PROCESSES CONTROLLING GEOCHEMICAL VARIATIONS IN THE SOUTH PIT LAKE, ELIZABETH MINE SUPERFUND SITE, VERMONT, USA

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Abstract. The Elizabeth mine Superfund site offers unique opportunities to investigate the interplay between geochemical and physical processes in the geochemical evolution of an acidic pit lake. The mine exploited a steeply dipping massive sulfide ore body. Ores contained pyrrhotite and chalcopyrite and were hosted by siliciclastic sedimentary rocks and amphibolites. An open pit that accessed part of the ore body is filled by a long (380 m), narrow (< 25 m), and shallow (< 7 m) lake, which is divided into two parts by a rock slide. The southern end serves as a decant point, and discharges for most of the year. Quarterly sampling and continuous temperature monitoring of the water column in the lake document geochemical variations that depend on seasonal variations in the amount of precipitation and the presence or absence of ice. From spring to fall, parameters show limited variation with depth except for temperature, which decreases with depth. The lake experienced overturn in the fall. During winter under ice cover, the lake developed a chemocline shown by a sharp decrease in pH, a doubling of total dissolved solids (TDS), and a ten-fold increase in dissolved Fe with depth (0.4 - 55.2 mg/L). Oxia throughout most of the year causes removal of Fe, but low pH prevents significant sorption of Cu and other metals. Ca (25 - 72 mg/L), Mg (9.6 - 15.0 mg/L), K (6.0 – 8.3 mg/L), Si (6.7 – 9.6 mg/L), and SO$_4^{2-}$ (210 - 280 mg/L) are the major dissolved constituents during non-stratified ice-free periods; Fe (0.2 - 0.5 mg/L), Al (1.0 – 3.1 mg/L), Cu (0.6 – 1.2 mg/L), and Zn (0.3 - 0.5 mg/L) are important minor dissolved constituents. Throughout the year, the water quality is dependent upon a variety of factors including the geometry of the pit, the short residence time of water within the pit, wind mixing and fall overturn, the oxidation of sulfides on the pit walls and in the unsaturated waste on the floor of the pit south of the haulage way, oxidation of iron within the water column, and mixing of surface waters with high TDS waters entering the bottom of the lake.

Additional Key Words: acid, copper, iron, massive sulfide, sulfate, seasonal

1 Paper presented at the 7th International Conference on Acid Rock Drainage (ICARD), March 26-30, 2006, St. Louis MO. R.I. Barnhisel (ed.) Published by the American Society of Mining and Reclamation (ASMR), 3134 Montavesta Road, Lexington, KY 40502

7th International Conference on Acid Rock Drainage, 2006 pp 1936-1951
DOI: 10.21000/JASMR06021936

https://doi.org/10.21000/JASMR06021936

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Introduction

The Elizabeth Cu mine Superfund site, in east-central Vermont, was placed on the National Priorities (Superfund) List in 2001 because of aquatic ecosystem impacts due to acidity and high concentrations of dissolved metals (Al, Fe, Cu, Zn, Cd, and Co) (Hathaway et al., 2001: URS Corporation, 2006). The site has since been found to pose a number of chemical and physical threats to human health related to contaminated ground water, Pb in soils around a former ore-processing facility, and the physical instability of tailings piles. The site consists of four related hydrogeochemical settings, all of which resulted from the exploitation of a Besshi-type massive sulfide deposit. These settings include waste-rock piles, tailings piles, flooded underground workings, and a flooded pit – the subject of this paper (Fig. 1).

The geochemical complexity of the site results from changes in the commodities of economic interest, and in the mining and ore-processing techniques used from the discovery of the deposit in 1793, through an intermittent mining history, until the cessation of mining in 1958 (Kierstead, 2001). The earliest operation began as an open pit, which was transitioned into underground workings. Ore was roasted and leached in a pile currently known as TP3; the leachate was fed into a copperas (FeSO₄ heptahydrate) factory, which operated until about 1882. Copper smelting began on the site around 1830 and continued until 1930, and also contributed waste rock to TP3. Mining resumed in 1941, the ore being processed using modern flotation techniques, and continued until 1958 when the mine closed. The waste material from this period is found in tailings piles 1 and 2 (TP1 and TP2, respectively). Mining in the open pit, currently filled by the lake, began in 1950 as part of this campaign.

The purpose of this paper is to describe the physical and geochemical characteristics of the small pit lake developed at the abandoned Elizabeth Cu mine. The characteristics were determined through a combination of a bathymetric survey, continuous monitoring of temperature at various depths within the lake for a year, and quarterly water-quality sampling for an annual cycle. The results of this study will form the basis for the evaluation of various remediation options for the lake.

Setting

Water from the Elizabeth mine Superfund site drains into the West Branch of the Ompompanoosuc River, which is part of the Connecticut River watershed. The headwaters of the West Branch are underlain by the Devonian Waits River Formation, consisting of metamorphosed calcareous shale, shale, and minor quartzose limestone and dolomite, which in turn, is overlain by the Devonian Standing Pond Volcanics, a metamorphosed basalt, followed by the Devonian Gile Mountain Formation, which hosts the deposit and consists of metamorphosed black shale and graywacke, with lesser sandstone, calcareous shale, and amphibolite (Slack et al., 2001). The host rocks are dominated by quartz, feldspar, muscovite, biotite, and amphibole, and lesser amounts of garnet and calcite. The ore body crops out, and is tabular and elongate; it dips steeply and plunges to the north beneath the West Branch. The hypogene ore mineralogy is dominated by pyrrhotite, with lesser chalcopyrite and minor pyrite and sphalerite (Slack et al., 2001).
Figure 1. Maps and cross section showing main features of the Elizabeth mine Superfund site and Elizabeth mine pit lake. Location of cross section is shown on the map on the right as dashed line marked A – A’. Note lack of hydrologic connection between pit lake and underground workings (shown in pink). On the site map on the right, the pink indicates mine waste; blue indicates surface water. Contours of lake depth are shown in color in one meter intervals. Depth profile and sampling locations are shown by the encircled black stars.
Water-quality impacts from the Elizabeth mine to the West Branch come from three sources, going from upstream to downstream: (1) the Artesian Vent; (2) Copperas Brook; and (3) Lord Brook (Seal et al., 2001; URS Corporation, 2006; Fig. 1). The Artesian Vent on the southern bank of the West Branch is the only known discharge from the flooded underground mine workings. It is inferred to be recharged by surface-water inflow to the North Pit and by ground water along the length of the flooded mine workings. The underground mine workings extend from the North Pit over 2,400 m to the north, reaching approximately 500 m north of the river. Copperas Brook drains most of the abandoned mine site. Its source is a series of low-pH, high TDS seeps at the base of TP3. It then flows through an incised channel in TP2 into a pond on top of TP1, where it is currently diverted to the northeast corner of TP1 through a decant system constructed as part of a time-critical removal action that occurred in 2004. Several seeps at the base of TP1 join and enter Copperas Brook as it flows down to the West Branch; several small neutral tributaries contribute to the flow before reaching the confluence. The confluence of Copperas Brook and the West Branch is less than 1 km downstream from the Artesian Vent. Lord Brook receives impacts from a small mined area to the south known as the Old South Mine, the open pit filled by the lake, and seepage from a waste rock pile associated with the pit. Lord Brook enters the West Branch approximately 3.5 km downstream of Copperas Brook. Copperas Brook provides, by far, the greatest metal and acidity loads to the West Branch, followed by the Artesian Vent, and then Lord Brook.

The site is in a temperate climate zone (National Climatic Data Center, 2003; 2004). January is the coldest month having a mean temperature of -10 °C (average low = -17 °C) and July is the warmest month having a mean temperature of 19 °C (average high = 27 °C). Average annual precipitation is 98.5 cm and is fairly evenly distributed throughout the year. However, for the study period, the site received below average amounts of precipitation during the winter. The average monthly high precipitation (10.2 cm) is in August and the average monthly low precipitation (5.5 cm) is in February.

**Geometry of the Lake**

The pit, known as the South Open Cut, is elongated in a north-south direction along the strike of the steeply dipping ore body (Figs. 1 and 2). It is located near the crest of the hill. The total catchment area for the pit is less than 80,000 m². The pit deepens gently to the north. The total length of the excavation is approximately 550 m, but it only reaches approximately 25 m in maximum width and for most of its length, the width is less than 15 m. The southern 150 m of the pit is exposed up to the point of the haulage way, which was excavated during mining to the east to provide access to the pit. The southern, subaerial part of the pit, herein referred to as the “south arm”, includes exposed rock on the walls of the pit as well as sand- to boulder-sized mine waste on its floor. The south arm funnels drainage to the north toward the lake and haulage way. The haulage way serves as a decant point at the southern end of the lake. Water flows through the haulage way for most of the year except during winter freeze and the driest parts of the summer. The lake is not connected hydrologically to the mine pool in underground workings north of the North Pit. Shallow ground water seeps into the lake through fractures in the western wall of the pit. Limited data from a single monitoring well (MW16C) located approximately 75 m east of the pit at the approximate latitude of the rock slide indicates that ground water also flows toward the lake from the east (URS Corporation, 2006). Bedrock hydraulic conductivities near the pit average 1.06 x 10⁻⁴ cm/sec (URS Corporation, 2006). Another well in the vicinity of the lake (MW15C) is located approximately 150 m east of the lake, near the haulage way.

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Figure 2. Photographs of the pit lake and vicinity. a. Aerial view of the lake and vicinity looking north. The south part, the rock slide, and the partially ice covered northern part of the lake are visible. The North Pit and TP3 are visible at the top of the photo. Photo courtesy of Matt Kierstead (PAL). b. View of south part of the lake looking north from east bank, just north of the haulage way. Orange buoy (indicated by arrow) marks the sampling station in the south part (June 2003). c. North part of the ice-covered lake looking north into the enclosed northern extent of the lake (January 2004).
The lake, which is approximately 380 m long, is divided into two parts by a rock slide that fills approximately 50 m of the length of the lake (Fig. 1). The rock slide consists of boulder-sized material; individual boulders are as much as several meters across. The two parts of the lake, therefore, are hydraulically well connected. The southern part is 240 m long and reaches a maximum depth of 6.6 m. The northern part is 90 m long, and reaches a maximum depth of 4.3 m. The northern half of the northern part is sheltered by overhanging rock in a tunnel-like excavation (Fig. 2c). On the basis of a bathymetric survey, the southern part of the lake has an estimated volume of 12,450 m$^3$ and the northern part has an estimated volume of 2,990 m$^3$ for a combined volume of 15,440 m$^3$.

**Methodology**

Volume estimates for the lake were made on the basis of 95 bathymetric measurements using ArcGIS 9.1, and Visual Nature Studio. Two locations, one in the southern part of the lake and one in the northern part of the lake, were chosen for detailed study; both were near the sites of maximum depth in their respective basins (Fig. 1). The study investigated an annual cycle within the lake and included the continuous monitoring of water temperature and the quarterly water sampling (five quarters). Water samples were collected at depths of 0.3, 1.5, 2.7, 4.0, 5.2, and 6.4 m in the south and 0.3, 1.5, 2.7, and 4.0 m in the north. Temperature was monitored using Hobo temperature data-loggers from June 25, 2003 to June 22, 2004. Water-quality parameters (depth, temperature, pH, specific conductance (SC), dissolved oxygen (DO), oxidation-reduction potential (ORP), and turbidity) were measured using a Hydrolab mini-Sonde. Water was sampled using a peristaltic pump. Filtered (< 0.45 μm) splits were collected for cation and anion analysis. Unfiltered splits were also collected for cation analysis. Cation splits were preserved with ultra-pure nitric acid; anion splits were preserved by refrigeration. Dissolved total iron and ferrous iron concentrations were determined using colorimetric kits containing 1, 10 phenanthroline indicator with a Hach DR/2000 spectrophotometer.

Major and trace cation concentrations were determined in USGS laboratories (Denver, Colorado) by ICP-AES and ICP-MS. Anion concentrations were determined by ion chromatography also in U.S. Geological Survey laboratories (Denver, Colorado and Ocala, Florida). Laboratory and field methods are described by Crock et al. (1999), Ficklin and Mosier (1999), and Taggart (2002).

**Results**

Field and laboratory results for depth profiles within the lake, for discharge from the haulage way, and for surface drainage from the exposed south arm of the pit are summarized in Table 1. Results from both the northern and southern parts of the lake are similar, but the south has more dramatic variations than the north, presumably because unlike the north, the south is not partially sheltered, and thus is more vulnerable to climatic and other effects such as precipitation, evaporation, and surface-water inputs. Therefore, the discussion will be largely restricted to the southern part of the lake because results from this area are more informative about the most important processes controlling the chemistry of the pit lake.

During the summer of 2003, the temperature of the water column decreased steadily with depth for the first meter or two, and then more gradually below that (Figs. 3 and 4). The temperature difference from top to bottom was about 9.5 °C. About September 29, 2003, the
lake experienced overturn at which point the temperature was homogeneous from top to bottom. The lake continued to cool homogenously until it froze in December. The ice thickness was less than 0.5 m in January 2004. After freezing, the temperature of the water column increased with depth during the winter and into early spring. Near the top, the temperature approached 0 ºC. Throughout much of the water column, the temperature ranged between 3.5 and 5.5 ºC, near the temperature of maximum density of water. Near the bottom, temperatures reached a maximum of over 8 ºC. After the ice melted in mid- to late April, the water column gradually warmed to produce a profile where temperature decreased with depth with the thermal inversion occurring in late April.

Table 1. Selected dissolved (<0.45 m) water-quality data for the Elizabeth pit lake and associated settings. Pit lake samples are from depth. Ice-covered periods include January and April 2004; ice-free periods include June and October 2003, and June 2004.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Acute Toxicity*</th>
<th>South Lake No Ice</th>
<th>South Lake Ice Covered</th>
<th>North Lake With and Without Ice</th>
<th>Haulage way</th>
<th>South Arm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Low</td>
<td>High</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td>3.6</td>
<td>4.8</td>
<td>3.5</td>
<td>4.9</td>
<td>3.4</td>
</tr>
<tr>
<td>S.C. µS/cm</td>
<td></td>
<td>440</td>
<td>535</td>
<td>470</td>
<td>841</td>
<td>432</td>
</tr>
<tr>
<td>ORP mV</td>
<td></td>
<td>478</td>
<td>701</td>
<td>530</td>
<td>730</td>
<td>296</td>
</tr>
<tr>
<td>D.O. mg/L</td>
<td></td>
<td>7.4</td>
<td>9.7</td>
<td>3.8</td>
<td>10.7</td>
<td>3.3</td>
</tr>
<tr>
<td>Fe²⁺/Fe_total</td>
<td></td>
<td>0.3</td>
<td>1.0</td>
<td>0.1</td>
<td>1.0</td>
<td>0.3</td>
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<tr>
<td>SO₄²⁻ mg/L</td>
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<td>210</td>
<td>280</td>
<td>230</td>
<td>390</td>
<td>210</td>
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<tr>
<td>Ca mg/L</td>
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<td>71.4</td>
<td>57.2</td>
<td>77.5</td>
<td>49.9</td>
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<tr>
<td>K mg/L</td>
<td></td>
<td>6.0</td>
<td>8.3</td>
<td>6.6</td>
<td>9.3</td>
<td>6.0</td>
</tr>
<tr>
<td>Mg mg/L</td>
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<td>15.0</td>
<td>11.6</td>
<td>16.6</td>
<td>9.8</td>
</tr>
<tr>
<td>Na mg/L</td>
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<td>1.8</td>
<td>1.7</td>
<td>2.0</td>
<td>1.6</td>
</tr>
<tr>
<td>Si mg/L</td>
<td></td>
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<td>9.6</td>
<td>8.2</td>
<td>10.5</td>
<td>6.7</td>
</tr>
<tr>
<td>Al mg/L</td>
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<td>2.4</td>
<td>2.0</td>
<td>7.6</td>
<td>0.9</td>
</tr>
<tr>
<td>Fe mg/L</td>
<td></td>
<td>0.2</td>
<td>0.5</td>
<td>0.2</td>
<td>5.5</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Mn mg/L</td>
<td></td>
<td>0.4</td>
<td>0.7</td>
<td>0.5</td>
<td>0.9</td>
<td>0.4</td>
</tr>
<tr>
<td>As µg/L</td>
<td></td>
<td>&lt;1</td>
<td></td>
<td>&lt;1</td>
<td></td>
<td>&lt;1</td>
</tr>
<tr>
<td>Cu µg/L</td>
<td>18 (3)</td>
<td>612</td>
<td>1,000</td>
<td>508</td>
<td>1,290</td>
<td>617</td>
</tr>
<tr>
<td>Cd µg/L</td>
<td>3.9 (0.5)</td>
<td>1.6</td>
<td>2.5</td>
<td>1.5</td>
<td>2.2</td>
<td>1.5</td>
</tr>
<tr>
<td>Ni µg/L</td>
<td>1,418 (285)</td>
<td>42</td>
<td>60</td>
<td>41</td>
<td>53</td>
<td>42</td>
</tr>
<tr>
<td>Pb µg/L</td>
<td>81.7 (7.3)</td>
<td>0.1</td>
<td>0.9</td>
<td>0.2</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>Zn µg/L</td>
<td>117 (240)</td>
<td>322</td>
<td>500</td>
<td>336</td>
<td>464</td>
<td>303</td>
</tr>
</tbody>
</table>

*Acute toxicity for aquatic ecosystems is based on a hardness of 100 mg/L CaCO₃ equivalent (or 15 mg/L in parentheses), which is representative of the hardness of receiving water bodies (U.S. Environmental Protection Agency, 2004).

Depth profiles of specific conductance, pH, and dissolved oxygen also had distinct seasonal variations (Fig. 4). The specific conductance of the water column above 5 m depth was fairly constant during the June 2003 through April 2004 samplings, averaging 525 ± 8 µS/cm. Below 5 m during the ice covered periods, the specific conductance increased steadily with depth reaching a maximum of 840 µS/cm at the deepest point in the lake. In June 2004, the specific conductance profile was again constant from top to bottom, but the average value (450 ± 9 µS/cm) was significantly lower than the previous year. Quarterly profiles of pH have
variations consistent with those observed for specific conductance. During the first two samplings in June and October 2003, the pH was constant from top to bottom and averaged 3.7 ± 0.1. During January 2004 under ice cover, the pH decreased steadily with depth with a pH of 4.1 at the top and 3.5 at the bottom. During April 2004, the pH of the upper 5 m of the lake was fairly constant at 4.7, but a distinct chemocline was encountered at 5 m, at which point pH decreased steadily, reaching a value around 3.6 near the bottom. Thus, the chemocline distinctly marked by pH coincides with the departure in specific conductance noted in January and April 2004. In June 2004 after spring thaw, the pH profile was again constant (4.8 ± 0.1) from top to bottom, but was approximately one unit higher than the previous June, consistent with the significant dilution recorded by the specific conductance values. Quarterly profiles of dissolved oxygen concentrations are fairly constant with depth, being greater than 50% saturated (> 6 mg/L). The most notable exception was during the periods when the lake was covered by ice and a chemocline had developed at about 5 m depth. Below the chemocline, DO concentrations steadily decreased to below 2 mg/L. The pH of the drainage from the haulage way and from the exposed south arm of the pit ranged from 3.1 to 3.4, specific conductance ranged from 297 to 654 µS/cm, and the DO concentrations ranged from 2 to 10 mg/L.

Figure 3. Seasonal variations of water temperature at various depths in the southern part of the pit lake. Arrows indicate water-quality sampling dates.
Figure 4. Seasonal depth profiles of water temperature, specific conductance (SC), pH, and dissolved oxygen (DO) for the southern part of the pit lake.
The water chemistry of the pit lake is characterized by Ca as the dominant cation, followed by Si, Mg, and K. Sulfate is the dominant anion; Cl⁻ and nutrient concentrations are all less than 1 mg/L. Iron, Al, and Cu, followed by Zn and Mn are the most abundant trace metals. The concentrations of Fe and Cu within the lake are similar to one another, which are in marked contrast to Fe to Cu ratios in mine drainage for other deposits of this type, which typically are greater than 1:1 (Seal and Hammarstrom, 2003). Concentrations or ranges of concentrations are summarized in Table 1. The concentrations of most aqueous constituents have limited variations in the water column as typified by SO₄²⁻ and Ca (Figs. 5 and 6). Minor variations can be attributed to either dilution or evaporation. The most distinctive concentrations for most constituents are found in the deepest samples in the southern part of the lake when the surface of the lake was frozen. Iron is anomalous in that it has a much greater range of dissolved concentrations because of the influence of oxidation state on its solubility (Fig. 5). Even within this context, the deepest samples from the winter are distinctively high compared to the other water column samples. The chemistry of the water draining the subaerial south arm of the pit is distinctive in that it has the lowest pH and one of the highest conductivity values in the vicinity of the pit. Dissolved concentrations of various constituents, such as Fe and SO₄²⁻, also reach some of the highest values in the vicinity of the pit. The water chemistry discharging through the haulage way is intermediate between that of the lake and that of the south arm drainage, consistent with the mixing of these two sources (Table 1).

The most interesting variations in lake chemistry involve Fe, Cu, Al, and SO₄²⁻ during the winter periods when the surface of the lake was covered by ice. For Fe, Al, SO₄²⁻, and to a lesser extent K, concentrations show significant increases with depth beginning at the chemocline near 5 m depth (Fig. 6). In the case of Fe, the increase exceeds two orders of magnitude (0.4 to 55.2 mg/L); increases for the other constituents noted above are less. In contrast, Cu has decreases below the chemocline (Fig. 6). Less significant decreases with depth are also apparent for Cd and Zn.

Water quality within the pit lake exceeds acute criteria for the protection of aquatic ecosystems for both Cu and Zn assuming a hardness of 100 mg/L CaCO₃, a typical value for the West Branch of the Ompompanoosuc River – the main water body impacted by the mine site (Table 1). The pit lake has a mean hardness of 214 ± 25 mg/L. Lord Brook, a tributary of the West Branch that receives discharge from the pit lake, has a lower hardness of around 15 mg/L. Therefore, exceedances of acute criteria for selected metals at this lower hardness are also given in Table 1.
Figure 5. Variations of dissolved SO$_4^{2-}$ and Fe with pH for the northern and southern parts of the pit lake, and for miscellaneous waters in the vicinity of the pit. HW indicates surface waters draining through the haulage way, SA indicates surface water draining from the south arm of the pit, and GW indicates ground water in the vicinity of the pit (MW12C). The theoretical solubility limit for amorphous Fe(OH)$_3$ is shown for reference and was calculated using PHREEQC with the WATEQ database (Parkhurst and Appelo, 1999).
Figure 6. Seasonal depth profiles of dissolved Ca, $\text{SO}_4^{2-}$, Fe, and Cu for the southern part of the pit lake.
Discussion

The most important factors affecting the chemistry of the pit lake appear to be the input of dilute surface water, the input of solutes at the bottom of the lake, fall overturn, wind mixing, and precipitation of secondary phases. Water is dominantly delivered to the lake by recharge from surface water and seepage at the base of the lake. Because the pit is near the crest of the hill, its total catchment area is only 80,000 m², of which approximately two-thirds drains into the lake and one-third drains into the subaerial south arm (Figs. 1 and 2). Thus, on the basis of the average annual precipitation for the area (98.5 cm), the lake receives approximately 53,000 m³/year compared to a total volume of 15,440 m³, suggesting that the residence time of water in the lake is roughly 0.30 years (<4 months) ignoring ground-water inputs and losses due to evaporation. The only water in the vicinity of the pit lake that approaches the concentrations found in waters below the chemocline in the winter is surface drainage from the south arm area (Figs. 2 and 5). Ground waters upgradient from the pit do not appear to be impacted. Bedrock ground waters from the monitoring well nearest to the pit (MW16C) have near-neutral pH (7.3), low specific conductance (161 µS/cm), high DO concentrations (6.6 mg/L), and low Fe (<1 mg/L) and SO₄²⁻ (22.2 mg/L) concentrations (URS Corporation, 2006). Surface run off from the exposed south arm of the pit drains through the haulage way, the common discharge point for both the southern and northern parts of the pit. However, shallow subsurface drainage from the south arm into the lake through the sand- to pebble-sized fill in the floor of the pit may occur because the haulage way was excavated from bedrock and may act as a shallow dam. The sand- and pebble-sized fill may act as a shallow aquifer transferring water to the low point of the pit. Field-parameter and geochemical profiles of the water column of the southern part of the lake during the winter months when the surface is frozen indicate the input of warmer waters into the bottom of the lake with low pH and high TDS, dominated by Fe, Al, K, and sulfate (Figs. 3, 4, 5, and 6), characteristics similar to the surface drainage from the south arm. Other inputs of solutes also may come from the weathering of sulfide minerals on the pit walls above the lake surface. Subaqueous oxidation of sulfides in the wall-rock or floor material of the lake is considered to be of limited importance because of the low concentrations of DO and dissolved Fe³⁺ iron.

Mixing of the lake is accomplished both by overturn in the fall and by the action of wind. Overturn provides important mixing (ventilation) in the water column as indicated by the greater uniformity of pH and DO in the water column. In addition, the steep walls of the pit focus air flow, and facilitate mixing in the upper part of the lake. Wind mixing is less likely to be important in the sheltered northern part of the lake (Figs. 1 and 2).

The precipitation of secondary phases exerts an important control on the Fe chemistry of the water column (Fig. 5). Iron precipitation requires oxidation of Fe²⁺ iron, neutralization of Fe³⁺ iron-bearing fluids, or both. Overturn of the water column in the fall provides a mechanism (i.e., ventilation) to oxidize the water column and promote Fe precipitation. Evidence for this process is found in the observation of a ring of Fe³⁺ Fe precipitates at the water line during the October 2003 sampling, just a few days after overturn. The Fe²⁺/Fe total ratios for the water column (0.2 to 0.6) were also distinctly lower compared to other times of the year (Table 1). Mixing of low pH, high TDS shallow ground waters entering in the bottom of the lake with the higher pH water column may also lead to Fe precipitation. During ice covered periods, the decrease in DO concentrations between January and April, particularly at depth suggests that iron oxidation may be important in the consumption of DO. Other factors, such as lower DO concentrations in the
waters mixing into the lake and decomposition of organic matter, may also contribute to the lower DO concentrations in the lower water column. The lower concentrations of dissolved Cu in the deepest samples compared to those shallower in the water column during January and April suggest that the sorption of Cu on Fe(OH)$_3$ may be a locally important process for the removal of base metals from the water column in spite of evidence for its general absence throughout the remainder of the water column in all seasons. Similar, but less dramatic depth profiles are found for Cd and Zn during ice-covered periods.

**Conclusions**

The Elizabeth pit lake is dynamic. Its water quality is dependent upon a variety of factors including the geometry of the pit, the relatively short residence time of water within the pit, wind mixing and fall overturn, the oxidation of sulfides on the pit walls and in the unsaturated waste on the floor of the pit south of the haulage way, the oxidation of iron within the water column, and mixing of surface waters with high TDS shallow ground waters. The geometry of the pit is conducive to sulfide oxidation on the pit walls above the lake and in the unsaturated zone of wastes in the floor of the pit south of the haulage way. The slope of the subaerial portion of the pit toward the north facilitates the movement of solutes in the shallow subsurface to the deepest part of the lake. The elongate nature of the pit also focuses wind action, which along with fall overturn, promotes oxidation of Fe through partial or complete ventilation of the water column during the ice-free months. The relatively short residence time of water in the lake makes the water quality especially vulnerable to fluctuations in the amount of precipitation on an annual or seasonal basis. The precipitation of Fe at moderately low pH tends to leave Cu in solution due to the pH dependence of sorption on ferric hydroxides (Smith, 1999), producing mine water with subequal amounts of dissolved Fe and Cu. Thus, remediation strategies using only CaCO$_3$ for the neutralization of acid may not significantly affect the Cu concentration of the water because of the limitation on the potential number of sorptive sites associated with the precipitation of ferric hydroxides.

**Acknowledgements and Disclaimer**

This study was funded by the Mineral Resources Program of the U.S. Geological Survey, and by the U.S. Environmental Protection Agency – Region 1. The encouragement and support of Kathleen Johnson (USGS) is greatly appreciated. This paper benefited from reviews by Devin Castendyk, I-Ming Chou, Avery Drake, Chris Gammons, Larry P. Gough, and Brian Park. The use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

**Literature Cited**


