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Quantifying Surface Water Capture by Municipal Pumping Wells in an Urban Watershed Impacted by Road Salt

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QUANTIFYING SURFACE WATER CAPTURE BY MUNICIPAL PUMPING WELLS IN AN URBAN WATERSHED IMPACTED BY ROAD SALT

by

Austen York

A thesis submitted to the Graduate College
in partial fulfillment of the requirements
for the degree of Master of Science
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Austen York, M.S.

Western Michigan University, 2021

The Spring Valley sub-watershed is located within the Kalamazoo Township contains Spring Valley Lake, a man-made impoundment that ultimately discharges into the Kalamazoo River. Elevated chloride levels in pumped water from the Kalamazoo Station 14 municipal wellfield, located along the shoreline of Spring Valley Lake, has resulted in less than ideal corrosivity values for the water distribution system. Specific project objectives include: (1) identifying the cause of elevated chloride, (2) assessing surface water capture by the Station 14 wellfield, and (3) characterizing of water quality in Spring Valley Lake. Monitoring along a series of sampling transects spanning the sub-watershed, focused stormwater sampling, and deployment of field conductivity probes, were used to study the timing and quantify fluxes of major ions through the sub-watershed. These data conclusively demonstrate that winter application of road salts is the primary source of chloride in the sub-watershed. Vertical hydraulic gradients indicate aquifer recharge from the lake. Surface water capture by the wells is quantified using three methods: chloride mass balance, stable isotope mixing model, and water balance. These estimates provide a reliable capture range of 0.26-0.31 defined from common overlap of the three estimates.

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Austen York

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INTRODUCTION

Road salt, mostly in the form of sodium chloride, has been used as a deicing agent in the United States since the 1938, with some estimates claiming that road salt has prevented weather related collisions by up to 88% (American Highway Users Alliance, 2015). The use of road salt has steadily increased over time, with over 1.2 billion metric tons used in the last 25 years (Bolen 2021; Bolen 2016; Kostic 2010; Kostic 2005; Kostic 2000). Sodium chloride is highly soluble in water, and during snowmelt events, the sodium chloride ions will and are transported to surface water bodies during pronounced precipitation and snowmelt events (Daley et al., 2009; Novotny et al., 2007; Ramakrishna and Viraraghavan, 2005; Thunquist, 2004). While road salt is commonly the dominant source of chloride in urban watersheds (Novotny et al., 2009), other anthropogenic sources of chloride in declining order of significance include fertilizer, water treatment plant discharge, residential septic systems, permitted industries, atmospheric deposition, and dust suppressants (Overbo et al., 2021).

Elevated chloride concentrations in surface water systems have demonstrated to positively correlate with impervious surface cover in urban and suburban areas, around the United States (Kaushal et al., 2005). Dugan et al. (2017) reviewed data from over 38,603 lakes in the northeastern United States and found that 70% of lakes with greater than 1% impervious surface coverage within a 500 m buffer of the lake perimeter (approximately one-third of the lakes studied) exhibited increasing chloride levels from 1985 to 2010. A follow up study by Dugan et al. (2020) concluded that approximately 2000 lakes in the Midwest and northeast U.S. likely have chloride concentrations exceeding 50 mg/L.

Surface water located within urban and suburban watersheds are particularly prone to elevated chloride concentrations due to the combined effects of significant impervious area, heavy road salt applications, and runoff routing through engineered structures to surface water outfalls (Ledford et al., 2016). Urban lakes can be expected to experience long-term increases in chloride levels as long as road salt continues to be applied as a deicing agent. Elevated chloride in surface water can adversely impact surface water quality and aquatic ecosystems, such as alterations of fish assemblages in streams at chloride concentrations of 33 to 106 mg/L (Morgan et al., 2012), and reduced survival rates for amphibians in wetlands at chloride concentrations of 145 mg/L (Karraker et al, 2008). Adult and embryo fish death have been observed at chloride concentrations of 900 mg/L (Findlay and Kelly, 2011). The U.S. EPA has set acute ambient and chronic ambient water quality limits for chloride at 860 mg/L and 230 mg/L, respectively (EPA 1986), though negative effects of chloride on surface water have been observed at lower concentrations. Enrichment of sodium in surface water can also stimulate algal growth. Briggins and Walsh (1989) reported that sodium concentrations over 40 mg/L may trigger overgrowth of blue-green algae.

Lakes that experience high influxes of road salt may transition to monomixis or meromixis due to density stratification caused by increased salinity (Koretsky et al., 2011; Wyman and Koretsky 2018) These changes in lake geochemistry and seasonal mixing have significant impacts on redox stratification, resulting in shallower and more persistent anoxia and greater accumulation of reduced solutes, including dissolved ferrous iron, manganese, methane, phosphorous, and sulfide in the lake water column (Wyman and Koretsky 2018; Dupuis, 2017). Elevated chloride in surface water can lead to increases in water corrosivity, and in cases where corrosive chloride impacted waters reach pumping wells and water distribution pipes, galvanic corrosion of lead bearing materials can occur (Stets et al., 2018). Since road salt is a major contributor of chloride to surface water and chloride and corrosivity are often interlinked (Stets et al., 2018), surface water corrosivity should exhibit similar spatiotemporal trends as road salt applications.

Groundwater and surface water continuously interact across the landscape (Miller et al., 2016; Sophocleous, 2002; Winter et al., 1998; Zomlot et al., 2015). Subsurface zones of high permeability can function as drains to surface water features and enhance downward movement of surface water as recharge (Freeze and Witherspoon 1967). Confined aquifers are commonly thought to be isolated from surface water and shallow groundwater; however, aquitard windows in heterogeneous systems, such as glacial deposits, function as recharge zones to deeper aquifers (Martin and Frind, 1998). Groundwater extraction from wells located near surface water bodies can draw infiltration of surface water into an aquifer (Sophocleous, 2002). Induced infiltration of surface water can even occur in systems where aquitards serving as confining units under ambient conditions leak under the influence of pumping (Butler et al., 2007; Zhang et al., 2017).

Surface water capture by municipal wells has been shown to degrade well water quality in many environments. Capture of Palette River water by municipal wells supplying Lincoln, Nebraska was confirmed using a dye tracer, and caused degradation of well water by transport of atrazine from the river to the alluvial aquifer supplying the municipal wells (Verstaeten et al., 1999). Enteric viral contamination of a municipal well was caused by the induced infiltration of Mississippi River water through an alluvial sand and gravel aquifer, and stable isotopes were used to confirm that the evaporative signature in the well water could only be explained as river water capture (Borchardt et al., 2003). Chloride transport to municipal wells through an aquitard was observed in a study conducted glacial materials in Waterloo Ontario in 2006 (Bester et al., 2005). Non-uniform and discontinuous stratigraphic units created aquitard windows that allowed downward movement of road salt to the municipal pumping wells.

This study investigates the impacts of road salt application on water quality in the Spring Valley sub-watershed to the Kalamazoo River. Systematic water quality monitoring throughout a two-year period revealed clear trends in road salt accumulation and transport within the sub-watershed. The capture of chloride enriched surface water by the Kalamazoo, MI Station 14 municipal wellfield leads to elevated corrosivity in the municipal water supply system. Unique to this study is the quantification of surface water capture by the municipal wells using three independent methods: chloride mass balance, stable isotope mixing model, and water balance. The close agreement of the three estimates lends a robustness to and increases confidence in the results, and this approach can be applied to any urban watershed with road salt applications. The organization of the rest of the paper begins with the methodology in Section 2, results, and discussion in Sections 3 and 4, and study findings in Section 5.

METHODS

Site Description and Sub-Watershed Delineation

The Spring Valley sub-watershed is located within Kalamazoo, Michigan and covers an area of approximately 6.5 km^2 (Figure 1). The sub-watershed trends northeast to southwest and accumulated surface and subsurface flows discharge to the Kalamazoo River. The surface water flow system consists of a small stream that interconnects three lakes (Figure 1). Groundwater flow is parallel with the orientation of the sub-watershed (COK & PMI, 2002). Kalamazoo has a temperate climate, with daily temperatures typically remaining near or below freezing from December to March, and exceeding 20˚C from May through September. The area receives 91 cm of rain and 173 cm of snow annually. Most of the snowfall and road salt application occur from December through February, with intermittent rain during this period that can generate rain-on-snow runoff events. Much of the snowfall in this area can be attributed to lake affect, where the cold air masses absorb evaporative water as they move across Lake Michigan and then release as precipitation across southwest Michigan.

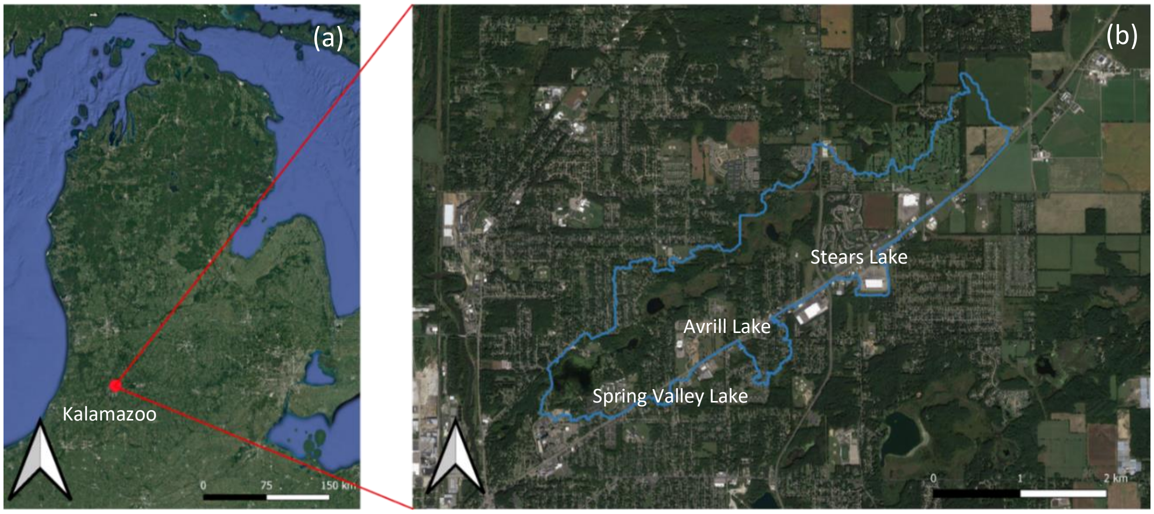

Figure 1. Study Site

Surface features in the Kalamazoo area are glacial in nature and consist of unconsolidated outwash plains, morainal highlands, and glaciated channels that overlie the Coldwater Shale (Deutsch et al. 1960). High permeability glacial deposits at depth serve as the regional aquifer system, which is principally recharged by atmosphere precipitation. Within the Spring Valley sub-watershed, a surficial sandy gravel unconfined aquifer up to 2.5 m below ground surface (bgs) overlies a sandy clay to clay aquitard located 2.5-23 m bgs. Below this aquitard is a sandy gravel aquifer system ranging from 23 to 35 m bgs. The clay aquitard is discontinuous, and the surficial sandy gravel aquifer and the deeper sandy gravel aquifer are directly connected in areas where the aquitard is not present. The Coldwater Shale is located at the base of the deeper aquifer system and is the primary bedrock unit for the Kalamazoo area (COK & PMI, 2002).

The deeper sand and gravel aquifer transmits water to five pumping wells of the Station 14 wellfield, located on the southeastern shoreline of Spring Valley Lake (Figure 2). Spring Valley Lake is a 3320 m^2 manmade impoundment with limited storage capacity. Each of the pumping wells have 0.3 m inner diameter casing and are designed for maximum pumping rates of 2.21×10^{-2} m^3/s (350 gpm). The production wells have 60-slot screens, surrounded by silica gravel packs, and are located 23 m to 31 m bgs with screen lengths ranging from 8 m to 11 m (COK & PMI, 2002).

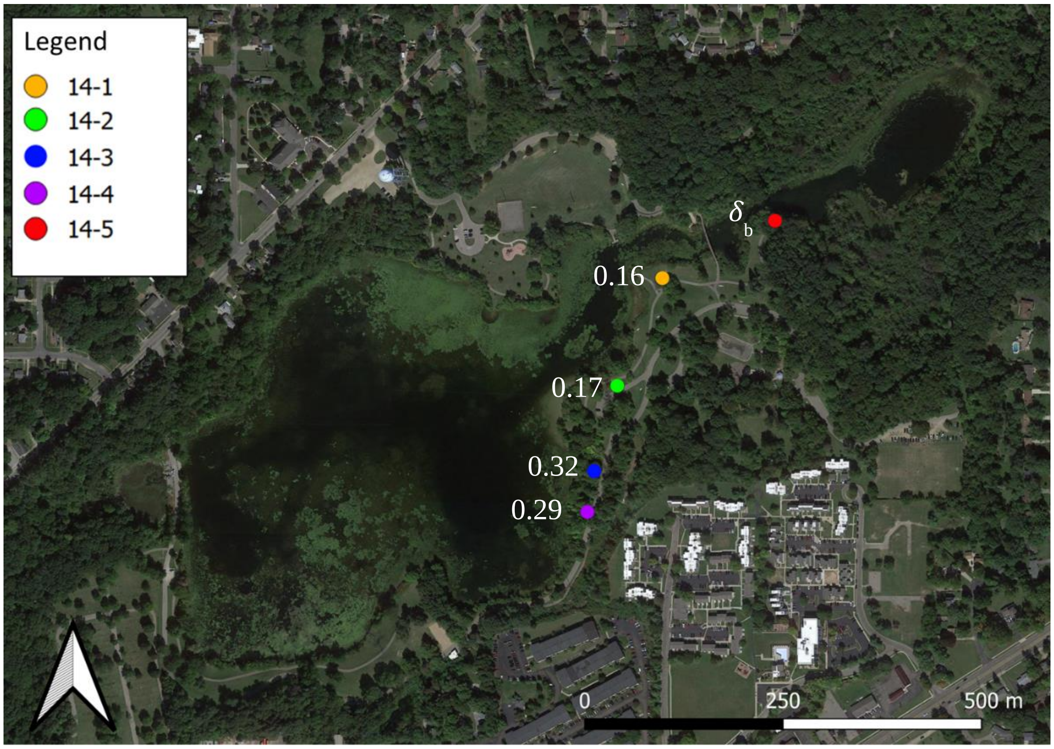

Figure 2. Spring Valley Lake pumping wells and isotope capture

The boundary of the Spring Valley urban sub-watershed was delineated using QGIS by applying an upslope area algorithm to the USGS NED one-meter elevation data at site 5 (Figure 1b). The sub-watershed boundary was manually expanded to the northeast of site 2 to account for stormwater routing. The raster layers generated from the upslope area algorithm were converted to vector layers, merged, and dissolved to create the urban watershed polygon. Total area of the watershed was computed using the field calculator area function in QGIS.

Seven outfalls contribute runoff to the Spring Valley surface water system (Figure 3). Two of the outfalls are located upgradient of Spring Valley Lake and discharge to the stream and five outfalls discharge to the lake. Five outfalls and associated drainage areas (1-5) (outlined in red on Figure 3) are owned and delineated by the City of Kalamazoo. Drainage area 6 is privately owned though it contributes to the adjacent public outfall. Drainage area 7 and the associated private outfall directs runoff from an adjacent apartment complex adjacent to the lake. Drainage area 8 and the associated private outfall are on the southwest portion of Spring Valley Lake and drain a portion of a nearby medical center. The municipal outfall and drainage area 5, to the east of the hospital outfall and drainage area 8, capture a portion of runoff from the medical center. Areas for each of the delineated 8 drainage regions are provided in Table 1. All public drainage areas were provided by the City of Kalamazoo, and private drainage areas were estimated using the field calculator area function in QGIS for each respective polygon.

Table 1. Drainage areas and associated data

Drainage Area	Ownership	Delineation	Area (m^2)	Discharge location
1	Public	City	91459	Lake
2	Public	City	487242	Stream
3	Public	City	201250	Stream
4	Public	City	145768	Lake
5	Public	City	4047	Lake
6	Private	Estimated	44516	Stream
7	Private	Estimated	56656	Lake
8	Private	Estimated	157828	Lake

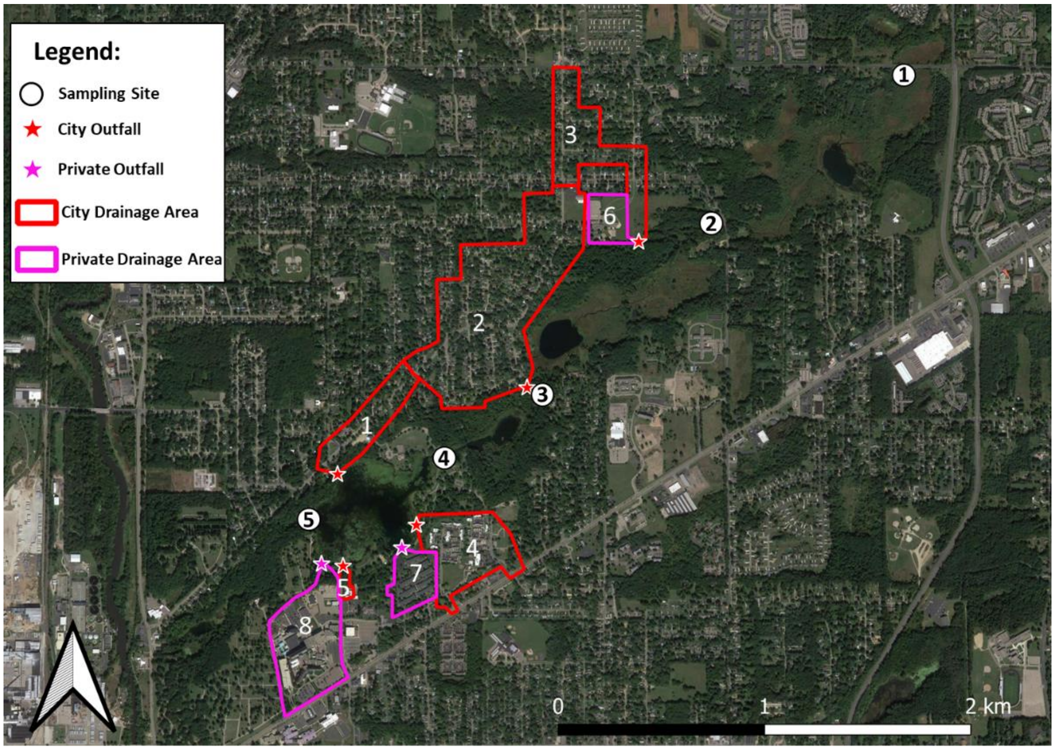

Figure 3. Sampling location and drainage areas

Surface Water Monitoring

A total of five sampling sites were established to monitor trends in major ions and nutrients within the sub-watershed (Figure 3). These locations are based on publicly accessible locations of suitable mixing in the surface water flow system. Site 1 is located at the headwaters of the surface water flow system where a culvert directs concentrated seepage from a groundwater dominated wetland directly to the north. Sites 2 and 3 are located along culverts directing surface flows under the roads to the southeast of Avrill and Stears lakes, respectively, which are located on private property and inaccessible during the study. Sites 4 and 5 are located at the inflow and outflow of Spring Valley Lake, respectively. These sites were sampled beginning on 3/20/2020, at a frequency of approximately once per month. Surface water outfalls were sampled during snowmelt events on 1/22, 2/23, and 4/10/2021, to quantify sodium chloride concentrations during peak snowmelt. The complete list of sampled parameters and associated analytical methods are listed in Table 2. Chloride, sodium, sulfate, alkalinity, phosphorus, and chlorophyll-a are of particular importance as these chemicals are representative of road salt, water corrosivity, and trophic state of surface water in the watershed. Major ions and nutrients were analyzed throughout the study by Trace Analytical Laboratory located in Muskegon, MI. Spring Valley Lake was sampled for chlorophyll in August 2021 at sites 4 and 5 and three locations between the inflow and outfall to obtain an average lake chlorophyll-a concentration. The chlorophyll-a samples were analyzed by the Michigan Department of Environment, Great Lakes, and Energy (EGLE) state laboratory in summer 2021.

Table 2. Parameters analyzed

Analyte	Method	Reference
Calcium	Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)	EPA 200.7 Rev. 4.4
Iron		
Magnesium		
Potassium		
Sodium		
Fluoride	Ion Chromatography	EPA 300.0 Rev. 2.1
Chloride		
Nitrate		
Nitrite		
Sulfate		
Total Kjeldahl Nitrogen	Semi-Automated Colorimetry	EPA 351.2
Total Alkalinity as CaCO3	Titration	SM 2320 B-11
Total Dissolved Solids	Gravimetry	SM 2540 C-11
Phosphorus	Spectrophotmetry	SM 4500-P E-11
Orthophosphate	Hach Pocket Colorimeter II	
Chlorophyll A	Fluorometry	SM 10200H
δ^{18} Oxygen	Off Axis Integrated Cavity Output Spectroscopy (Off Axis ICOS)	Los Gatos Triple Isotope Analyzer
δ^{2} Hydrogen		

A total of 10 Onset conductivity probes were deployed at the 5 sampling sites and at 5 surface stormwater outfalls located along the perimeter of Spring Valley Lake. The conductivity probes recorded conductivity and temperature from 1/14 – 5/5/2021 at 15-minute intervals to determine the duration and the timing of road salt inputs during melt events using electrical conductivity as a proxy for sodium and chloride entering the lake through the surface water outfalls

(Granto and Smith 1999; Morgan et al., 2012). Specific conductance was calculated from measurements of electrical conductivity and water temperature.

Surface Water Capture

A lake water balance, stable isotope two component mixing model, and chloride mass balance were all used to estimate the component of lake water captured by the Station 14 municipal pumping wells. The lake water balance estimates surface water capture from differences in surface water discharge at the inflow and outflow of Spring Valley Lake during the winter when evapotranspiration is negligible. Estimation of lake water capture by stable isotopes of water relies on evaporative fractionation of oxygen-18 in the lake in a two-component mixing problem that considers groundwater and lake water as isotopic endmembers. The chloride mass balance method was conducted over an annual water year and utilizes estimates of chloride mass flux computed at the inflow and outflow of the lake, chloride storage within the lake, and chloride concentrations in Station 14 water.

Lake Water Balance

MHE Products PushPoint piezometers were used to measure head differences between surface water and groundwater to determine the interaction and hydraulic function of Spring Valley Lake relative to the surrounding groundwater flow system. The PushPoint piezometer is a simple, machined tool consisting of a stainless-steel tubular body of 0.63 cm (0.25 in.) diameter with a 5 cm (2 in.) screened zone at one end and a sampling port at the other. A guard-rod provides support to the PushPoint during sediment insertion and prevents plugging and deformation of the screen; the guard rod is then removed when the desired depth is reached. Head measurements made with using the PushPoint device by pulling water with a polyethylene syringe through polyethylene tubing attached to the end (Cascarano et al., 2020).

Gradient measurements were measured in Spring Valley Lake during summer 2020 and 2021. The piezometer was driven into the lake sediment with screen depths ranging from 0.9 to 1.8 m. At some locations, piezometer insertion was rejected by layers of hard clay and a measurement was not taken. Vertical gradients are computed from the equation: $i_v = \frac{\Delta h}{\Delta z}$, where i_v is vertical hydraulic gradient [dimensionless], Δh is the difference in head in the lake sediments and lake water [L], and Δd is the depth of the mini piezometer screen in the sediment [L] (Freeze and Cherry, 1979). Positive vertical gradients indicate groundwater discharge into the lake, and negative vertical gradients indicate downward movement of surface water from the lake and to the aquifer as recharge.

Inflow and outflow to Spring Valley Lake was determined using an OTT MF pro electromagnetic current meter and water velocity sensor (accuracy ± 2%) attached to a Hatch topsetting wading rod. Stream gauging occurred during on 2/22, 5/5, and 10/7/2021, at the inflow (located in-between sites 3 and 4) and outflow (site 5) of Spring Valley Lake. The midpoint method developed by the U.S. Geological Survey was used to compute total flow or stream discharge as the sum of a series of regularly spaced rectangular subsections (Turnipseed and Sauer, 2010). Depth, velocity at d_{60}, and distance from the left bank (facing upgradient) were recorded for each subsection. Flow for each subsection is then computed as:

$$q_i = v\left(\frac{b}{2}\right)d \tag{1}$$

where q_i is discharge for the i^{th} rectangular subsection [L^3/T], v is water velocity [L/T], b is subsection width [L], and d is water depth [L]. Total flow Q [L^3/T] is then computed as the sum of subsection flows: $\sum_{i=1}^{n} q_i$.

Surface water capture for the study system using a water balance approach is best estimated as the difference between computed inflow and outflow during the winter months when the lake is completely frozen, evapotranspiration is negligible, and the difference in streamflow can be attributed to capture by the pumping wells. This approach greatly reduces uncertainty in the surface water capture estimate given the high degree of uncertainty in lake ET estimates (Winter, 1981). Pumping rates of the municipal wells at the time of stream gauging were provided by City of Kalamazoo. Surface water capture by the pumping wells is determined from:

$$SWC_{WB} = \frac{Q_i - Q_o}{Q_w} \tag{2}$$

where SWC_{WB} is the fractional component of surface water in the pumped well water computed from a water balance approach, Q_i streamflow inflow [L^3/T], Q_o stream outflow [L^3/T], and Q_w the cumulate flow rate of the five pumping wells [L^3/T].

Isotope Mixing Model

Contributions of surface water infiltration from Spring Valley Lake can be detected and measured by analyzing stable oxygen (^{18}O, ^{16}O) and hydrogen (^{1}H, ^{2}H) isotope ratios. Isotopic ratios are measured with respect to an international standard VSMOW (Vienna Standard Mean Oceanic Water) and are reported as "delta per mil" defined by the equation:

$$\delta‰ = \left(\frac{R_{sample}}{R_{standard}} - 1\right) 1000 \tag{3}$$

where R represents the ratio of heavy to light isotopes, i.e. $^{18}O/^{16}O$ or $^{2}H/H$.

Water samples were analyzed using a Los Gatos Triple Liquid Water Analyzer in the Stable Isotope Laboratory at Western Michigan University. The isotope analyzer employs off-axis integrated spectroscopy to measure the isotopic composition of the sample according to infrared absorption. One microliter of sample is converted into gas within the isotope analyzer and injected into a small cavity via a gas inlet. The cavity contains two high reflective (100% and 99.99%) mirrors. Photons are then sent into the cavity via a diode laser and bounce back and forth between the mirrors as some of the photons are absorbed by H2O gas. As photons leave the cavity through the 99.99% reflective mirror, they are directed to a detector, via a focusing lenses, where absorption and in turn isotopic composition is measured (Berman et al., 2013).Analytical precision of measurement is 0.2 ‰ of oxygen and 1.5 ‰ for hydrogen based on the internal control sample that is run with each analysis batch.

Man-made impoundments represent surface water reservoirs with enriched ^{18}O and ^{2}H due to evaporative fractionation of oxygen and hydrogen isotopes. An enriched ^{18}O and ^{2}H signal in the production well water at Station 14 indicates lake water infiltration. The fraction of well water sourced from lake water infiltration and the fraction sourced from groundwater can be determined using $\delta^{18}O$ values in the lake water and groundwater in a two-component mixing equation (4) derived from a mass balance equation (5) (Clark 2015):

$$SWC_{IMM} = f_a = \frac{\delta_w - \delta_b}{\delta_a - \delta_b} \tag{4}$$

$$\delta_w = \delta_a f_a + \delta_b (1 - \delta_a) \tag{5}$$

where δ_w is the $\delta\ ^{18}O$ value of the produced well water, δ_a and δ_b represent the two $\delta\ ^{18}O$ endmembers of lake water and groundwater respectively, and f_a represent the fractional component of lake water found in production well water. Values of f_a serve as estimates of surface water capture using an isotope mixing model (SWC_{IMM}) that are independent of physical flow measurements.

All precipitation isotope ratios define a straight line known as the global meteoric water (GMWL) (Craig, 1961) given by the equation: $\delta^2H = 8.13\delta^{18}O + 10.8$. The slope of 8 is an indicator that precipitation is an equilibrium process where at equilibrium the $\delta^2H/\delta\ ^{18}O$ is the ratio of vapor pressures of water containing the respective isotopes (Shelby and Krishnamurthy, 2019). The offset of 10 is the result of kinetic fractionation at source oceanic regions, where the diffusivity coefficient between ^2H and ^{18}O are different (Shelby and Krishnamurthy 2019).

The GMWL is a locus of all freshwater systems, so it is essential to define a Local Meteoric Water Line (LMWL) to better understand regional hydrology. The LMWL for Kalamazoo, MI is very similar to the GMWL, and has been obtained by years of analysis (Machavaram and Krishnamurthy, 1995; Shelby and Krishnamurthy, 2019). LMLW is given by the equation: $\delta^2H = 7.67\delta^{18}O + 12.03$. The groundwater endmember in this study should plot on the LMWL since precipitation is the primary source of recharge in the Kalamazoo area. The isotopic signature of ground water reflects the average isotopic ratio of precipitation, as seasonal changes is the isotopic composition of precipitation are averaged by groundwater mixing.

Chloride Mass Balance

Surface water capture of lake water in the pumping wells can be estimated by using an annual chloride mass balance:

$$M_w = M_i - M_o \pm M_l \tag{6}$$

where M_i is annual chloride mass entering the lake at the inflow (Site 4), M_o is annual chloride mass leaving the lake at the outflow (Site 5), M_l is chloride mass storage in the lake, and M_w is the mass of chloride captured by the pumping wells. Each of these mass components are computed for a water year defined from 10/1/2020 to 9/30/2021. Chloride mass at the inflows and outflows are the product of streamflow and chloride concentration. These measurements have different resolutions, with the chloride sampled approximately monthly and three sets of streamflows from surveys performed in February, May, and October of 2021. Each of these quantities are linearly interpolated to daily values and then summed to generate annual values. The lake storage term was computed as the product of lake volume and the difference in chloride mass in the lake at the beginning and end of the water year. Surface water capture is then estimated using:

$$SWC_{MB} = \frac{M_w}{[Cl] * Q_w} \tag{7}$$

where SWC_{MB} is fractional component of surface water capture from the chloride mass balance, M_w is the mass of chloride captured by the pumping wells, [Cl] is the average annual chloride concentration, and Q_w is the Station 14 average annual pumping rate for the 2020-2021 water year. Water chemistry at site 4 is assumed to be representative of the water chemistry captured by the pumping wells due to the proximity of site 4 to the pumping wells.

RESULTS

Hydrological Characterization

Weather trends for the 2020 water year are given in Figure 4. Average daily temperature ranged from -13°C to 28°C, with precipitation totals of 113.03 cm snowfall and 86 cm rain. The first significant snowfall event occurred on 11/24/2020 (3.05 cm) and was followed by 17.8 cm of snowfall from 12/24/2020 to 1/5/2021. Mid-January through late February (1/17-2/23/2021) marked a period of intense snowfall (89.4 cm), with average daily temperatures remaining near or below freezing and maximum daily temperature not exceeding freezing from 2/5-2/21. Temperatures suddenly increased after 2/21, with average daily temperatures remaining above freezing after 3/5. The approximate month period (2/21- 3/23) following the January-February snowfall period was exceptionally dry with only 0.7 cm of rain and 1.8 cm of snow. The majority of rainfall occurred from early summer to early fall (5/23-9/25) with 51.1 cm of total precipitation. The largest rain events occurred on 6/24-6/26 and on 7/23 with totals of 14.01 cm and 6.7 cm, respectively.

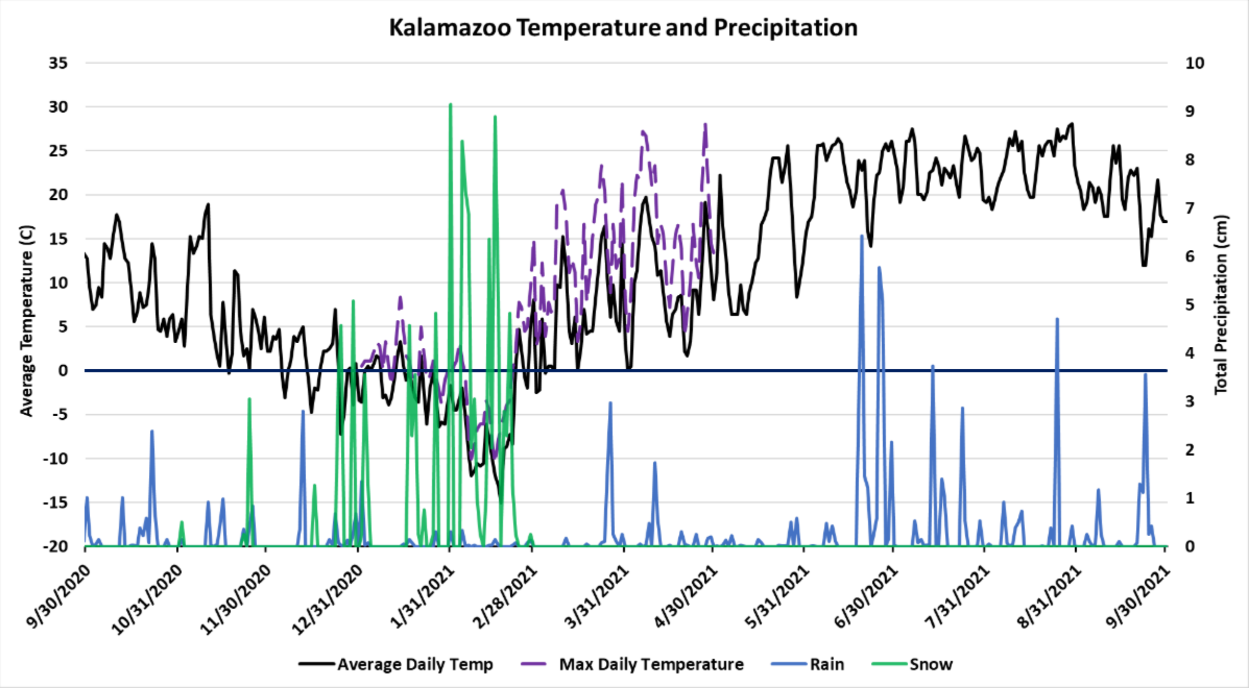

Figure 4. Weather data for 2020 water year

Spring Valley Lake inflows and outflows decreased from May to February and increased from February to October, with May and October representing the lowest and highest recorded flows, respectively. Inflows and outflows for February, May, and October were 0.063, 0.050, and

0.85 m^3/s and 0.050, 0.034, and 0.061 m^3/s, respectively (Table 3). Minimized and maximized flow values were obtained by applying the error associated with the instrument to the measured flow values. The pumping rates during February, May, and October are 3.9×10^{-2}, 4.2×10^{-2}, and 4×10^{-2} m^3/s, respectively.

Table 3. Streamflow, pumping rate, and residence time data

	February			**May**			**October**		
	Min	**Central Tendency**	**Max**	**Min**	**Central Tendency**	**Max**	**Min**	**Central Tendency**	**Max**
Q_{inflow} [m^3/s]	0.061	0.063	0.064	0.049	0.050	0.051	0.083	0.085	0.086
$Q_{outflow}$ [m^3/s]	0.049	0.050	0.051	0.033	0.034	0.034	0.059	0.061	0.062
Q_{wells} [m^3/s]		0.039			0.042			0.039	
r_t [d]	59	60	61	87	89	90		49	

Vertical gradients in Spring Valley Lake for the summer of 2020 were mostly negative, indicating downward flow (Figure 5a). One positive upward gradient (0.17) was observed along the northeast portion of the lake, near well 14-5, and one neutral gradient was observed along the northern shoreline, downgradient of site 4. Negative gradients ranged from -0.03 to -0.28, with the largest magnitude negative gradients occurring near the shoreline between wells 14-2 and 14-3 and in the west portion of the lake. Vertical gradients in the summer of 2021 were again largely negative though more positive gradients were measured in the northeastern portion of the lake near well 14-5 (0.07 and 0.13) (Figure 5b). The neutral gradient observed in summer 2020 was slightly positive during summer 2021 (0.01). Negative gradients ranged from -0.01 to -0.4, with the largest magnitude negative gradients occurring between wells 14-2 and 14-3, about 200 m southwest of well 14-4.

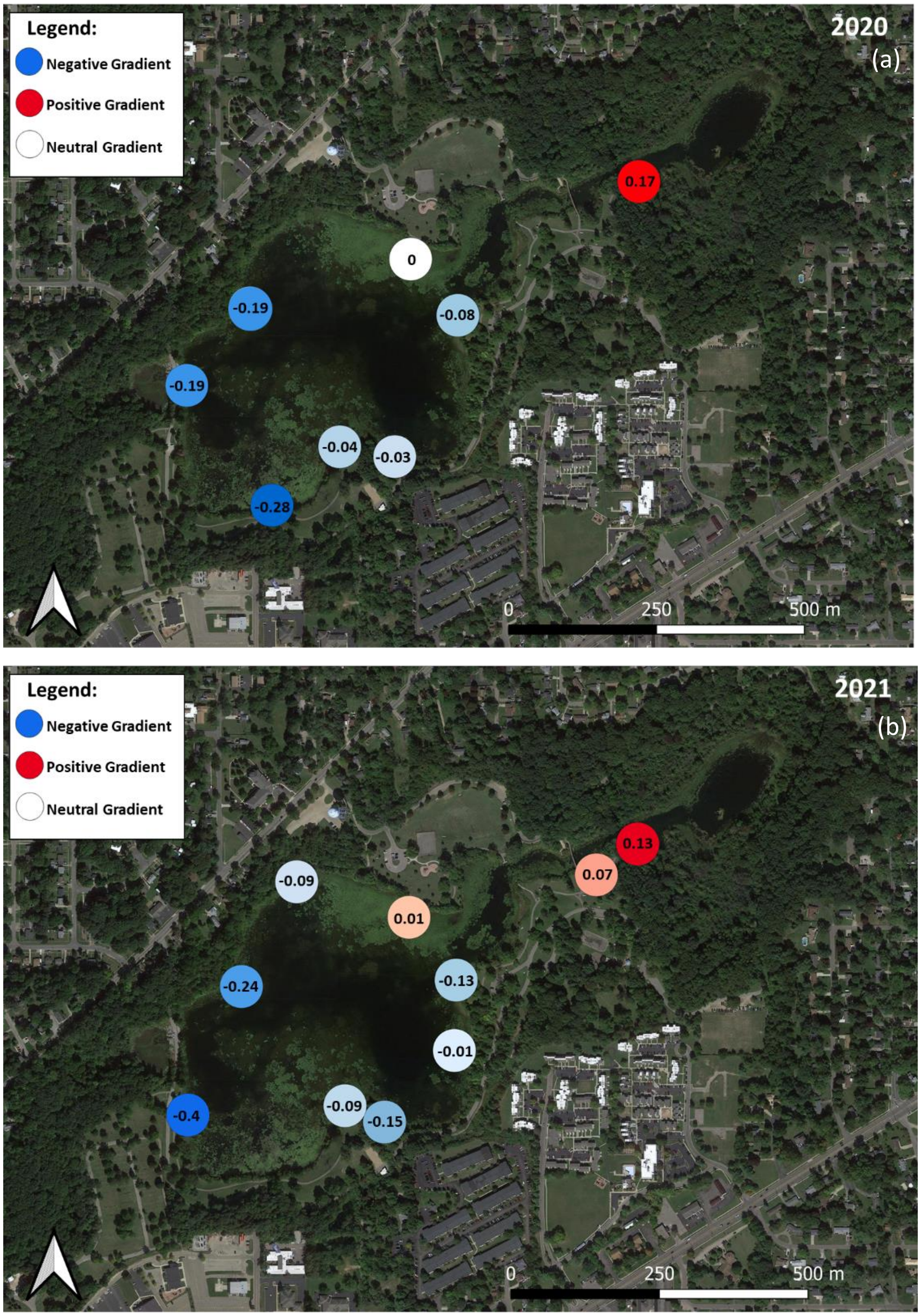

Figure 5. Vertical gradients in Spring Valley Lake

Lake bathymetry was determined by performing a multi-day survey using a Deeper sonar depth finder attached to a kayak. The survey identified a maximum lake depth of 7.4 m occurring approximately 100 m to the west of well 14-3, though the majority of lake depth is between 1 and 2 m. There is a distinct paleochannel with channel depth mostly ranging between 2 and 3 m. Lake stage varies approximately about 0.3 m annually. Residence time in the lake, computed by normalizing total lake volume by outflow rate, and ranged from 49 days to 89 days, with an average residence time of 66 days. Residence time increased from February to May and decreased from May to October.

Water Quality

The surface water flow system is of a magnesium bicarbonate type, with major cation and anion concentrations generally increasing from site 1 to 5 (Figure 6). Exceptions to this general trend occur for bicarbonate, calcium, magnesium, and sulfate. Magnesium and sulfate concentrations tend to remain similar at all sampling site, while bicarbonate and calcium concentrations decrease from site 1 to site 5. During 2020, the maximum sodium and chloride concentrations in Spring Valley Lake were concentrations of 53 mg/L and 110 mg/L, respectively, on 3/26 and gradually decreased in the summer. During 2021, sodium and chloride concentrations began trending upwards after 1/14, with sodium concentrations reaching a high of 54 mg/L on 3/11 and chloride concentrations reaching a high of 110 mg/L on 6/11. Sodium and chloride remained significantly elevated from 3/11 to 6/11 then returned to similar baseline concentrations observed in summer 2020.

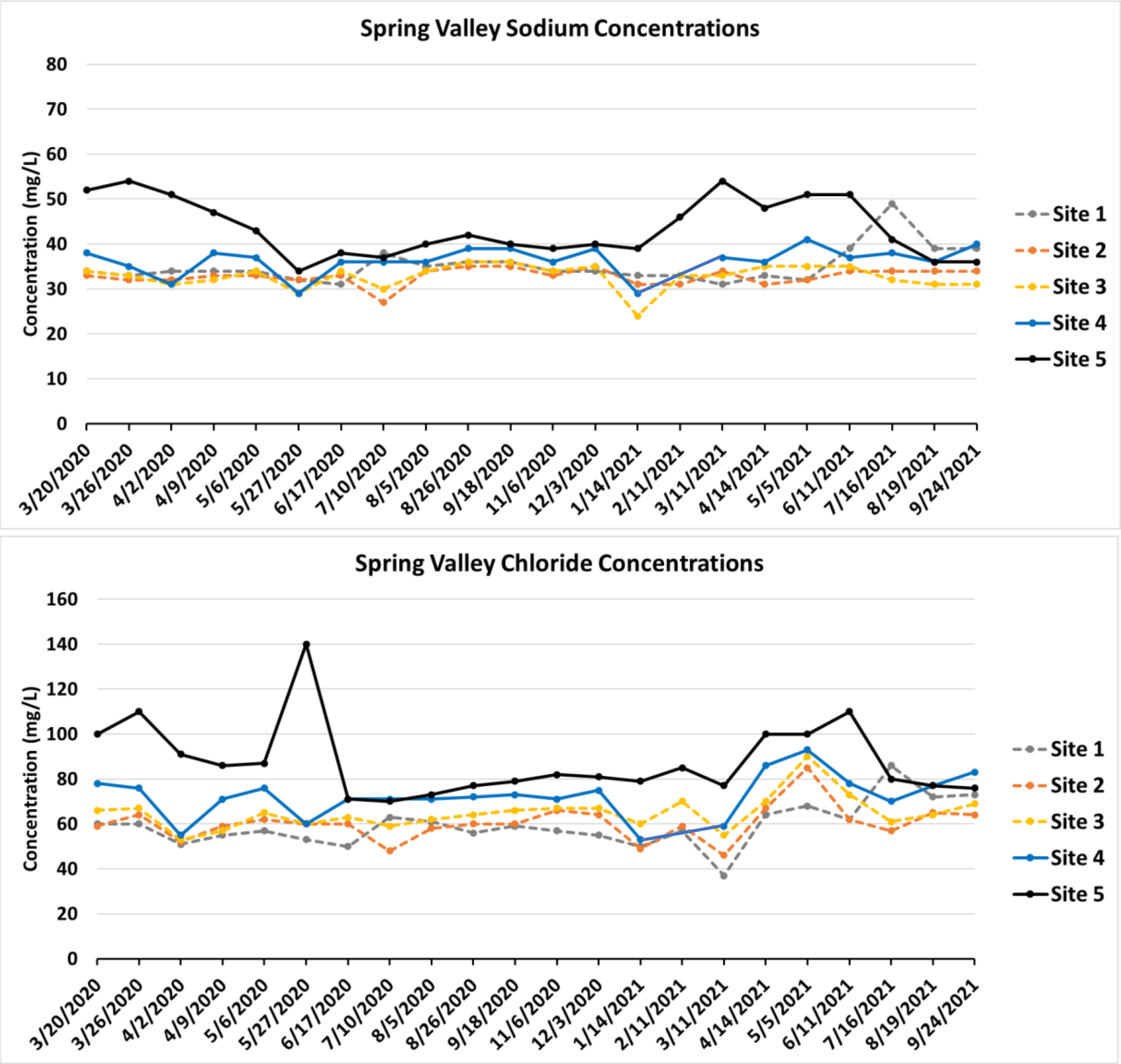

Figure 6. Sodium and chloride concentrations in watershed

Specific conductance (SC) trends for the outfalls discharging to Spring Valley Lake are given in Figure 7. A total of 5 distinct SC peaks are observed from 1/14 to 5/4/2021. Peak 1 is from 1/18 to 1/24 on south outfalls 1-3. Peak 2 was observed for south outfalls 1- 4 from 1/26 to 2/7. Peak 3 occurred from 2/12 to 2/18 at south outfalls 1, 2, and 4. The north side outfall logger shows continuously elevated SC from the beginning of peak 2 to the end of peak 3. From 2/19 to 3/1, peak 4 occurs at the northside outfall and southside outfalls 1-4 and was the only SC peak that was observed at all sites. Peak 5 was recorded from 3/10 to 3/22 and was only observed at south outfalls 3 and 4.

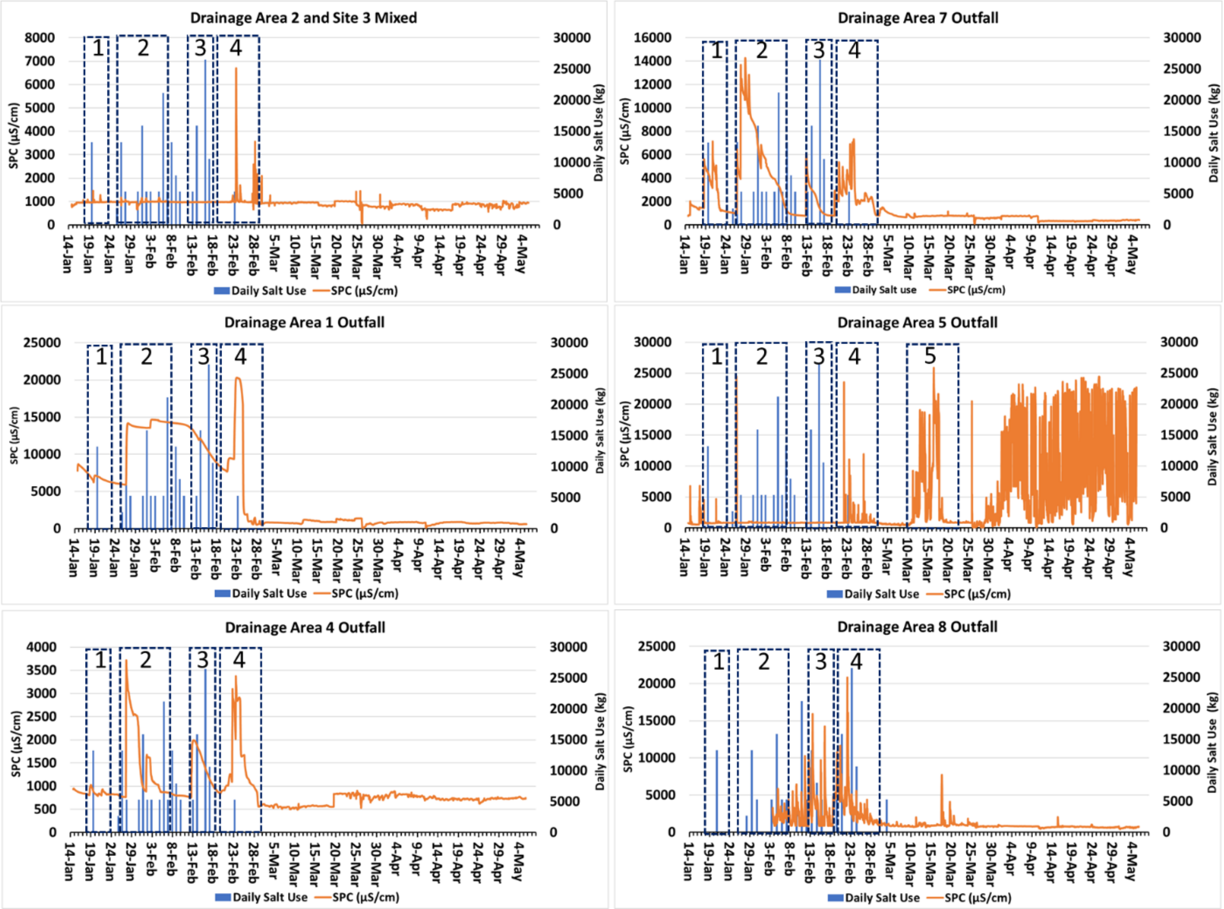

Figure 7. Specific conductance trends at Spring Valley Lake outfalls

Chloride-sulfate mass ratio (CSMR) is a simple mass ratio of chloride to sulfate:

$$CSMR = \frac{[Cl]}{[SO_4]} \tag{8}$$

and is a measure of corrosion potential for galvanic corrosion of lead soldered joints in copper and brass pipes. Values above 0.5 indicate moderate corrosion potential for systems with alkalinity greater than 50 mg/L and high corrosion potential in systems with alkalinity less the 50 mg/L (Belitz et al., 2016). CSMR values ranged from 1.65 to 5 in Spring Valley Lake for the study period, with the highest concentrations observed at site 5 during the spring (5) and fall (4.5) during 2020 and spring to early fall of 2021 (3.8-4.75) (Figure 8a).

The Larson Index indicates corrosivity of water to iron and steel, and is defined as the sum of moles/L of chloride and sulfate normalized by moles/L of bicarbonate (Belitz et al., 2016):

$$LI = \frac{[Cl]+[SO_4^2]}{[HCO_3]+[CO_3^2]}. \tag{9}$$

Larson Index values can be grouped into four ranges: 0.2 < LI ≤ 0.4, 0.4 < LI ≤ 0.5, 0.5 < LI ≤ 0.1, and LI > 1 represent light, low, moderate, and high metal corrosion tendencies, respectively. Trends in the Larson Index are given in Figure 8 and range from 0.44 to 1.32 with the greatest values during the summer months. Maximum LI values of 0.97 and 1.3 occur in summer 2020 and 2021, respectively (Figure 8b). Sulfate concentrations remained stable in the lake. Significant bicarbonate decreases occurred during both summers with concentrations declining to 120 mg/L and 140 mg/L during summer 2020 and 2021, respectively.

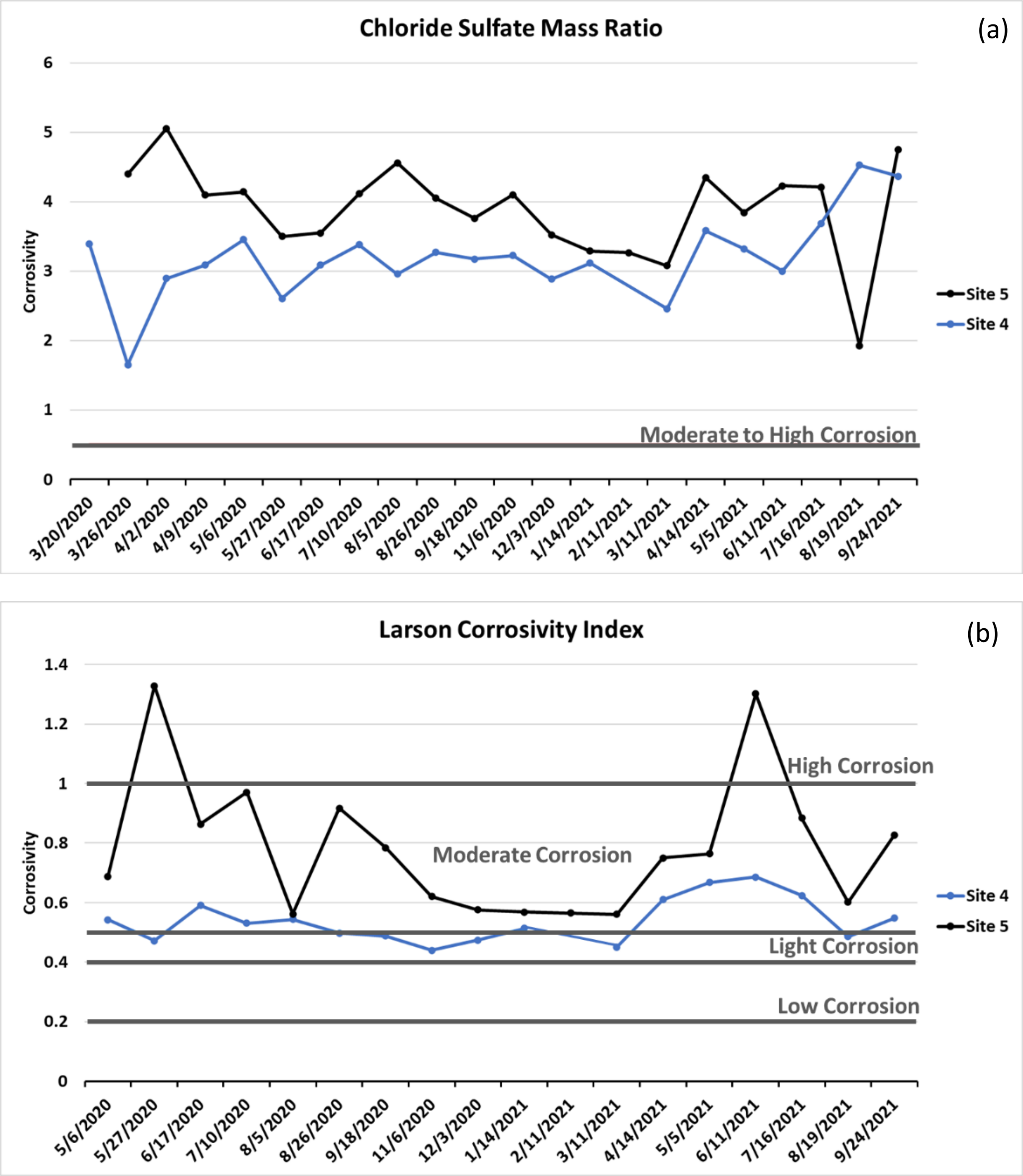

Figure 8. Chloride Sulfate Mass Ratio and Larson Index values in Spring Valley Lake

Trophic State Index (TSI) (Carlson 1977):

$$TSI(P) = 10\left(6 - \frac{ln\left(\frac{48}{[\mathrm{P}]}\right)}{ln(2)}\right); \qquad TSI\ (Chl) = \left(6 - \frac{2.04 - 0.68 \ln\ [\mathrm{Chl}]}{\ln\ (2)}\right) \tag{10}$$

where either total phosphorus [P] [mg/m^3] and chlorophyll [Chl] [mg/m^3] can be used to determine TSI (Figure 10). TSI obtained by total phosphorous generally ranged from 40 to 60 with occasional values exceeding 60. A TSI value of 44 was computed from the average chlorophyll-a concentration obtained from surface water sampling on 8/30/2021.

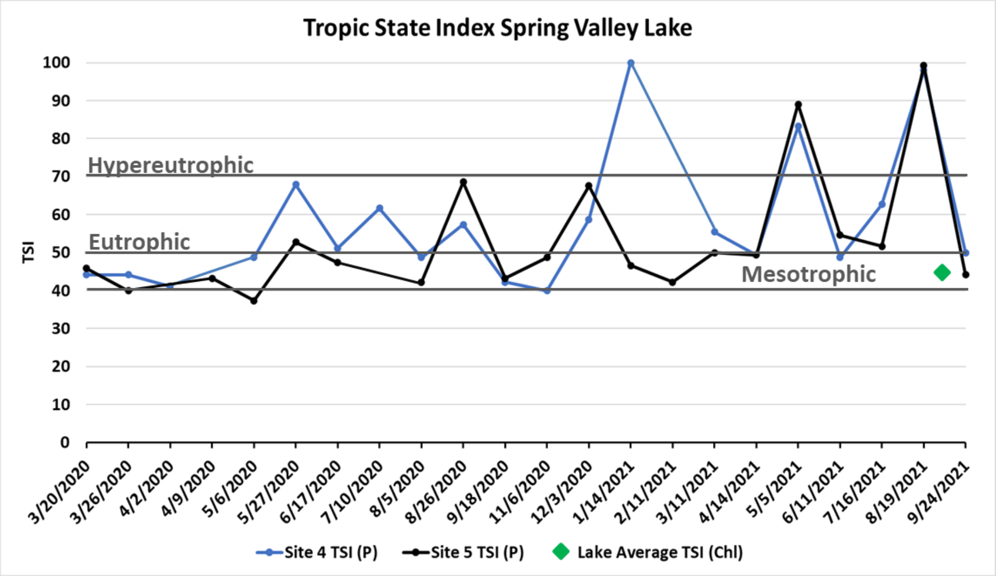

Figure 9. Trophic State Index values in Spring Valley Lake

Surface Water Capture

Values of Q_i, Q_o, , and Q_w are given in Table 3, and describe flow into the lake by the stream inflow, flow out of the lake at the exit of the impoundment, and average monthly flow of the 5 wells, respectively. Values obtained in February 2021, when the entire lake surface was frozen, provide the best estimate of surface water capture as evapotranspiration was negligible. Values of inflow (Q_i) and outflow (Q_o) decreased from May to February and increased from February to October. In February, differences in inflow and outflow (Q_i-Q_o) were lowest and increased to highest values during October. Values of average monthly pumping rates (Q_w) were similar for February, May, and October of 2021. Minimum and maximum bounds of surface water capture were established by applying sensor error to streamflows at the inflow and outflow. Error derived reductions at the inflow and increases at the outflow were used to produce the lower bound, while increases at the outflow and decreases at the inflow were used to create the upper bound.

Isotopic composition of surface water collected from site 5 shows $\delta^{18}O$ enrichment during summer 2020 and 2021. Well 14-5 represents the groundwater end member which is consistent with the positive vertical gradients measured near well 14-5. The isotope data plots below the LMWL for summer 2020 and on or above the LMWL for summer 2021. Wells 14-1, 14-2, 14-3, and 14-4 represent mixed well water and always plot between the surface water and groundwater end members. Summer 2020 mixed well water show strong $\delta^{18}O$ enrichment relative to well 14-5 groundwater endmember and all data plot below the LMWL (Figure 10), while summer 2021 mixed well water is less $\delta^{18}O$ enriched than summer 2020 data. Average $\delta^{18}O$ surface water (δ_a), groundwater (δ_b), and well water (δ_w) values for the study period were -6.76 ‰, -9.82 ‰, and -9.075 ‰, respectively

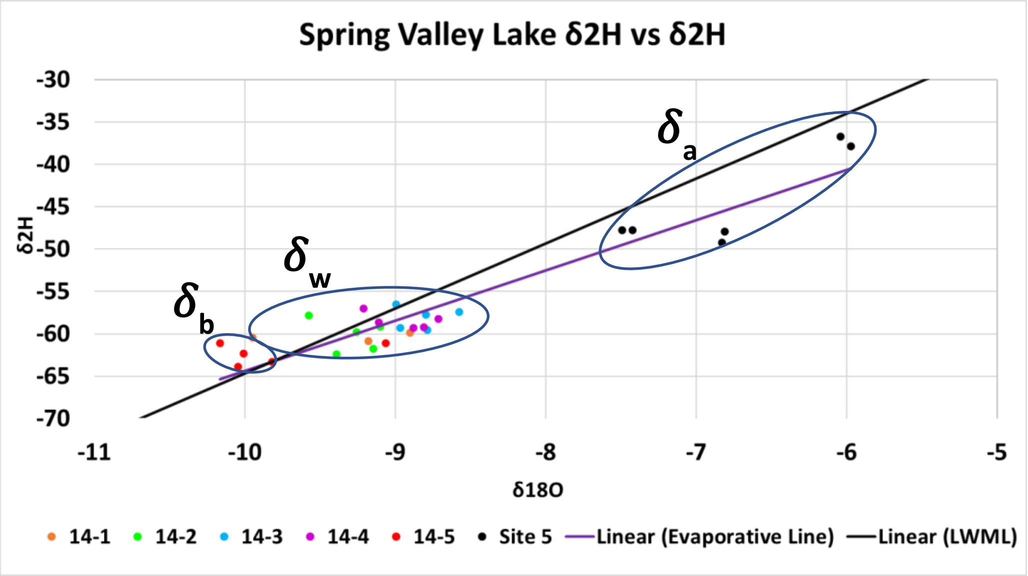

Figure 10. Spring Valley Lake stable isotope data

Annual chloride mass balance totals at the inflow (M_i) and outflow (M_o) are 153,332 kg and 130,755 kg, respectively. Annual mass storage of chloride in the lake (M_l) was calculated as 1032.9 kg. Average annual pumping rate of the five wells (M_w) was 4.07×10^{-2} m^3/s, and average chloride concentration as site 4 [Cl] was 72.39 mg/L. Concentrations of site 4 were used due to the close proximity of site 4 to the pumping wells. Minimum and maximum bounds were established by applying sensor error to inflow and outflow values used in the mass flux calculations as listed in Table 3.

Table 4. Surface water capture data from all methods

SW Capture	Cl Mass Balance	Isotope Mixing Model	Lake Water Balance
Minimum	0.19	0.16	0.26
Central Tendency	0.26	0.24	0.32
Maximum	0.31	0.32	0.38

Components of surface water capture by all methods are listed in Table 4. Capture by water balance method ranged from 0.26 to 0.38, with central tendencies of 0.32 and 0.40 for February and May, respectively. The February estimate 0.26 to 0.38 with a central tendency of 0.32 is the most reliable estimate as evapotranspiration does not occur. Higher estimates for May likely reflect the influence of evapotranspiration as the full water balance cannot be resolved. Derived surface water capture estimations from isotopic data were averaged for summer 2020 and 2021 and range from 0.16 to 0.32 with central tendency of 0.24. Surface water capture from the chloride mass balance method for the 2020 water year ranged from 0.19 to 0.31, with a central tendency of 0.26

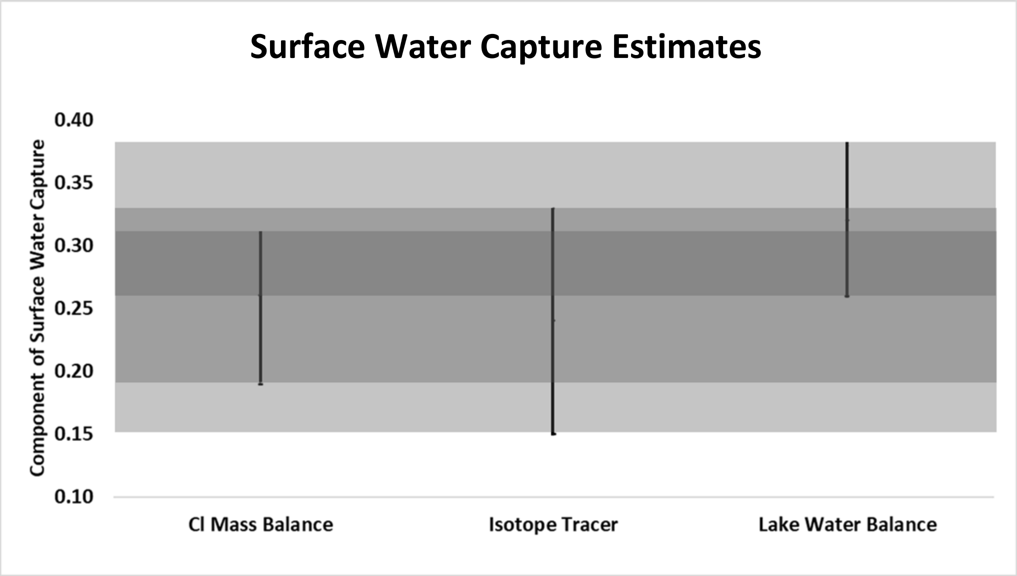

Figure 11. Surface water capture estimates by all methods

DISCUSSION

Road Salt Transport in Spring Valley Sub-Watershed

Sodium concentrations for sites 1-3 are generally similar. Downgradient enrichment of sodium begins to occur in the stream between sites 3 and 4 and is most pronounced between sites 4 and 5. Chloride enrichment in the stream occur incrementally from sites 1-3 with notable increases from sites 3 to 4 and 4 to 5. Increases in sodium and chloride can be correlated to the presence of stormwater outfalls between sampling sites. Between sites 2 and 3 one outfall is present, and while sodium does not appreciably increase between these sites, chloride has an average increase of 4.6 mg/L. A single outfall is also present from sites 3 to 4 with average increases in sodium and chloride of 1.9 mg/L and 7.6 mg/L, respectively. Greater concentration increases from site 3 to 4, relative to concentration changes from 2 to 3, are likely attributed to an approximate doubling in the size of the drainage area contributing to the outfall located between sites 3 and 4 (Table 1, Figure 3). The largest average increases in sodium and chloride, 8.9 mg/L and 15.6 mg/L, respectively, occur from sites 4 to 5, due to 5 stormwater outfalls with a combined drainage area of 455,758 m^2 discharging to the lake between the two sampling sites.

While the accumulation and enrichment of sodium and chloride in surface water were systematically observed downstream throughout the entire study, it was most pronounced from spring to early summer in 2020 and from spring to midsummer in 2021. Project monitoring began on 3/20/2020, and sodium and chloride concentrations may have been elevated in the early Spring prior to the late March sampling project start date. The chloride peak of 140 mg/L on 5/27/2020 at Site 5 is believed to have originated as an illicit discharge from a stormwater outfall with measured chloride concentrations - as high as 16,000 mg/L. This illicit discharge was traced to the source and no longer occurs.

From these data, road salt appears to be the primary source of sodium and chloride enrichment in the watershed. Correlation of sodium and chloride increases with outfall structures suggest that runoff is a controlling factor on sodium and chloride enrichment in the surface water. Given that the largest sodium and chloride increases occur from spring to summer after the application of road salts cease, it can be concluded pulses of sodium and chloride from road salt are transported through the watershed in the spring and reside in the lake for months after direct runoff. This finding is supported by lake residence time estimates ranging from 49 to 89 days (Table 3).

This interpretation is consistent with specific conductivity (SC) trends. During melt events, road salt is dissociated as sodium and chloride and transported by runoff to surface water from the stormwater outfalls, where it is detected as conductivity increases (Figure 7). SC peak 4 (Figure 7) represents the largest melt event during 2021, as it was the only melt event that was detect by all stormwater outfall conductivity loggers. Preceding SC peak 4 (2/19-3/1), maximum daily temperatures from 2/5-2/21 did not exceed freezing and likely resulted in a buildup of road salt and snow/ice on impervious surfaces. After 2/22, average daily temperatures were frequently above freezing (Figure 4), and significant snowmelt runoff and road salt transport to surface water outfalls occurred. The elevated sodium and chloride concentrations at site 5 span a longer period of time than the stream sites consistent with the lake residence time estimates.

Surface Water Capture

The estimates of surface water capture made using three independent methods are remarkably close and clearly demonstrate that Station 14 municipal wells capture a significant amount of lake water. The fraction of surface water captured ranges from 0.16 to 0.38, but the mutual overlap of three methods narrows the range to 0.26 to 0.31. This is a composite estimate distributed over the five wells. The isotope mixing model is useful for identifying surface water capture among the 5 wells and indicates a trend of increasing surface water component moving from north to south in wells 14-1 to 14-4 (Figure 2), consistent with the observed trend of increasingly negative vertical gradients (Figure 5). Differences in ^{18}O enrichment from summer 2020 to summer 2021 likely result from significant increases in precipitation during summer 2021. Rainwater is typically enriched in the lighter ^{16}O oxygen isotope and functions as a primary source of recharge of aquifers in the Kalamazoo area. Increased precipitation in summer 2021 would cause increased mixing of groundwater with the $\delta\ ^{18}$O depleted precipitation and decrease the $\delta\ ^{18}$O values of the well water.

Each of the three methods operate on distinct spatial and temporal scales. The isotope mixing model and water balance approaches provide instantaneous or near instantaneous estimates of surface water capture. The primary difference between the two methods is that the water balance is based on physical estimates of lake inflows and outflows, whereas the isotope mixing model provides estimates based solely on isotopic composition which is completely independent of flow measurements and other components of a water balance. The chloride mass balance method is based on an entire water year and encompasses the transport and retention of road salt throughout the entire sub-watershed along with annual pumping at Station 14. The utility of each method is strengthened when combined into a single estimate derived from common overlap. The horizontal distance of Spring Valley Lake to the pumping wells ranges from 20 m to 500 m, with an approximate vertical distance of 18-24 m from the lake bottom to the top of the well screens. Consistent with the observations from Spring Valley Lake and the spatial scales of surface water – ground water interaction by Kalabas et al. (2006), we anticipate that surface water capture can occur on a distance up to 1000 m from pumping wells.

Many definitions of well water capture exist in the literature. Capture estimates generated by Konikow and Leak (2014) range from 0.0 to 1, with a mean of 0.61, based on pumping wells in 31 large aquifer systems across the United States . In contrast with our study where capture is specifically defined as the component of surface water infiltration from an adjacent surface water body, Konikow and Leak (2014) defined capture as the sum of infiltration of water sourced from surface water bodies, decreases in surface water baseflow, and decreases in evapotranspiration caused by water table elevation decline. Generally, reservoir water will recharge groundwater without being induced by pumping. A study in semiarid southeastern Spain found that the component of recharge to groundwater, as a component of runoff volume, across 107 engineered check dams ranged from 0.03 to 0.50, with a mean value of 0.10 (Martin-Rosales, 2006). Luukkonen et al. (2004) used numerical simulations to estimate surface water capture from Allan Creek in Kalamazoo County, Michigan to pumping wells located in a confined aquifer. Their estimates of surface water capture ranged from 0.2 to 0.8, and generally decreased with increasing distance away from the stream. A follow up study to Borchardt et al. (2003), identified 7 of 13 municipal wells in La Crosse, WI, captured surface water with estimates by stable isotope methods ranging between 0.09 and 0.14 (Hunt et al., 2004).

All capture estimates have uncertainty which can be attributed to sensor error and environmental uncertainties associated with the respective methods. The water balance and mass balance methods both use the OTT MF Pro flow sensor which has an accuracy of ± 2%. Uncertainty in flow measurements by sensor error was taken into account by applying the flow sensor accuracy to the measured flows to create minimum and maximum bounds of capture. The water balance approach may overestimate capture, as the method assumes the difference between the inflow and outflow is entirely attributed to capture, while some component of the difference may be attributed to seepage to groundwater that is not captured by the pumping wells. Similarly, the mass balance approach may overestimate capture as some mass of chloride could escape the lake to groundwater which is not captured by the pumping wells. Additionally, the mass balance approach does not account for evapotranspiration in the lake which will result in the method to be biased high. Coarse resolution of stream gauging and the linear interpolation of flow between stream gauging events results in significant uncertainty in the mass balance method. Similarly, the monthly resolution of chloride sampling and the linear interpolation of values between sampling events also brings about uncertainty in the mass balance. The use of stable isotopes in estimating SWC relies on clearly pronounced and stable differences in ^{18}O in surface water and groundwater, which inherently incorporates some degree of uncertainty (Kalabus et al., 2006). Endmembers of the isotope tracer method were obtained by three sampling events and may be better constrained by additional sample collection which would yield more representative end members and a more accurate capture estimate.

Each of the methods in this study provides different spatial and temporal resolution where: (1) the water balance computations include total surface water contributions from the watershed to the lake and occur during the winter where evapotranspiration is negligible due to ice cover, (2) the isotopic fractionation is specific to the evaporative signal in the lake and are taken during the summer and fall, and (3) the chloride mass balance integrates all measurements of streamflow and chloride concentrations contribute to the lake by the watershed over the annual water year. Measurements by these different techniques and the agreement between each method on different temporal and spatial scales, increases confidence and constrains the estimations of surface water by the City of Kalamazoo Station 14 wellfield.

Lake Water Quality

Chloride-sulfate mass ratios (CSMR) exceeding 0.5 indicate that surface water in Spring Valley Lake is always moderately corrosive to lead at sites 4 and 5 (Figure 8b). The water would be ranked as highly corrosive if alkalinity fell below 50 mg/L (Belitz et al. 2016), however, alkalinity in Spring Valley Lake was never observed below 120 mg/L in this study. The LI differs from CMSR in that it describes the corrosivity of water to iron and steel, and discerns that the lake water has a low to moderate steel corrosion tendency at site 4, and low to high corrosion tendency at site 5. The highest LI values occur in Spring Valley Lake during the summer. While increases in chloride will generally elevate the LI, the observed increases in the Larson Index during summer 2020 are caused by reductions in lake alkalinity, as alkalinity and chloride were both at minimum concentrations. The high LI value on 5/27/2021 is not connected to road salt, and is attributed to the illicit, high-chloride discharge from an outfall. High Larson Index values in the lake during summer of 2021 can be attributed to the combination of low lake alkalinity and high lake chloride concentrations. Since alkalinity decreases seasonally, highest lake water corrosivity should be expected in the summers after road salt transport to Spring Valley Lake by snowmelt runoff has persisted into March.

LI and CSMR values at site 4 are more representative of surface water captured by the Station 14 wellfield than corrosivity values at site 5, due to the proximity of site 4 to the pumping wells. The City of Kalamazoo adds sodium hexaphosphate at a blending station for Station 14 water to negate the corrosivity of the well water. If untreated, steel and lead corrosion can prompt deterioration of water supply infrastructure and potentially lead to health impacts such as abdominal pain, depression, fatigue, forgetfulness, and developmental impacts in newborn children caused by elevated levels of lead (HHS, 2007; NIOSH 1995)

Seasonal reductions in Spring Valley Lake alkalinity are likely caused by biogenic calcite precipitation. In lakes where alkalinity is greater than 1 MEq/L, biogenic calcite precipitation can occur at the cost of lake alkalinity. Alkalinity greater than 1 MEq/L is common, with 57% of global lakes exceeding this concentration (Khan et al., 2020). Spring Valley Lake falls into this category of lakes as alkalinity in Spring Valley Lake ranges from 2.8 MEq/L to 5.6 MEq/L. In lakes where the 1 MEq/L alkalinity criteria are met, algae can act as nucleation sites during the summer for calcite precipitation leading to a reduction in lake alkalinity, as described by the mass balance equation: $Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O$. Note that 1 mole of CO_2 results in a net loss of 1 mole of dissolved inorganic carbon (DIC) and 2 moles of total alkalinity from the water (Khan et al., 2020).

The presence of algae in Spring Valley Lake has been confirmed by the trophic state index (TSI) that can be computed using both Chl-a as a proxy for algae and phosphorous (Figure 9). Determination of the trophic state of the lake should place greater weight on chlorophyll- a derived TSI values that are more of a direct measurement of algae in the lake. A composite sample during summer 2021 generated a TSI (Chl-a) of 44 (Figure 9), indicating a mesotrophic state, whereas TSI(P) typically ranks the lake as mesotrophic to eutrophic. The peaks where TSI (P) exceeds 70 indicates a hypereutrophic state, though this condition was not observed. More realistically, the lake likely remains mesotrophic and may occasionally rise to low value eutrophic status. Though large-scale algal blooms were not observed during this study, water was observed to have a green hue with good visibility.

CONCLUSIONS

The capture methods in this study can be applied to any road salt impacted surface water body with an inflow and outflow. While roads salt runoff to surface water has the potential to negatively impact aquatic ecosystems and municipal water supply infrastructure, the chloride enriched waters can also be helpful in determining surface water capture. In cases where pumping wells capture a significant fraction of chloride enriched surface water, corrosion of water distribution infrastructure is a concern that can be alleviated by the use of corrosion inhibitors. The primary findings of this study are:

- Pronounced sodium and chloride enrichment in surface water occurs from spring to early/mid-summer, after pulses of road salt derived sodium and chloride are transported through the watershed in the spring and reside in the lake for months after direct discharge from outfalls.

- Estimates surface water capture ranges from .16-.38, with a more confident range of .26-31 based on the overlap of each method.
- Chloride-sulfate mass ratios indicate that surface water in Spring Valley Lake is always in the moderately corrosive range for lead, and may be slightly corrosive to highly corrosive to steel according to the Larson Index.
- Trophic state of the lake ranges from mesotrophic to hypereutrophic by TSI(P) however visual inspection and the more reliable TSI(chl) index indicate a mesotrophic state of the lake.
- Seasonally enhanced corrosivity associated with reductions in lake alkalinity during the summer is likely caused by biogenic calcite precipitation.

Additional research is needed to further constrain estimates of surface water capture by the chloride mass balance approach. This can be achieved by: (1) increasing stream gauging frequency to a monthly resolution, and (2) reducing the sampling to sites 4 and 5 and increasing the frequency of sampling to bi-weekly. This approach would provide more accurate chloride data at the inflow and outflow of the lake and reduce analytical costs. Estimation of evapotranspiration during non-winter months would allow for year-round estimates of surface water capture by the water balance method. Continued sampling of well water and surface water for ^{2}H and ^{18}O isotope analysis would better constrain estimates of surface water capture over a longer time period to account for variations in stable isotope composition and obtain better end member values. Continued chlorophyll-a sampling during the summer would provide an improved trophic state index estimation of Spring Valley Lake and could further confirm the impact of biogenic calcite precipitation impacts on summer alkalinity reductions in lake water. A longer-term study would also provide the benefit of characterizing long term chloride trends in Spring Valley Lake. Generally, chloride concentrations in urban lakes have been observed to increase; however, it is currently unclear if this system, with limited storage, would continue to experience long-term chloride enrichment of surface water.

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