urban areas.[11,17−19] Groundwater chloride concentrations are impacted by chloride storage in soils,[20,21] delivery of chloride from the unsaturated zone,[22−24] and interaction with surface water.[25] Controls on surface water chloride concentrations in winter and spring are primarily impacted by flushing of salted impervious surface cover.[18,25,26] However, in streams receiving groundwater discharge, mixing of high salinity surface waters with low salinity groundwater decreases surface water concentrations in winter. Long-term salinization of floodplain groundwater is occurring throughout

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northern climates, but storage may help in the short term to mitigate potentially harmful effects of highly saline events.

In this study, we used field observations in conjunction with groundwater modeling to investigate the hydrogeological processes controlling chloride fate and transport in the saturated zone of an urban floodplain. As our study system, we used an urban stream in New York State that is subject to heavy applications of road salts in winter (Figure 1). The modeling approach simulated floodplain hydrologic processes that could retain excess chloride from deicers and slowly discharge it year-round. These processes focused on spatial and temporal interactions between the five principle controls on chloride transport in urban riparian floodplains (Figure 2a): surface water-groundwater interactions; hillslope groundwater discharge; push and pull of water to and from floodplains with changes in stream stage (e.g., bank storage); precipitation recharge; and groundwater recharge during overbank flooding events. The only process that removed water and chloride from groundwater was discharge to the stream. Finally, we discuss the implications of our findings for stream restoration projects, specifically those that restore riparian zones and promote hydrologic connection between urban streams and adjacent groundwater systems.

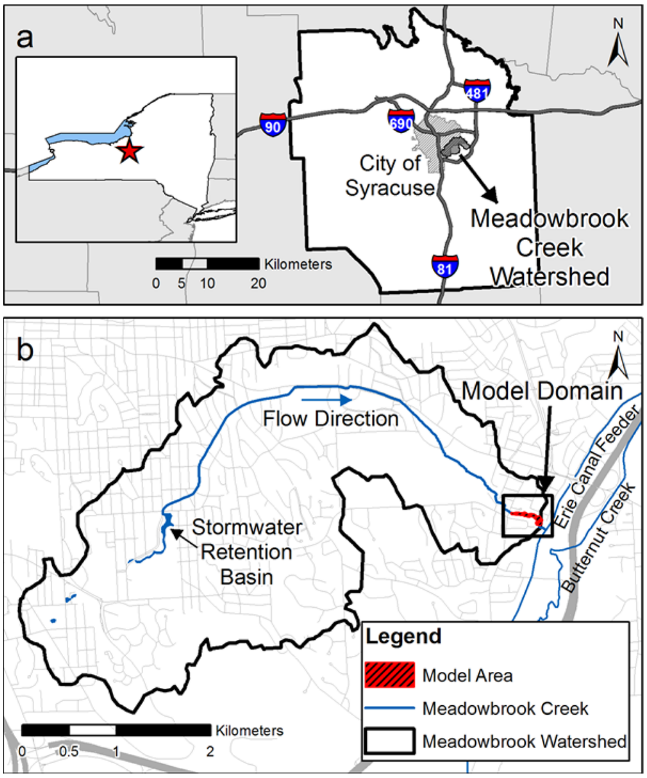

Figure 1. (a) Location of Meadowbrook Creek watershed within Onondaga County and in relationship to the City of Syracuse. (b) Meadowbrook Creek starts from a stormwater retention basin before flowing east into an Erie Canal feeder channel. The model domain is the floodplain located in the last 500 m of the stream.

■ MATERIALS AND METHODS

Study Site. Meadowbrook Creek is a first-order urban stream in Syracuse and DeWitt, New York (Figure 1). The study reach flows east for 5.6 km until it discharges into the Erie Canal system.[27] The upper 4.1 km of the stream is heavily impacted by road runoff and described in further detail in Ledford and Lautz.[25] The lower 1.5 km of the stream meanders through a large cemetery before flowing into a riparian floodplain for the final 500 m. The floodplain, with its mature and extensive riparian vegetation, complex channel morphology, and hydrologic connection to the riparian aquifer, is the model site of this study.

The area has a temperate climate, with an average annual snowfall of 315 cm and 98 cm of rain. Average monthly temperatures range from −4.7 °C in January to 21.8 °C in July.[28] Since 2009, the Onondaga County Department of Transportation has used 100% salt on the roads for deicing.[29]

Field Methods. Five piezometers were installed in the floodplain in September 2011 in a transect perpendicular to the stream (Figure 2b). P1 was closest to the stream, at a distance of 1.1 m, with approximately equal spacing of piezometers through P5, which was 12 m from the stream (Table S1). Piezometers were installed by hand augering a borehole up to 1.5 m below the land surface. Piezometers were cased with polyvinyl chloride (PVC) pipe (1.9 cm diameter) and had a 30.5 cm sand-packed screen. Sand was used to fill voids between the piezometer and the borehole sides. Hydraulic head at each piezometer during stream baseflow was measured on October 5, 2011.

Groundwater samples were collected from each piezometer on 20−22 different dates between June 8, 2012 until June 4, 2013, depending on whether the piezometer recovered quickly enough from purging to sample. Stream water samples were collected from the middle of the stream from May 11, 2012 until June 4, 2013 at 24 stations positioned longitudinally along the stream. Water samples were collected in 60 mL HDPE bottles, were stored at 4 °C, and were filtered within 24 h using Whatman GF/F 0.7 μm nominal pore size filters. Samples were analyzed for anion chemistry using a Dionex ICS-2000 Ion Chromatograph with five in-house standards for calibration and three U.S. Geological Survey standards for calibration verification. Measurement error was estimated as three times the standard deviation of replicate standard measurements. Wet precipitation data were collected on the green roof of the Syracuse Center of Excellence, approximately 2 km from the studied watershed (http://syracusecoe.syr.edu) and analyzed by ion chromatography (Driscoll, unpublished data).

A Solinst LTC Levelogger Junior pressure transducer and conductivity logger was calibrated and installed adjacent to the piezometer transect on January 19, 2013 (Figure 2b). It recorded water height and conductivity at 10 min intervals from that date until July 22, 2014. Logger conductivity measurements were converted to chloride concentrations by an empirical relationship between conductivity and chloride from grab samples taken at the same site (see SI).

Streambed elevations and piezometer casing elevations were surveyed using a Nikon Nivo Total Station. Groundwater discharge to the stream over the reach was measured using either a Sontek acoustic Doppler velocimeter (ADV) or by doing Rhodamine Water Tracer (RWT) or bromide injections over the reach. Road length and distribution data were downloaded from the NYS Office of Cyber Security.[30] All analyses of road densities and other watershed characteristics were completed using ESRI ArcGIS. Weather data were collected from the Community Collaborative Rain, Hail & Snow Network (CoCoRaHS) station NY-OG-2 from July 1, 2012 until July 1, 2014.[31] This station is located in the research

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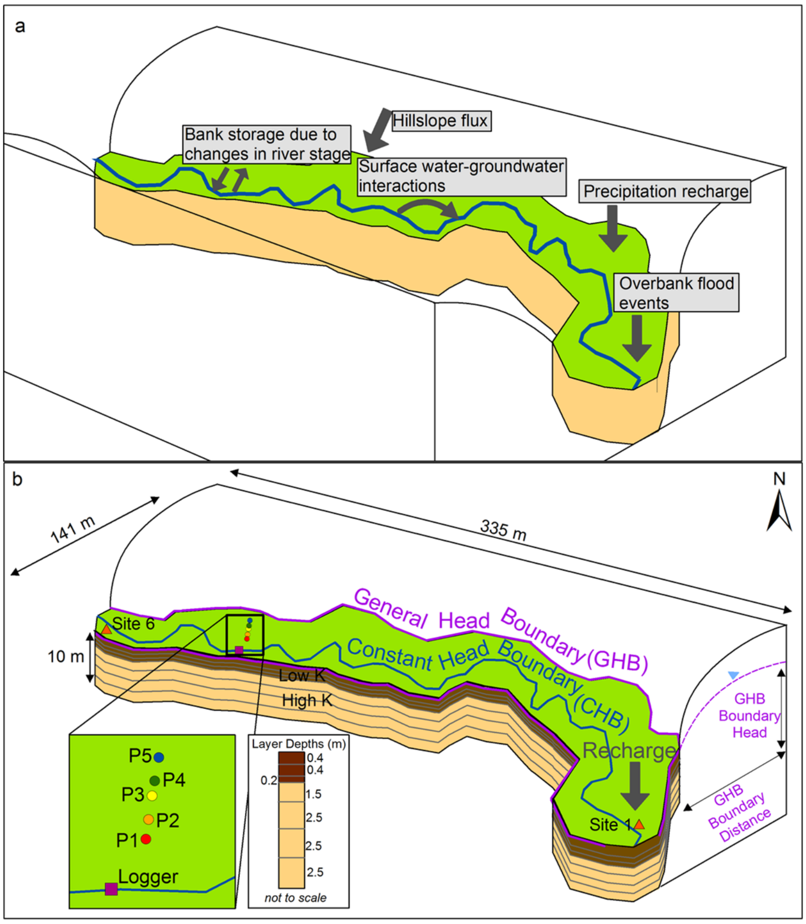

Figure 2. (a) Conceptual model of how chloride could enter the floodplain. (b) The model is made of 7 layers, with two hydraulic conductivities, a constant head boundary along the river, a general head boundary along the hillslope break, and recharge. Stream height and specific conductivity were recorded at the water level logger. Model results were compared to chloride grab samples collected from the piezometer transect and at the two grab sample locations indicated.

watershed, approximately 2.5 km from the model site. These data included precipitation, snowfall, and snow depth.

Groundwater Flow Modeling. We aimed to simulate annual patterns in groundwater hydrology and solute transport that are the dominant factors regulating the fate and transport of road salt runoff in a typical year. The model excluded the unsaturated zone due to its minimal thickness (generally <1 m) and our emphasis on understanding groundwater storage and transport processes. Our modeling approach uses a combination of calibration to multiple field observations (i.e., floodplain head measurements, discharge to the stream), comparing model output to observed groundwater chloride concentrations, and sufficient model simplicity to investigate the hydrogeologic processes of interest using a minimal number of model calibration parameters.[32]

The groundwater system was simulated using MODFLOW-2000, a block-centered, finite-difference computer code developed by the U.S. Geological Survey that solves the equation for groundwater flow.[33] We used Visual MODFLOW pre- and post-processors.[34]

The model domain consists of the field site floodplain, and is approximately 335 m by 141 m (Figure 2b). The active model domain was delineated based on the boundary between the riparian floodplain and the toe of the adjacent hillslope and covers an area 1.3 km^2 in size. Grid cells are uniformly 1.5 m × 1.5 m in the X and Y directions in the active model domain.

The model was 10 m in depth and contains seven layers. Changes in land surface elevation longitudinally along the floodplain were defined based on the average slope of the river bottom from field surveys. The slope of the floodplain toward the river from the hillslope was based on the observed slope in land surface along a piezometer transect (slope =0.01). Layer thicknesses range from 0.20 to 2.5 m (Figure 2b), with thinner layers within the top 1.5 where we had more detailed field data. All model layers have a constant thickness throughout the model domain.

Observations of drill cuttings during borehole augering show the floodplain sediments to be comprised of a surficial layer of silty-clay, underlain by a more permeable sandy-silt layer. The top three layers of the model domain were assigned a hydraulic conductivity two orders of magnitude lower than the bottom four layers of the model domain to represent the observed floodplain sediment structure. Conductivities of all layers were designated as anisotropic, with $K_{x,y}$:K_z of 10. Winkley[27] found that outwash sand and gravel surficial deposits in the area have bulk conductivities ranging from 10^{-2} to 10^{-5} m/s and are highly permeable. Literature values for hydraulic conductivity of floodplain sediments were used as initial conductivity values for layers four through seven, which were then adjusted during steady-state model calibration (Table 1).

The northern and southern boundaries of the model are located at the break in hillslope observed in the field and were

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Table 1. Sensitivity Analysis of Groundwater Model Parameters[a]

High K		Hillslope Hydraulic Gradient 2%	3%	4%
1×10^{-4} m/s	RMSE (m)	0.044	0.033	0.041
	groundwater Q (L/s)	2.2	2.7	3.2
	maximum chloride in P2 (mg/L)	616	598	532
	winter range of chloride in P1 (mg/L)	200	110	165
2×10^{-4} m/s	RMSE (m)	0.044	**0.032**	0.039
	groundwater Q (L/s)	4.1	**5.4**	6.4
	maximum chloride in P2 (mg/L)	676	**678**	490
	winter range of chloride in P1 (mg/L)	239	**166**	171
4×10^{-4} m/s	RMSE (m)	0.045	0.031	0.038
	groundwater Q (L/s)	8.8	10.7	12.7
	maximum chloride in P2 (mg/L)	639	583	560
	winter range of chloride in P1 (mg/L)	331	258	213

[a]Model outputs that were compared were the RMSE of the distribution of floodplain heads, the groundwater discharge to the river, the maximum chloride concentration at P2, and the range of chloride seen at P1 during the winter. Observed groundwater discharge to the stream was 8.9 L/s. Observed maximum chloride concentration in P2 was 655 mg/L and the range in P1 over the winter was 118 mg/L.

delineated using visual assessment of aerial photographs. These locations were assigned general head boundary (GHB) conditions to allow for flux of hillslope water into the model. The boundary was placed in the fourth layer of the model, in the higher conductivity material. The GHB uses hillslope conductivity and hillslope hydraulic head to derive a head-dependent flux into the model domain. The GHB was parametrized using the same conductivity as the high conductivity layers, which was determined by model calibration. The distance assigned to the GHB was 100 m, and the elevation of the water table at that distance was varied until the steady-state model simulated a reasonably accurate head distribution along the piezometer transect and a reasonably accurate discharge rate to the stream.

The stream was modeled using a spatially variable constant head boundary in the fourth layer of the model. The streambed longitudinal profile was interpolated from field surveys. The streamwater height was then assigned to be a minimum of 21 cm higher than the streambed, based on the minimum river height at the water level recorder, and to maintain a flat or down-valley water surface slope along the full longitudinal profile (Figure S1). Daily average water heights at the location of a pressure transducer were calculated using pressure transducer data from July 1, 2013 until July 1, 2014. We then assumed daily changes in stage height were spatially uniform over the study reach (Figure S1). Temporal gaps in data were filled by linear interpolation.

A recharge boundary was used to simulate groundwater recharge due to infiltrating precipitation and infiltration of standing water during overbank flooding events. Local residents report that the reach floods approximately 10−12 times a year, during heavy precipitation or snowmelt events, which is consistent with our observed changes in stream stage during the year. These flood events involve rapidly rising water that spills over banks onto the floodplain. While usually lasting only a short duration (<1 day), much of the overbank water infiltrates into the subsurface instead of discharging back into the stream, as there are minimal secondary and distributary channels throughout the reach.

Recharge due to infiltrating precipitation was set at 150 mm/year and did not change through time. This recharge rate is approximately 15% of the annual water equivalent precipitation. Occurrence of overbank events was defined using precipitation data from CoCoRaHS station NY-OG-2.[31] As a first approximation, overbank events were defined as occurring under two possible conditions: during precipitation events of >2.5 cm in a day, or when snow depth between consecutive days decreased by at least 13 cm, indicating a snowmelt event (Figure S2). On model days with overbank events, recharge was set to 1.5 cm/day.

The model was calibrated to hydraulic head observations along a piezometer transect and longitudinal changes in streamflow over the study reach, which are assumed equal to groundwater discharge rates to the stream, under steady-state conditions for summer baseflow. Steady-state model calibration was done manually by varying only two parameters: (1) the conductivity of layers four through seven (simultaneously adjusting the conductivity of layers one, two, and three to maintain 2 orders of magnitude difference), and (2) the hillslope hydraulic gradient for the GHB. These two parameters were adjusted until the model reproduced both the change in head along the piezometer transect and the discharge rate to the stream under summer baseflow conditions.

The model was initially run in steady-state using July baseflow conditions (conditions on day 0 of the subsequent transient model run), and the resulting head distribution was then used as the initial heads for a 2-year transient model run. The 2-year transient model run consisted of two repeating, identical years of model boundary conditions, with the first year as a "spin up" year. We conceptualize the head and solute concentrations in the modeled floodplain to vary cyclically on an annual basis, creating dynamic cyclical conditions over the long term. Such dynamic cyclical conditions were generated by running the model for multiple years using the same set of cyclic inputs. The second year of the 2-year transient model run was used to generate the output presented here.

Solute Transport Modeling. To simulate chloride concentrations throughout the saturated subsurface, we ran MT3DMS[35] using the Hybrid Method of Characteristics (HMOC) particle-tracking approach to minimize numerical dispersion at the sharp chloride concentration fronts.[36] Our effective porosity was 18% (Table S1). Longitudinal dispersivity was estimated using the Xu and Eckstein[37] relationship between apparent longitudinal dynamic dispersivity and flow length, as described in Fetter.[38] Using an average flow length of 10 to 15 m, a dispersion value of 1 m was chosen. Chloride transport was assumed to be conservative. A steady-state model run for summer baseflow conditions yielded a distribution of chloride concentrations on July 1, which were used as the initial conditions for a 2-year transient model, as described in the Groundwater Modeling section.

Daily average chloride concentrations for the stream were calculated using conductivity data recorded by the logger and an empirical relationship between conductivity and chloride

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concentrations (see SI). The daily average chloride concentrations were assigned to the constant head boundary as a point source boundary (Figure S3a).

The chloride concentration of hillslope water discharging from the GHB to the model domain was assigned based on field measurements of chloride through time in the piezometer closest to the hillslope break (P5, Figure 2b) from 2012 to 2013. The GHB chloride flux captures chloride derived from road salt that recharged groundwater in upslope areas and was subsequently transported to the floodplain as hillslope discharge. When plotted through time, a clear cyclical seasonal pattern appears, and we fit a trinomial equation to the points, which was used to calculate a daily chloride concentration for the hillslope water and assigned to the GHB using a point source boundary (Figure S3b).

Chloride concentrations in recharge were designed to reflect stream chloride concentrations during overbank events and wet deposition values during all other times. During overbank flood events, standing water on the floodplain is derived directly from spillover from the main channel and, as a result, recharge during these events is expected to have the same chemical composition as the water in the main channel during these times. The maximum chloride concentrations in the stream on days of overbank events were assigned as the chloride concentrations of recharge during modeled overbank events (Figure S3c). During nonoverbank time periods, recharge was assigned a concentration of 2 mg/L, a concentration obtained from wet precipitation data.

During piezometer installation, we observed that the floodplain sediments at the locations of P1, P4, and P5 transitioned to a sandy silt at depths of approximately 1 m, indicating those piezometers were screened in a higher permeability material. In contrast, sediments were consistently a silty clay to the screened depths of P2 and P3. Concentration observation wells in the model domain were screened in different hydraulic conductivity layers to mimic these observations. P1, P4, and P5 were screened in the lower conductivity layer while P2 and P3 were screened in the higher conductivity layer, although differences in elevation between screens was less than 50 cm (Table S1). Model parametrization used data from July 2013–July 2014, and we assessed the quality of solute transport model results by comparing to seasonal changes in groundwater chemistry observed in June 2012–June 2013.

Sensitivity Analysis. Model sensitivity to calibrated parameter values was evaluated by adjusting the hydraulic conductivity and the hillslope hydraulic gradient of the final model. For the sensitivity analysis, the hydraulic conductivity was doubled and also halved, and the hillslope hydraulic gradient was increased and decreased by 1%. We then compared the response of four key model outputs: the RMSE of head in the floodplain, the flux of groundwater to the stream during baseflow, the maximum chloride concentration in the piezometer transect through space and time, and the range of chloride concentrations in P1 (closest to the stream) over the winter (Table 1). This was done to identify the combination of parameters that best fit both the hydraulic properties (groundwater flux and water table head distribution) and the solute properties (chloride concentrations).

Although sensitivity analysis suggests model parametrization of the hillslope gradient and sediment hydraulic conductivity are sufficiently constrained to assess the dominant controls on water and solute fluxes in this study, additional data collection would further constrain the model results. In particular, additional data would provide information that could be used to calibrate to additional model parameters, including dispersivity. In particular, data on water level fluctuations in the piezometers, instead of only baseflow head values, would allow for validation of the simulated changes in head seasonally and during storm events. Additionally, multiple years of head and concentration data would allow for independent calibration and model validation data. Future studies should also consider the influence of biogeochemical cycling on chloride.[39−41]

Residence Time and Floodplain Storage Capacity. Residence time of chloride delivered to the floodplain during overbank events was evaluated by adding particles approximately every 10 m^2 to the top wetted cell on the day of the first winter overbank event. This was a sufficient point density to visualize paths and minimize model run time.

The ability of the aquifer to temporarily store chloride was evaluated by the change in chloride mass in the floodplain over the winter. Chloride storage capacity of the floodplain was defined as the difference between the maximum and minimum chloride masses in the floodplain during winter. This was compared to road salt applications using road lengths and application rates reported in Cunningham et al.[42]

RESULTS

Field Observations of Chloride in Stream and Groundwater. Stream chloride concentrations fluctuated seasonally, with concentrations remaining relatively low, between 245 and 288 mg/L, from May to late November (Figure S4a) and reaching a maximum of 1076 mg/L in winter months due to road salt runoff. Throughout the year, stream chloride concentrations remained above the EPA ambient water quality regulatory limit for chronic exposure of 230 mg/L.[16] Comparing chloride concentrations through time at Site 1 (downstream end) and Site 6 (upstream end), we saw that stream chloride concentrations were enriched longitudinally during nonwinter months and diluted during winter months (Figure S4a).

Groundwater chloride concentrations also fluctuated seasonally, but by a smaller magnitude (Figure S4b). In winter, measured groundwater chloride concentrations were lower than streamwater, falling between 70 and 655 mg/L. In summer, groundwater chloride concentrations in some floodplain locations were higher than streamwater chloride, with a maximum concentration of 439 mg/L. Based on these observations, Ledford and Lautz[25] hypothesized that groundwater discharge to the stream was responsible for stream chloride dilution in winter and enrichment in summer, although they did not explore mechanisms responsible for chloride storage and transport in the floodplain aquifer.

Model Simulation of Groundwater Flow. Steady-state groundwater model calibration, as described in the methods, resulted in a best-fit, steady-state model with a high hydraulic conductivity value of 2×10^{-4} m/s and a hillslope hydraulic gradient of 3%.

Following model calibration, the model reproduced fairly well the observed hydraulic gradient across the floodplain and the total groundwater discharge rate to the stream. For the steady-state model, the RMSE of hydraulic head was 0.03 m, which was 18.8% of the range of observed hydraulic heads. The simulated and observed hydraulic gradient between P1 and P5 were in good agreement, with values of 1.3% and 1.1%, respectively. The discharge of groundwater to the constant

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head boundary in the steady-state model was 5.5 L/s, which corresponds to an error of 38.5% from the average change in streamflow observed over the study reach of 9.0 L/s. While the percent error may seem large, the groundwater discharge component of total streamflow was similar between field observations and model results. Field measurements show that groundwater discharge to the reach in the modeled area contributes 15% of total surface water discharge at the reach outlet, whereas in the model the groundwater contribution is 10%.

Following steady-state model calibration, we also compared the simulated range of hydraulic head values at the piezometer locations during the transient model run to the observed values during baseflow conditions. In this way, we ensured that model conditions during the transient run remained consistent with field observations during baseflow. We compared hydraulic head along the piezometer transect during the transient run on a model day at a similar time of year to the field measurements and observed an R^2 of 0.75 (Figure 3a). During the transient run, the head values along the piezometer transect responded to both 20 cm variations in stream stage (Figure 3a) and high recharge during overbank events. The groundwater discharge

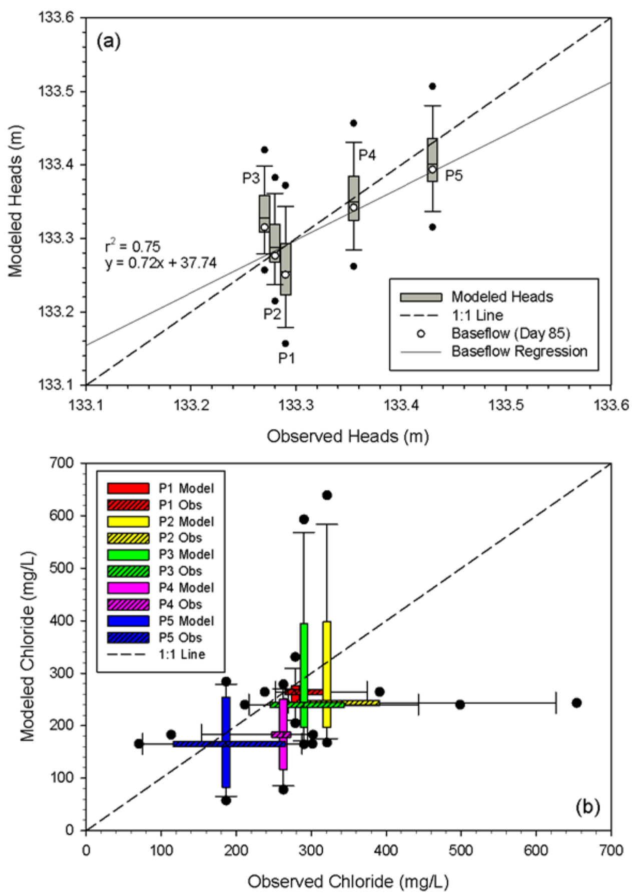

Figure 3. (a) Observed vs modeled heads along the piezometer transect. Open circles are the model output during baseflow, and the solid line is the regression for that day. Boxplots show the range of heads simulated over the model run, and 5th and 95th percentile outliers are shown as solid dots. (b) Boxplots of distributions of observed and modeled chloride concentrations along the piezometer transect. Observed values were recorded in 2012−13 and modeled values were for 2013−14. The 5th and 95th percentile values are shown as solid circles.

rates to the stream reach during the transient run varied from 4.5 to 7 L/s, remaining comparable to the average observed increase in discharge along the reach of 9.0 L/s (Figure S5).

Model Simulation of Solute Transport. The model was calibrated to hydrologic conditions and then solute transport modeling results were assessed by comparing results of the transient solute transport model to observed groundwater chloride concentrations along the piezometer transect. The model simulated two key conditions: (1) the range and distribution of chloride concentrations observed at each piezometer (Figure 3b) and (2) the seasonal timing of peak chloride concentrations in groundwater (Figure 4).

The model simulated annual ranges and distributions of chloride concentrations at each piezometer in response to stream concentrations and overbank events that were similar to the observed ranges and distributions during the previous year (Figure 3b). When comparing modeled and observed chloride concentrations, the model simulated minimal variation in chloride concentrations in P1, P4, and P5 over an annual time scale, similar to field observations (Figure 3b). The model simulated larger variations in chloride concentrations at P2 and P3, similar to field observations.

The model also simulated a similar seasonal timing of peak chloride concentrations, particularly in the low conductivity layer where chloride concentrations reach the highest values (Figure 4b). Chloride concentrations in P2 and P3, screened in low conductivity material, reached maximum values following overbank flood events in winter, when high salinity streamwater infiltrated to the shallow groundwater, peaking at 620 mg/L in the former and 606 mg/L in the latter. Chloride concentrations at P1, P4, and P5, screened in high conductivity material, never exceeded 324 mg/L in the model simulation results and never exceeded 393 mg/L in the field observations. The difference in timing of peaks between the observed and modeled years was due to different timing of overbank flooding between the two years, as indicated by the arrows (Figure 4), and differences in river chloride concentrations.

Particle travel times show a median simulated residence time of chloride in groundwater of 55 days, with a bimodal pattern (Figure 5). This distribution was controlled by the distribution of the top wetted layer in the model when particles are added. The first peak is particles that are added in the third layer, and thus closer to exiting the model through the constant head boundary. The second peak is particles that enter the second layer, and had to travel farther to reach the constant head boundary. The maximum time for a particle to stay in the floodplain was 189 days.

Model Sensitivity. Our calibration and sensitivity analysis show that the baseflow model we selected as optimal did not have the true minimum RMSE of all models, but did have groundwater discharge and chloride concentrations most similar to observed data (Table 1). The RMSE of the simulated heads in the floodplain was dependent on the hillslope hydraulic gradient, which is fixed by the GHB condition, while the magnitude of the groundwater discharge to the stream was more strongly related to the hydraulic conductivity. Increased hillslope flux flushed chloride out of the floodplain more rapidly, resulting in lower concentrations in P2. The range of chloride in P1 increased with lower conductivities, as they resulted in higher winter chloride concentrations. This combination of adjusting two model parameters and evaluating four model outputs led us to conclude that our chosen parameters produced the greatest degree of realism across

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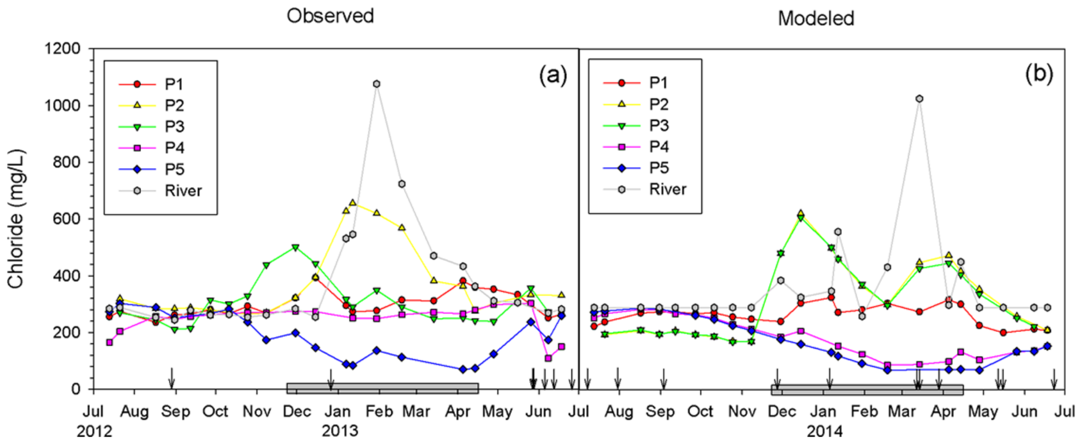

Figure 4. (a) Observed chloride concentrations in the piezometer transect and in the river from July 1, 2012 until June 30, 2013. (b) Modeled chloride concentrations in the piezometer transect and observed river chloride (derived from conductivity observations) from July 1, 2013 until June 30, 2014. In both figures, the arrows pointing to the *x*-axis indicate overbank flooding events determined from precipitation and the gray boxes along the *x*-axis indicate winter.

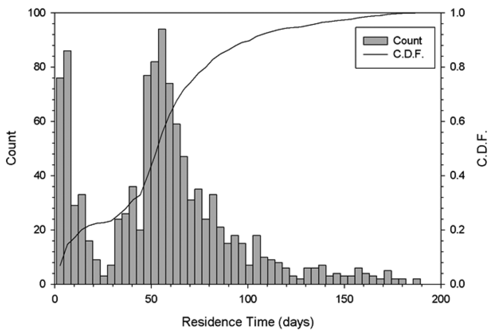

Figure 5. Histogram and cumulative density function (CDF) of modeled residence times for particles released on the first overbank event of the winter.

multiple observed data series, and thus robustly approximated the processes controlling water and solute fluxes in the floodplain.

DISCUSSION

What Hydrogeological Processes Promote Chloride Storage in Riparian Floodplains? Numerous studies have identified groundwater chloride storage as a mechanism to explain increased baseflow chloride concentrations over the past 50 years.[7,11,13,17,18,43] However, identifying specific processes controlling chloride transport to groundwater is less common, as noted by Roy and Bickerton.[19] While studies have identified soil storage and organic matter as potential reservoirs,[40,41,44,45] our study focused on chloride storage in the saturated zone. We hypothesized that five hydrogeologic processes controlled chloride fluxes to and from the urban riparian floodplain: surface water−groundwater interactions; bank storage due to fluctuating stream stage; hillslope groundwater discharge; precipitation recharge; and groundwater recharge during overbank flooding events.

The combination of discharge of groundwater to surface water (Figure S5) with the water table sloping toward the stream (Figure 3a) means that surface water−groundwater interactions, while present in the model, are not controlling chloride concentrations in the piezometers more than a few meters from the stream. Model results do show fluxes of water from the stream to the floodplain of 0.6 to 1.1 L/s during the transient model run, but these flux rates are small relative to the groundwater flux from the floodplain to the stream (4.4−7.0 L/s; Figure S5), and flowpaths originating at the stream do not extend beyond a few meters into the floodplain. Modeled chloride concentrations, even at the piezometer closest to the stream (P1; Figure 4b), do not clearly respond to changes in streamwater chloride concentrations (Figure S3a) through time. While bank storage may impact chloride concentrations at P1, if surface water−groundwater exchange were a primary control on chloride transport, we would expect to see the largest concentrations in P1. Instead, we see the highest chloride concentrations in P2, and the second highest values in P3, which is even further from the stream (Figure 4a). The minimal changes in chloride at P1, combined with observed maximum concentrations in the middle of the floodplain, indicate that bank storage is not the dominant process moving chloride into the groundwater.

Jin et al.[46] noted that streams dominated by groundwater hillslope discharge would have a strong seasonal response to road salting, where decreased hydrologic residence times result in faster chloride response in surface water. But, winter flux from the hillslope is a constant source of lower chloride groundwater in our study and so cannot be the source of the large winter groundwater chloride peaks seen in the floodplain (Figure S3b). The large contribution of hillslope flux to the total groundwater discharge to the stream (Figure S3b and Figure S5), combined with the low hillslope groundwater chloride concentrations annually instead work in combination to keep floodplain groundwater chloride concentrations low, particularly in the higher permeability sediments.

Our model shows that the main process promoting chloride storage in the urban floodplain is overbank flood events during the winter, when streamflow is heavily impacted by road salt runoff. Field observations show that the only source of high chloride water is surface water in the stream, and the only process that results in large quantities of surface water entering the groundwater is groundwater recharge during overbank flood events. The highest simulated chloride concentrations in the floodplain are found in lower permeability sediments during time periods immediately following overbank flood events in winter. With warmer weather and the cessation of road salt application, overbank flood events with lower chloride concentrations begin to flush the groundwater in spring. The

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temporary storage of road salt chloride (1−2 months in model simulations), along with the discharge of relatively low salinity groundwater during winter months, have the effect of reducing the chloride concentration in surface water during time periods most impacted by road salt runoff. This process supports the recommendations of Daley et al.,[47] who indicate that engineers could decrease the frequency and concentration of first-flush chloride pulses in urban areas by installing stormwater drainage methods that increase hydrologic residence time and decrease hydrologic connectivity between impervious surface cover and streams. Our sensitivity analysis indicates that even substantial variation in the most important model parameters (ex. hillslope hydraulic gradient, hydraulic conductivity distribution, etc.) would not change the primary mechanism of salt delivery (Table 1), even though the residence time or storage capacity of the floodplain vary somewhat.

How Much Chloride Can an Urban Floodplain Store? Cunningham et al.[42] reported that road salt application rates in New York state in 2006 were 19.6 kg NaCl/lane km. Using this road salt application rate and the length of roadways in the Meadowbrook Creek drainage basin, we calculate that the Meadowbrook floodplain can hold 0.2% of the chloride applied annually on all of the watershed roads. If we only consider roads closest to the stream (within 100 m), then the floodplain can hold 1.4% of the annual road salt load. These numbers indicate that the buffering impact we observed occurs despite the very small amount of applied chloride that is entering the groundwater. Our storage results are substantially different from those calculated by Novotny et al.[13] who estimated that 72−77% of salt applied in the Twin Cities metropolitan area (from both road salt and wastewater treatment plants) was retained in surface water, groundwater, or soils. This difference hints at scaling issues in chloride retention studies, along with the potential for large masses of chloride to be stored in watersheds in areas other than groundwater, such as in soils or surface water bodies, including lakes.

What Is the Residence Time of Chloride in an Urban Floodplain? The simulated median residence time of chloride entering the floodplain during overbank events is 55 days (Figure 5). The main mass of particles leaves the model between 50 and 70 days after entering, indicating the floodplain can store chloride for at least two months after it would have originally been flushed out of the system as high-concentration surface water. One quarter of the particles take longer than 70 days to flush out, and the maximum residence time was 189 days, indicating partial storage for as long as 6 months. Residence times observed in this study are much shorter than those observed in larger, intrawatershed studies, which show residence times of up to 50 years, but the residence times observed here are for the riparian floodplain specifically, rather than for the watershed as a whole.[48] This suggests that temporary storage of salt in urban riparian floodplains can provide a buffering effect, minimizing peak chloride concentrations in surface water in winter, without also elevating chloride concentrations in baseflow in subsequent years. Research has shown that groundwater storage of salt increases baseflow chloride concentrations through time.[8,10,11] Given the short residence times of chloride observed at our site, storage in surface aquifers with sufficiently high hydraulic conductivities is not a long-term process. Instead, the small storage capacity relative to annual salt loads (1.4%) indicates that the high conductivity material allows the floodplain to process large quantities of floodwater, while the size of the floodplain salt pool remains small.

What Are the Policy Implications of Our Findings? Urban managers need to consider the use of road salt and its impacts on ecosystems as they make policy choices.[26] Overbank flood events in restored sections of urban streams that include a riparian floodplain may help mitigate the high chloride concentrations seen in surface water due to "first-flush" effects of impervious surfaces.[17] Maintenance of intact urban riparian floodplains, or restoration of riparian floodplain connection in urban streams, provides a temporary storage zone for chloride delivered by road runoff in winter. For such urban riparian floodplains to be effective for buffering winter stream chloride concentrations, they must flood regularly during winter high flow events (e.g., rain-on-snow events) and have sediment properties and hydraulic gradients that allow for residence times of several months. Currently, the primary way to decrease chloride concentrations in streams appears to be reducing road salt usage on roads.[49] While groundwater is not a permanent sink for chloride,[50] our research shows that managers can take advantage of temporary storage of chloride in groundwater to help decrease the annual range of chloride concentrations in urban streams.[25] Such storage can be sufficiently temporary (e.g., discharged during the subsequent summer) that chloride concentrations in summer baseflow are elevated slightly during the following season, but do not continually increase over longer time periods (e.g., decades). However, this does not take into consideration the biogeochemical cycling of chlorine[39−41] and thus the potential for nonconservative behavior of chloride.

As restoration projects move forward to address the multiple benefits of naturally functioning floodplains,[51] we advise urban planners and engineers to consider increasing the number of engineered overbank flood events during winter and increasing the hydraulic conductivity of floodplain sediments. In combination with a primary goal of improved habitat or nitrogen removal,[51] the promotion of groundwater storage of chloride and subsequent buffering of surface water chloride concentrations will help minimize large annual variations in surface water chloride concentration, benefiting stream ecosystems that are sensitive to swings in concentration.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b00402.

> Detailed descriptions about the relationship between specific conductivity and chloride; Tables S1−S2 and Figures S1−S6 (PDF)

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Notes

The authors declare no competing financial interest.

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