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Hydrologic Balance, Water Quality, Chemical-Mass Balance, and Geochemical Modeling of Hyperalkaline Ponds at Big Marsh, Chicago, Illinois, 2016–17

Scientific Investigations Report 2019–5078

U.S. Department of the Interior
U.S. Geological Survey

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DAVID BERNHARDT, Secretary

U.S. Geological Survey
James F. Reilly II, Director

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Conversion Factors

U.S. customary units to International System of Units

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
acre	0.4047	hectare (ha)
square foot (ft^2)	0.09290	square meter (m^2)
Volume		
cubic foot (ft^3)	0.02832	cubic meter (m^3)
Hydraulic conductivity		
foot per day (ft/d)	0.3048	meter per day (m/d)
Flow rate		
cubic foot per day (ft^3/d)	0.02832	cubic meter per day (m^3/d)
inch per day (in/d)	0.0254	meter per day (m/d)

Datum

Except as otherwise noted, vertical elevation information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Elevation refers to distance above or below the vertical datum.

Supplemental Information

Abbreviated water-quality units used in this report are as follows: micrograms per liter are considered equivalent to parts per billion at the reported concentrations. Bottle volumes are reported in milliliters (mL) or liters (L).

Specific conductance is reported in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

Concentrations of chemical constituents in water are reported in either milligrams per liter (mg/L) or micrograms per liter (µg/L).

Abbreviations

$CaCO_3$	calcium carbonate
EPA	U.S. Environmental Protection Agency
PCO_2	partial pressure of carbon dioxide
USGS	U.S. Geological Survey

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Abstract

Hyperalkaline (pH greater than 12) ponds and groundwater exist at Big Marsh near Lake Calumet, Chicago, Illinois, a site used by the steel industry during the mid-1900s to deposit steel- and iron-making waste, in particular, slag. The hyperalkaline ponds may pose a hazard to human health and the environment. The U.S. Geological Survey (USGS), in cooperation with the Environmental Protection Agency (EPA) and in collaboration with the City of Chicago's Park District, completed a study to evaluate the hydrologic balance, water quality, and chemical-mass balance of hyperalkaline ponds at Big Marsh and geochemical modeling used to evaluate remediation options for water quality at the site based on data collected in 2016–17.

Synoptic measurements of surface-water and groundwater elevations were used to determine flow directions and to enable a preliminary estimate of the hydrologic balance for the ponds. Water-quality samples also were collected and analyzed for selected constituents including major anions and cations, nutrients, metals, and trace elements. The results of the water-quality analyses were used to develop a geochemical model to evaluate concentrations, factors affecting pH, and the state of equilibrium between surface waters and atmospheric carbon dioxide. The geochemical model was used to evaluate remediation scenarios using riprap, spillways, or active aeration. The results indicate that active aeration will decrease the pH to near 7.5 in about 8 hours, the fastest rate of the scenarios. Passive aeration, such as riprap or spillways, also can be effective at decreasing the pH in about 45 hours, but spatial obstacles limit their implementation. Seasonal variations in temperature also affect the rate of equilibration, where colder temperatures may have a lower pH than warmer temperatures and may affect the timing and frequency of remediation.

Introduction

Big Marsh, which is about 289 acres, is east of Lake Calumet in Chicago, Illinois (fig. 1). During the early to mid-1900s, several steel mills operated near Big Marsh. These mills produced large volumes of slag material, some of which was deposited as fill in Lake Calumet and Big Marsh (Kay and others, 1996). Hyperalkaline (pH greater than 12) surface water and groundwater are present at the site, which includes two ponds. The hyperalkaline drainage is the result of geochemical reactions among precipitation, surface water, and groundwater with the slag material. The weathering of the slag releases calcium and increases the pH of affected waters (Roadcap and others, 2005).

The City of Chicago applied for a U.S. Environmental Protection Agency (EPA) Brownfield grant to fund, in part, the redevelopment of Big Marsh to restore it to natural areas with recreational opportunities, such as a 40-acre bike park. The bike park was constructed between September and November 2016. Habitat of the remaining 249 acres of Big Marsh continues to be restored to hemimarsh conditions similar to natural environmental conditions. Restoration is limited by the ongoing presence of hyperalkaline water in the ponds at Big Marsh, which pose a threat to human health and the environment. The U.S. Geological Survey (USGS), in cooperation with the EPA and in collaboration with the City of Chicago's Park District, completed a study to evaluate the hydrology and geochemistry of the hyperalkaline ponds at Big Marsh to serve as an initial step for evaluating remedial options using data collected in 2016–17. This study focused on the known hyperalkaline conditions of surface water and groundwater at Big Marsh and sought to (1) characterize the hydrologic balance of the hyperalkaline ponds at Big Marsh, (2) characterize the quality of surface water and groundwater and chemical mass balance at the site, (3) identify environmental risks related to the inorganic water chemistry of the site, and (4) evaluate remedial options for the site that address the hyperalkaline surface water and groundwater and other environmental risks identified in the course of this study.
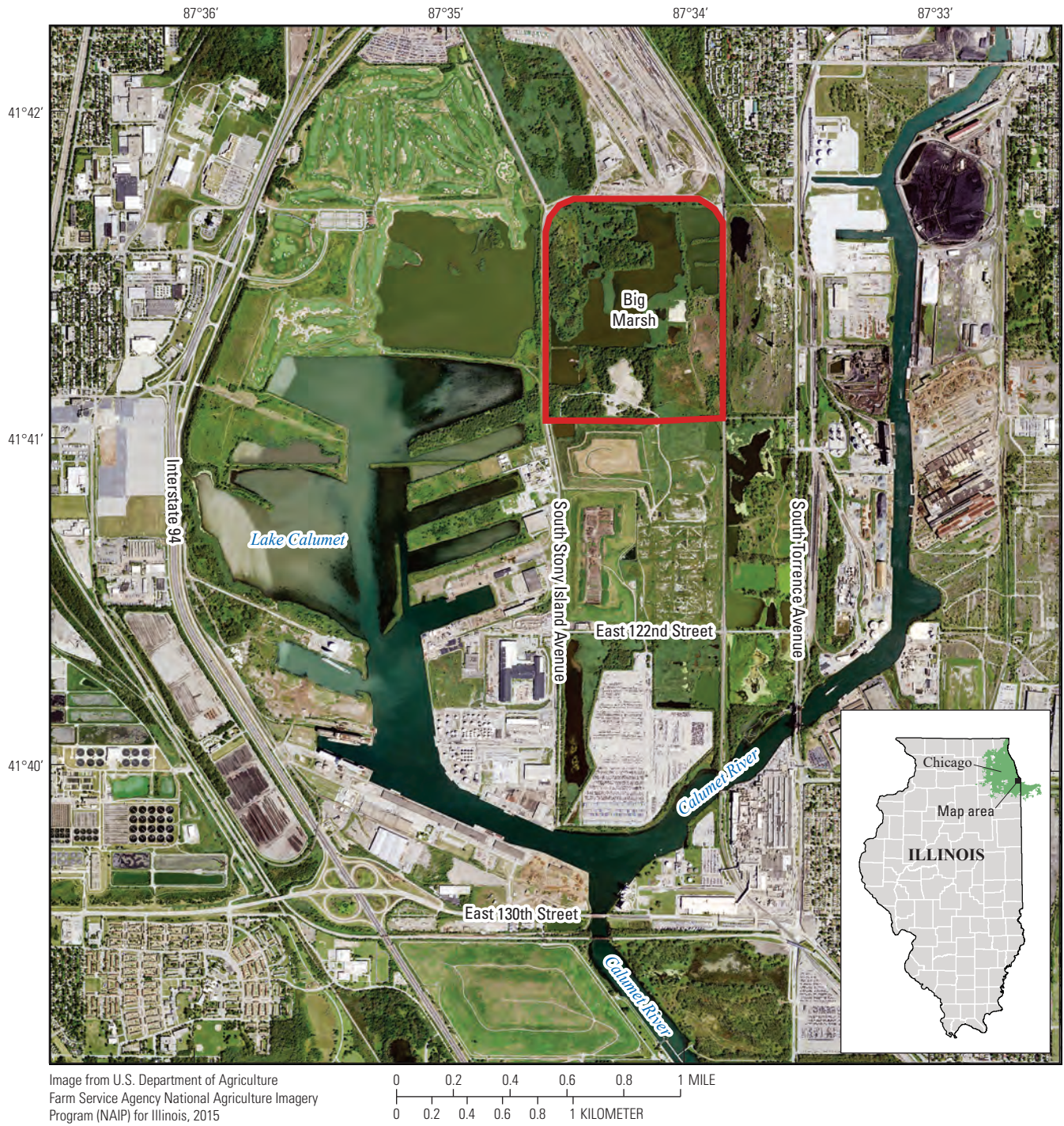
Figure 1.   Regional location of Big Marsh and Lake Calumet in Chicago, Illinois.

Purpose and Scope

The purpose of this report is to describe the hydrologic balance, water quality, and chemical-mass balance of hyperalkaline ponds at Big Marsh and to describe the geochemical modeling used to evaluate remediation options for water quality at the site using data collected in 2016–17. Specifically, this report presents a calculation of groundwater discharge into two hyperalkaline ponds and compares the results to a preliminary water-balance analysis estimated from flow measurements at inflows and outflows of surface water collected at selected locations throughout Big Marsh. The results of the water-balance analysis were estimated because of numerous past and ongoing changes to the site, and consequently, the results limited the utility of previously collected historical longer term data. Also presented are the results of the water-quality samples, chemical-mass balance, and geochemical model to determine the equilibrium state of the surface-water chemistry with respect to atmospheric carbon dioxide.

Description of Study Area

Big Marsh is bounded by Norfolk Southern Railroad Yard to the north, Indian Ridge Marsh to the southeast, South Stony Island Avenue to the west, and Paxton Landfill to the south (fig. 2). Big Marsh consists of several surface-water bodies, including Big Marsh Pond, Pond A, Pond B, Pond B West, Pond C, and Pond C West (fig. 2). The primary areas of focus for this study are hyperalkaline groundwater, seeps, and Ponds B and C, which are hydraulically connected to the surface waters of Pond C West, and Pond B West (fig. 3). Ponds are surrounded by fill deposits composed primarily of slag in the southern and eastern parts of Big Marsh and dredging spoils and construction debris in the western part (Kay and others, 1997). The slag-fill deposits at Big Marsh range from about 6.5 to 10 feet (ft) thick and consist of mainly steel slag and have lesser amounts of construction and demolition debris, and dredge spoils from Lake Calumet and the Calumet River (fig. 1; Kay and others, 1996). The extent of the slag-fill deposit area in figure 2 is estimated and mainly focuses on the slag-fill deposit area that contributes to the surface waters at Ponds B and C and does not include all the possible areas of slag-fill deposits, including those potentially underlying the ponds. Slag-fill deposits are underlain by 10 to 15 ft of sand (Kay and others, 1997) and together compose the Calumet aquifer (Hartke and others, 1975). The Calumet aquifer is underlain by a confining unit comprising about 70 ft of till and lacustrine silt deposits (Kay and others, 1997). Big Marsh is primarily a flow-through lake. Groundwater enters Big Marsh primarily from the east flowing through the slag-fill deposits and discharges into the surface waters of Ponds A, B, and C and into Big Marsh Pond and exits along the western edge of Big Marsh into Lake Calumet. The groundwater and surface-water bodies of Big Marsh are interconnected and responsive to fluctuations of Lake Michigan (2.45 miles northeast; not shown) water levels (V3 Companies, Ltd., 2006a).

Ponds B and C receive groundwater discharge along the eastern and southeastern banks, and from seeps with higher amounts of discharge, which were observed primarily along the eastern bank of Pond C. Ponds B and C receive discharge from groundwater seeps originating in the slag-fill deposits near the MW2 monitoring well 37N14E–13.3a1 (hereafter referred to as monitoring well "MW2") (USGS station 414121087335701; figs. 2 and 3). The concentration of slag-fill deposits in this area produces the high-pH groundwater and seeps at Ponds B and C (Roadcap and others, 2005).

The surface waters of Ponds B and C have a complex flow system (fig. 3). Pond B has a small rivulet that drains into Pond C West along the southwest corner of Pond B, depending on water elevation. Pond B West has a small component of surface-water flow into or out of Pond B, depending on the water elevation of Big Marsh Pond. The surface water at Pond C has a bifurcated flow where a part of the water flows into Pond B and a smaller, mostly surficial component flows through a small rivulet and emergent wetland along the southeastern bend and ultimately discharges to Big Marsh Pond.

The surface waters of Big Marsh are controlled by culverts that have undergone various design changes. In 2015, a channel was excavated through the earthen berm that originally separated Pond A from Big Marsh Pond. A 24-inch (in.) diameter culvert lies underneath the train tracks of the Norfolk Southern Railroad Yard and drains 250 acres of surface runoff into Indian Treaty Creek and into Big Marsh Pond (V3 Companies, Ltd., 2006b; fig. 2). In the spring of 2017, a second set of culverts, consisting of twin 24-in. diameter corrugated steel pipes, was installed south of the Norfolk Southern Railroad Yard culvert to accommodate a new access road. The Big Marsh Pond outlet was redesigned and installed on October 15, 2015, and set to allow the water levels at Big Marsh to be at their lowest level of 579 ft to stimulate plant growth in the marsh (Chicago Park District, written commun., May 11, 2017). The Big Marsh Pond outlet drains the surface water from Big Marsh, through twin 30-in. pipe culverts, toward Big Marsh culvert and out to Lake Calumet. Big Marsh culvert was redesigned as a second set of twin 30-in. pipes and installed to accommodate the new bike park entrance in early October of 2016 (Chicago Park District, written commun., May 11, 2017; fig. 2). This second set of culverts maintains the minimum water elevation for the Big Marsh at an elevation of about 581.13 ft above the North American Vertical Datum of 1988 (NAVD 88) to restore hemimarsh conditions at Big Marsh (Chicago Park District, written commun., May 11, 2017). Additionally, the newly installed bike park has stormwater drainage infrastructure to divert surface runoff into Big Marsh. Discharge and runoff from these drainage pipes and surface area have not been measured because it was outside the scope of this study.

Figure 2.   Big Marsh study area, sample and discharge measurement locations, and slag-fill deposit area, Chicago, Illinois.

Figure 3. Hyperalkaline ponds of Big Marsh, Chicago, Illinois, and locations of samples collected October 24–25, 2016, and discharge measurements collected May 3, 2017.

Previous Investigations

Previous studies have investigated the geochemistry of the groundwater in the Lake Calumet area including the Big Marsh site (Roadcap and others, 2005; Waska, 2013) and concluded that aeration and a permeable reactive barrier of Apatite-II™ could be an effective remedy to lower pH in surface water. Additional geochemistry and site-specific data were needed to evaluate aeration (active or passive) as a remedial treatment. Event-based and seasonal precipitation effects on the groundwater/surface-water interactions at Big Marsh were investigated by Duwal (1994). Some of the main conclusions from that study were that the hydraulic conductivity of the slag-fill deposits was about two orders of magnitude greater (170 feet per day [ft/d]) than that of the underlying sand deposits (2.83 ft/d). Water-level fluctuations correlated with precipitation events but with a lag time determined by soil moisture content in the unsaturated zone. Precipitation events greatly affect the seepage rates at seeps along the banks of Ponds B and C. Macropore systems within the slag-fill deposits affect the location of the springs or seeps within the ponds. Additionally, Duwal (1994) identified 11 seeps (springs) along the eastern edge of Ponds B and C. Duwal (1994) estimated the flow into Pond B to range from 0.85 to 6.78 cubic feet per day (ft³/d) based on data from seepage meters. The groundwater seepage flow into Pond C was measured to be 0.12 to 0.47 ft³/d, with the highest seepage rate along the southeast corner of the bank of Pond C measured at 356 ft³/d (Duwal, 1994). Large macropores throughout the slag-fill deposit area greatly affected the rate and amount of groundwater entering the ponds.

Waska (2013) investigated the microbiology of the hyperalkaline conditions and possible remedies at the site and concluded that the alkaliphilic and alkalitolerant microbes respond differently to varying environmental conditions and that the microbes adapt readily to changes in the extreme conditions. Column experiments were completed to evaluate the effectiveness of three permeable reactive barriers: quartz, dolomite, and Apatite-II™—a fish bone material (Waska, 2013). The results of the column study indicated that the Apatite-II™ permeable reactive barrier would be a potentially effective pH remedy (Waska, 2013); however, there is a concern that this remedial approach may add nutrients (phosphate and possibly nitrogen species) to the surface-water environment and cause algal blooms or eutrophication.

The geochemistry of the hyperalkaline groundwater within the slag in the Lake Calumet area was investigated and potential remediation options were evaluated by Roadcap and others (2005). The slag material consists primarily of calcium silicate with as much as 50 percent iron and manganese, and includes other elements such as chromium, molybdenum, and vanadium. An aeration technique called air sparging was determined to be a possible effective remedy for reducing the pH at the seeps. Carbon dioxide sparging and acid addition also were effective at rapidly reducing pH; however, both remedies may increase dissolution of the metals bonded to the calcite deposits, thereby increasing the metals concentrations in the surface water.

Methods

The USGS synoptically measured surface-water and groundwater elevations at selected locations around Big Marsh on October 24, 2016, with a Trimble™ R8 GNSS global positioning system using a virtual reference system using a Real-Time Network based on the single-base Real-Time Kinematic method (Rydlund and Densmore, 2012). The surface-water and groundwater-level elevations (table 1) were used to determine the hydrologic flow directions near the hyperalkaline ponds at Big Marsh. For groundwater, a depth to water reading from a measuring point was obtained using a calibrated electronic tape using methods presented by Cunningham and Schalk (2011). The height of the measuring point above land surface was measured with a calibrated tape measure, recorded, an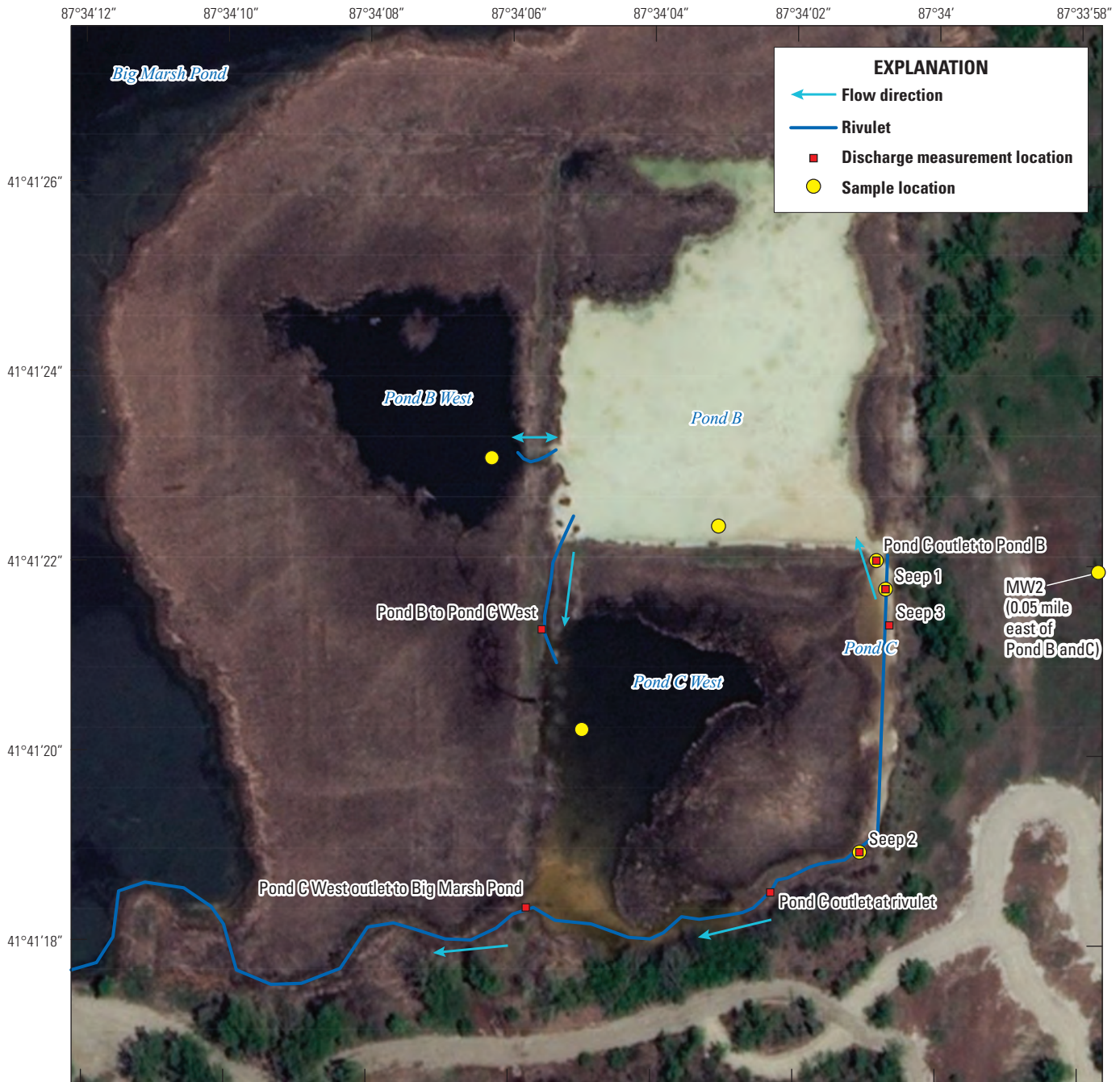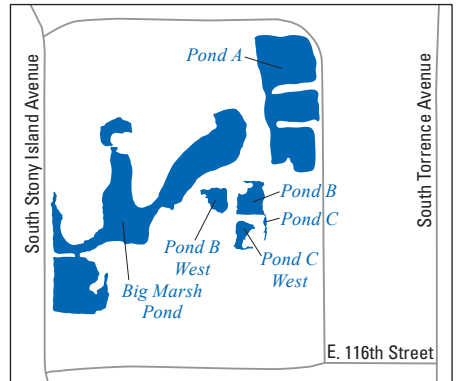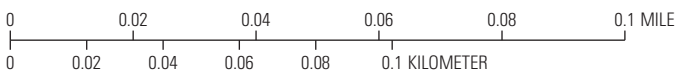d added to the land-surface elevation to obtain the elevation of the measuring point. Groundwater elevations were calculated by subtracting the depth to water level from the measuring point elevation. Additional groundwater-level measurements at MW2 were collected on May 3 and June 30, 2017 (U.S. Geological Survey, 2018).

Hydraulic conductivities of the slag deposits were estimated from slug tests completed on October 27, 2016, at the MW2 monitoring well (Gahala and others, 2019). Of the 6 tests (3 slug-in tests, 3 slug-out tests), the slug-out tests were determined to have adequate slug response curves for the application of the spreadsheet analysis. The procedure for completing the slug tests is presented in Groundwater Technical Procedures Document GWPD 17 (available at https://pubs.usgs.gov/tm/1a1/pdf/GWPD17.pdf). Slug-test data were analyzed using the technique of Bouwer and Rice (1976).

A total of 9 surface-water quality and 1 groundwater-quality samples were collected on October 24 and 25, 2016. Sample collection and processing followed procedures described by the "USGS National Field Manual for the Collection of Water-Quality Data" (U.S. Geological Survey, variously dated). Surface-water samples were collected from various locations throughout Big Marsh by use of a peristaltic pump and Teflon tubing (figs. 2 and 3). Water samples were filtered in the field using a 0.45-micrometer capsule filter. Field alkalinity included hydroxide, carbonate, and bicarbonate contributions as well as total alkalinity as calcium carbonate ($CaCO_3$). Alkalinity was measured in the field by adding phenolphthalein and bromocresol green-methyl red pH indicators to a known volume of sample and titrating with standardized sulfuric acid. Major cations and trace element samples were field acidified with 7.5 nitric acid. All samples were analyzed for laboratory alkalinity, major anions and cations, nutrients, metals, and trace elements by the USGS National Water Quality Laboratory in Lakewood, Colorado, using standard measurement methods (Fishman, 1993; Fishman and

Table 1.   Survey locations and water elevations throughout Big Marsh, Chicago, Illinois, collected by the U.S. Geological Survey on October 24, 2016.

[NAVD 88, North American Vertical Datum of 1988; ±, plus or minus; °, degree; ′, minute; ″, second]

Survey location[1]	Station number	Latitude	Longitude	Water elevation in feet above NAVD 88	Vertical precision ±, in feet
Groundwater					
MW1	414130087340101	41°41′30.20213″	87°34′00.61744″	582.9	0.02
MW2	414121087335701	41°41′21.60375″	87°33′57.10771″	584.0	0.03
Well Seep 1–D	414121087340004	41°41′21.49658″	87°34′00.15974″	582.6	0.08
Bend D	414118087340003	41°41′18.87251″	87°34′00.49945″	582.7	0.03
South Pond D	414127087340003	41°41′27.11177″	87°34′00.14668″	582.8	0.04
NW4	414125087335801	41°41′25.10402″	87°33′58.30521″	582.9	0.04
NW2	414126087335401	41°41′26.33131″	87°33′54.37312″	582.8	0.03
NW3	414127087335501	41°41′26.85920″	87°33′54.68780″	582.7	0.03
Surface water					
Pond A	414134087335601	41°41′28.38179″	87°33′59.85566″	581.0	0.04
Pond B	414123087340203	41°41′25.74041″	87°34′00.85776″	582.1	0.03
Pond C (Seep 1)	414122087340101	41°41′21.48304″	87°34′00.53368″	582.2	0.03
Big Marsh Pond	414121087342001	41°41′33.64427″	87°34′04.02211″	580.9	0.03
Unnamed pond	414126087335402	41°41′26.26251″	87°33′53.85386″	582.9	0.03

[1]Survey location names were modified from U.S. Geological Survey (2018).

Friedman, 1989; Garbarino, 1999; Garbarino and others, 2006; Patton and Kryskalla, 2003, 2011). The only groundwater sample was collected at monitoring well MW2. Other wells on site seemed to be in poor hydraulic connection with the surrounding deposits as evidenced by slow (greater than 3 days) recharge. To collect groundwater, low-flow methods were used with a peristaltic pump and Teflon tubing placed at the mid-screen level of the well. A total of three casing well volumes of water were removed from the well, and field measurements of water temperature, pH, specific conductance, turbidity, and dissolved oxygen were continuously monitored with a multi-parameter sonde and flow-through chamber during pumping and allowed to stabilize. This ensures collection of a representative water sample (U.S. Geological Survey, variously dated).

Locations of the surface-water and groundwater-level measurements and samples collected on October 24 and 25, 2016, and the discharge measurement locations collected on May 3, 2017, are shown in figures 2 and 3. Surface-water discharge was measured on May 3, 2017, at (1) the inflow from the newly installed culvert along Indian Treaty Creek, (2) the new channel from Pond A to Big Marsh Pond, (3) Pond C outlet to Pond B, and (4) Pond C outlet at rivulet to Big Marsh Pond. Discharge measurements at the Big Marsh Pond culvert could not be collected on May 3, 2017, because of obstructions. Discharge measurements were collected using flow meters following the standard techniques and methods (Turnipseed and Sauer, 2010) for measurements by wading. Either

the two-point method (depth greater than 2.5 ft) or six-tenths-depth method (depth 0.3–2.5 ft) was applied depending on the depth of the water.

Point velocity at the seeps was measured on May 3, 2017, by placing the flow meter near the middle of the seep where a positive flow could be obtained (fig. 3). Three measurements of velocity were recorded in field notes and averaged. A discharge from each seep was estimated by multiplying the velocity by the cross-sectional area (height and width) of the seep opening using a tagline ruler.

The groundwater discharges into Ponds B and C were estimated from the Dupuit-Forchheimer equation (Wang and Anderson, 1982), which accommodates a water table boundary condition. The Dupuit-Forchheimer equation includes water-elevation levels coupled with hydraulic conductivity. The Dupuit-Forchheimer equation assumes no vertical hydraulic gradient and flow is primarily horizontal and follows along the slope of the surface (Wang and Anderson, 1982). Horizontal flow generally exists where the groundwater discharges at the seeps, except for possible vertical flow during and after precipitation events along the bank of Pond C as observed in Duwal (1994). The groundwater discharge entering Ponds B and C was calculated from water elevations measured during the October 24, 2016, synoptic survey using the Dupuit-Forchheimer equation (eq. 1):

$$q = K(H^2_{MW2} - H^1_{Pond\ B}) / 2L \qquad (1)$$

where

q is the flow per unit width, in cubic feet per day;

K is the horizontal hydraulic conductivity, in feet per day, and is equal to the mean of the values obtained from the slug tests in the Calumet aquifer completed at well MW2 during this study (2.9 ft/d);

H is the height of the water column (water elevation) measured between two points, MW2 and Pond B (and C) elevation, in feet; and

L is the length between the two measured water-elevation points in feet.

Groundwater discharge is obtained by multiplying q by the area of the shoreline through which flow exists. The area of the shoreline was determined by multiplying the shoreline length by the maximum depth of Ponds B and C (2.0 ft).

A hydrologic balance attempts to account for all the water that flows into and out of a study area during a given period. A preliminary hydrologic balance was calculated for 1 day to determine the net groundwater discharge into and out of Ponds B and C. The general hydrologic balance equation is described as change in storage is equal to inputs minus outputs. To evaluate the net groundwater discharge into Ponds B and C, the change in storage was assumed to be equal to zero. The equation is rearranged so that inputs = outputs, so that,

$$P + SW_i + GW_i = E + SW_o + GW_o \tag{2}$$

therefore, solving for net groundwater discharge gives

$$(GW_i - GW_o) = E - P - SW_i + SW_o \tag{3}$$

where

$GW_i - GW_o$ is the net groundwater discharge (groundwater input minus groundwater output);

P is precipitation, determined from observed data for the date evaluated (May 3, 2017);

E is evaporation, determined from published graphs and measured discharge of surface-water input plus surface-water output;

SW_i is surface-water input; and

SW_o is surface-water output.

The change in storage at Ponds B and C was assumed to be zero, reflecting assumed steady-state conditions. The assumption of steady state is based on the zero precipitation during the October 24, 2016, surface-water and groundwater-level measurements and the May 3, 2017, surface-water discharge measurements. The assumption of steady state for 1 day allows for the calculation of groundwater inflows and outflows at each of the ponds. Groundwater discharge quantities were calculated from the Dupuit-Forchheimer equation

and compared to the results determined by the hydrologic balance.

Precipitation and Evaporation

Precipitation and evaporation are components of the water balance and contribute to the addition or removal of water. There were no observed precipitation events on October 24, 2016, or May 3, 2017, at Big Marsh (National Oceanic and Atmospheric Administration, 2017). Additional data are needed to verify the total volume of water added to ponds after a rain event. In addition, data may be needed for understanding the chemical response to groundwater discharge and surface-water runoff into the ponds.

The volume of water removed from the ponds by evaporation was determined using the techniques of Hamon and others (1954) and Roberts and Stall (1966), which required average temperature, average dew point, and average wind speed (Weather Underground, 2017). The daily evaporation rate for October 24, 2016, was estimated to be 0.05 inch per day (in/d), and evaporation rates for May 3, 2017, was estimated to be 0.10 in/d. The daily evaporation values are within the range of those determined by Duwal (1994).

Bathymetry

The surface area and volume of surface waters at Big Marsh (Big Marsh Pond, Pond A, Pond B and Pond B West combined, and Pond C and Pond C West combined) were determined using bathymetric data collected on September 23, 2014, by Integrated Lakes Management, Inc. (V3 Companies, Ltd., written commun., Feb. 24, 2017). Big Marsh Pond has an average depth of 1.95 ft (fig. 4). Ponds B and C also are shallow with an average depth of 1.05 and 1.50 ft, respectively, with a maximum depth of about 2 ft. Pond A was substantially deeper, having a maximum depth of 10 ft (V3 Companies, Ltd., written commun., Feb. 24, 2017). The surface area of Big Marsh Pond is 3,161,300 square feet (ft^2), and the volume of water at Big Marsh Pond is 4,756,000 cubic feet (ft^3). The surface area of Pond B and Pond B West is 182,917 ft^2 with a volume of 162,193 ft^3. The surface area of Pond C and Pond C West is 87,410 ft^2 with a volume of 149,258 ft^3. This information is used to calculate the volume of precipitation, evaporation, and the residence time at each of the ponds.

Surface Water

Surface-water elevation measurements collected on October 24, 2016 (table 1), reflect water levels after the stoplogs were set to lower the water levels at Big Marsh; therefore, surface-water discharge was collected at inflows and outflows of Big Marsh wetland in the spring and summer of 2017 to provide discharge data related to the lowered water level. Surface-water discharge measurements were collected at

Figure 4. Bathymetry of the ponds at Big Marsh, Chicago, Illinois, September 23, 2014. [Data from V3 Companies, Ltd., collected by Integrated Lakes Management, Inc.]

inflows and outflows of Ponds B and C to estimate a preliminary hydrologic balance, given all the changes.

Surface-water discharge measurements were collected at the locations indicated in figure 2 (or fig. 3) and are summarized in table 2. The overall quality of the discharge measurements was rated good to poor with the interpolated variance estimator ranging from 2.7 to 49.8 percent. The reasons for the poor ratings are the limited accessibility and difficulties during some of the measurements. Wading in certain parts of Pond C was not possible because of the soft bottom composed of about 5 ft of calcite precipitates, according to sediment data collected by Integrated Lakes Management, Inc., on September 23, 2014 (V3 Companies, Ltd., written commun., Feb. 24, 2017). In some instances, the ability to collect enough measurements along a transect to obtain a total discharge reading of less than 5-percent error was not possible because of the limited width of the outlet and inlet areas (Pond B outlet to Pond C, Indian Treaty Creek, and Pond C West outlet to Big Marsh Pond). Pond C outlet at rivulet is limited to the only measurable flow, which was about 3 ft wide and within a few tenths (0.20 ft) of a foot as the water fanned out into the wider marsh area. An interpolated variance estimator of error could not be measured but is expected to be poor. Only the discharge measurements collected on May 3, 2017, at the seeps, Pond C outlet to Pond B, and Pond C at rivulet were used in the hydrologic balance calculation.

Groundwater

Surface-water and groundwater-level measurements were used to construct a water-table contour map at Big Marsh for October 24, 2016 (fig. 5). Groundwater-flow directions are perpendicular to the contour lines. Groundwater flows west and north from the slag in the southeast part of the site toward Ponds A, B and C, and Big Marsh Pond. The flow direction is different from what was reported by Duwal (1994), which noted an east to west flow with Pond A, at times, flowing into Pond B. The new channel connecting the surface waters of Pond A and Big Marsh Pond has apparently lowered the water level in Pond A, resulting in a higher hydraulic gradient toward the north at Big Marsh. The water levels from the Duwal (1994) study; the V3 Companies, Ltd., (2006b) study; the EarthTech, Ltd., (written commun., 2005) study; and the October 24, 2016, synoptic survey are listed in table 3. Water elevations measured for this study at Pond A and Big Marsh Pond were lower than previous studies, but Pond B, Pond C, and MW2 (groundwater elevation) were within the range of previous studies. Pond B, Pond C, and MW2 seem to be less effected by the lowering of water levels at Big Marsh Pond outlet and Big Marsh culvert.

Table 2. Measured discharge at locations throughout Big Marsh, Chicago, Illinois, collected by the U.S. Geological Survey on May 3, 2017.

[E, estimated; --, not available; NM, not measured]

Location	Discharge for May 3, 2017, in cubic feet per day	Percent error[1]
Measured inflows		
Indian Treaty Creek culvert	58,311 E	17.8
Seep 1 at Pond C	2,411 E	--
Seep 2 at Pond C	674 E	--
Seep 3 at Pond C	202 E	--
Pond A outlet	35,493 E	21.5
Measured outflows		
Pond B outlet to Pond C West	NM	--
Pond C outlet at rivulet	795 E	--
Pond C West outlet to Big Marsh Pond	NM	--
Pond C outlet to Pond B	16,779 E	49.8
Big Marsh culvert[2]	283,392	2.7

[1]Interpolated variance estimator.

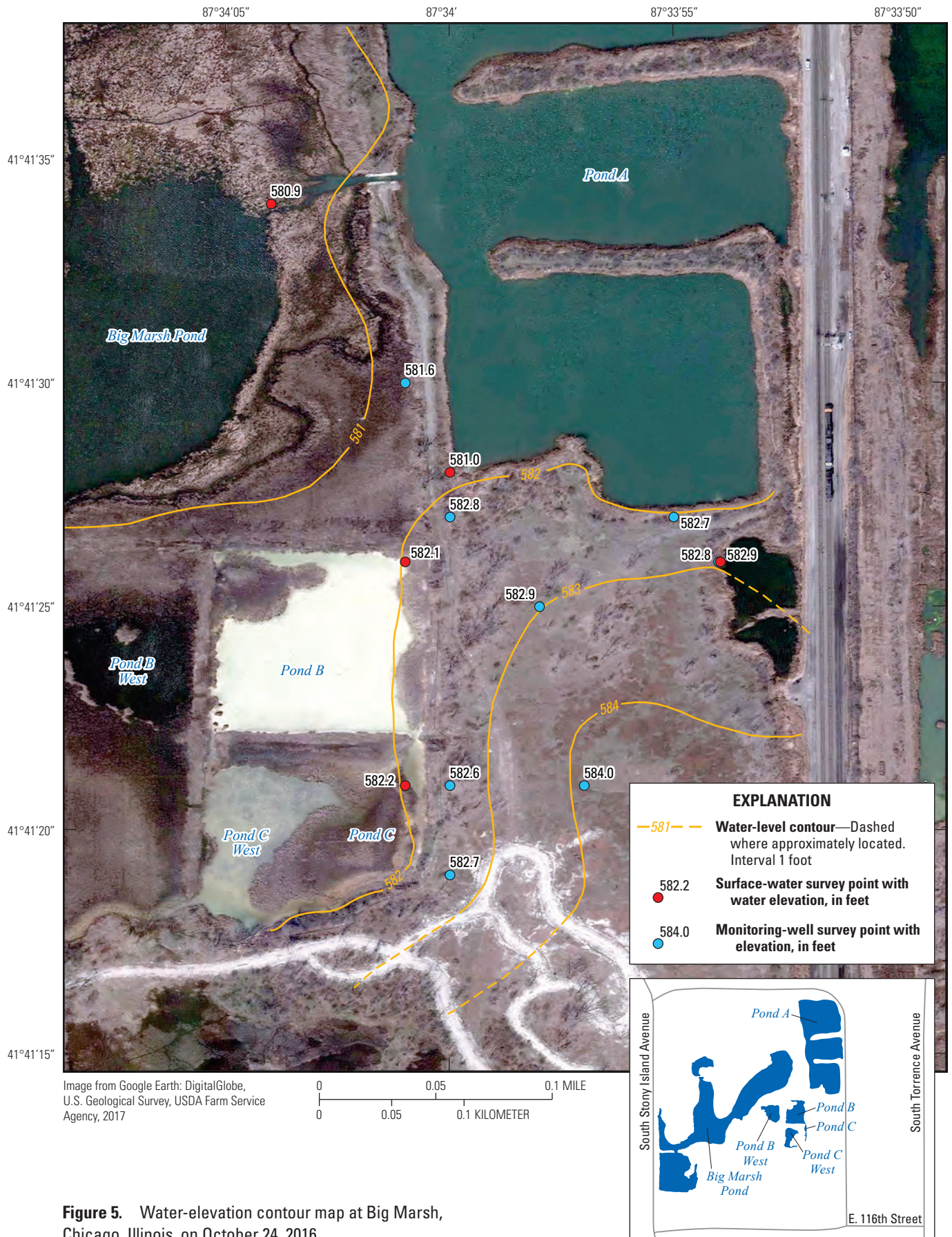[2]Measurement collected March 3, 2017.

Figure 5. Water-elevation contour map at Big Marsh, Chicago, Illinois, on October 24, 2016.

Table 3.   Comparison of water-elevation data at similar locations amongst four studies at Big Marsh near Lake Calumet, Chicago, Illinois.

[NM, not measured]

Location	Water elevation, in feet above North American Vertical Datum of 1988			
	Duwal (June 1994)[1]	V3 Volume V (October 2003)[2]	EarthTech, Ltd. (November 2005)[3]	U.S. Geological Survey (October 24, 2016)
Indian Treaty Creek	NM	NM	584.4	NM
Pond A	584.6	NM	582.4	581.0
Pond B	582.7	NM	581.4	582.1
Pond C	582.7	NM	581.5	582.2
Big Marsh Pond	582.7	582.41	581.4	580.9
Big Marsh Pond outlet	NM	581.49	580.2	NM
MW2	584.6	583.42	583.4	583.97

[1]Data are from Duwal (1994).

[2]Data are from V3 Companies, Ltd. (2006b).

[3]Data are from EarthTech, Ltd. (written commun., 2005).

The results of the Dupuit-Forchheimer calculation that estimates groundwater discharge into Ponds B and C on October 24, 2016, are presented in table 4. The hydraulic conductivity estimated from the slug tests averaged about 2.9 ft/d for the slag deposits (Gahala, 2019) and the results indicate that the groundwater discharged into Pond B at 11,615 ft³/d and into Pond C at 17,560 ft³/d (table 4).

Groundwater discharge into Pond B, as estimated from the Duwal (1994) study, was 2,543 ft³/d. The hydraulic conductivity as measured from the slug tests in the Duwal (1994) study may have been too low. Changing the horizontal hydraulic conductivity (1.64 ft/d; Duwal, 1994) to what was measured in this study (2.9 ft/d) increased the Duwal discharge values to similar flow results as the present study.

Additionally, during this study, only about five to six seeps were observed in Pond C, and the seep with the highest (356 ft³/d) flow measurement in the Duwal (1994) study could not be identified. The differences in seep observations from the Duwal (1994) study to the present study may have a few causes: (1) it is possible that seeps were not observed during this study because observations and site visits were generally during warmer months—seeps were easier to observe in the colder months because the slightly warmer flowing water from the groundwater melted the surface-water ice on the ponds; (2) the lower flowing seeps may have been filled in by the calcite precipitates, in effect, cutting off that flow or reducing flow enough to inhibit a direct observation. A few seeps were observed to have higher flow velocities and discharge potentially; however, they could not be measured because of inaccessibility.

Flow velocities were measured at three seeps identified along the banks of Pond C, and discharge was estimated based on the height and width of the seep opening. On May 3, 2017, the estimated discharge at seep 1 was higher (2,411 ft³/d)

than any other seep measurement, but on June 30, 2017, flow velocities could not be measured because flow was less than the sensitivity of the flowmeter instrument. These observations of differences in flow indicate a variable discharge rate of the seeps. It also is important to consider that these velocities are only estimates and have high uncertainties associated with them. Seepage meters are more accurate instruments for this type of measurement but were not available for this study. Discharge values estimated from these velocities exceeded the range from seepage meter measurements collected by Duwal (1994). Additional information on the quantity of seeps and the weekly to monthly flow rates in response to lower or higher water levels may be needed for future remediation considerations.

Hydrologic Balance

A water-balance equation assumed steady-state conditions (no change in water level) for 1 day to account for the direction, quantities, and residence time of groundwater discharge into or out of Ponds B and C. These quantities can provide some preliminary estimates of the volumes of groundwater and primary locations for where the groundwater is entering and exiting. The results for the computed groundwater discharge based on equation 3 are shown in table 5. For the computed groundwater discharge, inflows are negative, and outflows are positive; therefore, the negative flow at Pond B indicates the surface water is flowing into the groundwater as recharge through vertical flow (disregarding a nonmeasurable amount going from Pond B to Pond C West). In Pond C, about 1,244 ft³/d of surface water is lost to evaporation, plus an additional 17,574 ft³/d (16,779 ft³/d from Pond C outlet

Table 4.   Calculations of groundwater flow into Ponds B and C, Big Marsh, Chicago, Illinois, for October 24, 2016.

[NAVD 88, North American Vertical Datum of 1988; %, percent]

Date	Groundwater elevation, in feet above NAVD 88	Pond stage, in feet	Length of flow line, in feet	Length of shoreline through which flow exists along flow transect, in feet	Maximum depth of Ponds B and C, in feet	Area of transect along flow direction, in square feet	Flow per unit width, in square feet per day	Groundwater discharge, in cubic feet per day	Water-balance results
Pond B									
Oct. 24, 2016	584.0	582.1	260	470	2	940	11.84	11,615	15,427 (33%)
Pond C									
Oct. 24, 2016	584.0	582.2	260	750	2	1,500	11.84	17,560	15,531 (12%)

to Pond B plus 795 ft³/d at Pond C outlet at rivulet; table 5, fig. 3) of surface water flows from Pond C into Pond B and into Big Marsh Pond. Therefore, to accommodate this loss of surface water, about 15,531 ft³/d of water is entering Pond C from groundwater (as indicated by the positive net groundwater discharge [table 5]). The computed groundwater entering and exiting Ponds B and C indicates the assumption of steady state is reasonable.

The residence time of the groundwater entering and exiting at the ponds was determined by dividing the volume of each pond by the calculated net groundwater discharge per the water-balance results. Pond B has an approximate volume

Table 5.   Hydrologic balance for Ponds B and C on May 3, 2017, at Big Marsh near Lake Calumet, Chicago, Illinois.

[--, not applicable; NM, not measured; GW, groundwater; E, evaporation; P, precipitation; SW_i, surface-water input; SW_o, surface-water output]

Type of flow and description	Pond B	Pond C
Inflows (excluding groundwater), in cubic feet per day		
Precipitation	0	0
Seep 1 at Pond C	--	2,411
Seep 2 at Pond C	--	674
Seep 3 at Pond C	--	202
Pond C outlet to Pond B	16,779	--
Total inflows	16,779	3,287
Outflows (excluding groundwater), in cubic feet per day		
Evaporation	1,352	1,244
Pond B outlet to Pond C West	NM	--
Pond C outlet at rivulet	--	795
Pond C outlet to Pond B	--	16,779
Total outflows	1,352	18,818
Computed groundwater discharge, in cubic feet per day		
net $GW=E-P-SW_i+SW_o$	−15,427	15,531

of 162,193 ft³ and the net groundwater discharge was calculated to be –15,427 ft³/d; therefore, it takes about 10.5 days for the surface water of Pond B to be lost to the groundwater. Pond C has an approximate volume of 149,258 ft³ and a net groundwater discharge of 15,531 ft³/d; therefore, it takes about 9.6 days for the net groundwater discharge to replenish the surface water lost.

Because of the accuracy of the instrument, the application of the method, and limiting environmental conditions, it is important to stress that the results of the hydrologic balance have some uncertainties because of the errors (49.8 percent) associated with the direct surface-water discharge measurements. The Dupuit-Forchheimer equation was used to estimate the expected volumes of groundwater discharge for each pond. The groundwater discharge quantities calculated by the Dupuit-Forchheimer equation for October 24, 2016, indicated generally good agreement for Pond C with the quantities estimated from the hydrologic balance results for May 3, 2017 (tables 2 and 4). The Dupuit-Forchheimer equation overestimated the groundwater discharge into Pond C at 17,560 ft³/d (11.6 percent). The Dupuit-Forchheimer equation underestimated the groundwater discharge from Pond B by 33 percent; thus, there is considerable uncertainty with the net groundwater discharge estimated at Pond B. Additional surface-water and groundwater data are needed to confirm the volume of groundwater exiting Pond B.

Water Quality of Hyperalkaline Ponds and Groundwater at Big Marsh

A total of 9 surface-water samples and 1 groundwater sample were collected at Big Marsh (fig. 2) on October 24 and 25, 2016 (table 6, at the back of this report; water-quality data collected for this study also are available from the USGS National Water Information System database [U.S. Geological Survey, 2018]). Surface-water samples were collected at two

locations in Pond B (Pond B, Pond B West) and four locations in Pond C (Seep 1, Seep 2, Pond C West, and Pond C outlet to Pond B) (fig. 3). Additional surface-water samples were collected at Pond A outlet, Indian Treaty Creek, and Big Marsh Pond outlet (fig. 2). A groundwater sample was collected from well MW2. In general, the groundwater sample (MW2) had the highest concentrations of calcium, barium, strontium, and zinc, and the highest pH of any sample. Concentrations of major ions, metals, and trace elements, along with pH, were elevated at the seeps and decreased with distance from the seeps.

The surface-water and groundwater quality at Big Marsh had exceedances of EPA water quality and environmental criteria for pH, lead, and manganese (U.S. Environmental Protection Agency, 1986). The freshwater chronic aquatic toxicity criteria limit pH to between 6.5 and 9.0 (U.S. Environmental Protection Agency, 1986, 2013). The field pH of groundwater (MW2), Seeps 1 and 2, Pond B, Pond C outlet, Pond C West all exceeded the criteria and Big Marsh Pond outlet just meets the criteria at a pH of 9.0 (table 6).

Concentrations of barium (383 micrograms per liter [µg/L]), calcium (938 milligrams per liter [mg/L]), lead (17.9 µg/L), nickel (31.6 µg/L), strontium (2,320 µg/L), and zinc (73.4 µg/L) were elevated in groundwater relative to their concentrations in surface water. Metals and trace elements within the surface waters that receive discharge from the groundwater seeps were elevated for barium at Seep 1 (343 µg/L), Seep 2 (104 µg/L), and Pond A outlet (122 µg/L / 124 µg/L, duplicate) (table 6). All other surface-water locations had barium concentrations that ranged from 30.5 to 197 µg/L. Elevated calcium concentrations within the surface-water locations were 833 mg/L at Seep 1 and 167 mg/L at Seep 2. All other surface-water locations had calcium concentrations that ranged from 39.1 to 101 mg/L.

Lead concentrations at the seeps were an order of magnitude higher than at any other surface-water location. Seep 1 had a lead concentration of 4.23 µg/L, and Seep 2 had a lead concentration of 4.84 µg/L (table 6), nearly twice the amount of the EPA recommended Aquatic Life Criteria (2.5 µg/L) (U.S. Environmental Protection Agency, 2013). All other surface-water locations had lead concentrations that ranged from 0.069 to 0.175 µg/L. Lead concentrations in the groundwater sample were greater than the chronic aquatic toxicity criteria of 2.5 µg/L based on a hardness of 100 mg/L calcium carbonate ($CaCO_3$) from the EPA Aquatic Life Criteria (U.S. Environmental Protection Agency, 2013).

Alkalinity is an indication of the acid-neutralizing ability of water and is related to the concentration of carbonate compounds and hydroxyl (OH^-) dissolved in the water. For the Big Marsh site, these species are the predominant anions, which makes them essential for evaluating the geochemical evolution of the hydrological systems, in addition to enabling data-quality review for charge imbalance and conductivity imbalance (appendix 1). Alkalinity was measured at the time of sampling,

and the field result is the most representative of the conditions. Total field alkalinity was 1,946 mg/L as $CaCO_3$ in the groundwater, with 1,886 mg/L as $CaCO_3$ of the total coming from hydroxide alkalinity, 60 mg/L as $CaCO_3$ coming from carbonate alkalinity, and 0 mg/L from bicarbonate alkalinity. In surface water, total field alkalinity ranged from 34 (Pond B) to 1,665 mg/L (Seep 1) as $CaCO_3$. Of the total alkalinity of 1,665 mg/L as $CaCO_3$ for Seep 1, 1,535 mg/L as $CaCO_3$ was from hydroxide alkalinity, and 130 mg/L $CaCO_3$ was carbonate alkalinity. In general, alkalinity decreased farther away from the seeps. The second highest total field alkalinity was detected at Indian Treaty Creek at 650 mg/L $CaCO_3$, all of which was in the form of bicarbonate alkalinity.

Quality Assessment and Quality Control

A total of 12 water-quality samples (10 regular [environmental], 1 duplicate at Pond A outlet, and 1 field blank) were collected at Big Marsh. Concentrations measured in the duplicate sample (table 6) indicated consistent detections within 10 percent of the regular sample for major ions and nutrients. The duplicate metals and trace elements were generally consistent with less than 10-percent difference, with the exception of iron and lead (17 percent). The concentrations were near or less than the detection limit of 5 µg/L for iron and 0.02 µg/L for lead; therefore, the differences are not considered to have a substantial effect on the water-quality results for either iron or lead. The field blank had no detections above the detection limits, with the exception of cobalt, which was measured at the detection limit (0.03 µg/L).

Chemical-Mass Balance

In addition to the water balance, which accounts for the water inflow and outflow, a chemical-mass balance computes the chemical rate of change in storage within each pond according to the hydrologic balance results (Harvey, 2016). In this study, the chemical-mass balance provides a single-day quantification for the change in concentrations of selected chemicals based on the water balance of May 3, 2017, and estimates the quantities of chemical that would need to be treated during similar flow.

Chloride and sodium are the conservative tracers applied in this calculation to determine the chemical-mass balance or long-term steady-state conditions of Ponds B and C. The conservative tracer hypothetically is not involved in any geochemical or biological reactions that would alter its concentration. The results are compared to magnesium and calcium, which in this case, are nonconservative ions that react to atmospheric and surface-water conditions. The hydrologic balance equation (eq. 4) is combined with the tracer analyte as follows:

$$\Delta(VC_L)=PC_P-EC_E+SW_iC_i-SW_oC_L+GW_iC_{Gi}-GW_oC_L \qquad (4)$$

where

Δ	is the change of the mass of the tracer within the ponds (pond volume times the concentration of the tracer in the pond);
V	is the pond volume;
C_L	is the concentration of the tracer in the pond;
P	is precipitation;
C_P	is the concentration of the tracer in P multiplied by the volume of P added to each pond;
E	is evaporation;
C_E	is the concentration of the tracer in E (which, in this case, is assumed to be negligible);
SW_i	is the surface-water inflow;
C_i	is the concentration of surface-water inflows;
SW_o	is the surface-water outflow;
GW_i	is the groundwater inflow;
C_{Gi}	is the concentration in groundwater inflows; and
GW_o	is the groundwater outflow.

Surface-water inflow and groundwater inflow, and groundwater outflow and surface-water outflow, are multiplied by the concentrations detected at each inflow and outflow sample location (table 7). Concentrations in groundwater inflows were summed for MW2, Seep 1, and Seep 2. The groundwater discharge for each of the ponds, as determined from equation 3, was applied to the GW_i and GW_o for Ponds B and C in equation 4.

The results of the chemical-mass balance are shown in table 7. Because Pond B has a net surface-water recharge to the groundwater, the concentrations of chloride and sodium are negative, indicating a decrease in their concentration in Pond B as the surface water recharges the groundwater. Pond C had gains in chloride and sodium as the groundwater replenishes the surface water to equilibrate with losses of surface-water outflows. This change in concentrations of chloride and sodium is not equal to decreases at Pond B, indicating a lag time between groundwater and surface water added and removed from Ponds B and C.

The nonconservative tracer, magnesium, maintains an almost equal amount lost in Pond C versus gained in Pond B. The source of the magnesium does not seem to be substantial from the slag, as evident by concentrations below the detection limit at MW2 and Seep 1 (table 6). Magnesium increases in concentrations farther away from Ponds B and C outlet to Pond B. As the magnesium within Pond C outlet to Pond B gets carried toward Pond B and Pond C West, and farther out, the magnesium is reduced at Pond C West, whereas other locations increase in magnesium. The small concentrations of magnesium are added and removed at a steady state. Calcium, which is not conservative and indicates a decrease of 2,407 milligrams per cubic foot (mg/ft³; 85 mg/L), is likely accounting for the precipitation of the calcium into calcite as

it reacts to atmospheric carbon dioxide. The groundwater discharge into Pond C adds 5,350 mg/ft³ (189 mg/L) of calcium that then flows out toward Pond B and Big Marsh Pond and is removed as calcite precipitates farther away from the seeps.

The hydrologic balance and chemical-mass balance are only over a 1-day period. A range in discharge related to elevated water levels and precipitation events has not been investigated because of ongoing changes to Big Marsh. The chemical-mass balance generally supports the assumptions of a steady state (sodium and magnesium) between groundwater and surface-water inflows and outflows, with an indication of a lag time. Additional data regarding the total volume added during precipitation events and geochemical reactions may be needed for the design of a remediation system.

Geochemical Modeling

The conceptual model for the chemical evolution of groundwater and surface water at Big Marsh involves the infiltration of atmospheric precipitation into a shallow, unconfined aquifer comprising calcium-silicate-rich slag and other refuse. Chemical reactions in the calcium-rich slag effectively strip the infiltrating precipitation of its dissolved carbon dioxide, presumably by precipitation of $CaCO_3$. As the groundwater flows through the slag, it dissolves additional calcium as it reacts with a variety of calcium and iron silicates, and lime, which serves to raise the pH to hyperalkaline values above 12. The initial stripping of dissolved carbon dioxide from the infiltrating precipitation through reacting with calcium silicate minerals, such as larnite (Ca_2SiO_4), and the precipitation of calcite in the steel-slag aquifer (Piatak and others, 2015) can be described by the following reaction: $Ca_2SiO_4+2H_2O+2CO_2\rightarrow2CaCO_3+H_4SiO_4$. Once the dissolved inorganic carbon has been stripped from the solution by the precipitation of calcite, further reaction of groundwater with calcium silicate minerals in the aquifer serves to raise the pH of the groundwater as described, for example, by the dissolution reaction of larnite (Roadcap and others, 2005): $Ca_2SiO_4+4H_2O\rightarrow2Ca^{2+}+H_4SiO_4+4OH^-$.

As the groundwater that is devoid of dissolved inorganic carbon emerges into the surface-water environment at Big Marsh, it begins to absorb atmospheric carbon dioxide. The absorbed carbon dioxide reacts with the dissolved calcium to precipitate $CaCO_3$. The pH of the hyperalkaline water drops because of the absorption of atmospheric carbon dioxide as described by the following reactions: $H_2O+CO_2\rightarrow2H^++CO_3^{2-}$ (pH>~10.5) and $H_2O+CO_2\rightarrow H^++HCO_3^-$ (pH<~10.5) and the calcite precipitation reaction $H_2O+CO_2+Ca^{2+}\rightarrow2H^++CaCO_3$. The Big Marsh hydrologic system is actively capturing and storing carbon at the recharge and discharge ends of the shallow groundwater-flow path.

Geochemical modeling can be used to gain quantitative insights into the equilibrium state of groundwater and surface water at Big Marsh described by these reactions. Three

Table 7. Chemical-mass balance for May 3, 2017, at hyperalkaline ponds at Big Marsh, Chicago, Illinois.

[--, no data]

Chemical-mass balance, May 3, 2017	Precipitation, in milligrams per cubic foot per day	Evaporation, in cubic feet per day	Net groundwater discharge, in cubic feet per day	Surface-water inflow, in cubic feet per day	Surface-water outflow, in cubic feet per day	Change in concentration, in milligrams per cubic foot	Concentration divided by volume of pond, in milligrams per cubic foot	Concentration converted to milligrams per liter
			Pond B					
Pond B flux	0	1,352	−15,427	16,779	0	--	--	--
Chloride	0	--	−38,180,102	35,824,364	--	−2,355,738	−14.52	−0.5
Sodium	0	0	−11,532,662	10,452,732	0	−1,079,930	−6.66	−0.2
Magnesium	0	0	−12,013	769,701	0	757,688	4.67	0.2
Calcium	0	0	−409,758,991	19,337,554	0	−390,421,436	−2,407	−85
			Pond C					
Pond C flux	0	1,244	15,531	0	17,574	--	--	--
Chloride	0	--	128,154,288	0	84,547,787	43,606,501	292	10
Sodium	0	0	34,303,481	0	22,393,469	11,910,012	80	3
Magnesium	0	0	94,335	0	936,047	−841,712	−6	−0.2
Calcium	0	0	852,309,572	0	53,794,089	798,515,483	5,350	189

approaches have been used to model the geochemistry of Big Marsh:

1. Water speciation and saturation state modeling using PHREEQC, WATEQ4F, and REACT and Act2 from the Geochemist's Workbench (Bethke, 2008);

2. Aeration kinetic modeling using PHREEQC with the kinetic models of Cravotta (2015); and

3. Reaction path modeling using REACT from the Geochemist's Workbench (Bethke, 2008).

WATEQ4F was used in part to assess the quality of the complete water analyses as described in appendix 1. The kinetic modeling of hypothetical aeration of Big Marsh groundwater is described in the following section.

The equilibrium state of the water samples relative to atmospheric carbon dioxide can be assessed by considering dissolved concentrations of carbon in equilibrium with different partial pressures of carbon dioxide (fig. 6). The pH and

dissolved inorganic carbon concentration of the 10 water samples from Big Marsh are shown in figure 6. They span a range of pH from 7.5 to 12.2 and a range of dissolved inorganic carbon concentrations from 2.7 to 78 mg/L. The lines representing equilibrium with the atmospheric partial pressure of carbon dioxide (PCO_2; 100 percent), 10 percent of the atmospheric partial pressure of carbon dioxide, and 1 percent of the atmospheric partial pressure of carbon dioxide are shown for reference. The samples indicate a systematic progression towards equilibrium, and the groundwater and seep samples are the most out of equilibrium with the atmosphere, the water bodies closest to the seeps are closer to equilibrium with atmosphere, and finally the open water bodies and Indian Treaty Creek are close to equilibrium or slightly supersaturated with respect to atmospheric carbon dioxide. In other words, the groundwater and seeps are highly undersaturated, the proximal waters are moderately undersaturated, and the open waters are saturated or slightly supersaturated with respect to atmospheric carbon dioxide. Surface-water sample sites have
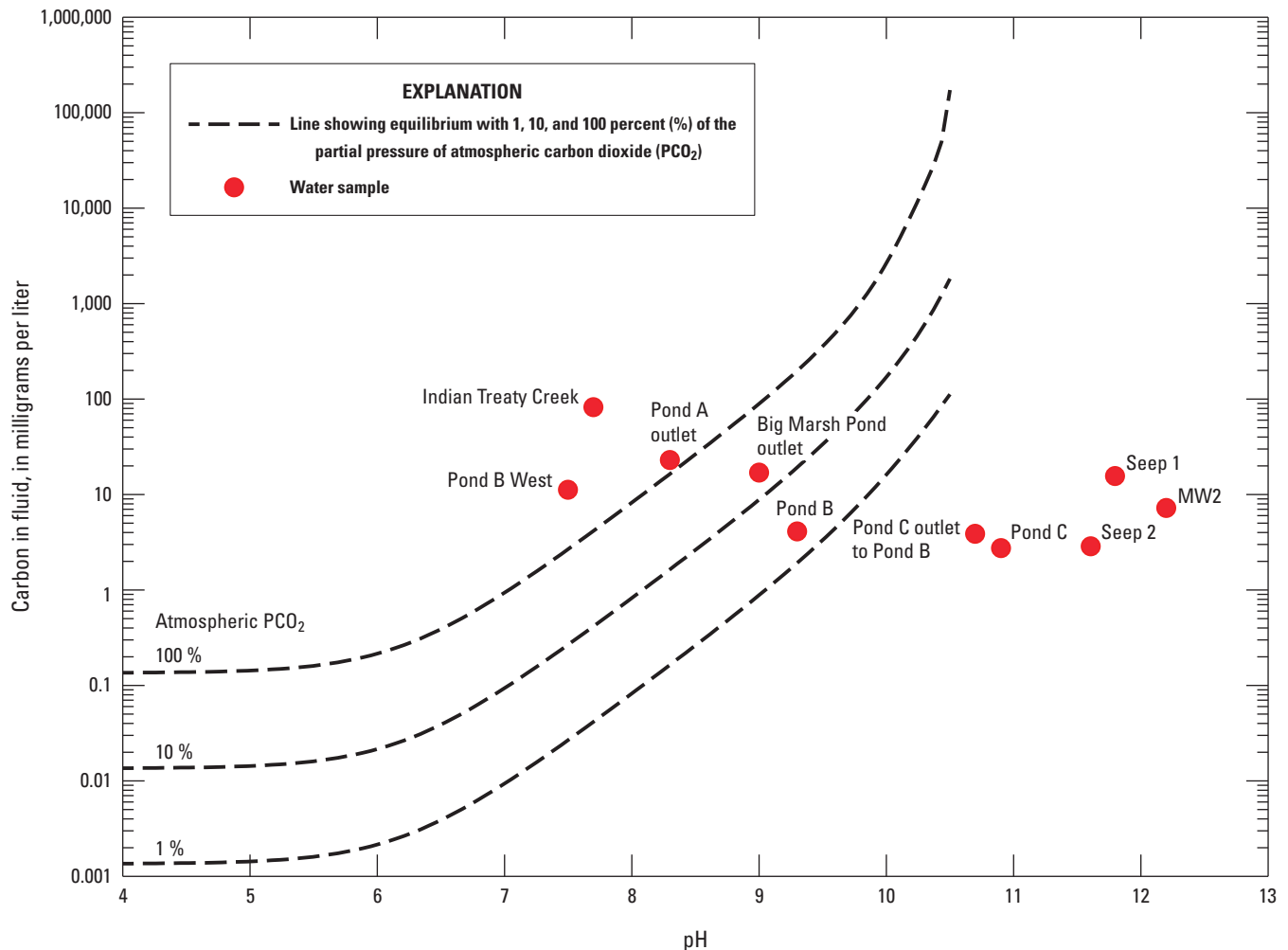

Figure 6.   The pH and dissolved inorganic carbon concentrations of water samples from the Big Marsh site, calculated using the REACT module of the Geochemist's Workbench.

unlimited access to the atmosphere and, therefore, have varying degrees of equilibrium reflective of mainly kinetic limitations on absorption of atmospheric carbon dioxide.

Effects on pH—one of the primary water-quality concerns at Big Marsh—can be evaluated by considering the stability of various minerals in the chemical system Ca-C-O-H under the specific geochemical conditions detected at Big Marsh. In a carbon-free chemical system, the only relevant solid phase is portlandite (Ca[OH]$_2$), the hydrated equivalent of lime (CaO). The distribution of aqueous and solid species in a carbon-free system (Ca-O-H) is shown in figure 7 as a function of pH and dissolved calcium concentration. The Big Marsh water samples also are plotted on this diagram. The distribution of aqueous and solid species in the Ca-C-O-H system is shown in figure 8 as a function of pH and dissolved calcium concentration in equilibrium with atmospheric carbon dioxide (log PCO$_2$=−3.4). The Big Marsh water samples also are plotted on this diagram. The carbon-free diagram (fig. 7) indicates the high-pH end of the range measured in the groundwater and seeps is limited by the stability of portlandite, whereas the diagram constructed, assuming equilibrium with atmospheric carbon dioxide, indicates that the precipitation of CaCO$_3$ may represent the lower limit of pH in these waters.

The saturation state of waters at Big Marsh relative to calcite can further be investigated by examining the saturation indices calculated using WATEQ4F. A saturation index (SI) is defined by the following formula:

$$SI = \log\left(\frac{IAP}{K_{sp}}\right) \tag{5}$$

where

IAP is the ion activity product from a water analysis and

K_{sp} is the solubility product for a specific mineral.

A negative saturation index indicates undersaturated conditions (the mineral dissolves), a saturation index of zero indicates saturation, and a positive saturation index indicates supersaturation (the mineral precipitates). The results of the saturation index calculations for the Big Marsh water samples are shown in figure 9. These results indicate that the lowest pH sample is undersaturated with respect to calcite and the slightly alkaline samples are saturated with respect to calcite, but high-pH samples are supersaturated with respect to calcite.

Figure 7.   Logarithm of the activity of the calcium ion (log aCa^{2+}) versus pH diagram showing the stability fields of solid and aqueous species at 25 degrees Celsius in the carbon-free system Ca-O-H, calculated using the Act2 module of the Geochemist's Workbench (Bethke, 2008).

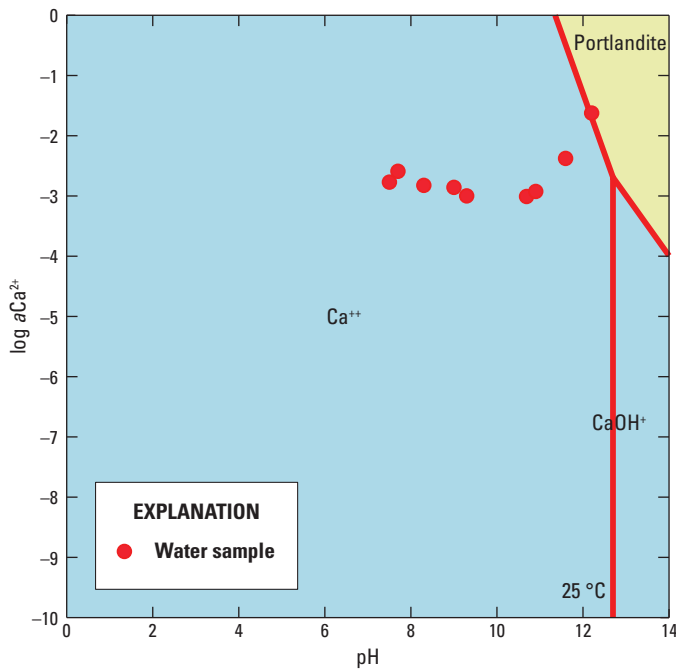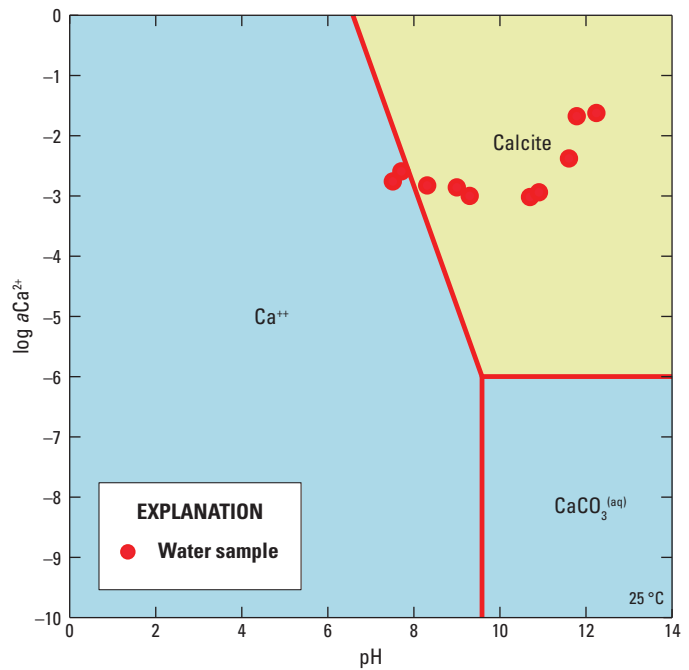**Figure 8.**   Logarithm of the activity of the calcium ion (log aCa^{2+}) versus pH diagram showing the stability fields of solid and aqueous species at 25 degrees Celsius in the system Ca-C-O-H, calculated using the Act2 module of the Geochemist's Workbench (Bethke, 2008).
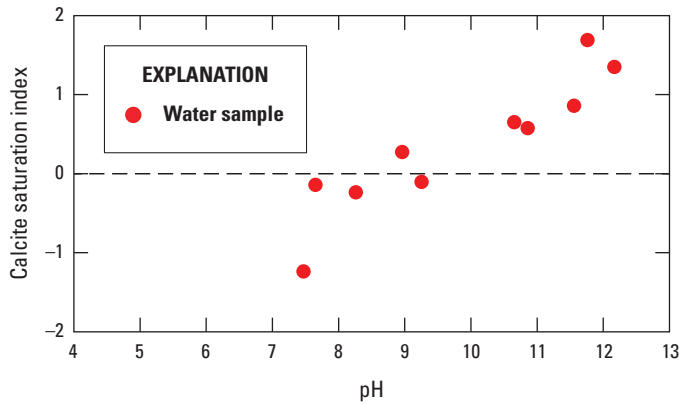
Figure 9. Variation of the saturation index of calcite with pH for the Big Marsh water samples.

Implications for Remediation

The primary concern for remediation at Big Marsh is the hyperalkaline pH of Ponds B and C, seeps, and groundwater. Several approaches have been indicated for the remediation of the hyperalkaline waters at Big Marsh (Roadcap and others, 2005; Waska, 2013). Roadcap and others (2005) considered carbon dioxide sparging, air sparging, and hydrochloric acid addition. They determined that carbon dioxide sparging and acid addition were the most efficient and that pH was stabilized at a pH near 7 by dissolution of preexisting calcite. Air sparging also was effective but was roughly 100 times slower than carbon dioxide sparging. Waska (2013) completed benchtop experiments with permeable reactive barrier materials and determined that Apatite-II™—a fish bone material—was effective in lowering pH; however, this material also released substantial amounts of nutrients, which may not be suitable at Big Marsh because of concerns about the potential for algal blooms and eutrophication.

Also of concern are water-quality issues related to trace elements, which are localized and limited to lead and manganese. The elevated dissolved lead concentrations are detected in the seeps and groundwater. Lead is known to be effectively removed by coprecipitation with calcite (Fulghum and others, 1988); thus, calcite precipitation at Big Marsh should eliminate water-quality issues related to lead. The 3 samples with elevated lead concentrations (2 seeps and 1 groundwater sample) have the highest pH and are all supersaturated with respect to calcite, indicating that calcite precipitation has not happened, and therefore, lead has not been removed from these waters (fig. 9). Cerussite ($PbCO_3$) and rhodochrosite ($MnCO_3$) are substantially undersaturated with saturation indices ranging from −8.5 to −2.8 and from −14.1 to −1.7, respectively. The factors that affect the rate of $CaCO_3$ nucleation at Big Marsh are uncertain but warrant further investigation for the design of treatment systems to remediate the high-pH waters.

Geochemical modeling indicates the waters should reach a pH near 7.5 if they are in equilibrium with atmospheric carbon dioxide. Techniques to accelerate this process can partially be assessed using the models of Cravotta (2015) to describe the outgassing and ingassing of carbon dioxide and oxygen in the context of treatment systems for coal mine drainage. The model assumes that outgassing and ingassing happen at the same rate and are driven by the compositional gradient of the gas species between water and atmosphere. Examples of gradient-driven gas exchange include the ingassing of atmospheric oxygen into anoxic waters upon emergence from the subsurface or the outgassing of carbon dioxide because of supersaturation related to aquatic plant respiration in wetland settings. The applicability of the outgassing and ingassing model of Cravotta (2015) to Big Marsh warrants further evaluation because it was designed for near neutral to slightly acidic conditions. The model uses a first-order asymptotic function where the driving force is the gradient of the carbon dioxide concentration dissolved in water relative to the ambient atmosphere. The rate should slow over time as the gradient diminishes.

The flux of atmospheric carbon dioxide to emerging groundwaters at Big Marsh is further complicated by uncertainties in the role that calcite nucleation plays in establishing and maintaining compositional gradients of carbon dioxide between the atmosphere and water. Specifically, a key question is whether the atmospheric carbon dioxide absorption reaction or the calcite nucleation reaction is the rate-limiting step. The supersaturated state of the high-pH waters at Big Marsh indicates that the nucleation of calcite is the rate-limiting step in the overall process, which means that the kinetic model for carbon dioxide ingassing may be directly applied to Big Marsh. In a situation where calcite precipitation is rapid relative to carbon dioxide absorption, calcite saturation would serve to buffer dissolved inorganic carbon concentrations and, thus, the gradient between atmosphere and water. In contrast, if calcite precipitation is slow relative to carbon dioxide absorption, then rates would slow as surface water approaches saturation with respect to the partial pressure of atmospheric carbon dioxide.

An additional key uncertainty in the current model is how well the field-derived rate constants for carbon dioxide outgassing and ingassing apply to Big Marsh. This model provides insights into the relative efficiencies of various aeration approaches, although quantitative application to the Big Marsh setting is questionable. The four aeration scenarios for which rate constants are available are (1) aeration of a stagnant, nonflowing waterbody; (2) aeration using a riprap channel; (3) aeration using a long spillway that maximizes the ratio of surface area to depth of water flowing over the spillway; and (4) active mechanical aeration.

In the aeration simulations (scenarios 1, 2, 3, and 4), all water starts at a pH of about 12.7 (fig. 9). With ongoing aeration, the pH drops over time. Based on the model, diffusion of carbon dioxide into stagnant, mainly nonflowing water (scenario 1) is extremely slow, requiring more than 20,000 hours
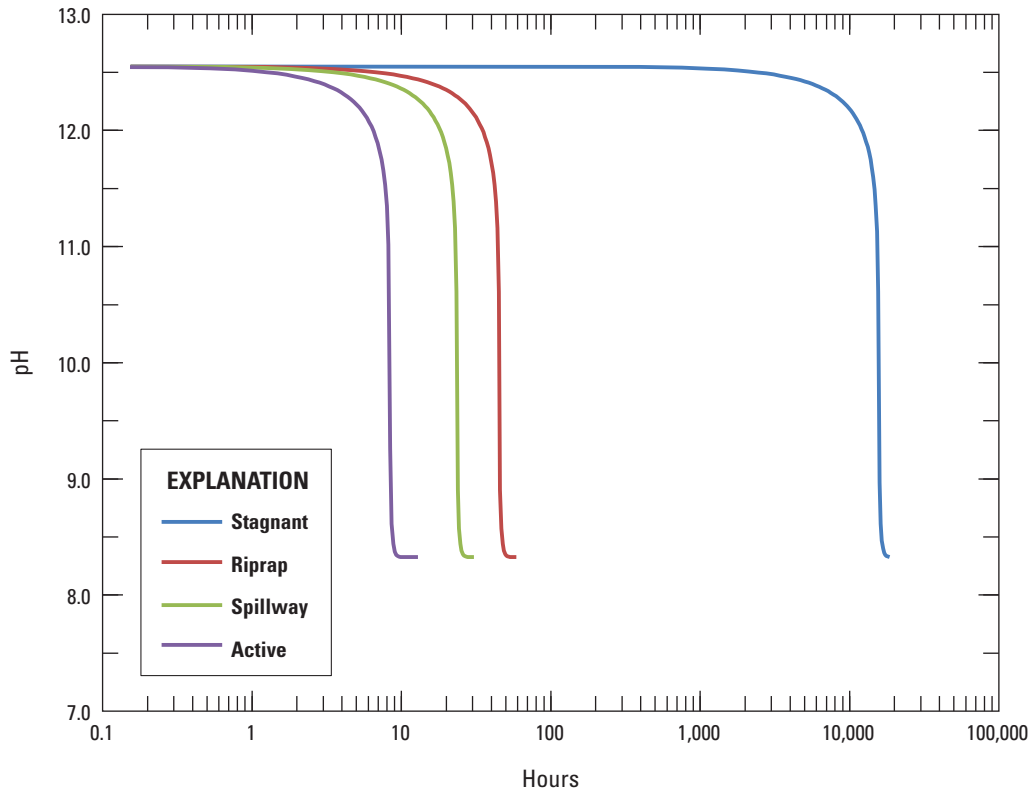
Figure 10.   Variation of pH with time for Big Marsh groundwater because of the absorption of atmospheric carbon dioxide at 10 degrees Celsius using various modes of aeration, calculated using the PHREEQC using the kinetic model of Cravotta (2015).

to reach equilibrium with the atmosphere. All types of passive (scenarios 1, 2, and 3) and active (scenario 4) aeration accelerate this process with equilibration times varying between 8 hours for active aeration and 45 hours for riprap channels.

The temperature of the process also affects the rate of equilibration. Gases, such as carbon dioxide, are more soluble in water at lower temperatures than higher temperatures. The increased solubility at a low temperature makes the compositional gradient of partial pressure of carbon dioxide in the atmosphere relative to its solubility in water greater, which in theory, should drive the reaction faster according to the model (fig. 10). The temperature-dependent solubility of carbon dioxide also affects the final pH of the water equilibrated with the atmosphere, as shown in figure 11. Equilibration at cooler temperatures should have a lower pH than equilibration at warmer temperatures. The mean annual temperature in the Chicago area is 13.7 degrees Celsius (°C). The average low temperature is in January (−7.7 °C), and the average high temperature is in July (27.2 °C) (U.S. Climate Data, 2019).

The final selection of a remediation strategy for water quality at Big Marsh and its eventual implementation will require additional investigation. Enhancing natural processes, either passively or actively, to accelerate the absorption of

atmospheric carbon dioxide probably offers the least long-term environmental risk because it relies on the natural acid-buffering capacity of $CaCO_3$ and avoids challenges, for example, in trying to add acid to maintain surface waters within a restricted range of pH. Permeable reactive barriers, using fish bone or other organic materials (Waska, 2013), risk nutrient loading to and eutrophication of Big Marsh. Acid addition, for example, by dosing with hydrochloric or some other acid; the amendment of soils with acidic material (ferrous or ferric sulfate salts); or permeable reactive barriers containing acid-generating materials (pyruite), will likely present long-term challenges with respect to maintaining pH within acceptable limits because of a lack of natural geochemical buffers.

The development of an implementation presents some surmountable challenges. The flat land surface in the area and the similar water levels of the Big Marsh and Lake Michigan limit the potential for turbulent surface-water flow, making passive aeration using a riprap channel or spillway difficult to achieve. Mechanical means to achieve equilibrium with atmospheric carbon dioxide include air sparging of existing water bodies, as indicated by Roadcap and others (2005), or the pumping of groundwater to an above-ground holding tank to achieve the gradient needed for "passive" aeration using the
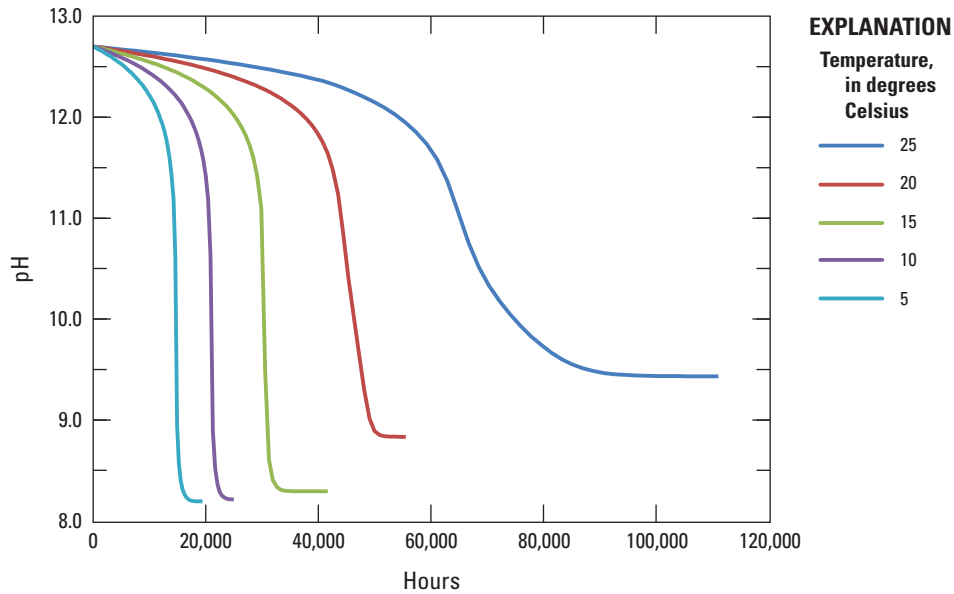
Figure 11. The effect of temperature (in degrees Celsius [°C]) on the variation of pH with time for Big Marsh groundwater because of the absorption of atmospheric carbon dioxide in a stagnant water body, calculated using the PHREEQC using the kinetic model of Cravotta (2015).

approaches modeled by Cravotta (2015) or other approaches. The ultimate selection of sparging versus aeration warrants consideration of factors such as energy requirements, failure modes because of scaling on mechanical components and other factors, and physical footprint.

Several data gaps remain before a final remedial strategy can be selected and designed for Big Marsh. These data gaps include the documentation of the spatial extent of high-pH groundwater and its discharge areas, validation of the geochemical model under these extreme conditions of hyperalkaline pH, and the scalability of a selected approach. These data gaps can be addressed through three tasks:

1. Complete benchtop experiments to refine rate constants for carbon dioxide absorption and calcite nucleation using "synthetic" groundwater that is geochemically similar to hyperalkaline groundwater at Big Marsh. Using "synthetic" groundwater is more feasible than trying to collect groundwater from the site, isolating it from interactions with atmospheric carbon dioxide, and transporting it to the laboratory. The identification of the rate-limiting steps (carbon dioxide absorption versus calcite nucleation) will be essential for design. The calibration of rate constants for Big Marsh conditions will also be essential for scaling the treatment system to

an appropriate size. Additional seasonal measurements of water levels, flow, and pH measurements are needed to understand the full range of high-pH water needing to be treated. The quantity of groundwater discharging at Pond B also needs additional data to refine the results of this preliminary water balance.

2. Complete pilot tests in the field. Small-scale pilot tests represent an inexpensive means of evaluating candidate technologies using the actual water being treated under the climate conditions of the site. Ideally, the pilot test should minimally span the time from high summer temperatures to colder fall and winter temperatures.

3. Delimit the extent of the hyperalkaline plume requiring treatment at the site by installing a series of monitoring wells or piezometers along the eastern part of Big Marsh. The current extent of high-pH waters and calcite precipitates delimit the general extent of the hyperalkaline groundwater, but effective remediation will require finer resolution. Consideration of potential future needs for pumping groundwater for treatment relative to the cost of installation may be helpful in the selection of the number and size of monitoring wells or piezometers.

Summary and Conclusions

Big Marsh is a hemimarsh area undergoing reclamation for higher value use because of historical impairment because of slag-fill material deposited throughout the area during the early to mid-1900s. Ponds within Big Marsh have hyperalkaline (pH greater than 12) waters and pose a human and ecological risk. Through cooperation with the U.S. Environmental Protection Agency, Brownfields Program, and collaboration with the City of Chicago's Park District, the U.S. Geological Survey investigated remediation options of the hyperalkaline ponds to inform future remedial designs. A water-level survey, water-quality samples, and flow measurements were completed to calculate a water-balance analysis and a chemical-mass balance analysis. The water-quality data were applied in geochemical modeling to understand the current conditions and evaluate various remediation options for reducing the pH within the ponds.

A water-balance analysis determined that the ponds are at a steady-state condition where the water entering the ponds is equal to the water exiting the ponds. The hydrologic balance indicated that Pond B recharges the groundwater and Pond C receives the most groundwater from the slag-fill aquifer.

The chemical-mass balance also confirmed that Pond B is recharging the groundwater as indicated by the chloride and sodium concentrations, but there may be a lag time between groundwater and surface water added and removed from Ponds B and C. Magnesium concentrations in Ponds B and C were near equilibrium, indicating the assumption of hydrologic steady-state conditions applied to the hydrologic balance equation is reasonable. Calcium concentrations decrease as dissolved calcium reacts with carbon dioxide to produce calcite as it precipitates out and settles along the bottom of Ponds B and C.

The hydrologic balance and chemical-mass balance only apply to a 1-day period. A range in water-balance component values such as the discharge rates of the surface water during high and low precipitation events may be needed to create a more robust hydrologic balance and chemical-mass balance. Geochemical responses to high precipitation events and drought (low water conditions) may be necessary for the design of a future remediation system.

A total of three approaches were used to interpret the aqueous geochemistry of Big Marsh and evaluate remediation options. Water speciation determined that the system indicated a progression with the groundwater and seep samples as being the most out of equilibrium and were undersaturated with respect to atmospheric carbon dioxide. Proximal waters were moderately saturated whereas the more distal open waters were saturated or slightly supersaturated with atmospheric carbon dioxide.

The initial pH of the groundwater is largely controlled by the stability of portlandite and other calcium silicates in the steel-making slag that composes the shallow, unconfined aquifer at the site. Upon emerging from the subsurface, the water absorbs atmospheric carbon dioxide, which results in a lowering of the pH, and the dissolved calcium reacts to produce calcite.

The results of the geochemical modeling indicate that the facilitation of the equilibration of groundwater with atmospheric carbon dioxide may be the best approach for achieving water-quality goals at Big Marsh. This approach has the advantage of buffering pH through the precipitation of calcium carbonate—a feature that various acid addition strategies lack. Implementation of a remedial approach will likely require mechanical pumping of either air or water because the shallow topography and small difference in elevation between the Big Marsh ponds and Lake Michigan mean that the limited natural gradient will be difficult to use. Final selection of a remedial strategy will require an improved understanding of the rates of relevant reactions under these high-pH conditions and the nature and extent of the hyperalkaline groundwater plume.

References Cited

Bethke, C.M., 2008, Geochemical and biogeochemical reaction modeling, 2d ed.: New York, Cambridge University Press, 543 p.

Bouwer, H., and Rice, R.C., 1976, A slug test for determining hydraulic conductivity of unconfined aquifers with completely or partially penetrating wells: Water Resources Research, v. 12, no. 3, p. 423–428. [Also available at https://doi.org/10.1029/WR012i003p00423.]

Buchanan, T.J., and Somers, W.P., 1969, Discharge measurements at gaging stations: U.S. Geological Survey Techniques of Water-Resources Investigations, book 3, chap. A8, 65 p. [Also available at https://pubs.usgs.gov/twri/twri3a8/.]

Cravotta, C.A., III, 2015, Monitoring, field experiments, and geochemical modeling of Fe(II) oxidation kinetics in a stream dominated by net-alkaline coal-mine drainage, Pennsylvania, USA: Applied Geochemistry, v. 62, p. 96–107. [Also available at https://doi.org/10.1016/j.apgeochem.2015.02.009.]

Cunningham, W.L., and Schalk, C.W., comps., 2011, Groundwater technical procedures of the U.S. Geological Survey: U.S. Geological Survey Techniques and Methods, book 1, chap. A1, 151 p., accessed October 2016 at https://pubs.usgs.gov/tm/1a1/.

Duwal, K., 1994, Event-based and seasonal precipitation effects on ground water-wetlands interactions near Lake Calumet, southeast Chicago, Illinois: University of Illinois at Chicago, master's thesis, 78 p.

Fishman, M.J., ed., 1993, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of inorganic and organic constituents in water and fluvial sediments: U.S. Geological Survey Open-File Report 93–125, 211 p. [Also available at https://doi.org/10.3133/ofr93125.]

Fishman, M.A., and Friedman, L.C., 1989, Methods of determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, book 5, chap. A1, 545 p. [Also available at https://doi.org/10.3133/twri05A1.]

Fulghum, J.E., Bryan, S.R., Linton, R.W., Bauer, C.F., and Griffis, D.P., 1988, Discrimination between adsorption and coprecipitation in aquatic particle standards by surface analysis techniques—Lead distributions in calcium carbonates: Environmental Science & Technology, v. 22, no. 4, p. 463–467. [Also available at https://doi.org/10.1021/es00169a016.]

Gahala, A.M., 2019, Water level data from single-well (slug) tests at a monitoring well in Big Marsh, Chicago, Illinois: U.S. Geological Survey data release, https://doi.org/10.5066/P9VUAQ35.

Garbarino, J.R., 1999, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of dissolved arsenic, boron, lithium, selenium, strontium, thallium, and vanadium using inductively coupled plasma-mass spectrometry: U.S. Geological Survey Open-File Report 99–093, 30 p. [Also available at https://doi.org/10.3133/ofr9993.]

Garbarino, J.R., Kanagy, L.K., and Cree, M.E., 2006, Determination of elements in natural-water, biota, sediment, and soil samples using collision/reaction cell inductively coupled plasma-mass spectrometry: U.S. Geological Survey Techniques and Methods, book 5, chap. B1, 88 p. [Also available at https://pubs.usgs.gov/tm/2006/tm5b1/.]

Hamon, R.W., Weiss, L.L., and Wilson, W.T., 1954, Insolation as an empirical function of daily sunshine duration: Monthly Weather Review, v. 82, no. 6, p. 141–146. [Also available at https://doi.org/10.1175/1520-0493(1954)082%3C0141:IAAEFO%3E2.0.CO;2.]

Hartke, E.J., Hill, J.R., and Reshin, M., 1975, Environmental geology of Lake and Porter Counties, Indiana—An aid to planning: Bloomington, Ind., Indiana Geological Survey Special Report no. 11, 57 p.

Harvey, J.W., 2016, Hydrologic exchange flows and their ecological consequences in river corridors, chap. 1 *of* Jones, J.B., and Stanley, E.H., eds., Stream ecosystems in a changing environment: Reston, Va., Elsevier, 83 p., accessed March 8, 2018, at https://doi.org/10.1016/B978-0-12-405890-3.00001-4.

Kay, R.T., Duwelius, R.F., Brown, T.A., Micke, F.A., and Witt-Smith, C.A., 1996, Geohydrology, water levels and directions of flow, and occurrence of light-nonaqueous-phase liquids on ground water in northwestern Indiana and the Lake Calumet area of northeastern Illinois: U.S. Geological Survey Water-Resources Investigations Report 95–4253, 84 p. [Also available at https://doi.org/10.3133/wri954253.]

Kay, R.T., Greeman, T.K., Duwelius, R.F., King, R.B., Nazimek, J.E., and Petrovski, D.M., 1997, Characterization of fill deposits in the Calumet region of northwestern Indiana and northeastern Illinois: U.S. Geological Survey Water-Resources Investigations Report 96–4126, 36 p. [Also available at https://doi.org/10.3133/wri964126.]

National Oceanic and Atmospheric Administration, 2017, Record of climatological observations: National Centers for Environmental Information web page, accessed February 23, 2017, at https://www.ncdc.noaa.gov/.

Patton, C.J., and Kryskalla, J.R., 2003, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Evaluation of alkaline persulfate digestion as an alternative to Kjeldahl digestion of determination of total and dissolved nitrogen and phosphorus in water: U.S. Geological Survey Water-Resources Investigations Report 2003–4174, 33 p. [Also available at https://doi.org/10.3133/wri034174.]

Patton, C.J., and Kryskalla, J.R., 2011, Colorimetric determination of nitrate plus nitrite in water by enzymatic reduction, automated discrete analyzer methods: U.S. Geological Survey Techniques and Methods, book 5, chap. B8, 34 p. [Also available at https://doi.org/10.3133/tm5B8.]

Piatak, N.M., Parsons, M.B., and Seal, R.R., II, 2015, Characteristics and environmental aspects of slag—A review: Applied Geochemistry, v. 57, p. 236–266. [Also available at https://doi.org/10.1016/j.apgeochem.2014.04.009.]

Roadcap, G.S., Kelly, W.R., and Bethke, C.M., 2005, Geochemistry of extremely alkaline (pH>12) ground water in slag-fill aquifers: Ground Water, v. 43, no. 6, p. 806–816. [Also available at https://doi.org/10.1111/j.1745-6584.2005.00060.x.]

Roberts, W.J., and Stall, J.B., 1966, Computing lake evaporation in Illinois: Water Resources Research, v. 2, no. 2, p. 205–208. [Also available at https://doi.org/10.1029/WR002i002p00205.]

Rydlund, P.H., Jr., and Densmore, B.K., 2012, Methods of practice and guidelines for using survey-grade global navigation satellite systems (GNSS) to establish vertical datum in the United States Geological Survey: U.S. Geological Survey Techniques and Methods, book 11, chap. D1, 102 p. with appendixes. [Also available at https://doi.org/10.3133/tm11D1.]

Turnipseed, D.P., and Sauer, V.B., 2010, Discharge measurements at gaging stations: U.S. Geological Survey Techniques and Methods, book 3, chap. A8, 87 p. [Also available at https://pubs.usgs.gov/tm/tm3-a8/.]

U.S. Climate Data, 2019, Climate Chicago, Illinois: U.S. Climate Data web page, accessed August 14, 2019, at https://www.usclimatedata.com/climate/chicago/illinois/united-states/usil0225.

U.S. Environmental Protection Agency, 1986, Quality criteria for water, 1986: Washington D.C., U.S. Environmental Protection Agency, Report 440/5–86–001, 453 p.

U.S. Environmental Protection Agency, 2013, Aquatic life ambient water quality criteria for ammonia—Freshwater: Washington D.C., U.S. Environmental Protection Agency, Office of Water, Report 822–R–13–001, 253 p.

U.S. Geological Survey, variously dated, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1–A10, accessed October 2016 at https://pubs.water.usgs.gov/twri9A.

U.S. Geological Survey, 2018, USGS water data for the Nation: U.S. Geological Survey National Water Information System database, accessed September 2018 at https://doi.org/10.5066/F7P55KJN.

V3 Companies, Ltd., 2006a, Calumet area hydrologic master plan (HMP)—Executive summary (volume I): Chicago, Ill., V3 Companies, Ltd., 36 p.

V3 Companies, Ltd., 2006b, Volume V—Water level monitoring, groundwater seeps and water quality monitoring report: Chicago, Ill., V3 Companies, Ltd., 17 p.

Wang, H.F., and Anderson, M.P., 1982, Introduction to groundwater modeling—Finite differences and finite element methods: San Diego, Calif., Academic Press, Inc., 52 p.

Waska, K., 2013, Hyperalkaline aquifers of Calumet wetlands—Environmental interactions between geochemistry and microbiology: DeKalb, Ill., Northern Illinois University, Ph.D. dissertation, 311 p.

Weather Underground, 2017, Weather history for KORD—June 2017: The Weather Channel web page, accessed August 23, 2017, at https://www.wunderground.com/history/airport/KORD/2017/6/30/DailyHistory.html?&reqdb.zip=&reqdb.magic=&reqdb.wmo=.

Table 6 and Appendix 1

Table 6. Water-quality results of surface-water and groundwater samples at Big Marsh, Chicago, Illinois.

[mg/L, milligram per liter; --, no sample; µS/cm, microsiemens per centimeter; °C, degrees Celsius; NTU, nephelometric turbidity unit; <, less than detection limit; E, estimated; NA, not available; µg/L, microgram per liter; d, diluted; n, below the laboratory reporting level and above the long-term method detection level]

Sample metric	Groundwater sample			Surface-water samples		
	37N14E-13.3a1 (MW2)	Seep 1	Seep 2	Pond B	Pond C outlet to Pond B	Pond B West
Station number	41412087335701	414122087340101	414119087340101	414123087340203	414118087341201	414123087340202
Date	Oct. 25, 2016	Oct. 24, 2016	Oct. 24, 2016	Oct. 25, 2016	Oct. 25, 2016	Oct. 25, 2016
Time	1030	1310	1457	1024	1400	952
Field measurements						
Dissolved oxygen, in mg/L	5.0	0.3	6.9	8.9	7.3	4.0
pH	12.2	11.8	11.6	9.3	10.7	7.5
Specific conductance, in µS/cm at 25 °C	9,760	8,890	5,330	418	438	608
Temperature, in °C	16.7	17.6	16.1	10.6	11.9	9.8
Turbidity, water, NTU	0.4	--	--	25	9.1	21
Total alkalinity, field, as calcium carbonate, in mg/L	1,946	1,665	280	34	36	94
Hydroxide alkalinity, field, as calcium carbonate, in mg/L	1,886	1,535	256	0	3.2	0
Carbonate alkalinity, field, as calcium carbonate, in mg/L	60	130	24	0	32.8	0
Bicarbonate alkalinity, field, as calcium carbonate, in mg/L	0	0	0	34	0	94
Major cations and anions, in milligrams per liter unless otherwise noted, dissolved						
Calcium	938	833	167	40.7	39.1	69
Magnesium	<0.055	<0.055	0.162	1.62	1.47	3.68
Potassium	25.3	22.7	23.1	18.4	17.7	21.6
Sodium	26.4	26.3	25.3	22.0	20.8	23.4
Alkalinity, laboratory, in milligrams per liter as calcium carbonate	E 2,420	E 2,250	293	37.9	26.1	127
Chloride	87.4	110	94	75.4	70.3	88.9
Fluoride	E 3	E 2.84	E 1.56	2.08	2.2	1.48
Silica, as silicate nutrients	0.176	0.354	3.48	4.5	5.29	10.5

Table 6   27

Table 6. Water-quality results of surface-water and groundwater samples at Big Marsh, Chicago, Illinois.—Continued

Sample metric	Groundwater sample	Surface-water samples				
	37N14E–13.3a1 (MW2)	Seep 1	Seep 2	Pond B	Pond C outlet to Pond B	Pond B West
Nutrients						
Sulfate	3.81	9.82	10.8	23	24	17.2
Ammonia, as nitrogen	4.69	3.52	0.84	0.33	0.58	2.78
Nitrate plus nitrite, as nitrogen	E 0.277	E 0.297	E 0.045	E 0.002	E 0.369	E 0.071
Nitrite, as nitrogen	E 0.091	E 0.281	E 0.114	E 0.109	E 0.154	E 0.007
Orthophosphate, as phosphorus, in µg/L	E 0.002	E 0.00011	E 0.00015	E 0.003	E 0.0005	E 0.004
Metals and trace elements, in micrograms per liter						
Aluminum	19.6	18.0	10.5	44.3	41.2	3.3
Barium	383	343	104	30.5	32.5	79
Beryllium	<0.04	<0.04	<0.03	<0.01	<0.01	<0.01
Cadmium	<0.12	<0.12	<0.09	0.08	0.08	0.04
Chromium	<2	<2	<1.5	0.53	0.83	<0.5
Cobalt	0.15	0.26	0.17	0.17	0.18	0.18
Copper	<0.8	2.2	2.2	1.4	1.8	<0.2
Iron	48.8	52.7	12.2	70.5	56.2	110
Lead	17.9	4.23	4.84	0.905	0.987	0.069
Lithium	34.2	50.7	41.2	34.4	33.1	29.5
Manganese	<1.6	<1.6	<1.2	5.69	2.77	270
Molybdenum	3.97	4.89	6.13	19.1	20.1	12.8
Nickel	31.6	22.4	10.1	4.5	4.4	1.9
Silver	<4	<4	<3	<1	<1	<1
Strontium	2,320	1,480	549	266	260	323
Thallium	<0.08	<0.08	<0.06	<0.02	<0.02	<0.02
Vanadium	<0.4	<0.4	0.69	4.1	5.8	0.2
Zinc	73.4	<8	<6	<2	<2	<2
Antimony	<0.12	<0.12	0.26	0.98	0.94	0.80
Arsenic	1.3	1.2	1.0	1.6	1.5	1.8
Boron	157	123	99	145	145	18
Selenium	0.22	0.33	0.21	0.49	0.57	0.16
Uranium	<0.04	<0.04	<0.03	0.16	0.09	0.39

Table 6. Water-quality results of surface-water and groundwater samples at Big Marsh, Chicago, Illinois.—Continued

Sample metric	Surface-water samples					Field blank sample
	Pond C West	Pond A outlet	Pond A outlet (duplicate)	Big Marsh Pond outlet	Indian Treaty Creek	
Station number	414123087340201	414134087335601	414134087335601	414121087342001	414121087342002	414134087335601
Date	Oct. 25, 2016	Oct. 25, 2016	Oct. 25, 2016	Oct. 25, 2016	Oct. 25, 2016	Oct. 25, 2016
Time	1050	1230	1230	1500	1530	1645
Field measurements						
Dissolved oxygen, in mg/L	3.3	10	10	15.2	5.5	--
pH, field (standard units)	10.9	8.3	8.3	9.0	7.7	--
Specific conductance, in µS/cm	523	672	672	982	1,890	--
Temperature, in °C	10.8	10	10	12.4	10	--
Turbidity, water, NTU	1,280	10	10	14	12	--
Total alkalinity, field, as calcium carbonate, in mg/L	36	193	188	142	650	--
Hydroxide alkalinity, field, as calcium carbonate, in mg/L	13.4	0	0	0	0	--
Carbonate alkalinity, field, as calcium carbonate, in mg/L	22.8	0	0	0	0	--
Bicarbonate alkalinity, field, as calcium carbonate, in mg/L	0	193	188	142	650	--
Major cations and anions, in micrograms per liter unless otherwise noted, dissolved						
Calcium	47.1	59	58.9	55.4	101	<0.022
Magnesium	0.411	28.4	28.4	38.1	48	<0.011
Potassium	20.7	9.22	9.17	21.9	43	<0.06
Sodium	24.2	29.5	29.6	80.3	200	<0.01
Alkalinity, laboratory, in milligrams per liter as calcium carbonate	25.4	161	161	147	570	<4
Chloride	99.6	45.7	46.4	128	204	<0.02
Fluoride	1.48	1.36	1.35	0.59	1	<0.01
Silica, as silicate nutrients	4.61	13.2	12.9	6.63	21	<0.018

Table 6   29

Table 6. Water-quality results of surface-water and groundwater samples at Big Marsh, Chicago, Illinois.—Continued

Sample metric	Surface-water samples					Field blank sample
	Pond C West	Pond A outlet	Pond A outlet (duplicate)	Big Marsh Pond outlet	Indian Treaty Creek	
Nutrients						
Sulfate	12.5	105	107	149	18	<0.02
Ammonia, as nitrogen	0.19	0.23	0.24	<0.1	9	<0.1
Nitrate plus nitrite, as nitrogen	E 0.009	NA	NA	NA	E 0.109	NA
Nitrite, as nitrogen	E 0.063	E 0.008	E 0.007	E 0.008	E 0.133	NA
Orthophosphate, as phosphorus, in µg/L	E 0.0031	E 0.002	E 0.001	E 0.01	E 0.0173	NA
Metals and trace elements, in micrograms per liter						
Aluminum	22.3	4.1	4.0	3.4	<6	<3
Barium	54.9	122	124	49.6	197	<0.1
Beryllium	<0.01	<0.01	<0.01	<0.01	<0.02	<0.01
Cadmium	0.04	0.06	0.09	<0.03	<0.03	<0.03
Chromium	<0.5	<0.5	<0.05	<0.5	3.48	<0.05
Cobalt	0.20	0.08	0.08	0.33	2.93	0.03
Copper	1.8	0.6	0.6	0.84	1.01	<0.2
Iron	6.1	8.9	<5	16.4	202	<5
Lead	0.091	0.06	0.05	0.139	0.175	<0.02
Lithium	40.9	58.9	60	43.7	106	<0.15
Manganese	0.48	2.28	2.32	3.32	450 d	<0.4
Molybdenum	6.83	15.3	15.4	7.97	2.98 d	<0.05
Nickel	8.2	1.3	1.4	2.9	9.15	<0.2
Silver	<1	<1	<1	<1	<1	<1
Strontium	356	425	437	361	462	<0.5
Thallium	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Vanadium	1.0	1.1	1.2	1.4	1.13	<0.1
Zinc	<2	<2	<2	<2	3.7 n	<2
Antimony	0.32	0.90	0.91	1.06	0.33	<0.03
Arsenic	1.0	1.3	1.42	2.0	1.75	<0.05
Boron	103	325	321	547	1,212	<5
Selenium	0.19	0.14	0.15	0.25	0.51	<0.05
Uranium	<0.01	1.12	1.18	0.86	0.57	<0.01

Appendix 1.   Quality-Assurance and Quality-Control Implications of High-pH Waters

Water-quality analysis in high-pH waters, particularly when carbonate concentration is low, presents some unique challenges because of interactions with atmospheric carbon dioxide. Charge balance and, to a lesser extent, the comparison of measured and calculated specific conductance are common tools used to evaluate the overall quality of major element analyses. In theory, a complete analysis of a water sample should be electrically neutral, and the measured specific conductance should match a calculated specific conductance. In practice, a charge imbalance within 10 to 20 percent and a specific conductance imbalance within 10 percent are considered acceptable (McCleskey and others, 2011). Charge imbalance (represented in eq. 1.1 as $CI\%$) is calculated using the following formula (Ball and Nordstrom, 1991):

$$CI\% = \frac{(sum\ of\ cations\ species - sum\ of\ anions\ species) \times 100}{(sum\ of\ cations\ species + sum\ of\ anions\ species)/2} \quad (1.1)$$

which gives a maximum value of plus or minus 200 percent. The specific conductance imbalance (represented in eq. 1.2 as δK_{25}) is calculated using the following formula:

$$\delta K_{25} = \frac{K_{25\ calculated} - K_{25\ measured}}{K_{25\ measured}} \times 100 \quad (1.2)$$

where

K_{25} is the specific conductance standardized to 25 degrees Celsius (McCleskey and others, 2011).

Plots of CI percent versus δK_{25} can be used to determine if cations or anions are too low or too high in a sample based on deviations of charge balance and a perfect match between measured and calculated specific conductance (McCleskey and others, 2011). Some of the Big Marsh samples plot within an acceptable range, but many plot in the field indicative of anion deficiencies (fig. 1.1). The three samples that indicate the greatest deviation are the ones with the highest pH: Seep 1, Seep 2, and MW2. The charge imbalance and specific conductance imbalance calculations were repeated for these three samples by progressively increasing the pH by 0.1 unit to evaluate the potential for deficiencies of hydroxyl (OH−)—the dominant anion species—being the source of the imbalance problems. For two of the samples (Seep 1 and MW2), increasing pH by 0.6 to 0.9 unit reaches an acceptable combination of charge and specific conductance imbalance (fig. 1.2). For the third sample (Seep 2), no change in pH results in an acceptable outcome. Possible causes for this discrepancy are unclear but center on anion deficiencies. After hydroxyl, the next common anion species in sample Seep 2 is sulfate followed by carbonate.
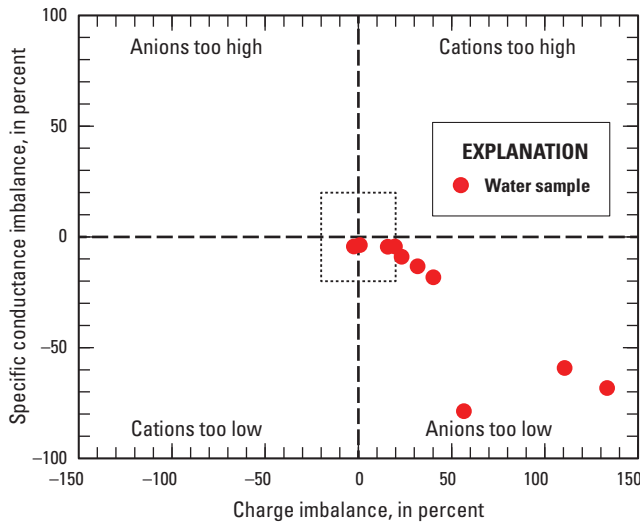

Figure 1.1.   The variation of charge imbalance and conductivity imbalance for samples from the Big Marsh study area. The dashed rectangle represents a variation of plus or minus 20 percent.
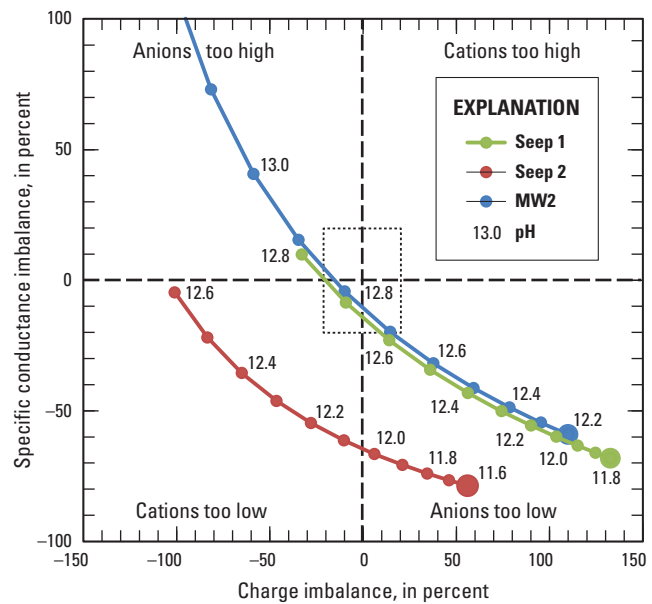

Figure 1.2.   The hypothetical effect of increasing pH on the charge imbalance and specific conductance imbalance for samples from the Big Marsh study area. The dashed rectangle represents a variation of plus or minus 20 percent.

References Cited

Ball, J.W., and Nordstrom, D.K., 1991, User's manual for WATEQ4F, with revised thermodynamic database and test cases for calculating speciation of major, trace, and redox elements in natural waters: U.S. Geological Survey Open-File Report 91–183, 193 p. [Also available at https://doi.org/10.3133/ofr91183.]

McCleskey, R.B., Nordstrom, D.K., and Ryan, J.N., 2011, Electrical conductivity method in natural waters: Applied Geochemistry, v. 26, p. S227–S229. [Also available at https://doi.org/10.1016/j.apgeochem.2011.03.110.]