Hydrograph and chloride pollutograph analysis of Hobbs Brook reservoir subbasin in eastern Massachusetts

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SUMMARY

Hyetographs, hydrographs, pollutographs, and deicing agent applications are analyzed with linear reservoir theory to explain the fate and transport of water and chloride in a small (1 km²) urban watershed subbasin. The subbasin delivers highway runoff to a public supply reservoir in eastern Massachusetts. Aquifer, vadose zone, and highway drainage systems deliver hydrographs with physically plausible exponential decay constants and seasonally varying discharge fractions. Continuous data from November 2005 to August 2012 suggest that baseflow contributes 48% of the water volume past a USGS gaging station at the subbasin outlet, while interflow and runoff calibration of 162 hydrographs yield respective water volume estimates of 21% and 31%. Specific conductivity, also measured continuously at the gage, is a surrogate for dissolved chloride concentration. The average chloride concentration for the 82 month period of record is 0.334 kg Cl⁻/m³ at the gage, which exceeds the USEPA secondary drinking water standard of 0.250 kg Cl⁻/m³ for dissolved chloride. Model calibration of 162 pollutographs suggests that baseflow contributes 61% of the chloride mass past the gage over the period of record, while the interflow and runoff chloride mass fractions are 17% and 22%. Most (85%) of the chloride flux past the gage is attributable to state application of chloride based deicing agents on major highways, with the remaining 15% due to municipal applications on local streets in the subbasin. A perennial stream with a small, urban watershed in a cold climate is likely to discharge an appreciable flux of subsurface chloride all year long.

1. Introduction and site description

1.1. Introduction

The increased use of road salt since World War II (Jackson and Jobbagy, 2005) reflects its low cost (TRB, 1991), effective deicing (Trost et al., 1987), and public safety (Usman et al., 2010) benefits, and is driven by the demand of the driving public for bare pavement under all weather conditions (AASHTO, 1999). These benefits and expectations should be weighed against the potential environmental costs of chloride based deicing agents (Ramakrishna and Viraraghavan, 2005), suggested by accumulating evidence of water quality impacts to lakes (Kelting et al., 2012), rivers (Godwin et al., 2009), watersheds (Rhodes et al., 2001), and unconfined aquifers (Kelly, 2008), with attendant effects on aquatic toxicity (Corsi et al., 2010), vegetation (Viskari and Kärenlampi, 2000), soil moisture (Norstrom and Bergstedt, 2001), and soil microbiology (Gryndier et al., 2008).

The potential impacts were identified as early as the 1970s (Little, 1972; Judd, 1970), and initial remedial responses included carbon (acetate, alcohol, or fermentation) based deicing alternatives and low salt zones featuring salt and abrasive mixtures. The former exert a dissolved oxygen demand on receiving water (Rabideau et al., 1987; Ostendorf et al., 1993), while the latter has its own set of environmental issues (Fay and Shi, 2012). Decreased deicing effectiveness due to problems with handling (Harris et al., 1993) and retention on the pavement (Nixon, 2001) increases the application rates and associated costs and impacts for these alternatives, so that snow and ice engineers are using them less. Rather, the current state of the art trends toward the use of chloride based deicing agents, but at reduced application rates (Shi et al., 2013), optimized by improved road weather information systems, prewetting and anti-icing techniques, pavement sensors, and closed loop spreader technology (TRB, 2005).

1.2. Linear systems applied to an urban, cold weather watershed

Calibrated water and chloride mass balances (Rosenberry et al., 1990; Kelly et al., 2008; Novotny et al., 2009) introduce transport models and data into the cost/benefit process, so that decisions and impact assessments for chloride based deicing practices can be made on a more deterministic basis that is less reliant on correlations and simulations. Longer term periods of record over multi-
### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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</thead>
<tbody>
<tr>
<td>( A )</td>
<td>subbasin area (( L^2 ))</td>
</tr>
<tr>
<td>( A_{AVE} )</td>
<td>state maintained pavement area in subbasin (( L^2 ))</td>
</tr>
<tr>
<td>( C_p )</td>
<td>empirical coefficient relating specific conductivity to dissolved chloride (( M/\ell^2\cdot S ))</td>
</tr>
<tr>
<td>( c )</td>
<td>dissolved chloride concentration of gage discharge (( M/L^3 ))</td>
</tr>
<tr>
<td>( c_B )</td>
<td>baseflow chloride concentration (( M/L^3 ))</td>
</tr>
<tr>
<td>( c_r )</td>
<td>dissolved chloride concentration in interflow (( M/L^3 ))</td>
</tr>
<tr>
<td>( c_t )</td>
<td>dissolved chloride concentration on the pavement (( M/L^3 ))</td>
</tr>
<tr>
<td>( c_{RD} )</td>
<td>first flush of dissolved chloride concentration (( M/L^3 ))</td>
</tr>
<tr>
<td>( c_{RO} )</td>
<td>dissolved runoff chloride concentration when storm stops (( M/L^3 ))</td>
</tr>
<tr>
<td>( E )</td>
<td>evapotranspiration rate (( L/T ))</td>
</tr>
<tr>
<td>( F_f )</td>
<td>vadose zone discharge fraction</td>
</tr>
<tr>
<td>( F_{ER} )</td>
<td>highway drainage system discharge fraction</td>
</tr>
<tr>
<td>( g )</td>
<td>gravitational acceleration (( L/T^2 ))</td>
</tr>
<tr>
<td>( h )</td>
<td>depth of sheet flow on pavement (( L ))</td>
</tr>
<tr>
<td>( k )</td>
<td>permeability of vadose zone (( L^2 ))</td>
</tr>
<tr>
<td>( L_B )</td>
<td>characteristic aquifer distance (( L ))</td>
</tr>
<tr>
<td>( L_B )</td>
<td>characteristic distance of the vadose zone (( L ))</td>
</tr>
<tr>
<td>( M_B )</td>
<td>fraction of chloride mass past the gage due to baseflow for period of record</td>
</tr>
<tr>
<td>( M_I )</td>
<td>fraction of chloride mass past the gage due to interflow for period of record</td>
</tr>
<tr>
<td>( m_B )</td>
<td>fraction of chloride mass past the gage due to baseflow for event</td>
</tr>
<tr>
<td>( M_I )</td>
<td>fraction of chloride mass past the gage due to interflow for event</td>
</tr>
<tr>
<td>( m_R )</td>
<td>fraction of chloride mass past the gage due to surface runoff for period of record</td>
</tr>
<tr>
<td>( m_B )</td>
<td>fraction of chloride mass past the gage due to surface runoff for event</td>
</tr>
<tr>
<td>( P )</td>
<td>intensity of precipitation (( L/T ))</td>
</tr>
<tr>
<td>( P_C )</td>
<td>characteristic precipitation intensity (( L/T ))</td>
</tr>
<tr>
<td>( Q )</td>
<td>total volumetric water discharge (( L^3/T ))</td>
</tr>
<tr>
<td>( Q_B )</td>
<td>baseflow of groundwater (( L^3/T ))</td>
</tr>
<tr>
<td>( Q_I )</td>
<td>interflow of subsurface moisture from the vadose zone (( L^3/T ))</td>
</tr>
<tr>
<td>( Q_{RD} )</td>
<td>interflow at end of storm (( L^3/T ))</td>
</tr>
<tr>
<td>( Q_0 )</td>
<td>initial total water discharge (( L^3/T ))</td>
</tr>
<tr>
<td>( Q_R )</td>
<td>surface runoff of water from the highway drainage system (( L^3/T ))</td>
</tr>
<tr>
<td>( Q_{RD} )</td>
<td>surface runoff at end of storm (( L^3/T ))</td>
</tr>
<tr>
<td>( S )</td>
<td>characteristic matrix pressure head gradient of vadose zone</td>
</tr>
<tr>
<td>( s_1 )</td>
<td>solid chloride mass in i-th deicing agent application per unit pavement area (( M/L^2 ))</td>
</tr>
<tr>
<td>( T )</td>
<td>aquifer transmissivity (( L^2/T ))</td>
</tr>
<tr>
<td>( t )</td>
<td>time (( T ))</td>
</tr>
<tr>
<td>( t_F )</td>
<td>time when precipitation stops (( T ))</td>
</tr>
<tr>
<td>( t_{D} )</td>
<td>time to dry the pavement (( T ))</td>
</tr>
<tr>
<td>( u_B )</td>
<td>fraction of water volume passing the subbasin gage due to baseflow</td>
</tr>
<tr>
<td>( u_I )</td>
<td>fraction of water volume passing the subbasin gage due to interflow</td>
</tr>
<tr>
<td>( u_R )</td>
<td>fraction of water volume passing the subbasin gage due to surface runoff</td>
</tr>
<tr>
<td>( z )</td>
<td>evapotranspiration exponent</td>
</tr>
<tr>
<td>( \delta_c )</td>
<td>root mean square of pollutograph model error (( M/L^3 ))</td>
</tr>
<tr>
<td>( \delta_N )</td>
<td>logaritmic mean hydrograph model error</td>
</tr>
<tr>
<td>( \delta_R )</td>
<td>root mean square of hydrograph model error (( L^3/T ))</td>
</tr>
<tr>
<td>( \nu )</td>
<td>kinematic viscosity of soil moisture (( L^2/T ))</td>
</tr>
<tr>
<td>( \lambda_c )</td>
<td>exponential decay constant of the aquifer (( L^3/T ))</td>
</tr>
<tr>
<td>( \lambda_B )</td>
<td>exponential decay constant of the vadose zone (( L^3/T ))</td>
</tr>
<tr>
<td>( \lambda_I )</td>
<td>exponential decay constant of the highway drainage system (( L^3/T ))</td>
</tr>
<tr>
<td>( \mu )</td>
<td>depression storage layer thickness (( L ))</td>
</tr>
<tr>
<td>( \mu_B )</td>
<td>specific conductivity of gage discharge (( S/L ))</td>
</tr>
<tr>
<td>( \Omega )</td>
<td>baseflow specific conductivity (( S/L ))</td>
</tr>
<tr>
<td>( \Omega_0 )</td>
<td>zero order source term for chloride dissolution (( M/L^3\cdot T ))</td>
</tr>
<tr>
<td>( \omega )</td>
<td>chloride dissolution source strength (( L/T ))</td>
</tr>
<tr>
<td>( \xi )</td>
<td>accumulated depth of precipitation (( L ))</td>
</tr>
</tbody>
</table>

Plate deicing seasons reduce the importance of storage change and seasonal variability, and inspire more confidence in the balances as a result. In this regard, chloride mass residence times are generally longer than hydraulic response times because the former reflect water velocity while the latter depend on pressure wave velocity. If there are spatial data describing piezometric head, hydraulic properties, and deicing agent concentration gradients, these balances can be analytical (Ostendorf et al., 2004, 2006a) or numerical (Bester et al., 2006) solutions to partial differential transport equations. In the absence of spatial details, the balances revert to the input/output formalism of linear hydrologic systems (Dooge, 1973; Bruinsma, 2005), although the reservoir parameters can be assessed in physically plausible terms (Gelhar and Wilson, 1974). This latter approach is followed in the present analysis.

The present study features temporal, not spatial detail in a relatively small watershed with a long period of record. Water and chloride based deicing agents interact at storm, weekly, and seasonal time scales in the highway right of way through the subbasin, as documented by a gaging station at the outlet that measures flow and specific conductivity. The specific conductivity data complement the hydrologic measurements because the analysis of the solutions and physical plausibility of the parameter values endorse the approach, and the fractions are readily understood by completing users of the subbasin and right of way.
1.3. Site description

The data are from the Lincoln Street subbasin of the Hobbs Brook reservoir of the Cambridge Water Department (CWD, 2011) in eastern Massachusetts, located in Fig. 1 and described in detail by Waldron and Bent (2001) and CWD (2006). Constructed in the 1890s, the reservoir has a capacity of 10.7 million m³, and, along with the adjacent Stony Brook reservoir, meets the average demand of 0.613 m³/s provided by CWD for the 95,000 permanent resident and 60,000 student population. The Lincoln Street subbasin drains a 1.07 × 10⁶ m² area A, or 5.3% of the Hobbs Brook reservoir watershed (Fig. 2 and Table 1).

A subsurface investigation was conducted in the subbasin (service area in Fig. 2) in the 1990s by the University of Massachusetts Transportation Center (UMTC, 1995) for the Massachusetts Department of Transportation (MassDOT). Soil borings and hydraulic tests indicate an unconfined, nonuniform sand aquifer 6 m thick that overlies crystalline bedrock, and in turn underlies a 2 m thick vadose zone. The aquifer permeability is 10⁻¹¹ m² with an average water table slope of 0.02 towards the perennial subbasin tributary, so that the specific discharge of the groundwater is 2 × 10⁻⁹ m/s and the aquifer transmissivity T is 6 × 10⁻⁴ m²/s. Gelhar and Wilson (1974) suggest that the basinflow decay constant i₀ is about 37/L₀ in magnitude. A horizontal basinflow length scale L₀ of 100 m then implies a i₀ value of 2 × 10⁻⁵ s⁻¹, and a hydraulic response time (1/i₀) of several months. Basinflow responds seasonally at the subbasin. Fiori (2012) uses a rigorous solute transport model to suggest that the contribution of old (prestorm) recharge to the basinflow output volume varies directly with the product of i₀ and the storm duration. A long storm duration of 1 day at the Lincoln Street subbasin would have a 0.02 product value and an old basinflow fraction 0.98; the aquifer contribution to the tributary pollutographs reflects historical, not current contamination.

Interstate 95 and State Route 2A cross in the subbasin, and MassDOT maintains 15.7 lane miles of pavement in the subbasin, including ramps of the interchange and feeder lanes and parking lot of the rest area (CWD, 2006). The standard lane width of 3.65 m (Garber and Hoel, 1999), multiplied by the lane mile total, yields a state maintained paved area Aowed of 9.2 × 10⁶ m², or 8.5% of the subbasin area. Fig. 2 suggests that local streets are distributed among residential neighborhoods east of the right of way. A 4 lane mile paved area is ascribed to these streets, which are the responsibility of the Town of Lexington; this latter is 2.2% of the subbasin area.

The Interstate, State Route interchange, and service area all feature drainage systems with curbs, catch basins, storm drains, and retention pools that flow directly and indirectly to an unnamed tributary of the Hobbs Brook reservoir (CWD, 2006). This tributary, though small, is perennial, suggesting that vadose zone soil moisture and groundwater also contribute flow. Thus, drainage from the Interstate, interchange, and service area right of way all generate interflow and basinflow in addition to the surface runoff collected by the closed drainage system. The local roads are assumed to recharge the aquifer, and are not directly connected to the state maintained drainage system (Waldron and Bent, 2001).

The Interstate serves an average daily traffic volume of 160,000 vehicles through the subbasin (MassDOT, 2012). The heavy volume is much higher than the “Super Commute” minimum of 30,000 vehicles per day, and is sensitive to delays. The American Association of State Highway and Transportation Officials (AASHTO, 1999) recommends the highest level of deicing service for this highway designation: maintenance of bare pavement 24 h a day. MassDOT deices the subbasin pavement from the Lexington 2A salt/premix storage facility, using a combination of four chloride based deicing agents. The storage facility is responsible for a total of 136 lane miles of pavement, including the 15.7 lane miles in the subbasin. The Lexington Public Works Department (DPW, 2012) maintains the local streets in the subbasin with a lower level of service among its 284 lane mile total.

1.4. Output and input data

The United States Geological Survey (USGS, 2012a) operates a gage (number 0104415) on the tributary, 80 m upstream of its res-
ereoir outlet. Established in October 1997, the station has maintained 15 min frequency (or shorter) discharge and specific conductivity data sets since November 1, 2005, using standard USGS instrumentation, methods, and telemetry (Smith, 2007). The period of record extends through August 2012: two continuous time series of 82 months’ duration comprise the output dataset. Monthly and total averages are extracted from these data, and 162 individual hydrographs and pollutographs from the record elucidate the subbasin response to storms and interstorm periods.

The USGS (2012b) measures precipitation at 15 min intervals at a station (01104430) between the Hobbs and Stony Brook reservoirs (shown in Fig. 1). MassDOT logs volumes or weights of the deicing agents used in the study area on an event basis. Woodard and Curran (2011) provide the total deicing application agent applied by the Town of Lexington for the 2010 deicing season (November 2009–April 2010). The hydrograph time series and discrete deicing agent logs are the input dataset. Simple linear models of the runoff (Nash, 1959), interflow (Ostendorf et al., 2001), and baseflow (Celhur and Wilson, 1974) relate the output to input.

The relatively large paved fraction and multyear, temporally resolved database prompted CWD to request MassDOT to support the continued USGS maintenance and monitoring effort at the Lincoln Street gage, with UMASS interpretation of the data. The proximity of this instrumented subbasin to the deicing agent source elucidates the impact of historical deicing agent practices on water quality, and provides a baseline for the assessment of effects of future changes in these practices.

2. Hydrograph analysis

2.1. Precipitation and total hydrograph

Fig. 3 summarizes 82 months of hydrologic data from the Lincoln Street subbasin, expressed as discharges. The circles denote precipitation, expressed as the monthly change in the equivalent water depth \( \Delta \), multiplied by \( A \), then divided by the seconds in a month. The \( \Delta \) value at end of the period of record is 9.29 m, which implies that an average annual precipitation depth of 1.36 m falls on the subbasin each year. The circles in Fig. 3 suggest that precipitation does not vary seasonally, though there is considerable scatter each month: March 2010 witnessed over 0.43 m of precipitation, while March 2006 featured a 0.017 m depth of water equivalent. These extremes plot as 0.175 and 0.007 m/s in Fig. 3, respectively.

The monthly average of the total discharge \( Q \) observed to pass the gage plots as squares in Fig. 3. Each symbol represents thousands of individual samples, since the sampling interval is 15 min or less over the period of record. The average \( Q \) past the gage for the period of record is 0.0259 m/s, which corresponds to a depth of 0.763 m per year on the subbasin area (Table 1). Thus 56.1% of the precipitation over the 82 month period passed over the Lincoln Street gage, while 0.60 m was lost to evapotranspiration, groundwater flow directly to the Hobbs Brook reservoir, or to transport out of the subbasin. The latter two losses are neglected in this analysis: Fig. 3 suggests that the monthly averages decline during the late summer, consistent with an evapotranspirative loss. Furthermore, the 0.60 m per year loss rate is comparable to the water surface evaporation rate of 0.63 m per year for eastern Massachusetts (Linsley et al., 1982). In the latter regard, Chaudhury (1999) uses an empirical exponent \( z \) of about 2 to estimate mean annual evapotranspiration from precipitation and water equivalence of net annual radiation.

\[
\text{Evapotranspiration} = \frac{\text{precipitation}}{1 + (\frac{\text{precipitation}}{\text{radiation}})^{z}}
\]  

The substitution of 2 for \( z \) and 0.63 m for radiation in Eq. (1) yields an evapotranspiration estimate of 0.57 m, comparable to the observed loss rate in the subbasin.

2.2. Baseflow

The perennial nature of the tributary suggests that groundwater contributes baseflow to the Lincoln Street gage. An array of models can be used to separate baseflow from surface runoff hydrographs (Eckhardt, 2008) in the absence of precipitation input data. Low flow behavior elucidates the baseflow (Smakhtin, 2001), and a

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Lincoln Street</th>
<th>Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
<td>Subbasin area</td>
<td>1.07 × 10^6</td>
<td>USGS (2012a)</td>
</tr>
<tr>
<td>( Q_{t} )</td>
<td>Total discharge (average)</td>
<td>0.0259</td>
<td>USGS (2012a)</td>
</tr>
<tr>
<td>( Q/\text{PFA} )</td>
<td>Average discharge fraction</td>
<td>0.561</td>
<td>USGS (2012a)</td>
</tr>
<tr>
<td>( E_{c} )</td>
<td>Evapotranspiration (average)</td>
<td>1.90 × 10^{-6}</td>
<td>USGS (2012a)</td>
</tr>
<tr>
<td>( c )</td>
<td>Gage chloride (average)</td>
<td>0.334</td>
<td>USGS (2012a)</td>
</tr>
<tr>
<td>( Qa )</td>
<td>Baseflow (average)</td>
<td>0.0125</td>
<td>USGS (2012a)</td>
</tr>
<tr>
<td>( k_b )</td>
<td>Baseflow decay constant</td>
<td>2 × 10^{-7}</td>
<td>USGS (2012a)</td>
</tr>
<tr>
<td>( M_a )</td>
<td>Baseflow chloride fraction</td>
<td>0.61</td>
<td>USGS (2012a)</td>
</tr>
</tbody>
</table>

Table 1. Subbasin and aquifer parameter values.
The recession curve for the Lincoln Street gage can be assembled from a composite of droughts over the period of record for the gage (Hall, 1988). A simple variant of these more sophisticated models is adopted in the present analysis, since precipitation is known, the subbasin area is small, the baseflow hydraulic response time is seasonal, and unsteady interflow is considered separately. Baseflow \( Q_8 \) is approached asymptotically over the interstorm period, and taken as a constant for the storm. Fig. 3 plots (as triangles) these asymptotes for the 162 storms analyzed at the Lincoln Street gage.

The average of all 162 baseflow estimates is 0.0125 m\(^3\)/s, which equates to a 0.368 m depth each year, 27.1% of the precipitation. The steady specific discharge estimated by the UMTC (1995) site investigation, when multiplied by the 6 m unconfined aquifer depth and 1 km streamwise length of the aquifer implied by Fig. 2, yields a baseflow estimate of 0.012 m\(^3\)/s. The agreement of this independent \( Q_8 \) estimate, obtained by a thorough, but local subsurface site characterization effort, with the hydrologic Fig. 3 based estimate is striking, particularly since the latter reflects a temporally resolved, but spatially blind site wide assessment of the quantity.

The aquifer water volume fraction \( V_a \) of the total volume of water passing the subbasin gage is the ratio of the period of record averages for baseflow and total discharge. Table 1 cites the \( V_a \) value of 48.3%; baseflow is significant at the site. The triangles in Fig. 3 display an order of magnitude drop of baseflow during the summer, as vegetation and stronger vapor pressure gradients withdraw groundwater from the aquifer. This behavior is typical of New England, where baseflows are smallest in August and September while precipitation is uniform throughout the year (Hodgkins and Dudley, 2011).

### 2.3. Surface runoff hydrograph and decay constant

The total hydrograph past the outlet gaging station is analyzed as a superposition of linear reservoir outputs for seasonal baseflow from the aquifer, diurnal interflow from the vadose zone (R subscript), and hourly scale surface runoff from the highway drainage system (R subscript). The surface runoff system is assumed to have a discharge proportional (by the decay constant \( i_R \)) to its volume (Chow, 1964), so that the conservation of water mass balances storage, outflow, and inflow in simple fashion

\[
\frac{1}{i_R} \frac{dQ}{dt} + Q_e - A_F a_P = 0
\]  

\( Q_0 - Q_R + Q_I + Q_e \) \hspace{1cm} (2a)

\[ Q_R(t) = 0 \quad (t < t_0) \]  

\[ Q_I(t) = 0 \quad (t > t_0) \]  \hspace{1cm} (2b)

\[
\frac{1}{i_R} = \int_{0}^{t_0} P(t) \, dt
\]  

\( \zeta = \int_{0}^{t_0} P(t) \, dt \) \hspace{1cm} (3a)

\[
\frac{Q_m}{Q_m} - \frac{Q_m}{Q_m} = 1 + i_R A_F a_P \Delta t
\]  

\[
Q_m - Q_m \exp \left[ -i_R (t - t_0) \right] \quad (t_0 < t < t_0)
\]  

\[ Q_e = Q_e \left( \frac{1}{i_R} \right) \quad (t < t_0) \]  \hspace{1cm} (3b)

\[ Q_e = Q_e \left( \frac{t - t_0}{i_R} \right) \quad (t_0 < t) \]  \hspace{1cm} (3c)

\[ Q_e = Q_e \left( \frac{1}{i_R} \right) \quad (t < t_0) \]  \hspace{1cm} (3d)

\[ Q_e = Q_e \left( \frac{T}{i_R} \right) \quad (t > t_0) \]  \hspace{1cm} (3e)

Eq. (3d) defines the depression storage layer thickness \( \zeta \), which must be filled before runoff can begin at time \( t_0 \) (Linsley et al., 1982). Time \( t \) is zeroed at the beginning of the calibration period of interest. Eq. (3d) is a forward finite difference approximation of the governing Eq. (3a), with known prior conditions used to estimate the runoff \( Q_0 \) at the initial step \( \Delta t \). The exponential recession [Eq. (3c)] with decay constant \( i_R \) proceeds after the storm stops at time \( t_0 \), as a closed form solution of Eq. (3a). The surface runoff at time \( t_0 \) is \( Q_0 \). The recession is the instantaneous unit hydrograph of the system, and the analysis could proceed in terms of a convolution integral (Chow, 1964), although the numerical integration takes a longer time to run on a computer than does Eq. (3d). The runoff system routes a fraction \( F_R \) of the precipitation intensity \( P \) falling on the watershed area to the gage with a decay constant \( i_R \) that reflects pavement attributes and configuration of the highway drainage system configuration. The discharge fraction varies due to evapotranspiration, antecedent moisture content, and other seasonal fluctuations.

The storm of September 6–7, 2008 calibrates the runoff decay constant for the subbasin, with the results summarized in Fig. 4 and Table 2. The storm was intense and significant, with a peak intensity of 2.5 inches per hour and a total depth of 6.06 cm. The first 11 h of runoff data calibrate the runoff decay constant, depression storage layer thickness, and runoff fraction in accordance with a simplification of Eqs. (2) and (3)

\[ Q_{\text{predicted}} \approx Q_0 + Q_e \quad (t \sim 1/i_R) \]  \hspace{1cm} (4)

Baseflow and interflow additions during the storm are ignored, as is the recession of the observed initial discharge \( Q_0 \). This holds because surface runoff dominates the hydrograph during the first few hours after an intense storm. A nested Fibonacci search (Knuth, 2005) minimizes the root mean square \( \delta_R \) of the difference between measured and predicted [Eq. (4)] discharge

\[ \delta_R = \left[ \frac{1}{N} \sum_{N} \left( Q_{\text{measured}} - Q_{\text{predicted}} \right)^2 \right]^{1/2} \]  \hspace{1cm} (5)

This search yields a runoff fraction of 0.353, much larger than the paved fraction of 8.6%. The unpaved areas and retention basins of the right of way contribute direct surface runoff during intense precipitation. The calibrated depression storage layer thickness of 0.51 mm lies within the 0.2–4 mm range of pavement texture cited by Coney and Coney (1997) as has been found by hydrograph analysis at other highway sites (Ostendorf et al., 2001, 2005).

The calibrated runoff decay constant is 2.49 \times 10^{-4} \text{s}^{-1}. The \( i_R \) value is retained as record of storm, as cited in Table 2, and implies a 1 h runoff response time of \( \frac{1}{2} \text{h} \text{s}^{-1} \) for the closed drainage system of the subbasin. The physical plausibility of \( i_R \) can be
assessed by equating it to the inverse of the travel time of a disturbance through the subbasin

$$\frac{1}{i_1} \approx \sqrt{\frac{A}{g h}} \tag{6}$$

with gravitational acceleration is g. The denominator of Eq. (6) is the celerity of a long wave in an open channel (Henderson, 1966), while the numerator characterizes the horizontal distance of the subbasin. The runoff decay constant calibration implies a thickness $h$ of 6.8 mm for the Lincoln Street subbasin. The thickness is the same scale as pavement texture: the runoff does not puddle on the pavement surface.

### 2.4. Interflow hydrograph and decay constant

The storm of June 14, 2006 and following 9 day interstorm period calibrated the decay constant $i_1$ of the interflow hydrograph with the results summarized in Fig. 5 and Table 2. This storm, like its Fig. 4 counterpart, was intense and brief enough to calibrate subbasin runoff response; the following 1 week dry period was long enough to elucidate the vadose zone attributes while preserving a constant baseflow contribution. The interflow model is analogous to its runoff counterpart

$$\frac{1}{i_1} \frac{dQ_t}{dt} + Q_t - A F_i P$$

### Fig. 5. Observed (symbols) and calibrated (line) (a) hyetograph and (b) hydrograph, Lincoln Street subbasin, June 2006. Calibrated interflow decay constant is cited in Table 2, and used for all other storm and interstorm periods.

### Table 2

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Lincoln Street</th>
<th>Basis</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{pav}$</td>
<td>MassDOT pavement area</td>
<td>$5.2 \times 10^4$</td>
<td>CWD (2008)</td>
</tr>
<tr>
<td>$c_m$</td>
<td>Deposition storage layer (average)</td>
<td>$4.0 \times 10^{-6}$</td>
<td>Hydrograph calibration</td>
</tr>
<tr>
<td>$i_n$</td>
<td>Runoff decay constant</td>
<td>$7.7 \times 10^{-6}$</td>
<td>Hydrograph calibration</td>
</tr>
<tr>
<td>$i_R$</td>
<td>Runoff discharge fraction (average)</td>
<td>0.22</td>
<td>Hydrograph calibration</td>
</tr>
<tr>
<td>$i_V$</td>
<td>Runoff volume fraction</td>
<td>0.31</td>
<td>Hydrograph calibration</td>
</tr>
<tr>
<td>$M_{Ch}$</td>
<td>Runoff chloride fraction</td>
<td>0.22</td>
<td>Pollutograph calibration</td>
</tr>
<tr>
<td>$j_n$</td>
<td>Interflow decay constant</td>
<td>$4.34 \times 10^{-6}$</td>
<td>Hydrograph calibration</td>
</tr>
<tr>
<td>$j_I$</td>
<td>Interflow discharge fraction (average)</td>
<td>0.21</td>
<td>Hydrograph calibration</td>
</tr>
<tr>
<td>$M_I$</td>
<td>Interflow volume fraction</td>
<td>0.15</td>
<td>Hydrograph calibration</td>
</tr>
</tbody>
</table>

Eq. (2a) predicts $Q_t$ with constant baseflow and Eqs. (3) and (7) modeling runoff and interflow. The curve in Fig. 5 shows the calibration. The $i_R$ and $i_I$ values for the Lincoln Street are $0.283$ and $0.381$ and the interflow decay constant is $4.34 \times 10^{-6}$ s$^{-1}$ for this storm. While the discharge fractions vary from storm to storm, the calibrated interflow decay constant is cited in Table 2 and adopted across the period of record: the interflow response time ($1/i_1$) of 4 days is an order of magnitude longer than its runoff counterpart in the subbasin. Fig. 5b is semilogarithmic. It recovers the classical break in slope as the runoff attenuates and reveals the latter dominance of the slower responding vadose zone. The hydraulic diffusivity governs the propagation of a disturbance through the vadose zone (Eagleson, 1970). Ostendorf et al. (2001) use diffusivity to assess the plausibility of the calibrated interflow system response time

$$\frac{1}{i_d} \approx \frac{\nu L_d}{k g S} \tag{9}$$

The characteristic length $L_d$ of the vadose zone is 10 m, the soil moisture kinematic viscosity $\nu$ is $10^{-6}$ m$^2$/s, and the matrix pressure head gradient $S$ is 1. The calibrated decay constant then implies a vadose zone permeability $k$ of $5 \times 10^{-12}$ m$^2$ for Lincoln Street—about half of the saturated value found during the (UMTC, 1995) site characterization.

The decay constants for the three systems distinguish linearity superimposed hydraulics at hourly, diurnal, and seasonal scales, since $i_R > i_I > i_D$. The magnitude of the system discharge varies directly with the time scales. $Q_R > Q_I > Q_D$. 

![Observed (symbols) and calibrated (line) (a) hyetograph and (b) hydrograph, Lincoln Street subbasin, June 2006. Calibrated interflow decay constant is cited in Table 2, and used for all other storm and interstorm periods.](image-url)
Fig. 6. Calibrated runoff $F_R$ (red circles) and interflow $F_I$ (black squares) discharge fractions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.5. Hydrograph calibration across the period of record

Eqs. (2a), (3), and (7) are applied to 162 storm and interstorm hydrographs across the subbasin period of record, using Table 2 values for the decay constants. The linear error of Eq. (5) calibrates $F_R$, while the logarithmic error of Eq. (8) calibrates $F_I$ and the asymptotically approached $Q_e$. The calibrated depression storage layer thickness ranges from 0 to 9.4 mm with an average value of 4.0 mm (cited in Table 2). The average depression storage layer thickness is used to model chloride dissolution kinetics, coupling the hydrograph and pollutograph models.

Fig. 6 indicates that $F_I$ generally declines during the summer, as evapotranspiration withdraws more soil moisture from the vadose zone, as is the case for the aquifer. The averages of the 162 $F_R$ and $F_I$ calibrations shown in Fig. 6 are 0.22 and 0.15, respectively. The two period of record averages combine with the 27% baseflow fraction to total 84% of the precipitation, close to the 56% value implied by the observed total precipitation and total hydrograph averages. The average $F_R$ and $F_I$ values also suggest that the highway drainage system and vadose zone contribute appreciable water volume fractions $V_R$ and $V_I$ to the subbasin gage over the period of record. Since baseflow accounts for 48% of the gage volume, Table 2 cites runoff and interflow volume fractions of 0.31 for $V_R$ and 0.21 for $V_I$ based on the relative values of the discharge fractions.

The baseflow index is the sum of the subsurface (interflow and baseflow) volume fractions (Eckhardt, 2008)

$$\text{Baseflow \ Index} = V_R + V_I$$

(10)

The long term volume fractions imply a baseflow index of 0.69 for the Lincoln Street gage, which lies in the mid-range of the indices estimates for 65 North American catchments by Eckhardt (2008).

3. Pollutograph analysis

3.1. Specific conductivity and total chloride pollutograph

The advective flux of specific conductivity past the gage is the product of $Q$ and the specific conductivity $\mu$. It couples water mass transport to contaminant mass transport models, and also provides a useful basis for assessing urban runoff (USEPA, 1983) and watershed loading (USEPA, 1987). In this latter regard, the circles in Fig. 7 are monthly average specific conductivities passing the subbasin gage, obtained by dividing the monthly average $Q$ values of Fig. 3 into monthly average values of $Q_0$. The monthly average specific conductivity varies seasonally with highest values in winter. The figure features a low value of 0.34 mS/cm in August 2010, an order of magnitude less than the maximum value of 4.5 mS/cm in December 2007. The sum of the 82 months of data in Figs. 3 and 7 represents the total specific conductivity passing the gage over the period of record, an amount equal to $6.93 \times 10^8$ mS/cm. This total, divided by the total volume of water discharged past the gage, yields a period averaged specific conductivity of 1.24 mS/cm.

Fig. 8 displays (as symbols) measured specific conductivity and measured dissolved chloride in samples from the Lincoln Street gage, as reported on the USGS (2012a) website. The line is a regression through the data [Eq. (11)].

$$c = C_p \mu$$

(11a)

$$C_p = 0.27 \text{ kg(Cl)} \cdot \text{cm} \cdot \text{m}^3 \cdot \text{mS}$$

(11b)
The empirical coefficient $C_p$ [Eq. (11b)] relates specific conductivity to dissolved chloride throughout this analysis. The value agrees with empirical coefficients found at other chloride based deicing agent field sites in eastern Massachusetts: a range of 0.23 - 0.30 kg·cm·m²·s⁻¹ describes highway runoff in Dedham (Ostendorf and Kilbridge, 2011), Wilmington (Heath and Belaval, 2011), and Cohasset (Ostendorf et al., 2001). The period averaged $\mu$ corresponds to a period averaged $c$ of 0.334 kg·Cl⁻¹·m⁻³, in excess of the United States Environmental Protection Agency (USEPA, 2012) secondary drinking water standard of 0.250 kg·Cl⁻¹·m⁻³ for dissolved chloride. The monthly average chloride concentrations of Fig. 7 range from 0.092 to 1.22 kg·Cl⁻¹·m⁻³.

### 3.2. Baseflow chloride concentration

The baseflow specific conductivity $J_e$ like $Q_e$ is approached asymptotically over each interstorm period. Fig. 7 displays the estimated values as squares. These groundwater conductivities are more stable than their total counterparts, and vary from an October 2006 minimum of 1.05 mS·cm⁻¹ to a July 2006 maximum of 2.85 mS·cm⁻¹. Eq. (11b) converts the specific conductivity to baseflow chloride concentration $C_e$, as indicated by the right axis of Fig. 7. The groundwater $C_e$ values range from 0.237 to 0.741 kg·Cl⁻¹·m⁻³, and nearly all exceed the secondary standard value.

Eq. (11b) also converts the $6.89 \times 10^{-5}$ mS·cm⁻¹ total specific conductivity amount to a total mass of $1.87 \times 10^6$ kg of chloride that past the Lincoln Street gage during the 62 month period of record. The product of $Q_e$ and $C_e$ is the flux of chloride from the aquifer to the drainage system. Minimal first flushes are assessed here for each storm and interstorm period by definition. The integral of this flux over the period of record may be estimated from monthly averages of the quantity, an exercise which yields a mass of $1.14 \times 10^9$ kg chloride. This baseflow mass fraction $M_e$ is 61%; the aquifer provides a significant fraction of the total flux of chloride passing the Lincoln Street gage over the period of record.

### 3.3. Runoff chloride pollutograph model and deicing agent dissolution kinetics

Advection transports dissolved chloride through the runoff and interflow systems, whose output fluxes $Q_e$ and $Q_C$ mix with the baseflow chloride flux to generate $Q_r$.

$$Q_r = Q_e + Q_C$$  \hspace{1cm} (12)

The drainage system routes input chloride $F_cP_c$ from the pavement through the surface drainage system as a balance of storage and outflow that can be expressed as

$$\frac{dC_e}{dt} + AF_eC_R - AF_eC_P = 0$$  \hspace{1cm} (13a)

$$C_R = C_P \left( t \leq t_f \right)$$  \hspace{1cm} (13b)

$$C_R = \frac{Q_{c_R} \left( t > t_f \right)}{Q_{c_R} \left( t \leq t_f \right) + 1/AF_e \left( t > t_f \right)} \left( t_f \leq t \leq t_o \right)$$  \hspace{1cm} (13c)

The runoff concentration when the storm stops is $C_R$. Solid deicing agent dissolves into precipitation on the highway, generating the dissolved chloride concentration on the pavement $C_R$. Ostendorf et al. (2001) model the term as a balance of storage, outflow and zero order dissolution through an elemental control volume centered on a deicing agent granule on the pavement.

$$C_R - C_P \left( 0 < t < t_f \right)$$  \hspace{1cm} (14a)

$$\frac{dC_R}{dt} + \frac{\rho}{t} - \Omega \left( t_f < t < t_o + t_{dRV} \right)$$  \hspace{1cm} (14b)

The depth of the elemental control volume is the average (4.0 mm) depression storage layer thickness, so that the hydrographs and pollutographs are coupled. The zero order source term $\Omega$ models the dissolution of solid deicing agent chloride granules, and stays constant during each storm and interstorm period. The granules dissolve so long as there is water in the depression storage layer, and this period persists for a time $t_{dRV}$ after the end of precipitation at time $t_p$.

The observed “first flush” chloride concentration $Q_{f,0}$ is the minimum or maximum value at the gage just after the onset of runoff at time $t_p$ when the discharge (and advective chloride flux) is dominated by surface runoff. Minimal first flushes and weak source strengths are created by most summer storms (Fig. 9a), whose runoff dilutes the more stable saline contributions of the vadose zone and aquifer. The maximal first flushes and strongest sources primarily occur in winter (Fig. 9b), when deicing agent applications contaminate the winter runoff more strongly than the subsurface moisture. Ostendorf et al. (2008b) found a similar range of first flush specific conductivities (shown in the left axis of Fig. 10) in 4 years of calibrated storm pollutographs at State Highway 25 in southeastern Massachusetts. Ostendorf et al. (2001) found a similar range of $Q_{f,0}$ values in 3 years of storm pollutographs at the closed drainage system outlet of a salt/presmelt storage facility in Cohasset, Massachusetts. Indeed, these latter data established the zero order dissolution model [Eq. (14)].

The observed first flush concentrations can be used to construct the limits of source strength calibration by ignoring precipitation in Eq. (14b) with the result

$$\Omega_{MIN} < \Omega < \frac{Q_{f,0}}{I_o + I_{dRV}}$$  \hspace{1cm} (15a)

$$\Omega_{MIN} \approx \frac{Q_{f,0}(minimum)}{I_o + I_{dRV}}$$  \hspace{1cm} (15b)

A lower limit $\Omega_{MIN}$ of $3 \times 10^{-2}$ kg·Cl⁻¹·m⁻³·s⁻¹ is imposed by the minimum observed first flush chloride concentration in the period

![Fig. 9. Observed (symbols) and calibrated (lines) chloride pollutographs. (a) Typical (May 12-19, 2006) summer storm and interstorm period and (b) typical (December 16-21, 2005) winter storm and interstorm period.](image-url)
Fig. 10. Observed first flush chloride concentrations. Eq. (11) converts specific conductivities to dissolved chloride concentration.

of record and a conservative $t_D + t_{DST}$ value of 10$^2$ s. A finite difference approximation of Eqs. (14b) and (15) is used in runoff pollutograph analysis

$$c_{Pn} = c_{Pm} + \frac{1}{1 + \frac{1}{\Omega \Delta t}}$$  

(16)

3.4. Interflow chloride pollutograph model, seasonal calibrations, and chloride fractions

The conservation of chloride through the vadose zone balances storage, efflux to the gage, and influx from the ground surface and water table

$$\frac{Q_m c_m}{Q_m} \frac{dc}{dt} + Af \frac{Q}{Q_m} = Af \frac{Q}{Q_m} (E_P + E_c)$$  \hspace{1cm} (17a)

$$\frac{Q}{Q_m} c_m - \frac{Q}{Q_m} c_c = \frac{Q}{Q_m} c_c - \frac{Q}{Q_m} c_c$$  \hspace{1cm} (17b)

$$c_{m} = c_{m} + \frac{2 \pi Af}{Q_m} (E_P + E_c) \Delta t$$  \hspace{1cm} (17c)

The pavement concentration characterizes the fraction of precipitation that infiltrates into the vadose zone, carrying dissolved deicing agents with it. This contribution is significant during winter months. The last term in Eq. (17a) models evapotranspiration (at a rate $E$), which advects dissolved groundwater chloride upwards across the water table. The chloride remains in the vadose zone, while the soil moisture changes phase on its way back to the atmosphere. This portion of the interflow chloride assumes importance in the summer, as $c_{Pn}$ declines. The hyetographs and hydrographs suggest an annual evapotranspiration loss of 0.60 m from the subbasin, with a seasonal maximum in the summer. The interflow pollutograph model sets $E$ equal to zero for December through March, $1.8 \times 10^8$ m/s for April, May, October, and November, and $3.6 \times 10^8$ m/s for June through September in Eq. (17c).

With $c_{Pm}$ and $q_0$ observed and all decay constants estimated, the $\Omega$ and $c_c$ values calibrate the 162 storm and interstorm pollutographs. The root mean square error $\delta_c$ of the pollutograph is used in the calibration

$$\delta_c = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (c_{Pm}(measured) - (Qc)(predicted))}$$  \hspace{1cm} (18)

A nested Fibonacci search minimizes the error, with typical results shown as the lines in Fig. 9. The $c_{Pn}$ values are 0.24 and 0.38 l<g/m$^3$ for the summer and winter pollutographs of the figure. This uniformity contrasts with the seasonal first flush values mentioned earlier.

The individual chloride pollutographs may be integrated in order to estimate the fractions contributed by the drainage system $m_R$ and vadose zone $m_I$ to the total chloride mass for each storm and interstorm period

$$m_R = \frac{\int_{0}^{\text{event}} Q \cdot c_{Pn} \cdot dt}{\text{event} \cdot \text{Q} \cdot \text{c}_{\text{Pn}}}$$  \hspace{1cm} (19a)

$$m_I = \frac{\int_{\text{event}} Q \cdot c_{Pn} \cdot dt}{\text{event} \cdot \text{Q} \cdot \text{c}_{\text{Pn}}}$$  \hspace{1cm} (19b)

Fig. 11 displays the results, which feature an average surface runoff system chloride fraction of 0.22 and an average vadose zone chloride fraction of 0.18. These latter are assumed to represent the entire period of record, so that $M_R$ is 22% and $M_I$ is 17%, as cited in Table 2. The interflow fraction is rounded down, so that the chloride fractions from all three systems sum to one.

4. Deicing agent applications

4.1. MassDOT and Lexington municipal applications

Fig. 12 displays the chloride masses $n_I$ in deicing agents applied by MassDOT to the 136 lane miles of highway served by the Lexington 2A salt/premix storage facility during the study period. Two solid agents, road salt and premix, and two liquid agents, calcium chloride and magnesium chloride, were applied over the seven deicing seasons from 2005 to 2012. The solid applications are reported in tons, while the liquid agents are reported in gallons. All four agents have chloride (Cl$^-$) as the sole anion, so that chloride is
a logical constituent for mass transport estimation. Road salt is NaCl, and the stoichiometry suggests that 1 ton of road salt has a (solid) chloride mass of 551 kg. Premix blends 80% road salt with 20% CaCl\textsubscript{2} by mass, so that one ton of premix has a solid chloride mass of 556 kg. MassDOT used a 32% by mass solution of liquid CaCl\textsubscript{2} as a prewetting agent for the first six deicing seasons of the study. One gallon of this deicing agent solution has a chloride mass of 0.945 kg, based on a pure CaCl\textsubscript{2} density of 2340 kg/m\textsuperscript{3} (Weast, 1967). MassDOT switched to a 30% by mass solution of liquid MgCl\textsubscript{2} for the 2012 deicing season. One gallon of this deicing agent solution has a chloride mass of 1.02 kg, based on a pure MgCl\textsubscript{2} density of 2320 kg/m\textsuperscript{3}.

Fig. 12 distributes the chloride in 12,600 tons of road salt and 11,800 tons of premix over seven deicing seasons on the 136 lane miles served by the Lexington 2A facility, at an annual rate of 14.5 kg of solid deicing agents per lane meter. This rate exceeds the 5.4 kg deicing agents per lane meter annual rate for Maine (Mason et al., 1999), the 7.2 kg deicing agents per lane meter rate applied by MassDOT to State Route 25 in southeastern Massachusetts (Ostendorf et al., 2006b), the 9.2 kg deicing agents per lane meter rate for New York and New Hampshire reported by the Transportation Research Board (1994), and the 12 kg deicing agents per lane meter rate for Sweden cited by Lofgren (2001). The high rate reflects the heavy traffic volume on the Interstate and MassDOT sensitivity to weather related interruptions of service.

Fig. 12 includes the much smaller chloride masses of prewetting agent applications: 145,000 gallons of CaCl\textsubscript{2} for six seasons and 17,400 gallons of MgCl\textsubscript{2} for the 2012 season. The chloride factors, when applied to the solid and prewetting amounts, yield a total applied chloride mass of 1.37 \times 10\textsuperscript{7} kg applied to the 136 lane miles served by the Lexington 2A facility, an annual rate of 1.44 \times 10\textsuperscript{4} kg Cl per lane mile. This total, scaled by the 15.7 subbasin lane miles to facility lane mile ratio, suggests that 1.58 \times 10\textsuperscript{6} kg of chloride was applied to the study area pavement over seven deicing seasons. The total specific conductivity observed to pass the Lincoln Street gage, multiplied by Eq. (11b), yields a dissolved chloride mass of 1.85 \times 10\textsuperscript{6} kg over the period of record. Thus, ignoring storage change, MassDOT applications account for 85% of the total chloride pollutograph. Local and private deicing applications are likely responsible for the remainder.

In this regard, Woodard and Curran (2011) state that the Lexington Department of Public Works applied 5480 tons of road salt to town streets in the 2010 deicing season. The road salt stoichiometry and 284 lane mile municipal total yield a chloride application rate of 6.6 kg chloride per lane meter per year. This total, when multiplied by the 4 lane miles of municipal pavement in the subbasin area, leads to a town chloride mass of 4.2 \times 10\textsuperscript{8} kg per year, or 3.0 \times 10\textsuperscript{9} kg chloride over the 7 year period of record. This is about 15% of the total chloride mass that passed the Lincoln Street gage. All of this local total passed through the aquifer, where it combined with 46% from the state maintained pavement to comprise the 61% baseflow total inferred from the pollutographs. The remaining 39% of the MassDOT chloride applications divided between the surface runoff and interflow as \( M_R \) and \( M_p \).

### 4.2. A seasonal model for deicing agent solid dissolution

The \( j \)th deicing agent application \( s_j \) per unit horizontal area contributes an increment \( \Delta \Omega_j \) to the dissolved chloride source. The deicing agent solid is immobile upon its application, so that the incremental solid deicing agent mass conservation equation balances storage and dissolution

\[
\frac{d \Delta \Omega_j}{dt} = -\frac{\partial}{\partial t} - \frac{\partial}{\partial t} - \frac{\partial}{\partial t}
\]

The dissolution proceeds so long as the pavement texture remains wet, so that time can be more conveniently expressed in terms of the accumulation depth of precipitation \( \bar{z} \). The characteristic precipitation intensity is \( P_c \). Since the surface area of the deicing agent solid varies directly with its mass, Ostendorf et al. (2001) suggest first order dissolution kinetics on a seasonal time scale

\[
\Delta \Omega_j = -\omega \Omega_j
\]

with source strength \( \omega \) characteristic of the pavement texture and type of deicing agents used, but constant across the period of record.

Eqs. (20a) and (21) govern the seasonal dissolution of the \( j \)th deicing agent application as precipitation accumulates

\[
\frac{d s_j}{d \bar{z}} = -\frac{\omega}{P_c} s_j
\]

The source at a given time (hence \( \bar{z} \)) is the sum of all the prior attenuated applications

\[
\Omega_j - \Omega_j + \omega \sum_{\bar{z} = \bar{z}} \exp \left[ \frac{-\omega}{P_c} (\bar{z} - \bar{z}) \right]
\]
The calibrated source strength for the Lincoln Street subbasin is larger than the $2.6 \times 10^6$ s$^{-1}$ and $2.0 \times 10^6$ s$^{-1}$ values found by Ostendorf et al. (2006b, 2001) for similar seasonal calibrations at State Route 25 in southeastern Massachusetts and an access road in eastern Massachusetts. The Lincoln Street subbasin salt dissipates more rapidly than these other MassDOT study areas, so that surface runoff is not as saline in the summer. The calibration is less than the $3.0 \times 10^5$ s$^{-1}$ value fit to data from surface drainage at an outdoor storage and loading area, and comparable to the $7.3 \times 10^5$ s$^{-1}$ value describing surface drainage from indoor storage and loading at a remediated salt storage facility (Ostendorf et al., 2012).

5. Discussion

The annual MassDOT application of $2.26 \times 10^6$ kg chloride and annual town of Lexington application of $4.2 \times 10^6$ kg chloride, divided by the annual discharge volume of 8.17 $\times 10^6$ m$^3$ water, yield a 0.33 kg Cl$^-$/m$^3$ dissolved chloride concentration well beyond the secondary drinking water standard of the USEPA (2012). The concentration is a consequence of the large area of heavily traveled pavement, high level of service demanded by the drivers, and small area of the watershed subbasin. The construction of detention ponds in the Lincoln Street subbasin is a best management practice for mitigation of particulates, heavy metals, and other highway runoff constituents (TRB, 1993), and as such reflects MassDOT's awareness of the sensitive location of the Interstate right of way in the CWD reservoir watershed. Detention basins, however, deliver runoff and conservative chloride to the groundwater, ensure the large $V_G$ and $M_D$ fractions cited in Table 1, and a perennial discharge of water and dissolved chloride past the gage. Fig. 7 confirms the chronic, year round exceedance of the chloride standard at the gage. These would have been more acute, but seasonal, if more of the deicing agents remained in the surface runoff.

Fortunately, the Lincoln Street subbasin is a small (5.9%) fraction of the Hobbs Brook reservoir watershed area (Fig. 1), which relies on dilution from more pristine subbasins to preserve its quality. Smith (2007) measures an essentially uniform annual distribution of specific conductivity downstream of the Hobbs Brook reservoir (at station 01104430, where the precipitation was also measured). The 0.70 mS/cm Hobbs Brook specific conductivity at this station, when Eq. (11b) is invoked, yields a dissolved concentration of 0.150 kg Cl$^-$/m$^3$. This is less than the secondary standard, but bears watching – as suggested by the cooperative interest of two state, two federal, and one municipal agency in the Lincoln Street subbasin. Nonetheless, it is clear that dissolved chloride concentration decreases with distance from the pavement due to increased dilution.

6. Conclusions

Hytographs, perennial hydrographs, specific conductivity pollu­tophraphs, and deicing agent applications are analyzed with simple linear reservoir theory to explain the fate and transport of chloride in a small urban watershed subbasin delivering highway drainage to a public water supply reservoir in eastern Massachus­setts. Highway drainage, vadose zone, and aquifer systems describe 82 months of continuous outlet gage data as a superposition of runoff, interflow, and baseflow hydrographs with physically plausible exponential de­cay constants and seasonally varying discharge fractions. The inverse of the decay constants imply hydraulic response times of 60 days for the aquifer, 60 h for the vadose zone, and 70 min for the drainage system. The baseflow contributes 48% of the water volume passing the gage over the period of record, the interflow adds 21%, and the runoff 31% of the water volume.

Specific conductivity is a surrogate for dissolved deicing agent concentration, and 82 months of continuous data suggest that the average gage chloride concentration of 0.334 kg Cl$^-$/m$^3$ exceeds the USEPA secondary drinking water standard of 0.250 kg Cl$^-$/m$^3$. The chloride hytographs feature zero dissolution order kinetics on the pavement, infiltration and evaporation of chloride into the residual soil moisture of the vadose zone, and perennial contamination of the aquifer. Baseflow contributes 61% of the chloride mass flowing past the gage over the period of record. The respective fractions for interflow and runoff are 17% and 22% of the dissolved chloride past the gage.

Solid deicing agents are the source for the pollu­tophraph model, so that individual events in turn calibrate a coupled seasonal model of application rates and chloride dissolution kinetics. This exercise yields a source strength commensurate with other long term field studies, and an accounting of all the reported state and local deicing agent applications. In the latter regard, 85% of the chloride flux past the gage is attributable to documented state application of deicing agents on the highway, with the remaining 15% due to distributed, deicing applications by the town of Lexington on local streets.

The data and interpretations elucidate the impact of historical deicing agent practices on water quality at a relatively undisturbed subbasin chosen by the stakeholders, and can serve as a baseline for comparison of future changes in these practices, should CWD, MassDOT, regulatory, and public safety officials deem them necessary. These changes could include more emphasis on road weather information systems, prewetting and anti-icing techniques, pavement sensors, and closed loop spreader technology, all geared towards optimal application of chloride based deicers on the highway. Continued monitoring of specific conductivity and discharge would be needed for the comparison, of course, and the sampling frequency would need to be high and multyear in order to distinguish the contributions from the drainage system, vadose zone, and baseflow.

Acknowledgments

The Massachusetts Department of Transportation Highway Division funded this research under Interagency Service Agreement No. 56565 with the University of Massachusetts Amherst. The surface water quality stations were operated and maintained by the United States Geological Survey, with cooperation by the
Cambridge Water Department. The assistance is acknowledged and appreciated, although the views, opinions, and findings contained in this paper are those of the author and do not reflect MassDOT, USCS, or CWD official views or policies. This paper does not constitute a standard, specification, or regulation by any agency.

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