Monitoring the water quality of pit lakes

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Abstract

This chapter reviews some of the important chemical and physical properties of pit lakes that should be monitored during and after flooding. At a minimum, seasonal depth profiles should be collected that show changes in water temperature, salinity (specific conductance), pH, turbidity (total suspended solids), and redox state (ORP/Eh). Based on the pit lake profile, water samples should then be collected at enough depths to adequately characterise different lake layers. Besides the usual list of major and trace solutes, suggested analytes include dissolved Fe(II)/Fe(III), nutrients and dissolved organic carbon, and dissolved gases (including O_2, CO_2, H_2S, and ammonia). Secchi depths or Photosynthetically-Active Radiation (PAR) sensors give useful information on sunlight penetration. With new benchtop instrumentation, stable isotope analysis of water (both O and H) is very inexpensive. Such data can be used to gain insights into lake stratification, sources of water filling the lake, and the extent of evaporation of different layers in the lake. Stable isotopes of dissolved inorganic carbon, also inexpensive, can be used to track sources of alkalinity, as well as biological reactions such as respiration and photosynthesis. Isotopic analysis of dissolved sulfate may be used to better understand sources of sulfate loading to a lake (e.g. oxidation of sulfide minerals versus dissolution of sulfate minerals), mechanisms of pyrite oxidation (e.g. by O_2 or by Fe^{3+}), and redox reactions involving bacterial sulfate reduction.

The well-known Berkeley Pit lake, in Butte, Montana, is used as an example of how pit lake monitoring can inform management decisions. A monthly water-level monitoring and semi-annual water quality monitoring programme for the Berkeley Pit was implemented by the state and federal regulatory agencies as a tool to determine when in-perpetuity treatment of the lake system will begin, and to track changes within the lake and surrounding flooded underground mines which may or may not affect treatment. Additionally, the monitoring data are being used to optimise an ongoing resource recovery project that is extracting copper from the lake.

1 Introduction – why monitor water quality?

Lakes formed by flooding of abandoned open pit mines can have a very wide range of water chemistries, depending on factors such as local geology, climate, pit morphometry, rate of filling and the type of water used to fill the lake (Eary, 1999). Although progress has been made, the science of predicting the future water quality of pit lakes is still in its infancy. For this reason, determining the chemical characteristics of a given pit lake must rely on direct observation, i.e. monitoring.

Water quality monitoring plays a critical role in many aspects of pit lake management. Long-term monitoring of pit lakes is often required by state, provincial, or federal agencies to ensure that changes in water quality do not pose a threat to human and/or aquatic health. Possible threats include unusually high or low pH, elevated concentrations of metals or metalloids, elevated concentrations of cyanide, thiocyanate, or other anthropogenic compounds, high partial pressures of dissolved gas (e.g. CO_2, H_2S), and the presence of pathogens. Increased attention is being paid to the possibility that mining lakes may have beneficial end uses, such as recreation, water supply, or habitat for aquatic life (McCullough and Lund, 2006; Gammons et al., 2009a). Monitoring is obviously needed to inform managers whether the desired end use is being attained, or if management intervention is needed to get there. The use of amendments, addition of lime or nutrients, during pit filling could help avoid or minimise future water quality problems (see Dowling et al. (2004) for a good example). Water quality profiling is needed to determine the presence

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or absence of vertical stratification in a lake, and whether the stratification is permanent (meromictic case) or seasonal (holomictic case). In some cases (Island Copper, BC, Canada, Pelletier et al., 2009), a meromictic lake may be engineered so that more saline, contaminated water is stored permanently in the bottom of a lake while more dilute, high-quality water floats on top. In other cases (e.g. Colomac Zone 2 pit, Northwest Territories, Canada, Chapman et al. (2007) meromixis may be a hindrance to achieving water quality targets, in which case the lake may need to be artificially mixed.

The purpose of this chapter is to provide an adaptable framework for monitoring the water quality of pit lakes. Because every lake has its own unique set of physical, chemical, and biological characteristics, there is no single set of measurement protocols that will be optimal (i.e. best balance between measurement intensity and cost) for all cases. The following discussion focusses mainly on inorganic solutes. Some important concepts are illustrated using the Berkeley Pit lake (Montana, USA) as an example. This lake (Figure 1) is well-known amongst the mining community, and has a much longer record of water quality monitoring than most other pit lakes. It is also a good example of how monitoring of pit lake water quality has informed the application of management strategy.

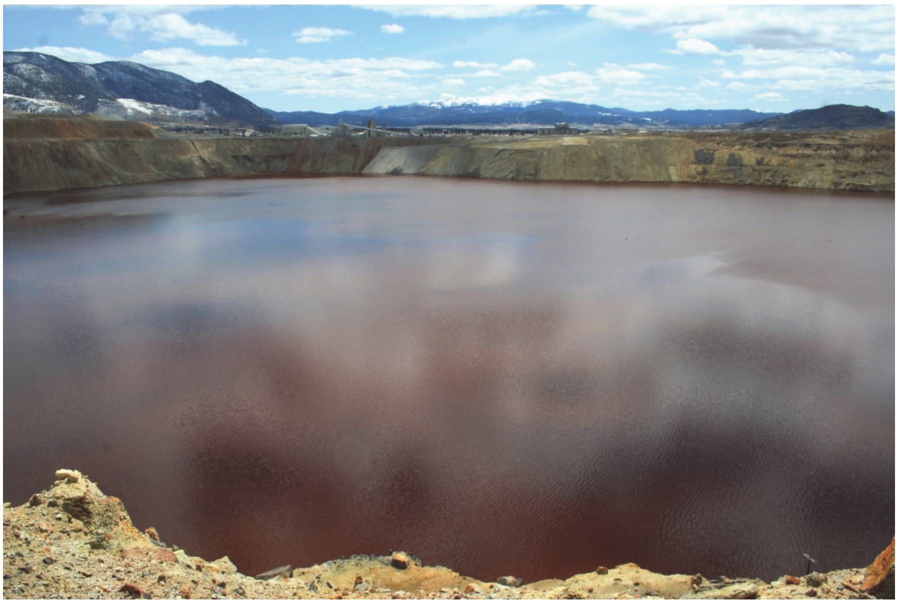

Figure 1 Photograph of the Berkeley Pit lake, looking south (Photo courtesy of C. Gammons, May, 2009)

2 When, where and how to collect samples

2.1 When to sample

Ideally, water quality monitoring should begin during the active mine life. Locations to collect samples include major seeps and springs, nearby surface waters (including tailings ponds, ditches), and groundwater collected from dewatering pumps. After closure, it is important to begin a pit lake sampling regimen immediately, so that any developing water quality problems can be recognised as soon as possible and early enough that management intervention can be successfully implemented. Most large open pits will take several decades to fill, unless large volumes of water are diverted into the pit from external sources. If water quality problems are found in the early stages of flooding, mitigation strategies can be identified and implemented. Once a pit lake has filled to a steady-state volume, it is important to continue water quality monitoring. All young, artificial lakes (including reservoirs) go through an extended period of transition where solute chemistry, nutrients, and aquatic life are continuously adjusting to the new hydrologic regime. Some lakes that are meromictic upon flooding may transition to being holomictic over time, either through incremental processes such as erosion of the chemocline during seasonal turnover or mixing events triggered by physical processes such as a major landslide down the pit walls. Alternatively, some lakes that are holomictic after flooding may slowly develop permanent stratification, e.g. by release of solutes (such as Fe^{2+}) from the pit lake sediment resulting in the development of a high-density bottom layer.

The number of times that a given pit lake should be sampled each year depends on how the lake is stratified, and to what degree the limnology changes on a seasonal basis. If access is good and funds are available, collection of monthly depth-profiles is recommended. Continuous data on lake stratification can be obtained at low cost by deploying small, submersible temperature-loggers on a cable at different depths. After a period of several months, the data are downloaded and the temperature traces can then be used to pick dates when partial or total lake turnover occurred, and which portions of the lake were vertically mixed (see below for an example from the Berkeley Pit). Collection of water samples for chemical analysis should be done seasonally.

2.2 Where and how to sample

Most pit lakes differ from natural lakes in that they are deep and often have no major surface water inlets and outlets. The majority of pit lakes therefore have relatively minor gradients in chemistry in a horizontal direction, and much greater changes in a vertical direction. Nonetheless, it is important early in a monitoring programme to collect samples at different x-y locations to test for lateral heterogeneity. If horizontal gradients are minimal, then the best location to collect long-term data will be in the deepest portion of the lake. A complete depth profile of field parameters (i.e. depth, pH, SC, dissolved oxygen, redox) is usually sufficient to locate vertical discontinuities in temperature or salinity.

Enough water samples for chemical analysis should be collected to represent each of the vertical compartments of the lake, with closer-spaced samples through zones of transition. Lake samples are typically collected using point samplers (e.g. Van Dorn or Niskin samplers) or by pumping water to the surface with a submersible or peristaltic pump. Each of these methods has its advantages and disadvantages. Peristaltic pumps may result in loss of dissolved gas (e.g. CO_2) due to depressurisation, with subsequent pH change. Submersible pumps avoid this problem but are more expensive and more sensitive to corrosion. Point samplers are the least expensive method, but are more prone to atmospheric contamination.

Whenever possible, field parameters, such as water temperature, pH, and dissolved oxygen, should be collected using a submersible multi-parameter meter that is capable of withstanding pressures corresponding to the maximum lake depth. Field parameters can change as water is pumped or hauled to the surface. A number of commercially available multi-parameter meters are available, most of which will cost in the range of US$ 4,000–8,000. Individual sensors (e.g. pH electrode) have a finite working life, and therefore an ongoing operational budget needs to be developed to cover replacement parts and maintenance. CTD (conductivity-temperature-depth) sensors, widely used by oceanographers, are more expensive but have greater precision than most conventional multi-parameter probes due to the addition of an internal circulating pump and other features (see Stevens and Lawrence, 1988).

Besides the pit lake itself, it is also recommended to collect samples of nearby surface waters, groundwaters, storm runoff, and, in some cases, precipitation. Any prominent groundwater inflows (e.g. seeps or springs) should be sampled prior to flooding as this information may be critical later on to understand the factors driving the development of pit lake chemistry. All surface water inputs should be sampled frequently enough to define seasonal or long-term changes in chemistry and flow. If possible, it is recommended to capture mine-wall runoff during storm events (Morin and Hutt, 2001). Finally, if a weather station exists near the mine site, it is recommended to collect composite monthly samples of precipitation for later water chemistry and stable isotope measurement. Such samples are relatively easy to collect and archive.

It is possible to collect samples of suspended sediment falling through the water column using an Imhoff cone (Figure 2a) or similar device. The mass of sediment collected over an integrated time period can be used to estimate the vertical flux of particulate matter to the lake bottom. Samplers can be deployed at different depths to see if there are changes in particulate mineralogy or if dissolution of solids occurs as they settle below the chemocline. If the pit lake is shallow, pore-water samplers (e.g. “peepers”) can be deployed into the lake sediment (Figure 2b). These samplers are very useful to document cm-scale vertical gradients in solute chemistry near the sediment-water interface. Vertical concentration gradients can be used to estimate the diffusive flux of solutes from the sediment into the overlying water column (Martin and Pedersen, 2002). Finally, if possible, lake-sediment cores should be retrieved for mineralogical, chemical, or microbiological testing (Figure 2c). As such sediment is likely to be anaerobic, special precautions need to be taken to prevent sample oxidation prior to analysis (Twidwell et al., 2006).

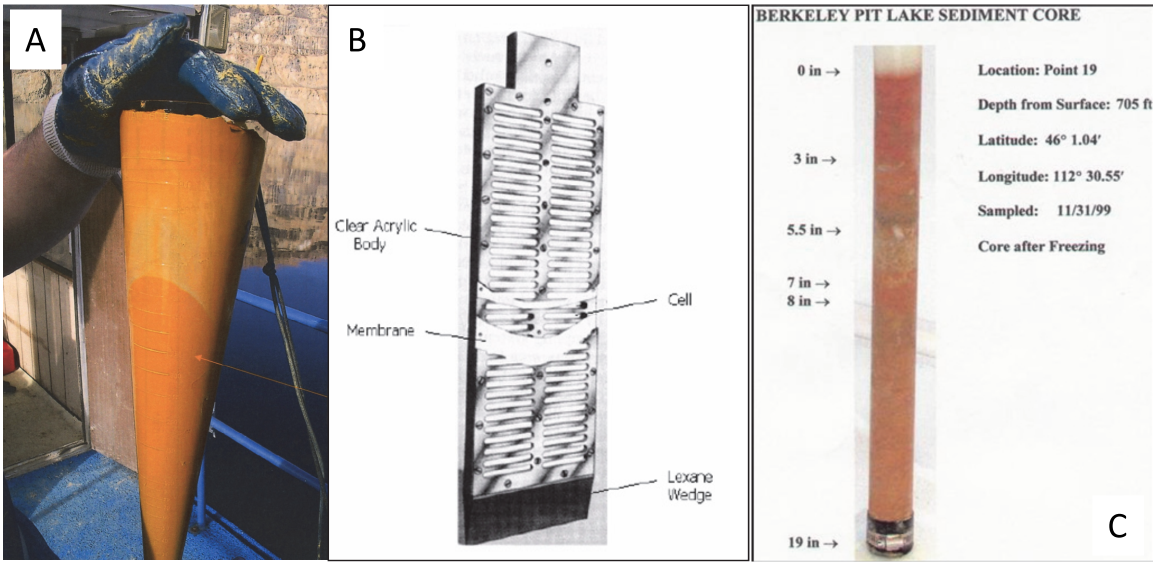

Figure 2 Miscellaneous sampling devices: A) an Imhoff cone being retrieved after deployment in the Berkeley Pit lake for four months. The cone is filled with a large mass of secondary mineral precipitates that descended through the water column; B) diagram of a peeper used for sampling sediment pore water (modified design of Hesslein, 1976). This sampler is approximately 40 cm tall and each cell has a volume of roughly 6 cm^3; C) sediment core (~ 50 cm long) collected from the bottom of the Berkeley Pit lake in 1999

3 What to measure

Table 1 provides an annotated list of important analytes that could be included in a pit lake monitoring programme. Some of these are critical for virtually any study, e.g. temperature, specific conductance (SC), major and trace element chemistry, whereas others are optional, but nonetheless may provide unique and valuable information that can help define processes driving water quality in the lake. A brief discussion is provided for each of the parameters listed in Table 1. Although not discussed further in this chapter, it is highly recommended to install a permanent weather station near the pit lake. Data such as solar radiance, temperature, relative humidity, precipitation, surface wind speed, and wind direction are needed to perform detailed limnological modelling.

Most multi-parameter probes used in pit lake monitoring studies are equipped with sensors to record water temperature, specific conductance (SC) (also known as EC or C25), pH dissolved oxygen (DO), and some measure of redox potential. Special attention should be paid as to whether conductivity measurements are “actual” (i.e. referenced to the temperature of the water sample) or “specific” (i.e. adjusted to 25°C). One of the ways that SC measurements are commonly used in pit lake studies is to estimate the concentration of total dissolved solids (TDS) and salinity, which, in turn, is needed to calculate water density. A correlation first needs to be established between SC and TDS, where the latter is determined from a complete chemical analysis. Since each lake has its own unique mixture of cations and anions, it is not recommended to use a generic formula to compute TDS from SC, even though your meter may give you this option. “Clark-cell” DO electrodes consume DO near the tip of the probe, and water must be stirred to get an accurate reading. Many newer multi-parameter instruments use a luminescent DO sensor that does not require stirring, and holds its calibration longer. For electrical potential measurement, it is crucial to know whether the instrument is reporting mV relative to an Ag-AgCl reference solution (often referred to as "Oxidation-Reduction Potential", or ORP), or relative to the standard hydrogen electrode, i.e. Eh. This is a very common source of error in the reporting of redox data.

Table 1 Annotated list of parameters that may be monitored in pit lakes

Parameter	Comments
Water temperature (T_w)	Needed to estimate water density. Collect T_w in situ, with a submersible sonde or a string of temperature loggers.
Specific conductivity (SC)	Needed to estimate water density. Know whether your meter is reading raw conductivity or SC (adjusted to 25°C).
pH	The pH of a deep water sample may change during pumping to the surface or during storage.
Dissolved oxygen (DO)	Always calibrate to local barometric pressure. Values < 1.0 mg/L should be interpreted with caution. Use a mixer for Clark-type electrodes.
Eh and ORP	Know whether your meter is reading ORP or true Eh. Eh/ORP has limited utility in toxic waters.
Turbidity or TSS	Establish a relationship between TSS and turbidity. Deploy samplers to estimate vertical flux of solids.
Light penetration or PAR	Secchi disks provide a rapid measure of light extinction. Submersible sondes can be equipped with PAR and/or chlorophyll a detectors.
Major and trace elements	Decide whether you want filtered or non-filtered (total) concentrations (good to include both). Usually analysed by ICP-AES or ICP-MS.
Alkalinity or acidity	Perform titrations as soon as possible after sampling, especially if samples are rich in ferrous iron. Follow a standard method.
Dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC)	Usually quantified by a total carbon analyser. Needed to quantify dissolved CO_2 for waters with pH < 4.5.
Major anions	Usually quantified by Ion Chromatography (IC). IC is the best method for analysis of sulfate, chloride, and nitrate.
Nutrients and H_2S	Colorimetric methods have low detection limits for H_2S and nutrients, but are prone to chemical interferences (e.g. with Fe).
Weakly-acid dissociable (WAD) cyanide, total cyanide and degradation products	Especially critical for mines where cyanide was used for metal recovery (e.g. most gold mines). Degradation products of cyanide include thiocyanate, ammonium, and nitrate.
Stable isotopes of O and H in water	Useful to examine lake stratification, evaporation, and different sources of water.
Stable isotopes of S and O in sulfate	Can be used to determine sources of dissolved sulfate and whether or not bacterial sulfate reduction is occurring.
Stable isotopes of N and O in nitrate	Can be used to determine sources of nitrate, and to track nitrate-attenuation mechanisms, such as denitrification.
Stable isotopes of C in DIC	Can be used to discriminate between DIC sourced from dissolution of carbonate minerals versus microbial respiration.

Turbidity and total suspended solids (TSS) are important data to collect for most pit lakes. Fine-grained suspended matter is often enriched in trace metals, microorganisms, and nutrients. Turbidity sensors can be attached to a multi-parameter probe or CTD probe to obtain a continuous depth profile. By collection of a subset of samples for conventional TSS measurement (filtering and weighing), one can establish a correlation between turbidity and TSS. If TSS is high, then this influences water density, which could be important for lake stratification. For example, some waters discharged into a pit lake, such as mill tailings or lime-treatment sludge, may have relatively low TDS but very high TSS. Such waters will normally sink to the bottom of the lake because of the contribution of suspended sediment to the total density.

Sunlight penetration is important to determine the depth range where primary production of O_2 takes place in a lake (often approximated by the 95% light-attenuation threshold). This can be quantified using a light sensor, usually set to measure a range of wavelengths corresponding to photosynthetically active radiation (PAR). Depth of the photic zone can also be approximated by lowering a secchi disk and recording the depth where the black and white quadrants on the disk can no longer be discerned to the observer. Turbidity is the most common reason for rapid attenuation with depth of sunlight in pit lakes. However, some lakes with low pH contain a high concentration of dissolved ferric iron which is also a strong absorber of visible light. Such lakes appear black when observed from above.

After a representative water sample is collected, it is usually split into several containers for different laboratory analyses. One bottle is typically used for analysis of a suite of major and trace elements by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The sampling plan should decide early on whether samples for ICP-AES analysis should be filtered or non-filtered, and how much acid of what type and purity should be added to preserve the samples. If filters are used, then the same filtration procedure should be followed for each visit. A common procedure is to use filters with a nominal pore size of 0.45 µm, which is sufficient to exclude most of the suspended sediment, plankton, and bacteria. Smaller pore sizes (e.g. 0.2, 0.1 µm) will capture more of the colloidal-sized particles, as well as the smaller bacteria, but are more prone to clogging. Procedure blanks made from de-ionised water should be prepared to test for the presence of trace elements (e.g. Zn) leached from sampling apparatus (e.g. gloves, syringes, filters, tubing, bottles) or preservation reagents. For trace metal work, it is recommended to acid-rinse bottles and syringes and to flush filters with de-ionised water prior to use. The analytical detection limits of inductively coupled plasma atomic emission spectroscopy (ICP-AES) are typically >1 to 10 ppb, and may be insufficient for analysis of some trace metals. Inductively coupled plasma mass spectroscopy (ICP-MS) or graphite furnace atomic absorption spectroscopy (GF-AAS) have greater sensitivity, but are also more expensive.

A 250 or 500 mL sample of raw (unfiltered) water should be collected for alkalinity and/or acidity titration, as well as laboratory checks on field parameters such as pH and SC. Alkalinity is a critical measurement that is used, along with pH and temperature, to speciate DIC between carbonic acid (H_2CO_3 or dissolved CO_2), bicarbonate ion (HCO_3^-), and carbonate ion (CO_3^{2-}). Alkalinity titrations should be performed as soon as possible after sample collection. This is especially critical for samples that contain dissolved ferrous iron: oxidation of Fe^{2+} produces ferric hydroxide and releases protons that will react with bicarbonate ion to form CO_2. Samples of raw water that turn orange or red during storage have “gone off”, and will give falsely low alkalinity values. If this problem persists, it might be a good idea to train samplers to perform alkalinity titrations in the field immediately after the water samples are collected. This can be done quickly using field alkalinity kits that employ a hand-held digital titrator and pH-sensitive indicator dyes. Acidity titrations are less commonly included in pit lake sampling plans, but provide useful information on the total acidity (i.e. sum of dissolved acids, including species such as Al^{3+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, HSO_4^-, and dissolved CO_2) in a water sample, which must be known to predict how much lime or other reagent will need to be added during future chemical treatment. Compared to alkalinity titrations, acidity titrations are somewhat complex to set up and interpret (see Kirby and Cravotta (2005) for a good review on the subject).

If the pH of a lake is <4.5, then the concentration of DIC cannot be determined by alkalinity titration, and a carbon analyser must be used. This method involves conversion of DIC to CO_2(g), which is measured spectroscopically. If DOC is present, then the carbon analyser can quantify both forms of carbon. DOC is important for several reasons, including its role in photochemical and microbial reactions and its ability to bind with heavy metals which, coincidently, decreases their toxicity to aquatic organisms, such as fish. The so-called "Biotic Ligand Model" incorporates DOC-metal interactions (Niyogi and Wood, 2004), and is being used by the US Environmental Protection Agency to set new regulatory targets for protection of aquatic life.

Major ions, including chloride (Cl^-), nitrate (NO_3^-), phosphate (PO_4^{3-}), and sulfate (SO_4^{2-}), are usually determined on filtered, non-preserved samples using ion chromatography (IC). Bicarbonate ion cannot be quantified by IC. Colorimetric analysis is also possible, and indeed the detection limits for several important nutrient species such as nitrate, phosphate, nitrite (NO_2^-) and ammonium (NH_4^+) are typically orders of magnitude lower using colorimetry as opposed to IC. The problem with colorimetry is that the results are often subject to matrix interferences. Method development is recommended using spiked samples and certified standards to confirm the reliability of any colorimetric test. Portable, battery-powered spectrophotometers are commercially available that can perform hundreds of separate tests. One test that is particularly useful is the analysis of dissolved sulfide ($H_2S + HS^-$). If free sulfide is present at depth, the chemistry of the lake waters will be drastically changed compared to shallower water that is devoid of sulfide. Dissolved sulfide is toxic to most aerobic organisms (including humans) and for this reason any lake with high sulfide concentrations at depth should be monitored for a possible release of H_2S gas. Colorimetry is also commonly used to speciate total dissolved Fe between ferrous and ferric species, i.e. Fe(II) and Fe(III), respectively, as shown in the example from the Berkeley Pit.

Dissolved cyanide (CN^-) may be an important contaminant of concern, especially if a pit lake is located near an active or former cyanide mill or heap-leach pad. The chemistry of cyanide is complex (Smith and Mudder, 1999), and often requires analysis of more than one chemical form. Total cyanide and WAD cyanide are the two most common types of analyses. The difference between total and WAD cyanide represents cyanide that is bound up in strong complexes, such as $Fe(CN)_6^{3-}$. In a pit lake environment, WAD cyanide will break down fairly quickly to a mixture of bicarbonate ion and ammonium ion (NH_4^+). If DO is present, the latter will be oxidised to nitrate. In contrast, strong metal-cyanide complexes are resistant to degradation and may persist long after all of the WAD cyanide is gone. If sulfate is present (which is usually the case in mine lakes), high concentrations of thiocyanate (SCN^-), another toxic compound, may build up as the WAD cyanide is broken down. Any monitoring programme for a pit lake where cyanide is a concern should also monitor thiocyanate.

Isotopic data may not be a critical component of a pit lake sampling plan, but nonetheless could provide unique insights that conventional chemical analysis would miss (Seal, 2003). With the advent of new bench-top instrumentation, stable isotope analysis of water samples has become both rapid and inexpensive, e.g. < US$ 20 for a combined O- and H-isotopic analysis. Different water inputs into a pit lake may have different isotopic signatures, making it possible to determine sources of recharge and to develop a water budget for the lake. Stable isotopes can also be used to estimate the mass of water lost to evaporation. Other stable isotopes may be useful to address specific questions, such as the identity of sources of S, N, or DIC. For example, is sulfate in a given lake sourced by oxidation of pyrite, or by dissolution of gypsum or hydrothermal sulfate minerals? Is bacterial-sulfate reduction occurring in the deep lake? Did nitrate come from blasting explosives or the oxidation of cyanide? Is denitrification occurring in the deep lake? Did high concentrations of CO_2 or bicarbonate ion come from the oxidation of organic matter, or dissolution of carbonate minerals? Like water, many laboratories now provide C- and O-isotopic analysis of DIC for surprisingly low cost. S and N isotopes are more expensive, but may still cost less than a complete inorganic suite of chemical analysis.

Samples for stable isotopic analysis of water need no special preparation, can be small volume (e.g. 10 mL), and, if tightly sealed with no head space, can be stored indefinitely. Thus, it is a simple matter to collect and archive water samples for later analysis. Samples for isotopic analysis of sulfate are processed by acidification with HCl, followed by addition of $BaCl_2$ to produce a $BaSO_4$ precipitate (Carmody et al., 1998). Samples for isotopic analysis of DIC are obtained by addition of $SrCl_2$ to make a $SrCO_3$ precipitate. The $BaSO_4$ or $SrCO_3$ precipitates are filtered, dried and weighed, and can be stored indefinitely. Isotopic analysis of nitrogenous species (e.g. nitrate, ammonia) usually requires a large volume, filtered sample (e.g. > 1L) which is processed at the isotope laboratory. If stored in plastic containers with a small amount of head space, the water samples can be frozen for longer-term storage.

4 Case study — the Berkeley Pit

The Berkeley Pit (Figure 1) is one of the largest and most acidic mining lakes in the world, with extremely high concentrations of dissolved metals (e.g. > 100 mg/L each of Al, Fe, Mn, and Zn). The pit began filling with water shortly after mining ceased in 1982, and continues to fill at a rate of $7.8e^{06}$ to $1.1e^{07}$ L/day, mainly from deep groundwater and underground mine pools (Gammons and Duaime, 2006). Since 2002, a monthly water level monitoring and semi-annual water quality monitoring programme has been conducted by the Montana Bureau of Mines and Geology (MBMG). This monitoring programme was implemented by the state and federal regulatory agencies as a tool to determine when in-perpetuity treatment of the lake system will begin, and to track changes within the lake and surrounding flooded underground mines which may or may not affect the quality and volume of the water to be treated. Additionally, the monitoring data are being used to optimise an ongoing resource recovery project that is extracting copper from the lake.

4.1 Berkeley Pit — field measurements

Figure 3 is an example set of field profiles collected from the Berkeley Pit in June, 2008, as part of the semi-annual MBMG sampling programme. The temperature and specific conductance (SC) profiles clearly show the vertical stratification in the lake, with a shallow, poorly mixed layer (epilimnion), an intermediate, well-mixed layer (hypolimnion), and a deep, well-mixed layer (monimolimnion). Profiles for other parameters, such as pH and Eh, show inflections at the limnological boundaries. Dissolved oxygen (DO) was present at detectable levels only in the epilimnion. The surface layer also had very high turbidity owing to oxidation of dissolved Fe^{2+} to secondary Fe(III) precipitates (Figure 2a).

The MBMG typically collects vertical profiles of field parameters prior to collection of water quality samples. By examining the field profiles, it is easy to pick which depths to collect discrete water samples. This is important because, in some years, there are only funds to analyse a small number of samples. Given this constraint, the samplers must be sure to collect at least one water sample from each of the major water layers in the lake.

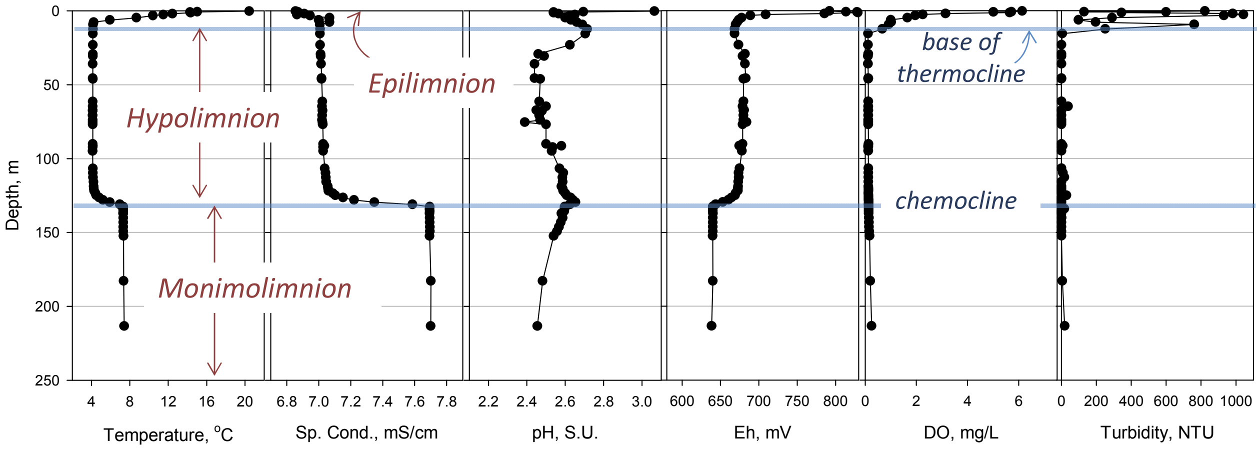

Figure 3 Berkeley Pit profiles collected in June, 2008 (MBMG, unpublished data). Sp. Cond. = Specific Conductivity, DO = dissolved oxygen, NTU = nephelometric turbidity units (Duaime and Tucci, 2009)

Five months of time-series data collected from temperature loggers suspended in the lake at different depths are shown in Figure 4. The data indicate that the surface layer of the lake during this time was poorly mixed. In contrast, the temperature traces between 15 and 61 m depth plotted right on top of each other, suggesting continual mixing of the hypolimnion. A third layer of water between 137 and 229 m (monimolimnion) had a constant temperature of 7.3°C until late September, at which time the chemocline of the Berkeley Pit lake was drawn down below an elevation of 137 m causing the two temperature traces to diverge. The lake mixed to a depth of at least 61 m following a sharp cold weather pattern in early October. However, due to its higher TDS, the deep lake (shown by the 229 m trace) remained stratified.

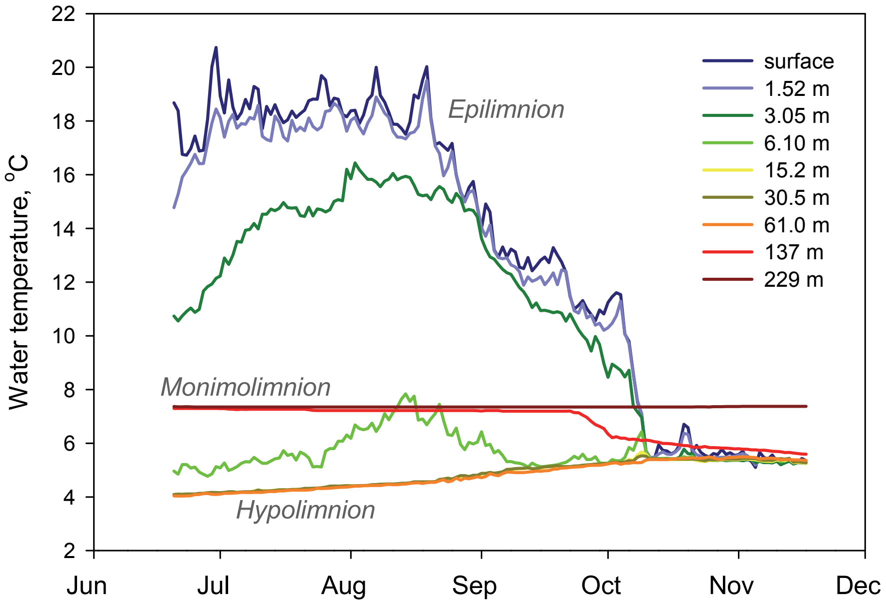

Figure 4 **Trends in water temperature with time at selected depths in the Berkeley Pit lake, 2008 (Duaime and Tucci, 2009)**

4.2 Berkeley Pit— chemical analyses

All chemical analyses of the Berkeley Pit lake collected as part of the MBMG semi-annual monitoring are available electronically at GWIC (2011). Summaries of these data are published annually by the MBMG as Open File Reports (Duaime and Tucci, 2009, 2011), many of which are available in PDF format at MBMG (2011). In this chapter, we have chosen to show some example data for dissolved iron (Fe). Figure 5a shows changes with depth in the concentration and redox speciation of Fe in June 2008. Note the abrupt transition from Fe^{2+} > Fe^{3+} at depth to Fe^{3+} > Fe^{2+} above the chemocline. This was important information for the active mining company, who is recovering dissolved copper from the pit lake by a cementation process. Water from the lake is pumped to the surface where dissolved Cu^{2+} is plated onto scrap iron as Cu metal. The Cu-depleted water is then returned back to the surface of the lake. Because high concentrations of ferric iron (Fe^{3+}) interfere with the Cu recovery process, the pump intake needs to be placed below the Fe^{3+}/Fe^{2+} transition. Figure 5b shows how the ongoing Cu recovery operation steadily drew down the elevation of the chemocline in the lake between 2005 and 2009, effectively changing the lake from being meromictic to being vertically mixed.

The dramatic decrease in the concentrations of dissolved Fe shown in Figure 5b was an unexpected consequence of the Cu recovery operation that may have a beneficial impact with respect to future pit lake management. Recent calculations suggest that the total acidity (i.e. sum of H^+ + dissolved metals) of the lake has decreased significantly compared to pre-2005 levels. This may translate into a substantial savings in the cost of lime when full-scale treatment of the lake begins, sometime after 2020.

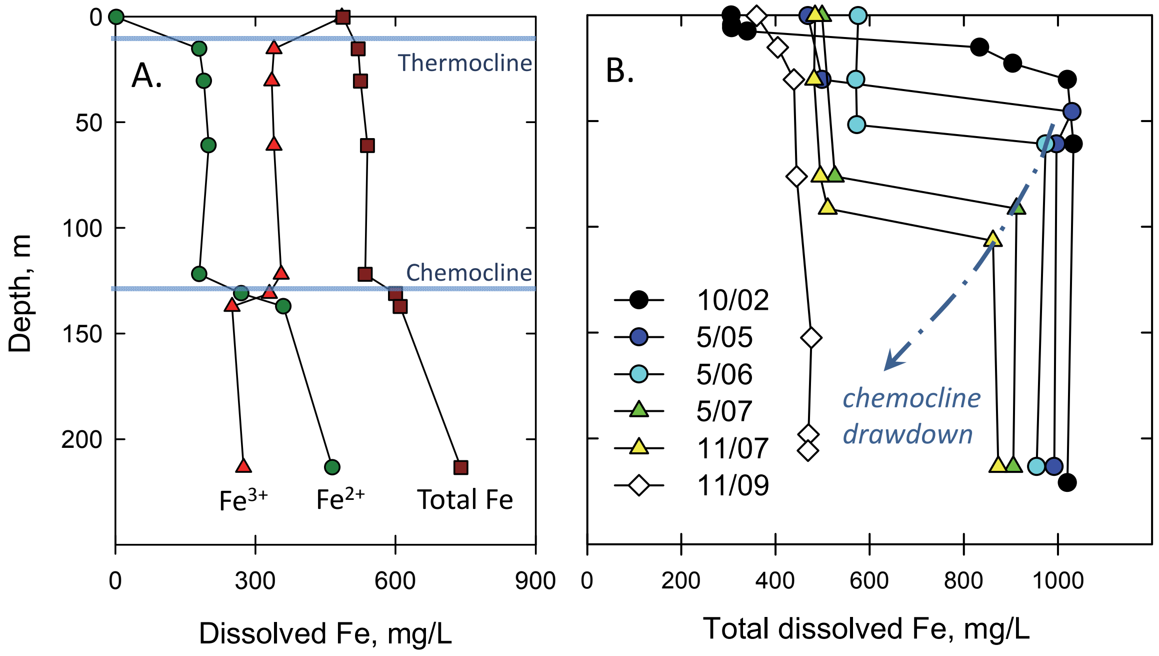

Figure 5 **Trends in Fe concentration and speciation with depth and time in the Berkeley Pit lake: A) data from June, 2008; B) comparison of total Fe data from 2002 to 2009, showing drawdown in the chemocline (Duaime and Tucci, 2011)**

4.3 Berkeley Pit — stable isotope analyses

Although not part of the MBMG's routine sampling plan, samples for stable isotope analyses have been collected from the Berkeley Pit and surrounding mine waters by researchers at Montana Tech. Trends in the stable isotopic composition of water in the Berkeley Pit lake are shown in Figure 6. The pit lake water was approximately 10–25% evaporated in 2003, with an increase in the extent of evaporation towards the surface, i.e. above the elevation of the 2003 chemocline, at about 50 m. In contrast, the isotopic compositions of the surrounding flooded mine shafts in Butte plot close to the local meteoric water line, indicate minimal evaporation prior to recharge. At the other extreme, water contained in a large tailings pond north of the Berkeley Pit was highly evaporated in 2003 (>40% water loss).

Trends in the stable isotopic composition of dissolved sulfate in the Berkeley Pit and surrounding mine waters of Butte are summarised in Figure 7. The Berkeley Pit lake has extremely high concentrations of sulfate (> 7,500 mg/L as SO_4). The isotopic composition of this sulfate is homogenous with depth in the lake, and overlaps with that of pyrite from the Butte orebody (Figure 7). This result is consistent with the hypothesis that most of the sulfate in the lake was sourced by oxidation of pyrite. In contrast, the sulfate-S present in the surrounding flooded mine shafts in Butte consists of a mixture of pyrite-derived S and sulfate released by dissolution of the mineral anhydrite ($CaSO_4$). Anhydrite is a common high-temperature alteration mineral in porphyry copper deposits, and is moderately soluble in cold water. In Butte, most of the early anhydrite that formed in the vicinity of what is now the Berkeley Pit was destroyed during later hydrothermal events, being preserved only in the deeper and more peripheral parts of the district. This interpretation of the geologic history is consistent with the isotope data since the water from the mine shafts flooded with water that is deeper and located outwards from the centre of the district contains sulfate that has a partial anhydrite signature.

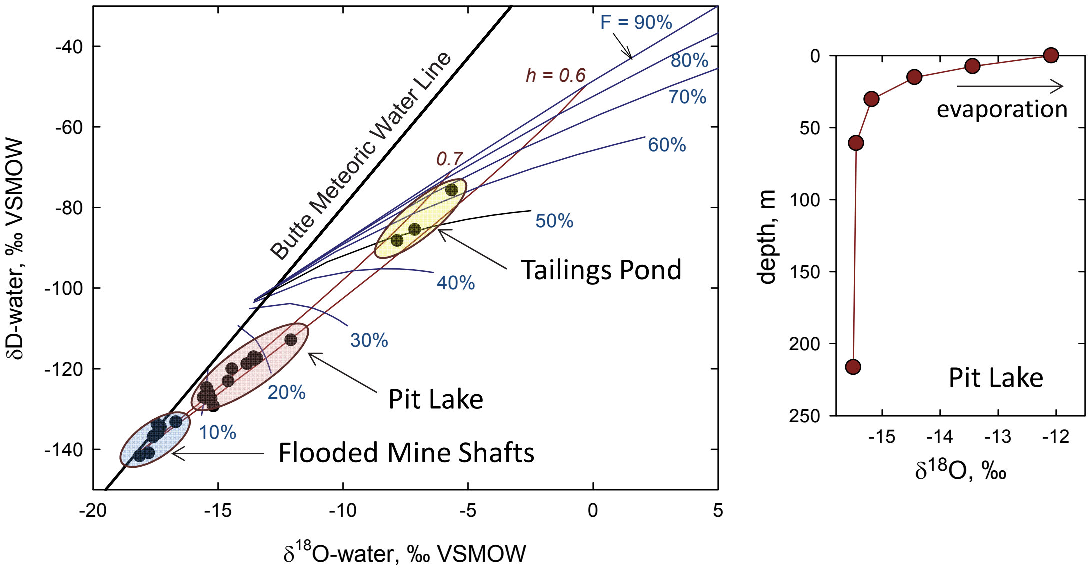

Figure 6 A) Stable isotopic composition of the Berkeley Pit lake and surrounding waters. F = fraction of water evaporated; h = relative humidity. B) Changes in O-isotopic composition of the Berkeley Pit lake (October, 2003) with depth. Both graphs are modified from Gammons et al. (2006)

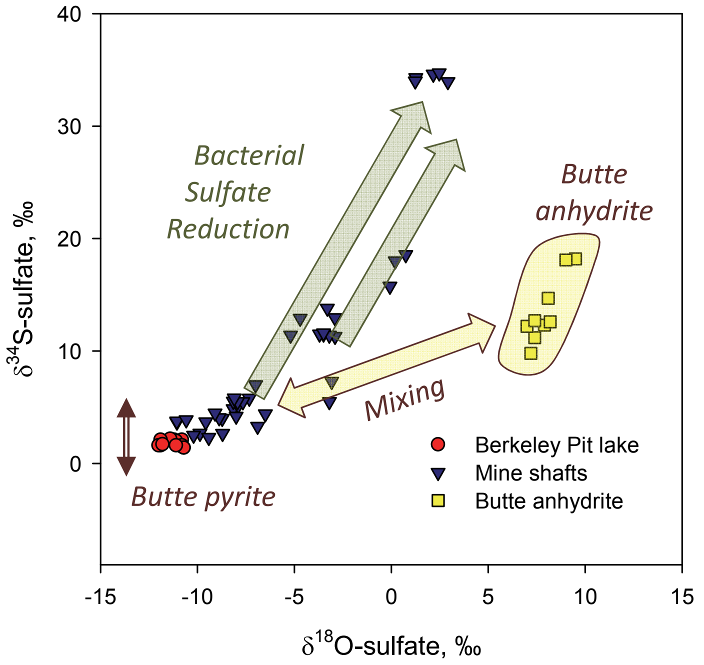

Figure 7 A) Stable isotopic composition of dissolved sulfate in the mine waters of Butte compared to the isotopic composition of pyrite and anhydrite in the orebody. Sulfate in the pit lake was derived almost entirely from oxidation of pyrite, whereas sulfate in the flooded mine shafts is a mixture of pyrite-S and dissolution of anhydrite, modified by bacterial sulfate reduction (adapted from Gammons et al., 2009b)

A few mine shafts plot off the mixing line between anhydrite and pyrite, and contain sulfate that was noticeably enriched in both ^{34}S and ^{18}O (Figure 7). These waters had a sharp odour of hydrogen sulfide (H_2S). The S-isotope ratio data confirmed that the dissolved sulfide was formed by bacterial sulfate reduction (Gammons et al., 2009b). Despite the fact that the deep Berkeley Pit lake is anoxic, no chemical or isotopic evidence has been found for significant activity of sulfate-reducing bacteria (SRB) in the lake. The lake sediment contains abundant organic carbon in both dissolved and solid form (Cameron et al., 2006). Thus, the paucity of SRB is probably due to the low pH of the lake, coupled with the extremely high concentrations of dissolved metals, such as Cu and Zn, which are known to be toxic to many species of SRB.

5 Conclusion

This chapter has outlined a framework to assist with the development of an appropriately focussed sampling plan to monitor the water quality of a pit lake. Although no single sampling design will be optimal for all lakes, the basic tenants of good measurement design and quality assurance/quality control (QA/QC) are universally applicable (see EPA, 2002). Namely:

1. The sample database must be representative of the environmental condition (i.e. make sure enough samples are collected to fully characterise the lake, and that the samples do not degrade prior to laboratory analysis);
2. The data collected in a given year must be comparable to similar data collected in other years (i.e. use standard field and laboratory methods);
3. The database must be complete (i.e. avoid large data gaps in the types of analyses performed or the dates of sampling);
4. The data must be accurate (i.e. follow proper calibration procedures to optimise precision and eliminate systematic error);
5. The analysis method used must be sufficiently sensitive (i.e. choose a method with a detection limit that is low enough so that the data can be interpreted within the context of relevant applicable water quality guideline criteria).

In most cases, certified laboratories will provide a full QA/QC report on demand, at no additional cost. This information should be archived as part of the project database. If analyses are done in-house, then QA/QC protocols can be customised to address the needs and capabilities of the monitoring plan.

In the authors' experience, and in conversations with other pit lake researchers, it appears that there are relatively few mining lakes world-wide with a water quality database that meets all of the measurement design and data-quality criteria outlined above, and even fewer where the data are publically available. Sufficiently comprehensive high-quality time-series databases are essential not only to empirically understand the status of a pit lake but to enable the refinement and calibration of physico-chemical prediction models. Lack of such comprehensive data is probably the single biggest factor that is holding back the science of pit lake research.

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