Chapter 3
Limnology of Pit Lakes

3.1 Physical Properties of Acidic Pit Lakes

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Mine water in pit lakes can have a pH of 3 or even less. In some cases, we find gradients of pH within the same lake extending from acidic to neutral. In addition, pH-neutral water can possess the potential to turn acidic when brought into contact with oxygen. In acidic waters, the concentrations of heavy metals can be high, which differentiates such lakes from 'natural' lakes, except for a few volcanic ones. Given these high concentrations, common approximations for electrical conductivity or density that may be reasonable in less contaminated water will not necessarily be accurate. In conclusion, alternative approaches need to be developed. In the following subsection, the most common approaches to deal with these properties are presented.

3.1.1 Electrical Conductivity

Acidity represents a reactive constituent. When iron rich, monimolimnetic waters of Waldsee are brought into contact with dissolved oxygen, iron is precipitated. The resulting hydrolysis of ferric iron, releases H^+ ions, which directly affect the carbonate buffering system and hence lower the conductivity. As a consequence, the implementation of electrical conductivity as a tracer underlies some severe restrictions.

Natural freshwater lakes usually have an electrical conductivity in the range of 0.1–0.5 mS/cm at 25°C. Mine drainage can have considerably higher conductivities (see Fig. 3.1). As a consequence, the precipitation versus evaporation deficit in the eastern German summer shows up in high values of conductivity during summer stratification (Karakas et al. 2003), while during deep circulation and in
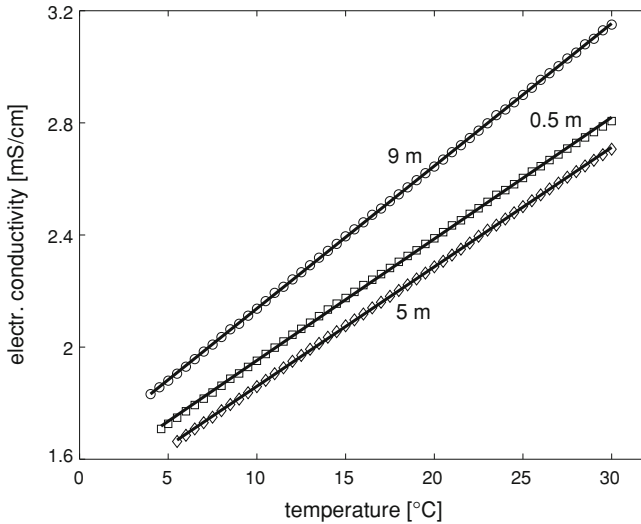
Fig. 3.1 Temperature dependence of electrical conductivity in water samples from several depths in Mining Lake 111 versus temperature (0.5 m—epilimnion, 5 m—hypolimnion, 9 m—monimolimnion; modified after Karakas et al. 2003)

the hypolimnion conductivity remains roughly constant. High concentrations of dissolved substances can contribute to epilimnetic water density. Especially in areas of dry summers, this effect can contribute to deep mixing when the higher epilimnetic concentrations of dissolved substances help overcome temperature stratification when falling autumn temperatures allow deep mixing. Ocean waters have an electrical conductivity of around 42 mS/cm at 25°C, while some (natural) salt lakes show an electrical conductivity even higher than 200 mS/cm (Dead Sea, Akawwi 2006; case study 5.3).

Acidic waters contain a considerable concentration of dissolved substances, i.e. the H^+ ions and corresponding ions to balance the electric charge. The specific electrical conductivity of H^+ is particularly high, i.e. a factor of 5–10 higher than most other ions (see Millero 2001). The conductivity contribution of H^+ ions (and OH^-) can be evaluated for infinite dilution, which of course is not realistic for pH values below 1 or above 13. The conductivity contribution of H^+ and OH^- give a lower limit of the electrical conductivity at 25°C of lake water (for the pH range 0–14, see Fig. 3.2). If the conductivity of a water sample is at least an order of magnitude above the curve in Fig. 3.2, H^+ (and OH^-) ions contribute a much lower portion to electrical conductivity, compared to other ions.

If lakes are neutralized by the addition of buffers, conductivity may remain high, as seen in the example of Lake Bockwitz, where soda was added to reduce acidity. The situation is less drastic if, during the filling period, water had been introduced from natural systems to dilute the highly mineralized (acidic) drainage from the mined area (e.g. Lake Goitsche, Boehrer et al. 2003).
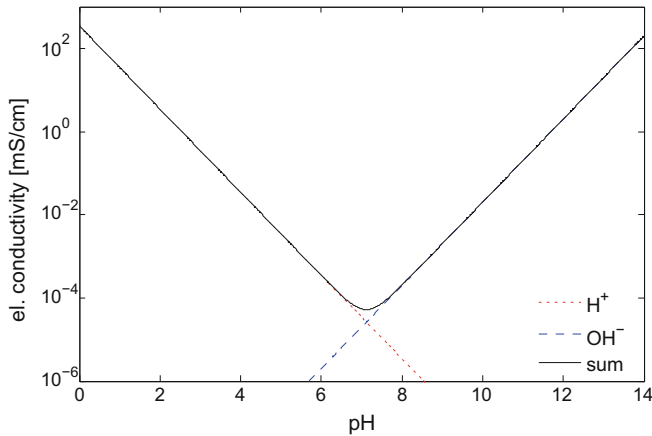
Fig. 3.2 Electrical conductivity at 25°C of the water ions, H^+ and OH^- and the sum against pH, calculated for infinite dilution

Electrical conductivity is a function of dissolved substances and temperature. To use it to assess the concentration of dissolved substances, the temperature effect is commonly removed by referring to the conductivity, as it were at a certain reference temperature, usually 25°C. Experience shows that the effect of temperature can be approximated quite well using linear regression, $C(T) = aT + b$ (see Fig. 3.1). This yields an equation for calculating κ_{25} from a field measurement of pairs of temperature T and in situ conductivity $C(T)$, using Eq. 3.1,

$$\kappa_{25} = \frac{C(T)}{\alpha_{25}(T - 25°C) + 1} \tag{3.1}$$

where α_{25} is commonly set to 0.02/K, or rarely to slightly lower values for natural neutral lakes.

All ions show specific temperature dependences, though, except for H^+, they lie within a relatively narrow band (see Sorensen and Glass 1987). As a consequence, the electrical conductivity of neutral waters calculated in this manner aligns well with Eq. 3.1. In acidic waters, however, the temperature dependence must be quantitatively analysed. In lakes with a low pH, a value for α_{25} considerably smaller than 0.02/K must be used (see Table 3.1).

For temperature compensation, the most common reference temperature is 25°C, though tables have also been developed for 20°C. Choosing a reference temperature closer to the temperatures found in the lake can improve the accuracy of the results (e.g. Boehrer et al. 2009b).

Oceanographers define salinity S as a function of temperature T and electrical conductivity C. Values are given in practical salinity units [psu], which give a good indication of dissolved salts in g/kg of ocean water and brackish water.

Table 3.1 List of empirically determined α_{25} values for various lakes

Lake	Sampling date	pH	α_{25}, 1/K	κ_{25}, mS/cm	Reference
Waldsee monimolimnion	2006-12-12	6.6	0.0194	0.974	Boehrer et al. (2009a)
Waldsee mixolimnion	2006-11-16	7.2	0.0194	0.481	Boehrer et al. (2009a)
RL 111 epilimnion	2001-08-21	2.67	0.0163	2.603	Karakas et al. (2003)
RL 111 hypolimnion	2001-08-21	2.67	0.0165	2.601	Karakas et al. (2003)
RL 111 monimolimnion	2001-08-21	2.8	0.0173	2.899	Karakas et al. (2003)
Moritzteich mixolimnion	2006-11-15	3.2	0.0178	0.970	Here
Moritzteich monimolimnion	2006-12-12	6.7	0.0194	1.497	Here

$$S = S(C, T) \tag{3.2}$$

Salinity is calculated over several steps, involving a number of empirical constants. The exact numerical approach can be read in the original literature or—in a more comprehensible way—in the review by Boehrer and Schultze (2008). At the time of writing this manuscript, UNESCO is providing a calculator on the internet for assessing properties of ocean water using coefficients by Fofonoff (1985). For low salinity limnetic water (<0.6 psu), Chen and Millero (1986) introduced a correction factor.

$$S = 1.00488_{\text{ocean}} \tag{3.2a}$$

In limnic waters, salinity has no clear definition. It would be better to refer to total dissolved substances, which is more clearly defined. However, as the most commonly accepted density formulae refer to this definition of salinity as an intermediate step, it is still in common use. Oceanographic equipment, e.g. multiparameter probes, often supply the salinity value in psu from measurements of temperature and electrical conductivity conveniently in the data output. It must be kept in mind that this value has been evaluated under ocean condition assumptions.

3.1.2 Density

Density gradients, i.e. potential density gradients contrary to in situ density (see e.g. Boehrer and Schultze 2008), in lakes control whether stratification is stable or whether density differences drive vertical exchange flows. An accurate approach for density is mandatory for any quantitative work on the stability of stratification. Density differences in lakes usually lie in the range of a few per mill, i.e. some kg/m^3, which are responsible for stable stratification during summer, and stable stratification in meromictic lakes.

There are four approaches to calculating density in lakes:

1. Using temperature and electrical conductivity data, while implementing ocean assumptions,

2. Making freshwater assumptions (of natural lakes) at low salinity,
3. Evaluating lake-specific regressions between temperature, conductivity, and density, and
4. By adding partial molal volumes and masses, when concentrations of all relevant dissolved substances are known.

1. Oceanographers use the so-called UNESCO formula by Fofonoff and Millard (1983) to evaluate density. This approach is valid only between 2 and 42 psu of salinity, and hence should only be used for a small number of lakes. In addition, the salt composition must be similar to brackish water (e.g. Rassnitzer See, Wallendorfer See in mining area Merseburg-Ost; Böhrer et al. 1998). This is the most commonly used approach for calculating density in numerical stratification models of lakes, and so this formula has become very important in limnology.
2. For natural lakes with salinities below 0.6 psu, Chen and Millero (1986) proposed using a different approach to calculate density. They suggested using a term that is based on the above definition of salinity for limnic waters to incorporate the density contribution of solutes. However, for acidic lakes, and also for most natural lakes, the composition of dissolved substances does not concur with the waters used for the regressions by Chen and Millero.
An alternative was offered by Bührer and Ambühl (1975) for alpine lakes (in Europe): They used a third order polynomial for density against temperature and added the density of dissolved substances with a linear term for conductivity. This formula at least seems to satisfy the density requirements in several natural lakes, possibly with a small adjustment for the coefficients (e.g. Heinz 1990). The numerical approaches, including the required coefficients, were listed by Boehrer and Schultze (2008).
3. In many cases, these approaches are not accurate enough to calculate density in pit lakes, as the differences due to chemical composition of solutes lead to considerable errors. In these cases, an empirical approach should be used.
If concentration changes of solutes are found, but the composition of the solutes does not change much, the best approach is probably the following: a lake water sample is investigated for its electrical conductance ($\kappa_{25sample}$ see Eq. 3.1) and its density over the required temperature range is measured in a densitometer. Usually a forth order polynomial is required to fit the density curve within the accuracy that is delivered from high accuracy densitometers (relative accuracy, e.g. PAAR Graz). A "pure water" sample is also measured in the same densitometer. The density difference between the samples is attributed to the conductivity of the lake water sample, as a measure of the solute concentration. The density formula hence has the general form (e.g. Karakas et al. 2003)

$$\rho = \rho_W + \frac{\kappa_{25}}{\kappa_{25sample}} \Delta\rho \tag{3.3}$$
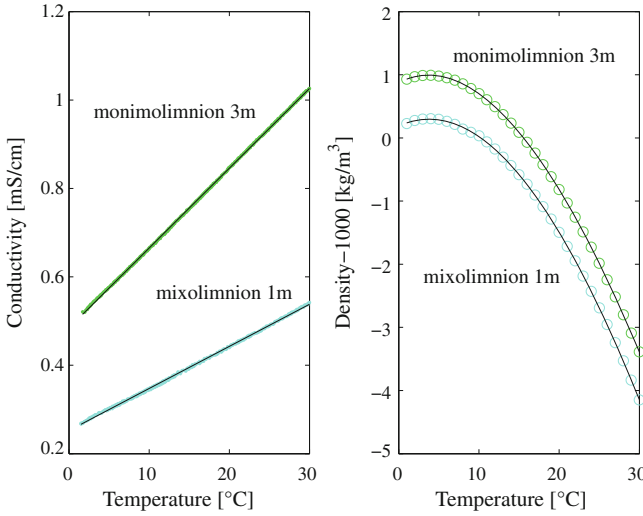
Fig. 3.3 Conductivity (*left panel*) and density (*right panel*) of a mixolimnion sample and a monimolimnion sample from Waldsee, Germany versus temperature (from Boehrer et al. 2009a, with permission of American Geophysical Union)

Nowadays, the pure water reference ρ_W can be taken from Kell (1975) or Tanaka et al. (2001). The density difference $\Delta\rho$ can be a constant or a polynomial in temperature $\Delta\rho(T)$. Conducting a dilution series can improve the accuracy, especially in highly saline systems (e.g. Jellison et al. 1999).

If a lake consists of two layers that differ in their chemical composition, as in meromictic lakes (see below), the gradient can be reflected in the following approach: starting from Eq. 3.3, the lake sample is replaced by the monimolimnion sample (higher conductance from deep waters) and the pure water sample by a mixolimnion sample (lower conductance from shallow waters), e.g. Boehrer et al. (2009a). A density regression $\rho_{\text{mixo}} = \sum_{i=0}^{4} p_i T^i$ (see Fig. 3.3) is produced, and a corresponding ρ_{monimo} for the monimolimnion sample. The density difference between both samples $\rho_{\text{monimo}} - \rho_{\text{mixo}} = \sum_{i=0}^{4} q_i T^i$ is attributed to the higher conductance of the monimolimnion sample.

Now, any sample of conductance κ_{25} can be linearly interpolated for density calculation, under the assumption that any water parcel behaves similar to a linear combination of the samples measured in the laboratory. Thus, a lake-specific density function can be attained for calculating density profiles from field measurements of temperature, T, and in situ conductivity, C (yielding κ_{25} following Eq. 3.1):

$$\rho = \sum_{i=0}^{4} q_i T^i \rho_W + \frac{\kappa_{25} - \kappa_{25-\text{mixo}}}{\kappa_{25-\text{monimo}} - \kappa_{25-\text{mixo}}} \cdot \sum_{i=0}^{4} q_i T^i \tag{3.4}$$

The evaluated coefficients for Waldsee (Boehrer et al. 2009a) are lake-specific and hence have not been listed here.

4. Finally, density of lake waters can be calculated from partial molal volumes of solutes. This approach requires that all substances contributing significantly to density are known. The approach is straightforward, but has not been widely used in limnological practice: adding the masses of water plus the concentrations in molal units b_n of substances of molar mass M_n yield the mass m of the solution, while the volume of water at the respective temperature plus the molal volumes $V_n = \frac{\partial V}{\partial b_n}$ yield the volume V of the solution (Millero 2001, Table 3.19).

$$\rho_{mv} = \frac{m}{V} = \frac{m_W + m_W \sum_n b_n M_n}{m_W/\rho_W + m_W \sum_n b_n V_n} = \frac{1 + \sum_n b_n M_n}{1/\rho_W + \sum_n b_n M_n} \qquad (3.5)$$

Molar masses of solutes are easily available, but molal volumes depend on temperature and ionic strength. A numerical approach can be found in the work of Boehrer et al. (2010), where the required coefficients of limnologically important substances are also given. The numerical approach RHOMV can be accessed via the internet (www.ufz.de/webax).

3.1.3 Optical Properties of Lake Water

Due to high concentrations of dissolved substances, mine lakes can have very distinct coloring. Below pH of about 3, ferric iron is soluble in water; a pronounced red color is often encountered. In the aluminum buffered pH range of about 5, mine water can show a turbid blue to turquoise color. Light attenuation in these colored lakes can be very high.

Measurements in Moritzteich show the spectrum of irradiated light against depth (Fig. 3.4), which shows pH values of about 3.2 in the mixolimnion (above 10 m depth). While directly below the surface there is considerable input of near infrared light and near UV, wave lengths below 300 nm and above 750 nm have been (nearly) completely attenuated before reaching a depth of 1 m. Hence light attenuation is a function of wave length. This is also reflected in the perception of water color.

While light intensities of wave lengths between 400 and 700 nm can decrease by 50% from a depth of 0.01–1 m, attenuation is much less below 1 m. At a depth of 2 m, about 80% of the light intensity at 1 m depth can be recorded. Here, light attenuation is also a function of water depth. In conclusion, the common assumption of exponential light intensity decrease with depth is a rough approximation, at least in some cases.

Vertical gradients of dissolved substances result in variable water properties. In the case of meromictic lakes, such a transition can be very sharp, as seen in Moritzteich where water properties go from oxic mixolimnion to anoxic monimolimnion conditions within several decimeters (see Fig. 3.5). While mixolimnetic
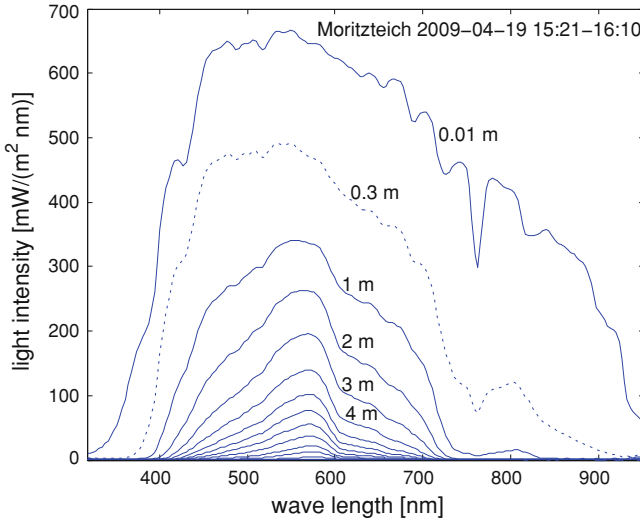
Fig. 3.4 Spectrum of irradiated light in Moritzteich against depth. Interval of solid lines is 1 m, broken line at 0.3 m depth. Measurements were taken under a clear sky in the afternoon between 15:21 and 16:10 Central European Time

waters are clear, monimolimnetic waters have a distinct reddish color, which is attributed to the very high concentrations of iron and dissolved organic matter. A narrow turbid band about 15 cm thick separates the two layers (Figs. 3.5 and 3.6).

Optical properties in these transitions can be investigated more closely with multiparameter probes. Profiles of turbidity (i.e. backscattered white light) and light transmissivity can be acquired. Data from Moritzteich (Fig. 3.5) quantify the optical impression of Fig. 3.6. The turbidity maximum and transmissivity minimum can be seen in acquired data sets at a depth of about 10 m, where oxygen drops from mixolimnetic values to monimolimnetic values and electrical conductivity rises sharply.

In addition to particularly high light attenuation, we can find extremely clear water in acidic pit lakes. Mine Lake 117 represents this type of lake, where visibility is very high, and the lake bed at a depth of about 7 m can be visible from the lake surface. The variability of optical properties in acidic lakes is demonstrated in Fig. 3.7. Light absorption data can be compared for clear Mine Lake 117, a residual turbid, acidic, iron-rich lake (residual lake Niemegk, now part of neutral Lake Goitsche), and a highly acidic, non-turbid, red mine lake (107). In general, the lakes form two groups, where the red color seems to dominate spectral absorption, while the effects of turbidity are reflected in the shallower depths, where similar light intensities are found (see depiction of the spectra in Fig. 3.7).
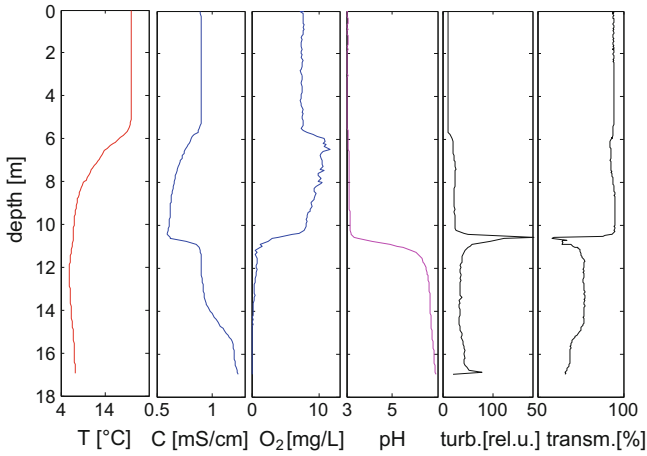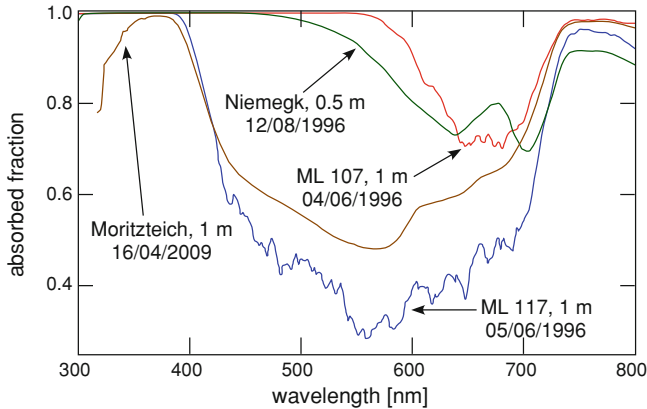
Fig. 3.5 Profiles of temperature, electrical in situ conductivity, dissolved oxygen (numerically corrected for response time of 5.5 s), pH, turbidity, and light transmissivity against depth in Moritzteich on 5th July 2007

Fig. 3.6 Water sample from a depth of about 10 m from Moritzteich, showing the transition from mixolimnion to monimolimnion
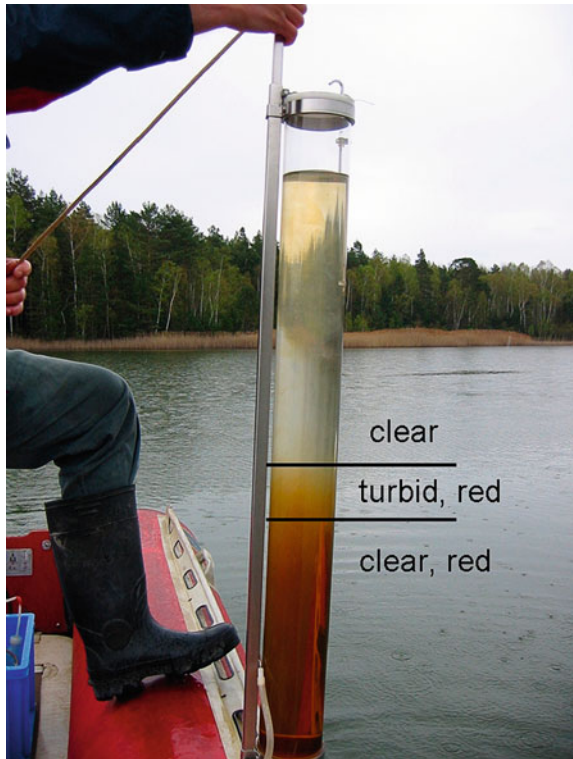
Fig. 3.7 Light attenuation in acidic pit lakes: ML 117: Mining Lake 117 (pH = 3, very clear), ML 107: Mining Lake 107 (pH = 2.4, clear and red) and residual lake Niemegk (acidic, pH = 2.7, turbid red; all data from Schimmele and Herzsprung 2000) in comparison to Moritzteich (mixolimnion pH = 3.2)

3.1.4 Stratification and Circulation

At the surface, lakes are exposed to seasonal changes in weather conditions. Exposed to sensible heat exchange with the atmosphere and irradiation from the sun, surface waters show a pronounced annual temperature cycle (see Fig. 3.8). As diffusive transport through water is slow, deeper layers are shielded from heat input from the atmosphere. Consequently temperature excursions at greater depths are generally much smaller over an annual cycle (Fig. 3.8). For general features of lake stratification, we refer to Boehrer and Schultze 2008.

During stratification, the density at the lake surface is less than in deeper water. As a consequence, vertical exchange of water parcels requires energy. If not enough energy is available to overcome the density difference, the lake remains stratified. Usually a strong temperature gradient (thermocline) is formed. Lower autumn temperatures allow deeper mixing due to falling surface temperatures and higher water density at the surface. As a consequence, the annual cycle of a lake is divided into stratification and circulation periods (see Fig. 3.9).

During stratification periods, vertical exchange of dissolved substances is very much restricted to vertical circulation of the epilimnion in cold and windy periods. Below the thermocline, vertical transport is generally small. In areas of high density gradients, transport coefficients can be close to the molecular level (von Rohden et al. 2009) while at depths that are weakly stratified, transport coefficients can be larger by several orders of magnitude (e.g. von Rohden and Ilmberger 2001).

In small- to medium-size lakes, this turbulent transport mainly happens at the side boundaries where waves and currents interact with the slope of the side walls (Gouldsmit et al. 1997). Turbulence created in the open water only contributes a
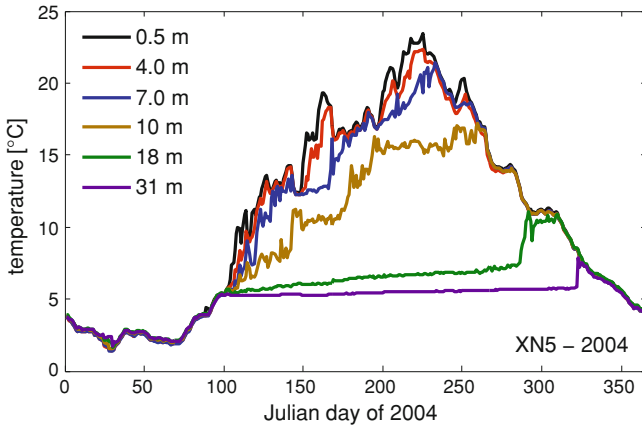
Fig. 3.8 Temperature time series acquired at several depths in Lake Goitsche at sampling site XN5
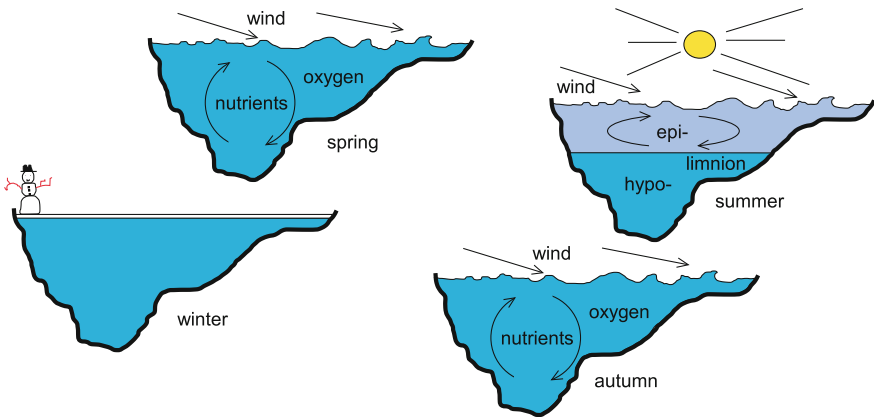
Fig. 3.9 Circulation pattern of a dimictic lake, with a circulation period in spring and autumn, separated by stagnation periods during summer, and periods of ice cover in winter

large portion of the vertical transport in larger lakes (e.g. Lake Constance, Boehrer et al. 2000; Kocsis et al. 1991). As the density gradient is the crucial quantity to overcome, transport coefficients have been correlated with the potential density gradient in the form of a stability frequency

$$N^2 = -\frac{g}{\rho}\frac{\partial\rho}{\partial z} \tag{3.6}$$

for an empirical correlation of transport coefficients under given stratification conditions (Heinz et al. 1990; von Rohden and Ilmberger 2001).

In contrast, during circulation periods, vertical transport happens at a fast rate. Oxygen is supplied to deeper layers of the lake and dissolved substances, which have accumulated in the deep waters during the stratification period, are redistributed through the lake.

If a lake is temperature stratified during summer and covered by ice during winter, it usually experiences two separate stratification periods (stagnation), separated by two deep circulation periods. Such lakes are called dimictic. Usually lakes without an ice cover circulate sporadically during winter under appropriate weather conditions. These lakes are called monomictic, as they show one extended period of stratification and one period of (intermittent) full vertical circulation over an annual cycle.

Only very deep lakes without gradients of dissolved substances can have continuous stratification throughout winter without an ice cover. These lakes may exhibit other specialties of permanent stratification due to pressure effects on the temperature of maximum density (see Crawford and Collier 1997; Petterson 1902; Yoshimura 1936). This kind of stratification has been observed in very deep crater lakes in Japan (Fig. 3.10, Boehrer et al. 2009b), which have a similar shape and size as large mine pits (several kilometres in diameter and depths that can exceed 200 m). Due to the small horizontal dimension, the deep water stratification in these lakes corresponds to model results derived under consideration of horizontal homogeneity and stability criteria (Boehrer et al. 2008).

Deep water renewal by thermobaric instabilities, as postulated for the deep water renewal in Lake Baikal (Weiss et al. 1991), do not play an important role at this size of lake basins. In very deep lakes, the difference between potential temperature and in situ temperature can become important, especially if deep water temperatures differ much from the temperature of maximum density (see e.g. Boehrer and Schultze 2008).

If surface temperatures of a lake never fall below the temperature of maximum density around 4°C, the deep water will have a temperature above 4°C. Hence, these lakes can only circulate vertically when surface waters have cooled sufficiently to overcome the density of the deep water. Due to the variability of winter temperatures, this is not necessarily the case every winter, especially if the lakes are deep. Such lakes are termed oligomictic.

In cases where gradients of dissolved substances contribute significantly to the density stratification, concentrations in the deep water may suffice to prevent a lake from a full overturn (e.g. Findenegg 1933; Hutchinson 1957). Isolated from exchange with the atmosphere, the deepest layers in the lake develop a chemical milieu different from the waters above. Such a bottom layer is called a monimolimnion, contrary to the mixolimnion, i.e. the ensemble of epilimnion and hypolimnion above (see Fig. 3.11). A zone of high chemical gradients, a 'chemocline' separates the two layers. Such lakes are called meromictic, as opposed to holomictic, when a full overturn of the water masses takes place at regular or irregular intervals.

Many lakes in deep mine pits will develop meromictic conditions (e.g. Boehrer and Schultze 2006; Stevens and Lawrence 1997, 1998). Analogies have been reported between volcanic lakes and lakes forming in abandoned opencasts
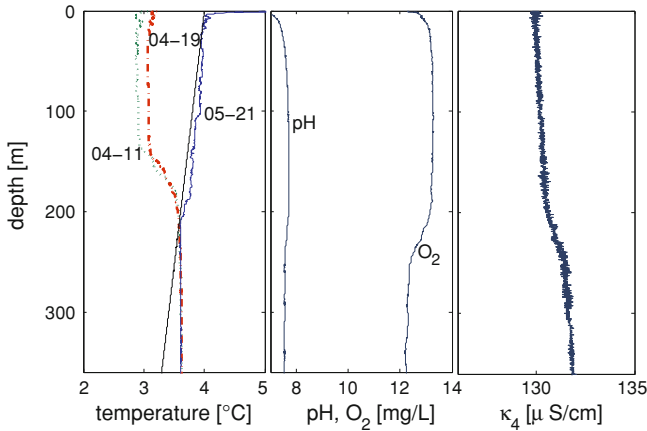
Fig. 3.10 Profiles of temperature, electrical conductivity, pH, and dissolved oxygen in Lake Shikotsu in Japan from 21st May 2005 (and other dates where annotated, modified after Boehrer et al. 2009b)

concerning shape and size (Boehrer et al. 2009b), geochemistry and microbial activity (e.g. Wendt-Potthoff and Koschorreck 2002), and meromixis (e.g. Boehrer and Schultze 2006; Murphy 1997; Sánchez-España et al. 2008; Stevens and Lawrence 2006).

A number of geochemical processes can be involved in sustaining the density stratification (see Table 3.2), including the iron cycle as the most prominent for lakes originating from mining (see Boehrer and Schultze 2006, 2008). In addition, the groundwater connection plays an important role in many meromicitic pit lakes (von Rohden and Ilmberger 2001; Seebach et al. 2008; von Rohden et al. 2009). Quantification and numerical simulation of processes controlling meromixis remain a challenge (Böhrer et al. 1998; Jellison et al. 1998; Heidenreich et al. 1999; Fig. 3.12).

Besides iron, the anoxic decomposition of organic material, manganese, and calcite precipitation must be included in stability considerations. Many other elements experience co-precipitation, when the above-mentioned chemicals form solids in the water column. For a proper meromixis prognostication, a full geochemical model is required. Geochemical models have been developed (Müller et al. 2008; Salmon et al. 2008), but they still require the proper coupling of geochemical processes to density effects to properly reflect the evolution of stratification (Moreira et al. 2011).

In many cases, mining has disrupted an equilibrium that had existed for many centuries or even millennia before. Removal of an overburden and lowering the water table has provided oxygen to layers where input had previously been very low. As a consequence, some mineral deposits have gained mobility, such as metal ions after oxidation of their sulfide deposits. Depending on the paths they have taken before entering a pit lake, groundwaters from various aquifers can greatly vary in their concentrations of dissolved substances. As a consequence, pit lakes in general are exposed to high mineral gradients.
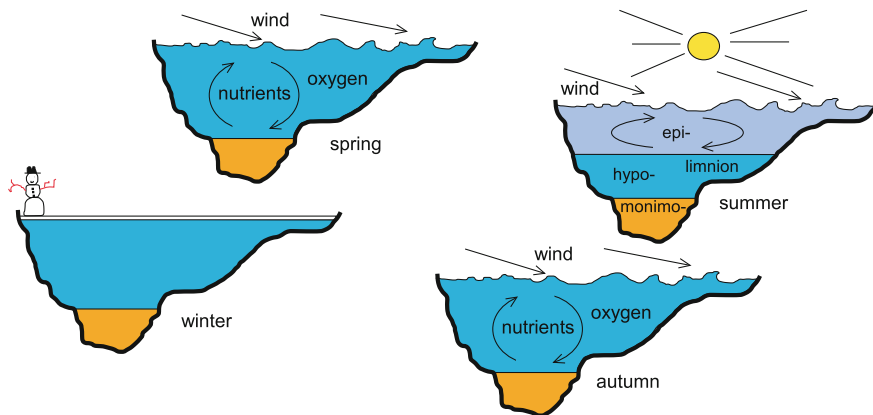
Fig. 3.11 Circulation pattern of a meromictic lake; the chemically different monimolimnion remains in the deepest depression of the lake bed throughout the year

Table 3.2 Documented precipitation processes responsible for sustaining meromixis

Substance	Lake, country	Reference
Sodium sulphate	Shield lakes, Canada	Rawson and Moore (1944)
Organic material	Längssee, Austria	Frey (1955)
Calcite	Lake La Cruz, Spain	Rodrigo et al. (1998)
Iron	Swinsjöen, Norway	Kjensmo (1967)
Manganese	Lake Nordbytjernet, Norway	Hongve (1997)
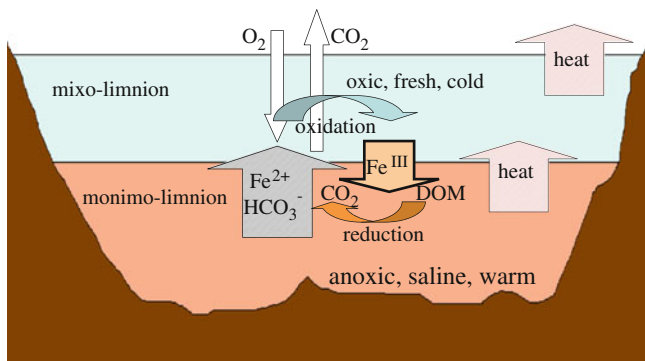
Fig. 3.12 Geochemical cycle sustaining the iron meromixis in Waldsee (from Boehrer et al. 2009a, with permission of the American Geophysical Union)

Monimolimnia, however, do not represent entirely isolated water bodies. There is a certain minimum diffusive exchange with the overlying mixolimnion. In addition, small-scale turbulence may transport dissolved substances across the chemocline.

In many cases, monimolimnia receive inflows from the groundwater domain, and discharge into it (Heidenreich et al. 1999). Pit lakes are young aquatic systems, where time has been short to form a sediment layer that could isolate the lake water from the groundwater domain. As a result, highly dynamic systems are formed that can be closely linked to groundwater flows that may have unusually high gradients.

To confine hazardous substances to deeper waters, it may be desirable to reduce vertical exchange (Schultze and Boehrer 2009). At least in two cases, resulting meromictic conditions have been induced or retained intentionally (Island Copper Mine Lake in Canada: Fisher 2002, Fisher and Lawrence 2006; Lake Vollert-Süd: Stottmeister et al. 1998). In both cases, dissolved substances were considered a hazard to the surface waters. Confined to deeper layers of the water column, they do not pose a danger to the fauna around the lake. In the case of Island Copper Mine Lake, anoxic conditions in the deep water are anticipated after oxygen is depleted, which should induce precipitation of metal sulfides.

Decomposition of organic material and co-precipitation leads to accumulation of dissolved substances in the deep water. These substances contribute to density and thus sustain the presence of meromixis. Accumulation continues until formation is balanced by exports out of the monimolimnion into the mixolimnion or groundwater space. Some of these dissolved substances are gases. In addition to passive transport by the water, gases can escape by forming bubbles, which move due to their own buoyancy. Bubbles form when the sum of partial pressures overcomes the local pressure (e.g. Halbwachs et al. 2004), which essentially is the sum of hydrostatic pressure and air pressure. Concentrations in the water and partial pressures are linked by the so-called Bunsen coefficient.

Amongst gases, carbon dioxide plays a particular role. As its Bunsen coefficient is much larger (≈ 1) than most other gases (≈ 0.01), a much higher volume of CO_2 can be dissolved in water. Above pH $= 5$, part of the carbonate is dissolved as bicarbonate ions or carbonate ions. In addition, the density contribution of CO_2 is positive, while other common gases such as O_2 and N_2 contribute negatively to density, i.e. dissolving oxygen in water decreases the density due to an expanding volume. As a consequence, a water column can be stably stratified due to its increasing CO_2 concentration towards greater depths.

The sudden release of large volumes of dissolved gases has been documented from tropical volcanic lakes. Such limnic eruptions have cost the lives of 1,700 human beings in the neighborhood of Lakes Monoun and Nyos, both located in Cameroon, in 1984 and 1986, respectively. Despite much research, the release mechanisms of these events are not agreed upon.

3.1.5 Waves and Currents in Mining Lakes

Like natural and neutral lakes, acidic lakes are exposed to meteorological forcing. Winds and differential cooling, for example, drive currents and create surface and internal waves. There are differences in the flow behavior of mine pit lakes and
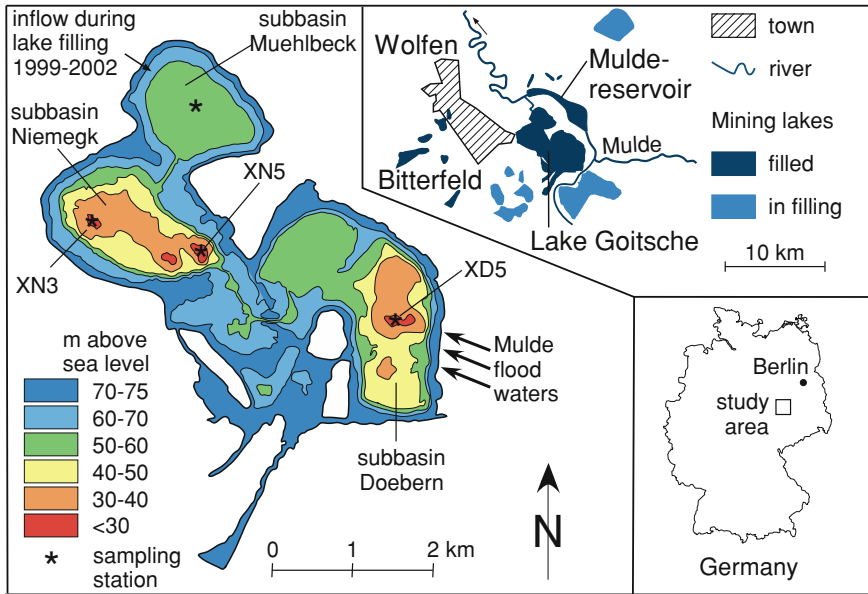
Fig. 3.13 Lake Goitsche and major measuring sites in the lake (map dated 2003; modified after Boehrer et al. 2003)

natural (and neutral) lakes, beyond what was discussed about deep recirculation, which are due in most cases to the morphometric peculiarities of the pits rather than the water properties. In this subsection, we refer to a number of special stratification and flow features that may be encountered in mine pit lakes and which are not commonly discussed when referring to currents in lakes in general. For the general context of currents in lakes, we refer to the literature of physical limnology (e.g. Fischer et al. 1974; Hutter 1987; Imberger and Patterson 1990; Imboden and Wüest 1995).

As mining followed the deposits, many mining lakes are subdivided at depth into basins, connected across sills that extend close to the surface (e.g. Mining Lake 111). This basin structure can result in different water conditions in the deep depressions as exchange between basins is very restricted below the sill depth (e.g. Boehrer et al. 2003, 2005). Between 1999 and 2006, Lake Goitsche contained meromictic patches in some places (e.g. XN3 see map in Fig. 3.13), while even deeper depressions of the lake basin (XN5, XD5) were filled with mixolimnetic waters (Boehrer et al. 2003).

Internal waves may be able to lift water from a greater depth across a sill ("internal wave pumping", Van Senden and Imboden 1989). The excursion height and the amount of water that will cross a sill from a lower location are limited by the amplitude of internal waves and the number of events in a certain time period.

When lakes are stratified, internal seiches can form. Usually, the first internal vertical mode dominates the water movements in a lake during stratification periods. If the equilibrium position is disturbed by the surface stress of wind, the
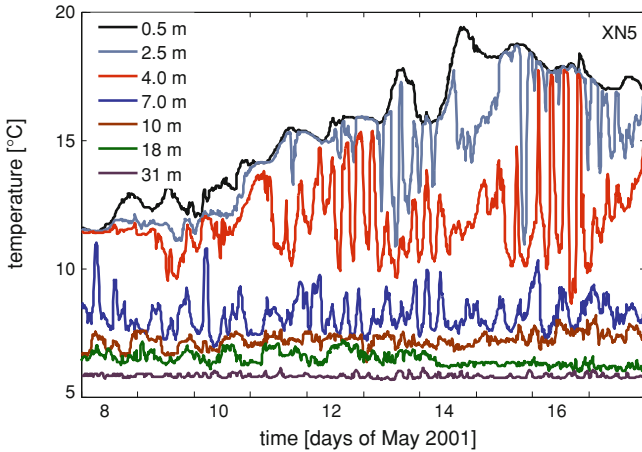
Fig. 3.14 Temperature time series at several depths in Lake Goitsche, subbasin Niemegk (position XN5), showing oscillations

cessation of the wind will result in internal waves, where the epilimnion and hypolimnion usually move in opposite directions in a frequency determined by the lake morphometry and the density stratification of the water column. At a fixed position, temperature oscillations of a distinct frequency can be recorded (Fig. 3.14). Higher modes have also been reported, and in a few cases, they are dominant (Vidal et al. 2005), but usually, their influence on currents is small, and can be quantified numerically (Boehrer 2000).

Lake Goitsche consists of several subbasins, which were interconnected by channels for the flooding procedure. By the year 2001, the subbasins had reached a common water surface, slightly greater than 70 m above sea level (see Fig. 3.13). The thermocline of the subbasin Niemegk (between 7 and 10 m water depth, Fig. 3.14) lay below the sill depth of the neighboring Mühlbeck and Döbern subbasins. Interfacial waves on the thermocline (i.e. first mode internal waves), were not able to leave the basin. The internal wave recorded at location XN5 had a period of 4 h. This oscillation period was clearly related to the size of the Niemegk subbasin. The oscillation of the thermocline induced currents in the epilimnion (and hypolimnion). However, as the thermocline oscillation was confined to the subbasin, surface currents must have felt the sill although they flowed clearly above the sill depth.

Boehrer and Stevens (2005) pointed out that the distribution of kinetic energy may be affected by the fact that reflection conditions for internal (ray) waves in many mine lakes are different than in natural lakes. Natural lakes typically have a shallow near-shore zone that acts as a ray wave trap (e.g. Turner 1973). In addition, benches left from mining produce even steeper walls. Furthermore, such benches act as discrete locations that can create internal wave rays of defined wave length and imposed frequency, such as the internal seiche in Island Copper Mine Lake. The observed turbulence pattern below the chemocline (Stevens et al. 2005) may be connected to the uniform wavelength (Boehrer and Stevens 2005).
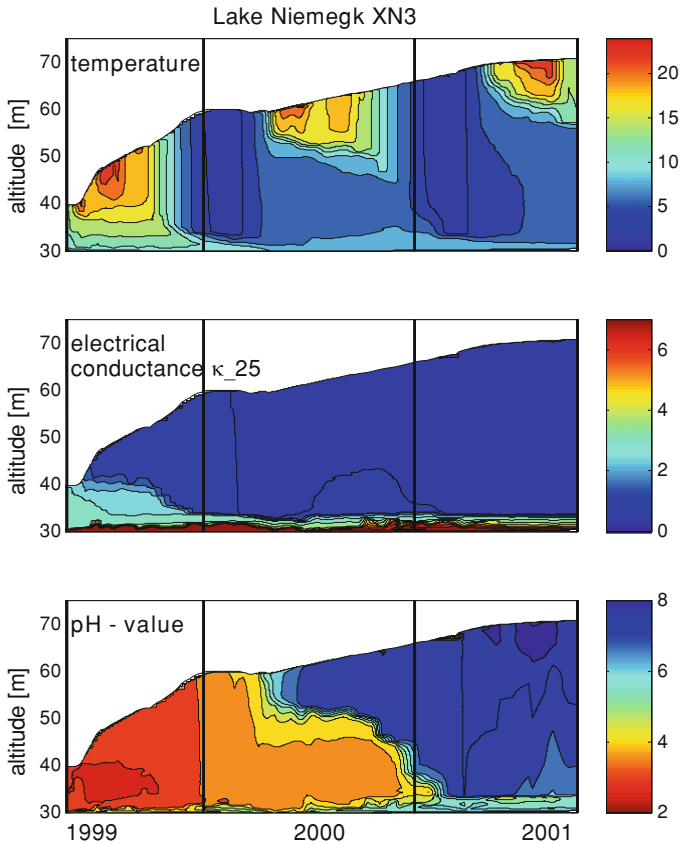
Fig. 3.15 Contour plots of temperature (in °C), electrical conductivity at 25°C (in mS/cm), and pH at measuring site XN3 over the period of regular flooding of the Goitsche pit (modified after Boehrer et al. 2003)

3.1.6 Mixing and Vertical Transport

Gradients of dissolved substances can be sustained for longer time periods, if density stratification restricts vertical transport. This was verified when the previously acidic residual lake Niemegk was filled with river water to reduce acidity. While the introduced flooding water had neutralized the epilimnetic waters within a short time period during 2000, the deep waters retained their low pH until deep recirculation later during the year allowed for vertical exchange of dissolved substances, such as buffering chemicals, into the deeper water (Fig. 3.15, Boehrer et al. 2003). Gradients of pH are stable over longer time periods only where density gradients reduce vertical mixing.

Meromictic lakes can show especially high vertical density gradients. Von Rohden and Ilmberger (2001) measured the spreading of an introduced tracer
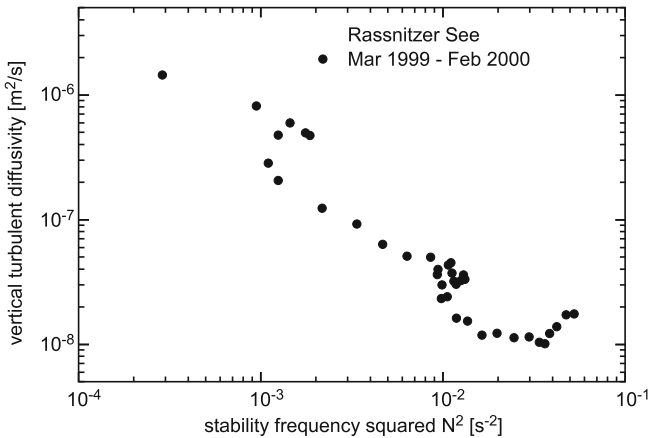
Fig. 3.16 Vertical diffusivity versus stability (modified after von Rohden and Ilmberger 2001)

cloud over periods of two years and calculated vertical transport coefficients from their measurements. A strong correlation of vertical diffusivity and density gradient could be verified. High gradients in the deep waters limited vertical transport to values little above molecular diffusion (Fig. 3.16; von Rohden and Ilmberger 2001; von Rohden et al. 2009).

Goudsmit et al. (1997) showed that in a lake that is several kilometers long (Alpnacher See), nearly all mixing happened along the side boundaries. Even in lakes as large as Lake Constance, mixing due to friction and shoaling at the side walls can still overcome pelagic mixing (Boehrer et al. 2000; Kocsis et al. 1998). Hence, the generally steep side walls in mine pits can affect vertical mixing. And, as mentioned above, the steepness of sidewalls and benches can produce different wave patterns and can alter distribution of internal wave energy at depth.

Transport can be established by double diffusion. This occurs when two species of different diffusivities contribute to density, one in a stabilizing and one in a destabilizing configuration. In meromictic lakes especially, we find examples where the temperature and concentration of dissolved substances both increase with depth. This usually results in staircases of temperature and conductivity profiles (Newman 1978; Schmid et al. 2005). This process is well established in tropical lakes, but has also been discovered in meromictic lakes of the temperate climate zone (von Rohden et al. 2010; case study 5.3).

Despite the overall stable density stratification in meromictic lakes, double diffusion can greatly enhance vertical transport (Brandt and Fernando 1995; Schmid et al. 2005). If temperature increases with depth, and hence opposes the density gradient implied by dissolved matter, the previously continuously density stratified water column is broken up into convection layers alternating with layers of high gradients.

Double diffusion also happens at chemoclines, where waters of different properties meet. In the case of Waldsee near Döbern, the density difference can be

largely due to dissolved ferrous iron in the monimolimnion, which cannot enter the oxic mixolimnion, as biochemical oxidation will cause it to precipitate back into the monimolimnion (Boehrer et al. 2009a). The configuration approaches the case of two immiscible layers in thermal contact (Fig. 3.12). As a consequence, double diffusive convection cells are not restricted to the step size derived for conservative salts (e.g. Federov 1988), and a full monimolimnetic overturn has been observed, resulting in the redistribution of dissolved substances within the monimolimnion (Boehrer et al. 2009a).

3.1.7 Concluding Remarks

Pit lakes have quite a few peculiarities. This section has discussed special features of pit lakes that are not usually covered sufficiently in books about limnology. Some of these aspects have developed from site-specific solutions to more general considerations, e.g. temperature compensation of electrical conductivity, and the implementation of density functions based on partial molal volumes in numerical models. The effect of (biogeo-)chemical transformations on stratification still needs to be quantitatively investigated. Numerical models must be developed and used to improve prognostication of the evolution of water quality in pit lakes and to demonstrate remediation strategies for pit lakes. Such prognosticative tools may also prove useful for predicting changes in "natural" lakes that may result under change of use and climate variability.

3.2 Limnochemistry of Water and Sediments of Acidic Pit Lakes

3.2.1 Pit Lakes from Coal and Lignite Mining

3.2.1.1 Water, Sediment, and Pore Water

Kurt Friese, Peter Herzsprung and Martin Schultze

Introduction

Hard coal and lignite are important raw materials for energy and steel production. Coal provides 26.5% of global primary energy needs and generates 41.5% of the world's electricity. Over 5,560 million tons (Mt) of hard coal and ca. 890 Mt of brown coal/lignite are currently produced worldwide. There are over 847 billion tons of proven coal reserves worldwide and recoverable reserves in about

Table 3.3 Top ten coal and lignite producers and worldwide production in 2008 (Mt—million tonnes; from Statistik der Kohlewirtschaft 2010)

Hard coal	(Mt)	Lignite	(Mt)
China[a]	2,586	Germany	175
USA	1,000	Russia	76
India	436	Turkey	71
Australia	334	USA	68
Russia	247	Australia	67
Indonesia	150	Greece	63
South Africa	250	Poland	59
Kazakhstan	104	Czech Republic	47
Poland	84	Serbia	36
Colombia	70	Romania	35
World	5,562	World	892

[a] including lignite

70 countries (World Coal Institute 2009). About 47% of power generated in Germany (the world's largest lignite producer), is provided by coal and lignite whereas, for example, in Poland, it exceeds 90% (Euracoal 2009). Hard coal and lignite is the principal source of energy production for several countries in Europe and elsewhere (e.g. Australia, China, India, Indonesia, Republic of South Africa, Russia (and the former states of the USSR), USA, and to a lesser extent, other countries in Africa, Asia, and Latin America). Table 3.3 shows the 10 major coal and lignite producing countries.

This chapter provides an overview of the chemistry of water and sediment in pit lakes from former coal and lignite open cast mines, mainly by comparing results from Australia, Germany, Poland, and the United States. Results of studies on pit lake water chemistry from India are considered as well. Generalized results of the chemistry of sediments and their pore waters were mainly deduced from studies on Australian and German pit lakes because comparable results were not found elsewhere. A review paper covering water chemistry and sedimentary processes of acidic coal mine pit lakes in Germany was published recently by Blodau (2006).

The geological conditions that lead to the formation of lignite and hard coal, mainly the anoxic conditions in the presence of sulfur and iron in a brackish environment, also favor the formation of pyrite or marcasite (FeS_s), and to lesser extent, mackinawite (FeS). Hence, lignite and hard coal deposits are often accompanied by pyrite/marcasite in the strata. The content and distribution of pyrite can vary over a broad range from 0.1 to 5% by weight (e.g. Knöller et al. 2004; Ludwig and Balkenhol 2001; Ludwig et al. 1999; Rolland et al. 2001; Seoane and Leiros 1997; Tiwary 2001) in disseminated occurrence, concentrated in clusters or in scattered pockets (Evangelou and Zhang 1995) depending on the mechanism of pyrite formation (e.g. syngenetic or epigenetic). Therefore, it is not surprising that mining opens the pathways for the oxidation of this pyrite. Surface mining needs dry conditions; consequently, before a mine pit can be opened, the groundwater table has to be lowered to an appropriate depth below the coal seams.

This is the first step in exposing the pyrite to oxygen, which afterwards is accelerated when the strata and coal are excavated.

When the mine is closed and operations cease, groundwater pumping, which normally is contemporaneous with increasing depth of the mine pit, stops. Consequently, the groundwater table rebounds until hydrological equilibration is reached. The ascending groundwater enters the pit by passing through the dewatered strata. On its way, the groundwater transports the products of pyrite oxidation, mainly sulfate, iron, and acidity (see Sect. 2.2) or dissolves secondary minerals that might have formed, in particular in overburden dumps.

The hydrochemistry of coal mine pit lakes is the result of the geological background, the hydrologic situation, the amount of sulfur within the strata, the extent of pyrite oxidation, and the mining technology used (e.g. Blodau 2006; Rolland et al. 2001; Wisotzky and Obermann 2001). Consequently, lake water chemistry has to be generalized with care and several exceptions might exist.

Pit Lake Water Chemistry

The first examples of strip mine pit lake water chemistry were from hard coal mining in the USA and were published by Campbell and Lind (1969), Campbell et al. (1964), and Parsons (1964), based on initial studies of Crawford (1942; cited in Campbell et al. 1964) and Heaton (1951, cited in Campbell et al. 1964) from coalfields in the Cedar Creek region of Missouri. Parsons (1964) described six acid strip mine pit lakes with a pH between 2.5 and 3.0 and ferric iron concentrations from 1 to 300 mg L^{-1} and sulfate concentrations from 2000 to 8,400 mg L^{-1}. Typically, all these lakes could be classified as acidic, hard water lakes of the Ca–SO_4-type. The Al concentrations in these lakes were quite high, ranging from 96 to 183 mg L^{-1}. In the same region (about 20 km north of the lakes investigated by Parsons (1964), Campbell et al. (1964) and Campbell and Lind (1969) investigated five acid strip mine pit lakes over a period of five to six years. The pH of these lakes ranged from 2.3 to 8.2. The concentrations of dissolved substances depended on the pH and on the depth of water sampling, showing increased concentrations with lower pH and greater depth. The maximum concentrations reported by Campbell et al. (1964) were 4,350 mg L^{-1} of ferric iron, 7,600 mg L^{-1} of sulfate, and 83 mg L^{-1} of manganese, whereas Campbell and Lind (1969) reported 426 mg L^{-1} of aluminum and 217 mg L^{-1} for zinc as maximum values from the bottom of the most acidic pit lake from this series. According to Campbell et al. (1964), similar conditions of strip mine pit lake water chemistry could be expected for coalfields in Arkansas, Oklahoma, Kansas, and Iowa from the same geological formation.

The first summary of existing and expected pit lake water chemistry of hard coal mines in the western USA was given by Miller et al. (1996). The main ion composition of these lake types defines them as Ca–SO_4 waters with high iron contents in the range of 200 mg L^{-1}. Due to the low sulfur content of the hard coal deposits in Montana, Wyoming, and Dakota (an average of about 0.6% S, Turbak

et al. 1979) and alkaline groundwaters, most of these hard coal mine pit lakes have a neutral pH (Anderson and Hawkes 1985). Similar observations were reported from a set of coal mine pit lakes from Illinois (Gibb and Evans 1978, cited in Castro and Moore 2000).

Further sets of geochemical data were available from 14 pit lakes in former hard coal mines in the Collie region in Western Australia (Lund and McCullogh 2008; Salmon et al. 2008; McCullough et al. 2010; see also case study 5.4), from 71 pit lakes in former lignite mines in Western Poland (Samecka-Cymerman and Kempers 2001; Solski and Jedrczak 1990, 1991a, b; see also case study 5.2) and from even more pit lakes in former lignite mines in Germany (for data sources and further details, see case study 5.1). These data are used to illustrate how the concentrations of dissolved substances are related to pH (Fig. 3.17 a–c). The ranges within the datasets are compared and discussed (Figs. 3.18 and 3.19).

The solubility of many constituents increase with decreasing pH, in particular carbonates, metal (hydr)oxides, and silicates. Magnesium (Fig. 3.17a), aluminum, the heavy metals including iron (Fig. 3.17b), and silicon (Fig. 3.17c) follow this pattern. Whereas ferric iron and oxidized manganese species increasingly precipitate with increasing pH, concentrations of iron and manganese can still be elevated under neutral conditions due to the high solubility of iron(II) and manganese (II) at anoxic conditions. Figure 3.17 a–c shall be used for a brief discussion of some fundamental biogeochemical rules in pit lake water; these rules are well established in geochemistry and have been discussed in more detail by Eary (1999).

The relevance of iron and aluminum buffering in pit lakes has often been demonstrated (e.g. Totsche et al. 2004; Uhlmann et al. 2004). Totsche et al. (2006) demonstrated that zinc also may buffer pH. However, those investigations were done in water originating from a waste rock dump of a Canadian base metal mine. In pit lakes resulting from coal and lignite mining, only iron and aluminum reach concentrations high enough to form relevant buffering systems.

Calcium, sodium, and potassium (Fig. 3.17a) do not show a clear concentration dependence on pH. This may be due to the formation of secondary minerals, such as gypsum and jarosite. In the case of German pit lakes, another reason is the intrusion of saline groundwater from Permian salt deposits into some of the pit lakes (see case study 5.1). For at least some of the Australian pit lakes, the diversion of highly saline water into lakes from the local rivers during the first flush at the beginning of the wet season would have likely disrupted any relationship between these cations and pH. The source of the salt in the river water was agricultural land use (McCullough et al. 2010), which is causing salinization of soil, groundwater, and river water in many regions of Australia. For more details on the mechanisms behind this phenomenon see e.g. Jolly et al. (2001). The absence of any relationship of chloride concentrations to pH supports this conclusion (Fig. 3.17a).

The decrease of sulfate concentrations with increasing pH (Fig. 3.17a) probably reflects that less pyrite oxidation occurs in certain lake catchments, which therefore have higher pH-values and lower acidities. To some degree, this might also
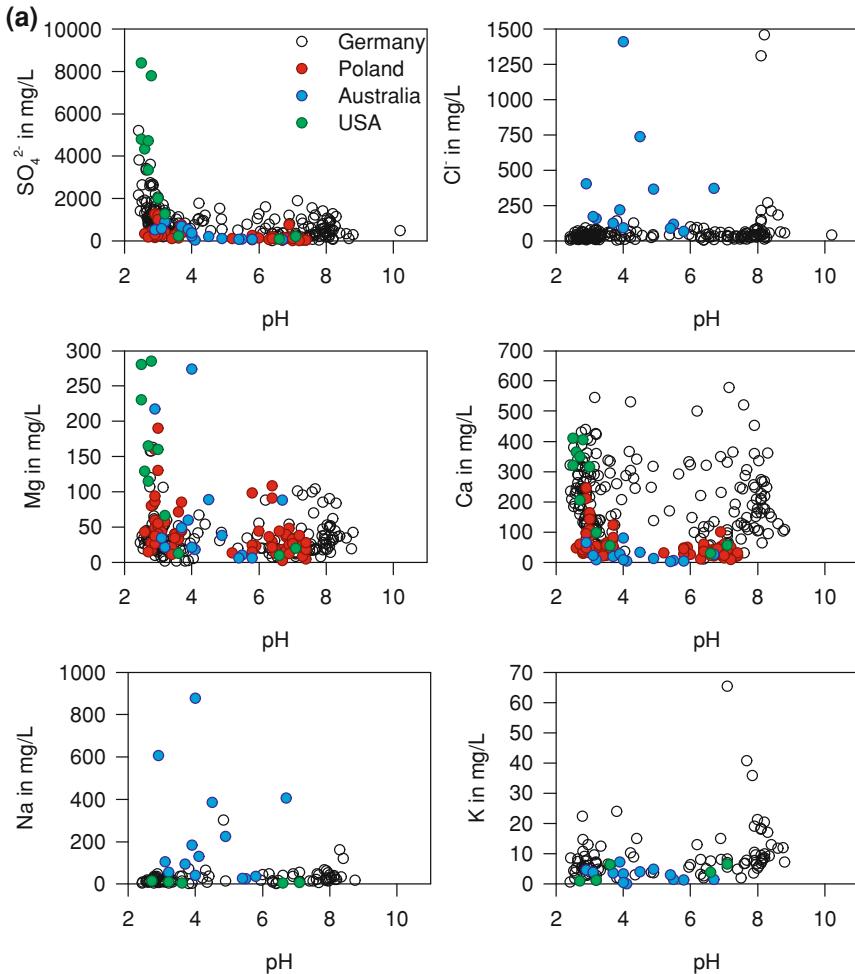
Fig. 3.17 Compilation of water chemistry data versus pH for pit lakes from Germany, West Poland, the Collie region (Australia), and the Cedar Creek region (USA). **a** Sulphate, chloride, magnesium, calcium, sodium, and potassium. **b** Acidity, Fe, Al, Mn, Zn, and Cu. **c** Ammonia, nitrate, SRP, TP, DOC, and Si

explain similar behavior of other constituents. In addition, pit lakes that became neutral over time due to natural flushing by neutral superficial and subsurface inflows are usually diluted with respect to all water constituents.

The decrease of ammonia concentrations with increasing pH (Fig. 3.17c) can likely be attributed to the inhibition of nitrification under acid conditions. Lignite is believed to be the source of ammonia in acidic pit lakes resulting from lignite mining. In former hard coal mines, where blasting is a common step in mining, explosives are probably the main source for ammonia. However, the missing inhibition of nitrification at neutral pH obviously did not result in a strong increase
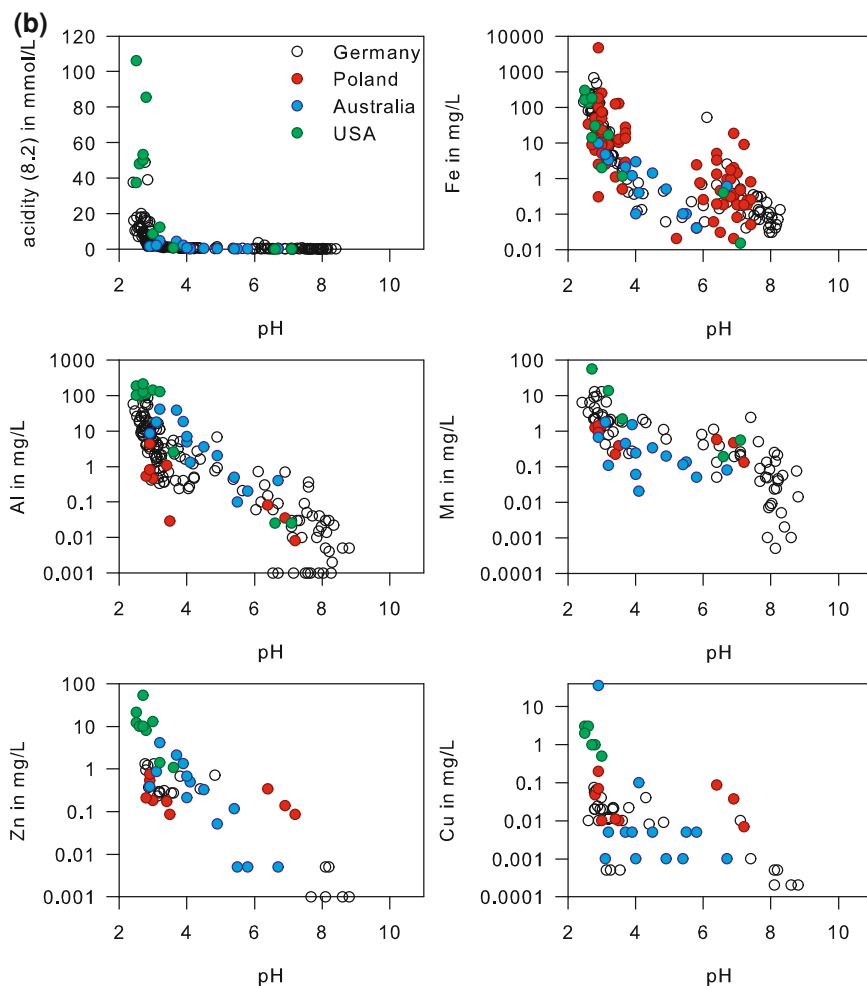
Fig. 3.17 (continued)

of nitrate with increasing pH (Fig. 3.17c). Other microbial processes, like uptake of nutrients and denitrification, may have also influenced the concentrations of nitrate.

The relation of pH to the concentration of dissolved organic carbon (DOC) is also not well understood (Fig. 3.17c). The increase of DOC at pH above 5 may result from better solubility of humic acids at higher pH and from less intense co-precipitation of organic compounds with precipitating iron and aluminum due to the much lower availability of the metals at neutral pH. Furthermore, the oxidation of organic carbon, i.e. its consumption during photo-reduction of ferric iron, is occurring only under acid conditions. The concentrations of SRP and total phosphorus (TP; Fig. 3.17c) are generally low. This is due to their strong binding
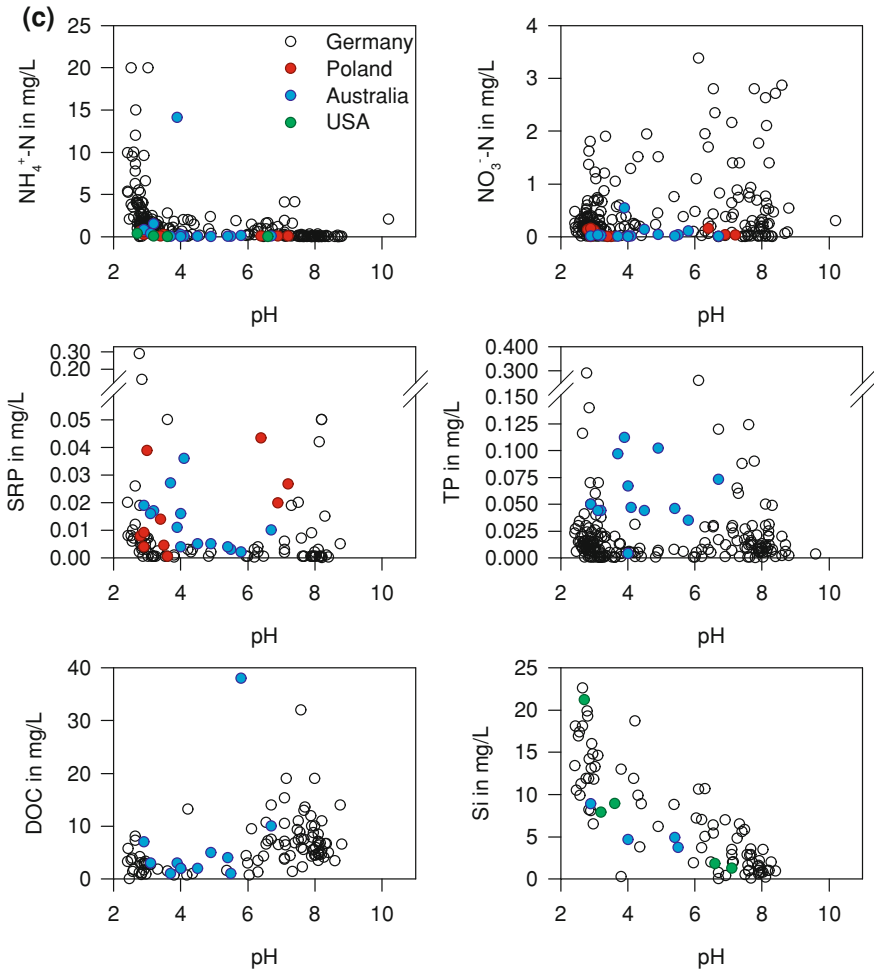
Fig. 3.17 (continued)

to surfaces of precipitates of iron and aluminum (see Sect. 3.2.1.3). In the few cases where high concentrations occur, source contributions (i.e. high loads from the catchment areas, inflow of waste water, inadequate fishery) rather than pH was apparently responsible.

In summary, there are no clear differences obvious between the relationships of ion concentrations to pH for the compared mining regions.

Figures 3.18 and 3.19 compare the ranges of the data from the pit lakes in Australia, USA, Poland and Germany. There are several close similarities between the German pit lakes and the pit lakes in western Poland. In addition to the fact that both groups of lakes originate from lignite mining, the Polish lakes belong to a geological structure, a moraine arc formed by Quaternary glaciation (Kupetz
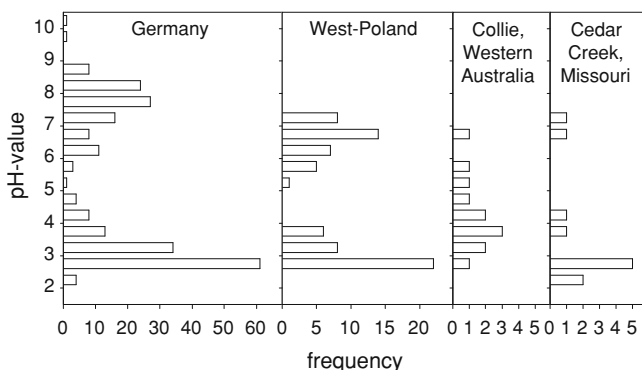
Fig. 3.18 Comparison of the frequency distributions of pH in pit lakes from Germany (data sources described in case study 5.1), from West Poland (data from Solski and Jedrczak 1990; Samecka-Cymerman and Kempers 2001), from the Collie region of Western Australia (data from McCullough et al. 2010) and from the Cedar Creek region in Missouri (data from Parsons 1964; Campbell and Lind 1969). Note the different scales for the frequency
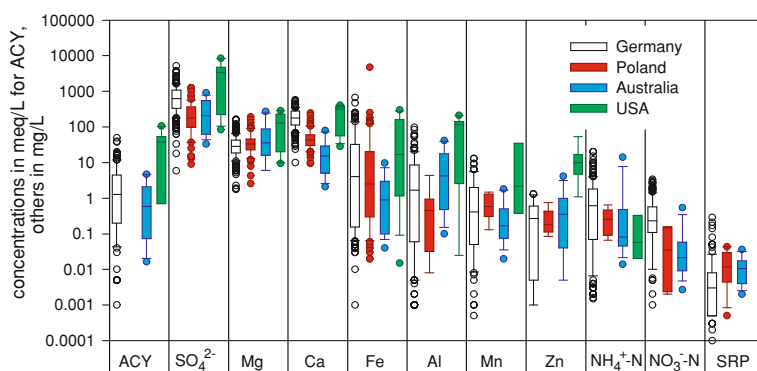
Fig. 3.19 Comparison of concentrations of major constituents characterizing the water chemistry in pit lakes from Germany (data sources described in case study 5.1), from West Poland (data from Solski and Jedrczak 1990; Samecka-Cymerman and Kempers 2001), from the Collie region of Western Australia (data from McCullough et al. 2010) and from the Cedar Creek region in Missouri (data from Parsons 1964; Campbell and Lind 1969). Lines within the boxes are median values, box limits 25 and 75%, and whiskers show the 10 and 90% values, respectively. ACY—acidity. Please note the different number of values behind the plots: 121–221 for the German pit lakes, 9–71 for West Poland, 12 for the Collie region and 4–11 for the Cedar Creek region

1996), that crosses the border into Germany. Lignite was mined there very early, mainly during the first half of the 20th century, since the seams reached the surface as a result of deformation by the pressure of the glaciation.

The frequency distribution of pH in the pit lakes in all of these regions had a statistical mode in the acidic range (Fig. 3.18). In Germany and in Missouri, the pH range indicated buffering by iron. The maximum frequency distribution of pH

in the pit lakes of the Collie region lay at higher pH, which is closer to the pH range typical for buffering by aluminum. Only the Polish and the German pit lakes showed a second maximum in their pH frequency distribution in the neutral range. It could be that the datasets from the Collie region and from the Cedar Creek region were not large enough to show a second maximum. Alternatively, the relative absence of neutral pit lakes in the Collie and Cedar Creek regions may be due to the limited age of the pit lakes at the time of the investigation and the lack of broad remediation programs, comparable to those conducted in Germany during the last 20 years (see case study 5.1). The findings of Campbell et al. (1964) and Campbell and Lind (1969) support this assumption. They found that pH increased in three of the investigated lakes from 1940 to the 1960s due to natural processes like long term wash out, natural buffering by slow weathering processes (e.g. dissolution of silicates), and microbial alkalinity production by sulfate reduction.

On average, i.e. according to the median, the pit lakes in Missouri showed the highest concentrations of the solutes in Fig. 3.19, except for ammonia. The concentrations of acidity, sulfate, calcium, iron, and manganese all followed the same pattern: the highest concentrations were found in the pit lakes in Missouri, with intermediate concentrations in Polish and German pit lakes, and the lowest concentrations in the pit lakes in Western Australia. The concentrations of magnesium, aluminum, and zinc followed different patterns. Data on the concentrations of dissolved organic carbon (DOC) and the nutrients nitrogen and phosphorus were only available for the pit lakes of Germany and the Collie region in Western Australia (Figs. 3.17, 3.19). The occurrence of many neutral pit lakes in Germany is assumed to be one reason for the higher concentrations of DOC and nitrate in the German pit lakes. The embedding of the German pit lakes in sand and gravel additionally allows more intense interaction between remnant lignite in the overburden and the groundwater than is possible under the hydrogeological conditions of the Collie region (hard coal, sandstone, mudstone, shale). This probably also contributed to the lower concentrations of ammonia in the pit lakes of the Collie regions. The reasons for the differences in soluble reactive phosphorus (SRP) are not known. The different geological conditions of the various mining regions (hard coal in Missouri and Western Australia versus lignite in West Poland and Germany, and the different ages of the coal and lignite (Carboniferous in Missouri, Permian in the Collie region, and Tertiary in Poland and Germany)) probably contribute to the other notable differences in water quality, as do the different ages of the pit lakes at the time of their investigation and differences in how they were filled (natural rebound of groundwater or flooding with river water).

Published hydrochemical data from coal mine pit lakes outside of the United States of America, Australia, Poland, and Germany are rare. Denimal et al. (2005) reported on three pit lakes in former coal mines at the north-eastern edge of Massif Central (France). The lakes had a circumneutral pH and two of them were meromictic. Sulfate concentrations ranged from 500 mg L^{-1} to 1,500 mg L^{-1}. Iron concentrations were low at the surface (0.01–0.11 mg L^{-1}) and at depth (0.06–0.3 mg L^{-1}), whereas manganese concentrations were at rather typical levels (0.02–0.2 mg L^{-1} at surface, 1.4–4.5 mg L^{-1} at depth). Water chemistry

comparable to the German lignite pit lakes was reported from acid mine waters (not pit lakes) from coalfields in India (Singh 1988; Tiwary 2001). Furthermore, there are also several coalfields in India producing neutral and less contaminated mine waters (e.g. Choubey 1991; Gupta 1999; Khan et al. 2005; Tiwary 2001). Similarly, few data (only sulfate and zinc) were given by Geldenhuis and Bell (1997) for acid overspill water (pH range 2.0–3.4) collected in control reservoirs of the Loubert Mine in South Africa (Witbank coalfield, eastern Transvaal). Although, electric conductivity (EC) in these overspill water was in the same range as EC values measured in lignite mine pit lakes of Germany (e.g. 2–6 mS/cm), sulfate and zinc concentration were much higher in the overspill water (up to 5 g/L and up to 4.7 mg/L, respectively).

Sediment Chemistry

The authigenic sediments from coal mine pit lakes are generally very fine grained with a near-surface (upper 5–10 cm) high water content (>40%; Friese 2004; Friese et al. 1998b). In several cases, water contents of 60–80% were detected in the top 5 cm (e.g. Fritz and Carlson 1982; Langner 2002). The amount of in-lake sedimentation depends strongly on local conditions (e.g. amount and rate of groundwater inflow or precipitation). As much groundwater and seepage or drainage water enters the lake, precipitation of solid phases from the oxidation of pyrite and—if they exist—secondary minerals will occur. Typical sedimentation rates are on the order of 5–10 mm/y (deduced from 10 to 20 cm sediment layers in 10–40 years old pit lakes; e.g. Bachmann et al. 2001; Friese 2004; Friese et al. 1998b; Peine 1998; Peine and Peiffer 1996, 1998; Peine et al. 2000).

   The main component of the sediment is often iron (iron oxides, hydroxides, and hydroxosulfates), ranging from only 5% to 45% of the dry weight (Bachmann et al. 2001; Blodau et al. 1998; Brugam et al. 1988; Lessmann et al. 1999; Meier et al. 2004; Peine et al. 2000). Other major components are generally Si, Ca, Mg, Na, K, and Al (Friese 2004; Friese et al. 1998a, b; Read et al. 2009). All of these can be attributed to the dissolution of silicates, like quartz, feldspar, or clay minerals. Mineralogical analyses of sediments from coal mine pit lakes are scarce in the literature. Göttlicher and Gasharova (2000) described the precipitation of goethite and jarosite as the main iron precipitates in the lignite mine pit lake ML-111 (see also case study 5.6), whereas Peine et al. (2000) found mainly schwertmannite in mine pit lake 77 from the same German mining district. Our own mineralogical analyses (not yet published) of sediment cores from the Lusatian mine pit lakes ML-111 and ML-107 confirm the precipitation of iron hydroxosulfates, like K-jarosite, and of iron-oxides like goethite (Table 3.2) in the upper 15–20 cm of the lake sediments. Quartz and clay minerals are also common throughout the lake sediments. Geochemical analyses by XRF (X-ray fluorescence) show that iron predominates in these sediments.

   A generalized sequence of typical sediment from the acid lignite mine pit lakes of Lusatia (Germany) is given in Table 3.4. Often, the top 1–2 cm layer of the

Table 3.4 Typical sequence of the sediment structure and composition in acid pit lakes of the Lusatian lignite mining district, Germany

Unit	Depth (cm)	Color	Structure	Grain size	Main mineralogy	Main geochemistry
1	0–2	Red–brown	Without any texture	Fine clay	Amorphous or less crystalline; Fe-hydroxosulfates (jarosite, schwertmannite)	Water content: 70–80%; LOI: 20–40 wt%; Fe_2O_3: 30–45 wt%; SiO_2: $\approx$ 10 wt%
2	2–3	Black	Without any texture	Fine clay	Amorphous or less crystalline FeS, FeS_2, Me(Zn, Ni)S	Water content: 70–80%; LOI: 20–40 wt%; Fe_2O_3: 10–20 wt%; S: 2–3 wt%
3	3–20	Reddish yellow to brown	Laminated	Clayey	Fe-oxides, Fe-hydroxides, Fe-hydroxosulfates, clay minerals, quartz, feldspar	Water content: 60–70%; LOI: 20 wt%; Fe_2O_3: 10–30 wt%; S: 1–2 wt%; Al_2O_3: 5–10 wt%
4	>20	Grey	Grained	Silty to sandy	Quartz, feldspar	SiO_2: >80 wt%; Al_2O_3: 10–15 wt%

Please note that differences in the thickness of units occur from lake to lake as well as within a particular lake depending on the bottom morphology and the individual sedimentation. Additionally, unit 1 is not observed in every lake

sediment is a very fluffy and water-rich layer of freshly precipitated iron hydroxosulfates. The form of the iron precipitated from the water column strongly depends on the pH-Eh conditions (e.g. Stumm and Morgan 1996). Since iron is a key factor in the water–sediment system for this type of lake, the iron cycle is described in detail separately (Sect. 3.2.1.2). In several cases, this layer is not apparent and the top unit consists of a very dark black, water- and organic-rich, strongly reduced layer (named unit 2 in Table 3.4) that is enriched with reduced sulfur compounds like FeS, FeS_2, and probably other metal sulfides (ZnS, NiS). The occurrence of reduced sulfur compounds and the precipitation of secondary iron sulfides within this layer were proven by sulfur isotope measurements (Fauville et al. 2004; Knöller et al. 2004). However, most of the sediment is a unit of laminated precipitates of iron-hydroxosulfates, -oxides and -hydroxides, quartz, and clay minerals (unit 3 in Table 3.4). Since this laminations is very fine (within the mm to sub-mm range), it is not yet clear what causes the lamination (Table 3.4).

In general, trace elements are of minor importance in German lignite mine pit lake sediments. As, Cd, Co, Cu, Cr, Pb, and Zn all display mass concentrations below 50–70 mg/kg (dry weight). In some cases, there is a close positive correlation found between iron and arsenic, iron and copper, and iron and cobalt within the depth profiles of the sediments, which is probably the result of co-precipitation onto iron-hydroxides/hydroxosulfates. On the other hand, in sediment cores with strong anoxic conditions and a pronounced unit 2 (Table 3.4), positive correlations can be found between S and Ni and S and Zn within the top 5 cm due to precipitation of metal sulfides, as mentioned above. Similar high correlations between S and Cu and Ni were reported by Brugam et al. (1988) from near-surface sediments of coal mine lakes from the midwestern U.S. (about 30 lakes). The amount and distribution of trace metals co-precipitated onto iron hydroxides/hydroxosulfates and the precipitation of metal sulfides varies from year to year and also within a year, depending on the stability of oxic and anoxic conditions at the sediment surface or within the top 5 cm, respectively.

Sediment Pore Water Chemistry

Pore water is an interface and transfer component between the solid (sediment) and liquid (lake water) phases, and between the groundwater and lake water, so its composition can play a major role in pit lake water chemistry. Thus, analysis of pore waters gives information about transport and transformation processes within the sediment (e.g. Blodau et al. 1998; Koschorreck et al. 2007 a, b; Regenspurg et al. 2004). Chemical (Knorr and Blodau 2006) and microbiological (Meier et al. 2004) transformative processes are both responsible for cycling elements between the pore water and sediment. Researchers have focussed on chemical processes that can be derived from pore water profiles in acid lignite and coal mine pit lake sediments (Herzsprung et al. 2002; Knorr and Blodau 2006; Peine et al. 2000);

the most important of these involve transformations of ferric and ferrous minerals (see also Sect. 3.2.1.2). Generally, the researchers analyzed pH, dissolved oxygen (or redox potential; Koschorreck et al. 2007a), ferrous iron, total dissolved iron, sulfate, and DOC (Laskov et al. 2002) in the pore water. To complete process understanding and enable geochemical modeling (PHREEQC or similar programs), additional analysis of remaining major ions (calcium, magnesium, sodium, potassium, and chloride), other metal ions like aluminum, manganese, and zinc, and nutrients like ammonia and soluble reactive phosphate may be required (Herzsprung et al. 2002).

Diagenesis of minerals like schwertmannite, jarosite, and goethite occurs in acidic pit lake sediments (Bozau et al. 2007; Knorr and Blodau 2006; Peine et al. 2000; Regenspurg et al. 2004). The pore water composition reflects the steady state resulting from all transformation and transport processes in the sediment (Knorr and Blodau 2006). The influence of biogeochemical transformations on pore water chemistry will be discussed using examples from the literature (Herzsprung et al. 2002; Knorr and Blodau 2006; Laskov et al. 2002; Peine et al. 2000).

Investigating the electron flow in the iron-rich Mining Lake 77, Peine et al. (2000) found a predominant pH gradient in the sediment pore water (Fig. 3.20). Protons are transferred by diffusion from acidic pelagic water to the sediment and are produced by transformation of schwertmannite to goethite and by precipitation of solid ferric iron minerals at the oxic/anoxic boundary. In deeper sediment layers, protons are consumed by reductive dissolution of ferric minerals and by sulfate reduction. The precipitation or dissolution of manganese oxides (MnOx) produces similar effects (Tan et al. 2010).

Figure 3.20 demonstrates the dependence of pore water chemistry on the geochemical conditions of acid pit lake sediments. ML 111 is extremely acidic; pore water pH values < 3.5 were found at sediment depths up to more than 20 cm (Herzsprung et al. 2002; Koschorreck et al. 2007a). ML 77 contains less acidity than ML 111. The pore water pH of ML 77 rises to higher values (up to 6) with increasing sediment depth (Peine et al. 2000). Ferrous iron and sulfate pore water concentrations are influenced by transport, dissolution, and precipitation processes. Knorr and Blodau (2006) demonstrated that pore water gradients change dramatically with groundwater percolation (upward). AMD-polluted groundwater (from dump sites with high ferrous iron and sulfate concentration) percolates the sediment of ML 77, so the concentration gradients are considerably less distinct than would be the case without percolation (Fig. 3.20). A local maximum of ferrous iron and sulfate pore water concentration (as shown in Fig. 3.20) qualitatively indicates transformation of schwertmannite to goethite (Knorr and Blodau 2006).

The DOC content in acid pit lake sediment pore water typically exceeds pelagial water DOC by at least an order of magnitude (Friese et al. 1998a, b; Laskov et al. 2002). As assumed by Laskov et al. (2002), the release of DOC into pore water is linked to the transformation of schwertmannite to goethite by desorptive processes. All parameters involved in redox cycling (ferric and ferrous iron, sulfate, pH, ORP, and DOC) were intensively investigated in pit lake pore waters, with minor consideration given to the other inorganic parameters mentioned above
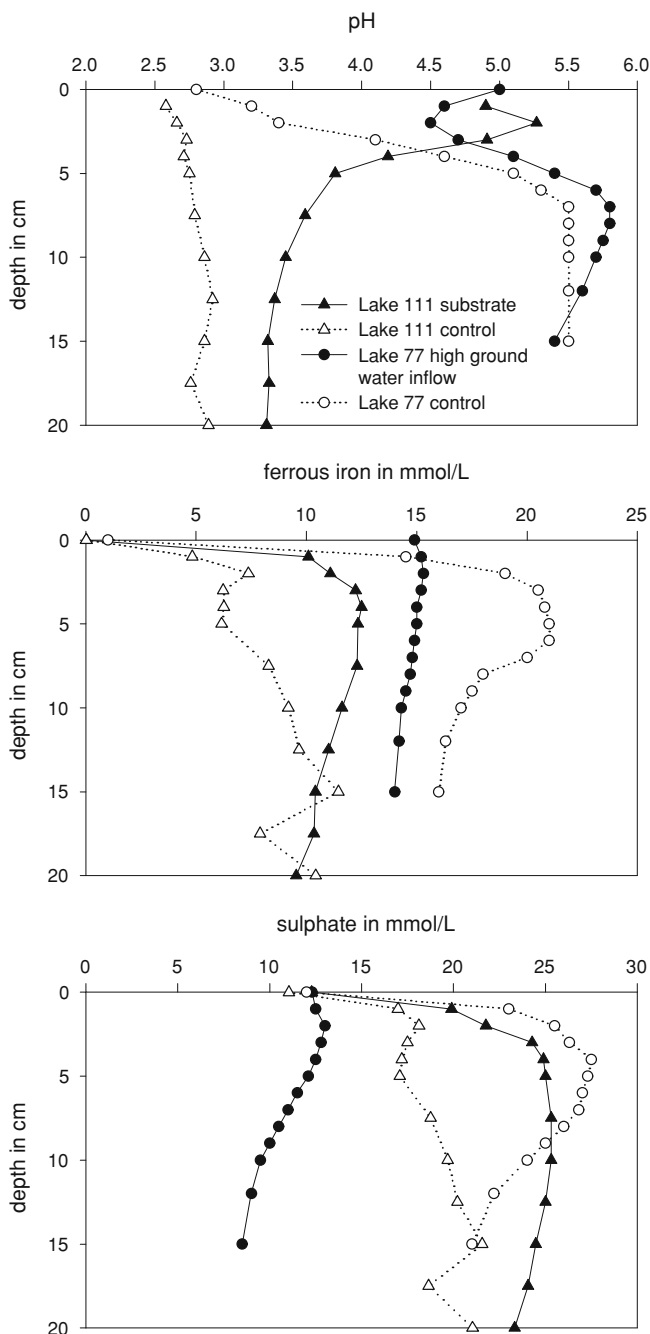
Fig. 3.20 Profiles of pH, ferrous iron and sulphate concentrations in pore water of sediments from two different pit lakes of the Lusatian lignite mining district, Germany. The sediment of Mining Lake 77 was treated by a high upward flow of groundwater (data from Knorr and Blodau 2006) and the sediment of Mining Lake 111 by the addition of Carbokalk on the sediment surface (data from Herzsprung et al. 2002; for details see text)

(other major ions, metal ions). Blodau et al. (1998) stated that concentration gradients of calcium, magnesium, potassium, sodium, and chloride were less pronounced. Herzsprung et al. (2002) investigated pore water chemistry after organic substrate (carbokalk, a by-product of the sugar industry, cf. Frömmichen et al. 2003, 2004) and lime were added to stimulate alkalinity production. As shown in Fig. 3.20, pH values were elevated in the uppermost sediment layers after addition of substrate to lake water in an enclosure of mine pit lake ML-111 (Lusatia, Germany; cf. Geller et al. 2009). The concentrations of sulfate and ferrous iron increased due to reductive dissolution of ferric minerals. The pore water composition changed considerably. Ferrous iron, sulfate, potassium, and ammonia were released into the pore water while aluminum and silica concentrations were depleted by precipitation. The release of potassium indicated the dissolution of K-jarosite, which is probably also the source of enriched ammonia concentrations within the pore water; both ions have a similar ionic radius and so NH_4^+ might replace K^+ in K-jarosite.

In a similar study conducted by Read et al. (2009), the change of pore water pH, iron, and sulfide after addition of DOC was investigated in a laboratory experiment on sediments from two Australian pit lakes and compared to the ML-111 results. Reductive processes were induced in all experiments, leading to increased concentrations of iron and ammonia in the overlying water, but sulfide was only measurable in the pore water in the Australian pit lake sediments. The high concentrations of ferric iron in the ML-111 sediment inhibited the formation of sulfide (see also Sect. 3.2.1.2). Consequently, a shift to increased pH within the top layer of the sediment was only observed in the Australian pit lake sediments.

Observations (Blodau et al. 1998; Herzsprung et al. 2002; Peine et al. 2000) indicate that the concentrations of calcium, magnesium, sodium, and chloride in pore water are not very different from pelagial water concentrations (exception: calcium in pore water after treatment with lime). These parameters seem to be neither involved in biogeochemical transformations nor in groundwater/lake water interactions. The concentration of manganese is elevated in acidic lake water and nearly equal in pore water and pelagial water (Herzsprung et al. 2002). In neutral coal mining affected lakes, manganese concentrations are low under oxic conditions (Wu et al. 2001). However, in the corresponding pore water, peak manganese concentrations can be found near the sediment water boundary. Manganese cycling in pit lake sediments after remediation and neutralization by flooding with river water is discussed by Herzsprung et al. (2010) and Wu et al. (2001). The behavior of phosphorus in acidic pit lake sediment pore water was explored by Kleeberg et al. (2005, see also Sect. 3.2.1.3).

Concluding Remarks

In the past 15 years, remarkable progress has been made in understanding pit lake chemistry and pit lake processes, mainly through research at pit lakes in Germany and Australia. Lakes in former hard coal mines have been much less intensively

investigated than at lignite mines. Although many results from the German and Australian pit lakes can be generalized, a more international database is needed to better understand the relationships between the geological conditions of the deposits and the final chemical conditions in the lakes. This includes differences resulting from being in unconsolidated or in solid rock, which affects the interaction between the pit lakes and groundwater, and the contribution of residues of coal and lignite to the organic matter in the pit lakes. Furthermore, a detailed structural characterisation of this organic matter and quantification of its degradability and its contribution to reductive alkalinity production is needed.

3.2.1.2 The Role of Iron Minerals in the Biogeochemistry of Acidic Pit Lakes

Stefan Peiffer, Klaus-Holger Knorr and Christian Blodau

Predominant Iron Minerals in Acidic Mine Pit Lakes

Environments affected by acidic mine drainage (AMD) are characterized by the occurrence of a large variety of iron oxy (hydroxy) sulfates. Depending on the redox state of Fe and the degree of dilution, a broad range of sulfate and hydroxide minerals can form, ranging from pure melanterite ($FeSO_4$) in highly concentrated very acidic waters to goethite (FeOOH) in dilute waters (for a review cf. e. g. Nordstrom and Alpers 2000). A mineral characteristic to rivers affected by AMD is schwertmannite. It has the general formula, $Fe_8O_8(OH)_x(SO_4)_y \times n\ H_2O$, where $(8–x)/2 = y$ and $1.0 < y < 1.75$ and a mineral structure probably akin to akaganéite (γ-FeOOH; Bigham et al. 1994). The exact structure is, however, still a matter of discussion (Majzlan and Myneni 2005; Waychunas et al. 2001). The occurrence of schwertmannite was demonstrated also in the sediment of an acidic pit lake (APL) in layers up to 5 cm thick (Peine et al. 2000). In a survey performed in APLs from 17 pit lakes of three different lignite mining districts (Regenspurg et al. 2004), schwertmannite was the predominant iron mineral in fresh sediments. In addition to environments affected by AMD, it has been found in acidic sulfate soils, where it is subject to a dynamic iron turnover (Burton et al. 2006)

Schwertmannite is restricted to a geochemical window characterized by pH values between 2.5 and 4.5 and sulfate concentrations between 10 and 30 mmol L^{-1} (Bigham et al. 1994; Yu et al. 1999). At pH < 2.5, jarosite predominates (Cravotta et al. 1999). Geochemical modelling revealed that there is a chemical equilibrium between Fe^{3+} dissolved in lake water sampled from these lakes and schwertmannite (Regenspurg et al. 2004, Fig. 3.21). It can therefore be postulated that the geochemical window reflects a pH buffering system established by schwertmannite precipitation. This seems to be characteristic for many APLs, buffering the pH to values between 2.6 and 3.3 (Peine et al. 2000). An extensive review on acidity generation and consumption in APLs has been provided by Blodau (2006).
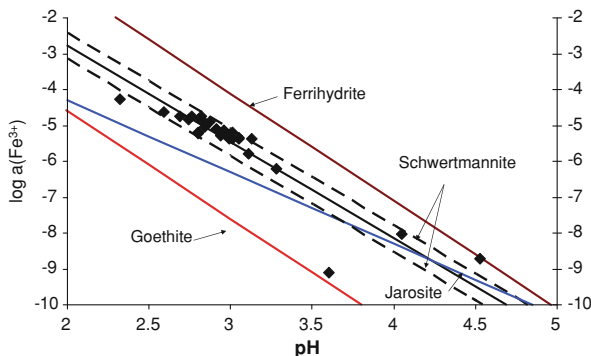
Fig. 3.21 Plot of the logarithm of the Fe^{3+} activity (mean values of measured data) versus pH for surface waters of 17 APLs. Solubility lines were calculated for goethite (log $a(Fe^{3+}) = 1.4$–3 pH), ferrihydrite (log $a(Fe^{3+}) = 4.83$–3 pH), K-jarosite (*mid-line* log $a(Fe^{3+}) = -0.19 - 2$ pH), and schwertmannite (*mid-line* log $a(Fe^{3+}) = 2.7$–2.63 pH). Maxima and minima (*dashed lines*) for the solubility window of schwertmannite are for the range of log $a(SO_4^{2-}) = -1$ to –1.5, that of jarosite –1.85 to –2.5, and for log $a(K^+) = -3.5$ to –4.07 (after Regenspurg et al. 2004)

Formation and Stability of Schwertmannite

In the APLs studied by Regenspurg et al. (2004), a redox equilibrium between Fe^{2+} and schwertmannite was detected, which implies that schwertmannite is the first mineral formed after Fe(II) oxidation in these environments. Given the slow oxidation kinetics of Fe(II) at low pH, this observation implies that schwertmannite formation is controlled by the oxidation kinetics of Fe^{2+}. This assumption was confirmed by a mass balance of dissolved Fe(II) and suspended Fe(III) established for a specific, yet typical APL studied by Peine et al. (2000). In this lake, solid Fe(III) was identified to be exclusively bound to schwertmannite, of which the sedimentation rate was measured to be 2.6×10^{-3} mol Fe(III) m^{-2} $year^{-1}$ on average, which agreed well with the Fe(II) oxidation rate of 3.0×10^{-3} mol Fe(II) m^{-2} $year^{-1}$.

Schwertmannite formation seems to be directly linked to bacterial oxidation of Fe^{2+} (Kawano and Tomita 2001). The bacterial cell appears not to be involved in the precipitation of either jarosite or schwertmannite (Eneroth and Bender Koch 2004), although direct contact between the bacterial cells and the crystal surface was demonstrated (Ferris et al. 2004). In a study of the bacterial community at a plant that generates pure schwertmannite while treating acidic waters from an active lignite surface mine (Glombitza et al. 2007), strains of Fe(II) oxidizing bacteria belonging to the class of beta-proteobacteria, closely related to the neutrophilic iron-oxidizing *Gallionella ferruginea*, were the dominant group (Hedrich et al. 2007; Heinzel et al. 2008).

Schwertmannite has been demonstrated to be metastable with respect to goethite (Bigham et al. 1996). Once suspended in water, it ultimately transforms into goethite, thereby lowering the pH (Jönsson et al. 2005; Knorr and Blodau 2007;
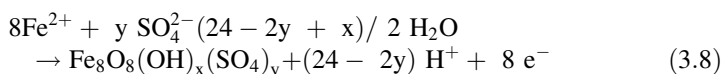
Regenspurg et al. 2004; Schwertmann and Carlson 2005). The transformation rate is slow under acidic conditions (pH $\approx$ 3) and increases significantly at higher pH (Regenspurg et al. 2004; Schwertmann and Carlson 2005), being driven by a supply of alkalinity (Peine et al. 2000). This transformation also seems to be dependant on temperature and concentrations of sulfate and dissolved organic carbon (DOC; Jönsson et al. 2005; Knorr and Blodau 2007), factors that can be highly variable under field conditions. High concentrations of sulfate and DOC probably also impede or at least retard the formation of well-crystalized goethite; instead; low-sulfate but poorly crystalline, x-ray amorphous iron oxyhydroxides form (Knorr and Blodau 2007).

Transformation to goethite has been demonstrated to occur in the sediment of an APL (Peine et al. 2000) at a rate of 3.5 mol m^{-2} $year^{-1}$. This reaction generates additional acidity in the sediment:

$$2y\ H_2O\ +\ Fe_8O_8(OH)_x(SO_4)_y \rightarrow 8FeOOH\ +\ y\ SO_4^{2-}\ +\ 2y\ H^+ \qquad (3.7)$$

The Role of Schwertmannite for the Element Cycles in APLs

As discussed above, schwertmannite plays a prominent role in the acid–base budget of APLs and is abundant in their sediments (e.g. Sánchez-Espana et al. 2008). This has consequences for the nature and rates of elemental cycling in APLs. The stability of acidic conditions in APLs is enhanced by the acidity-driven iron cycle at the sediment–water interface, where acidity generated by oxidation of Fe^{2+} to schwertmannite (1.0–4.7 mol m^{-2} $year^{-1}$ in the sediment of Mining Lake (ML) 77, Lower Lusatia, Eastern Germany; Eq. 3.2) is balanced by alkalinity gained by microbial reduction of schwertmannite in this zone (0.65–4.0 mol m^{-2} $year^{-1}$ in ML 77; Peine et al. 2000).

$$8Fe^{2+}\ +\ y\ SO_4^{2-}(24 - 2y\ +\ x)/\ 2\ H_2O$$
$$\rightarrow Fe_8O_8(OH)_x(SO_4)_y + (24 -\ 2y)\ H^+ +\ 8\ e^- \qquad (3.8)$$

Contrary to other minerals, schwertmannite is easily microbially reduced under acidic conditions by acidophilic bacteria, such as *Acidophilium cryptum JF*-5 (Küsel et al. 1999). This is reasonable, minding the strong dependence of microbial reducibility of iron minerals on factors such as crystallinity and surface area (Lovley and Phillips 1988; Roden 2003). Goethite is reduced at significantly lower rates by acidophilic bacteria than dissolved Fe(III) or amorphous ferric hydroxide by *Acidiphilium SJH* (Bridge and Johnson 2000). The reducibility of jarosite by *Acidiphilium SJH* is even lower than that of goethite (Bridge and Johnson 2000). In the acidic, schwertmannite-enriched zone of APL sediment, a rate of 6–25 nmol g^{-1} h^{-1} (Peine et al. 2000) was measured. Addition of schwertmannite to APL sediment-peat slurries also stimulated the Fe(II) release rate compared to both unamended controls and goethite addition in incubation experiments (Blodau and Gatzek 2006), which clearly indicated Fe(III) reduction.

Table 3.5 Quality of organic carbon in different density fractions as indicated by C/N-ratio, lignine content, and the amount of aromatic polycarbonic acids, a marker for coal carbon

Density (g cm^{-3})	C/N ratio (g/g)	Σ Lignine (μg/mg C)	aPCA (μg/mg C)
<2.0	56	9.0	95
2.0–2.4	23	4.0	68
>2.4	19	3.3	48

The lowering of pH and potentially the increase in dissolved ferric iron appeared to be critical to the increase in bacterial iron reduction in these schwertmannite-amended incubation experiments.

The alkalinity derived from reductive dissolution was, however, completely consumed by the transformation of schwertmannite into goethite and the reoxidation of Fe(II) (Peine et al. 2000). Sulfate reduction only took place at a depth where the transformation was complete and the pH increased. The rate of alkalinity formation from sulfate reduction (2.0 eq m^{-2} year^{-1}) in deeper zones (≈ 10 cm) of the sediment from ML 77 was in the range of the acidity generated by schwertmannite transformation (3.5 eq m^{-2} year^{-1}) at ≈ 5 cm depth. It appeared that these two processes balanced each other. Thus, the pH did not increase in the lake water or in the top 5 cm of the sediment (this picture can, however, be changed by advective groundwater flow conditions, cf. below). Under these low pH conditions and without a supplemented carbon source, sulfate reduction is inhibited (Küsel and Dorsch 2000; Meier et al. 2004), so that Fe(II) cannot be fixed as iron sulfide in the top layers of the sediment. Reprecipitation of iron sulfides, however, would be a prerequisite for long-term neutralization of APLs (Blodau 2006).

Moreover, schwertmannite also appears to control metabolic activity in the sediment by selectively retaining microbially labile organic carbon (Laskov et al. 2002). Less than 10% of the organic carbon in the top sediment of a lignite APL were identified as autochthonous; the other fractions were either terrestrial (30–40%) or coal carbon. A density fractionation revealed that in the upper 4 cm of the sediment, 70% of the total carbon were associated with the heaviest, hence, iron-containing fraction, which itself made up 95% of the total mass. The iron fraction consisted of pure schwertmannite (Peine et al. 2000). A detailed analyis of the quality of the carbon pools in the three density fractions revealed that the carbon associated with the iron fraction was of the "best" quality with respect to its microbial availability (Table 3.5). It had the lowest C/N ratio, and the lowest content of lignite and aromatic polycarbonic acids, a marker for coal carbon (Glaser et al. 1998).

These observations may imply restrictions with regard to the primary production in APLs. Primary production in APLs seems to depend on the benthic supply of dissolved inorganic carbon (DIC), due to the low concentrations of DIC in acidic waters (Nixdorf and Kapfer 1998; see also Sects. 3.3.1.1 and 3.3.1.4). This supply may be severely affected by the availability of labile organic carbon being used for respiration by dissimilatoric bacteria associated with the large iron (schwertmannite) pool.

In addition to the impact of schwertmannite on pit lake geochemistry and metabolism, the mineral may also strongly influence the mobility and sequestration of trace elements. The mineral has a high affinity to anions and is, due to its large surface area, an efficient sink for As(V) (e.g. Acero et al. 2006; Schroth and Parnell 2005) and As(III) (Paikaray et al. 2011) in mine waters (see also case study 5.5). The adsorption of arsenate has been demonstrated to be an exchange reaction with non-structural sulfate (Fukushi et al. 2003). Similarly, phosphate can be retained, although at high concentrations, phosphate and arsenate may lead to destruction of the schwertmannite structure (Regenspurg and Peiffer 2005). Schwertmannite may therefore be regarded as an effective sink for both toxic anions and essential nutrients that control primary production, and can also enhance carbon sequestration in these waters.

Hydrogeochemical Effects on Schwertmannite Stability Under Transient Hydrological Conditions

APLs are hydrologically characterized by a strong interaction with groundwater (Werner et al. 2005; Fleckenstein et al. 2009). Influent groundwater tends to be only weakly acidic, due to intensive buffering activites in the adjacent dump materials, but rich in Fe(II) and sulfate (Bozau and Strauch 2002; Rolland et al. 2001; Werner et al. 2001). The extent of exchange with groundwater has a significant effect on biogeochemical processes in the sediments. Pore-water pH values, concentrations of Fe(II), sulfate reduction rates, and iron sulphide content were higher in areas of groundwater inflow (Blodau 2004, see also Sect. 3.2.1.1). The proton balance within the sediments was negative in areas with groundwater inflow and positive in those without groundwater inflow (Blodau 2005).

It appears that these observations are strongly linked to the reactivity of schwertmannite exposed to different flow rates in combination with different loads of $FeSO_4$ and DOC (Blodau und Knorr 2006; Knorr und Blodau 2006). Percolation in columns filled with schwertmannite-containing sediment material stimulated transformation of schwertmannite and thus acidity export. Mobilization increased with flow rates and decreased $FeSO_4$ concentration.

In order to quantify these relationships, we reanalyzed the data from Knorr and Blodau (2006) under conditions of pseudo steady-state. Acidity formation rates were calculated as the difference between acidity concentration at the inflow and the outflow of the columns times the flow rate. Acidity was calculated from the concentration of the following species and components

$$\text{Acidity} = 2\, c\!\left(Fe^{2+}\right) + 3\, c\!\left(Fe^{3+}\right) + 2\, c\!\left(FeOH^{2+}\right) + 3\, c\!\left(Al^{3+}\right) + c\!\left(HSO_4^-\right) + c\!\left(H^+\right) \tag{3.9}$$

The acidity formation rate decreased non-linearly with the load of sulfate (Fig. 3.22). This variable shows the same dependence on sulfate load as the ratio between inflow and outflow sulfate concentration, which suggest a relationship between the dissolution rate of schwertmannite and sulfate load. The acidity

Fig. 3.22 Acidity formation rate and ratio between inflow and outflow sulfate concentration as a function of sulfate load measured in column experiments by Knorr and Blodau (2006) under pseudo steady-state conditions
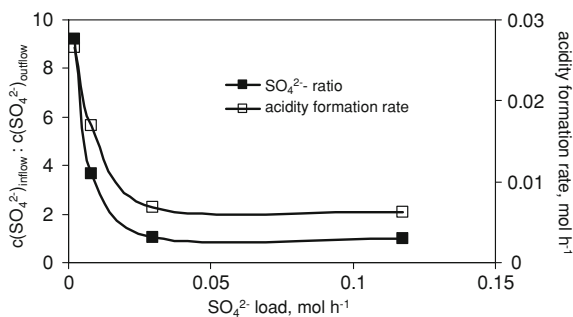
formation rate therefore seems to be proportional to the degree of undersaturation $(K_{sp} - IAP)/K_{sp}$, with IAP being the ion activity product of schwertmannite and K_{sp} its solubility product.

The implication of these considerations for APL water quality could be severe when groundwater inflow changes compared to conditions under which schwertmannite deposits formed. Such a scenario can be expected when the regional groundwater flow field is altered by the cessation of water drainage in pit mines. Influent groundwater will tend to dissolve sedimentary schwertmannite, thereby amplifying acidity flow into a lake. This effect becomes even more relevant if sulfate load is low. On the other hand, exfiltrating lake water will export acidity into the groundwater. The sediment layers underlying the schwertmannite-containing layer in such areas will thus receive acidity, inhibiting sulfate reduction and long-term neutralization of the acidity.

3.2.1.3 Phosphorus in Acidic Mining Lakes: Importance and Biogeochemical Cycling

Björn Grüneberg and Andreas Kleeberg

Because phosphorus (P) availability often limits phytoplankton growth, elevated concentrations of P usually accelerates freshwater eutrophication. A large body of knowledge exists on P in neutral freshwater lakes and lakes acidified by airborne pollutants, but the role of P as a key nutrient in geogenically acidified mining lakes (MLs) is not adequately considered. This is important because many MLs are subject to rapid P import by ecotechnological measures or flooding with river water. Changes in pelagic and benthic conditions (e.g. pH, redox potential, C, and Fe supply), either through natural development or due to anthropogenic manipulations, affect P mobility (Kleeberg and Grüneberg 2005). Independent of velocity and grade of manipulation during ML development, a low trophic state (oligo- to mesotrophic) has to be maintained, either to satisfy utilization concepts (e.g. recreation) or to meet regulatory standards (e.g. the EU water framework directive).

Acid MLs are usually characterized by low pelagic concentrations of total P (TP, < 5–38 μg L^{-1}, n = 23 MLs; Nixdorf et al. 1998; Fig. 3.23) and soluble reactive P (SRP, 6–26 μg L^{-1}, n = 4 MLs; Spijkermann 2008). These lakes are usually oligotrophic (Nixdorf et al. 2003). High TP concentrations (42–230 μg L^{-1}) occur in meromictic or sewage-impaired MLs (Fig. 3.23). Exceptionally high SRP concentrations (3.5–14.8 mg L^{-1}), derived from the dissolution of phosphorite-nodules by highly aggressive acid mine drainage (AMD), were reported for an acid (pH 2.5) pond (Woelfl et al. 2000).

The vulnerability of MLs to critical P loads from river flooding (Schultze and Klapper 2004), P loading due to in-lake measures (e.g. Lessmann et al. 2003), and fish farm emissions for neutral MLs (Axler et al. 1996, 1998; Rümmler et al. 2003; Yokom et al. 1997) is of present and future concern. Hence, the prediction of future trophic state requires knowledge of mechanisms of import and accumulation of P in relation to that of other substances during ML succession, particularly on P pelagic settling and scavenging, benthic P diagenesis, and mobility aspects known to influence P retention and pelagic P availability.

The objectives of this section are to: (1) review the state of knowledge concerning P in acidic MLs in order to evaluate its actual import paths, accumulation, and retention mechanisms, (2) assess recent and future sedimentary P mobility in young MLs, and (3) address open and critical research and management questions. Due to the dynamic development of the young (only a few decades old) MLs, the discussion refers in some cases (e.g. sedimentation, P forms) only to conditions of the current (acid) phase of succession. Furthermore, the number of studies on P in MLs is limited and little long-term data exists, so some conclusions are preliminary.

Import of Phosphorus

Soil erosion, in the form of transported suspended sediment in overland flow, is often associated with high rates of particulate P transfer from land to water bodies. A review of P loss from land to water by Sharpley et al. (2001) revealed that the loss of P originates mostly from small areas within watersheds, and typically during a few periods of high rainfall intensity. However, the results of common soil erosion processes are not transferable to the dumps of the post-mining landscape (e.g. Abel et al. 2000; Biemelt et al. 2005).

A year of monitoring and ten short rainfall simulations have revealed high erosion rates and loss rates for P and Fe from bare lignite mining dumps at Schlabendorf, Lusatia, Germany (Kleeberg et al. 2008). The hydrophobicity led to very low infiltration, thus generating surface runoff even at low rainfall intensities. The mean annual soil erosion rate from the monitoring site was 18×10^6 kg km^{-2} year^{-1}. Loss rates for P and Fe were 470–650 kg km^{-2} year^{-1} and 37.9×10^3–71×10^3 kg km^{-2} year^{-1}, respectively. These rates are equivalent to those of intensively used agricultural catchments. However, P import from

these P-poor (17–90 µg g^{-1}) tertiary spoil materials into MLs will hardly affect their trophic state due to the accompanying high Fe import (Fe:P $\approx$ 60).

The diversion of river water into mining pits, both to quickly fill the pit and, at some sites, as flow-through to maintain sustainability, is one of the major management strategies to prevent (hydraulic gradient towards the dumps) or to combat acidification by dilution and import of alkalinity (see Sects. 4, 5.1).

Primary filling can cause extremely high short-term P loading for the new pit lakes. For example, various MLs in Saxony-Anhalt, Germany, have been flooded with river water (TP 110–160 µg L^{-1}), resulting in short-term P loading between 0.07 and 3.15 g m^{-2} year^{-1} for ML Merseburg Ost to 3.6 g m^{-2} year^{-1} for ML Runstädt (Schultze and Klapper 2004; see also case study 5.1). In-lake TP concentration during flooding ranged between <3 and 160 µg L^{-1} and usually decreased rapidly for MLs with significant 'mining impact' (metal import). As documented for ML Goitsche, Germany, which was flooded by River Mulde water (TP $\approx$ 110 µg L^{-1}), P was efficiently removed from the water column by Fe- and Al-compounds adsorbing riverine P, leading to low TP concentrations of 6–11 µg L^{-1} a few months after flooding (Duffek and Langner 2002; Herzsprung et al. 2010). However, elevated TP concentrations (12–70 µg L^{-1}) after flooding of other MLs, such as ML Runstädt, depict the limits of this technique and the risk of eutrophication.

Through flow of alkaline river water is required for many MLs as a continuous management measure to buffer acidity (Senftenberger See, ML Dreiweibern) or to use MLs as reservoirs to buffer variable discharge. Most examples show that MLs can compensate for this extra nutrient load (e.g. 20% for ML Dreiweibern) by high P retention, depending on the degree of mining impact, thus retaining a meso- or oligotrophic state.

Groundwater (GW) often dominates the water budgets of acid and neutral MLs after cessation of flooding (Hofmann et al. 2008; Werner et al. 2001). Despite the availability of high quality water mass balances from three-dimensional GW modeling (Heidenreich et al. 1999; Knoll et al. 1999), it is difficult to quantify P import because: a) TP concentrations in GW vary over a wide range (e.g. 101–254 µg L^{-1} for ML 117; 50–1,700 µg L^{-1} for ML Dreiweibern, Germany), and b) the P concentration is altered substantially during sediment passage.

The composition of GW after sediment passage as measured by seepage meters differs considerably from that in the vicinity of a lake (e.g. Driescher et al. 1988; John and Lock 1978). During passage through mining-influenced sediment, which typically has an elevated Fe content in both acid and neutral MLs compared to sediment of near naturally neutral lakes (Fig. 3.23), it is very unlikely that substantial amounts of P initially reach the ML water. Due to the high P sorption capacity of Fe-rich sediments (e.g. 5.6–9.1 mg g^{-1} in ML 117), predominantly adsorption of P onto Fe oxyhydroxides, P levels rarely exceed the sorption equilibrium concentration of about 3 µg L^{-1}. With typical Fe contents >70 mg g^{-1} and Fe:P ratios >60 for acid ML sediments (Fig. 3.23) there is no case where P is close to saturation, i.e. Fe:P < 10 (Lijklema 1977).

Complete P mass balances allow the estimation of the TP concentration in GW after sediment passage if whole lake retention (R) is assumed. For ML Dreiweibern, a GW TP concentration of 0–75 μg L^{-1} was calculated (for R = 0.85–0.88), which is considerably less than measured in GW wells. However, preferential flow is probably important due to small-scale bottom inhomogeneities that are influenced by the regional surface excavation technique. Preferential flow into deeper parts of e.g. ML 117 by means of electrical conductivity and seepage meter measurements revealed a 82–93% reduction of TP concentration to 17–71 μg L^{-1}, compared to GW, despite high discharge at these locations and a short, i.e. <10 cm sediment passage (Hofmann 2003; Hofmann and Lessmann 2006). From a whole-lake sediment P budget, we estimated that the GW infiltrating the sediment had a TP concentration of 200–300 μg L^{-1}, which was almost completely adsorbed during sediment passage, generating a mean in-lake SRP concentration of <4 μg L^{-1}.

Role of Phosphorus in Mine Lake Remediation

In the dumps, phosphate (PO_4^{3-}) additions can reduce the potential of Fe^{3+} to act as a pyrite oxidant if PO_4^{3-} precipitates with Fe^{3+}, forming relatively insoluble iron phosphate minerals, such as amorphous $FePO_4$ and $FePO_4 \cdot 2H_2O$ (strengite; e.g. Baker 1983; Hood 1991). However, experiments to verify the P control on pyrite oxidation indicated that the inhibition is only temporary because of iron armoring (Huang and Evangelou 1992; Fytas and Evangelou 1998). An example of natural phosphate rock application to precipitate iron is also described in case study 5.7. To our knowledge, practical application of this technique is limited because of the high costs, and the potential adverse environmental effects of P fertilization.

The approach of neutralizing poorly buffered airborne acidified lakes by treatment with P fertilizer has been known for a long time (Davison et al. 1995). In recent years, some have attempted to use single P amendments to reduce AMD from mine dumps, or to stimulate a ML's primary production to enhance the C supply for benthic alkalinity generation. Additions of P should be most effective in removing acidity via iron sulfide sequestration. Theoretically, to remove 1 mol acid, it is necessary to form 1 mol of FeS_2. This can be achieved by applying either 0.05 mol PO_4^{3-} ('controlled eutrophication', Fyson et al. 1998a), or 0.5 mol $CaCO_3$ ('lake liming', e.g. Lindmark 1982), or alternatively 3.75 mol of organic matter <CH_2O> ('saprobization', Fyson et al. 1998b). However, the following few examples show that single P additions have had limited effects.

Fyson et al. (1998a, b) tested amendments of organic C and hydroxyapatite in lab mesocosm experiments with sediment of an acid (pH 3.1) ML. Additions of potatoes at rates of 51–348 g dry weight (dw) m^{-2}, equivalent to a P load of 0.13–0.88 g m^{-2} (P content 1.8 mg g^{-1}) resulted in anoxic conditions above the sediment, and an increase in dissolved Fe, SRP, NH_4^+, and organic and inorganic C as the potatoes decomposed. In contrast, a single hydroxyapatite addition (692.9 g P m^{-2}) was not effective in supplying organic C via planktonic

Source

		Surface Sediment							Water		

acid MLs

Label	TP_Sed (mg g⁻¹)	TFe_Sed (mg g⁻¹)	S_Sed (mg g⁻¹)	Fe:P	Fe:S	LOI (%)	TP_water (µg L⁻¹)	TFe_water (mg L⁻¹)	pH_water	Source
ML 107 (98)	0.50	300	73	332	2.3		18	420		p
Sedlitz (93)	0.50	2.4		5			8	28		e
ML113 (01)	0.29	91	14	112			40	135		a
ML 111 (98–00)	0.45	140		369			11	218		e, f, s
Lichtenauer See (93)	0.21	71		131		14	9	49		e
Skado (93)	0.30	100	9	62	6.3	19	11	105		g, h
ML 117 (02–04)	0.90	200		246		29	6	9		n
ML 112 (01)	0.45	300		332		26	11	33		d, o, j
Niemeck (Goitsche) (99)	0.50	220		182		25	6	230		e
Halbendorf (93)	0.67	140		199		19	5			e, r
Koschen (93)	0.39			354			6	25		d, o, j
Doebern (Goitsche) (02)	0.50	320		135		28	9.5	5		e
Bärwalde (09)	0.48	117	25	203	6.6	29	2	4.1		c
Senftenberg Südfeld (93)	0.79	290	6	35	4.2	14		4.2		a
Gobpile (<86)	0.40	25		44	1.0		5	0.3		e
Felixsee (01)	0.40	32								a

neutral MLs

Label	TP_Sed	TFe_Sed	S_Sed	Fe:P	Fe:S	LOI	TP_water	TFe_water	pH	Source
Senftenberg (93)	2.4	140		32		21	6	1.8		e
Senftenberg (09)	1.6	137		46		22	15	0.2		a
Dreiweibern (01)	0.61	90	5	82	10	11	12	0.5		a
Dreiweibern (08)	1.25	243		108		18	10	0.5		a
Gräbendorf (09)	0.72	86		66		23		0.3		a
Kulkwitz (01)	0.48	27	2	31	7.7		11	0.0		q
Haselbach (07)	0.18		3.3	148			4	0.1		e
Schönfelder See (95)	0.86	100		64		22	12	0.2		q
Baß (<(86)	1.50	45	5	17						c
Linden (<86)	1.00	58		32	6.6					c
Spremberg Reserv. (01)	2.8	133	5.5	26	4.2		43	0.4		i
Laubusch (Hypo) (98)	4.5	40	54	5	1.0	25	27	13		r
Golpa IV (95)	15	196		4			124			m

meromictic MLs

Label	TP_Sed	TFe_Sed	S_Sed	Fe:P	Fe:S	LOI	TP_water	TFe_water	pH	Source
Walds. Döb. (Monim) (03)	0.60	300	170	277	1.0	36	50	129		a, g
Moritzteich (Monim) (04)	1.10	277	82	139	1.9		30	400		t
Lugteich (Monim) (01)	5.0	190	93	21	1.2	40	140	826		a

natural lakes

Label	TP_Sed	TFe_Sed	S_Sed	Fe:P	Fe:S	LOI	TP_water	TFe_water	pH	Source
natural lakes	2.3 (n=105)	34 (n = 26)		8						a, l, m

< 4   > 6

◄**Fig. 3.23** Sediment and water data for MLs with emphasis on sediment P and mining indicators (Fe, S) for acid, neutral, and meromictic MLs; (Hypo: hypolimnion; Monim: monimolimnion). Sources: a) own unpublished data; b) Borovec and Hejzlar (2001); c) Brugam et al. (1988); d) Duffek and Langner (2002); e) Friese et al. (1998); f) Frömmichen et al. (2004); g) Grüneberg and Kleeberg (2005); h) Grüneberg (2006); i) Heidenreich and Kleeberg (2003); j) Herzsprung et al. (2004); k) Herzssprung et al. (2010); l) Hupfer (1998); m) Hupfer et al. (1998); n) Kleeberg and Grüneberg (2005); o) Langner (2004); p) Lessmann et al. (1999); q) LMBV (various unpublished reports and monitoring data from state company responsible for the remediation of former lignite mines in eastern Germany; www.lmbv.de); r) Nixdorf et al. (2000); s) Saballus (2000); Stellmacher (2004)

production. The studies demonstrated that organic wastes remove acidity in the short-term by generating reducing conditions around the sediment surface and stimulating P release to the overlying water.

To study whether self-sustaining acidity removal is possible by 'controlled eutrophication', enclosure experiments were run in dimictic, acidic (pH $\approx$ 3) ML 117-Grünewalder Lauch (A = 0.94 km^2, z_{max} = 14.4 m) from August to October 2002. 12 enclosures ($\varnothing$ = 1 m) were installed at a water depth of 6 m. Two were neutralized by adding Na_2CO_3, two were neutralized and fertilized (Na_2CO_3 + P with 3 g m^{-2}), two were only fertilized with P (3 g m^{-2}), two were neutralized and fertilized with 3 kg fresh potatoes (309 g C m^{-2} incl. 1.44 g P m^{-2} on a dw basis), two were only fertilized with 3 kg potatoes, and two were left untreated as controls.

Neutralization and C addition in combination was most efficient in terms of sustainability of increased pH and decreased Eh at the sediment water interface and secondary supply of particulate organic C (POC) from primary production towards the sediment. There was no permanent effect after single neutralization, C addition, or P fertilization. In the neutralized and P-fertilized enclosures, the Na_2CO_3 additions led to a rapid decrease of TP concentration from 500 to 15 µg L^{-1} by co-precipitation with Fe carbonate and Fe hydroxide, and so significantly decreased the pelagic P availability for primary producers. Consequently, there was (at least for the amounts added) no long-term effect as a consequence of the diminished phytoplankton production and the corresponding POC flux. In summary, there was a gradual component-specific effect on pH in the sequence: 'potatoes' > 'Na_2CO_3 + P' > 'P' > 'control' indicating that biogenic alkalinity generation due to organic C supply is more efficient than liming or P amendments.

Lessmann et al. (2003) reported on in-lake treatment by the addition of organic waste material to increase primary production and to form anoxic microbial reaction compartments and thereby stimulate biogenic alkalinization via sulfate reduction. The small (A = 10 ha, V = 10^5 m^3), shallow (z_{max} = 2.5 m) acidic mining lake Koyne 113, Germany, was treated four times in three consecutive years with a total of 243 t of a mixture (C: 486 g kg^{-1}, N: 6.36 g kg^{-1}, P: 94 mg kg^{-1}) of cut-up beer and water bottle labels in jute bags. These additions resulted, from before the treatment to the third year, in increased lake water concentrations of organic C from 2.9 to 8.0 mg L^{-1}, of TP from 10 to 43 µg L^{-1}, and of chlorophyll a from 28 to 85 µg L^{-1}. However, acidity ($K_{B4.3}$ = 10.4 ± 0.4 mmol l^{-1}; $K_{B8.2}$ = 13.9 ± 0.6 mmol l^{-1}) and pH (2.5 ± 0.05) did not change.

This approach obviously failed because the import of acidity-forming constituents was not stopped. For example, within the observation period, sulfate concentrations increased from 1.59 to 2.86 g L^{-1}, i.e. by 79.9%. This increase showed that either no sulfate reduction occurred in the shallow lake, or sulfides were re-oxidized due to constant high oxygen saturation >90% in the water column. Even if part of the sulfate was stored in the sediment, such an oxygen supply favors a re-oxidation of sulfides as shown by Koschorreck et al. (2002).

Furthermore, the addition of C (mostly C_{org}) with 1,181 g m^{-2}, of N with 15.5 g m^{-2}, and of P with 0.23 g m^{-2} corresponds to a ratio of $C_{13,356}:N_{150}:P_1$. This ratio differs quite a lot from the mean composition of phytoplankton with $C_{106}:N_{16}:P_1$ (Redfield 1934), which indicates that the nutrient mixture was not appropriate. The total P amount of waste material addition should theoretically lead to a pelagic TP concentration of 228 μg L^{-1}, representing an already highly eutrophic lake. However, the TP concentration monitored after the measure (43 μg L^{-1}) revealed that most of the P (77.6%) was precipitated due to surplus of P-binding partners, such as Fe, Al, and Mn (Fe:P 6366, Al:P 4248, and Mn:P 180) in the water. Metal concentrations even increased during the experiment.

Phosphate and nitrate have also been directly applied to surface waters of pit lakes to reduce metal concentrations and toxicity. Island Copper pit lake (Fisher and Lawrence 2006; Pelletier et al. 2009), and enclosures in Main Zone and Waterline pit lake, Canada (Martin et al. 2003) received P additions between 0.1 and 2.0 mmol m^{-2} d^{-1}. Due to increased primary production, a pronounced removal of dissolved and total Zn, Cu, and Cd was attained by active uptake or sorption to algal surfaces and subsequent particle settling, and by metal-sulfide precipitation under anoxic conditions. Combined limestone neutralization and P amendment reduced Al and Zn metal toxicity by shifting metal species to predominantly non-bioavailable forms in mesocosms with Lake Kepwari water, West Australia (Neil et al. 2009; case study 5.4).

To summarize, it is best to lower the import of AMD to a minimum prior any in-lake manipulations. In the case of P fertilization, the concomitant import or pelagic and benthic surplus of P-binding partners, such as Fe, Al, and Mn, has to be adequately considered in terms of a mass balance and respective sediment. Even a surplus of P and organic C by waste materials does not guarantee effective acidity sequestration, even though it bears the risk of eutrophication.

Sedimentation and Accumulation of Particulate Matter and Phosphorus

Composition and sedimentation of particulate matter in MLs has rarely been studied. High deposition rates for dry weight (dw; 3.8 g m^{-2} d^{-1}) and Fe (1.45 g m^{-2} d^{-1}) were reported for acidic (pH 2.9) ML 77, Germany (Peine et al. 2000). Similar dw deposition rates (2.1 g m^{-2} d^{-1}) were reported for meromictic ML Waldsee, Germany (Dietz, unpubl.), and considerably lower rates (dw: 0.94 g m^{-2} d^{-1}, Fe: 0.2 g m^{-2} d^{-1}) for ML 117 (Grüneberg 2006). Due to the high Fe content of settling matter (210–363 mg g^{-1}), Fe fluxes are an order of

Fig. 3.24 Monthly mean of sedimentation rate at the deepest site of acid (pH ≈ 3) ML 117, Germany, for the epilimnetic 7 m trap (open symbol) and hypolimnetic 12 m trap (closed symbol) for: **a** total Fe, **b** total P, and **c** the atomic C:P ratio of material entrapped
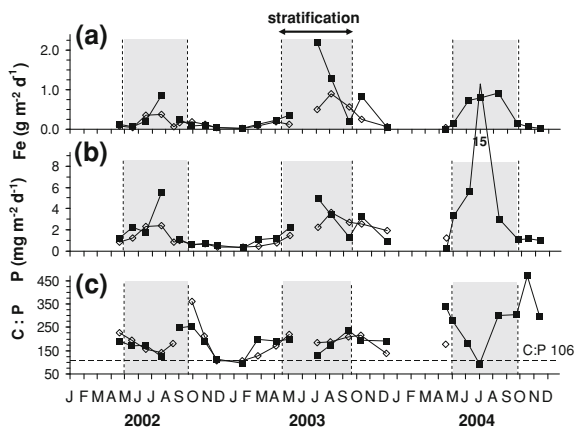
magnitude higher than in natural lakes. A three-year sediment trap study in acidic (pH 3.0) dimictic ML 117, representing moderate Fe concentrations (9.3 mg L^{-1}) revealed, first, annual mean epilimnetic sedimentation rates of organic C (101 mg m^{-2} d^{-1}) and TP (1.4 mg m^{-2} d^{-1}) were similar to those of natural oligotrophic lakes. Second, Fe oxyhydroxide precipitation dominated sedimentation only for a short time, between mid June and August (max. 2.2 g Fe m^{-2} d^{-1}; Fig. 3.24a), inducing low C:P ratios during summer (Fig. 3.24c) by scavenging of organic C, a seasonal trend opposite to that of natural neutral lakes. Third, even during periods of intensive Fe oxyhydroxide floc formation, low concentrations of SRP ≈ 3 µg L^{-1} limited P adsorption, so downward P transport was mainly organic (algae; 39–71% TP).

Sediment composition and accumulation rates differ for shallow and deep parts of ML 117 due to different rates of lateral Fe oxyhydroxide and organic particle transport and mobilization. The sediment formed at a shallow water depth (2.5–8 m) has a high P sorption potential due to a high Fe (400 mg g^{-1}) and low P content (0.4 mg g^{-1}). In contrast, an Fe-poor (24–250 mg g^{-1}) but C- and P-rich (loss on ignition: 32–70%; TP: 0.9–3.4 mg g^{-1}) sediment formed at deeper (8–14 m) water depths. Although these results are from a single case study, differentiation in small deep and extended shallow areas is characteristic for a number of MLs (Nixdorf et al. 2001). Thus, the effects of morphometry-triggered sediment accumulation and composition patterns for P retention or for processes depending on POC supply have to be considered as likely to occur in other MLs as well.

Phosphorus Adsorption Properties of Mining Lake Sediments

The low trophic state of acid MLs is, to a great extent, a consequence of the high P adsorption capacity of metal oxyhydroxides (e.g. 37.3 mg P g^{-1} Fe for fresh Fe hydroxide at pH 7; Parfitt et al. 1975). Phosphorus adsorption capacities (batch experiments, Langmuir isotherm) varied between 0.3 and 3.3 mg g^{-1} dw for sediment of neutral Spremberg reservoir, Germany, receiving river water

discharged by AMD (Heidenreich and Kleeberg 2003), and 3.8–9.1 mg g^{-1} dw for three ML sediments (Grüneberg 2006) with P adsorption clearly depending on sedimentary Fe content ($R^2 = 0.90$; $n = 8$). These numbers are significantly higher than those known from natural lakes ranging from 0.03 to 3.0 mg g^{-1} dw (e.g. Detenbeck and Brezonik 1991; Pant and Reddy 2001), and are similar to other Fe hydroxide media (Adler and Sibrell 2004; Zeng et al. 2004).

Working with these numbers, it should be considered that P adsorption a) is lower (e.g. 5.6–8.5 mg g^{-1} for ML 117) if determined in continuous flow experiments as to mimic GW sediment passage with more realistic (0.4 and 2.0 mg L^{-1}) adsorbate concentrations (Grüneberg 2006), and b) may significantly decline under anoxic conditions (e.g. Pant and Reddy 2001).

The significance of the very efficient non-redox sensitive Al–P sorption (Lijklema 1980; Parfitt 1989) has been documented for rain-acidified lakes (e.g. Kopáček et al. 2004), but not for MLs. There are contradictory views on the influence of humic substances on metal-P adsorption, which compete with P for adsorption sites at metal surfaces (Antelo et al. 2007; de Vincente et al. 2008), but may also increase P sorption (Bloom 1981; Gerke and Herman 1992). This might be especially significant for MLs, giving the substantial amounts of partly lignite-derived C associated with metal oxyhydroxides (Laskov et al. 2002).

Phosphorus Forms in Mining Lake Sediments

The stability of P binding in acid ML sediments was highlighted by Brugam et al. (1988). They found that only a small fraction of P dissolves in 0.1 N HCl (representing inorganic metal-bound P) and that most P (and other elements) is released only in ashed sediment by hot HCl. Thus, most P is strongly adsorbed or in organic form.

Many authors apply a sequential extraction (e.g. Hupfer 1998; Psenner et al. 1984) to identify operational phases and to interpret pools and mobility of benthic P forms. Because of the high Fe contents of ML sediments, the procedure was modified (Grüneberg 2006; Saballus 2000), and a simple method for TP and TFe determination was tested for sediments with Fe contents up to 450 mg g^{-1} (Grüneberg and Kleeberg 2005).

Iron is regarded the predominant sorption partner for P in MLs due to the abundance of Fe oxyhydroxides. However, BD-P (Fe-bound P) comprised only 17–30% of TP in oxic sediments of acid ML 112 (Kleeberg and Grüneberg 2005) and ML 117 (Grüneberg and Kleeberg 2005). The potential for P adsorption to Fe oxyhydroxides (BD-P) is not completely fulfilled in these acid MLs due to an excess of Fe compared to P.

Aluminum contributes differently to P sorption in MLs depending on the geochemical setting. Despite high atomic Al:P ratios ($13 - 440$; n = 8) in acid ML surface sediments, Al is of minor importance for P binding if mainly present as constituent of clay particles, as found for ML Golpa IV (Hupfer et al. 1998), and by means of energy-dispersive X-ray analysis and sequential extraction for ML 117 (Grüneberg and Kleeberg 2005). The increase of NaOH-P (metal-bound P,

mainly Al, and organic P) at the expense of BD-P between pH 4 and 7 was interpreted as a shift of relevance from Fe− to Al−oxydroxides for P sorption in ML Goitsche (Duffek and Langner 2002; Duffek and Schultze 2002). Dominance of Al–P binding was also demonstrated for rain-acidified (pH 4.9) Lake Plešne due to high Al import (Kopáček et al. 2004) and for Mud Pond Lake (pH 4.8), as evidenced by 80% solubility of Al and >95% solubility of P in the NaOH-fraction (Wilson et al. 2008).

Vivianite [$Fe_3(PO_4)_2$] is known to be a long-term P sink in anoxic lake sediments (e.g. Holdren and Armstrong 1980; Nriagu and Dell 1974). Positive vivianite saturation indices were determined by chemical equilibrium calculations for the highly anoxic deeper sediment of ML Golpa IV (Hupfer et al. 1998) and in mesocosm experiments with organic C and P additions to ML sediments (Grüneberg 2006; Langner 2004). These authors concluded that the high Fe content of ML sediments and the dominance of Fe reduction over SO_4^{2-} reduction result in excess Fe^{2+} in pore water, which allows concurrent sulfide and vivianite formation not possible under most conditions (Nriagu 1972).

Metal–organic complexation was assumed to be an important P binding mechanism as it offers an explanation for the high BD- and NaOH-NRP (non-reactive P) content of ML sediments (Grüneberg and Kleeberg 2005) that is consistent with the finding that organic matter is preserved after degradation due to adsorption to Fe oxyhydroxide surfaces (Antelo et al. 2007; Laskov et al. 2002; Tipping 1981).

To summarize, there are indications of Al control of P binding for MLs at pH 4–6.5, based on one case study and analogous rain-acidified lakes. For acid (pH < 4) MLs, high organic P contents were found in two cases (up to 36–42% NaOH-NRP in ML 112 and 117 surface sediment), while most Fe-based P adsorption capacity remains unfulfilled due to the high Fe contents. Evidence for vivianite as well as metal–organic complexation is vague despite their potentially high relevance as long-term sinks for P in MLs.

Phosphorus Mobility and Availability: Implications for Mine Lake Succession

There are mechanisms and indications for both very efficient P binding in ML sediments and also for increased mobility of P with ML succession. Four mechanisms that could lead to increased P mobility and potentially higher trophic state have been identified. First, the import of Fe and Al into MLs will decrease with maturation and reclamation of their catchments; thus, the supply of P binding partners will decline (Kleeberg and Grüneberg 2005). Second, the P adsorption capacity of Fe oxyhydroxides will decline with increasing pH due to transformations to more crystalline forms. Third, the burial of metal-rich sediments by particles from river flooding or increased primary production may render the Fe oxyhydroxides from the acid phase inactive for P adsorption (Schultze and Klapper 2004). And finally, natural maturation or artificial neutralization will lead to P and C accumulation in MLs, which may cause anoxic conditions at the

sediment, reductive dissolution of Fe oxyhydroxides, immobilization of Fe as FeS_x, and consequent mobilization of Fe-bound P analogous to natural lakes (Caraco et al. 1993; Kleeberg 1998).

However, anoxic conditions do not inevitably cause P release. SRP concentration remained close to the detection limit of ≈ 3 μg L^{-1}, despite anoxic conditions (Eh < 150 mV) and periodic neutralization of hypolimnetic water to pH 5–6.4 in ML 117 (Grüneberg 2006). The meromictic and anoxic ML Goitsche showed no sign of eutrophication (TP 8 μg L^{-1}), despite a short-term high P import by a river flood (Herzsprung et al. 2010). In both cases, the re-oxidation of Fe^{2+} from reductive dissolution in anoxic sediment layers at the sediment water interface ('ferrous wheel'; Campbell and Torgersen 1980; Davison 1993) allowed continuous P precipitation by newly-formed Fe oxyhydroxides. Thus, a high Fe:P ratio in pore water ($\approx 10,000$ for ML Goitsche, basin Niemegk) was suggested as an indictor for a low trophic state (Herzsprung et al. 2010; Sect. 3.2.1.1).

The longevity of an effective Fe–P co-precipitation is elucidated by the case of natural lake Groß-Glienicker See, Germany (A = 0.67 km^2, z_{max} = 10.8 m). P sorption capacity has remained high for 16 years (13 cm of new sediment) after iron hydroxide and iron chloride treatment (Hupfer 2004), as evidenced by an elevated Fe content, low pore water SRP, and a high Fe:P ratio in sediment (7.5) and pore water (15.0; Fig. 3.25).

Conversely, batch and column experiments involving the addition of organic C have shown that P release from Fe-rich ML sediments is possible under permanent anoxic conditions. However, P release rates between 0.15 and 0.46 mg m^{-2} d^{-1} (Grüneberg 2006) and 6.2 mg m^{-2} d^{-1} (Langner 2004) are low compared to those of oligotrophic (0–1 mg m^{-2} d^{-1}) and mesotrophic (2.1–6.7 mg m^{-2} d^{-1}) lakes (Nürnberg and Lazerte 2004). Grüneberg (2006) found that P release occurred only from ML sediments where Fe was largely immobilized as FeS_x, as evidenced by a low atomic Fe:S ratio (1.4–2.0). The measured SRP pore water concentrations were in adsorption equilibrium with the fraction of Fe not immobilized as FeS_x.

Explanations for high P retention, the limits of P binding, and conditions that cause high pelagic P concentrations can also be derived by analyzing the geochemisty of ML water and sediment (Figs. 3.23 and 3.26): MLs without additional nutrient inputs are characterized by low TP concentrations in water column (<12 μg L^{-1}) and sediment (<0.5 mg g^{-1}). Additional nutrients provided by river flooding or wastewater discharge results in high sediment TP, but pelagic TP concentration increases only if the P loading exceeds sedimentary P sorption capacity (e.g. ML Golpa IV). Elevated P concentrations (30–50 μg L^{-1}) in the monimolimnion of meromictic MLs Moritzteich and Waldsee Döbern, which receive only natural low P imports, highlight that high Fe contents (≈ 300 mg g^{-1}) and Fe:P ratios (140–280) in the sediment are insufficient indicators for P mobility (Fig. 3.26c). For most cases, prerequisites for high P concentrations are anoxic conditions in the hypolimnion and sediment as well as immobilization of Fe as FeS_x as indicated by low atomic Fe:S ratio <2 (Fig. 3.26e). Kleeberg (1998) already identified the 'degree of pyritization' (DOP),
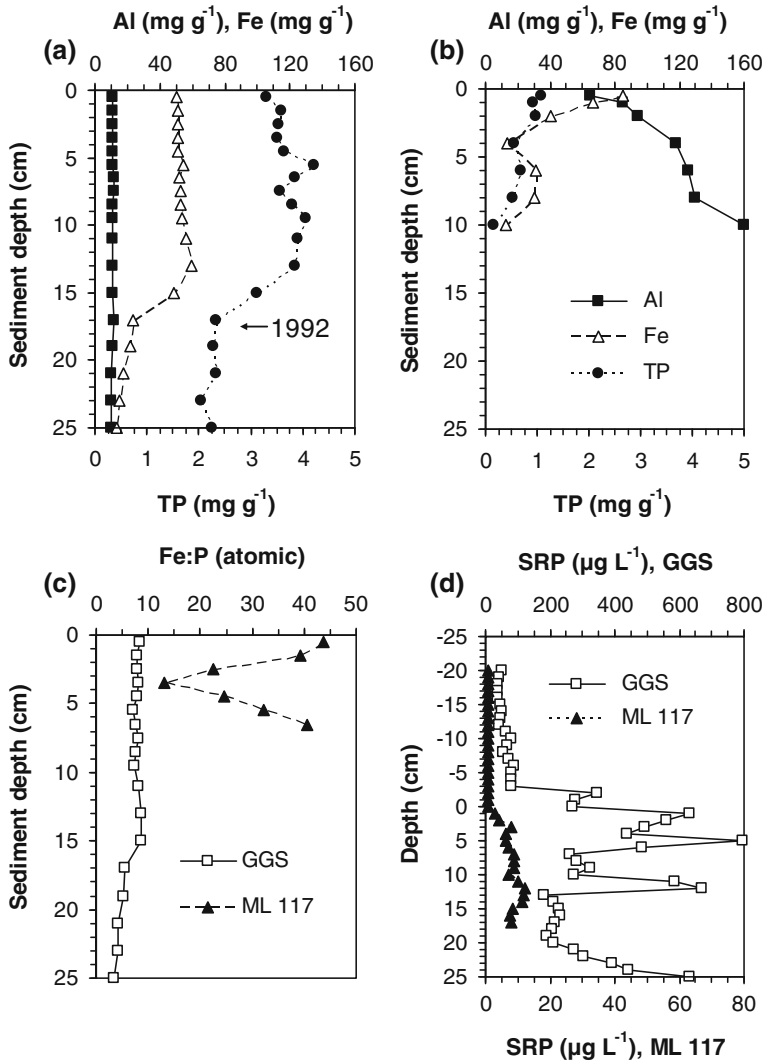
Fig. 3.25 Vertical profile of sedimentary Al, Fe, and total P (TP) for **a** neutral lake Groß Glienicker See, Potsdam, Germany, which has been treated by ferric Fe in 1992 (see *arrow*), and **b** for acid ML Grünewalder Lauch (ML 117), Lauchhammer, Germany; **c** respective atomic Fe:P ratio for both lakes; **d** vertical profile of soluble reactive P (SRP) in pore water at the deepest site of lake Groß-Glienicker See (GGS) in September 2008, and for ML 117 in June 2003

an expression of the percentage of Fe sequestered in FeS_x form, as an essential indicator for P mobility.

Groundwater seepage into MLs largely determines water geochemistry due to the import of elevated quantities of dissolved metals and sulfur associated with mining activities (Blodau et al. 2006; Graupner et al. 2005; Wisotzky and Obermann 2001). As the cycling of P relates to the quantity of this mining impact, various indicators for P mobility have been used, reflecting the interconnections between P, Fe, Al, and S (Fig. 3.27). A high mining impact (metal import and their pelagic precipitation as oxyhydroxides) leads to very low benthic P mobility in acid MLs. Under anoxic conditions, P mobility remains low due to: a) upward propagation of the aforementioned 'ferrous wheel,' which leads to a high P binding capacity of Fe-rich ML sediments beyond the period of a massive AMD, despite decreasing Fe- and Al-import and ongoing deposition of organic and P-rich sediment; b) the possibility of vivianite formation as a permanent P sink concurrent with sulfide formation, given a Fe^{2+} surplus; and c) the higher thermodynamic stability of the $Fe(OH)_3$–P complex, compared to $Fe(OH)_3$, so that an almost complete transformation of ferric Fe to FeS_x (>75%) is required before P release becomes significant (Golterman 1995).

A high pore-water Fe:P ratio and low SRP concentrations was found to assure efficient adsorption onto re-precipitated Fe oxyhydroxides, an indicator concept also suggested for natural lakes (e.g. Baccini 1985). The surface sediment Fe:P ratio, suggested as an indicator for shallow oxic lakes (Jensen et al. 1992; Sondergaard et al. 1993), can be used for MLs only when the DOP is low. Analogously, the Al:P ratio (Rydin et al. 2000; Welch and Cooke 1999) may be used with Al hydroxide as the binding partner. Kopáček et al. (2005) proposed the ratio NaOH-Al: $BD + H_2O$–$P > 25$ as an indicator for efficient Al-based P sorption. Maaßen (2003) and Jin et al. (2006) suggested combined Al and Fe indicators, a concept not tested for MLs yet. We recommend the application of the Fe:S ratio or $\log(Fe:S) \times \log(Fe:P)$ ratio to account for the fact that DOP determines the availability of Fe as binding partner.

Phosphorus Retention in Mining Lakes and Prognosis of Trophic State

Acid MLs exhibit a high availability of P binding partners as a result of mining activities, as indicated by sediment Fe:P ratios up to 370 (Fig. 3.23). Even neutral MLs (without unusually high P loading) have significantly higher sediment Fe:P ratios (17–148) than natural lakes (≈ 8; Fig. 3.23). As a consequence of this elevated sediment-based P binding capacity, whole lake P retention for a set of eight Lusatian MLs was $14.7 \pm 5.5\%$ higher than predicted from the empirical OECD (1982) model (Grüneberg, unpublished). Data indicate that even a slight mining impact (e.g. Fe surplus) leads to significantly increased P retention. We suggest that empirical P retention models be adapted for MLs since this underestimation of permissible loading may, for instance, lead to usage restrictions.
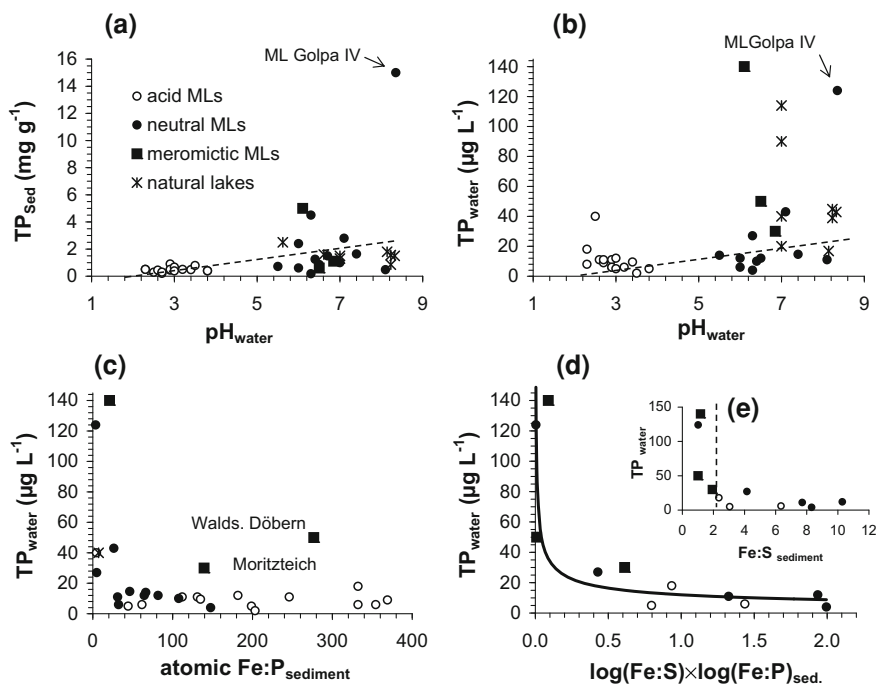
Fig. 3.26 Concentration of total P of water (TP_{water}) and sediment ($TP_{sediment}$) versus indicators (ratios in water and sediment) supposed to indicate conditions of low and high P concentrations in MLs ($n = 27$, see Fig. 3.23) compared to natural lakes ($n = 5$)
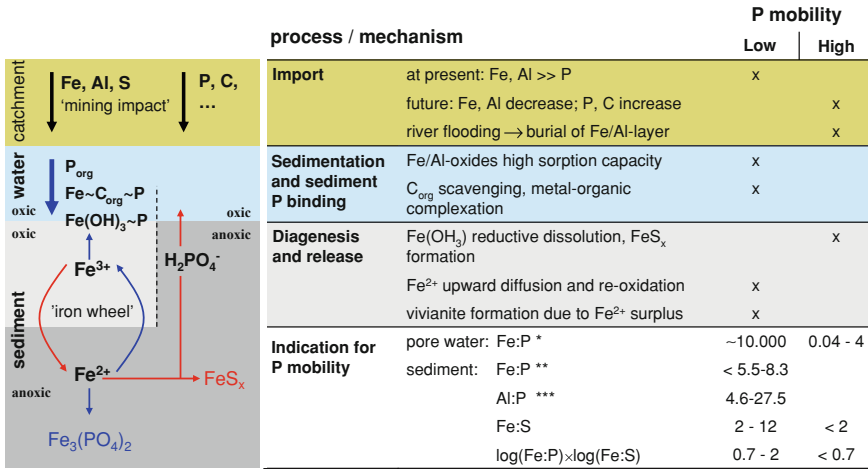
3.2.2 Hardrock Metal Mine Pit Lakes: Occurrence and Geochemical Characteristics

L. Edmond Eary and Devin N. Castendyk

3.2.2.1 Introduction

Pit lakes are an increasingly common legacy of modern, large-scale surface mining operations. Pit lakes formed in open pit metal mines, where base and precious metals are extracted from ore deposits hosted in predominantly igneous and metamorphic silicate rocks, comprise one category of pit lakes. This category is referred to as hardrock metal-mine pit lakes, to distinguish them from pit lakes formed in above-ground hydrocarbon, industrial minerals, and aggregate mining operations.

   Ore deposits exploited by mining consist of rock assemblages with naturally elevated concentrations of metals. These include the base metals (e.g. Co, Cu, Pb, Mo, Ni, and Zn) and precious metals (e.g. Ag and Au). Base metals are typically

process / mechanism		P mobility	
		Low	High
Import	at present: Fe, Al >> P	x	
	future: Fe, Al decrease; P, C increase		x
	river flooding → burial of Fe/Al-layer		x
Sedimentation and sediment P binding	Fe/Al-oxides high sorption capacity	x	
	C_{org} scavenging, metal-organic complexation	x	
Diagenesis and release	$Fe(OH)_3$ reductive dissolution, FeS_x formation		x
	Fe^{2+} upward diffusion and re-oxidation	x	
	vivianite formation due to Fe^{2+} surplus	x	
Indication for P mobility	pore water: Fe:P *	~10.000	0.04 - 4
	sediment: Fe:P **	< 5.5-8.3	
	Al:P ***	4.6-27.5	
	Fe:S	2 - 12	< 2
	log(Fe:P)×log(Fe:S)	0.7 - 2	< 0.7

Fig. 3.27 Processes in MLs with implications for low or high P mobility and indicators for P mobility; (*) no quantitative relation for P mobility versus pore water Fe:P or threshold value for MLs established yet; (**) only if Fe is not immobilized as FeS_x; (***) only as Al hydroxide, not as clay constituent

found as metal sulfides and sulfosalt minerals, and precious metals as sulfide minerals (e.g. acanthite—Ag_2S) or as native metals (gold, silver, electrum), in association with iron sulfides. Accessory minerals containing As and Se are common. Due to the ubiquitous presence of iron sulfides, acid rock drainage is a major water quality problem in metal-mine pit lakes. Thus, the environmental problems with metal-mine pit lakes are similar to those at coal and lignite pit lakes, where acid rock drainage from iron sulfide oxidation occurs, but hardrock metal-mines often have a more diverse set of metals at high concentrations available for dissolution and release to surface and groundwater systems, compared to coal and lignite pit lakes.

Water quality in pit lakes is often an important issue that affects permitting of new mines, expansion of existing mines, and planning for closure. There are numerous approaches for using numerical models to predict future water quality in pit lakes (e.g. Balistrieri et al. 2006; Castendyk and Webster-Brown 2007a, b; Eary et al. 2008; Kempton et al. 1997; Schafer et al. 2006). However, one of the best ways to assess whether predictions are credible is to compare them to water quality patterns that occur in existing pit lakes located in ore deposits with similar geo-environmental characteristics. This chapter provides an overview of the geoenvironmental characteristics and associated water quality patterns for metal-mine pit lakes that provides a starting point for comparative purposes. The frequency of occurrence of metal-mine pit lakes is also discussed. These topics are fundamental to understanding the importance of geoenvironmental models for guiding the setup of numerical models of future pit lake water quality and assessing the credibility of the resulting numerical predictions.

3.2.2.2 Occurrence of Hardrock Metal-Mine Pit Lakes

The metal mining industry has faced an increasing challenge of meeting society's demand for metals to maintain economic growth while ore grades in metallic ore deposits have steadily declined. For example, worldwide production of copper has steadily increased at an annual rate of about 4% since 1910 while average ore grades have declined by about 50% (Fig. 3.28). The long term trends in worldwide gold production and ore grade are similar to copper (Fig. 3.29), although the trend data for gold show more ups and downs due to various factors, such as economic disruptions, opening of new mining districts, and improvements in extraction technologies. Since 1910, worldwide gold production has increased from about 700–2,500 t/year in 2006. This increase in production has taken place even though ore grades have decreased by 50–75% since the early 1900s (Fig. 3.29). Obviously, gold recovery from lower and lower grade ores has become increasingly important for maintaining production rates.

An important technology for efficiently extracting gold from low grade oxide ores is heap leaching with cyanide. In this process, crushed ore is saturated with a cyanide solution which dissolves microscopic grains of gold. The solution is recovered and processed to extract the gold. First trialed in New Zealand at the turn of the 20th century, gold heap leaching became a primary extraction method for oxide ores starting in the 1970s. By 1986, about 30% of the world's production of gold was through heap leaching with cyanide (Dorey et al. 1988).

Increasing metal production from decreasing ore grades requires processing more material. Thus, open pit mining has become the dominant method for metal recovery over time because it is a more efficient method of excavating huge amounts of ore. The dominance of open pit mining can be seen in a compilation of data on yearly worldwide investments in mining projects from 2001 to 2007, which was a period of rapid increase in mine production. Figure 3.30 shows these data for all base metals, precious metals, iron, and diamonds. Figure 3.31 shows data specifically for gold and copper. Each of these charts shows that the proportion of mines planned to be operated as open pits has increased coincident with the recent increase in mining activity. This trend is especially evident for gold and copper mines (Fig. 3.31). For all metal mines, the proportion planned to be operated as open pits increased from 61% in 2001 to 79% in 2007 (Fig. 3.31). For copper and gold mines, the proportion planned as open pits increased from 63% in 2001 to 87% in 2007 (Fig. 3.31). While these data represent only a short time span, they show how open pits have become the dominant mining method for metals due to the need to increase production while ore grades have decreased.

The data on mining project investments also provides a good depiction of where metal mines are located and where they will be located in the future. Figure 3.32 shows the trends in investment by region. Australia (included as part of Oceania) has consistently been the leading country for investments in metal mining projects since 2001. Overall, investments are distributed across all geographic regions, and the proportions of investments by region have remained roughly constant, except for small increases for Latin America at the expense of other regions.
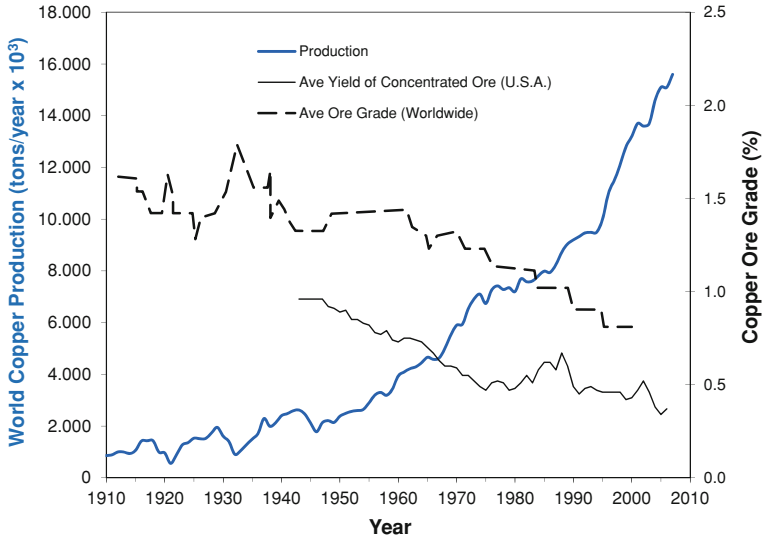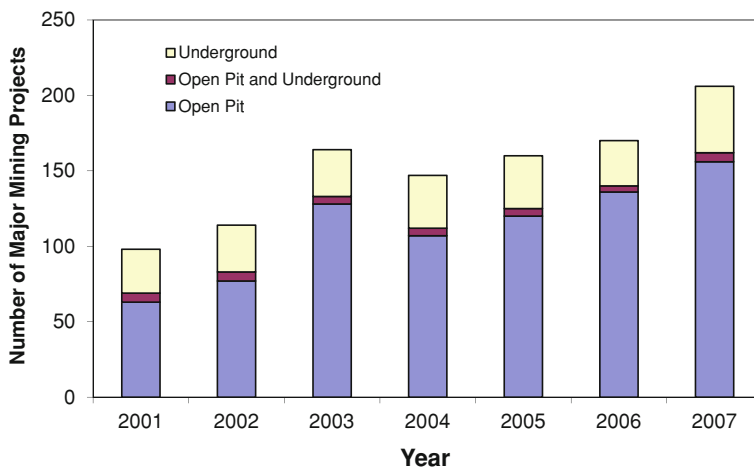
Fig. 3.28 Trends in worldwide copper production (Kelly and Matos 2008a) and ore grades (Kelly and Matos 2008a; Gerst 2008) since 1910
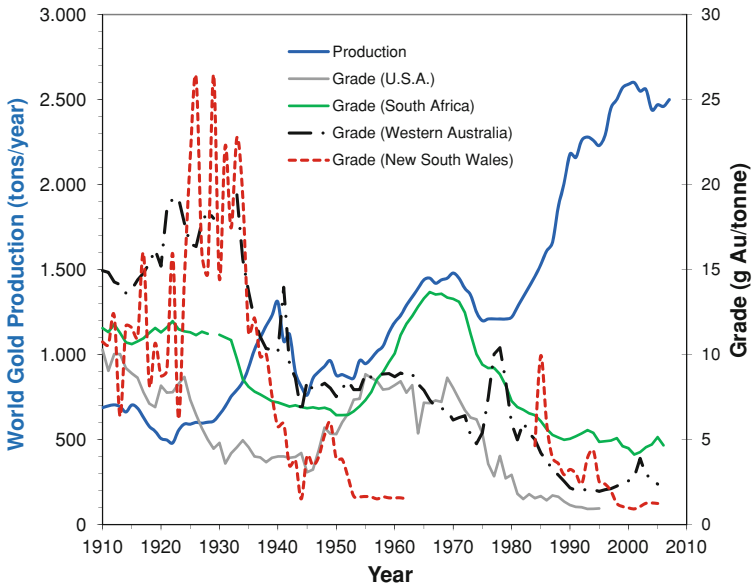
Fig. 3.29 Trends in worldwide gold production (Kelly and Matos 2008b) and gold ore grades (Craig and Rimstidt 1998—U.S.A.; Mudd 2007—South Africa and Australia) since 1910

Fig. 3.30 Trends in major mining projects (copper, gold, iron, lead, nickel, platinum group metals, silver, diamonds, zinc; E&MJ 2002–2008)

The global distribution of pit lakes can be expected to resemble the distribution of investments in mining (Fig. 3.32) because the trends shown in Figs. 3.30 and 3.31 indicate that a high percentage of metal mines will be open pit operations. Given the past exploitation of many prospects in the established mining districts of Canada, the United States, and South Africa, it is anticipated that the number of open pit mines (and therefore pit lakes) in East and Central Africa, Central Asia, and Latin America will increase in the future (Castro and Moore 2000).

Metal-mine pit lakes have the potential to cause long-term changes to hydrologic systems and water quality (National Research Council 1999). The creation of lakes in areas where no lake existed prior to mining can potentially affect the viability of nearby water resources. Given their potential volumes, mine pit lakes comprise a potentially large water resource in arid to semi-arid regions and mountainous areas, where potable water is a valuable commodity. For example, Miller (2002) estimated that 35 pit lakes in Nevada have the potential to store 1.85×10^9 m^3 of water, compared to 0.74×10^9 m^3 of water in all the reservoirs in Nevada constructed for water storage. However, the resource value of water in pit lakes is greatly diminished if the water is of poor quality or lost to evaporation. Evaporative loss from large-surface-area pit lakes in arid regions effectively "pumps" stored groundwater from aquifers to the atmosphere while simultaneously increasing the concentration of dissolved metals in residual lake water. Conversely, pit lakes in humid climates may undergo more extensive sulfide oxidation and generate larger volumes of acidic discharge owing to higher inputs of direct precipitation, runoff, and groundwater.

The sections below describe the typical causes of poor water quality at metal-mine pit lakes based on known geochemical processes and observed trends in chemical compositions of existing pit lakes. While these descriptions are useful for making generalizations about the characteristics of metal-mine pit lakes, there are
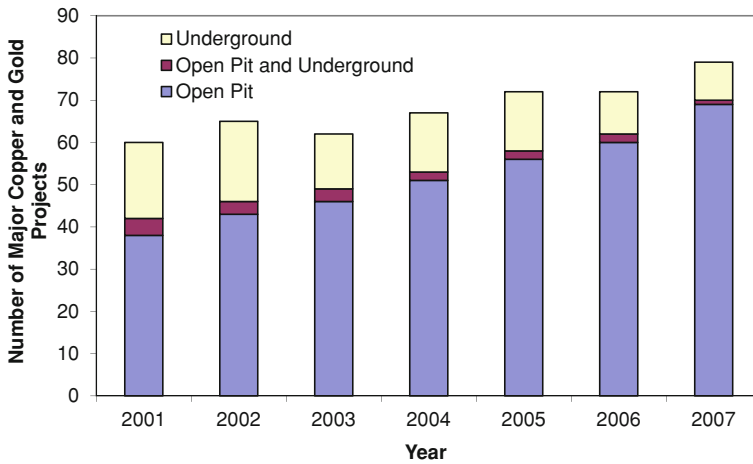
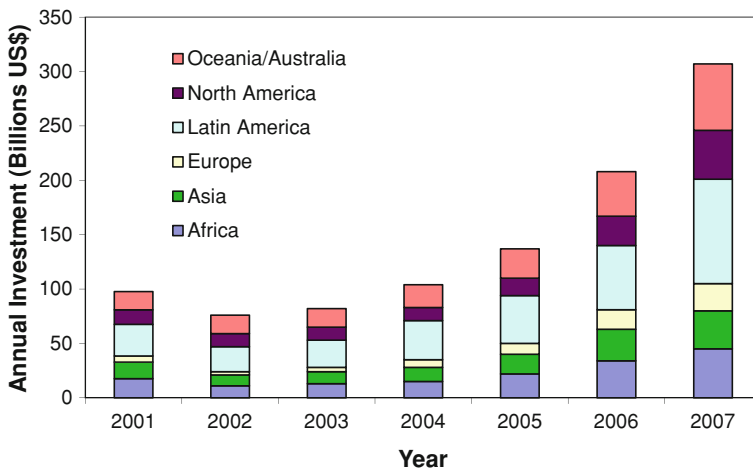**Fig. 3.31** Trends in major mining projects for copper and gold (E&MJ 2002–2008)

Fig. 3.32 Annual investments in metal mining projects by region (E&MJ 2002–2008)

many deviations from such generalizations due to differences in the geoenvironmental characteristics of specific mine sites.

3.2.2.3 Hydrogeochemical Processes in Metal-Mine Pit Lakes

There are a number of hydrochemical processes that can affect water quality in metal-mine pit lakes over the long term, including:

- Geoenvironmental characteristics
- Sulfide mineral oxidation
- Water balance
- Mineral solubility
- Surface adsorption
- Water column dynamics
- Sediment biogeochemical processes
- Mitigation and remediation efforts

This list of processes is not meant to imply rank in importance but is merely a generalized compilation of the numerous factors that influence water quality in pit lakes. The following sections discuss the importance of these processes in more detail.

3.2.2.4 Geoenvironmental Characteristics

The geoenvironmental characteristics of an ore deposit generally exerts the primary influence on water quality in pit lakes in the absence of remedial measures. The characteristics of ore deposits are often discussed in terms of geoenvironmental models, which are a convenient way to categorize geologically similar mineral deposits and their wastes with respect to their geochemical, mineralogical, geological, geophysical, hydrological, and climatic properties. Summaries and examples of geoenvironmental models can be found in duBray (1995), Plumlee (1999), Plumlee and Nash (1995), Plumlee et al. (1999) and Seal et al. (2007).

Two of the more important aspects of geoenvironmental models are host rock reactivity and alteration mineralogy. Host rock reactivity is important because a portion of the wallrock that surrounds a pit lake is usually comprised of partially mineralized and/or sub-ore grade host rocks that typically contain metal sulfides. Alteration mineralogy is important because the secondary minerals left exposed in the pit walls (host rocks, remnant ore, and adjacent rocks) after mining is completed represent potential sources of leachable metals and acidity. Table 3.6 provides a list of ore deposit types arranged by major metal commodity and their typical assemblages of host rocks. The reactivities of the host rocks are also indicated for each deposit type in terms of typical acid neutralization potential and acid generation potential. The predominant theme that can be gained from the data in Table 3.6 is that most metal ore deposits are contained in silicate rock types that typically have more acid generation potential than acid neutralization potential. The few exceptions to this generalization, such as the lead–zinc Mississippi Valley deposits and Carlin-type gold deposits, are hosted in carbonate rocks, and hence tend to have moderate to high acid neutralization potential. However, the host rocks of most metal ore deposits have an excess of acid generation potential relative to acid neutralization potential.
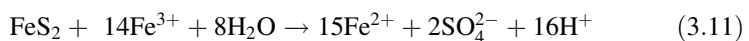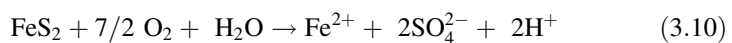
Table 3.7 lists typical alteration types and secondary mineral assemblages that may be overprinted on host and ore rocks at metal ore deposits. The effects of the secondary minerals on acid neutralization and acid generation potential are also qualitatively estimated in Table 3.7. Most types of alteration result in a decreased potential for acid neutralization because the metasomatic processes involved in secondary mineral formation usually remove or replace reactive primary carbonate and silicates with less reactive silicates and, in some cases, iron sulfides and metal sulfates (e.g. alunite, jarosite), depending on redox conditions. The primary exception to this generalization is carbonitization, in which primary minerals are replaced by carbonate minerals.

The geoenvironmental characteristics of an ore deposit, such as those listed in Tables 3.6 and 3.7, cannot be used to predict absolute values of water quality parameters, such as pH or metal concentration, but they can provide a useful qualitative guide about what type of water quality should be expected in a pit lake. For example, a prediction of neutral pH and low metal concentrations for a future pit lake in a porphyry copper deposit with pervasive argillic alteration should be questioned to identify what mitigating characteristics make it an exception when its geoenvironmental characteristics would predict that acidic water quality should occur. For existing pit lakes, an examination of the geoenvironmental characteristics of the deposit can provide context for explaining observed water qualities. This information may be used to identify the range of conditions that may occur based on comparison to pit lakes in similar deposit and host rock types, which may be useful in the design of remedial strategies for final closure of the pit lake.

3.2.2.5 Sulfide Mineral Oxidation

The primary processes responsible for poor water quality in metal-mine pit lakes is acid mine drainage due to the oxidation of iron sulfide minerals, such as pyrite, marcasite, and pyrrhotite. Sulfides are present in the floors and wallrocks of most metal-mine pit lakes and in the groundwater flow paths leading to pit lakes. In the groundwater flow paths, oxidation may take place in dewatered aquifers, providing a potential source of solutes that could be rinsed and transported into a mine (above and below ground) after mining has ended and the groundwater level recovers to its natural elevation. Sulfides may also be present in waste rock and ore stockpiles sometimes left in the pits after closure.

Iron sulfide is oxidized by molecular oxygen and ferric iron through reactions such as:

$$FeS_2 + 7/2 \, O_2 + \, H_2O \rightarrow Fe^{2+} + \, 2SO_4^{2-} + \, 2H^+ \tag{3.10}$$

$$FeS_2 + \, 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \tag{3.11}$$

A similar type of reaction can be written for pyrrhotite oxidation. Depending on pH conditions, dissolved oxygen concentrations, and microbial activity, ferrous

Table 3.6 Summary of major ore types and acid–base characteristics for hardrock metal-mine pit lakes

Primary metal	Deposit type	Typical host rocks	Host rock acid–base character[a]	Expected lake water quality
Au	Adularia-sericite epithermal vein	Silicic—volcanics: rhyolite, dacite, latite, andesite	Low NP; moderate to high AGP	Acidic to circumneutral
	Epithermal quartz-alunite	Silicic—volcanics	Low NP; high AGP	Acidic
	Carlin type (silicic)	Silicic—siltstone, sandstone, shale, ± igneous intrusive	Low NP; low to moderate AGP	Mildly acidic to circumneutral
	Carlin type (calcareous)	Carbonates—calcareous siltstone, silty, cherty or dolomitic limestone, siltstone, limestone	Moderate to high NP; low to moderate AGP	Circumneutral to alkaline
	Low sulfide quartz-gold veins	Silicic—granitic intrusives, greenstone, gneiss	Low NP; moderate AGP	Acidic
	Au–Ag telluride veins	Silicic—alkalic porphyritic igneous (syenite, monzonite diorite, phonolite), volcanic breccia, diatremes, stockworks	Low NP; moderate AGP	Acidic
	Quartz-pebble conglomerate	Silicic—Clastic sediment, igneous (granite, greenstone, ± volcanics)	Low NP; moderate AGP	Acidic
	Skarn	Carbonates—limestone, dolomite, marble, metasediments	Moderate to high NP; moderate AGP	Acidic to alkaline
Ag	Sedimentary exhalative	Silicic—silicified metasediments, sandstone, siltstone, mudstone, shale	Low NP; moderate AGP	Acidic
	Adularia-sericite epithermal vein	Silicic—volcanics (rhyolite, dacite, latite, andesite)	Low NP; moderate to high AGP	Acidic
	Polymetallic veins	Silicic—igneous intrusives (diorite, granodiorite, monzonite), volcanics (andesite to rhyolite), metasediments	Low NP; moderate to high AGP	Acidic
	Au–Ag telluride veins	Silicic—alkalic porphyritic igneous (syenite, monzonite diorite, phonolite), volcanic breccias, diatremes, stockworks	Low to moderate NP; moderate to high AGP	Acidic

Table 3.6 (continued)

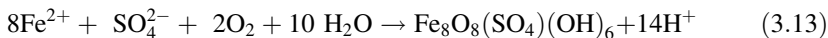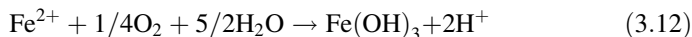| Primary metal	Deposit type	Typical host rocks	Host rock acid–base character[a]	Expected lake water quality
Cu	Seafloor massive sulfide	Silicic—mafic to felsic volcanics, metasediments	Low to moderate NP depending on mineral assemblage; high AGP	Acidic
	Magmatic massive sulfide	Silicic—mafic volcanic: diabase, gabbro, pyroxenite	Low to moderate NP depending on mineral assemblage; high AGP	Acidic to neutral
	Sedimentary exhalative	Silicic—silicified metasediments, sandstone, siltstone, mudstone, shale	Low to moderate NP; moderate AGP	Acidic
	Porphyry	Silicic—igneous intrusives (tonalite to monzogranite, syenite porphyries)	Low NP; moderate to high AGP	Acidic
	Sediment hosted	Silicic—red-beds (green shale, gray shale, siltstone, sandstone, ± carbonates, evaporites)	Low to moderate NP; low to moderate AGP	Acidic to neutral
	Skarn	Carbonate—Limestone, dolomite, marble, calc-silicate metasomatic, igneous intrusives (tonalite to monzogranite, syenite porphyries)	Moderate to high NP; moderate AGP	Neutral
Mo	Porphyry	Silicic—igneous intrusive: granitic-rhyolitic porphyries	Low NP; moderate AGP	Acidic
Pb–Zn	Seafloor massive sulfide	Silicic—mafic to felsic volcanics, metasediments	Low to moderate NP depending on mineral assemblage, High AGP	Acidic
	Sedimentary exhalative	Silicic—silicified metasediments, sandstone, siltstone, mudstone, shale	Moderate NP; low to moderate AGP	Acidic
	Mississippi Valley type	Carbonate—dolostone, ± limestone, sandstone–siltstone, shale	Moderate to high NP; moderate AGP	Neutral to alkaline
	Manto/skarn	Carbonate—limestone, dolomite, sandstone–siltstone	Moderate to high NP; moderate AGP	Acidic to alkaline

[a] *NP* neutralization potential, *AGP* acid generation potential

Table 3.7 Summary of acid–base characteristics of major alteration types found in metallic ore deposits based on the summary in Plumlee (1999)

Alteration	Secondary minerals	Acid–base characteristics[a]
Acid sulfate (alunite)/ advanced argillic	Quartz/chalcedony, pyrite, alunite, jarosite, kaolinite, ± pyrophyllite, dickite	Greatly decreases NP, increases AGP; increases potential for rapid initial release of acid + sulfate
Argillic	Kaolinite, illite, montmorillonite, ±pyrite, ±chlorite	Decreased NP; possible increase in AGP
Phyllic	Quartz, sericite, pyrite	Decreased NP; increased AGP
Potassic	K-feldspar, biotite, ±anhydrite	Decreased NP; possible rapid release of sulfate
Propylitic	Epidote, chlorite, calcite, albite, ±pyrite	Increased NP depending on amount of calcite formed; Possible increase in AGP from pyrite
Silica	Silica (quartz, chalcedony)	Decreased NP; AGP not substantially changed
Jasperoid	Silica (quartz, chalcedony)	Greatly decreased NP due to replacement of sedimentary carbonates with silica; AGP not substantially changed
Greisen	Quartz, muscovite, fluorite, cassiterite, magnetite	Potential for decreased NP; AGP not substantially changed
Skarn	Ca silicates, silica, magnetite, ±pyrite	Decreased NP; increased AGP
Dolomitization	Dolomite	Decreased effective NP due to formation of potentially less reactive dolomite; AGP not substantially changed
Carbonitization	Calcite, dolomite, siderite, rhodochrosite	Potentially large increase in NP (but neutralization from siderite is countered by oxidation of Fe^{2+}; AGP not substantially changed)
Sulfidation	Pyrite	Decreased NP; increased AGP

[a] *NP* neutralization potential, *AGP* acid generation potential

iron is fairly rapidly oxidized to ferric and precipitated as ferric hydroxide and schwertmannite, producing more acid, as in:

$$Fe^{2+} + 1/4O_2 + 5/2H_2O \rightarrow Fe(OH)_3 + 2H^+ \tag{3.12}$$

$$8Fe^{2+} + SO_4^{2-} + 2O_2 + 10\,H_2O \rightarrow Fe_8O_8(SO_4)(OH)_6 + 14H^+ \tag{3.13}$$

It is generally recognized that dissolution reactions involving carbonates (calcite and dolomite) have a high potential to neutralize the acid generated by sulfide oxidation through reactions such as:

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \tag{3.14}$$

Silicates also have the capacity to neutralize acidity through dissolution reactions, such as the following reaction for anorthite:

$$CaAl_2Si_2O_8 + 2H^+ + 6H_2O \rightarrow Ca^{2+} + 2Al(OH)_3 + 2H_4SiO_4 \tag{3.15}$$
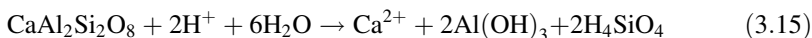
There are numerous detailed descriptions of the above types of reactions involved in sulfide mineral oxidation in the literature (e.g. Nordstrom and Alpers 1999; White et al. 1999) and it is not the purpose of this paper to discuss them in detail. However, a comparison of the kinetics of acid generation reactions (Eqs. 3.10 and 3.11) to the rates of acid neutralization (Eqs. 3.14 and 3.15) is useful for illustrating why some metal-mine pit lakes become acidic and some do not.

Williamson and Rimstidt (1994) describe the abiotic rate of pyrite oxidation by oxygen for a reference system with a surface area to water ratio of 1 m^2 pyrite/ 1 kg of solution:

$$Rate(mol\,pyrite\,m^{-2}s^{-1}) = 10^{-8.19}\left(\frac{m_{O_2}^{0.5}}{m_{H^+}^{0.11}}\right) \tag{3.16}$$

These authors also describe the abiotic rate of pyrite oxidation by ferric iron for conditions where both dissolved oxygen and ferric iron are present in solution for a reference system (Williamson and Rimstidt 1994):

$$Rate(mol\,pyrite\,m^{-2}s^{-1}) = 10^{-6.07}\left(\frac{m_{Fe^{3+}}^{0.93}}{m_{Fe^{2+}}^{0.4}}\right) \tag{3.17}$$

For carbonate minerals, Palandri and Karaka (2004) describe the rates of calcite and dolomite dissolution:

$$Rate(mol\,calcite\,m^{-2}s^{-1}) = 10^{-0.3}[H^+]^{1.0} + 10^{-5.81} + 10^{-3.48}P_{CO_2} \tag{3.18}$$

Finally, the rates of dissolution of silicates can be described by the general form of the following rate expression (Casey and Ludwig 1995; Chou and Wollast 1985; Palandri and Karaka 2004):

$$\text{Rate}(\text{mol silicate } m^{-2}s^{-1}) = k_H[H^+]^a + k_w + k_{OH}[OH^-]^b \qquad (3.19)$$

Palandri and Karaka (2004) provide a detailed summary of the values of rate constants and exponents for Eq. 3.19 for silicate minerals.

Figure 3.33 shows a comparison of the above reaction rates for a range of pH for equivalent quantities and surface areas. The rates of pyrite oxidation by both oxygen and ferric iron are more rapid than neutralization by the types of silicates most commonly found in silicic intrusive rocks hosting metal sulfide ores, such as quartz, feldspars, clays, and micas. The dissolution rates of some mafic silicates (e.g. olivine and anorthite) approximate the rate of pyrite oxidation by oxygen, suggesting that they may be good sources of neutralization. However, few economic grade metallic ore deposits mined in open pits are hosted in mafic silicates; hence, their importance for preventing acid generation for most pit lakes is minimal.

In comparison, the rates of carbonate mineral (calcite and dolomite) reactions are more rapid than pyrite oxidation (Fig. 3.33). That is why carbonate minerals, when present in sufficient quantities, can prevent acid generation in metal-mine pit lakes; they react rapidly enough to keep up with the rate of iron sulfide oxidation, assuming that they are not completely consumed before the sulfides.

The conclusion that can be drawn from Fig. 3.33 is that most silicate minerals generally do not dissolve fast enough to preclude acid generation under most circumstances, in contrast to carbonate minerals. This conclusion is not surprising; otherwise, acid rock drainage would not be the common phenomena that it is given the predominance of silicate rock types over carbonates in most mineralized districts. Similar observations have been made for natural, closed-basin lakes located in volcanic terrains with high sulfur contents where the buffering capacities of silicate minerals have been overwhelmed by pervasive acid alteration from sulfur and sulfide oxidation, resulting in naturally acidic, saline lakes (Risacher et al. 2002).

3.2.2.6 Water Balance

Water balance, which describes the inputs and outputs of water and their associated solute loads to a pit lake, has a fundamental control on water quality in metal-mine pit lakes, especially during the initial period of infilling. Solutes enter the lake primarily through groundwater inflow, leaching of wallrocks, leaching of backfill material (if present), and the dissolution of secondary minerals and metal-salts, some of which may exist as efflorescence on pit walls and in pore spaces prior to lake filling. Salts may also exist in the dewatered parts of aquifers surrounding a mine due to oxidation processes. Because solute influxes are functions of flow rates, they are directly dependent on the rates of water inflow from the different hydrologic sources that make up the water balance of the pit lake watershed. Sources may include groundwater, pit wall runoff, direct rainfall, and
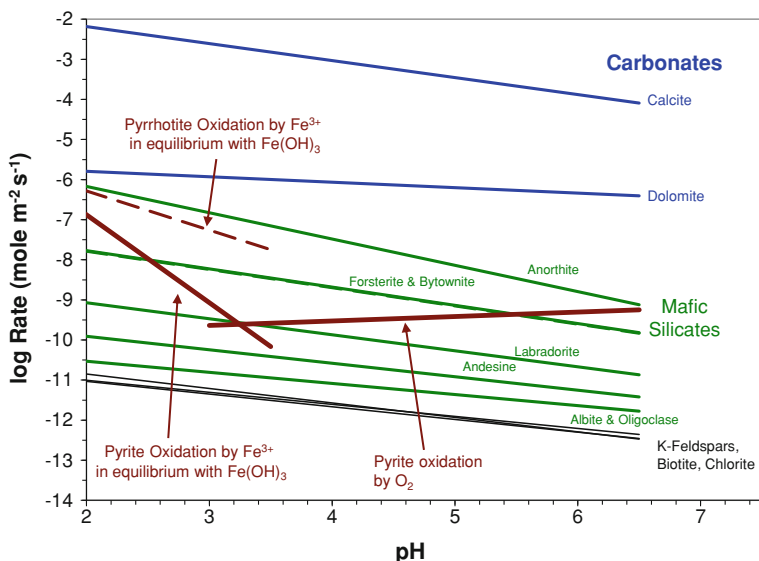
Fig. 3.33 Comparison of reaction rates for acid generation and acid neutralization reactions relevant to metal-mine pit lakes (reference surface area to solution ratio of 1 m^2/kg H$_2$O). Sources of rate data are Williamson and Rimstidt (1994) for pyrite and Palandri and Karaka (2004) for pyrrhotite, carbonates, and silicates

possibly surface water diverted into the open pit to accelerate lake filling. The rates of inflow of different hydrologic sources may change over time as the pit lake fills. For example, the proportion of the water balance from groundwater inflow may decrease over time as the local groundwater table recovers and hydrologic gradients diminish, whereas the relative proportions of water from runoff and direct precipitation may increase, depending on the pit morphology and catchment area. Sulfide mineral oxidation will slow as the wallrocks are increasingly inundated, thereby slowing the rates of acid and metals release. In some cases, the rinsing of sulfide oxidation products from wallrocks and backfill materials may provide a short-term high influx of solutes during the early stages of pit filling (see also case study 5.1). If evaporation is the only route for water loss from the pit lake, many solute concentrations not affected by solubility will increase slowly over time due to evapoconcentration. Biogeochemical processes and surface adsorption reactions taking place in the water column and sediments may moderate the concentrations of some solutes, but for the most part, the water and chemical balance will primarily control water quality.

The water balances for most hardrock mining pit lakes can be categorized in general terms as either: terminal pit lakes, in which outflow occurs only as evaporation or; flow-through pit lakes, in which surface and/or groundwater flow into and out of the pit lake (see also Sect. 4.1.2). The typical trends in water quality

dynamics for each type are likely to be different for different water balance scenarios.

A common situation for many hardrock mining pit lakes is that the wallrock leachates are acidic due to sulfide mineral oxidation, whereas the inflowing groundwater has a circumneutral to alkaline pH and some amount of acid-buffering capacity. As a result, the dynamics in water quality are controlled by the relative influx proportions from these two sources. For example, most terminal pit lakes with low influxes of acid solutes from wallrock leaching and high influxes of alkalinity from groundwater will evolve to water qualities with one of the following sets of characteristics: (1) circumneutral pH values, gypsum saturation, and low cationic and anionic metal concentrations due to solubility and adsorption constraints, or (2) alkaline pH values, calcite saturation, and low cationic metal concentrations but potentially elevated concentrations of arsenic and selenium (Davis and Eary 1997; Eary 1998). In either case, the total dissolved solids concentrations will continue to increase over time in terminal pit lakes due to evapoconcentration (Fig. 3.34). Pit lakes formed in Carlin-type gold deposits are examples of circumneutral to alkaline pit lakes with occasional instances of elevated arsenic and selenium (Davis and Eary 1997; Eary 1998).

For pit lakes with high influxes of acid equivalents from wallrocks compared to groundwater inflow, the initial and long-term water quality can be expected to be acidic, with high total dissolved solids (TDS) due to elevated metal concentrations and sulfate (Fig. 3.34; Eary 1999). The pH will most commonly stabilize over time between 2.5 and 4, but the TDS will continue to increase due to evapoconcentration (Fig. 3.34). Over the long-term, some amount of microbial activity in the sediments of anoxic lower layers of meromictic lakes may produce small increases in pH and decreases in metal concentrations due to sulfate reduction, but the lakes are likely to remain acidic in the absence of remedial measures due to their large volume and the isolation of meromictic waters from shallower lake layers. The acidic pit lakes of the Iberian Pyrite Belt (Sánchez-España et al. 2008) associated with polymetallic massive sulfide deposits and the former Spenceville pit lake (Levy et al. 1997), which formed in a silicic polymetallic vein deposit, are examples of terminal pit lakes with high rates of acid influx and evapoconcentration.

Bowell and Parshley (2005) documented the existence of a variety of secondary iron sulfates and arsenic oxyhydroxides on pit wallrocks that may act as sources of easily leachable metals to pit lakes during the initial stages of pit infilling and potentially on a seasonal basis thereafter. Pit lakes receiving high initial loads of metals and sulfate from the wash off of oxidation products may initially have acidic pH values that eventually rise as the effects of the wash off of acidic solutes diminish and the pit walls become inundated, slowing further sulfide mineral oxidation (Fig. 3.34). The TDS trends for this situation may show an initial period of decrease due to dilution from inflowing groundwater with lower TDS concentrations, but over time, the trend for TDS will be upward (Fig. 3.34). This type of TDS trend may be most applicable to arid climate pit lakes.

Flow-through and terminal pit lakes with high influxes of acidity from wallrocks relative to groundwater inflow are likely to remain acidic in the absence of
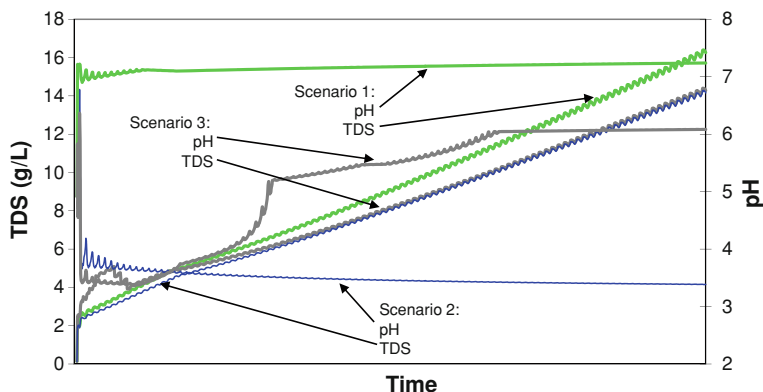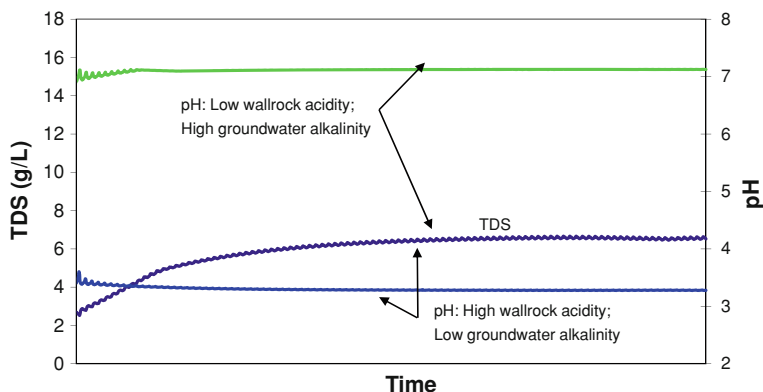
Fig. 3.34 Generalized time trends in pH and TDS for terminal pit lakes for Scenario 1—high groundwater alkalinity and low wallrock acidity; Scenario 2—high wallrock acidity and low groundwater alkalinity; and Scenario 3—moderate groundwater alkalinity with initial acid wash off

remedial measures (Fig. 3.35). Conversely, flow-through pit lakes with low acid loads from wallrocks and high influxes of alkalinity from groundwater are most likely to have circumneutral pH values. An important difference with terminal pit lakes is that TDS concentrations in flow-through pit lakes will only increase until the lake reaches hydrologic steady state with the groundwater system (Fig. 3.35). At that point in time, the TDS should stabilize as a balance is reached between chemical inputs and losses to and from the pit lake. The Berkeley pit lake is an example of an eventual flow-through system in which total solute concentrations have slowly increased over time as the lake approaches its hydrologic spill-over point (Gammons and Duaime 2006), although its water quality dynamics are also affected by water management systems associated with metal extraction and inflows from underground workings. An important consideration for both terminal and flow-through pit lakes is that the time scale for the dynamics in chemical processes may be different from hydrologic processes (Schafer and Eary 2009). A flow-through pit lake may reach hydrologic equilibrium in a relatively short period of time, but various chemical processes and water column dynamics in terminal pit lakes may continue to evolve and result in changes in water quality.

3.2.2.7 Water Column Dynamics

It is generally recognized that metal-mine pit lakes have substantially different shapes than natural lakes. Pit lakes tend to have lower ratios of surface area to depth and are steep-sided compared to natural lakes. This difference is evident in a comparison of relative depths for pit lakes. (Relative depth is defined by Wetzel (2001) as the ratio of the maximum depth to the average diameter, in percent.

Fig. 3.35 Generalized time trends in pH and TDS for flow-through pit lakes

See also Sect. 2.1) Natural lakes usually have relative depths in the range of 2% or less, whereas metal-mine pit lakes have much higher values, from 15 to 45% (Castendyk 2009). Highwalls, which are common on one or more sides of pit lakes, may also decrease the transfer of wind energy to the lake surface, decreasing the potential for mixing of the water column.

Based on these general characteristics, it has been thought that pit lakes should be more likely to be permanently stratified (meromictic) than natural lakes, which commonly experience seasonal overturn (holomictic), and that a calculation of relative depth may be sufficient to predict water column dynamics (Castro and Moore 2000; Doyle and Runnells 1997; Lyons et al. 1994). However, Schultze and Boehrer (2009) and Castendyk (2009) independently showed that relative depth is a poor predictor at best of the tendency for stratification in pit lakes. For example, a plot of maximum depths against surface areas for metal-mine pit lakes shows that, as might be expected, meromictic lakes tend to have slightly higher depths than holomictic lakes, there is a great deal of overlap between the two sets of data (Fig. 3.36). Many steep-sided pit lakes have high depths and small surface areas yet show holomictic water column dynamics. These data indicate that while the shape of a pit lake undoubtedly has an important influence on the water column dynamics, numerous other factors, such as the chemistry and density of lake water inputs, climate, and hydrology, are also important (see also Sect. 3.1).

The data in Fig. 3.36 show that predicting whether a pit lake will become permanently stratified or experience seasonal or occasional overturn cannot be based solely on shape. Knowledge of water column dynamics is important for predicting long term water quality and designing mitigation strategies to improve water quality. For example, a lake that experiences seasonal overturn may be expected to remain oxygenated for most of the year. This factor that can be used to parameterize predictive models for future pit lakes or interpret water quality models of existing pit lakes where redox processes are important for controlling metal concentrations. In comparison, a pit lake that experiences permanent
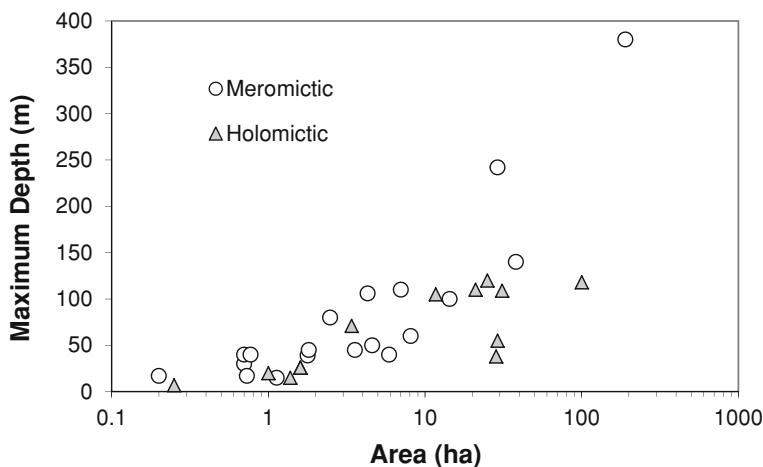
Fig. 3.36 Maximum lake depth versus area for meromictic and holomictic metal-mine pit lakes from the compilations of Castendyk (2009) and Sánchez-España et al. (2008)

stratification may have substantially different redox conditions and water qualities in different lake layers. Oxygenated conditions may exist near the surface whereas anoxic conditions may exist at depth, leading to sulfate reduction and alkalinity production in bottom sediments.

Permanent stratification and associated effects on biogeochemical processes may be incorporated into approaches for improving water quality. For example, the strategies employed at the Island Copper pit lake in British Columbia have resulted in greatly improved water quality in surface layers, even though the lake experienced inputs of acid mine drainage water (Pelletier et al. 2009). In a different study, Colarusso et al. (2003) determined that density stratification of the water column in the South Mine Pit lake at the Copper Basin Mine, Tennessee would be stable for a range of potential conditions. This result was used by Wyatt et al. (2006) to justify development of an in-pit lime treatment system to improve the water quality of discharges from the top, low-TDS water layers.

3.2.2.8 Mineral Solubilities

Mineral and gas solubilities play an important role in affecting rates of solute release in pit lakes similar to contaminant attenuation processes observed in some surface groundwater systems. Numerical models of pit lakes typically rely at least in part on thermodynamic-based geochemical models of aqueous speciation, solubility, and surface adsorption, as well as kinetic formulations for predicting water quality trends in future pit lakes and interpreting water quality conditions in existing pit lakes. Pit lakes, however, are dynamic systems in which both kinetically controlled abiotic and biotic chemical processes occur, producing conditions

of disequilibrium that may metastably persist. Eary (1999) reviewed equilibrium trends in pit lakes to provide guidance to numerical modelers about which solubility reactions are reasonably well represented by chemical equilibrium and which are more likely to be affected by kinetic processes.

A summary of potential solubility controls for different solutes from Eary (1999) and supplemented by a few more recent studies is given in Table 3.8. The review by Eary (1999) showed that sulfate is the dominant solute in most metal-mine pit lakes, especially acidic pit lakes, and sulfate concentrations are typically limited by gypsum solubility. Gypsum is indicated to be a solubility control based on its trend in saturation indices calculated for a number of metal-mine pit lakes as a function of sulfate concentration (Fig. 3.37). Other important solubility controls for major ions indicated from saturation indices were calcite, fluorite, and barite. In addition, the data trends from numerous acidic pit lakes indicated that reasonably well defined solubility controls include alunite for aluminum, ferrihydrite for iron, and manganite and birnessite for manganese. Schwertmannite may also be an important solubility control for iron in acidic pit lakes, based on evaluations provided by Nordstrom and Alpers (1999) and Sánchez-España et al. (2009).

Solubility controls for divalent minor metals are much less well established, but data trends suggest otavite for cadmium, brochantite and malachite for copper, cerrusite and pyromorphite for lead, and hydrozincite and zinc silicate for zinc (Table 3.8). Concentrations of As and Se are not represented by any established mineral solubilities and may be primarily affected by adsorption to aluminum and iron oxyhydroxide minerals under acidic conditions. For example, Sánchez-España et al. (2008) report that arsenic concentrations are significantly lower in acidic pit lakes that have pH values within the pH stability field of schwertmannite (i.e. $pH < \approx 4$) compared to pit lakes in which schwertmannite is not stable. Arsenic may also be incorporated into uncommon mixed hydroxyl sulfate minerals, such as beudantite $[PbFe_3(AsO_4)(SO_4)(OH)_6]$ (Romero et al. 2007). Adsorption processes are less effective for removing arsenic and selenium from solution in high sulfate concentrations or in higher pH (i.e. >pH 6) solutions and their concentrations can be expected to increase linearly with evapoconcentration.

In summary, mineral solubilities provide reasonable representations of maximum concentrations for many major solutes (e.g. Ca, Mg, HCO_3^-, SO_4^{2+}, F, Al, Fe^{3+}, and Mn) in metal-mine pit lakes (Eary 1999; Eary and Schafer 2009), but they are much less reliable for predicting the concentrations of divalent minor metals (e.g. Cd, Cu, Pb, and Zn) and metalloids (e.g. As and Se). In most cases, predictive models will need to rely on empirical formulations to represent metal and metalloid concentrations derived from either experimental, field data, and/or comparisons to existing pit lakes in similar geoenvironmental settings.

Trend data for $CO_{2(g)}$ partial pressures as a function of pH for metal-mine pit lakes are shown in Fig. 3.38. These $CO_{2(g)}$ levels are calculated from measurements of pH and bicarbonate alkalinity and carbonate equilibrium speciation. They show that most acidic metal-mine pit lakes can be expected to be oversaturated with $CO_{2(g)}$ compared to the atmospheric level of $10^{-3.5}$ atm (Fig. 3.38). The degree of oversaturation increases in acidic pH conditions and reaches about

Table 3.8 Summary of potential solubility controlling minerals for metal-mine pit lakes (Bowell and Parshley 2005; Eary 1999)

	Acidic (pH < ≈4.5)	Circumneutral (pH ≈ 4.5 to ≈ 7.5)	Alkaline (pH > ≈ 7.5)
Al	Alunite, basaluminite	Gibbsite, kaolinite, allophane, sericite	Gibbsite, kaolinite, allophone, sericite
Alkalinity	Not applicable	Calcite[b]	Calcite[b]
As	Adsorption to ferrihydrite and schwertmannite[h], scorodite[j], bukovskyite[k], scorodite-mansfieldite[k], weilite[k], pharmacolite[k]	Adsorption to ferrihydrite[h]	None identified
Ba	Barite	Barite, witherite	Barite, witherite
Cd	None identified	Adsorption to ferrihydrite	Otavite
Ca	Gypsum	Gypsum	Gypsum, calcite
Cu	Copper sulfates[j]	Brochantite[g]	Malachite, brochantite[g]
Fl	Fluorite	Fluorite	Fluorite
Fe[c]	Ferrihydrite, schwertmannite, melanterite[j]	Siderite (Fe^{2+})j	Siderite (Fe^{2+})j
Pb	Anglesite[f], chloropyromorphite[d], plumbojarosite[j]	Anglesite[f], chloropyromorphite[d], adsorption to ferrihydrite	Cerrusite[f], chloropyromorphite[d]
Mn	Manganite, birnessite	$MnHPO_4^d$	Rhodochrosite
Se	Adsorption to ferrihydrite[i]	Adsorption to ferrihydrite	None identified
Strontium	Celestite	Celestite, strontianite	Celestite, strontianite
Sulfate	Gypsum, copiapite[k], melanterite[k], mirabolite[k], halotrichite-pickeringite[k]	Gypsum	Gypsum
Zinc	None identified	Hydrozincite[e], $ZnSiO_4^g$	$ZnSiO_4^g$, zincite, smithsonite[j]

[a] Oversaturation with calcite is typical in most pit lakes; [b] Oversaturation with CO_2 at $10^{-3.5}$ atm typically occurs for pH < 8.5 and undersaturation for pH > 8.5; [c] Assumed to be ferric iron; [d] Dependent on the presence of phosphate; [e] Requires the presence of carbonate alkalinity; [f] Requires relatively high sulfate concentration such as those reached at gypsum saturation; [g] Requires the presence of dissolved silica near or approaching saturation with chalcedony; [h] Decreases in efficiency with increases in sulfate concentration; [i] Negligible for sulfate concentration >100 mg/L; [j] From compilation for acid mine waters in Nordstrom and Alpers (1999) [k] From compilation of Bowell and Parshley (2005)

**Fig. 3.37** Gypsum saturation indices for metal-mine pit lakes (Eary 1999)
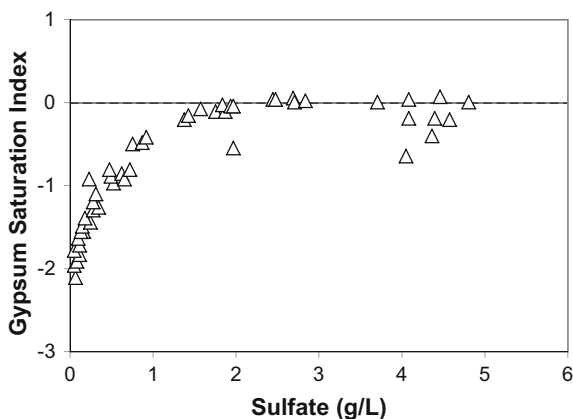
10^{-2} atm or about 30 times atmospheric $CO_{2(g)}$ for pH less than 7. These data are important for providing information on the levels of oversaturation that should be expected to occur when parameterizing geochemical models of pit lakes. Models of metal-mine pit lakes should expect conditions of disequilibria with respect to $CO_{2(g)}$, particularly for lakes with pH less than the circumneutral range. This is an important point for modelers to remember when predicting pit lake geochemistry. By specifying $CO_{2(g)}$ in equilibrium with the atmosphere, the model will force $CO_{2(g)}$ out of solution, resulting in a higher pH than would otherwise be calculated. This can lead to predicted higher pH values than observed pH values.

3.2.2.9 Surface Adsorption

At a microscopic scale, charged ions and molecules are attracted to electrically-charged surfaces of suspended particulate matter (SPM) within pit lake water. Positively-charged cations (e.g. Cu^{2+}, Pb^{2+}, Zn^{2+}) are attracted to negatively-charged surfaces, whereas negatively-charged anionic metalloids (e.g. SeO_4^{2-}, SeO_3^{2-}, AsO_3^{3-}, AsO_4^{3-}) are attracted to positively-charged surfaces. Once the ion or molecule adsorbs onto a surface, it will remain there until the pH of the surrounding solution changes or the SPM decomposes. Under optimal conditions, the water quality of a pit lake may improve due to metal adsorption to SPM and the SPM settles to the bottom of the pit lake where it is buried. With this goal in mind, improving water quality via surface adsorption forms the basis of many contemporary remediation strategies for pit lakes (Kalin and Wheeler 2009; Pelletier et al. 2009).

Hydrous ferric oxides (HFO), such as ferrihydrite and schwertmanite, which are produced by the oxidation of iron sulfides in acidic pit lakes, typically provide abundant surface area for adsorption. Webster et al. (1998) discuss the effects of surface adsorption on the water quality of acid mine drainage. Castendyk and Webster-Brown (2007b) demonstrate the effects of surface adsorption on predicted pit lake water quality by comparing As, Cd, and Cu concentrations modeled

Fig. 3.38 Trends in equilibrium partial pressures of $CO_{2(g)}$ in metal-mine pit lakes (Eary 1999)
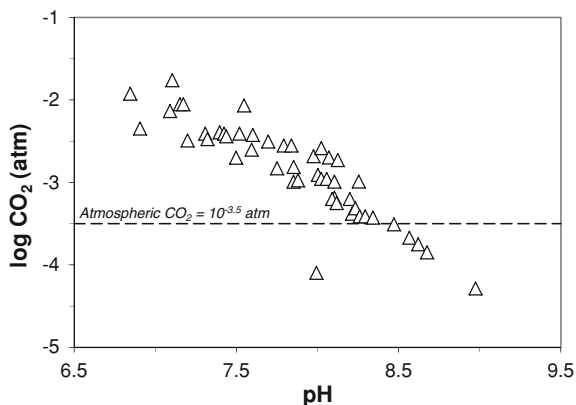
without surface adsorption to concentrations modeled with surface adsorption onto freshly precipitated ferrihydrite.

The surfaces of other particles, such as Al and Mn hydroxides and clays minerals (e.g. smectite, illite, kaolinite) that develop surface charges in response to cation substitutions may also be adsorption substrates. Furthermore, the surfaces of suspended organic matter, such as phytoplankton and diatoms spines, provide adsorption sites; hence, some remediation strategies endeavor to stimulate biological productivity of pit lakes by the addition of nutrients (Kalin and Wheeler 2009; Pelletier et al. 2009).

General depictions of percent adsorption of various dissolved cations and anionic metalloids onto a sample of HFO as a function of pH (Figs. 3.39 and 3.40 partially explain why low pH pit lakes tend to have elevated concentrations of cationic metals whereas high pH pit lakes may exhibit elevated concentrations of anionic metalloids (see below). However, these diagrams should only be used as general indicators of adsorption trends as each pit lake will contain different surface adsorption surfaces and different water chemistry.

3.2.2.10 Sediment Biogeochemical Processes

Geochemical processes occurring in bottom sediments have the potential to affect metal cycling in metal-mine pit lakes in ways similar to natural water bodies. These reactions are driven in large part by the oxidation of carbon catalyzed by microbial processes. In simple terms, the oxidation of organic carbon can be described by:
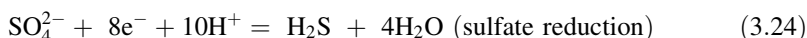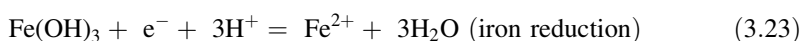
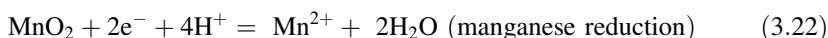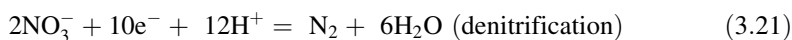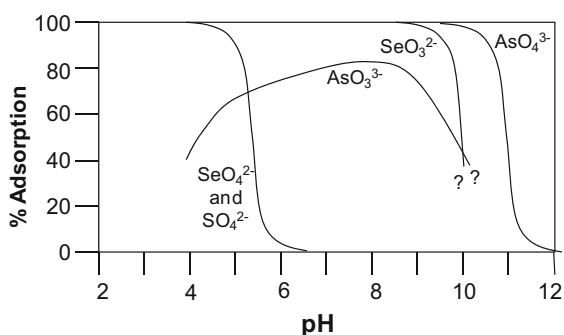$$C_{organic} + 2H_2O = CO_2 + 4H^+ + 4e^- \tag{3.20}$$
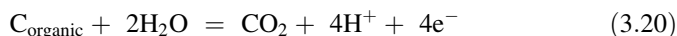
In the anaerobic environment at the bottom of a pit lake, anaerobic microorganisms derive energy from the oxidation of organic carbon coupled with the following reduction reactions, which are listed in order of decreasing redox potential:
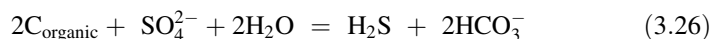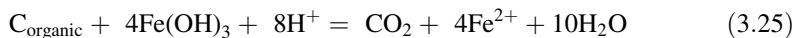
Fig. 3.39 Approximate adsorption of cations onto generic HFO as a function of lake pH (after Drever 2002, with data from Dzombak and Morel 1990)
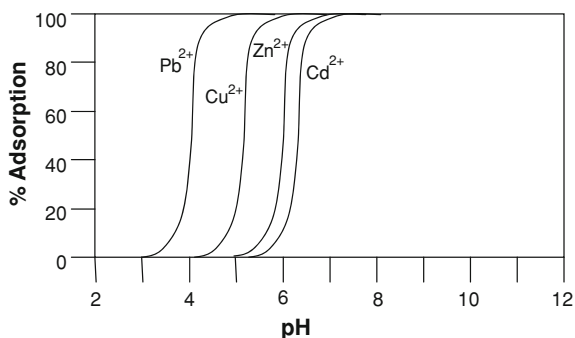
Fig. 3.40 Approximate adsorption of anionic metals onto generic HFO as a function of lake pH (after Drever 2002, with data from Dzombak and Morel 1990)

$$2NO_3^- + 10e^- + 12H^+ = N_2 + 6H_2O \text{ (denitrification)} \qquad (3.21)$$

$$MnO_2 + 2e^- + 4H^+ = Mn^{2+} + 2H_2O \text{ (manganese reduction)} \qquad (3.22)$$

$$Fe(OH)_3 + e^- + 3H^+ = Fe^{2+} + 3H_2O \text{ (iron reduction)} \qquad (3.23)$$

$$SO_4^{2-} + 8e^- + 10H^+ = H_2S + 4H_2O \text{ (sulfate reduction)} \qquad (3.24)$$

When combined with reaction 3.20, the net oxidation–reduction reactions for iron and sulfate by organic carbon may be written as follows:

$$C_{organic} + 4Fe(OH)_3 + 8H^+ = CO_2 + 4Fe^{2+} + 10H_2O \qquad (3.25)$$

$$2C_{organic} + SO_4^{2-} + 2H_2O = H_2S + 2HCO_3^- \qquad (3.26)$$

While these types of reactions are well established as important controls on sediment chemistry, there are few investigations specific to metal-mine pit lakes available in the literature that can be used to develop detailed understanding of sediment mineralogy, chemical composition, pore water chemistry, biogeochemistry, and their effects on water quality. Information gleaned from a few available studies is summarized in Table 3.9, although most of these studies were focused

on acidic, stratified (i.e. meromictic) pit lakes. The common characteristics of the lakes summarized in Table 3.9 are acidic compositions, seasonal or permanent stratification, oxygenated upper portion of the water column, and anoxic conditions at depth and in sediments. Iron and aluminum oxyhydroxide and sulfate minerals are commonly found in sediments along with gypsum. These minerals are most likely to have formed as secondary phases in wallrocks and carried into the pit lakes by erosion or formed in the water column and subsequently settled to the bottom. Triantafyllidis and Skarpelis (2006) also report the presence of a number of metal sulfate minerals present as a thin layer of precipitants in the bottom of a shallow, highly acidic pit lake that is oxygenated throughout the water column.

Accompanying the anoxic conditions at depth are increases in pH in the sediment pore water relative to the overlying water column and occasional presence of hydrogen sulfide (Table 3.9). These characteristics are indicative of biologically-mediated reduction of sulfate and Fe^{3+}, potential for release of metals due to reductive dissolution of metal oxyhydroxides, and potential for re-precipitation of some metals as metal sulfides. Biological reduction of sulfate requires an energy source for microbial activity in the form of organic carbon. However, there are few data on organic carbon levels in metal-mine pit lakes. Levy et al. (1997) found low concentrations of dissolved organic carbon (DOC) in the water column of the acidic Spenceville pit lake, although concentrations were greater in the sediment pore water (Table 3.9). Levy et al. (1997) speculated that the low DOC levels in combination with high Fe^{3+} levels limited the extent to which microbial processes resulted in sulfate reduction in the sediments of the Spenceville pit lake. Cameron et al. (2006) reported low DOC concentrations in the water column but relatively high concentrations in the sediment pore water from the acidic Berkeley pit lake (Table 3.9). However, there is little evidence of sulfate reduction in the Berkeley pit lake sediments, which Cameron et al. (2006) interpreted as an indication that highly acidic, metal laden conditions are hostile to supporting high populations of sulfate-reduction bacteria. In contrast, the less acidic Udden pit lake shows low TOC and evidence of some amount of sulfate reduction. Some of the highly acidic pit lakes of the Iberian Pyrite Belt also show increased pH values in sediments compared to the overlying water column and hydrogen sulfide has been detected in some deep water samples, indicative of sulfate reduction (Sánchez-España et al. 2009).

It is important to note that biogeochemical reactions do not always improve pit lake water quality. Wendt-Pottoff et al. (2004) observed that stimulation of sediment biogeochemical processes in an acidic pit lake in Germany released Fe^{2+} to the overlying water column, which in turn oxidized and counteracted neutralization.

Also, the concepts and data discussed in this chapter are directed at natural factors that affect water quality in metal-mine pit lakes in the absence of mitigation and remediation efforts. Many different remedial approaches exist for improving water quality in pit lakes. The reader is referred to the appropriate chapters or sections in this volume and also discussions in Kalin and Wheeler (2009), Pelletier et al. (2009), and Wielinga (2009).

Table 3.9 Summary of sediment geochemistry characteristics for acidic, metal-mine pit lakes

Pit lake	Limnology	pH/Redox conditions	Organic carbon	Secondary minerals in sediments	Reference
Spenceville Pit, California[b]	Meromictic	pH 2.4–2.9 in water column; pH 3.42 in sediment pore water; DOC and H$_2$S in sediments	DOC: 7 mg/L water column; DOC: 110 mg/L in sediment pore water	Jarosite, gypsum[a], unidentified amorphous Al phase	Levy et al. (1997)
Kirki (Agios Filippos) Pit, Greece	Not reported	pH 2.9–3.1 in water column; oxidizing	Not reported	Jarosite, wroewolfeite, beaverite, gypsum, anglesite, scorodite, bukovskyite, goethite, melanterite, rozenite, butlerite	Triantafyllidis and Skarpelis (2006)
McLaughlin South Pit, California	Holomictic	pH 4 in water column; anoxic in lower lake layers	Not reported	Ferrihydrite floc in water column adsorbs As and Sb	Rytuba et al. (2000)
Udden Pit, Sweden	Dimictic	pH 4.8 in surface increasing to 6.4 at the bottom of water column; anoxic in lower lake layers; increased Fe, As, and Mn with depth	TOC: 0.4–0.6 mg/L in surface layers increasing to 2.7 mg/L at depth	Ferrihydrite[a], gibbsite[a]	Ramstedt et al. (2003)
Berkeley Pit, Montana	Meromictic (may have been holomictic in the past)	pH 3.1–3.4 in sediment pore water; anoxic at depth	TOC: 0.3–0.4% in sediments; DOC: 2.5–4.5 mg/L in water column and 50–380 mg/L in sediment pore water	Jarosite, gypsum, AlOHSO$_4$[a], schwertmannite (water column)[a]	Twidwell et al. (2006; Cameron et al. 2006)
Numerous pit lakes of the Iberian Pyrite Belt	Meromictic and holomictic	pH 1.2–4.7 in water column; typically oxidizing in surface water layers and anoxic at depth; evidence of Fe^{3+} and SO$_4$ reduction in sediments in the form of H$_2$S odor	Not reported	(Ferrihydrite, alunite, schwertmannite, jarosite, gibbsite, jarbanite)[c]; Efflorescent minerals on shorelines include gypsum, pickeringite, and hexahydrite	Sánchez-España et al. (2008; 2009)

[a] Inferred from solubility calculations
[b] Spenceville pit was backfilled in 2001
[c] Inferred from elemental analyses of colloids collected from the water column and solubility calculations

3.2.2.11 Water Quality Trends

Inspection and analysis of data trends from existing metal-mine pit lakes can provide useful knowledge about important factors affecting water quality, such as ore deposit type, geochemical processes, and hydrologic cycles. However, there are no publicly accessible, comprehensive international databases on pit lake water quality currently in existence that can be used for thorough assessment of chemical trends. Various amounts and detail on water quality data are available in open literature reports and scientific papers for individual and collections of pit lakes. The water quality data collected for this paper and discussed below are summarized in Table 3.10. Data from these sources were compiled for the purpose of summarizing trends in water quality and comprise 144 water quality analyses for 49 pit lakes. This dataset is predominantly reflective of pit lakes formed in gold mines in the western U.S. and is relatively old. Hence, it is recognized that these data represent, at best, only snapshots of water quality at the time of study and thus not a completely accurate representation of all types and variabilities of all types of metal-mine pit lakes. However, taken together, these water quality data do provide useful context for identifying trends generally common to metal-mine pit lakes.

TDS is an important parameter in the evaluation of water quality trends to provide context for more detailed inspection of other solutes, such as metals (discussed below). Figure 3.41 shows a plot of TDS as a function of pH for metal-mine pit lakes where the data are categorized according to the ore deposit type. The TDS concentration can be strongly affected by evapoconcentration; hence, the age of the pit lake may be an important factor. The data shown in Fig. 3.41 represent lakes at all ages of maturity. While the factor of age may obscure some details in TDS trends, the data in Fig. 3.41 indicate that elevated TDS concentrations occur most frequently under acidic conditions (pH $< \approx$ 4.5), although a few alkaline (pH $> \approx$ 7.5) pit lakes also show elevated TDS (Fig. 3.41). Lakes with a pH between pH 4.5 and 7.5 generally have low TDS concentrations. Overall, the highest TDS concentrations occur for acidic pit lakes formed at mines of massive sulfide, high sulfidation polymetallic vein, and porphyry types of deposits.

A closer inspection of the major components of TDS indicates that the percentage comprised of sulfate increases as TDS increases (Fig. 3.42). The percentage of TDS as alkalinity decreases as TDS is increased as it is increasingly supplanted by sulfate. Sulfate is, by far, the dominant solute in nearly all pit lakes with highly elevated TDS concentrations. The majority of the high TDS, high sulfate pit lakes included in the datasets shown in Figs. 3.41 and 3.42 are acidic. A direct reflection of high acidity can be seen by the increase in the percentage of TDS comprised of metals (Al + Fe + Mn) with an increase in TDS. These metals comprise 5–20% of the TDS concentrations in most acidic pit lakes, such as those of the Iberian Pyrite Belt in Spain (Sánchez-España et al. 2008) and the Berkeley pit lake in Montana (Pellicori et al. 2005). These highly acidic pit lakes contain predominantly acidic sulfate solutions in which metals, sulfate, hydrogen ion, and to a lesser extent, base cations, make up most of the TDS concentrations.

Table 3.10 Summary of water quality data sources for metal-mine pit lakes

| Deposit	Pit lakes	Location	Number of water quality values	Reference
Low sulfide gold-quartz deposit	Harvard	California	1	Ashley and Savage (2001)
Volcanogenic low sulfidation	Sleeper	Nevada	8	Dowling et al. (2004)
Quartz adularia	Boss, Aurora, Tuscora	Nevada	25	Price et al. (1995)
Carlin-type	Cortez, Big Springs, Adelaide, Getchell (south, center, north)	Nevada	16	Price et al. (1995)
Porphyry	Yerington, Liberty, Ruth, Kimbley, Cypress-Tonapah, Anaconda, Berkeley	Nevada Montana	35	Bird et al. (1994; Davis and Ashenburg 1989; MacDonald 1993; Price et al. 1995; Pellicori et al. 2005)
Quartz alunite	Ketchup Flat	Nevada	6	Price et al. (1995)
Skarn	Fortitude	Nevada	3	Price et al. (1995)
High sulfidation polymetallic vein	Spenceville McLaughlin (south, north), Kirki	California California Greece	16	Levy et al. (1997; Rytuba et al. 2000; Triantafyllidis and Skarpelis 2006)
Massive sulfide	22 Iberian District pit lakes, Udden, Elizabeth (south, north)	Spain Sweden Vermont, New Hampshire	34	Sánchez-España et al. (2008; Ramstedt et al. 2003; Seal et al. 2006)
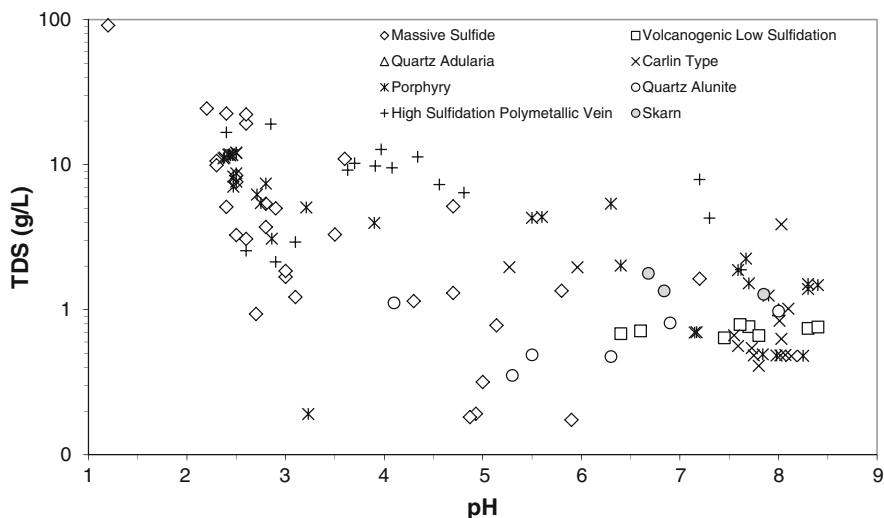
Fig. 3.41 Trends in total dissolved solids in metal-mine pit lakes

Iron, Al, and Mn are most commonly the dominant dissolved metals in acidic pit lakes due to the increased solubilities of the minerals that contain these elements. This effect can be seen in plots of Fe, Al, and Mn as functions of pH (Figs. 3.43, 3.44 and 3.45 respectively). Iron concentrations may exceed 1,000 mg/L in the most acidic pit lakes formed in massive sulfide, polymetallic high sulfidation, and porphyry deposits (Fig. 3.43). Only total Fe concentrations are shown in Fig. 3.43, but both ferrous and ferric iron are usually present when pH values are less than about 4.5 due to slow oxidation kinetics and absence of dissolved oxygen in the lower layers of acidic pit lakes. Iron concentrations tend to be low in pit lakes formed in Carlin type, quartz adularia, and low sulfidation deposits due to circumneutral to slightly alkaline pH conditions resulting from low sulfide content in the host rocks of many of the pit lakes included in this dataset. The secondary minerals reported to best explain iron concentrations in acidic pit lakes are schwertmannite and ferrihydrite, whereas siderite may be a reasonable solubility control for neutral to alkaline pit lakes (Table 3.8), depending on redox conditions. Trends in Al and Mn concentrations with pH (Figs. 3.44 and 3.45) are similar to Fe, although there are fewer data for Al, and Mn shows much more variability through the mid-pH range. Most secondary oxyhydroxide and sulfate minerals containing Fe, Al, and Mn have amphoteric solubilities, and hence show similar trends in concentrations with pH. Secondary solids such as gibbsite and various Al-sulfates, such as jurbanite, alunite, and basaluminite, are important solubility controls for dissolved Al in acidic pit lakes. For slightly acidic to alkaline pit lakes, poorly crystalline clay-type minerals, such as kaolinite and allophane, may be the most common secondary minerals incorporating dissolved Al.

Concentration data for divalent cationic metals are shown in a Ficklin-type plot in Fig. 3.46. These metals show the expected trend of greatly increased
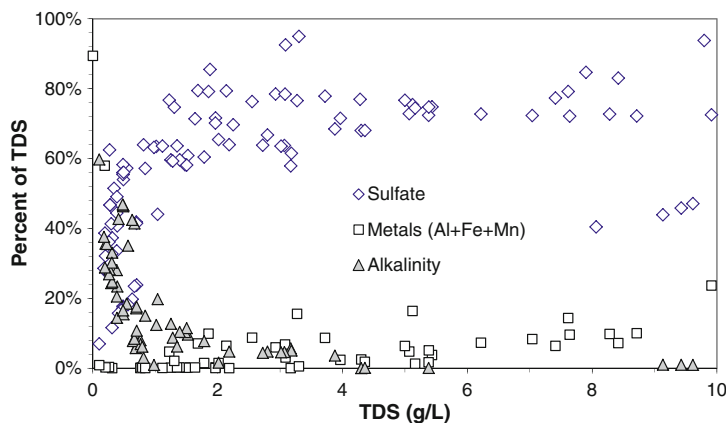
Fig. 3.42 Major components of TDS in metal-mine pit lakes expressed as percentages of TDS

concentrations in acidic pit lakes formed in massive sulfide, polymetallic high sulfidation, and porphyry deposits. A number of circumneutral lakes (pH $> \approx 4.5$ and $< \approx 8$) formed in massive sulfide and porphyry deposits also show relatively high metal concentrations due primarily to Cu and Zn (Fig. 3.46). Secondary minerals incorporating Cu and Zn are relatively soluble in the slightly acidic to neutral pH range. High solubilities allow high concentrations of these metals to occur in pit lakes due to the combined effects of sulfide oxidation and evapo-concentration, although adsorption to iron oxides may partially moderate cationic metal concentrations under these conditions (Fig. 3.39).

A final group of solutes is the anionic metalloids of As and Se. The trends for As concentrations in metal-mine pit lakes show a more complex relationship to pH than the cationic metals. Arsenic concentrations are highest at low pH, decrease to their lowest values in the pH range from about 4.5–7, and then tend to be higher at pH > 7 (Fig. 3.47). On the acidic end, pit lakes formed in massive sulfide deposits have the highest As concentrations due in part to the mineral arsenopyrite, whereas pit lakes formed in quartz adularia deposits tend to have the highest As concentrations for alkaline pH conditions. Selenium concentrations show a different pattern: the lowest concentrations (generally below detection limits) occur in acidic pit lakes and the highest concentrations occur in neutral to alkaline pit lakes (Fig. 3.48). Pit lakes formed in quartz adularia and porphyry deposits tend to have the highest Se concentrations (Fig. 3.48).

The tendency for elevated As and Se concentrations to occur in quartz adularia and porphyry pit lakes has been previously recognized by Shevenell et al. (1999), who examined water quality trends for 16 pit lakes in Nevada. Neither As or Se form low solubility secondary minerals under most pH conditions and the adsorption of As and Se anions is minimized under alkaline pH conditions. Because of these adsorption characteristics, the highest concentrations of As and Se tend to occur in alkaline pit lakes that have or are expected to evapoconcentrate (Eary 1998). A similar phenomenon is seen in natural evaporative lakes of the
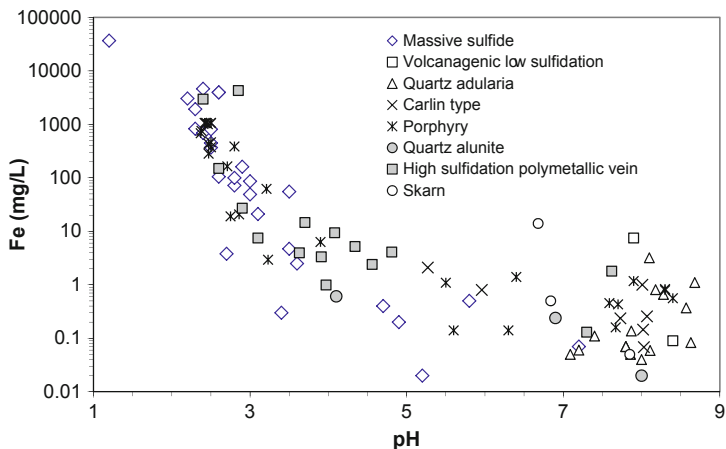
Fig. 3.43 Trends in total Fe concentrations with pH in metal-mine pit lakes
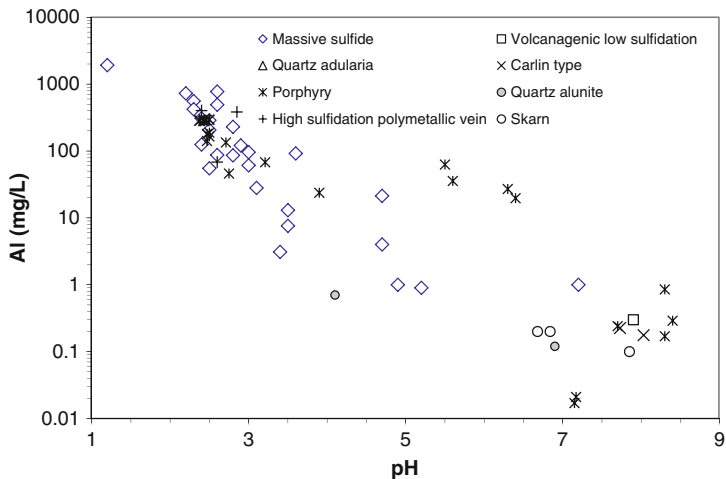

Fig. 3.44 Trends in Al concentrations with pH in metal-mine pit lakes

western USA that also contain elevated alkalinities and As concentrations, such as Mono Lake, California (Maest et al. 1992), Toulon and Upper Humboldt Lake, Nevada (Seiler et al. 1993), and Abert Lake, Oregon (Whitehead and Feth 1961).

3.2.2.12 Conclusions

The concentrations of solutes in metal-mine pit lakes show distinct trends that are primarily related to pH. The pH, in turn, is a complex function of the geoenvironmental characteristics, sulfide mineral content and oxidation rates, water
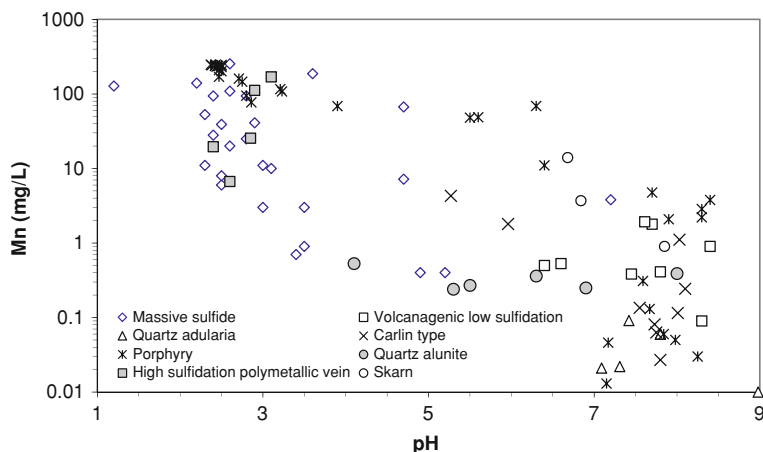
Fig. 3.45 Trends in Mn concentrations with pH in metal-mine pit lakes
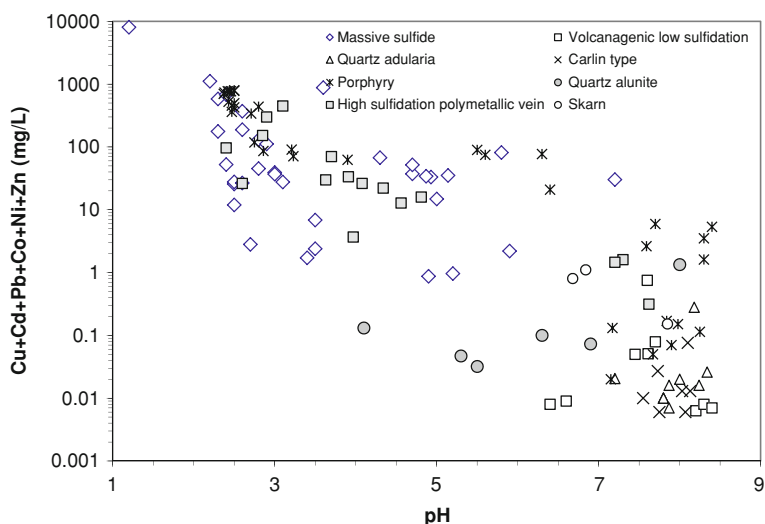
Fig. 3.46 Ficklin plot of divalent cationic metal concentrations with pH in metal-mine pit lakes

balance, solubilities of secondary mineral phases, water column dynamics, sediment biogeochemical processes, and remediation efforts. Thus, geoenvironmental characteristics can provide a useful framework for interpreting the hydrochemistry of existing pit lakes, making predictions of water quality for future pit lakes, and designing remedial strategies. However, there are still many areas where research could greatly improve our understanding of metal-mine pit lakes. A regularly
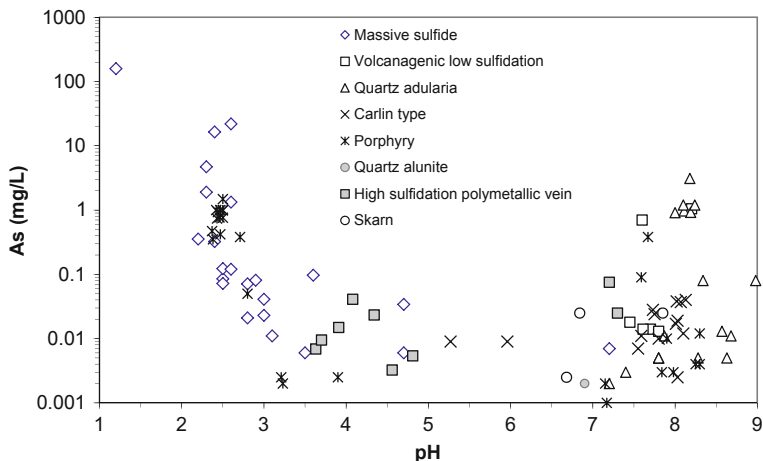
Fig. 3.47 Trends in As concentrations with pH in metal-mine pit lakes
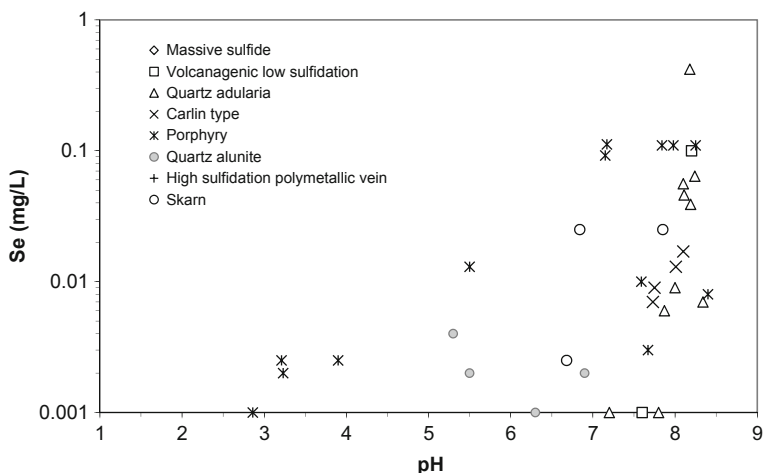
Fig. 3.48 Trends in Se concentrations with pH in metal-mine pit lakes

updated, international database on water quality from existing pit lakes in different types of mining regions, deposit types, metal resource, climate, and hydrologic environment could be valuable for identifying important factors affecting water quality, testing numerical models, and tracking remediation effectiveness. In addition, detailed studies on metal and nutrient cycling in the water column and sediments of pit lakes are needed to better understand the role of biogeochemical processes on water quality.

3.3 The Biology and Ecosystems of Acidic Pit Lakes

Katrin Wendt-Potthoff

Acid Pit Lakes as Special Habitats

Compared to typical acid mine drainage and chemically-similar hydrothermal solutions, the ionic composition of acid pit lakes is generally less concentrated, due to dilution of acid-generating oxidation products with groundwater or rainwater. The dissolved metal concentrations are typically elevated compared to natural lakes, but not necessarily at levels considered toxic for freshwater biota—this depends largely on the origin of the pit (lignite/coal versus metal ore mining, Sects. 2.2 and 3.2). As in natural lakes, stratification and mixis depend on the ambient climate, but also on the chemical influence of catchment and in-lake processes (Sects. 3.1 and 3.2.2). Iron and sulfur cycling determine the biogeochemistry, especially in the anoxic zones, in contrast to natural freshwater lakes, where the main anaerobic process is typically methanogenesis. The high iron concentrations of pit lakes also bring about significant photochemical reduction of Fe(III) near the lake surface, which is coupled with photochemical oxidation of dissolved organic carbon, a process that further diminishes the available organic carbon for organisms. The food webs of acidic pit lakes have much fewer levels and species than those of natural freshwater lakes. This makes them interesting locations for studying fundamental ecological processes. Therefore, the trophic interactions and flow of energy have been comprehensively investigated (Sect. 3.3.1.4). Much less is known about the taxonomy and physiology of bacterioplankton components and fungi in the water column, since microbiological studies have mainly focused on the sediments, where anaerobic, alkalinity-generating processes are common. Besides their extreme chemistry, many pit lakes are quite young (decades or years), which might also explain deficits in their colonization.

3.3.1 Plankton

3.3.1.1 Phytoplankton

Dieter Lessmann and Brigitte Nixdorf

Phytoplankton plays a key role in the biocoenotic structure of lakes—in acidic lakes just as in pH neutral lakes, although the importance of biotic factors decreases with increasing acidity, in contrast to abiotic conditions (Arnott and Vanni 1993). Phytoplankton species composition, in terms of species-related characteristics such as size, edibility, preferred nutrient sources, together with species abundance and biomass, profoundly influence other trophic levels (see also Sect. 3.3.1.4).

Phytoplankton coenoses of acidic pit lakes differ considerably from those of lakes in the circumneutral pH range due to their low species diversity, low biomass, different seasonal patterns, and utilization of resources. This is similar to findings for the phytobenthos of these lakes and of rivers and lakes that are acidified by acid mine drainage (AMD) or from volcanic sources.

During the past 15 years, scientists from different institutions have focussed their research on acidic pit lakes in the Lusatian and central German lignite mining district in the southeastern part of Germany, where this specific type of lake is relatively abundant. Other acidic water bodies that have been studied intensively by limnologists recently include streams in the Iberian Pyrite Belt (e.g. Sabater et al. 2003; Aguilera et al. 2007), streams affected by AMD in New Zealand (e.g. Niyogi et al. 1999, 2002; Bray 2007), and lakes and streams influenced by volcanism in the Argentinean Andes (e.g. Beamud et al. 2007; Pedrozo et al. 2010).

Species Diversity and pH

The biocoenotic structures of acidic lakes are determined by multiple abiotic stressors (Frost et al. 1999; Nixdorf et al. 2003b), which becomes especially evident in the correlation of species diversity with pH (Fig. 3.49). The plankton coenosis is less diverse as pH decreases, and the structure of the food web becomes simpler (see also Sects. 3.3.1.2 and 3.3.1.4). Only a small number of phytoplankton species tolerate the high proton and metal concentrations; the latter are site-specific and of different composition and importance. The loss of biodiversity and its effects are also well known from waters acidified by acidic deposition, whose lowest pH is around 3.5 (e.g. Baker and Christensen 1991; Matschullat et al. 1994; Steinberg and Wright 1994).

In Lusatian pit lakes, which have been regularly sampled for several years, the number of phytoplankton taxa in the pH range 2.5–3 is mostly between 7 and 9, whereas at pH values around 4, the taxa number increases to 17–25 (Fig. 3.49; Lessmann and Nixdorf, unpubl.; 2000). The majority of these algae belong to the nanoplankton or picoplankton (20–2 and 2–0.2 μm, respectively). These groups are usually underestimated in Lugol's samples (Sorokin 1999; Woelfl and Whitton 2000), and many algae have not yet been identified to the species level due to a lack of distinctive morphological characteristics. Comprehensive molecular biological studies are needed. The approach of Aguilera et al. (2007) for the investigation of the eukaryotic benthic community of Rio Tinto is an example how molecular approaches and traditional techniques can be combined to analyse the biocoenoses of acidic waters with greater accuracy.

Algal Communities at a pH of About 3

Most acidic pit lakes have a pH of about 3 due to iron buffering (Geller et al. 1998; Totsche et al. 2003). In Lusatian pit lakes with pH ≤ 3, the typical phytoplankton community is dominated by the genera *Ochromonas* and

Fig. 3.49 Relationship between the number of phytoplankton taxa and the mean pH of 17 acidic pit lakes in Lusatia regularly sampled for several years, based on microscopic analyses
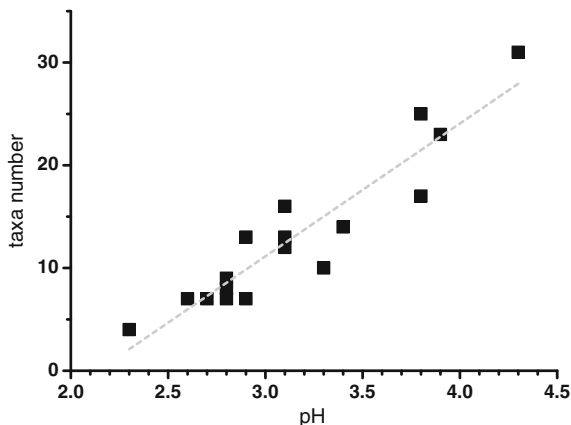
Chlamydomonas (Table 3.11; Lessmann et al. 2000; Nixdorf et al. 1998). Both are ubiquitous taxa in waters acidified by AMD (Lackey 1939; Sheath et al. 1982). *Chlamydomonas acidophila* is probably the only widespread species of its genus in these lakes and can be the most abundant phytoplankton taxon (Spijkerman 2008; Spijkerman et al. 2007). It is also a very common species in other extremely acidic waters, such as volcanic lakes, which can have even lower pH ranges than acidic pit lakes (Rhodes 1981; Satake and Saijo 1978; Sheath et al. 1982; Twiss 1990). The genus *Ochromonas*, with six morphologically distinct types, was eudominant in all lakes surveyed by Lessmann et al. (2000), who found that it constituted more than 50% of the annual total biovolume. *Lepocinclis teres*, *Euglena mutabilis* and *Chromulina* sp. can also be found frequently in several lakes. Two phytobenthic diatom species, *Eunotia exigua* and *Nitzschia* sp., occurred in most samples, but their contribution to total phytoplankton biomass is low in deep lakes (Lessmann et al. 2000). *E. mutabilis* is especially abundant in the littoral zone of the lakes, forming dense mats on the sediment surface (Kapfer 1998a, b).

Nevertheless, there is high variability in the phytoplankton community. Recent data show that *Peridinium umbonatum* and *Scourfieldia cordiformis* can be common in some of these lakes, in addition to *Chlamydomonas* and *Ochromonas*, and can represent a high portion of the annual total biovolume (Lessmann and Nixdorf, unpubl.).

In acidic pit lakes of the central German mining district around Leipzig, with a pH of 2.7–3.3, the dominant taxa, before remediation, were *Ochromonas* and *Chlamydomonas*, together with *Cryptomonas* and *Chrysococcus*, respectively (Rönicke et al. 2001, 2010). Another pit lake in that region that had a pH 3.4–3.6 was inhabited by five phytoplankton species, with *Chlamydomonas* being the most dominant, followed by *Chrysococcus* (Rönicke et al. 2002).

Many diatom species are unable to maintain a population at pH values below 4.5. DeNicola (2000) reviewed the occurrence of diatom species at pH ≤ 3.5. He identified less than nine species as real inhabitants in this pH range, most belonging to the phytobenthos.

Table 3.11 Presence and dominance of phytoplankton taxa that occur in pit lakes with pH ≤ 3. Data are based on 14 pit lakes of the Lusatian mining district

Class	Taxon	Presence (%)	Dominance
Chrysophyceae	*Chromulina* sp.	53	subd–eu
	Ochromonas spp. (6 types)	100	eu
Bacillariophyceae	*Eunotia exigua* Rabenhorst	73	subr–dom
	Nitzschia sp.	40	subr–dom
Cryptophyceae	*Cyathomonas* sp.	40	subr–eu
	Rhodomonas minuta Skuja	7	eu
Dinophyceae	*Gymnodinium* sp.	20	subr–eu
	Peridinium umbonatum Stein	13	subr–rec
Euglenophyceae	*Euglena mutabilis* Schmitz	60	subr–dom
	Lepocinclis teres f. *parvula* (Schmitz) Francé	67	subr–eu
Prasinophyceae	*Scourfieldia cordiformis* Takeda	27	subr–eu
Chlorophyceae	*Chlamydomonas* spp.	100	subd–eu
Trebouxiophyceae	*Nanochlorum* sp.	7	eu

Range of mean dominance: eu (dominant) with >10% of the total annual biovolume; dom(inant) with 5–10%; subd(ominant) with 2–5%; rec(edent) with 1–2%; subr(ecedent) with <1% (acc. to Schwerdtfeger 1975; after Lessmann et al. 2000)

Usually, Cyanobacteria are absent in such acidic water. Steinberg et al. (1998) detected the phycobilins phycocyanin and phycoerythrin (using fluorescence signals in flow-cytometry) in a pit lake with pH 3.0 and attributed them to filamentous Cyanobacteria. However, these fluorescence signals could not be assigned to specific cells by direct microscopic evidence (Whitton, Wendt-Potthoff, pers. comms.); so the detected pigment fluorescence might have come from eukaryotic algae with phycobilins (Rhodophyta, Cryptophyta, Glaucophyta). Unquestionable is that the green sulphur bacterium *Chlorobium limicola* can occur in extremely acidic waters (Overmann, pers. comm.).

The phytoplankton inhabitation of extremely acidic pit lakes can be compared with acidic volcanic water systems and streams receiving AMD. An unknown green alga occurs in high densities in the Indonesian crater lake Kawah Ijen with pH < 0.3 (Löhr et al. 2006). *Ch. acidophila* is known to be highly productive in the Japanese volcanic lake Katanuma at a pH of 1.9 (Satake and Saijo 1974).

The volcanic Río Agrio/Lago Caviahue acidic water system in the Argentinean Andes has been studied intensively for more than 10 years. The system comprises a crater lake from which the upper Río Agrio originates, which has a pH gradient of 0.4–1.5, Lago Caviahue, with a pH of about 2.3, and the lower Río Agrio (Pedrozo et al. 2010). In contrast to most pit lakes, the waters are rich in metals and phosphorus. The chemistry varies due to fluctuations in the activity of the volcano Copahue. While the crater lake lacks any phototrophic organisms, the upper Río Agrio is inhabited predominantly by the Chrysophycean genus *Gloeochrysis* (Table 3.12), which contributes 99% of the relatively low epilithon biomass, which totals <5 mg m^{-2} Chl-*a* (Baffico 2007; Baffico et al. 2004). The Chlorophycean species *Keratococcus rhaphidoides* represents more than 90% of the total annual abundance in Lago Caviahue, with eight other algal taxa also present (Table 3.12; Beamud et al. 2007; Pedrozo et al. 2001, 2010).

Table 3.12 Algal species, pH, and electrical conductivity (EC, mS cm^{-1}) in the upper Río Agrio/Lago Caviahue water system (after Pedrozo et al. 2010)

Site	pH	EC	Taxa
Crater Lake	1.2	500	(no phototrophs)
Upper Río Agrio	1.3–1.8	7.9–14.2	*Gloeochrysis* sp., *Euglena mutabilis*
Lago Caviahue	2.3	2.1	*Keratococcus raphidioides*, *E. mutabilis*, *Watanabea* sp., *Palmellopsis* sp., *Ulothrix* sp., *Nitzschia capitellata*, *Diatoma mesodon*, *Mougeotia* sp., Haptophyta

In addition to high acidity and high metal concentrations, autotrophs in streams that receive AMD are usually confronted with metal oxide deposition, which can cover all substrates where flow velocity is low (Bray 2007; Niyogi et al. 1999, 2002). Bray (2007) analysed the effects of AMD on algae in streams that show acidity gradients and identified pH as the most important controlling factor of the algae assemblage structure. With 15 taxa, algal diversity is low at pH < 3.6. This corresponds with the taxa number of the phytoplankton occurring in pit lakes with the same pH range. Certain species tend to dominate, especially filamentous *Klebsormidium acidophilum*. Other abundant species are *E. mutabilis*, *Navicula cincta*, *Microspora quadrata*, and *Microthamnion kuetzingianum*.

The benthic eukaryotic community of Rio Tinto, with a pH between 0.9 and 2.5 due to pyrite oxidation and AMD, comprises 10 algal taxa. The lowest taxa numbers are associated with the most acidic sites. Members of Chlorophyta, such as *Chlamydomonas*, *Dunaliella*, *Chlorella*, and *Euglena*, are the most frequent species, forming large green patches along the riverbed. *Dunaliella* and *Cyanidium* related species inhabit the most acidic site (Aguilera et al. 2007). Sabater et al. (2003) found low taxa and dominance structure fluctuations in Rio Tinto within the year and that the dominant taxa were *Klebsormidium flaccidum*, *Pinnularia acoricola*, and *Euglena mutabilis*. In acidic effluents from abandoned mines in Portugal, Valente et al. (2007) observed an algal flora that was dominated by *Euglena mutabilis* and *Klebsormidium* sp.

According to these findings, the dominant phytoplankton taxa in extremely acidic pit lakes are typically *Ch. acidophila* and species of the genus *Ochromonas*. The most common species in all kinds of extremely acidic waters is *E. mutabilis*. *Klebsormidium* appears to be a typical algal taxon in extremely acidified streams. However, large fluctuations in the biocoenotic structures can occur in these extremely acidic waters.

Phytoplankton Communities at pH 3.5 to 5

The phytoplankton community changes with increasing pH. Compared with lakes with a mean pH of 3 or lower, the taxa number increases and other species become dominant. At pH 4, the most common species in Lusatian pit lakes are *Peridinium umbonatum*, *Cryptomonas* spp., and in some lakes, *Amphidinium elenkinii*. Due to

the lack of a stabilising buffering system, only a small number of these lakes show pH values between about 4.3 and 5.5. In this pH range, the phytoplankton community of Lusatian pit lakes is mostly formed by *Scourfieldia cordiformis*, *Cryptomonas* spp., *Peridinium umbonatum*, *Amphidinium elenkinii*, and *Gymnodinium* sp. (Lessmann and Nixdorf, unpubl.).

A few studies have monitored changes in the phyoplankton during an increase of pH due to remediation. Rönicke et al. (2010) found an increase in diversity slowly following the changes in pH during chemical neutralisation. The most common phytoflagellates (*Chlamydomonas*, *Ochromonas*, *Chrysococcus*) from the extremely acidic phase continued to dominate at the beginning of lake neutralisation. *Chromulina*, diatoms (*Synedra acus*, *Nitzschia acicularioides*, *Eunotia exigua*), Cryptomonads (*Cryptomonas ovata*, *Rhodomonas minuta*) as well as Dinoflagellates (*Peridinium umbonatum*) became increasingly important during the following years. Cyanobacteria did not occur until circumneutral conditions were achieved.

Kalin et al. (2006) describe the effects of pH changes in a pit lake in Canada where pH decreased from 5 to 3. Phytoplankton diversity dropped from 52 to 42 taxa, the number of taxa with a frequency >10% from 39 to 10. Only *Ochromonas* and *Chlamydomonas* were consistently present. *Peridinium*, *Pinnularia*, and *Euglena* were frequent during the pH 5 phase and declined at lower pH. *Lepocinclis* proliferated when pH decreased and metal concentrations increased.

Control Mechanisms of Primary Production and Seasonal Succession of Phytoplankton

The biocoenotic structures are not the only difference between acidic pit lakes and circumneutral lakes; primary production control mechanisms also differ. Intense productivity studies and analyses of primary production and seasonal phytoplankton succession are available, especially from pit lakes of the Lusatian mining district.

Primary production is low in most lakes and does not exceed bacterial production, even during daylight. This leads to high differences on daily basis, with an average primary production rate of about 31 mg C m^{-3} d^{-1}, in contrast with a bacterial production rate of 186 mg C m^{-3} d^{-1}. The algal to bacterial production ratio identifies the lakes clearly as heterotrophic systems, which results in oxygen undersaturation of the water bodies (Nixdorf et al. 2003a). Beulker et al. (2002, 2004) measured autotrophic production of mining lake (ML) Plessa 117 (mean pH 2.9) regularly for more than a year. Primary production rates ranged from less than 1– 12.5 mg C m^{-3} h^{-1} in the upper water body. The wide range reflects the high seasonal fluctuation. With 278 mg C m^{-2} d^{-1}, the mean annual lake area related rate was low compared with natural lakes of the region (Beulker et al. 2004).

In general, mean annual phytoplankton biomass seems to be independent of the degree of acidification and to depend primarily on the availability of nutrients. In oligotrophic acidic pit lakes at pH values around 3 and 4, mean phytoplankton biovolume is within a similar range, between 0.3 and 0.7 mm^3 L^{-1}. At certain

Fig. 3.50 Scheme of the seasonal pattern of phytoplankton biomass succession in ML Plessa 117 (pH 2.9), usually formed by specific algae and indicating, in particular, the significance of the availability of increased inorganic carbon concentrations for phytoplankton growth in this lake
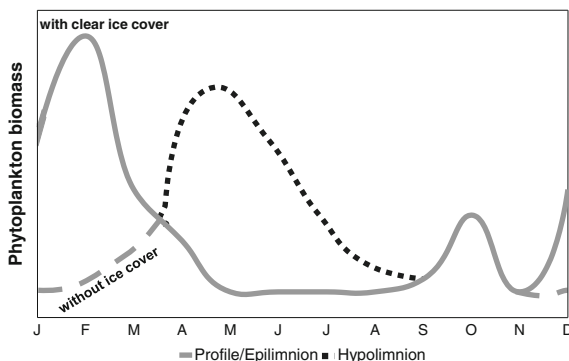
times of the year, maxima of 2–3 mm^3 L^{-1} can occur (Lessmann and Nixdorf unpubl.; Nixdorf et al. 1998). As in natural pH-neutral lakes, the increase in phosphorus concentrations can significantly increase phytoplankton biomass and can lead to eutrophication despite the high phosphorus binding capacity of the iron-rich water and sediments (Lessmann et al. 2003; Tittel and Kamjunke 2004; Woelfl et al. 2000).

Nevertheless, large seasonal fluctuations of primary production and biomass are typical for oligotrophic acidic pit lakes and can generally be attributed to inorganic carbon limitation rather than to changes in phosphorus concentrations. Under acidic conditions below pH 4.3, CO_2 is the only available inorganic carbon source for photosynthesis. As long as the water body is in exchange with the atmosphere, the equilibrium between water and atmosphere and the uptake by autotrophs lead to dissolved inorganic carbon (DIC) concentrations that are far lower than in pH-neutral waters with bicarbonate buffering and their high availability of inorganic carbon.

However, CO_2 can accumulate in water layers isolated from the atmospheric exchange, i.e. in the hypolimnion or under ice. This can cause a fast increase in phytoplankton biomass. In contrast, during circulation periods and especially in the epilimnion of the summer stagnation phase, CO_2 concentrations are low. Increasing CO_2 concentrations are typical for the hypolimnia due to the inflow of CO_2-rich groundwater and respiration and decomposition of organic matter as major sources. During winter, ice cover can significantly reduce inorganic carbon loss to the atmosphere and lead to an increase in DIC concentrations and in phytoplankton biomass, if there is no shading by snow.

As an example, in ML Plessa 117 a typical pattern of seasonal phytoplankton succession was observed with the highest biomass in winter under an ice cover free of snow, followed by a second phytoplankton bloom in the upper hypolimnion at the beginning of the summer stratification and a small increase during the autumnal overturn (Fig. 3.50). In ML Plessa 117, these blooms are usually formed by a small number of species, with *Ochromonas* and *Chlamydomonas* being the most important ones. In consequence, mild winters without long-lasting ice cover show no algal bloom, and the maximum phytoplankton biomass occurs during the summer stratification as a deep chlorophyll maximum (DCM) in the metalimnion

and upper hypolimnion (Lessmann and Nixdorf 2002; Beulker et al. 2003; Lessmann et al. 2006). DCMs are also characteristic of other oligotrophic acidic pit lakes (Tittel et al. 2003).

In addition to pelagic primary production, benthic algae can be important contributors to primary production of acidic lakes. A dense layer of the diatoms *Eunotia* spp. and *Pinnularia obscura* covers the sediment surface in a lake with pH 2.6 (Koschorreck and Tittel 2002, see also Sects. 3.3.2.2 and 3.3.2.3). The microphytobenthos in the littoral zones of the Lusatian pit lakes Plessa ML 111, ML 108, and ML 117 is dominated by *E. mutabilis*, *Eunotia* spp., and *Nitzschia paleaeformis*. Chlorophyll-*a* concentrations, primary production rates, and specific primary production were strikingly higher at *Euglena* dominated sites (12–176 mg Chl-*a* m^{-2}; 2.99–7.84 mg C m^{-2} h^{-1}; 0.30–0.47 mg C (mg Chl-*a*)$^{-1}$h^{-1}) than at sites dominated by *Eunotia* (1–89 mg Chl-*a* m^{-2}; 0.46–3.84 mg C m^{-2}h^{-1}; 0.03–0.35 mg C (mg Chl-*a*)$^{-1}$h^{-1}) (Kapfer 1998a, b). Elevated phytobenthos production may be attributed to higher concentrations of soluble reactive phosphorus (SRP), dissolved inorganic carbon (DIC), and dissolved organic carbon (DOC) in the sediment pore water than in the pelagic water, especially where groundwater inflow occurs (Hofmann and Lessmann 2006; Kapfer 1998a, b).

The presumed limitation of primary production by phosphorus and inorganic carbon in ML Plessa 117 is supported by laboratory experiments. To increase the volume-specific primary production rates, it was necessary to increase the inorganic carbon concentrations above 0.6 mg L^{-1} and the total phosphorus concentrations above 10 μg L^{-1} (Beulker et al. 2002, 2004).

Calculation of the carrying capacity for autotrophic phytoplankton shows changes in primary production limitations with water depth during the summer stratification of partly meromictic ML 111. While primary production is limited by inorganic carbon in the epilimnion, phosphorus becomes the limiting nutrient in the hypolimnion. Light limitation occurs only in the deepest parts of the lake (Fig. 3.51; Krumbeck et al. 1998).

In contrast to Lusatian mining lakes, in volcanic Lago Caviahue (pH about 2.5), primary production is primarily limited by nitrogen (dissolved inorganic nitrogen: 30–150 μg L^{-1}; compare also Berkeley Pit Lake, case study 5.5). The N:P ratio ranges from 0.03 to 0.11. A seasonal succession is missing and variations can mostly be attributed to volcanic activity. In addition to ammonium, phytoplankton biomass is also controlled by inorganic and, for mixotrophic species, by organic carbon (Pedrozo et al. 2008, 2010). Despite the lack of seasonal gradients of phytoplankton biomass in the water column, sometimes DCMs can be observed in the upper hypolimnion due to locally increased nutrient concentrations (Beamud et al. 2010).

Adaptation Strategies of Phytoplankton

Protists with fast asexual reproduction potential under favourable conditions form the most important group of the phytoplankton in the most acidic pit lakes. *Ch. acidophila* is able to survive at pH 1.0 for short time; its limit for sustained growth
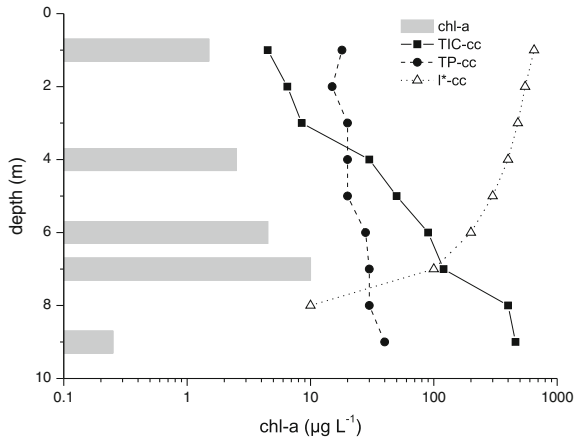
Fig. 3.51 Realized biomass and carrying capacity (cc) of phytoplankton expressed as Chl-*a* concentrations with regard to the available resources of inorganic carbon (TIC), phosphorus (TP), and light (l*) in the water column of ML 111 during summer stratification. The water column is divided into the epilimnion, down to a depth of about 3 m, the hypolimnion, from about 3 m to about 7 m, and the monimolimnion below (after Krumbeck et al. 1998)

is pH 1.5–2.0 (Pollio et al. 2005). Acidophilic algae developed different physiological adaptations to be able to maintain their cytoplasmatic pH in the circumneutral range or to increase pH in the water layer adjacent to their cell surface for the control of their osmoregulation (Pick 1999).

The two most common taxa *Ch. acidophila* and *Ochromonas* have a different pH niche width. While *Ch. acidophila* is an obligate acidophilic species, *Ochromonas* is acidotolerant, because *Ch. acidophila* has its fitness optimum under extremely acidic conditions, whereas *Ochromonas* grows best under moderately acidic conditions. That shows that in extremely acidic pit lakes, the phytoplankton coenosis is formed by a mixture of acidophilic specialists and acidotolerant generalists (Moser and Weisse 2011).

With regard to the occurrence of light and nutrient gradients, especially the lack of inorganic carbon in the epilimnion during summer, motility and the ability for fast reproduction under optimized conditions (C-strategists acc. to Reynolds 1997) are major advantages for phytoflagellates in acidic pit lakes (Fyson and Rücker 1998; Lessmann and Nixdorf 2000; Nixdorf et al. 1998).

Analysing the trophic spectrum that the dominant species are able to use, it is apparent that there is a high proportion of mixotrophs (Beulker et al. 2004; Nixdorf et al. 1998). These can either live as photoautotrophic organisms or (additionally) change to osmotrophy and feed on the organic carbon available in the water column or on bacteria, as phagotrophic organisms. *Chlamydomonas* and *Scourfieldia cordiformis* combine phototrophy with osmotrophy; *Ochromonas*, *Gymnodinium*, *Lepocinclis*, and *Cryptomonas* combine phototrophy with phagotrophy. In this group, *Ochromonas* can also feed on *Chlamydomonas* (Beulker et al. 2004; Tittel et al. 2003).
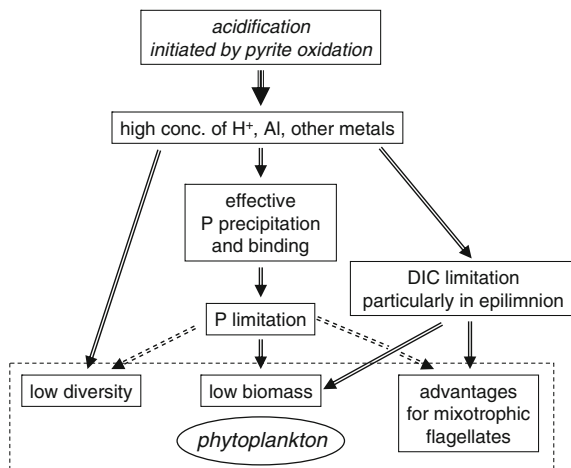
The ecosystem of ML 111 is very well investigated (see also Sects. 3.3.1.4 and 5.6). The plankton consists of single-celled and filamentous bacteria, mixotrophic flagellates with *Ch. acidophila* and *Ochromonas*, the Rotifera *Elosa worallii* and *Cephalodella hoodi*, and Heliozoa as the most important taxa of the food web. Heterotrophic flagellates, Crustacea, and fish are missing; Ciliata and Rhizopoda are rare. While bacterial filaments, *Ochromonas*, *Elosa*, and Heliozoa dominate in the epilimnion, the hypolimnion is dominated by single-celled bacteria, *Chlamydomonas* and *Cephalodella*. *Chlamydomonas* is primarily phototrophic and limited by light and inorganic carbon and is grazed by *Ochromonas* in the epilimnion. However, *Ochromonas* is primarily phagotrophic and controlled by prey availability (Kamjunke et al. 2004). Tittel and Kamjunke (2004) and Tittel et al. (2005) were able to show in experiments that the phototrophic growth of *Ch. acidophila* is limited at the water surface and that the addition of DIC leads to an increase in the growth rate. Despite significant photosynthetic activity, the alga also reduced the high DOC concentrations. Mixotrophic phytoflagellates are also important bacterial grazers. In ML 111, *Ochromonas* grazes 88% of the daily bacterial production of the epilimnion and 68% of that of the hypolimnion (Schmidtke et al. 2006).

Top-down control of the phytoplankton is only likely with the occurrence of larger zooplankton in high abundance, such as *Brachionus sericus* and *Chydorus sphaericus* (Wollmann and Deneke 2004; Wollmann et al. 2000); otherwise, the influence of higher trophic levels on phytoplankton is negligible (Lessmann et al. 1999; Weithoff 2004; see also Sects. 3.3.1.2 and 3.3.1.4).

To summarize, the extreme environmental conditions of acidic pit lakes, with high proton and metal, and low nutrient concentrations (limitation of primary production by P and C), control phytoplankton coenoses, resulting in low diversity and biomass (Fig. 3.52). On the other hand, several taxa show adaptations to the extreme habitat, especially physiological adaptations to the low pH, which allow them to thrive there. Mixotrophy, motility, and high reproduction potential are additional features for successful colonization of acidic pit lakes.

3.3.1.2 Zooplankton

Maria Belyaeva and Rainer Deneke

Relationship of Species Occurrence and Taxonomic Diversity to pH

Species richness of metazoan zooplankton is typically very low in acidic pit lakes, as few species can tolerate their harsh abiotic conditions (Nixdorf et al. 1998). As in other extreme environments, one or very few species dominate, resulting in low community evenness. Regarding the taxonomic composition of zooplankton in acidic pit lakes at pH 2.3–4.5, rotifers clearly outnumber crustaceans. Cladocera are represented by few species, but they can be important colonizers in lakes with pH ≥ 3, whereas Copepoda are rare (Deneke 2000).

Despite unfavorable abiotic conditions, even extremely acidic lakes are colonized by zooplankton: at pH 2.3, two rotifer species—*Cephalodella hoodi* and *Rotaria rotatoria*—were observed in the pelagic zone of Lake Plessa 107—a pit lake in northeast Germany (Lessmann et al. 1999). These two species, together with *Elosa worallii*, *Cephalodella gibba*, and *Brachionus sericus* constitute the core zooplankton community in highly acidic pit lakes with pH around 3 (Deneke 2000). A number of rotifer species from the genera *Lecane*, *Colurella*, *Trichocerca*, *Lepadella*, and *Philodina* are occasionally found in highly acidic pit lakes, but they are never very abundant (reviewed in Deneke 2000). All of the acid-tolerant rotifer species also occur in less acidic pit lakes (Wollmann et al. 2000), above their species-specific lower in situ pH thresholds (Table 3.13); however, they disappear from the pelagic zone of neutral and alkaline pit lakes, being replaced by a species assemblage typical of natural non-acidic lakes (Nixdorf et al. 1998). *Chydorus sphaericus* (Cladocera, Chydoridae) is the most acid-tolerant crustacean species that colonizes acidic pit lakes, with an in situ pH threshold of 3.0 (Wollmann et al. 2000). At pH > 3.5, two more crustaceans occur in acidic pit lakes—another cladoceran, *Scapholeberis mucronata*, and the most tolerant cyclopoid copepod, *Diacyclops* sp. (Wollmann et al. 2000). Remarkably, calanoid copepods that often dominate zooplankton communities in soft-water acidic lakes (Brett 1989) are completely lacking in acidic pit lakes.

The majority of acidic pit lakes fall into the pH range of 2–4.5. At pH 4.5–6, chemical conditions become unstable due to the lack of a buffer system; thus, weakly acidic pit lakes are rare (Nixdorf et al. 2003). Hence, field studies on colonization patterns along the entire pH gradient from acidic to circumneutral conditions in pit lakes are methodologically hampered. The very few pit lakes with a pH range of 4.5–6 are recently or incompletely neutralized lakes, where water chemistry has not yet stabilized. These lakes are valuable sites to study colonization patterns and ecology of colonizing species under weakly acidic pit lakes conditions. For example, littoral Cladocera have been studied within a horizontal pH gradient in Lake Senftenberger See, formed within a channel connecting the acidic (pH 3) and the neutral (pH 7.5) basins of the lake (Belyaeva and Deneke

Table 3.13 Zooplankton species occurring in acidic pit lakes and the lowest in situ pH at which they were recorded

Taxonomic group	Species	pH	Sampling site	Reference
Extremely acidic pit lakes				
Rotifera, Monogononta	Cephalodella hoodi (Gosse 1896)	2.3	Lake Plessa 107	Lessmann et al. (1999)
Rotifera, Bdelloidea	Rotaria rotatoria (Pallas 1766)	2.3	Lake Plessa 107	
Rotifera, Monogononta	Cephalodella gibba (Ehrenberg 1838)	2.5	Pit lakes, Illinois, USA	McConathy and Stahl (1982)
Rotifera, Bdelloidea	Philodina sp.	2.5	Pit lakes, Illinois, USA	
Rotifera, Monogononta	Elosa worallii Lord 1891	2.6	Lake Plessa (ML 111)	Wollmann et al. (2000)
Rotifera, Monogononta	Lecane (Monostyla) lunaris Ehrenberg 1832	2.6	Pit lakes in Lusatia	Deneke, unpubl
Very acidic pit lakes				
Rotifera, Monogononta	Brachionus urceolaris O. F. Müller 1773[a]	2.6	Pit lakes, Illinois, USA	McConathy and Stahl (1982)
Rotifera, Monogononta	Colurella sp.	2.7	Pit lakes in Lusatia	Deneke, unpubl
Rotifera, Monogononta	Trichocerca similis Wierzejski 1893	2.7	Pit lakes in Lusatia	
Rotifera, Monogononta	Lecane stichaea Harring 1913	3.0	Pit lakes in Lusatia	
Rotifera, Monogononta	Lepadella sp.	3.0	Pit lakes in Lusatia	
Rotifera, Monogononta	Lecane (Monostyla) bulla (Gosse 1886)	3.0	Pit lakes, Illinois, USA	McConathy and Stahl (1982)
Cladocera, Chydoridae	Chydorus sphaericus (Müller 1776)	3.0	Grünewalder Lauch (ML 117)	Wollmann et al. (2000)
Moderately acidic pit lakes				
Cladocera, Daphniidae	Scapholeberis mucronata (Müller 1776)	3.5	Geierswalder See	Belyaeva and Deneke, unpubl
Copepoda, Cyclopidae	Diacyclops sp.	3.5	Felixsee	Wollmann et al. (2000)
Weakly acidic pit lakes				
Rotifera, Monogononta	Polyarthra sp.	4.7	Gräbendorfer See	Deneke, unpubl
Rotifera, Monogononta	Keratella cochlearis (Gosse 1851)	4.7	Gräbendorfer See	
Rotifera, Monogononta	Keratella testudo (Ehrenberg 1832)	4.7	Gräbendorfer See	
Rotifera, Monogononta	Filinia longiseta (Ehrenberg 1834)	4.7	Gräbendorfer See	
Cladocera, Daphniidae	Ceriodaphnia sp.	4.7	Gräbendorfer See	
Cladocera, Bosminidae	Bosmina coregoni Baird 1857	4.7	Gräbendorfer See	
Cladocera, Chydoridae	Eurycercus lamellatus (Müller 1776)	4.9	Senftenberger See	Belyaeva and Deneke (2007)

Table 3.13 (continued)

Taxonomic group	Species	pH	Sampling site	Reference
Cladocera, Chydoridae	*Pleuroxus truncatus* (Müller 1785)	4.9	Senftenberger See	
Cladocera, Bosminidae	*Bosmina longirostris* (Müller 1785)	5.0	Senftenberger See	
Cladocera, Sididae	*Sida crystallina* (Müller 1776)	5.0	Senftenberger See	
Cladocera, Chydoridae	*Alona affinis* (Leydig 1860)	5.0	Senftenberger See	
Cladocera, Chydoridae	*Acroperus harpae* (Baird 1835)	5.7	Senftenberger See	
Cladocera, Chydoridae	*Alona costata* Sars 1862	5.7	Senftenberger See	
Cladocera, Daphniidae	*Ceriodaphnia pulchella* Sars 1862	5.7	Senftenberger See	
Cladocera, Polyphemidae	*Polyphemus pediculus* (Linne 1761)	5.7	Senftenberger See	
Cladocera, Chydoridae	*Alona guttata* Sars, 1862	5.7	Senftenberger See	
Cladocera, Sididae	*Diaphanosoma brachyurum* (Liévin 1848)	5.7	Senftenberger See	
Cladocera, Daphniidae	*Simocephalus vetulus* (Müller 1776)	6.1	Senftenberger See	

Classification of lakes is according to Nixdorf et al. (2005), slightly modified. Core species that dominate zooplankton communities in acidic pit lakes are underlined. Lakes are in Germany unless otherwise specified

[a] Although this species was recorded from North American pit lakes as *Brachionus urceolaris*, it is likely *B. sericus*, which appears to be much more acid-tolerant than the former species. The observed minimum in situ pH of 2.6 for the North American populations differs from that in German lakes, where this species has only been found at a pH of 2.7 and above (Deneke 2000)

2007). Only two cladoceran species, *C. sphaericus* and *S. mucronata*, were found at pH below 4.9, whereas rather diverse communities occurred at pH ≥ 4.9 (Table 3.13). Dramatic changes in cladoceran species composition were observed within a distance of several hundred meters along the pH gradient, despite the lack of any physical barriers that might have limited the dispersal of species. Thus, the loss of species towards the acidic part of the lake can be attributed to the adverse effects of the chemical conditions. To our knowledge, no published studies report on the species composition of Copepoda and Rotifera within the pH range of 4.5–6 in pit lakes, although both groups do occur at these conditions (Belyaeva and Deneke unpubl.; Woelfl et al. 1998).

Most zooplankton species that are found in acidic pit lakes have been recorded from different continents and appear to be cosmopolitan. However, it should be noted that most data on zooplankton communities come from studies on pit lakes in Germany, while less is known about the biota of these habitats outside Europe. *C. hoodi*, *C. gibba*, and *B. sericus* have been recorded in both European and North American acidic pit lakes (Deneke 2000). There is a lack of detailed taxonomic studies confirming the co-specificity of geographically distant populations. Particularly, uncertainties exist concerning the taxonomic status of *B. sericus*. Although Rousselet (1907) described *B. sericus* as a separate species, it was often later regarded as a variety of *B. urceolaris* (e.g. Koste 1978). Hence, some records of *B. sericus*, *B. urceolaris* var. *sericus*, and *B. urceolaris* by different authors may possibly refer to the same taxon. If so, it colonizes acidic hard-water lakes separated by large geographical distances, being also found in Australian billabong ponds affected by mine drainage (Tait et al. 1984), geogenically acidified lakes in Japan (Uéno 1958), and in the Canadian Arctic ponds acidified by burnt bituminous shales (Havas and Hutchinson 1983). On the other hand, *Elosa worallii* is very common in acidic hard waters, but only in Europe (Nixdorf et al. 1998; Vallin 1953), while a detailed study of North American pit lakes by McConathy and Stahl (1982) did not detect this species. *C. sphaericus* has been recorded in hard-water acidic lakes on different continents (Deneke 2000). Yet, these populations probably belong to distinct, though closely related species (Belyaeva and Taylor 2009).

Volcanic and coastal sulfur lakes are natural analogues of acidic pit lakes, with similar water chemistry (Geller et al. 1998); they are also inhabited by similar zooplankton communities (Deneke 2000). However, there are some differences in species occurrence patterns, e.g. occurrence of copepods at pH around 3 in volcanic lakes in Japan (Uéno 1958), but not in pit lakes. This may be related to adaptation of species in the regions, where hard-water acidic lakes have existed over evolutionary relevant time scales.

Factors Influencing Colonization of Acidic Pit Lakes by Zooplankton

Zooplankton species richness and community composition in acidic pit lakes are both highly predictable from the lake pH value (Deneke 2000). The strong correlation between zooplankton species richness and pH (Fig. 3.53) exists
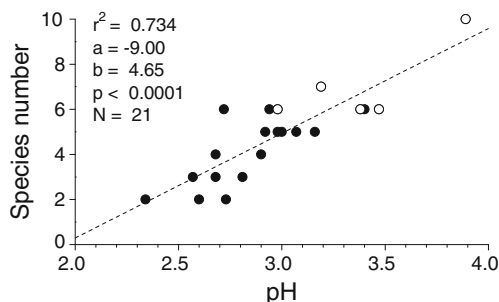
Fig. 3.53 Zooplankton species richness along a pH gradient in acidic pit lakes, based on monthly samples from 21 lakes in Lusatia, Germany, over a period of at least one year. Indicated are parameters of linear least square regression fitted to the data. Filled circles indicate that the communities lacked crustaceans; open circles indicate that crustaceans were observed

despite considerable variability in lake morphology, mixis regime, and trophic status of pit lakes. This, however, does not necessarily mean that high concentration of protons alone limits species occurrence. Generally, multiple abiotic stressors act in acidic lakes (Frost et al. 1999). Zooplankton species composition in acidic pit lakes differs greatly from that in soft-water acidic lakes, which indicates that other water chemistry parameters might be crucial for biological colonization. Laboratory tests with cladocerans have shown that aluminum, iron, and heavy metal ions (Lopes et al. 1999; Soucek et al. 2001) as well as high sulfate content (Kennedy et al. 2005) can contribute to the toxicity of waters affected by acid mine drainage. Metal ions may be elevated in soft-water acidic lakes as well, but their toxicity is mitigated by colored dissolved organic carbon (cDOC; Williamson et al. 1999). As cDOC content is usually very low in acidic pit lakes (Friese et al. 2002), its beneficial effects are diminished. Therefore, abiotic conditions in acidic pit lakes should be more toxic for organisms than those in naturally acidic lakes at the same pH values. Indeed, in our study on littoral Cladocera (Belyaeva and Deneke 2007), we reported higher species-specific in situ pH thresholds for most species in a pit lake vs. soft-water acidic lakes (Fig. 3.54). As a result, species diversity in acidic pit lakes is expectedly lower than in naturally acidic soft-water lakes.

Acidity reflects buffering capacity, i.e. the stability of pH conditions. Soft-water lakes are rather poorly buffered, and spatial as well as seasonal pH fluctuations occur, whereas acidic pit lakes at pH < 4.5 are well-buffered and display very little within-lake variation in pH, with the exception of meromictic pit lakes. At pH > 4.5, soft-water lakes are buffered by cDOC, but in pit lakes, this buffer system is lacking, and so the pH is very unstable (Nixdorf et al. 2003). Precipitation of metal compounds occurs during pH changes, which can adversely affect organisms (Belyaeva and Deneke 2007; Weatherley et al. 1991). This may occur, for example, during whole-lake neutralization or within mixing zones, where neutral river water enters a highly acidic pit lake. Thus, the detrimental effect of metal precipitation should be taken into account while planning neutralization measures.
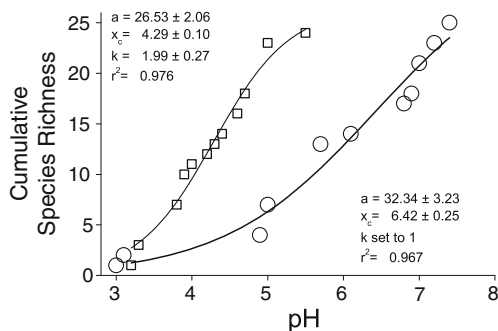
Fig. 3.54 Logistic regression curves for the potential cumulative species richness of littoral Cladocera within a horizontal pH gradient from 3 to 7 in a pit lake Senftenberger See (*circles*) and natural soft-water lakes (*squares*) based on in situ pH thresholds for individual species. Lower potential species richness predicted for acidic pit lakes, as compared to soft-water lakes, results from higher species-specific pH thresholds (modified from Belyaeva and Deneke (2007), with kind permission from Springer Science + Business Media)

Evidently, specific water chemistry in acidic pit lakes exerts profound effects on the zooplankton species diversity and composition. Secondary production and biomass in acidic lakes seem to be less affected, due to compensating shifts in biomass of tolerant species (Frost et al. 1995). On the other hand, food availability is believed to control zooplankton biomass in acidic lakes (Havens and Carlson 1998; Nixdorf et al. 1998) as well as within-lake distribution (Weithoff 2004) and seasonal dynamics of populations, but it is unlikely to limit species occurrence. Another limiting factor is, possibly, availability of micro-habitats in the littoral zone. Many acidic pit lakes are characterized by low macrophyte growth (Pietsch 1998); hence, plant-associated zooplankton species may be rare or completely excluded due to a lack of suitable micro-habitats. Biotic factors, such as predation and competition, play an important role in natural lakes. Yet, in acidic lakes, the importance of biotic factors decreases at low pH, where abiotic conditions become increasingly more stressful (Arnott and Vanni 1993). In the most extremely acidic pit lakes (pH < 2.8), neither predation nor competition seem to be important (Weithoff 2004), whereas at pH > 2.8, some effects of biotic interactions may be present, although water chemistry is still the major determinant of zooplankton community structure (Wollmann and Deneke 2004).

Dispersal of zooplankton may be hindered by the young age and/or isolated character of many acidic pit lakes. However, no published data is available on the primary colonization of newly created pit lakes, and it is unknown how long it takes the core zooplankton community to get established. Another interesting question for future studies would be the genetic structure and exchange among populations colonizing acidic pit lakes, i.e. metapopulation dynamics. It is possible that it would be reduced due to isolation of pit lakes, yet, many zooplankton species colonizing these habitats are pioneer species with high dispersal capabilities (see below), which can enhance metapopulation dynamics.

Ecology of Species Colonizing Acidic Pit Lakes

Anthropogenically stressed environments, such as acidic pit lakes, are commonly colonized by extremophilic specialists as well as generalist species with broad tolerance ranges to a number of environmental factors. In contrast to bacteria, algae, and protists, which are often represented by acidophiles in acidic pit lakes, the evidence for acidophily among zooplankton is rather weak (but see Sect. 3.3.1.4). Most of the zooplankton species occurring in acidic pit lakes have been also found in natural lakes at acidic and neutral conditions (Deneke 2000), although they exhibit somewhat different abundance patterns and habitat preferences there (see below). Furthermore, core species from acidic pit lakes—*C. sphaericus*, *B. sericus*, *E. worallii*, and *C. hoodi*—cultured at ambient pH, could be successfully transferred to neutral pH under laboratory conditions (Belyaeva and Deneke 2007; Deneke unpubl.). Hence, zooplankton community in acidic pit lakes largely, if not exclusively, comprises generalist species. In contrast, there are possibly some specialists among zooplankton species colonizing acidic soft-water lakes that have not been recorded in acidic pit lakes or in neutral hard-water lakes, e.g. the rotifers *Lecane acus*, *Habrotrocha lata*, *Keratella serrulata* (Bērziņš and Pejler 1987), and the cladocerans *Acantholeberis curvirostris* and *Streblocerus serricaudatus* (Flößner 2000). However, the designation of these species as specialists is derived from field occurrence data alone. It remains unclear whether their physiological optima lie under soft-water acidic conditions, or if they are simply weak competitors that are outcompeted in species-rich neutral lakes. Still, many soft-water acidic 'specialists' have not been found in species-poor acidic pit lakes, which suggests that they are not capable of tolerating the abiotic stresses there. The complete absence of specialists in acidic pit lakes is probably explained by insufficient time for adaptive evolution, since those are young habitats with peculiar abiotic conditions, and their natural counterparts, such as volcanic lakes, are rare.

Zooplankton species found in acidic pit lakes can be characterized as pioneers that also colonize newly created and perturbed water bodies. Pioneer species are r-strategists (meaning they have high growth rates) with efficient dispersal mechanisms, and they are able to use a wide range of food sources. For example, *C. sphaericus* is often the first crustacean species colonizing new sites (Louette et al. 2008); it is capable of using different food sources (De Eyto and Irvine 2001), tolerates a wide range of abiotic conditions (Belyaeva and Deneke 2007), and is often abundant in anthropogenically disturbed environments, e.g. highly eutrophic lakes (De Eyto 2001). Despite their large potential for colonization, pioneer species are presumably weak competitors. Their mass development is only observed in species-poor communities, such as acidic pit lakes, or in natural lakes, when superior competitors are (temporarily) absent, e.g. *C. sphaericus* developing in the absence of *Daphnia* and copepod nauplii (Matveev 1986).

Absence of pelagic forms and a simultaneous habitat shift of littoral species to the pelagic zone is a common observation in all kinds of acidic lakes, including soft waters (Nilssen 1980; Nilssen and Wærvågen 2003). This is probably due to the lack of competition and predation pressure under acidic conditions (Locke and

Sprules 2000). In European acidic pit lakes, no zooplankton species were found exclusively in benthic or littoral habitats (Deneke 2000), although rotifers and crustaceans exhibited heterogeneous distributions within the water column (Weithoff 2004; Wollmann and Deneke 2004). In North American acidic pit lakes, two species, *Lecane bulla* and *Philodina* sp., were found only in benthic algal clumps, but not in plankton (McConathy and Stahl 1982). The absence of large pelagic species in acidic pit lakes results in a shift towards species with body size <500 μm. A similar shift in size structure has been documented for naturally acidic and atmospherically acidified lakes (Schindler et al. 1985).

It is not quite clear what physiological adaptations of tolerant zooplankton species have led to successful colonization of acidic pit lakes. In general, organisms living at low pH are capable of maintaining a circum-neutral internal pH via passive or active mechanisms (Rothschild and Mancinelli 2001). Additional challenge for colonization of pit lakes is seemingly provided by the high total ionic content and high metal concentrations typical of these waters. Hence, it is possible that survival of zooplankton in acidic pit lakes is ensured due to different physiological mechanisms than those that are employed in soft-water acidic lakes. There is still a lack of knowledge concerning particular mechanisms of ion regulation in metazoan zooplankton species under acidic hard-water conditions. A study on a rotifer, *C. hoodi*, from extremely acidic pit lakes failed to detect any additional physiological costs or specific ecological adaptations (Weithoff 2005).

Ecological Characteristics of Zooplankton Communities in Acidic Pit Lakes

The major features of biological communities in acidic pit lakes are greatly reduced species diversity and extirpation of fish, so that the role of top predators is taken over by invertebrates (Wollmann et al. 2000). This leads to truncated and very simple food webs (Sect. 3.3.1.4). In acidic pit lakes, zooplankton community composition is controlled by pH and related water chemistry parameters, whereas zooplankton biomass is possibly controlled by food availability (Wollmann and Deneke 2004; Sect. 3.3.1.4), as in soft-water acidic lakes (Havens and Carlson 1998). Biotic interactions seem to be rather weak, at least in the most acidic pit lakes (Weithoff 2004). However, some ecological patterns occurring in natural lake ecosystems, such as niche separation among different species (Weithoff 2004), seasonal succession, and top-down and bottom-up effects on zooplankton (Wollmann and Deneke 2004; Wollmann et al. 2000), have been observed in acidic pit lakes as well. On the other hand, zooplankton community composition is rather peculiar and unique in acidic pit lakes, what may result in rather specific biotic interactions.

Nixdorf et al. (2005) proposed a classification scheme for acidic pit lakes based on pH, chemical buffer system, and colonization patterns by phyto- and zooplankton (Table 3.14). The defined lake groups can also be viewed as successive stages of habitat maturation, as acidic lakes should become neutral with time due to natural alkalinity generation by chemical and biological processes. Characteristic core species occur in each group of lakes (Table 3.14), whose presence often has a pronounced

Table 3.14 Classification of acidic pit lakes based on water chemistry and zooplankton colonization (modified from Nixdorf et al. 2005)

Lake group	pH	Conductivity (mS cm^{-1})	Acidity (mmol L^{-1})	Buffer system	Characteristic zooplankton species
Extremely acidic	<2.8	>3	>15	Iron	*Cephalodella hoodi*, *Elosa worallii*
Very acidic	2.8–3.5	1.5–3.0	>1.6–15	Iron	*Brachionus sericus*, *Chydorus sphaericus*
Moderately acidic	3.5–4.5	< 1.5	0–1.6	Aluminum	*Diacyclops* sp., *Scapholeberis mucronata*
Weakly acidic	4.5–6.5	< 1.5	ca. –0.5	Lacking buffer system	Diverse littoral Cladocera

effect on the food web structure and seasonal population dynamics (Wollmann and Deneke 2004). In 'extremely acidic' pit lakes (pH < 2.8), the zooplankton community is dominated by two small rotifer species, *C. hoodi* and *E. worallii*, and potential community grazing rates are very low (less than 1% per day). Hence, the impact on primary producers is negligible; indeed, no top-down effects on phytoplankton have been observed in extremely acidic pit lakes even during metazooplankton abundance peaks (Lessmann et al. 1999; Weithoff 2004). Heliozoa play the role of top predators in the pelagic food web; however, it appears that they are not capable of exerting any noticeable effect on zooplankton (Weithoff 2004).

In 'very acidic' pit lakes (2.8 ≤ pH < 3.5), the appearance of larger zoo-plankton species with higher clearance rates—*B. sericus* and *C. sphaericus*—leads to top-down effects on phytoplankton (Wollmann and Deneke 2004). As a result, a seasonal pattern is observed with a break-down of phytoplankton biomass following mass development of both zooplankton species in summer (Wollmann et al. 2000). Corixidae prey on both dominant zooplankton species here, while heliozoans disappear from pit lakes at pH > 2.8. As corixids can feed both on benthos and zooplankton, they enable benthic-pelagic coupling in the food webs (Wollmann et al. 2000).

In 'moderately acidic' pit lakes (pH 3.5–4.5), zooplankton communities are more diverse, including several additional rotifer species, a cladoceran *S. mucronata*, and copepods (Wollmann et al. 2000). The community composition is intermediate between the acidic and neutral pit lake communities (Wollmann and Deneke 2004). Still, acid-tolerant species that are characteristic of very acidic pit lakes also dominate here. Weakly acidic pit lakes with pH > 4.5 are very rare due to the lacking buffer system.

The metazooplankton community can serve as a reliable and simple biological indicator of water quality in acidic pit lakes (Nixdorf et al., 2005). Colonization patterns mostly reflect physiological thresholds of individual species. Hence, species composition and community structure is intimately related to chemical conditions, whereas variation due to biotic interactions and within-lake habitat heterogeneity is almost absent. Pit lakes with similar water chemistry conditions, though they

might be different in their morphology, mixis regime and trophic status, are still remarkably similar with respect to their zooplankton communities. All this makes zooplankton well-suited for bio-indication of ecological quality in acidic pit lakes.

3.3.1.3 Prokaryotic Microorganisms, Protists, and Fungi

Katrin Wendt-Potthoff

Bacterial Numbers and Biomass in Acidic Pit Lakes

Total bacterial numbers determined by epifluorescence microscopy in acidic pit lakes are similar to those of natural lakes and in many cases correspond to the trophic state of the lake inferred from primary production. Most acidic pit lakes in Germany are oligotrophic, and their bacterial counts normally do not show distinct vertical or seasonal patterns. Generally, the bacterial counts are roughly 10% of those from natural hard-water lakes (Nixdorf et al. 2003). Spanish pit lakes, which result from ore mining and include many meromictic lakes, often show pronounced vertical differences in bacterial numbers. For the numerous Australian pit lakes, no data on bacterioplankton, fungi, or heterotrophic protists are available.

Bacterial cell counts in acidic pit lakes are positively correlated to DOC concentrations (Kampe et al. 2010). In a comparative study of four pit lakes in Lusatia, average values lay between 1.6 and 3.4×10^5 cells mL^{-1}, with the highest values found in the most acidic (and oldest) lake. However, a neutral pit lake in the same region, which was studied as a reference, had bacterial counts of 4.9 $(\pm 4.4) \times 10^5$ cells mL^{-1} (Table 3.15). For Lake 111, bacterial cell numbers were confirmed by subsequent studies (Müller 2004; Pöhler et al. 2002), so they appear to be stable with time. The bacterial counts of acidic lakes correspond to bacterial biomass and production, which are negatively correlated with pH and in the same range as those of natural lakes (Kamjunke et al. 2005). In contrast to the Lusatian lakes, pronounced vertical gradients of bacterial counts were found in Spanish pit lakes, with maxima at the surface in a dam (Malki et al. 2006) and in the rather young and meromictic San Telmo lake (Sánchez-España et al. 2007). In the latter, bacterial counts reached 10^8 cells mL^{-1} in the upper 5 m, showed a minimum of $\approx 10^6$ cells mL^{-1} in the deeper mixolimnion, and increased again to 3.6×10^6 cells mL^{-1} in the anoxic monimolimnion. The Berkeley Pit in Montana, USA, had bacterial counts around 10^5 mL^{-1} in the upper part and lower counts at depths >55 m (Mitman 1999).

The percentage of filamentous organisms in bacterioplankton is often high in pit lakes and seems to be negatively correlated with pH. When filaments longer than 10 μm were considered, their proportion was below 1% in 11 of 12 samples in the neutral pit lake, Lake B. Bacterioplankton of the acidic pit lakes, Lake 111 (pH 2.6) and Lake 107 (pH 2.3), comprised 13 ± 9 and 17 ± 7% filaments (median $\pm$ standard deviation, $n = 12$ and 10, respectively; Babenzien and Meier

Table 3.15 Bacterial counts and percentage of cells forming microcolonies on polycarbonate filters (mean ± standard deviation), determined by epifluorescence microscopy after staining with acridine orange

Lake	117 (pH 3.0)	107 (pH 2.3)	111 (pH 2.6)	B (pH 8.0)	F (pH 2.8)
Total bacterial counts (mL^{-1})	$1.8 \pm 0.5 \cdot 10^5$ ($n = 12$)	$3.4 \pm 2.0 \cdot 10^5$ ($n = 8$)	$2.8 \pm 2.0 \cdot 10^5$ ($n = 24$)	$4.9 \pm 4.4 \cdot 10^5$ ($n = 23$)	$1.6 \pm 1.0 \cdot 10^5$ ($n = 23$)
% of cells forming microcolonies	23 ± 12 ($n = 12$)	n.d.	26 ± 9 ($n = 20$)	23 ± 10 ($n = 22$)	25 ± 19 ($n = 21$)
% of microcolonies with 2–3 cells	82 ± 8 ($n = 11$)	n.d.	60 ± 25 ($n = 20$)	70 ± 21 ($n = 22$)	71 ± 12 ($n = 20$)
% of microcolonies with 4–11 cells	11 ± 6 ($n = 11$)	n.d.	15 ± 11 ($n = 20$)	21 ± 17 ($n = 22$)	21 ± 19 ($n = 20$)
% of microcolonies with >12 cells	7 ± 3 ($n = 11$)	n.d.	9 ± 8 ($n = 20$)	9 ± 8 ($n = 22$)	9 ± 5 ($n = 20$)

Sampling took place between 1995 and 1997. Microcolony formation was not determined (n.d.) for Lake 107 because of the large fraction of filamentous cells. Applying one way ANOVA and subsequent pairwise comparison by the Holm-Sidak method, total bacterial counts in the neutral Lake B were significantly different from Lake 117, 111 and F, but not from the most acidic Lake 107
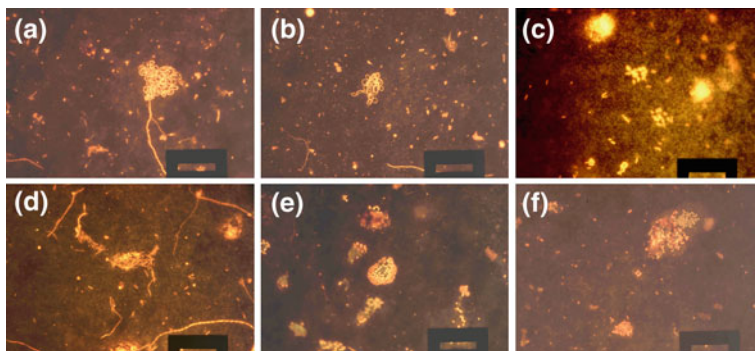
Fig. 3.55 Micro-organisms with "curled" morphology from **a** Lake 111 and **b** Lake 107. Microcolonies grown on polycarbonate filters from **c** Lake 117, **d** Lake 107, **e** Lake F, **f** the neutral pit lake, Lake B. Bars indicate 10 μm

1998, unpublished report); a later study (Müller 2004) reported around 11% filamentous cells in Lake 111 with a total cell count around 10^6 mL^{-1}. In addition to straight filaments of various sizes, conspicuously curled morphologies also occurred (Fig. 3.55a, b). A high proportion of filamentous forms can be a consequence of grazing pressure. In acidic pit lakes, bacteria are mainly grazed by phago-mixotrophic flagellates of the genus *Ochromonas* (Sect. 3.3.1.4).

Since microscopic counts of fixed cells not necessarily represent viable organisms, and microorganisms from the environment mostly fail to grow on solid culture media, dilution cultures in liquid media or microcolony assays using membrane filters (Straskrabova 1972) are used to enrich organisms or to test the viability of microscopically visible cells. Microcolony assays using white polycarbonate membranes have been successfully applied for acidophiles (de Bryun et al. 1990); this method has been modified to assess the ability of acidic pit lake microorganisms to divide with only their original 0.2 μm filtered lake water as a substrate (Wendt-Potthoff, unpublished). After 48 h, cells were fixed and stained with acridine orange following the protocol of Binnerup et al. (1993), and cell and microcolony numbers were counted using a filter immediately fixed after sampling as a reference. Some typical microcolonies are shown in Fig. 3.55 (c–f). Roughly 25% of total cells were able to divide on the polycarbonate membranes in both the neutral and acidic pit lakes. Most of the colonies (around 70%) were small, indicating that time and resources were only sufficient for one to two divisions (Table 3.15). However, larger colonies also formed with all of the studied lake waters, and their percentages were similar (Table 3.15). There is little published information to rank these results. They are within the range found for marine bacteria in membrane cultures with seawater and mud extract (0.8–66.1%, Bianchi and Giuliano 1996) and similar to those obtained with a slide culture approach without additional nutrients on freshwater and sewage samples (Fry and Zia 1982). Bartscht et al. (1999) found a higher percentage of $58.3 \pm 23.1\%$ dividing cells with a synthetic freshwater medium, but in this case, 15 mg L^{-1} of natural DOC was added, and the incubation time was 10 days.

In addition to the high percentage of cells able to divide with only lake water as a substrate, pit lake microbiota also showed a high potential to utilize ^{14}C-glucose during incubation at in situ temperature (Babenzien and Meier 1998, unpublished report). The process was temperature-dependent; in summer, uptake rates of 0.13–0.67 μg C L^{-1} h^{-1} were measured in Lusatian acidic pit lakes. These are in the range of activities measured in natural mesotrophic lakes and above that of the neutral reference pit lake, Lake B (0.12 μg C L^{-1} h^{-1}). The fraction of ^{14}C-glucose converted to CO_2 was not considered in these experiments. Metabolism of ^{14}C-glucose was also studied in summer samples from Reservoir 29, a lake that receives acidic drainage from coal refuse piles (Gyure et al. 1987). In this study, both uptake and respiration were considered, and there was a clear trend of increasing glucose utilization with depth. When converting these data, their range was either 0.04–8.6 or 0.2–43 μg C L^{-1} h^{-1} because of inconsistent information about label addition. Assuming that respiration accounts for approximately 30% of the measured activity (Hobbie and Crawford 1969), rates are comparable except for the deep-water measurements from Lake 29, which are roughly tenfold higher. Together with the fact that bacterial growth in acidic pit lakes was greatly limited by DOC availability (Kamjunke et al. 2006), this confirms the importance of heterotrophic metabolism in acidic pit lakes. The role of substrates and energy flow within the pit lake food web is discussed in detail in Sect. 3.3.1.4.

In conclusion, the numbers, biomass, viability, and thus the acclimatization of acidic pit lake bacterioplankton to the prevailing conditions appears to be comparable to that of other aquatic habitats.

Taxonomic Composition of Bacterioplankton in Acidic Pit Lakes

Information regarding the taxonomic composition of bacterioplankton in acidic pit lakes is scattered and inconsistent. The diversity of bacteria does not generally decline with sinking pH values, and the bacterial community composition in geographically close pit lakes of different pH appears to be similar (Kampe et al. 2010). The communities consisted mainly of alpha-, beta-, and gamma-Proteobacteria (>90% in most samples); Actino- and Acidobacteria were only minor components. Despite similar bacterial counts throughout the year, strong seasonal changes of community composition became evident by sequencing PCR products obtained with universal bacterial primers after denaturing gradient gel electrophoresis (DGGE; Kampe et al. 2010).

In a separate study, a clone library was prepared from Lake 111 water by 16S rDNA amplification with bacterial primers. Sequences of obligately anaerobic microorganisms were not detected in the clone library, corresponding to the oxic status of the water column. Here, the most prominent groups among the bacteria were *Acidobacteria*, *Acidiphilium* and, surprisingly, organisms affiliated with *Nitrosomonas* and *Legionella* (Müller 2004, Fig. 3.56). Ammonia oxidizers have also been found to be important in mine waters in North Wales (Hallberg et al. 2006). The presence of *Legionellae* was confirmed by Kampe et al. (2010). Members of the genus *Legionella*
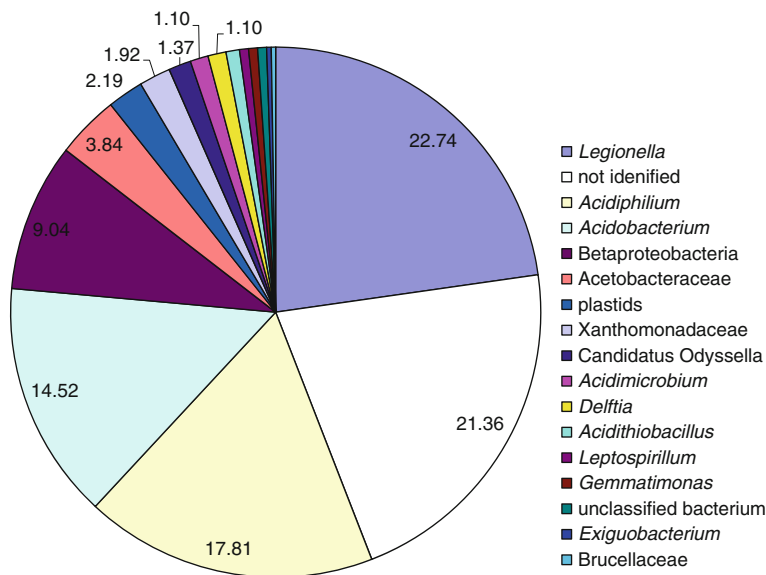
Fig. 3.56 Phylotypes detected in a clone library from a mixed water sample of Lake 111. The legend denotes taxa in decreasing order of percentage from *top* to *bottom*. The high fraction of clones that were not identified includes very rare phylotypes that were not further characterized. Percentages are given for taxa comprising more than 1% of the clones (data from Müller 2004)

(and of candidatus *Odyssella* as well) occur as endosymbionts in free-living amoebae (see review by Horn and Wagner 2004), and appreciable numbers of amoebae were also detected in Lake 111 (Müller 2004, see below). Although this association of microorganisms has not been reported from any other acidic pit lake, Legionellae and their potential host amoebae have been detected in a pH 2.7 geothermal stream in Yellowstone National Park (Sheehan et al. 2005). The fraction of unidentified clones in the Lake 111 clone library includes many rare phylotypes that were not further characterized. This indicates that the true diversity of Lake 111 bacterioplankton was not fully resolved by this clone library, though the phylotypes most frequent at the time of sampling could be classified. Müller (2004) also investigated Lake 111 bacterioplankton by whole cell hybridization. With eubacteria-directed probes, approximately 57% of all cells were marked. Among these, alpha-proteobacteria (27.6% of total cells) were most prominent, followed by gamma- and beta-proteobacteria and acidobacteria (7.2, 4.3, and 6.4% of total cells, respectively). The probe for alpha-proteobacteria stained many of the filamentous cells. For *Acidobacteria* subdivision 1, an improved oligonucleotide probe for whole cell hybridization was designed, and seasonally varying counts of $0.4–3.7 \times 10^4$ cells mL^{-1} were detected with this probe in Lake 111 bacterioplankton. This is equivalent to 37–70% of cells detected by the probe EUB338, and to 1.4–7.9% of all DAPI-stained cells (Kleinsteuber et al. 2008).

The Spanish pit lake San Telmo also showed a high percentage (47–78%) of alpha-proteobacteria (which include *Acidiphilium*) in the upper mixolimnion; in the lower part of the mixolimnion, *Leptospirillum*-like organisms (17–22%) were also important (Sánchez-España et al. 2007). *Acidithiobacillus*-related bacteria were generally rare in pit lake waters (Kamjunke et al. 2005; Sánchez-España et al. 2007). This is remarkably different from the prokaryotic diversity in the water column of the Río Tinto, about 80% of which was attributed to *Acidithiobacillus ferrooxidans*, *Leptospirillum ferrooxidans*, and *Acidiphilium* spp., all of which are involved in iron cycling (González-Toril et al. 2003).

Two reservoirs associated with the largest open pit copper mine in China (termed YTW and ZJ, both pH 3), which contained a mixture of acid mine drainage, infiltration water, and rain, were obviously dominated by gammaproteobacteria (61 and 90.1% of clones, Yin et al. 2008). This group includes *Acidithiobacillus ferrooxidans*, and 28.2 and 27.5% of clones from YTW and ZJ were related to this species. Despite their equal pH, the chemistry of the reservoirs exhibited pronounced differences, with YTW having similar concentrations of iron and aluminum (both between 900 and 100 mg L^{-1}) and ZJ being rich in aluminum and copper (1,588 ± 206 and 213 ± 26 mg L^{-1}) associated with moderate (198.61 ± 17.9 mg L^{-1}) iron concentrations. This may explain the much lower total bacterial diversity (a Shannon–Weaver diversity index of H = 2.23 compared to 4.16 in YTW) in that reservoir (Yin et al. 2008). Although much effort has been made to cultivate bacteria from tailings and acid mine drainage streams in recent years (e.g. Diaby et al. 2007; Johnson et al. 2001), there seems to be no such study on acidic pit lake water. However, an isolate from Lusatia was identified as *Acidiphilium organovorum* by fatty acid analysis (Wendt-Potthoff et al., unpublished).

In contrast to findings from extreme acid mine drainage, where archaea can account for up to 50% of prokaryotic cells in summer samples (Edwards et al. 1999), archaea seem to be less important in the cooler and more dilute waters of acidic pit lakes. Few archaea (3%) were detected in the water of the Spanish pit lake San Telmo (Sánchez-España et al. 2007). In Lake 111, abundance and diversity of archaea was also low. Except for some non-thermophilic Crenarchaeota, they were affiliated to Thermoplasmatales (Müller 2004). No archaea were found in clone libraries from three samples of the acidic river Rio Tinto in Spain, and few archaeal cells were detected by whole cell hybridization (Garrido et al. 2008).

The occurrence of live cyanobacteria has not been reported from acidic pit lakes so far, but related sequences have been detected in PCR products obtained with universal bacterial primers following DGGE and sequencing (Kampe et al. 2010). Sequences of other phototrophic prokaryotes were not found, and bacterial pigments indicative of such organisms are also generally absent (Kamjunke et al. 2005). A special situation may arise in meromictic pit lakes. If the monimolimnion is close to neutral and sulfidic, anoxygenic phototrophic bacteria may establish a presence at the chemocline. So far, only two such cases have been reported, in the small lakes Waldsee and Lugteich in Lusatia (Rücker et al. 1998). Waldsee has a naturally high input of organic matter in the form of leaf litter, and Lugteich had received municipal sewage that had only been mechanically treated from approximately 1970–1990.

Pigment analyses revealed the presence of green sulfur bacteria, Chlorobiaceae, with bacteriochlorophyll –d concentrations of up to 500 $\mu g\ L^{-1}$.

Generally, the taxonomic composition of bacterioplankton from pit lakes exhibits marked similarities with those of concentrated acid mine drainage and geothermally influenced waters. As a rule of thumb, acidic pit lakes tend to have a higher prokaryotic diversity as well as a higher proportion of heterotrophs and a lower proportion of archaea.

Fungi and Yeasts

Fungi and yeast are known to occur over a wide pH range, and a considerable diversity of isolates has been obtained from acidic habitats (e.g. Das et al. 2009; Joseph 1953). A high percentage (43% of 274 strains) of hyphomycete isolates from Rio Tinto was demonstrated to grow in Rio Tinto conditions (Lopez-Archilla et al. 2001). Fungal communities in pit lakes have not been as systematically studied as streams influenced by acid mine drainage or volcanic activity. Fungi in general have been termed "tolerant" to "common" in a collection of more than 200 mine water samples, which included pit lakes, as they were found in 8.05% of spring and 18.05% of summer samples (Lackey 1939). Yeast and fungal colonies regularly appeared on solid culture media inoculated with water samples from Lusatian lakes and were sometimes hard to separate from bacterial isolates, because fungicides were either not fully effective at pH 3, or the organisms were resistant to them. When carbon substrates were added to acidic pit lake water, fungal proliferation was observed within 24 h (Babenzien and Meier 1998, unpublished report). A yeast bloom has also been observed in situ after the addition of whey to an enclosure experiment in Lake 111 that was intended to consume the oxygen in the water column. However, none of these findings are quantitative. Colony counts of 6×10^4–$6 \times 10^5\ mL^{-1}$ have been reported from acid streams in northern West Virginia and Pennsylvania (Joseph 1953), and Gadanho et al. (2006) counted between 2 and >15,000 L^{-1} yeast colony forming units (cfu) in water samples from ponds and creeks in the Sao Domingos and Rio Tinto mines of the Iberian Pyrite Belt (pH 1.8–2.9). They used an acidified (pH 3) medium, which yielded higher counts than the conventional medium with pH 5.7. Tests with some samples revealed even higher counts when an acidic medium with water from the original sites was prepared. This shows that the yeast present in the acidic waters were well adapted to their habitat.

Using the same cultivation approach on a naturally volcanic-acidic water system in Argentina, Russo et al. (2008) counted lower yeast numbers (30–1,200 cfu L^{-1} for Rio Agrio and only 30–60 cfu L^{-1} for Lake Caviahue). Yeast diversity in a pit lake and a pond increased from spring to autumn, an as-yet unexplained observation that deserves further study (Gadanho et al. 2006). In total, 27 yeast species (both ascomycetous and basidiomycetous) were isolated, of which 48% might represent undescribed taxa. Among these, a *Cryptococcus* sp. required low pH for growth, a property that had not been observed before in yeasts (Gadanho et al. 2006). The

acid-tolerant yeasts belonged to other *Cryptococcus sp.*, *Lecytophora sp.*, *Candida fluviatilis*, *Rhodosporidium toruloides*, *Williopsis californica*, and *Rhodotorula* sp. A truly acidophilic *Cryptococcus* sp. was also isolated by Russo et al. (2008) from the volcanic-acidic Rio Agrio-Lake Caviahue environment. Moreover, a *Cryptococcus* sp. with a growth optimum at pH 3 and almost no growth at pH 8 was isolated from an acidic pond at Smoking Hills in Canada, and was shown to live in a mutualistic relationship with the acidophilic alga *Euglena mutabilis* (Nakatsu and Hutchinson 1988). This possibly indicates a widespread occurrence and environmental significance of such *Cryptococcus* species.

Regarding the in situ activity of fungi, Satake and Saijo (1974) postulated that the heterotrophic activity in waters below pH 3 were mainly attributed to molds, but at that time, there was no substantiating in situ data. Schlief and Mutz (2005), investigating fungal biomass and respiratory activity in a Lusatian pit lake, found maximum fungal biomass in autumn and winter, probably caused by leaf fall. At the time of maximum leaf-associated respiration, fungi were responsible for 47 (±7.7) % of total respiration.

After decades of acidic pit lake research, the taxonomic structure and in situ activity of their fungal communities is still not well known. However, refinement of culture media and isolation and molecular identification of both highly acid- and metal-tolerant as well as truly acidophilic species from various acid waters will hopefully help to close this gap in the near future.

Heterotrophic Protists in Acidic Pit Lakes

Heterotrophic protists found in acidic pit lake plankton comprise mainly heliozoa, ciliates, and amoebae; sometimes, heterotrophic nanoflagellates are also present. Due to the delicate structure of protists and the extreme chemical matrix of the lake water, sampling and preservation of protists requires special care (Woelfl and Whitton 2000). Among the ciliates, members of the orders Prostomatida, Hypotrichida, and Peritrichida were detected. They typically reached maximum cell densities of 5,000–30,000 cells L^{-1} or even 335,000 cells L^{-1} in an extreme case, which are comparable to densities known from natural lakes (Packroff 2000). Hypotrichida, mostly represented by large, slow-swimming forms, was also the dominant ciliate taxon in the Río Tinto system (Aguilera et al. 2007). The regular finding of hypotrich ciliates in plankton, which are typically benthic organisms, is an unusual feature of acidic pit lakes and acid rivers and may be attributed to a lack of predatory pressure (Aguilera et al. 2007; McConathy and Stahl 1982; Packroff 2000).

In some acidic pit lakes, heliozoa appear to be the main protistan component of the plankton. They can reach cell densities of 26,000 cells L^{-1} (Packroff 2000), and be the top predators in some acidic pit lakes (Bell et al. 2006; Woelfl et al. 1998). The heliozoa present in Lake 111 were putatively identified as *Actinophrys sol*, but their cells were smaller than those of the same species found in other aquatic habitats. They exhibited pronounced temporal and vertical patterns in abundance, biomass, and cell volume, with abundance and biomass maxima in late

Fig. 3.57 Phase contrast
image of sediment trap
material from Lake 111 with
cercomonad flagellates
(*arrow*)
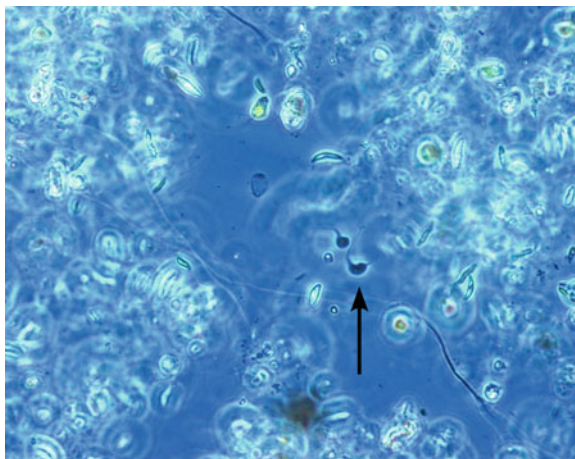
June/early July and September (Bell et al. 2006; for growth characteristics and
food web relations, see Sect. 3.3.1.4).

Müller (2004) reported 2.5×10^4 amoebae per mL in Lake 111. A high
diversity of amoebae has also been isolated from the extremely metal-rich
Berkeley Pit Lake in Montana, USA (Mitman 1999), and *Arcella vulgaris* has been
found to thrive in a highly acidic (pH 2.0) AMD-polluted lake in Ontario (Kumar
and Patterson 2000). Considerable benthic recruitment of heliozoa and rhizopods
takes place in Lake 111 (Bell and Weithoff 2003); this aspect deserves further
investigation in other acidic pit lakes.

Data on heterotrophic nanoflagellates in acidic pit lakes are scarce. As the
phytoplankton in these lakes is dominated by mixotrophic flagellates, their
heterotrophic counterparts are generally outcompeted in the illuminated part of the
water body (Rothaupt et al. 1996; Tittel et al. 2003). Packroff (2000) reported an
average heterotrophic flagellate density of 2.3×10^6 cells L^{-1} for Lake Cospuden
(East Germany), and Müller (2004) counted an almost identical value of
2.4×10^6 cells L^{-1} for Lake 111. Sediment traps deployed in Lake 111 regularly
contained some heterotrophic flagellates with a peculiar morphology, possessing
flexible cells with two flagella on opposite sides (Fig. 3.57). They were identified
as cercomonads. In addition, the widespread flagellates *Bodo saltans*, *Neobodo
designis*, *Neobodo covifilus*, and a taumathotomatid type were also found in these
samples (Markus Weitere, personal communication). A *Cercomonas* species was
also detected in a rRNA gene diversity study of the acidic river Rio Tinto (Amaral
Zettler et al. 2003), indicating that there might be cercomonads specifically
adapted to acid waters. Aguilera et al. (2007) observed a higher abundance of
cercomonads in winter months. This confirms the above-mentioned importance
of light for their distribution and biomass.

From the accessible data, it is hard to definitely judge microbial diversity in
acidic pit lakes. Often, species identification has not been possible, or clone
libraries are small and the information on seasonal patterns is missing. It appears

that microbial diversity in acidic pit lakes is higher than at extremely acidic mine sites, but lower than in natural lakes. Prokaryotic diversity is, however, higher in sediments than in the water column of acidic pit lakes (Sect. 3.3.2). Additional research is needed to understand the relationship between microbial community composition and environmental factors other than pH in acidic pit lakes.

3.3.1.4 Trophic Interactions and Energy Flow

Guntram Weithoff, Elly Spijkerman, Norbert Kamjunke and Jörg Tittel

Survival in acidic mine pits is possible for only a limited number of planktonic species (e.g. Lessmann et al. 2000; Wollmann et al. 2000; Sect. 3.3.1.1). Growth of the plankton and especially phytoplankton species has been suggested to be limited by pH, light quality and quantity, concentrations of ferric iron, zinc, aluminum, and manganese, CO_2, and inorganic phosphorus (P_i). The effects of these parameters will be evaluated separately, followed by field measurements of primary production, bacteria production, and their relation to each other. An analysis of the food web in extremely acidic lakes is provided, and the potential of "controlled eutrophication" for the abatement of acidification is discussed.

Adaptations to the Chemical Environment and to the Unusual Light Climate

pH

In many acidic mine pits, pH values are relatively stable over long time periods because the systems are buffered by high iron concentrations, which only fluctuate to a minor extent. Generally, pH values range between 2.0 and 3.5. Therefore, the lakes must be inhabited by species that are either acid tolerant or true acidophiles. In many such mine pits, a *Chlamydomonas* species can be found, often identified as *Chlamydomonas acidophila* (e.g. Gerloff-Elias et al. 2005a). *C. acidophila* can grow over a wide range of pH values, the lower pH limit lying at pH 1.5 and the upper limit at pH 7 (Fig. 3.58, Gerloff-Elias et al. 2005a; Nishikawa and Tominaga 2001; Spijkerman 2005). Its growth is optimal between a pH of 2.5 and 3.5, coinciding with the pH range of most acidic mine pits, and declines strongly at pH > 6. Maximum growth rates of *C. acidophila* at low pH are comparable to those of *Chlamydomonas reinhardtii* at pH 7 (Förster et al. 2001), indicating that low pH *per se* does not necessarily result in reduced growth.

Also, the maximum net photosynthetic rates of *C. acidophila* at pH 2.6 (308 mmol O_2 (g Chl a h)$^{-1}$) is comparable to that of *C. reinhardtii* at pH 7.0 (265 mmol O_2 (g Chl a h)$^{-1}$, Gerloff-Elias et al. 2005a; 300 mmol O_2 (g Chl a h)$^{-1}$, Förster et al. 1999), indicating that low pH also does not hamper maximum photosynthetic capacity. These results indicate that *C. acidophila* is well adapted to low pH and as this species is a main contributor to primary productivity

Fig. 3.58 Exponential growth rates of *Chlamydomonas acidophila* under non-aerated conditions over a range of external pH. Mean and SE of 3 independent replicates (modified after Spijkerman 2005)
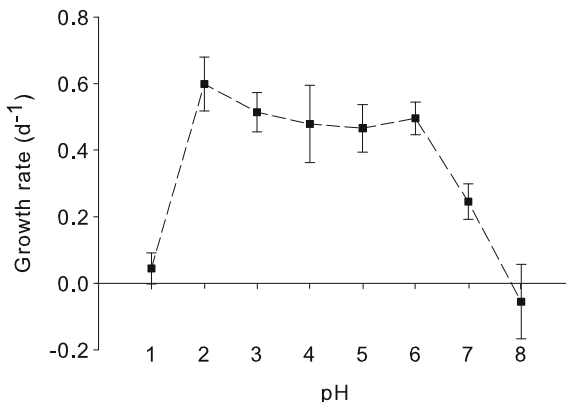
(Kamjunke et al. 2004), the relatively low primary production rates in acidic mine lakes (Kamjunke et al. 2005; Nixdorf et al. 2003) do not result from the low pH (Gerloff-Elias et al. 2005a).

Ochromonas spp. often dominates the plankton in the acidic mine pits in Germany, constituting 45–80% of plankton biomass (Kamjunke et al. 2004; Wollmann et al. 2000). An isolate of *Ochromonas* from one of these lakes, Lake 111, grew at pH 2.6 phototrophically with a rate of $0.07 \, \mathrm{d}^{-1}$, but could reach growth rates of 0.27 and $0.32 \, \mathrm{d}^{-1}$ mixo- or phagotrophically, respectively (Tittel et al. 2003). These rates are much lower than those obtained with neutral relatives who on average have growth rates of $0.46 \, \mathrm{d}^{-1}$ (max. $1.3 \, \mathrm{d}^{-1}$) under autotrophic, and $2.0 \, \mathrm{d}^{-1}$ (max. $3.14 \, \mathrm{d}^{-1}$) under mixotrophic conditions (Andersson et al. 1989; Maranger et al. 1998; Rothhaupt 1996; Sanders et al. 2001).

A dominant littoral microorganism in acid mine drainage is *Euglena mutabilis*. This algal species tolerates acid conditions down to pH 1.7, and its distribution is restricted to habitats with pH < 4.6, with prolific growth between pH 3.0 and 3.5 (Brake et al. 2001), possibly not much slower than mesophilic *Euglena* species.

Experiments with rotifer species from the genera *Cephalodella* and *Elosa* isolated from Lake 111, neighbouring lakes, and an acidic lake in Austria revealed a pH tolerance of 2.7–5 and 6, respectively (Weithoff, unpublished data). These results suggest that these rotifers are acidophiles. The calculated gross growth efficiency of *Cephalodella* sp. was in the range of isolates from neutral lakes (Weithoff 2005). In addition, the ciliate *Oxytricha* sp., also isolated from Lake 111, realised growth rates at pH 2.6 similar to that of mesophiles. It therefore appears that most species inhabiting acidic mine pits are acidophilic rather than acidotolerant, and most perform just as well at pH 2.6 as do their neutral relatives at pH 7.

Light

The underwater light spectrum in acidic mine pits is distorted and red-shifted. Contrasting to neutral lakes, only red light with a wavelength over 550 nm penetrates into the deeper water strata, whereas the blue light ($\lambda < 450$ nm) is already absorbed in the surface strata (Koschorreck and Tittel 2002;

Gerloff-Elias et al. 2005b). The light absorption in acidic mine pits results mainly from the high concentrations of dissolved ferric iron (for more detailed information, see paragraph 3.1). Consequently, the iron-rich Lake 111 (122 mg Fe L^{-1}) had an attenuation coefficient $K_d(PAR)$ of -0.7 m^{-1}, whereas it was only -0.2 m^{-1} in Lake 117 (5.5 mg Fe L^{-1}). In situ experiments revealed that *C. acidophila* exhibited a significantly higher absorption efficiency and a higher cellular chlorophyll b content when incubated in the red-shifted underwater light of Lake 111 than in the more typical, blue-green dominated light spectrum of Lake 117 (Gerloff-Elias et al. 2005b). At a depth of 7 m, where only 0.1–0.3% of surface irradiation arrives as a result of the high absorption coefficient of iron-rich lake water, benthic algal mats can still photosynthesize, using the red light very efficiently (Koschorreck and Tittel 2002).

Metals

In acidic mine lakes, concentrations of many metals are enhanced (Friese et al. 1998; Nixdorf et al. 1998; Packroff 2000), with high iron concentrations being the most striking feature. Compared with neutral lakes, Fe concentrations in acidic mine pits are about a thousand-fold higher, and they are a million-fold higher than in the Pacific Ocean, where Fe may limit phytoplankton growth (Timmermans et al. 2004). High concentrations of many metals can be toxic (Gross 2000), although acidophilic organisms are generally rather tolerant (Gimmler et al. 1991). A principal component analysis on data from the Rio Tinto (Spain) showed a cluster consisting of concentrations of most of the analyzed metals with *Dunaliella* sp., and an inverse relationship between this cluster and *Chlamydomonas* sp. (Aguilera et al. 2006). Possibly, *Chlamydomonas* sp. inhabits this site despite the high metal contamination, but its lesser pH tolerance than *Dunaliella* sp. should also be considered when looking at component analyses, as low pH and metal solubility negatively correlate (and *Dunaliella* sp. grows well at pH < 2.0).

There are several suggested compensatory mechanisms in extremophiles, such as increased accumulations of heat shock proteins (Hsps; Laksanalamai and Robb 2004). In comparison to the mesophilic *C. reinhardtii*, *C. acidophila* exhibited significantly higher accumulations of Hsps under non-contaminated culturing conditions, and an increased accumulation of small Hsps when incubated in metal-rich lake-water (Spijkerman et al. 2007a). Increased levels of small Hsps can protect photosynthesis from metal stress, as it supposedly does in higher plants (Heckathorn et al. 2004).

Gross (2000) evaluated a possible defence mechanism for acidophiles to withstand high metal concentrations via a highly positive surface charge of the outer cell membrane. The positively charged membrane and positive zeta potential allow *Dunaliella acidophila* to maintain a neutral intracellular pH, and results in both a high acid resistance and a high resistance against toxic di- and trivalent cations (Gimmler and Weiss 1999). The observed metal resistance in acidophiles can therefore be due to a general cation resistance rather than to a specific H^+ or metal resistance.
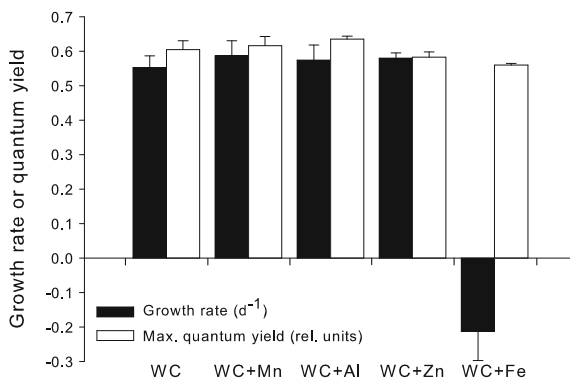
Fig. 3.59 Exponential growth rates over 5 days and maximum quantum yield after 3 days of *Chlamydomonas acidophila* cultivated in a minimal (WC) medium enriched with 11 mg Mn L^{-1}, 60 mg Al l^{-1}, 3.3 mg Zn L^{-1} or 800 mg Fe L^{-1}, reflecting metal concentrations in Lake 107 (modified after Spijkerman et al. 2007a). Results are mean and SE of 3 cultures

In *C. acidophila*, a large tolerance for Zn, Cd, Cu, and Co was described (Nishikawa and Tomanaga 2001). In contrast, after culturing the species in an Fe-rich medium, the maximum quantum yield was reduced, whereas high concentrations of Zn, Mn, or Al had no effect (Fig. 3.59, Spijkerman et al. 2007a). Repeating these experiments with $Fe_2(SO_4)_3$ instead of $FeCl_3$ revealed that it was the Fe speciation that caused the effect, and only very high concentrations of $Fe_2(SO_4)_3$ could inhibit the photosynthesis of *C. acidophila* (Spijkerman, unpublished data).

The periphytic green alga *Stigeoclonium tenue*, isolated from ditches containing mine water, was Zn-tolerant. It was able to grow and reproduce at external Zn concentrations $-\geq 1$ mg Zn L^{-1} (Pawlik-Skowronska 2003). In contrast to what would be expected, the Zn-tolerant ecotype of *S. tenue* significantly accumulated more Zn and Pb than a Zn-sensitive ecotype. Zn-toxicity experiments on neutrophiles often cover rather low concentrations; for example, the maximum concentration tested was 2.6 µg Zn L^{-1} in a marine *Chlamydomonas* sp., but resulted in a 10% decrease in growth rate (Sunda and Huntsman 1998), and similarly 5 µg Zn L^{-1} inhibited growth in *Selenastrum capricornutum* (Kuwabara 1985).

Similarly, the acidophilic protozoan *Euglena mutabilis* can grow at extremely high Fe concentrations (0.7–1.7 g Fe L^{-1}, Casiot et al. 2004) and has the ability to bio-accumulate Fe (Mann et al. 1987, 1989). *E. mutabilis* also contributes to formation of Fe-rich stromatolites by releasing intracellularly stored Fe compounds after death, which contribute to the solid material of stromatolites and act as nucleation sites for precipitation of authigenic Fe minerals (Brake et al. 2002). In addition, the acidophilic red alga *Cyanidium caldarium* also accumulated iron in acidic mine pits (Nagasaka et al. 2003). For neutrophilic algae, no Fe-toxicity values were found in the literature.

Little is known about the combined effect of metal ions and low pH on zooplankton. However, a study on several littoral crustaceans revealed that the

harmful effect of low pH can be enhanced by high concentrations of aluminum (Havens 1991a). Total cation concentrations in these experiments were much lower than concentrations typically found in acidic mine lakes. High concentrations of less toxic cations may counteract the harmful effect of low pH and high heavy metal concentrations.

In summary, multiple adaptations of acidophiles (high Hsp levels, decreased metal uptake as a result of a positive cell membrane, or storage and de-toxification of metals) increase their tolerance to high metal concentrations.

Phosphorus

One possible factor limiting primary production and biomass yield in acidic mine lakes is inorganic phosphorus (P_i; Nixdorf et al. 1996; Beulker et al. 2003, see also Sect. 3.2.1.3). Experiments performed using pulsed amplitude modulation (PAM) techniques suggested a P_i-limitation in the phytoplankton of some mine lakes in Lusatia, Germany (Lake 117 and 111, but not in Lake 107; Beulker et al. 2002). This result was explained by the higher P_i concentrations in Lake 107 (25 μg P L^{-1}) compared with those in Lake 117 (6 μg P L^{-1}) and 111 (12 μg P L^{-1}). Comparing the phytoplankton from 4 lakes containing different P_i concentrations showed a large biomass increase after P_i- enrichment experiments, suggesting that P_i is the main nutrient limiting algal growth (Fig. 3.60; Spijkerman 2008a). Also, in other acidic mine pits, P_i was acknowledged as the most important limiting factor for phytoplankton productivity (Simmons et al. 2004).

In an enrichment study performed on 4 acidic Lusatian lakes, *C. acidophila* appeared to be the most severely P_i-limited phytoplankton species (Spijkerman 2008a). In these lakes *Ochromonas* sp. dominates the biomass, but it is phagotrophic in nature and may avoid a P_i-limitation by engulfing P-rich particles such as bacteria (Schmidtke et al. 2006). *C. acidophila* is the dominant photo-autotrophic species and therefore primary productivity in the acidic mine lakes is most likely decreased by a P_i-limitation.

The minimum cell quota for phosphorus (Q_0) of *C. acidophila* (2.0–2.1 mg P g C^{-1}) was similar to that of *C. reinhardtii* (2 mg P g C^{-1}; Lürling and van Donk 1997), indicating no enhanced metabolic costs by the extreme environment (Spijkerman 2007; Spijkerman et al. 2007b). Enhanced metabolic costs should result in a higher cellular ATP content under all growth conditions, but it is best to compare species using a well-defined parameter, such as Q_0. Metabolic costs have been suggested in an isolate of *C. acidophila* from the Rio Tinto, but might consist of only a slightly increased ATP consumption rates (Messerli et al. 2005). Interestingly, the Q_0 of *C. acidophila* was higher at low than at high CO_2 conditions (Spijkerman 2007; Spijkerman et al. 2007b), demonstrating a relationship between CO_2 and P_i acquisition. Possibly, growth of *C. acidophila* in the acidic mine lakes is co-limited by CO_2 and P_i.

For bacterial production in Lake 117, indications were found for a P_i-limitation (Spijkerman 2008a), but it is acknowledged that bacterial production is generally limited by the low concentrations of organic carbon.
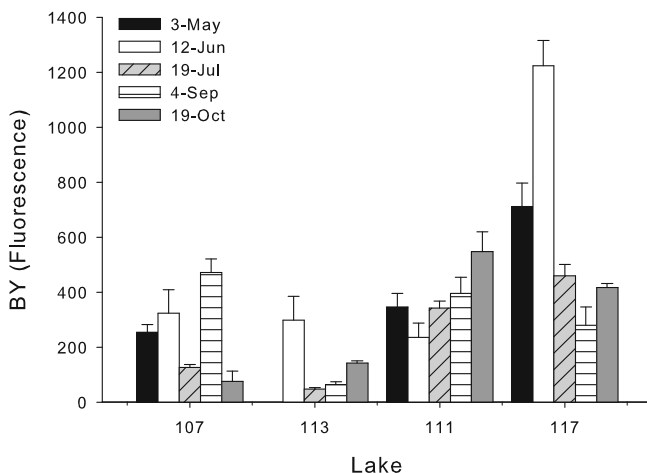
Fig. 3.60 Biomass yield (*BY*) of P-enrichment experiments after a one week incubation as measured by fluorescence of chlorophyll *a*. Lake P_i concentrations increase from *left* to *right*. Mean ± SD of 4 replicate measurements (from Spijkerman 2008a)

Carbon

In acidic waters below pH 4.0, inorganic carbon (C_i) is present only as CO_2, and HCO_3^- is virtually absent. Algae growing in acidic lakes are therefore often assumed to be C_i-limited in their natural environment (e.g. Nixdorf et al. 2003). However, adding CO_2 did not clearly enhance electron transport rates in phytoplankton samples from Lake 107, Lake 111, or Lake 117 (Beulker et al. 2002), although the phytoplankton succession revealed a clear dependence from the C_i concentration (Beulker et al. 2003). More precisely, rapidly increasing phytoplankton densities that were observed under ice and in the hypolimnion, correlated with enhanced C_i concentrations (Sect. 3.3.1.1). In addition, laboratory experiments with *C. acidophila* showed an increased maximum growth rate under high CO_2 conditions (Tittel et al. 2005). Concentrations of C_i in the upper water strata of acidic lakes are typically not much higher than equilibrium concentrations of CO_2 with the air (about 0.2 mg C l^{-1}, Tittel et al. 2003). This concentration of total C_i would limit photosynthesis and growth of algae in a neutral environment (e.g. Bozzo and Colman 2000). However, *C. acidophila* has a high affinity uptake system for CO_2 by photosynthesis, with an affinity constant of 0.025 mg C l^{-1} (Cuaresma et al. 2006; Spijkerman 2005, 2008b), similar to that in *C. noctigama* at pH 6.3 (van Hunnik et al. 2000) and *C. reinhardtii* (Bozzo and Colman 2000). Consequently, maximum photosynthetic rates can be realised in situ. Recent experiments suggest that high population densities, a P_i limitation and/or high concentrations of Fe might result in a CO_2 limitation, but much work still needs to be done. Only CO_2 enrichment experiments can reveal if C_i is indeed a growth limiting factor for the phytoplankton in acidic mine pits. These experiments will be difficult as the increased maximum growth rate at high CO_2 will likely not be realised in the field due to other population regulating factors.

Mixotrophy and Resource Limitation of Consumers

Mixotrophy as a Strategy to Overcome Resource Limitation

Mixotrophic organisms combine photosynthesis and the uptake of organic resources as modes of nutrition (Jones 1994, 2000). This phenomenon is especially common in flagellates. The relative contribution of mixotrophs to total phytoplankton biomass increases with increasing "extremeness" of the habitat. Two ways of mixotrophy can be distinguished: osmo-mixotrophy and phago-mixotrophy. Osmo-mixotrophic organisms can take up dissolved organic carbon compounds of both autochthonous and allochthonous origin. Phago-mixotrophic flagellates are able to ingest particles, e.g. bacteria or small algae. Both types supplement their photosynthetic carbon fixation by uptake of organic carbon when photosynthesis is limited. The degree of mixotrophy varies among species, that is, some use both carbon sources simultaneously most of their life, and some are mainly restricted to one carbon source and use the other only when the favourable carbon source is limited (Jones 1994). The uptake of dissolved organic carbon (DOC) in osmo-mixotrophic flagellates leads to potential competition with bacteria. In laboratory experiments, *C. acidophila* isolated from Lake 111 was capable of using the natural lake DOC for growth in the light, in the dark, and also in the presence of bacteria competitors. In addition, the alga readily assimilated aromatic compounds, typically occurring as light-degradation products of humic carbon of terrestrial origin (Tittel et al. 2009). In contrast, phago-mixotrophic flagellates act as predators on bacteria and algae. Since bacteria typically have a lower C: P ratio (i.e. they are relatively rich in phosphorus) than algae, phago-mixotrophs benefit from bacteria ingestion due to both the uptake of phosphorus and of carbon (Gaedke et al. 2002). This might be one driving factor for the high abundance of the phago-mixotrophic *Ochromonas* sp. in acidic mine pits.

Resource Limitation of Consumers

In principal, consumers can be limited either by resource quantity or by resource quality. When the first trophic level (i.e. the primary producers, such as phytoplankton) are limited by nutrient availability or other factors, then this translates directly to the first consumer level. Food supplement studies with rotifers from Lake 111 exhibited a quantitative resource limitation in the epilimnion over the whole vegetation period under ambient food conditions (Weithoff 2004). Indeed, artificially enriched enclosures in this lake exhibited both a higher biomass of phototrophs and an increased abundance of rotifers (unpublished data). Food quality also affects consumer growth in acidic lakes; besides potential mineral limitation due to low phosphorus availability, biochemical limitation might be important. Mixotrophic protists are abundant in extreme habitats and can adapt their mode of nutrition according to environmental conditions. These may change seasonally or vertically in the water column. Since the physiological pathways differ between autotrophic and heterotrophic nutrition, the biochemical
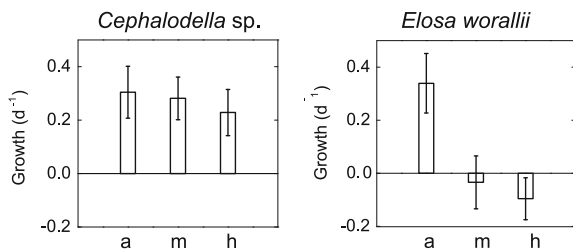
Fig. 3.61 Exponential growth rates of the rotifers *Cephalodella* sp. and *Elosa worallii* feeding on autotrophic (*a*), mixotrophic (*m*) and heterotrophic (*h*) *Chlamydomonas acidophila*. Data from life table experiments, error bars denote the 95% confidence interval (modified from Weithoff and Wacker 2007)

composition of protists strongly depends on their resource supply (Boechat et al. 2007; Poerschmann et al. 2004). Significant differences in the biochemical composition were found (e.g. in the composition and total amount of fatty acids). In particular, concentrations of polyunsaturated fatty acids are reduced when the heterotrophic pathway is employed (Boechat et al. 2007; Poerschmann et al. 2004). These fatty acids are often essential in zooplankton consumers and the lack of them may significantly reduce their growth. A case study with the osmo-mixotrophic *C. acidophila* grown heterotrophically (in the dark with glucose), mixotrophically (in the light with glucose), and autotrophically (in the light without any organic carbon source) demonstrated species-specific effects on the life history of rotiferan consumers. *Cephalodella* sp. achieved similar growth rates with all three types of *Chlamydomonas*, whereas *Elosa worallii* exhibited positive population growth only with autotrophic *Chlamydomonas* (Weithoff and Wacker 2007; Fig. 3.61). Thus, the competitive abilities of the consumers change according to the mode of nutrition of the mixotrophic flagellates (Hartwich et al. 2010). These results reveal that the performance of consumers is not only determined by the physical and chemical characteristics of mine lakes, but also by the biochemical composition of their resource.

Pelagic Primary Production and Bacterial Production in Lusatian Mine Lakes

In Lusatian mine lakes (Germany) of different pH, there was no relationship between pelagic primary production (PP) and pH. The highest PP was measured in the least acidic lake (Lake 117, pH 3.0), moderate values in the most acidic lake (Lake 107, pH 2.3), and the lowest PP in the lake with a pH of 2.6 (Lake 111). Overall, mean PP in all three mine lakes (14 μg C L^{-1} d^{-1}) was far below the means observed in many other lake systems (184 μg C L^{-1} d^{-1}, median 72 μg C L^{-1} d^{-1}; Cole et al. 1988). PP was in the range of values observed in polyhumic lakes, where PP was mainly limited by light (Ahtiainen et al. 1985;

Arvola 1984). PP in the acidic mine lakes could therefore be light limited, due to the high concentrations of dissolved ferric iron. Alternatively, the high seston C: P (mol:mol) ratio, ranging between 500 and 650 (Spijkerman 2008a), suggests that a P_i-limitation lowers PP. Overall, PP might be limited by a complex interaction of factors and vary with water depth (light availability), season, and among different lakes.

Bacteria

Most of the bacteria found in acidic mine lakes in Lusatia (Germany) were chemo-organo-heterotrophic, i.e. they take up organic compounds and gain energy from respiration. Chemolithotrophic bacteria (i.e. bacteria that use inorganic resources for gaining energy) of the genera *Acidithiobacillus* and *Leptospirillum* were found in very low numbers in the aerobic pelagic zone of the acidic mine lakes (Kamjunke et al. 2005; see also Sect. 3.3.1.3), so their metabolism can be assumed to be of minor importance compared to that of heterotrophic bacteria. Furthermore, no light absorption characteristic for bacterial pigments (bacteriochlorophyll or rhodopsin) was observed and, thus, no bacterial photosynthesis took place (Kamjunke et al. 2005). The bacteria comprised at least four species of the genera *Acidiphilium*, *Acidocella*, and *Acidosphaera* (Kamjunke et al. 2008). In contrast to mine waters in China (Yin et al. 2008), no differences in bacterial composition were observed in German lakes of different pH (Kampe et al. 2010).

Biomass and Production

In the Lusatian mine lakes, bacterial biomass showed values of 4–16 µg C L^{-1} in Lake 117, 8–59 µg C L^{-1} in Lake 111, and 22–82 µg C L^{-1} in Lake 107 (Kamjunke et al. 2005). Bacterial production (BP) ranged between 2–19 µg C L^{-1} d^{-1} in Lake 117, 4–17 µg C L^{-1} d^{-1} in Lake 111, and 8–45 µg C L^{-1} d^{-1} in Lake 107. The mean BP in all three mine lakes (10 µg C L^{-1} d^{-1}) was in the range of the mean (26 µg C L^{-1} d^{-1}, median 11.5 µg C L^{-1} d^{-1}) reported by Cole et al. (1988). The biomass-specific BP amounted to 0.06–1.8 d^{-1} (one value 2.6 d^{-1}, mean 0.78 d^{-1}) in Lake 117, 0.03–2.3 d^{-1} (one value 3.3 d^{-1}, mean 0.73 d^{-1}) in Lake 111, and 0.06–2.0 d^{-1} (mean 0.70 d^{-1}) in Lake 107, and fell in the range observed by Tremaine and Mills (1991) in acidic lakes with a pH of 3.6 (1.1–1.9 d^{-1}). Biomass-specific heterotrophic production (HP) in the mine lakes showed no dependence on pH but was positively related to water temperature ($p < 0.001$). The Q_{10} value (factor of increase within 10°C) amounted to 2.45 and agreed with literature values from non-acidic environments, which usually range between 2 and 3 (Lee et al. 2001; Pomeroy and Wiebe 2001; White et al. 1991).

Total bacterial biomass and production were negatively related to pH, and the highest values were observed in the most acidic, most iron-rich lake (Fig. 3.62; Kamjunke et al. 2005). Bacterial biomass was probably promoted by iron photoreduction. In non-acidic waters, DOC is photochemically degraded (Kieber et al. 1989)

Fig. 3.62 Negative correlation (p < 0.001) between the vertical means of bacterial biomass and bacterial production (*BP*) and the pH in three acidic lakes of eastern Germany with different, extremely low pH and high iron concentrations. Modified after Kamjunke et al. (2005)
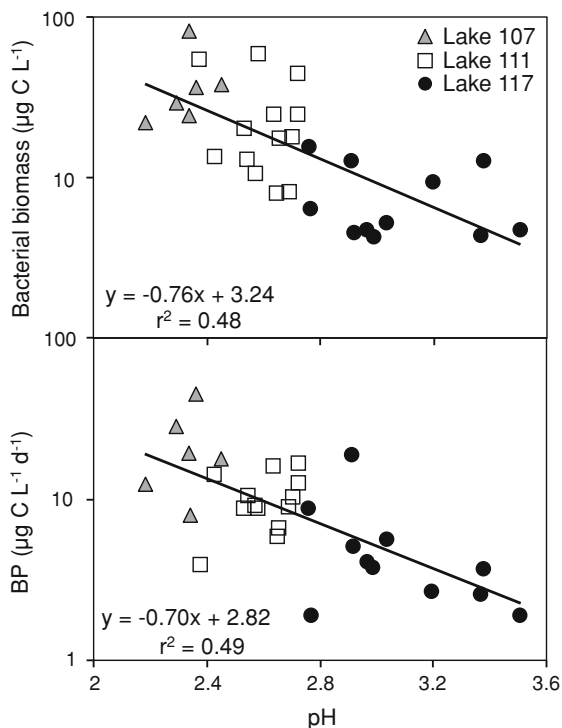
by UV irradiation and photosynthetic active radiation (PAR; Graneli et al. 1996, 1998; Wetzel et al. 1995). This mechanism differs in iron-rich mine lakes, where UV and short wavelength PAR are absorbed within the uppermost layer (Koschorreck and Tittel 2002) and the photolysis of Fe(III) aquo complexes generates hydroxyl radicals that react with refractory DOC (Brinkmann et al. 2003; Friese et al. 2002; Herzsprung et al. 1998). Light stimulated the formation of ferrous iron, changed the DOC composition (formation of low-molecular-weight organic acids, such as acetate, formate, and pyruvate), and increased the BP in laboratory experiments, suggesting that iron photoreduction caused DOC degradation (Kamjunke et al. 2005). Since the iron concentration in the mine lakes is negatively related to the pH of the waters, this may explain why measurements of BP were the highest in the most acidic and most iron-rich lake and lowest in the least acidic lake.

Carbon Sources

Vertical means of BP were not correlated with DOC concentrations, which ranged between 0.3 and 2.2 mg C L^{-1} in Lake 117, 0.7–2.9 mg C L^{-1} in Lake 111, and 0.1–1.8 mg C L^{-1} in Lake 107 (Kamjunke et al. 2005). The bulk of the DOC in the lake consists of polymeric fulvic acids (Poerschmann et al. 2004) that cannot be used directly by bacteria, whereas qualitative changes in chemical composition
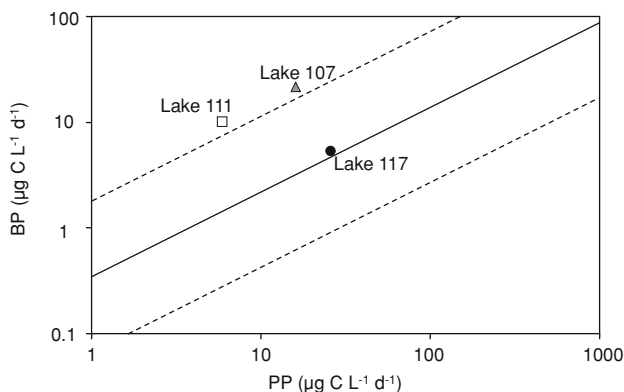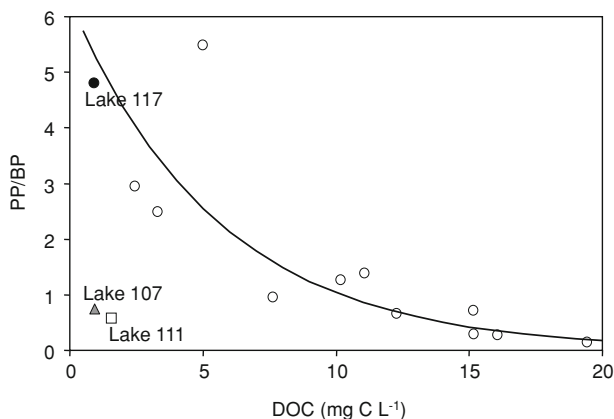
Fig. 3.63 Relationship between bacterial production (*BP*) and primary production (*PP*) of many water bodies. The line shows the regression of Cole et al. (1988; logBP = 0.8 logPP − 0.46) with 90% CI for the values. Data points represent data from acidic mine lakes of eastern Germany (modified after Cole et al. 1988)

of the DOC after degradation allow increased bacterial assimilation and utilization of the organic substrates (Wetzel et al. 1995). Unlike other lakes (Coveny and Wetzel 1995; Kamjunke et al. 1997; Robarts et al. 1994), there was no significant relationship between vertical means of BP and PP in the mine lakes (Kamjunke et al. 2005). This uncoupling is the first indication that planktonic PP was not the bacteria's main carbon source. Comparing average BP and PP of many waters, the data points of the more acidic, iron-rich, Lakes 111 and 107 are situated above the regression line (Fig. 3.63).

The high importance of other carbon sources is supported by high ratios of BP to PP, ranging between 0.08–2.0 in Lake 117, 0.7–10.8 in Lake 111, and 0.7–1.5 in Lake 107. Contrary to results from many other systems, BP was on the same order as PP in the lakes, and exceeded it in two-thirds of all cases. The majority of the values were far above the mean proportion of 20% BP compared to PP, as reported in many other lakes (Cole et al. 1988). Values above 100% have been observed, mainly from humic lakes with high DOC concentrations (above 10 mg C L^{-1}) from allochthonous inputs (Jansson et al. 2000), whereas such values were also observed for mine lakes at low DOC concentrations (Fig. 3.64). Karlsson et al. (2002) also found high BP/PP ratios in clear alpine lakes with low DOC concentrations, and their maximum ratio of 10 matched the maximum of 11 in the mine lakes. The exceptionally high ratios clearly indicate that BP in the lakes was supported by PP and additional carbon sources.

In one particular lake (Lake 111, pH 2.6), bacteria exhibited high growth rate and efficiency on exudates of pelagic and benthic algae. In contrast, they showed a lower growth rate and efficiency with organic carbon from groundwater, and grew at a very high rate but a very low efficiency on leaf leachate (Kamjunke et al. 2006). Given the magnitude of differential source inputs into the lake, benthic

Fig. 3.64 Relationship between the ratio of primary to bacterial production (PP/BP) and concentration of dissolved organic carbon (*DOC*) of many water bodies. The line with small open *circles* shows the regression of Jansson et al. (2000; PP/BP = $6.28e^{-0.18DOC}$). Large data points represent acidic mine lakes of eastern Germany (modified after Jansson et al. 2000)

primary production was probably the most important carbon source for pelagic bacteria.

Overall, it appears that bacteria play a more important role in the cycling of matter and as a basis for the whole food web in acidic mine lakes than in other lake ecosystems, and that their importance increases in more acidic and iron-rich lakes.

Accumulation of Algae in Subsurface Layers

In mesotrophic circumneutral lakes, algae often build up high biomasses at the thermo- or chemocline, leading to a deep chlorophyll maximum (DCM). These DCMs often comprise cyanobacteria and/or cryptophytes (Adler et al. 2000). A prerequisite for the formation of a DCM is a stable stratified water column. DCMs have also often been observed in mine pits. A case study of the DCM in Lake 111 revealed that the accumulation of the alga *C. acidophila* at depth was based on grazing losses in the upper water layers. *Chlamydomonas* was consumed by the pigmented flagellate *Ochromonas*. This mixotroph combined photosynthesis and prey uptake as substitutable energy resources. The abundance of prey alga reflected the critical food concentration of *Ochromonas*. The alga was reduced to low numbers if light was well available and vice versa, creating low *Chlamydomonas* abundances near the surface and a maximum at depth (Tittel et al. 2003). Such a situation leads to two partly segregated sub-habitats with differing trophic interactions and species composition (Kamjunke et al. 2004; Weithoff 2004).

Food Web Structure in Acidic Mine Lakes

The pH of the water is a major factor determining the distribution of zooplankton. For example, crustaceans, which need calcium carbonate for their carapax, suffer severely from low pH, because the dominant inorganic carbon species in such environments is CO_2. Thus, very few crustacean species occur in waters with a pH near 3 (Deneke 2000; Sect. 3.3.1.2). The lack of crustaceans and especially efficient filter-feeders such as *Daphnia* as well as the lack of higher invertebrates and vertebrates has considerable consequences for the structure of the food web and the flow of energy therein. The extreme nature of the habitat limits the length of the food chain to about two trophic levels due to the absence of higher trophic levels organisms (Gaedke and Kamjunke 2006) rather than low productivity, as suggested by Havens (1991b, which was derived from a field survey of rain-acidified lakes in North America). However, since most species are either mixotrophic or omnivorous, no straight food chains occur, though more complex interconnected trophic relations are common. Nevertheless, most of the carbon channelled through the trophic compartments is transferred by only one or two steps. Furthermore, the number of species of typical plankton groups (phytoplankton, heterotrophic protists, and rotifers) is also strongly reduced, leading to truncated pelagic food webs with a limited number of acting species (Gaedke and Kamjunke 2006; Kamjunke et al. 2004; Weithoff et al. 2010; Woelfl 2000, Wollmann et al. 2000). In neutral lakes with low abundances of cladocerans, the dominant bacterivores are phagotrophic flagellates (Jürgens 1994). This pattern was also found in a very acidic lake (Lake 111), where the estimated loss of bacterial production was mainly attributed to the phago-mixotrophic flagellate *Ochromonas* sp. The feeding of *Ochromonas* was size-selective, with highest volume-specific ingestion rates in a size range of 1.5–2 μm in diameter (Schmidtke et al. 2006).

Another key feature of these food webs is the dominance of mixotrophs and the prevailing omnivory of some consumers (e.g. Havens 1991b). As planktonic top predators, Heliozoa have been identified feeding on mixotrophic algae (*Chlamydomonas*) and on consumers such as rotifers (Bell et al. 2006; Woelfl 2000). However, as for rotifers, Heliozoa do not achieve positive growth rates with *Ochromonas* as the single food source (Bell et al. 2006; Weithoff 2004).

Increasing pH values in the range of 4–6 support an increasing number of phytoplankton and zooplankton and the resulting food web resembles the classical food web known from neutral lakes (Belyaeva and Deneke 2007; Havens 1991b; Keller and Yan 1991).

Potential of "Controlled Eutrophication" for Abatement of Acidification

Eutrophication is a classical field in limnology and the undesirable consequences of algal mass development are well known. With respect to acidic lakes and their neutralisation, however, the potential of a deliberate eutrophication has been debated for a long time (see also Chap. 4). The idea is based on the stimulation of

lake photosynthesis and organic carbon production (Davison et al. 1995) and differs from approaches in which organic carbon of external origin is supplied (Brugam et al. 1995; Klapper and Schultze 1997). Algae have also been used for the removal of heavy metals from acid mine drainage (see also case study 5.7). This has been reviewed by Das et al. (2009) and is not addressed here.

The growth and biomass production of algae can change the alkalinity directly by uptake and incorporation of inorganic nitrogen and its permanent burial in the sediment (Koschorreck and Tittel 2007). The assimilation of nitrate is associated with a gain in alkalinity, while assimilation of ammonia, which is the dominant form of inorganic nitrogen in acidic pit lakes, leads to a decrease in alkalinity (Wendt-Potthoff and Neu 1998). The photosynthetic uptake of inorganic carbon does not affect the pH, in contrast to circumneutral lakes, since bicarbonate and carbonate ions are practically absent below pH 4 and inorganic carbon is present only as dissolved CO_2 gas. Potentially more important is the indirect contribution of primary production if it serves as a carbon source for iron and sulfate reduction. These are the most significant processes of alkalinity generation in pit lakes (Blodau 2006) and their rates are typically limited by the availability of organic carbon compounds (Peine and Peiffer 1996).

There are examples indicating that internal organic carbon production can actually support iron- and sulfate reduction. In a productive lake having a moderately high phytoplankton biomass, the sediment top layer was characterised by higher organic carbon contents and lower C: P ratios compared to a less productive lake. More reduced sulfur was accumulated in the productive lakes' sediment and the pore water exhibited a neutral pH, in contrast to the lake with low phytoplankton production. The authors concluded that the potential of acidic lakes to be internally neutralised can be based on the supply of autochthonous carbon (Peine and Peiffer 1996). Other studies have also pointed to the significance of the origin and availability of organic substrates. For example, autochthonus carbon contributed 5–14% to total organic carbon in the sediment of three pit lakes but supported 50–75% of respiration (Blodau et al. 2000).

The idea that the addition of mineral nutrients stimulates the internal production of algal carbon and subsequently neutralisation has been applied to experiments at different scales. Laboratory-based mesocosms with a moderate to high base capacity of the water ($k_{B8.2}$ 2–15 mmol L^{-1}) were fertilised with phosphorus. Although dramatic increases of algal biomass could be observed, there were no significant effects on alkalinity or pH (Fyson et al. 1998a, 2006; Totsche et al. 2006). Mesocosms with a diameter of 30 m were mounted in the acidic Lake 111 (pH 2.6) and fed with straw and other substrates (Koschorreck et al. 2007a). Two years later, the leached mineral nutrients still supported a substantial algal biomass and carbon production. However, assuming that 30% of the production were channelled into iron- and sulfate reduction, the internal carbon production was sufficient to compensate for only 14% of ongoing inputs of acidity. The base capacity was very high and equalled 13–15 mmol L^{-1} (Tittel and Kamjunke 2004). The addition of organic waste products to Lake Koyne 113 (Lusatia, Germany) resulted in an increase of total organic carbon, phosphorus, and

phytoplankton biomass, up to 6 mm^3 L^{-1} and to 85 μg L^{-1} Chl *a*. However, no change of base capacity (13–15 mmol L^{-1}) was observed (Lessmann et al. 2003), and the pH remained at 2.6 (Spijkerman 2008a). In contrast to these examples from acidic pit lakes, moderate fertilization affected acidity in a rain-acidified softwater lake characterized by a low base capacity (0.01 mmol L^{-1}). The pH responded to phosphorus addition and subsequent phytoplankton growth with a moderate increase, from about 5–6 (Davison et al. 1995).

How much of the autochthonous carbon in fertilised mesocosms and lakes may be channelled into iron and sulfate reduction is not known. From planktonic organic carbon production, we can estimate an upper limit of acidity input that can be compensated for by internal lake processes. In general, acidic conditions do not prevent the development of a high phytoplankton biomass (Woelfl et al. 2000). In the acidic and polymictic Lake Niemegk (Lusatia, Germany), algal biomass peaks reached 22 g C m^{-2} and the production ranged from 0.23–11.5 g C m^{-2} d^{-1} (Zippel 2005), which is similar to biomass yield and production in hyper-eutrophic lakes. Assuming that 30% can be used for alkalinity generation, a theoretical removal of acidity of 2–117 mol m^{-2} a^{-1} can be calculated. The actual rates, however, strongly depend on the conditions at the sediment and are probably much lower (Blodau et al. 2000). This is illustrated by the example of Lake 117, where the actual rate of iron reduction was less than 1% of the potential rate derived from carbon supply (0.8 and 106 mol m^{-2} a^{-1}, respectively). The authors attributed this large difference to a possible limitation of iron availability and to competition with other processes, e.g. aerobic mineralization (Koschorreck et al. 2007b). Furthermore, high rates of gross sulfate reduction do not equal a long-term alkalinity gain, as a substantial proportion of reduced sulfur can be reoxidised and is not buried (Koschorreck et al. 2007a). In conclusion, deliberate eutrophication can be an option, if the standing stock of acidity and the inflow of acidity are low, the latter probably not higher than 0.5–1 mol m^{-2} a^{-1}. Candidates are lakes without a distinct red coloration of water. If neutral conditions are achieved, ongoing acidity inputs can be balanced by internal alkalinity generation of 0.24–1.4 and 1.6–9.5 mol m^{-2} a^{-1} in less productive and productive lakes, respectively (Koschorreck and Tittel 2007).

3.3.2 Littoral, Benthic and Sediment Zone

3.3.2.1 Macrophytes and Neophyte Invasions

Benedikt Beck and Arnulf Melzer

Introduction

The major reasons for macrophyte community changes during the last century have been eutrophication of freshwater ecosystems and acidification, caused by atmospheric deposition, and the consequences that these have had on lake water

and sediment chemistry (e.g. Arts 2002; Farmer 1990; Smolders 2002). Indicator systems based on characteristic macrophyte communities have been developed in Germany to assess the trophic status of lakes and running waters (e.g. Kohler and Schneider 2003; Melzer 1999). In addition to natural lakes, a large number of new artificial water bodies have formed in Germany over the last few decades or are in the process of being formed in the old open cast lignite mining pits (Nixdorf et al. 2005; see also Sects. 2.1 and 5.1). Many of these lakes are strongly acidified due to pyrite or marcasite oxidation. As a result, some of them offer living conditions comparable to extreme naturally occurring habitats, like volcanic crater lakes. Nevertheless, the lakes have been and are being colonized by specialized species. The most extensive work in the world on macrophyte colonization of this extreme environment was undertaken in the Lusatian Mining District (LMD) in Germany (Pietsch 1965, 1970, 1973, 1998). Overall, 234 water bodies ranging from acidic to neutral have been investigated since 1963, and a macrophyte community sequence has been developed that characterizes the aging process of the acidic mining lakes (Pietsch 1998). The latest research has focused on macrophyte species in strongly acidic mining lakes (e.g. Chabbi 1999, 2003; Chabbi et al. 2001; Fyson 2000; Küsel et al. 2003; Nixdorf et al. 2001).

There is an increasing demand for knowledge of macrophyte colonization of mining lakes. First, there are commitments to evaluate the ecological state of mining lakes larger than 50 ha to comply with the EU Water Framework Directive (WFD; Nixdorf 2005). Macrophytes are commonly used as an indicator for the ecological state of lakes and running waters (e.g. Meilinger et al. 2005; Schaumburg et al. 2004; Stelzer et al. 2005), but until now, no WFD classification for mining lakes has been developed that takes into account acidified mining lakes. In addition, mass development of indigenous and neophytic macrophytes is a problem in water ecosystems all over the world and threatens the planned usage of large mining lakes. The most prominent example is the invasion of the neophytic macrophyte species *Elodea nuttallii* in the formerly acidic mining lake Goitsche near Bitterfeld (Hilt et al. 2006; Rönicke et al. 2006). Here, the main macrophyte communities, the adaptations of selected species, and the possibility of invasions of unwanted aquatic weeds in mining lakes shall be discussed.

Vegetation of Mining Lakes

In the most acidic mining lakes, pHs down to 1.9 have been reported (Pietsch 1998). Their water is strongly buffered by an iron buffer system (Klapper and Schultze 1995; Nixdorf et al. 2003). At a pH between 4 and 5, the buffer system changes to an aluminum buffer system, which is also characteristic of acidified soft water ecosystems with a comparable pH. At a circumneutral state, a calcium bicarbonate buffer system prevails.

Pietsch (1998) identified four different stages of macrophyte colonization in mining lakes that are mostly concordant with these buffering systems. The so-called Initial and Early Stage referred to mining lakes that have a pH below 4.

The Transitional Stage included mining waters with a pH ranging from 4 to 6. The Climax Stage consisted of weakly acidic to weakly alkaline mining lakes with a pH of 6 to 8.

Young lakes of the Initial Stage were found to lack macrophyte vegetation due to extreme chemical conditions and other adverse factors, like unstable soil substrates (Pietsch 1998). The older Early Stage lakes (ca. 10 years) had somewhat mitigated chemical characteristics but still had a pH less than 4. An overview of macrophyte species occurring in these mining waters is provided (Table 3.16). The main types of vegetation described by Pietsch (1998) were dominant stands of the submerged growing bulbosus rush (*Juncus bulbosus*) and/or emergent reed species. Bog mosses (*Sphagnum* div. spec.), *Potamogeton natans*, and the neophytic *Myriophyllum heterophyllum* were also observed at a pH below 4 (Pietsch 1998; Pietsch and Jentsch 1984), and also commonly occur in Transitional Stage lakes.

In addition to the species mentioned by Pietsch (1998), Samecka-Cymerman and Kempers (2001) found the moss *Drepanocladus aduncus* as the only submerged macrophyte in a Polish mining lake at a pH of 2.8. Other mosses of the genus *Drepanocladus* are known to grow in volcanic crater lakes (e.g. Satake 2000) as well as acidic arctic ponds, at a pH from 2.8 to 3.8 (Havas and Hutchinson 1983; Hawes et al. 2002; see also Sect. 5.7.4).

Despite comparable chemical properties, the mentioned mosses do not seem to be common in acidic mining lakes. The moss *Leptodictyum riparium* has only been reported from a neutral mining lake (Hussner et al. 2005; own observation) even though it is able to survive at a pH down to 1.6 in a volcanic crater lake (Tamura 1936, cited in Havas and Hutchinson 1983). Additionally, it has been found together with a sedge, *Eleocharis acicularis*, in secondary acidified Canadian lakes (Gorham and Gordon 1963).

Flowing waters affected by acid mine drainage (AMD) in North America have often been found to be colonized by *E. acicularis* (e.g. Koryak and Reilly 1984; Kroh and Schein 1981; Rothrock and Wagner 1975). The lowest pH reported from these sites was 2.85. We have observed this species in mining lakes in Germany with a pH around 4 as well as in circumneutral pH mining lakes. Additionally Pietsch (1998) mentions an *E. acicularis* dominated vegetation type (Littorello—Eleocharietum acicularis) typical for fish ponds as one of the Climax Stages of macrophyte colonization in circumneutral mining lakes in the LMD. Other examples of submerged macrophytes in strongly acidic flowing waters affected by AMD are the liverwort *Scapania nemorosa* (Engleman and McDiffett 1996), *Sparganium emersum* (Sand-Jensen and Rasmussen 1978) and *S. americanum* (Rothrock and Wagner 1975).

For Transitional Stage mining lakes, Pietsch (1998) described various *J. bulbosus* associations that show some similarities to the vegetation of natural lakes. Massive growth of *Juncus bulbosus* together with bog mosses (*Sphagnum* div. spec.) was reported from secondarily acidified soft water lakes (e. g. Arts 2002; Melzer 1997; Melzer and Rothmeyer 1983; Melzer et al. 1985; Roelofs et al. 1995; Smolders et al. 2002). Outside of the Lusatian Mining District, this type of vegetation has been found in acidified Bavarian mining lakes near Schwandorf (C. Weilner, personal communication) and in mining waters of the Helmstedt Mining District in Lower

Table 3.16 Submerged and emergent macrophyte species occurring in mining waters with a pH below 4

Species	References
Submerged species	
Drepanocladus aduncus	Samecka-Cymerman and Kempers (2001)
Eleocharis acicularis	Rothrock and Wagner (1975)
Juncus bulbosus	Chabbi (1999), Nixdorf et al. (2001), Pietsch (1998), Wiegleb (1978)
Myriophyllum heterophyllum	Pietsch and Jentsch (1984)
Potamogeton natans	Pietsch (1998)
Sparganium americanum	Rothrock and Wagner (1975)
Sparganium emersum	Sand-Jensen and Rasmussen (1978), Nixdorf (2001)
Scapania nemorosa	Engleman and McDiffett (1996)
Sphagnum div. spec.	Pietsch (1998), Wiegleb (1978)
Emergent species	
Carex rostrata	Mayes et al. (2008), Nixdorf et al. (2001), Pietsch (1998)
Eriophorum angustifolium	Mayes et al. (2008), Nixdorf et al. (2001), Pietsch (1998)
Eleocharis acicularis	Rothrock and Wagner (1975)
Juncus bulbosus	Chabbi (1999), Nixdorf et al. (2001), Pietsch (1998)
Juncus effusus	Mayes et al. (2008), Nixdorf et al. (2001), Pietsch (1998)
Phragmites australis	Mayes et al. (2008), Nixdorf et al. (2001), Pietsch (1998)
Schoenoplectus lacustris	Mayes et al. (2008), Nixdorf et al. (2001), Pietsch (1998)
Typha angustifolia	Mayes et al. (2008), Nixdorf et al. (2001), Pietsch (1998)
Typha latifolia	Mayes et al. (2008), Nixdorf et al. (2001), Pietsch (1998)

Saxony (Wiegleb 1978). Other common species in the Transitional Stage are the fern *Pilularia globulifera*, the pondweeds *Potamogeton natans* and *P. polygonifolius*, and the mixotrophic bladderworts *Utricularia minor* and *U. ochroleuca* (Pietsch 1998). While the first three species are also known from acidic softwater lakes (e.g. Eriksson et al. 1983; Srivastava et al. 1995), the latter are typical for fens, bogs, or heath ponds (Pott 1995). As has been mentioned before, the neophytic species *M. heterophyllum* is also frequent in lakes of the Transitional Stage, developing dense dominant stands. In Germany, mainly manmade waters are colonized (Pietsch and Jentsch 1984).

Overall, Transitional Stage mining waters are rarely found in Germany outside of the LMD due to differing geological conditions. Klapper and Schultze (1995) showed that most mining lakes in the Central German Mining District (CGMD) are either strongly acidified or neutral. In the Lower Rhine Mining District (LRMD), only two small acidified mining lakes exist (Christmann 1998). The same can be assumed for some of the vegetation types of the Climax Stage displayed by Pietsch (1998). As he mentions himself, most of these are typical of the Lusatian region and mainly occur in bog and heath ponds.

Christmann (1998), in contrast, describes mainly typical hardwater macrophyte species in the LRMD. Similarly, we have found macrophyte communities known from neutral hardwater lakes in over 30 mainly neutral mining lakes in the most

Fig. 3.65 Dominant macrophyte vegetation in German mining lakes (modified and supplemented after Pietsch (1998))
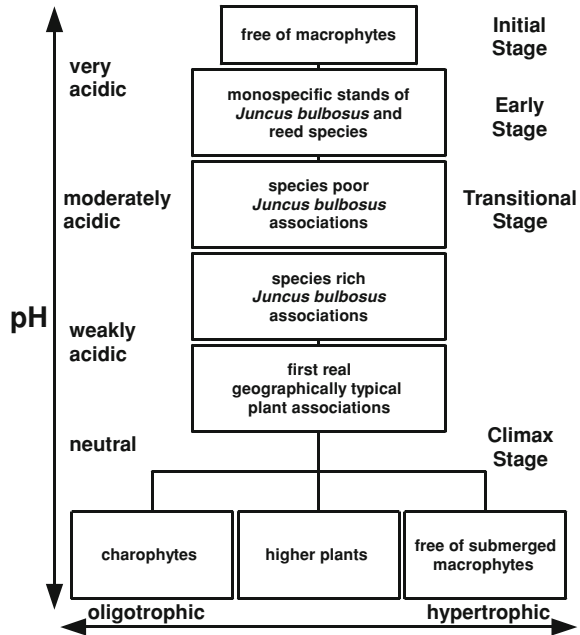
important lignite mining districts in Germany (Fig. 3.65). The species composition is mostly influenced by the trophic state, as also occurs in natural neutral hardwater lakes (Melzer 1999). Lackmann (1998) gives an example from the vegetation of three mining lakes from the LRMD. Charophytes dominate an oligotrophic lake while more eutraphent higher plants occur in the eutrophicated lakes. Pietsch (1998) mentions lakes dominated by *Chara hispida* as a possible climax state in neutral mining lakes, mainly outside of the LMD. Our investigations show that *C. hispida* is only one of several different charophyte species that frequently occur in oligotrophic mining lakes (see Table 3.17). These lakes are unusually transparent, which has allowed macrophyte vegetation down to a depth of 20 m. One intensively investigated example is the Kulkwitzer Lake west of Leipzig (Doege et al. 2006).

We have observed that mainly higher plants from the genera *Myriophyllum* and *Potamogeton* generally dominate mesotrophic to eutrophic mining lakes. Similar to natural lakes, very eutrophic mining lakes may lack submerged vegetation due to turbidity.

Strategies of Macrophyte Survival in Acidic Environments

In acidic environments, aquatic plants are faced with adverse conditions. One important peculiarity of most acidified waters is the low content of dissolved inorganic carbon (DIC) in the water column, which occurs almost totally as free CO_2, in equilibrium with the atmosphere below a pH of 4.5 (Klapper and Schultze 1995;

Table 3.17 Examples of dominant charophyte species in oligotrophic neutral mining lakes in Germany

Dominant charopyhte species	Bla	Bor	Hel	Kul	Mar	Wer
Chara contraria	▲	▲	▲	▲	▲	▲
Chara globularis	▲	▲	▲	▲		
Chara hispida			▲	▲		
Chara polyacantha			▲			
Chara vulgaris		▲			▲	▲
Nitella mucronata				▲		
Nitella opaca	▲	▲	▲	▲		▲
Nitellopsis obtusa			▲	▲		
Maximum macrophyte depth limit, m	16	19	16	19	10	13

Bla: Blausteinsee (LRMD), Bor: Borkener See (BMD), Kul: Kulkwitzer See (CGMD), Mar: Markkleeberger See (CGMD), Wer: Werbener See (CGMD), Hel: Helenesee with Katjasee (LMD); BMD: Borken Mining District (Hessen), unpublished data (Beck 2006–2007)

see also Sects. 3.3.1.1, 3.3.1.4 and 3.3.2.2). Low DIC concentrations can limit macrophyte growth at low pH more than the acidity (e.g. Pagano and Titus 2007; Roelofs et al. 1984; Titus et al. 1990). This is not the case for emergent macrophyte species, such as *Phragmites australis* or *Typha latifolia* (see Table 3.16), and species possessing floating leaves, like *Potamogeton natans* or *P. polygonifolius* (Maberly and Madsen 2002), due to their ability to use atmospheric CO_2. *Juncus bulbosus* has many adaptations that allow it to thrive in low DIC environments (Table 3.18). Wetzel et al. (1984) demonstrated the ability of bulbous rush to recycle CO_2 originating from its own respiration in the lacunar system of the plant. Additionally, the species can rely on higher DIC concentrations in sediment pore water (Roelofs et al. 1984; Wetzel et al. 1985). Root uptake can account for 15–35% of the total CO_2 demand of the plant (Raven et al. 1988), which is extremely high, second only to various isoetid species (Maberly and Madsen 2002). Additionally, the species benefits from bacterial CO_2 production in the rhizosphere as well as in the sediment–water interface (Wetzel et al. 1984, 1985). Comparable results were shown by Chabbi et al. (2001) and Küsel et al. (2003). They assumed greater CO_2 availability due to microbial decomposition of organic root exudates by bacteria inhabiting microspaces in iron plaques around the roots of *J. bulbosus*. The *Sphagnum* species that occur in acidified mining lakes or soft water lakes together with *J. bulbosus* are CO_2-dependent and do not possess roots. Observations of Roelofs (1983) show the highest sediment pore water DIC concentrations beneath *Sphagnum* beds. This indicates a "local CO_2" supply as would be the case near the sediment–water interface. Maberly and Madsen (2002) have suggested that this CO_2 uptake strategy is also used by species of the genus *Utricularia*. *Eleocharis acicularis* may possess a C_4-like carbon fixation (Keeley and Sandquist 1991) that is comparable to the crassulacean acid metabolism often found in isoetid species (Keeley 1998).

Another characteristic of acidified mining lakes is a high concentration of NH_4^+, which results from inhibited nitrification (Nixdorf et al. 2001), which can be

toxic to some aquatic plants (e.g. Glänzer et al. 1977; van Katwijk et al. 1997). Many submerged macrophyte species occurring in acidic mining lakes show a preference for ammonium uptake. *J. bulbosus* predominantly uses ammonium as a nitrogen source (Schuurkes et al. 1986) but can also use nitrate, to a lesser extent. Exclusive ammonium use and high tolerances have also been shown for different *Sphagnum* species (Paffen and Roelofs 1991; Schuurkes et al. 1986). It has been assumed that the elevation of ammonium together with DIC were key factors for extensive growth of *J. bulbosus* and *Sphagnum* in acidified softwater lakes (Arts 2002; Farmer 1990; Smolders et al. 2002). In situ experiments showed little nitrate reductase activity by *Potamogeton natans* (Melzer 1980), which implies preferential ammonium use. This is supported by reports of high ammonium concentrations in a typical *P. natans* association in a small stream influenced by acidic water from mining lake Bergwitzsee (Köck 1981). Pietsch and Jentsch (1984) describe habitats for *Myriophyllum heterophyllum* that are surprisingly low in ammonium concentrations unless it colonizes acidified sites with a pH down to 3.7. This may indicate that high ammonium concentrations negatively affect this species.

The high solubility of most metals under low pH conditions and the possibly phytotoxic effect of the resulting high concentrations is another characteristic of acidic mining lakes (Nixdorf 2001). Some macrophytes have been shown to accumulate high concentrations of heavy metals without toxic effects (e.g. Aulio 1986; Farmer 1990). This allows certain reed species to be used in wetlands constructed for remediation of polluted areas (e.g. Mayes et al. 2008). There are two principle ways for plants to avoid heavy metal toxicity; the first is to prevent the uptake of the toxic ions and the other is to dispose of any that enters the plant (Reichman 2002). Iron and manganese root plaque formation, which results from radial oxygen loss by aquatic plants and acts as a physical barrier or site of precipitation, is widely discussed as a heavy metal tolerance mechanism (e.g. Batty et al. 2002; Chabbi 1999, 2003; Ye et al. 2001). Different iron tolerances among fen plants have been shown to be related to iron plaque formation on the roots (Snowden and Wheeler 1993, 1995). Some of the most iron tolerant species of the study, like *Eriophorum angustifolium* or *Juncus effusus*, are found in strongly acidified mining lakes (Table 3.16). However, the role of the plaques is not clarified. Negative effects of root plaque formation have been shown for the acid-tolerant species *Lobelia dortmanna* (e.g. Christensen and Wigand 1998; Christensen et al. 1998). Organic acids exudation also plays a role in metal tolerance of plants by formation of complexes (Reichman 2002) but the function is also unclear and very species specific (Jones 1998). For *J. bulbosus*, organic acid exudation over the roots has been reported (Chabbi et al. 2001; Küsel et al. 2003), which might additionally favor the occurrence of the species in very acidic habitats. Internal mechanisms for metal tolerance have been reviewed by Reichman (2002) and include: compartmentation in vacuoles, complexing with phytochelatins, methallothioneins, organic acids, and inorganic and organic ligands, as well as alterations in cell metabolism. However, as the author mentioned, additional research is needed to reveal species specific mechanisms. For *J. bulbosus*, it has

Table 3.18 Effects of low pH-environment and adaptations of *Juncus bulbosus*

Effect	Adaptation	Reference
Low DIC in water column	Internal CO_2 recycling	Wetzel et al. (1984)
	CO_2 uptake from sediment and water	Wetzel et al. (1985), Roelofs et al. (1984)
	Microbial CO_2 production in iron root plaques	Chabbi (2001), Küsel (2003)
High NH_4^+ concentrations	Almost exclusive ammonium use	Schuurkes et al. (1986)
High concentrations of dissolved metals	Iron and manganese root plaque formation[a]	Chabbi (1999)
	Exudation of organic acids[a]	Chabbi (2001), Küsel (2003)
	Internal barriers	Chabbi (1999), Chabbi (2003)
High turbidity	Extremely low light compensation point	Roelofs et al. (1985)

[a] unclear function

been shown that metals are internally accumulated at the rhizodermis, exodermis, and endodermis (Chabbi 1999, 2003). Aquatic mosses have been found to accumulate metals in or at their cell walls (e.g. Crowder 1991; Engleman and McDiffett 1996; Satake 2000). In this context, cation exchange capacities of the species play an important role (Crowder 1991; Reichman 2002), which is especially high in *Sphagnum* mosses (e.g. Breuer and Melzer 1990a, 1990b; Clymo and Hayward 1982).

Macrophyte Invasions in Mining Lakes

The invasion of aquatic ecosystems by neophytic macrophyte species and their negative consequences to the ecosystem and to public use of the water bodies are known from all over the world (Willby 2007). The economical costs of invasions can be huge. For example, mass development of *Myriophyllum spicatum* has caused annual losses of 30–45 million US $ in the Truckee River watershed in the USA (Charles and Dukes 2007).

The impacts of a neophytic invasion were impressively demonstrated by the mass development of *Elodea nuttallii* in the formerly acidic mining lake Goitsche, near Bitterfeld (Hilt et al. 2006; Rönicke et al. 2006). It occurred in 2004 only two years after the pit was fully flooded with eutrophic river water, which also led to neutralization of the lake (Schultze and Geller 2004). The plants formed dense floating canopies more than 5 m deep, which seriously restricted the use of the lake for swimming, boating, and fishing. Subsequently, the mass development has been less intense although the only countermeasure that has been taken has been mowing stands of the species. Hilt et al. (2006) mentioned annual expenses ranging from 19,000 to 130,000 € spent in mowing *E. nuttallii* in other German

lakes. Like most other neophytic aquatic weeds, *E. nuttallii* is distributed easily by fragments of the plants (e.g. Di Nino et al. 2005). In the case of Lake Goitsche, the great flood in August 2002 caused the river Mulde to break through into the lake basin. This probably led to wide distribution of *Elodea* fragments which, along with nutrients provided by the flood water and other inflows, resulted in nuisance macrophyte developments and eutrophication. Nutrient-rich sediments can also promote eutraphent species like *E. nuttallii*, even under oligotrophic conditions (Angelstein 2008).

Typically, charophyte communities dominate nutrient-poor lakes. These are not problematic, even if occurring in masses. Additionally, they are beneficial since they help maintain the oligotrophic state by acting as a nutrient sink (Hilt et al. 2006; Kufel and Kufel 2002; Kufel and Ozimek 1994). In Lake Goitsche, charophytes can compete even with the very aggressive *E. nuttallii* during ongoing oligotrophication of the lake (personal observations).

In contrast to circumneutral mining lakes, the extreme habitat conditions of strongly acidified mining lakes restrict the occurrence of macrophytes to a small group of adapted species. Even so, mass developments of *Myriophyllum heterophyllum* in mining lakes with a pH down to 3.7 have demonstrated that such ecosystems can be invaded by neophytic species (Pietsch and Jentsch 1984). Additionally, some other invasive neophytic macrophytes can colonize acidified lakes. For example *Cabomba caroliniana* (Crow and Hellquist 2000; Hogsden et al. 2007) or *Crassula helmsii* (Klavsen and Maberly 2009) might be problematic in such lakes in the future, though there is no evidence of invasions in Germany yet.

No neophytic macrophyte occurrence has been reported in the most acidified mining lakes. However, the predominant indigenous species in these lakes, *J. bulbosus*, can be considered to be invasive as well. Examples of dense floating mats can be seen in Lake Senftenberg (see Fig. 4 C in Chabbi 1999) and were described by Pietsch (1998). From natural waters, problems with mass occurrences of bulbosus rush have been documented (e.g. Roelofs et al. 1994; Rorslett 1988). Dense stands of the species can produce impressive biomass of more than 1,000 g dry weight m^{-2} (Roelofs et al. 1994). In acidic mining lakes with extensive shallow areas, even extensive stands of reed species like *Phragmites australis* might interfere with planned uses of the lake (see Fig. 3.66).

At near-neutral pH, a great variety of neophytic as well as indigenous macrophyte species are capable of causing a nuisance. Gollasch and Nehring (2006) have provided a list of aquatic neophytes in Germany. Evidence of macrophyte mass developments, mainly in natural lakes, was shown by Hilt et al. (2006), while Table 3.19 lists examples in mining lakes. Rising water temperatures associated with climate change will further increase the number of potential invasive species (Hussner and Lösch 2005; Willby 2007).

Considering the great variety of possible invaders, it has to be realized that "… invasions are more than *just likely*, they are *inevitable*." (McIntosh et al. 2007). Nevertheless, some considerations might mitigate or even prevent macrophyte invasions in future mining lakes. As has been mentioned, flooding water plays an important role. Eutrophic flooding water should be avoided whenever possible.

Fig. 3.66 Examples of dominance stands of *Myriophyllum heterophyllum* (**a**) and *Phragmites australis* (**b**) in German mining lakes (Photos by B. Beck 2006–2007)

Table 3.19 Examples of mass developments of neophytic (N) and indigenous (I) macrophyte species observed in mining lakes from acidic to neutral

Species	pH preference	Example
Ceratophyllum demersum (I)	Circumneutral	Speicher Friedersdorf[a]
Elodea nuttallii(N)	Circumneutral	Goitsche [b, c, a]
Hippuris vulgaris(I)	Circumneutral	Möhlauer See [a]
Myriophyllum heterophyllum(N)	Moderately acidic to circumneutral	Heider Bergsee [d, c, a]
Myriophyllum spicatum(I)	Circumneutral	Speicher Knappenrode [a]
Myriophyllum verticillatum(I)	Circumneutral	Zechau III [a]

[a] own observation; [b] Rönicke et al. (2006); [c] Hilt et al. (2006), [d] Hussner (2005)

Additionally, knowledge about potential invasive species in the watershed of the river could be useful in assessing invasion risk. Another problem to be considered is the planned connection of mining lakes with channels for boating. If one lake is invaded, the invasion risk for connected lakes rises due to propagule dispersion by either boating or water flow (e.g. Jacobs and Macisaac 2009). Finally, the morphology of the lake basins can promote intensive macrophyte growth by offering wide areas of shallow water with an approximate depth of 5 m or less (see Sect. 2.1). The creation of steep shores in critical lake areas could at least prevent floating stands of rooted macrophyte species.

3.3.2.2   Zygnematalean Green Algae (Streptophyta, Zygnematales) in Lakes Impacted by Acidic Precipitation, Experimental Acidification, and Acid Mine Drainage

Andreas Kleeberg

Introduction

The green algal order Zygnematales has long been known to occur in diverse habitats worldwide (West and Starkey 1915). They occur in brackish and limnic waters, including natural acidic freshwaters (Greenwood and Lowe 2006; Hoshaw and McCourt 1988) and even in the Antarctic (Hawes 1989). Zygnematales typically colonize stagnant shallow lakes, ponds, pools, acidic wetlands (Greenwood and Lowe 2006), and the slow-flowing parts of running waters over a large pH range (Hoshaw and McCourt 1988). The dispersion of the Zygnemataceae due to acidification was documented for the first time in Scandinavia (Hendrey et al. 1976) and later in experimentally acidified (pH 4.5–6.2) lakes in North America (e.g. Stokes 1986). Zygnematalean green algae (ZGA) also occur in freshwaters that have been acidified by acid mine drainage (AMD; Bray 2007; Kleeberg et al. 2006).

Previous authors have focused on diverse facets of zygnematalean biology: (1) identification (France et al. 1992), (2) distribution (e.g. Howell et al. 1990; Turner et al. 1995a, b, c), (3) function as pH indicator species (e.g. Greenwood and Lowe 2006; Jackson et al. 1990; Verb and Vis 2005; Vinebrooke 1996; Vinebrooke and Graham 1997), (4) nutrient interactions (e.g. Fairchild and Lowe 1984; Hansson 1989; Graham and Vinebrooke 1998; Müller 1980; Niyogi et al. 1999; Pringle 1987), and (5) ecophysiology (Donahue et al. 2003; Graham et al. 1996; Gross 2000; Klug and Fischer 2000; Sheath et al. 1996). These studies, mostly for North America, further emphasize the importance of Zygnematales in acidic lakes. Several review articles provide useful general coverage of Zygnematales (Hoshaw and McCourt 1988), methodology (Aloi 1990), and the effects of acidification on Zygnematales (Planas 1996).

This chapter aims to summarize scientific knowledge on ZGA in freshwaters that have been impacted by acid rain, experimental acid additions, and acid mine

Table 3.20 Systematic classification of filamentous green algae of Zygnemataceae with the acidophilic genera occurring in acidic waters, with the number of their species and their percentages on species number of the family (Kadłubowska 1984; Hoshaw and McCourt 1988)

Taxon	Species	% total
Conjugatophyceae Streptophyta (Chlorophyta)		
Zygnematales Zygnemataceae		
Spirogyra	386	49.2
Zygnema	139	17.7
Mougeotia	138	17.6
Zygnemopsis	43	5.5
Zygogonium	29	3.7

effluents, and raise issues that require future study on this functional group in acidic mining lakes. For the purposes of this project, it was not appropriate to include coverage of humic (bog/peatland) lakes or acidic hot springs.

General Features of Zygnematales

Zygnematales and Desmidiales are exceptionally diverse and numerous in acidic (humic) lakes and bogs. The Zygnematales include the unicellular saccoderm desmids and closely related unbranched filamentous algae, such as the genus *Zygnema* (for which the order is named). Zygnematales are classified in the phylum Streptophyta, which includes the land plants (Bremer et al. 1987), or in Charophyta (Lewis and McCourt 2004), instead of in Chlorophyta. Modern systematic treatments apply the term Chlorophyta to groups of green algae that do not include the Zygnemataleans. It is important to note that the filamentous zygnemataleans do not form a separate clade from closely related saccoderm unicells. Zygnematales and Desmidiales are monophyletic sister clades that together form a monophyletic group/class, variously named Zygnemophyceae or Zygnematophyceae. The family Zygnemataceae represents unbranched ZGA, which sexually reproduce by conjugation as shared with Desmidiales. 13 genera with 784 species belong to the Zygnemataceae (Hoshaw and McCourt 1988). Only a few specialized genera occurring in acidic waters (pH < 5) are considered (Table 3.20).

Distinctive Features of Zygnematalean Green Algae

Conjugation distinguishes the Zygnemataceae from all other filamentous Streptophyta, except for a few species of filamentous desmids; for details, see Kadłubowska (1984) and Hoshaw and McCourt (1988).

ZGA, such as *Mougeotia* spp., *Spirogyra* spp., and *Zygogonium* spp., excrete copious amounts of muscilaginous substances, which prevent colonization by epiphytic algae (Vinebrooke et al. 2001). The metaphytic floating growth forms may also be unreliable and physically inaccessible to most littoral organisms.

Therefore, the blooms and mats, respectively, of ZGA occur because they out-compete other species at conditions of low concentrations of dissolved inorganic carbon (DIC) and grazing pressure (Vinebrooke et al. 2001).

Chloroplast movement is a light-driven phytochrome-mediated process. For example, in response to direct light, the chloroplast of *Mougeotia* spec. rotates about the long axis of the cell to change the amount of surface area exposed to light. In low light, the large flat side of the chloroplast faces the light. In bright light, the narrow edge profile is turned toward the light (Hoshaw and McCourt 1988).

Ecological Importance of Zygnematalean Green Algae

The acidification-induced growth of ZGA in lakes is most probably primarily a water temperature governed seasonal phenomenon, whereat the maximal abundances can fluctuate from lake to lake and from year to year (Morin and Cattaneo 1992; Planas 1996). While diatoms (e.g. Bacillariophyceae) have been used for a long time for pH indication (Hustedt 1939), the ZGA were linked to the acidification of lakes considerably later (Hendrey et al. 1976). In particular, the species of the genus *Zygogonium* (Table 3.20) are acidobiontic (dependent on acidity) indicator species, which exhibit broad acidity tolerance (Vinebrooke et al. 2001).

ZGA have an important influence on nutrient cycles (C, N, and P), and partly on the deposition of nutrients (Turner et al. 1995a, b), and can considerably contribute to the benthic C accumulation. They also influence the biogenic alkalinity generation via the sulfur cycle, by moving the horizon, in which the benthic sulfate reduction occurs, into larger sediment depth where the reoxidation of deposited reduced compounds is prevented (Koschorreck et al. 2007; Turner et al. 1995b). Thus ZGA can be important for the mediation of the internal alkalinity generation of acid mining lakes (Kleeberg et al. 2006; Koschorreck et al. 2007).

The respective zonation of the ZGA can be assigned to specific ecologically defined growth forms—mostly associated with the littoral sediment –according to morphology, chemistry, trophy and light climate of a lake:

- *Periphyton*—microfloral community, which lives on surfaces of submersed objects and substrates, respectively (Roll 1939), which does not include fungi, bacteria and protozoa and other animal components (unequal to the German term 'Aufwuchs', Weber 1973).
- *Metaphyton*—amounts of filamentous algae, which are conjunct with benthic substrates. However, these algae can also form loose flocs, mats or clouds, which lie on the bottom or which float above the bottom (Behre 1956; Wetzel 1983). Metaphyton is synonym to the older terms tychoplankton, pseudo-plankton (Naumann 1931) and pseudoperiphyton (Sládečková 1960).

The classification of ZGA to peri- or metaphyton is not always clear, since periphytic algae can pass into metaphytic aggregations in response to hydrostatic pressure (Howell et al. 1990), wind-induced water movement (Turner et al. 1987),
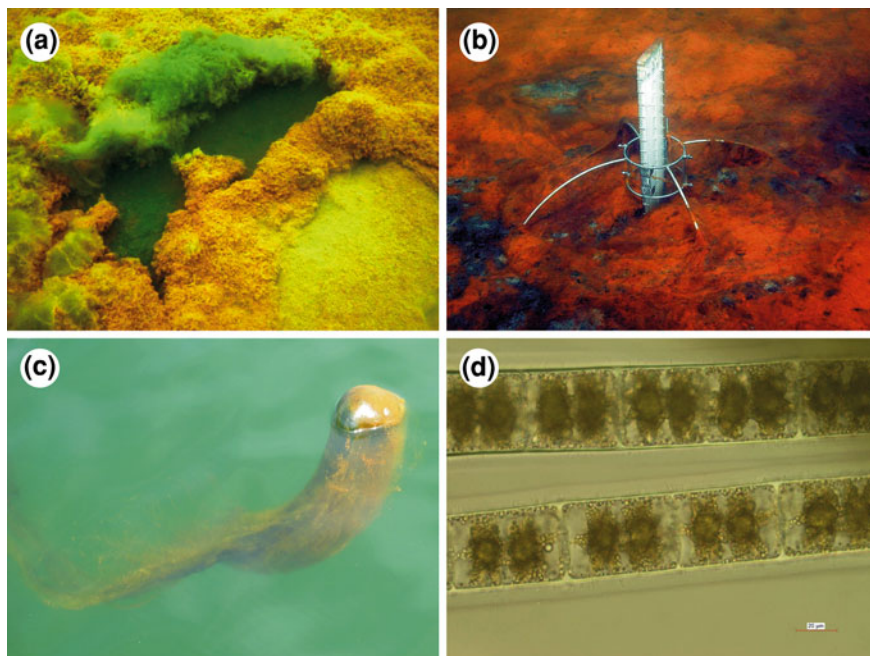
Fig. 3.67 a periphytic canopy of *Zygogonium ericetorum* at the sediment surface of acidic (pH ≈ 3) mining lake Grünewalder Lauch, Lusatia, Germany, **b** dense cover of *Z. ericetorum* at the sediment surface after 14 days of incubation of an *in situ* pore water sampler in the same lake (photos by M. Beyer), **c** momentary (jellyfish-like) flotation of *Z. ericetorum* at the water surface due to intensive O_2 production and its related enclosure of O_2 bubbles (photo by B. Grüneberg), and **d** microscopic picture of filaments of *Zygnema* spec. with the stellate and asteroidal chloroplasts, respectively (photo by H. Täuscher)

at changes of species composition along with a decreasing pH (Howell et al. 1990; Turner et al. 1995a). Intensive primary production (PP) at low depths, with simultaneous formation of O_2 bubbles within the densely-packed associations of the filaments (Fig. 3.67), supports the buoyancy of algal canopies (Hillebrand 1983).

Motility may be favored to best use environmental resources, light, CO_2, or to escape unfavorable conditions. Specific cell wall components such as algaenan, or possessing non-cellulosic cell walls may also facilitate growth and tolerance of low pH conditions (Bray 2007).

The pH-dependent Occurrence of Zygnematalean Green Algae

Acid and acidified waters are colonized by acidophilic (limited to growth in acidic conditions) and acid-tolerant (highly tolerant of acidic conditions) species of ZGA. Acidophilic algae, which occur down to pH values of 0.05, are not able to grow at neutral pH. For algae that live in very low pH conditions, several adaptations are necessary. For growth at low pH, a neutral cell pH must be maintained, which is

made possible by a relatively impermeable plasma membrane, reduced proton fluxes, and increased proton pump efficiency (e.g. Gross 2000). In addition, the algae have to cope with a restricted supply of CO_2 for photosynthesis since HCO_3^- is absent. Although DIC limits benthic PP in acid lakes (Klug and Fischer 2000), the species of Zygnemataceae are superior to other species (Vinebrooke 1996). Thus, most studies show that acidification increases the benthic algae biomass in both the littoral zones of lakes and in lotic systems (Planas 1996). Consequently, due to the high CO_2-requirements and ambient shortages, ZGA in acidic environments must have a CO_2 concentration mechanism (Gross 2000).

- Acidophilic to acid-tolerant peri- and metaphyton in lakes is composed mainly of the genera given in Table 3.20. At pH 5.5–4.8, acidophilic Zygnemataceae, such as *Spirogyra* spp. and *Mougeotia* spp., occur (Table 3.21).
- Usually, ZGA are found in monospecific aggregations below pH 4.8 (France et al. 1992). Usually a metaphytic coverage hardly exists below a water depth of 3 m. At all depths, the biomass and PP decreases with the lowering of light supply (e.g. Planas 1996; Schindler 1993). If the pH decreases < 4.8, *Spirogyra* spp. and *Mougeotia* spp. (Table 3.21) are displaced by *Zygogonium* spp. (Turner et al. 1995a, b), which are acid-tolerant over a wide span of pH (Table 3.22).
- Peri- and metaphytic aggregations, which are exposed to the conditions of a high acidity, often consist of dense filamentous canopies of *Zygogonium ericetorum* Kütz., 1843. Thus, this species paid attention to for a long time (Hodgetts 1918; West and Starkey 1915). While this acidobiontic indicator species colonized the whole shore area in an anthropogenic, acidified (pH < 5.6) lake (Planas 1996), it covered about 88.3% of the bottom in an acidic (pH ≤ 3) mining lake, Grünewalder Lauch, Lusatia, Germany (Kleeberg et al. 2006).

Factors that Determine the Distribution and Productivity of Zygnematalean Green Algae

Besides the direct physiological effects of the acid on the acid-tolerant ZGA (e.g. Klug and Fischer 2000), their species composition, biomass, and PP are determined by abiotic and biotic factors. The abiotic factors are: (1) pH, i.e. prevailing H^+ and metal concentrations; (2) limiting nutrients; (3) penetration depth of light, water temperature, and movement; (4) interfaces of the metaphytic mats, as well as; (5) substrate availability. The biotic factors include (1) the community of the littoral herbivorous macroinvertebrates and (2) competition for a limiting resource.

Abiotic Factors that Determine Distribution and Productivity

Ecosystematic disturbances that accompany the acidification of lakes, cannot be exclusively attributed to the potential toxicity of the H^+ and metal concentrations, particularly that of Al. The changed biogeochemical cycle of different components

Table 3.21 Occurrence and dominating growth forms of *Mougeotia* spp., Zygnemataceae, at respective pH in natural, acid and circum-neutral as well as artificial freshwater systems (according to Graham et al. 1996, changed and supplemented). AMD—acid mine drainage

Growth form	Occurrence	pH	Source
Benthic and planktonic	Tundra, pond, Kap Bathurst area	8.1–8.2	Sheath et al. (1982)[a]
Floating mats	Eutrophic pond, the Netherlands	7.5–9.9	Hillebrand (1983)
Floating mats	Pond in coastal dunes, the Netherlands	5.5–8.2	Simons (1987)
With the sediment associated filaments	Georgia Bay and North Tunnel, Ontario	6.6–7	Sheath et al. (1988)
Associated with stones	Streams of the Signy Islands, Antarctica	6–7	Hawes (1989)[b]
Aggregates associated with different substrates	Acidified soft water lakes, NE PA, USA	4.4–6.2	Fairshild and Sherman (1993)[c]
Metaphytic mats	Lake 223, experimental lake area, Ontario	5.1–5.6, 5.0–5.2	Schindler et al. (1985); Turner et al. (1987)
Algal mats	Groundwater influenced lake, mid-Wisconsin	4.7–5.6	Webster (1992)[d]
Metaphytic mats	Lake Little Rock, Wisconsin, enclosure	4.7	Klug and Fischer (2000)
Aggregate associated with diverse substrates	Acidified rivers, Scotland	4.4–6.7	Kinross et al. (1993)
Periphyton community	AMD stressed rivers, Westport, New Zealand[e]	3.2 ± 0.1	Bray (2007)
Macroalgal community	AMD impacted Hocking river sites, OH, USA	2.6–8.2	Verb and Vis (2001)
Periphyton assamblage	AMD impacted stream sites, unglaciated western Allegheny Plateau, OH, USA	1.6–4.7	Verb and Vis (2005)
Periphytic patches	Río Tinto, S Spain[f]	1.5–2.5	Sabater et al. (2003)

[a] *Mougeotia* did not occur in ponds with pH 3.6, 2.0, and 1.8; [b] in the cold streams grazers did not occur (see below); [c] for *Mougeotia*, the authors gave a pH optimum of 5.3 ± 0.8; [d] the maximum of biomass was determined at pH 5.2; [e] *Mougeotia* cf. *depressa*, (Hass.), *M.* cf. *laevis* (Kütz.) and *Zygnema* c.f. *cylindrospermum* (West et West); [f] in Río Tinto, at pH 0.8–3, *Zygnemopsis* spec., Zygnemataceae, also occurred (Aguilera et al. 2007)

Table 3.22 Occurrence and dominating growth form of *Zygogonium* spp., Zygnemataceae, and the pH of natural, circumneutral, and acidified freshwater systems reported in the literature

Growth form	Environment	pH	Source
Epilithic, epiphytic	Bowland Lake, Ontario	5.7–6.7	Jackson et al. (1990)
Metaphytic floating and semi-attached	0–2 m littoral of softwater lakes, Ontario, Canada	5.6–6.5	Howell et al. (1990)[a] France et al. (1991)
Periphyton	Low alkalinity lakes, Killarney Provincial Park, Ontario	< 5	Vinebrooke (1996)[b] Vinebrooke and Graham (1997)
Metaphyton	Experimentally acidified Lake 302S, NW Ontario	4.5	Turner et al. (1995a) Turner et al. (1995b)
Periphyton loosely attached, tall	Lake Ruth-Roy (Ontario)	4–4.6	Graham and Vinebrooke (1998)
Loose flocs	littoral of mining lake Koschen, Lusatia, Germany	3.2	Jacob and Kapfer (1999)[c]
Dense mats, peri- and metaphytic form	1.6–10.5 m depth in lake Grünewalder Lauch, Lusatia, Germany	2.9	Kleeberg et al. (2006)
Floating mats	Warm (30–31 °C) water near thermal springs, Yellowstone National Park, Wyoming	2.4–3.1	Lynn and Brock (19s69)

[a] predominant was *Z. tunetanum*; [b] *Z. ericetorum* and *Z. tunetanum*; [c] predominant during cold season was *Bumilleria klebsiana* (Xanthophyceae), and during warm season *Z. ericetorum* (Chlorophyceae)

(Fe, S, C, and N) can influence physical factors such as light climate, stratification, and/or substrate availability.

Effects of pH

Direct physiological effects of the acid on the ZGA, which determines their distribution and PP, are often difficult to assess because changes in pH are accompanied by changes in other potentially important factors such as dissolved inorganic carbon (DIC) and metals (Kleeberg et al. 2006; Klug and Fischer 2000). Appearance of *Mougeotia* and *Zygogonium* spp. with the (experimental) lowering of pH and their disappearance, if the pH was increased, e.g. by liming (Jackson et al. 1990; Turner et al. 1987) is well documented. However, these studies did not clarify whether the increase or decrease of dominating species are directly or indirectly attributed to pH.

Nutrient Limitation and Primary Production

Carbon—is known to be growth-limiting for the pelagic (e.g. Beulker et al. 2003; Nixdorf et al. 2003b) and benthic PP of ZGA (e.g. Mulholland et al. 1986; Turner et al. 1987, 1995a). HCO_3^- is virtually non-existent at pH < 5 and the dissolution of CO_2 from the atmosphere is very low. Consequently, at pH 3, for example, the

Table 3.23 Span of pH, of concentrations of total inorganic carbon (TIC), of ammonium (NH_4^+), and of dissolved reactive phosphorus (SRP) of acidic mining lakes of the Lusatian mining region, Germany (Nixdorf et al. 2003a)

Buffer system	pH	TIC (mg L^{-1})	NH_4^+–N (mg L^{-1})	SRP (µg L^{-1})	Number of lakes
Fe buffered	2.2–3.4	<0.2–18.3	0.12–14.2	1–30	15
Al buffered	3.8–4.0	<0.2–0.5	0.40–0.52	1–2	2
CO_3 buffered	6.0–8.0	0.8–36.7	0.02–3.65	1–8	8

atmospheric equilibrium concentration of CO_2 amounts to about 0.1 mg L^{-1} (Nixdorf et al. 2003b). Table 3.23 summarizes the span of nutrient concentrations of mining lakes.

Additions of N, P, and N + P alone in lab experiments did not stimulate the growth of ZGA (Fairchild and Sherman 1990). Moreover, the dense mats and missing water movement could hamper CO_2 diffusion (Turner et al. 1991, 1994). At the same time, the ZGA use the CO_2 originating from benthic mineralization (Wetzel et al. 1985). After additions of N and C, Fairchild and Sherman (1990) found a significantly increased abundance of *Mougeotia*, whereas not after single C additions. Thus, this species seems to be extremely efficient in CO_2 uptake at low pH, but less efficient in the uptake of HCO_3^- (Turner et al. 1987). For *Spirogyra*, it was hypothesized that this species can induce the formation of the carboanhydrase (Simpson and Eaton 1986), which supports the use of HCO_3^-.

Nitrogen—can be taken up by ZGA as nitrate (NO_3^-) or ammonium (NH_4^+), though NH_4^+ is preferentially used as a N source. In both rain-acidified soft water lakes and geogenically acidified mining lakes the concentration of NH_4^+ is relatively high (Table 3.23), in addition to the the NH_4^+ import caused by the inhibition of nitrification (e.g. Nixdorf et al. 2003a; Rudd et al. 1988). Consequently, the N supply for the benthic Zygnemataceae should be adequate, which is substantiated by the enrichment experiments with nutrient combinations by Fairchild and Sherman (1990). In an experimentally acidified lake (pH 4.5), the N:C ratio of ZGA, mainly of the genera *Mougeotia* and *Zygogonium*, was used to indicate the N limitation. With 0.11, i.e. between 0.1 and 0.13, it indicated a 'moderate' N deficiency (Turner et al. 1995a).

- *Phosphorus*—the availability of P is dependent on its import and the concomitant import of P-binding partners, particularly metals such as Fe, Al, Mn, and Ca, and the prevailing O_2, pH, and redox conditions (see also Sect. 3.2.1.3). Thus, in most acidic mining lakes the P concentrations are very low (Table 3.23). The co-precipitation of P by Al and Fe oxyhydroxides is documented for both acid rain-acidified soft water lakes (e.g. Kopáček et al. 2000) and geogenically acidified mining lakes (e.g. Kleeberg and Grüneberg 2005).
- The uptake of P by epilithic or periphytic mats has rarely been studied (Hansson 1989; Riber and Wetzel 1987; Tate et al. 1995). The activity of

Table 3.24 Span of biomass characteristica and net primary production (PP) of various zygnematalean green algae (ZGA) and the pH reported in the literature (dw: dry weight, Chl a: chlorophyll a)

ZGA	pH	Dw (g m^{-2})		Chl a (mg m^{-2})		Net PP (mg C m^{-2} d^{-1})		n	Number of References
		min	Max	min	Max	min	Max		
Periphyton	–	0.03	46.00	0.01	2385	0.6	2,510	#	a
Zygnema	6.7	21.7	39.80	20.00	400	31.7	32	4	b
Metaphyton	5.6	0.82	1.79	1.03	2.33	6.9	119	5	c
Zygogonium	4.5	0.30	32.40	–	–	16.8	2,222	7	d
Zygogonium	2.9	0.30	478.5	0.20	1,025	-12.0	851	4	e

[a] Morin and Cattaneo (1992); # 20 journals between 1975 and 1990 have been reviewed, i.e. $n = 187–1,194$; [b] Sheath et al. (1996); Tundra stream, Toolik region, Alaska; [c] Howell et al. (1990); predominately *Mougeotia* and *Zygogonium*; [d] Turner et al. (1995a); predominately *Mougeotia* and *Zygogonium*, data from 1991; [e] Kleeberg et al. (2006); *Z. ericetorum* in acid mining lake Grünewalder Lauch, Germany

indicators for P availability, such as phosphatases (Sabater et al. 2003), are also determined by other factors, such as available phosphate, and hence do not allow definite termination to an existing P limitation. Turner et al. (1995a) used the mass ratio of P:C $\times$ 1,000 as an indicator for the determination of P limitation. For a community of *Mougeotia* and *Zygogonium*, this ratio amounted to 5.8, i.e. was considerably smaller than 10, which indicates an extreme P deficiency. It is also known that benthic algae are able to store P if P is available in surplus. Whether the phosphate that is released (possibly quickly) after microbial mineralization is immediately taken up by the algae is unknown. It is also not clear whether the dominating meta- or periphytic growth form of ZGA preferentially uses the water body (Hansson 1990) or the sediment (Wetzel et al. 1985) as the major P source.

- *Primary production*—The determination of photosynthetic rates of the peri- and metaphytic ZGA is, because of their heterogeneous distribution between the growth forms, problematic. The variability of size of the metaphytic aggregates and concentration of algal filaments, which lie in high density within the associations close together and float, respectively, can significantly influence the biomass-specific PP due to the competition for light and nutrients (Mulholland et al. 1986; Turner et al. 1994, 1995a, c). This is reflected in the horizontal distribution of the biomass of ZGA in a lake and the span among different lakes (Table 3.24). The PP of ZGA can also be limited by temperature (see below), and is consequently seasonally very different (Graham et al. 1996; Howell et al. 1990). Moreover, the rate of net PP depends on the fall of slope of the littoral bottom, the amount of ZGA incubated for the measurements, and the amount of heterotrophic organisms associated with the algae (Howell et al. 1990; Kleeberg et al. 2006). The problem of comparing the benthic PP of the different waters becomes visible in the wide span of rates (Table 3.24; see also Sect. 3.3.2.3).

For example, in experiments with cultures of *Mougeotia* for the determination of PP and respiration as a function of pH, the production strongly decreased at pH = 3, but at pH < 3, the algae died (Graham et al. 1996a). 56 combinations of light and temperature with *Mougeotia* resulted in optimal conditions at 25°C and 300–2,300 μmol quanta m^{-2} s^{-1}, the net photosynthesis averaged 40.4 mg O$_2$ g^{-1} h^{-1} (Graham et al. 1996b).

In determining the PP of ZGA, beside the physical factors of light and temperature, pH-related factors such as the prevailing Al concentration and species have to be considered. Mulholland et al. (1986) determined the chlorophyll-specific rate of PP over a span of pH of 4.5–6.4. The lowest rates at pH 4.5 were not only determined by C and P limitation, but also by the toxicity of Al.

The rates of dark respiration of all benthic algae communities studied in acidified or acid lakes were higher than those of neutral references (Turner et al. 1991). A changed ratio between PP and respiration is generally regarded as an indicator of acid stress (Schindler 1993; Turner et al. 1995c). At pH < 5, the ratio of PP:respiration approached 1 (Schindler 1993).

Deposition and Toxicity of Metals

The most significant effect of AMD conditions on acid-tolerant communities is the deposition of metal oxides (e.g. Bray 2007; Niyogi et al. 1999). In comparison to the poorly buffered soft water lakes acidified by airborne pollutants, the metal concentrations in geogenically acidified mining lakes are much higher. For the latter, the concentrations of Fe vary between 0.09 and 170.2 mg L^{-1} and that of Al between 0.03 and 20.5 mg L^{-1}. In lakes with pH < 3.4, the molar proportion of Fe exceeds those of Al; at pH > 3.7, the relations are converse (Geller et al. 2000).

At pH < 6, Al becomes highly soluble; however, not all forms are toxic (Gensemer and Playle 1999). Inorganic monomeric forms are very toxic; Al fluoride complexes are not. An Al concentration of 50 μg L^{-1} was toxic for phytoplankton (Planas 1996). In acidified synthetic soft water, growth of the green alga *Chlorella pyrenoidosa* was inhibited after 96 h at an Al concentration of 162 μg L^{-1} (Parent and Campell 1994). In comparison, ZGA of the genus *Mougeotia* (Table 3.21) are distinctly tolerant of elevated Al concentrations. *Mougeotia* have been found in lakes at Al concentrations of 26–200 μg L^{-1} at pH 4.5–5.1, and in rivers at 41–1,410 μg L^{-1} at pH 4.4–7.3 (Graham et al. 1996). At higher experimental concentrations, Al caused a rapid decline in the ZGA growth rate and a lower final biomass (Kinross et al. 2000). The physiological mechanisms responsible for Al toxicity are still unknown (Gensemer and Playle 1999). The tolerance of *Mougeotia* to Zn depended on the level of concentrations (6–34,000 μg L^{-1}) in the waters from which they were isolated (Graham et al. 1996). Hence, in experimental cultures, *Mougeotia* tolerated a Zn concentration of 3,400 μg L^{-1}.

In acid mining lakes, the pH of the water is often seen as the primary variable that affects aquatic biota, but pH also acts as a master variable affecting metal hydroxide deposition. The high metal (particularly Fe) sedimentation rates should stress the ZGA in these lakes. For example, *Zygogonium ericetorum* was always associated

with Fe hydroxides in the mining lake Grünewalder Lauch, Lusatia, Germany (Kleeberg et al. 2006). In comparison, at pH < 4, periphytic *Ulothrix* sp. (Chlorophyceae) biomass accumulated only when the Fe deposition rate was below ≈ 1 g m^{-2} d^{-1} (Niyogi et al. 1999). Consequently, *Z. ericetorum* growth in Lake Grünewalder Lauch is obviously seriously stressed by high rates (around 0.9 g m^{-2} d^{-1}) of Fe deposition during summer at shallower sites. *Z. ericetorum* can become covered by Fe hydroxides (red–orange colour in Fig. 3.67) if it does not grow faster than the rate of Fe deposition, which is between 1.2 and 2.2 g m^{-2} d^{-1} at deeper sites. Moreover, these Fe hydroxides might also influence the extreme P deficiency of *Z. ericetorum* by their ability to efficiently adsorb phosphate (Kleeberg and Grüneberg 2005). This is supported by the *Zygogonium*-mediated diurnal Fe cycling, where about 34% of the dissolved Fe is reduced at night time and then oxidized and precipitated during the day (Koschorreck et al. 2007).

Physical Parameters that Determine Distribution and Productivity

Light—Oligotrophying factors such as a C limitation, particularly in shallow regions of acidified soft water lakes, can improve the light climate for ZGA and can lead to a shift of the light compensation point (Planas 1996; Turner et al. 1995a). In boreal lakes, Experimental Lake Area, NW Ontario, attached algal composition was mostly determined by photosynthetically active radiation and ultraviolet radiation fluxes. The community on rock surfaces exposed to high solar fluxes contained very high concentrations of a photoprotective scytonemin-like pigment, and was dominated by ZGA (Donahue et al. 2003). On the other hand, light can be a growth-limiting factor for ZGA. At low iron turbidity, as occurs in some acid mining lakes, ZGA development can be suppressed in the relatively clear water by oversaturation of light, and chlorophyll a concentrations (0.2–9 µg L^{-1}) remain at a low, C-limited, mostly oligotrophic level (Nixdorf et al. 2003b), which favors the yield of light at the sediment surface. In contrast, deep chlorophyll a maxima (Beulker et al. 2003; Nixdorf et al. 2003b) could deteriorate the light climate for benthic ZGA.

Water temperature—The species of the Zygnemataceae occur over a wide range of temperature. They can colonize both cold streams of the Antarctic (Table 3.21) and warm thermal springs (Table 3.22). The temperature dependency of growth, photosynthesis, and respiration is only known for a few species. Studies on the influence of light (10–2,338 µmol quanta m^{-2} s^{-1}) and temperature (5–30 °C) on the net PP of *Mougeotia* at pH 4.7 showed that the compensation point (net PP = zero) lies between 10 and 20 µmol quanta m^{-2} s^{-1} at 5 °C; the temperature optimum was at 25 °C (Graham et al. 1996b). Thus, different species within a lake (Table 3.22) can rotate in dependence on temperature (Jacob and Kapfer 1999).

Water movement—The ZGA prefer lentic water zones. Nevertheless, moderate water movement can increase the dispersion of benthic ZGA by modifying the boundary layer around the cells and increasing diffusion. Thus, water movement could increase the efficiency of ZGA in absorbing dissolved C (Planas 1996;

Turner et al. 1987, 1991). Excessive turbulence in lotic water zones, however, can be detrimental for the sediment-associated algae. Lower biomasses and abundances or absence of ZGA in low (littoral) water depth can be ascribed to wind-induced intensive water movements, when water velocity exceeds a threshold at which mechanical abrasion of turbulences surpasses the resistance limit of ZGA (Howell et al. 1990; Kleeberg et al. 2006).

Substratum—ZGA are often very heterogeneous and highly dynamic in their physical characteristics, so substrata are an important variable to consider when comparing the occurrence and the spatial distribution of the Zygnematacea. ZGA live beyond the very steep micro gradient zones within the upper sediment and influence buffering capacity by their presence and activity; they also influence the pH through their direct and indirect influence on alkalinity formation (Cook et al. 1986; Koschorreck et al. 2007). However, up to now, there are no specific studies showing any relationships between ZGA and the composition of the sediments or the effects of the influence of the sediment, e.g. the pH buffering onto the algae community, or the CO_2 supply from microbial mineralization and nutrient availability.

Biotic Factors that Determine Distribution and Productivity

The effects of biotic drivers (influencing factors) cannot always be definitely distinguished from abiotic (physical and chemical) factors, since different species have very different sensitivities to pH.

Grazers—The increase of ZGA biomass with decreasing pH is often ascribed to control by grazers, i.e. decreasing grazing pressure accompanying increased acidification. This hypothesis is supported by the fact that the acid-sensitive taxa of the macrozoobenthos, which need Ca for their shells or exoskeletons (like crustaceans and molluscs) disappear if the pH decreases < 5.5 (median). Around a pH of ≈ 6, the ZGA become dominant. The dominance coincided with the loss of gastropods and amphipods (Turner et al. 1991). However, at lower pH, no larger cell diameter ZGA dominated, which indicates that the grazing of invertebrates is not a determining factor for the composition of the algae community (Kinross et al. 1993). Tadpoles of an acid-tolerant frog, *Rana clamitans*, have suppressed Zygnemataceae associated with loose sediment and thereby stimulated closer sediment-associated species (e.g. *Coleochaete scutata*), i.e. supported a succession towards an algal physiognomy that is resistant to herbivores (Graham and Vinebrooke 1998). Only larger animal species, such as the algae-feeding cyprinids in soft water lakes (pH 5.6–5.9), can exert significant grazing pressure on the littoral metaphyton (France et al. 1991).

The relative effect of acidification and the total biomass of insects and productivity and the relationship between the grazer's abundance and the algae development are also not clear. In many acidified and acid lakes, chironomid larvae (Chironomidae, Diptera) dominate; according to different authors, their abundances and biomass seems to be pH-independent (Müller 1980; Planas 1996). The decrease in the number of different taxa and their biomass could be related to the fact that ZGA can shift from their two-dimensional periphytic into the three-

dimensional metaphytic growth form (Planas et al. 1989), and thus become physically inaccessible to most benthic taxa (Vinebrooke et al. 2001), since the metaphytic growth form represents a food item only available to herbivores with flexible life histories and feeding behaviors.

Traditionally, it has been argued that changes in the macroinvertebrate community can determine the composition of the algae (Harvey 1989). This implies that herbivores are selective. Their selectivity, in turn, is related to the physiognomy of the ZGA and their usability (Steinmann 1996). However, only a few observations deal with the food of acid-tolerant insects. Studies of Collier and Winterbourn (1990) showed that a large proportion ($> 60\%$) of the stomach content of fishflies (Ephemeroptera) and chironomids was detritus of a pH-independent origin. Donahue et al. (2003) found for ZGA species of *Spirogyra*, *Mougeotia*, and *Zygogonium* that chironomid density explained only 2% of algal species variance, suggesting that they were not overly important in determining ZGA community structure. Hence, so far, the increase in algal biomass and ZGA community structure cannot be definitely explained by the decrease of top-down regulation.

Competition—Increased ZGA biomass can be a consequence of lowered heterotrophic activity with a ratio growth:decomposition that favors Zygnemataceae (Stokes 1986). The balance between the different heterotrophic and autotrophic populations, representing the periphyton, could change the nutrient cycle and thereby decrease competition for a certain resource (Mulholland et al. 1986; Planas 1996). Whether the bacteria can outcompete the algae for a restricted P resource, as occurs in circumneutral lakes (Jansson 1988), remains an unanswered question.

Summary of Research Needed on Zygnematalean Green Algae in Acid-influenced Habitats

- *Occurrence*—Most studies of ZGA have only considered direct cause-effect relationships between two or a few environmental factors (e.g. pH, presence or absence of a ZGA species, distribution across AMD gradients), without considering other physical, chemical, and biological variables that might influence their presence or absence. Integrative bioassays (e.g. Pringle 1987) could contribute to a better elucidation of connectivity.
- *Long-term studies*—that document the situation before and along with acidification or after neutralization in conjunction with the occurrence and productivity of ZGA are needed. Spatial replications are often overlooked. An open question is why some ZGA species that occur together over a certain span of pH collectively disappear after neutralization, but only some of these species reappear after re-acidification (e.g. Jackson et al. 1990).
- *Ecological importance*—The importance of ZGA as an algae substrate and a food base for invertebrate benthic organisms is still not adequately known. The correspondence of acidification and total biomass of insects and productivity and the relationship between grazer abundance and algae development is also not clear. The increase in algal biomass and ZGA community structure cannot be definitely explained simply by decreased top-down regulation.

- *Productivity and nutrients*—Only a few scientific studies of circumneutral systems have paid attention to the interactions between the pelagic and benthic PP. However, they should be included in studies of mining lakes with pH < 5. Either the pelagic or benthic PP have been determined, rarely both. The C and P limitation of ZGA are mostly estimated using C:N:P relations. Lab experiments to estimate the degree of limitation have rarely been performed, and would, in conjunction with other environmental parameters, explain the respective occurrence, species composition, and productivity. It is also not clear whether the dominating meta- or periphytic growth form of ZGA preferentially uses the water body or the sediment as the major P source, and to what extent and by which mechanisms ZGA can mobilize and use P in the presence of a surplus of P-binding partners. How the densely packed filaments of mats influence nutrient exchange as conditions of diffusion change also needs to be studied.
- *Interplay with bacteria*—In most studies, the autotrophic components of the peri- and metaphyton, i.e. the ZGA itself are studied manifold, particularly with respect to chlorophyll a concentration and PP. The heterotrophic components with bacteria and fungi are significantly less considered. There are no specific studies on the relationships between ZGA and the composition of the sediments or the influence of the sediment, e.g. the effects of pH buffering onto the algae community or the CO_2 supply from microbial mineralization. The importance of bacteria is not only restricted to the effects of the nutrient transformations within the mats, since they also play a potential role as competitors for nutrients. Whether the phosphate that is released (possibly quickly) after microbial mineralization is immediately taken up by the ZGA is unknown. Also, whether the bacteria can outcompete algae for a restricted P resource, as shown for circumneutral lakes (Jansson 1988), remains an unanswered question.

Algal physiology—The physiologic adaptations of ZGA, such as the CO_2 concentration mechanism and the mechanisms responsible for Al toxicity, are not completely elucidated over the large span of extent of acidification and the respective water types.

Acid mining lake remediation—Information on the occurrence of acidophilic ZGA, their physiological adaptations, and their ecological functions are very useful pertaining the development of acid mining lakes and strategies for acid removal, i.e. particularly their role in benthic C accumulation, sediment early diagenesis, and biogenic alkalinity generation.

3.3.2.3 Benthic primary production

Matthias Koschorreck

If light reaches the bottom of an acidic pit lake, the sediment surface will be colonized by benthic algae. The sediment surface is a favourable place for primary producers since the concentrations of nutrients as well as dissolved inorganic
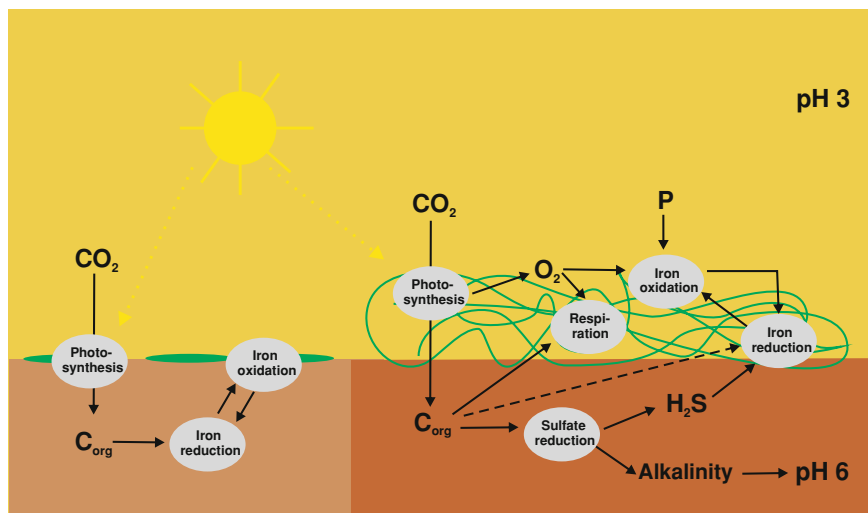
Fig. 3.68 Possible effects of benthic primary production in acidic pit mine lakes. The left part shows a benthic diatom biofilm, the *right* part shows a metaphyton layer covering the sediment

carbon are higher than in the open water (Nixdorf and Kapfer 1998). Although light intensities are often low, benthic algae can carry out photosynthesis directly at the sediment surface. This has important consequences for the biogeochemistry and also the acidity status of the lake (Fig. 3.68).

The sediment surface can be colonized by small unicellular algae, mostly diatoms such as *Eunotia exigua*, *Nitzschia palaeformis*, *Pinnularia acoricola*, or the Euglenophyte *Euglena mutabilis*, which shows highly variable abundance due to patchy growth (Lessmann et al. 1998; Kapfer, 1998). The phytobenthos can also consist of metaphytic filamentous algae, typically *Zygnemataceae* (Fig. 3.69; see also Sect. 3.3.2.2). In Mining Lake (ML) Grünewalder Lauch (ML117), 88% of the lake bottom was covered by several centimetre thick mats of *Zygogonium ericetorum* (Kleeberg et al. 2006; see also Sect. 3.3.2.2), with the highest abundance at water depths between 5 and 6 m and a mean biomass of 92 ± 96 g-dw m^{-2} (where dw indicates dry weight). These *Zygogonium* mats are P limited and seriously stressed by Fe deposition, which results in low annual primary production rates of 0.12 g C m^{-2} year^{-1}, which is in the range of literature values for filamentous green algae in lakes of various pH. Compared to the annual pelagic production of 43 g C m^{-2} year^{-1} (Nixdorf et al. 2003), primary production by *Zygogonium* is of minor importance in Lake Grünewalder Lauch. During summer, however, benthic net primary production can be as high as 21.4 mg C m^{-2} d^{-1}. This biomass production is the basis for high rates of microbial sulfate reduction observed in the permanently anoxic sediment below the metaphyton layer (Koschorreck et al. 2007).
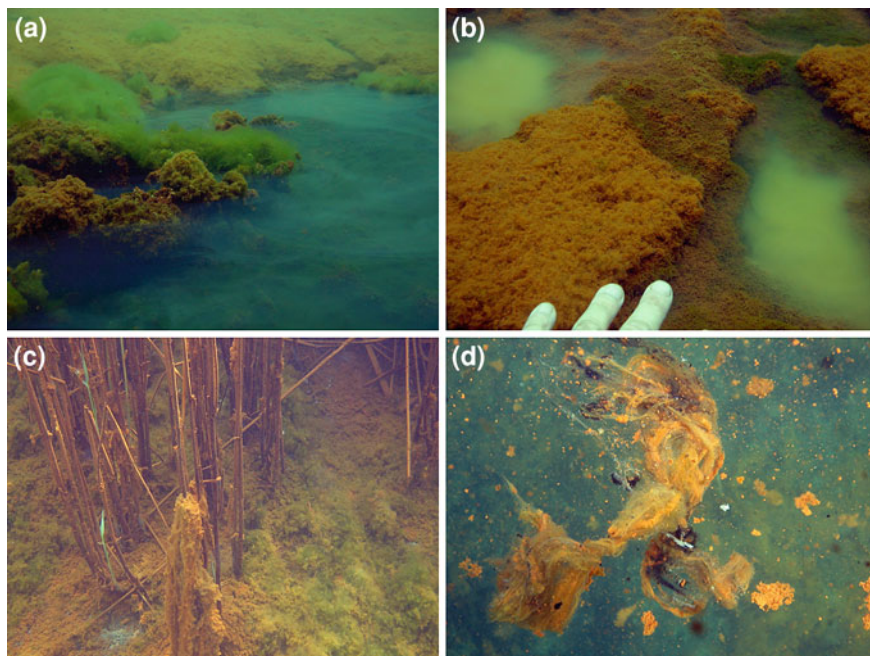
Fig. 3.69 Sediment surface of Mining Lake (ML117) Grünewalder Lauch (Germany) covered by periphytic filamentous algae (a–c) and suspended filamentous algae and iron precipitates (d; photographs: M. Beyer)

Photosynthesis carried out by the filamentous algae triggers diurnal fluctuations of oxygen in the metaphyton layer, which in turn leads to a diurnal redox-cycling of iron. Oxidation and precipitation of iron during the day scavenges phosphorus efficiently (Fig. 3.70).

Phytobenthic chlorophyll concentrations were 60 mg Chla m^{-2} in Lake Plessa 107 (pH 2.3; Lessmann et al. 1999) and in ML111 (pH 2.6; Koschorreck and Tittel 2002), about 10 mg m^{-2} in Lake 108 (pH 2.9), and about 110 mg m^{-2} in Lake Koschen (pH 3.1; Kapfer 1998).

Diatom-dominated benthic biofilms reached primary production rates of 1–5 mg C m^{-2} h^{-1} with specific rates being around 0.2 mg C mg-Chl^{-1} h^{-1}, as measured by the radiocarbon method (Kapfer 1998). Benthic gross and net primary production in ML111, as measured by oxygen microsensors, was 33 and 15 mg C m^{-2} h^{-1} at a light intensity of 15 µE m^{-2} s^{-1}, respectively (Koschorreck and Tittel 2002). The compensation irradiance of the photosynthetic benthic community was 6.8 µE m^{-2} s^{-1}, showing adaptation to low light intensities. The particular light spectrum in iron-rich acidic lakes fits the absorption spectrum of benthic diatoms better than the light in "normal", not coloured lakes. Thus, for a given photosynthetic active radiation (PAR), the benthic algae in ML111 could use 1.5 times more photons than in a non-acidic lake (Koschorreck and Tittel 2002).
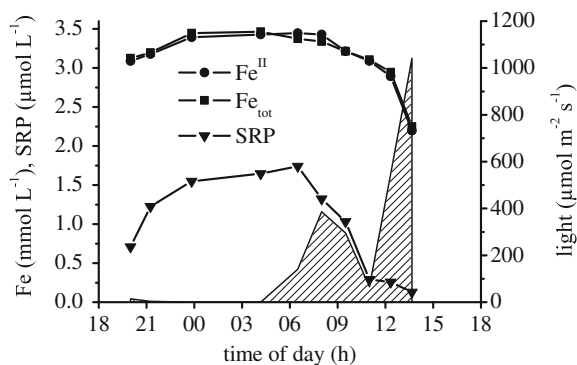
Fig. 3.70 Diurnal concentration fluctuation of dissolved iron and phosphorus in the metaphyton in lake Grünewalder Lauch (modified from Koschorreck et al. 2007). The shaded area indicates the light intensity
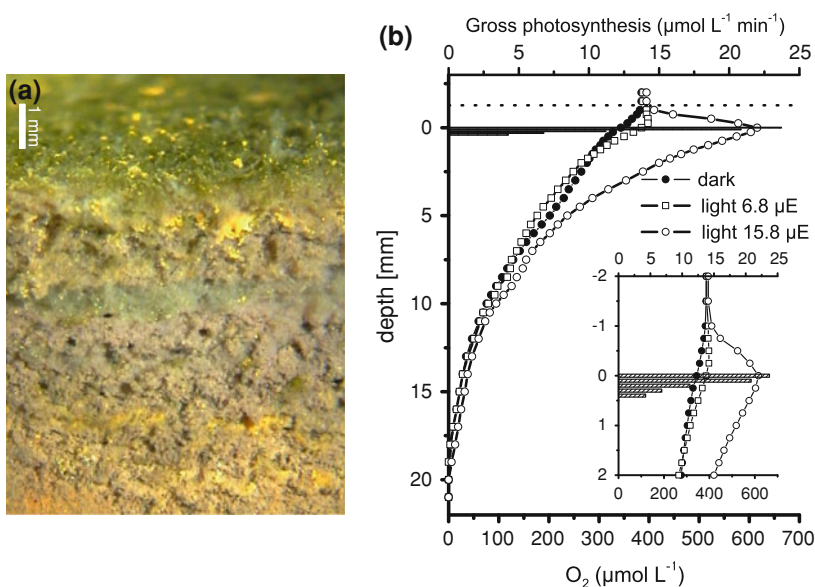
Fig. 3.71 Cross section of the sediment–water interface in ML111 showing a benthic phototrophic biofilm **a** and oxygen distribution in the light and in the dark (*lines*) as well as gross photosynthesis (bars). **b** Graph after Koschorreck and Tittel (2002). The insert shows a magnification of the water sediment interface

Although photosynthesis increased the oxygen concentration in the sediment, the oxygen penetration depth was not affected (Fig. 3.71). Thus, the direct influence of benthic diatom biofilms on the redox status of the sediments is probably of minor importance. Benthic primary production, however, is probably the most important source of organic carbon in shallow, extremely acidic mining lakes. It has been

Fig. 3.72 Contribution of different carbon sources in Mining Lake 111 (data from Kamjunke et al. 2006)

benthic primary production
22

groundwater
1.2

leaf input
1.9

pelagic primary production
8 $\mu g \, C \, L^{-1} \, d^{-1}$
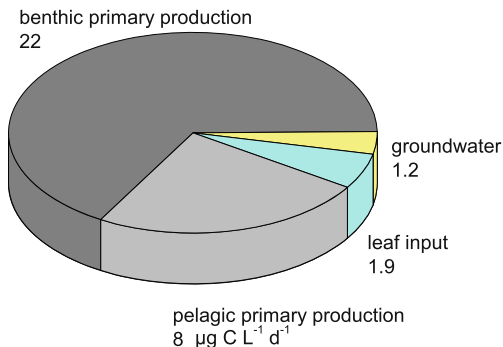
estimated that it contributes about 2/3 of the organic carbon in Mining Lake 111 (Fig. 3.72). Thus, with respect to the relative role of pelagic and benthic primary production, acidic pit mine lakes are comparable to "normal" shallow lakes (Ask et al. 2009; Vadeboncoeur et al. 2001).

3.3.2.4 Benthic and Sediment Community and Processes

Katrin Wendt-Potthoff

Zoobenthos

Due to the extreme chemistry, diversity of macrozoobenthos in acidic pit lakes is very restricted. Acid-tolerant predatory corixids are common (Wollmann 2000); however, they are not strictly benthic. Invertebrates that actively shred leaf litter are absent (Mutz et al. 2000). Aquatic insects are the most common group in acid waters, with 48.3% of total taxa being *Diptera*, mostly chironomids (Rodrigues and Scharf 2001). Apparently, chironomid larvae are able to withstand the high mineral acidity, and due to the very low predatory pressure, they can reach high abundances (Table 3.25, Zullo and Stahl 1988). A species that was mistakenly identified as *Tendipes plumosus* and later designated as *Chironomus* sp. was regularly found in 11 of 19 coal pit lakes in Missouri and Kansas, most of which had strongly acidic water and sediments (Harp and Campbell 1967). The authors reported that occurrence of the larvae was more related to the presence of leaf detritus than to pH, indicating that lack of food sources constrained them more severely than water or sediment chemistry. Only in the most acidic lake (Lake A_1, pH 2.3, potential free acidity 819–9,090 mg $CaCO_3 \, L^{-1}$ = 16.4–182 mmol L^{-1}) were pupae unable to emerge. A pit lake of the same pH and acidity ($K_{B4.3}$) of 30.9 mmol L^{-1} in Lusatia had a slightly lower chironomid density, and there was no data on emergence but evidence of predation by corixids (Lessmann et al. 1999, Table 3.25). Harp and Hubbard (1972) studied the benthic fauna of bauxite open-pit lakes in Arkansas, which resemble coal pit lakes with respect to pH, but have a different metal chemistry (iron = 0.2–13.9 mg L^{-1}, aluminum = 5.2–49.7 mg L^{-1}). Their sediments had a similar density of benthic animals as the iron-rich coal pit lake, Lake 111 in Lusatia, which

Table 3.25 Abundance of chironomid larvae in acidic pit lakes

Lake	pH	Individuals (m^{-2})	Comments	Source
A1	2.3–3.2	0–7,435	Pupae were unable to emerge	Harp and Campbell (1967)
A3	3.4–4.1	0–40,124		Harp & Campbell (1967)
Lake 107	2.3	0–430	*C. plumosus* group	Lessmann et al. (1999)
Bauxite pit lakes 1–4	2.9–3.4	511–5,479	Total benthic fauna counts, but almost entirely *Chironomus* sp.	Harp and Hubbard (1972)
Lake 111	2.6	0–4,500	*C. crassimanus*	Lagauzère et al. (2011)
Bradley's acidic pit	2.30–3.85	3,055–14,137 (49,972)[a]	*C.* near *maturus*	Zullo and Stahl (1988)
Bradley's acidic pit	2.30–3.85	0–17,352 (50,105)[a]	*Tanytarsus dendyi*	Zullo and Stahl (1988)

[a] The range given comprises all sampled depths and seasons with *: the range of numbers in transects and the maximum station density indicated with parentheses

appears to be a medium value (Table 3.25). Analysis of the gut contents of *Chironomus crassimanus* larvae from this lake revealed that they mainly fed on filamentous bacteria, fungal hyphae, and photosynthetic microorganisms (Rodrigues 2001).

The seasonal development and reproductive cycle of chironomids in acidic pit lakes have rarely been studied in detail (Zullo and Stahl 1988), and their relevance might have been overlooked by common episodic sampling. It has been demonstrated for natural freshwater environments that the bioturbation and feeding activity of chironomids play an important role in matter transport and sediment biogeochemistry (Nogaro et al. 2008). Therefore, in acidic pit lake sediment where they dominate the sediment macrofauna, effects of their bioturbating activity should be significant. To date, there is only one study dealing with the effects of burrowing chironomids on acidic pit lake sediments (Lagauzère et al. 2011). The authors found a three-fold increase of the diffusive oxygen uptake by the sediment, indicating a stimulation of organic matter mineralization. Iron transformations were also influenced (lower rates of oxidation and reduction, stimulation of mineral transformations, increased abundance of iron-oxidizing bacteria), but the flux of iron across the sediment–water interface was not affected.

Among the meiofauna, mites and nematodes are present in acidic pit lake sediments. Rodrigues and Scharf (2001) detected *Hydrozetes lacustris* in exposed leaf packs in three lakes, with increasing abundance from water pH 2.3 to 3, while nematodes were not found at pH 2.3. A later transect study by Traunspurger (pers. comm.) revealed the presence of both nematodes and water mites in Lake 111 sediment, which did not show a systematic relation to water depth. Nematodes

comprised 8 species feeding on bacteria and fungi, with *Prismatolaimus* sp. being dominant.

There is little information available on microzoobenthos of acidic pit lakes. Bell and Weithoff (2008) reported the importance of benthic recruitment of the dominant zooplankton organisms, rotifers and heliozoans, in littoral sediments in Lake 111 in Lusatia. Protozoan and metazoan abundance in the sediment did not exceed 25 individuals cm^{-3}; however, these values were comparable to rotifer densities of other, natural lakes. The testate amoeba, *Arcella vulgaris*, has been found to inhabit even the most acidic (pH < 2) part of James Lake, a lake acidified by dumping of waste rock from pyrite mining (Kumar and Patterson 2000).

Microbial Numbers and Biomass

Sedimentation rates have been determined for several acidic pit lakes (Siefert and Mutz 2001: 0.9–4.9 g m^{-2} d^{-1}). A considerable part of the sedimenting material may be ferric iron, as indicated by schwertmannite sedimentation rates of 1–4 g m^{-2} d^{-1} (Peiffer 1999) or iron sedimentation of 1.4 g m^{-2} d^{-1} in Lake 77 (Küsel 2003). This is in contrast to natural lakes of similar depth, where dead biomass is a more important fraction of sedimenting material. Despite this, sediment bacterial counts in acidic pit lakes appear to be similar to those of natural lake sediments. Average bacterial densities in the upper 2 cm of Lake 111 sediment, determined by epifluorescence microscopy, were $0.82 \pm 0.26 \times 10^9$ g-dw^{-1}, which corresponds to $1.01 \pm 0.34 \times 10^9$ cells cm^{-3} or a mean bacterial biomass of 22.48 ± 7.13 μg C cm^{-3} (Bell and Weithoff 2008). Maximum cell counts reached 1.6×10^9 g-dw^{-1} or 1.97×10^9 cm^{-3}. These numbers were approximately three orders of magnitude higher than pelagic counts and did not show pronounced seasonal trends. They were also in the same range as in other freshwater environments (Bell and Weithoff 2008). The sediments of the extremely acidic and metal-rich Berkeley Pit also contained 3×10^9 cells per gram sediment (Cameron et al. 2006). When bacterial counts are converted from phospholipid phosphate values instead of counting cells microscopically, values tend to be considerably higher for surface sediments. On a basis of 11 sampling campaigns from 2001–2004, the upper 2 cm of Lake 111 sediment yielded cell numbers of $3.4 \pm 1.2 \times 10^{11}$, corresponding to 9.5 ± 3.5 mg C g-dw^{-1} bacterial biomass (Wendt-Potthoff, unpublished). These values are roughly two orders of magnitude higher than the counts of Bell and Weithoff (2008). The discrepancy can be explained by the fact that the phospholipid phosphate method does not discriminate between bacteria and other viable microbial biomass such as fungi, microalgae, or protists. Phospholipid-phosphate based values for surface sediments of other pit lakes were similar (Table 3.26), and they did not show a clear relation to pH. This was further tested using a set of 194 sediment samples from different pit lakes (Fig. 3.73a). The data showed no correlation between biomass and pH, but illustrated that there are few sediment samples with intermediate pH values. A similar distribution has already been documented for the water column of such

Table 3.26 Biomass, cell counts and carbon contents in surface sediments (upper 2 cm) of pit lakes based on phospholipid phosphate extraction of duplicate samples

| Lake	N	Sediment pH	nmol P (g-dw^{-1})	Cells (g-dw^{-1})	Microbial carbon (mg g-dw^{-1})
Lake 111	11	2.8 ± 0.4	851 ± 310	$3.4 \pm 1.2 \cdot 10^{11}$	9.5 ± 3.4
Lake 117 with filamentous algae	1	6.2	1,066	4.3×10^{11}	11.9
Lake 117 without filamentous algae	1	4.2	1,242	5.0×10^{11}	13.8
Lake 107	1	2.3	93	3.7×10^{10}	1.0
Lake Niemegk	1	2.8	376	1.5×10^{11}	4.2
Lake B	1	7.0	221	8.8×10^{10}	2.5

N is the number of sediment samplings, and results for Lake 111 are given with standard deviation

lakes (Geller et al. 1998). However, microbial biomass was negatively correlated with sediment depth (Fig. 3.73b; Pearson Product Moment correlation: P value 3.26×10^{-9}).

Prokaryotic Diversity in Pit Lake Sediments

Some attempts have been made to obtain a general overview of the prokaryotes present in a pit lake, e.g. clone libraries were generated from pit lake sediment after amplifying the 16S rRNA gene. The prokaryotic diversity in acidic pit lake sediments is obviously higher than that of extremely acidic mine waters, but apparently these communities comprise a considerable number of similar organisms. However, since the detected clones are often only distantly related to known organisms, this approach is more suited to comparing different locations or sampling events than to infer microbial physiology at the studied site. Pham et al. (2007) found mostly Proteobacteria, Actinobacteria, and Firmicutes when applying DGGE profiling to a sediment transect of Lake Kepwari, an oligotrophic pit lake in Western Australia (pH 4.5–5). Bacterial diversity appeared to be higher in samples of intermediate depth (10 and 18 m) than in very shallow or deep water (0 and 29 m). Sulfate-reducing bacteria belonging to the genera *Desulfomonile*, *Desulfococcus*, *Desulfobacterium*, and *Desulfomicrobium* were detected except in the 10 m sample, which in contrast was the only one containing Acidobacteria. However, the number of analyzed bands and clones was low, so this picture is probably incomplete.

A rRNA-based clone library was generated from the sediment of the strongly acidic (water pH 2.7, sediment pH 2.5–3.6) Lake 111 (Meier et al., in revision; Müller 2004). In this study, sulfate reducing bacteria were not detected. Beside a large number of clones retrieved from algae chloroplasts, the largest group of clones was found within the Xanthomonadaceae. These clones are closely related to phylotypes and to cultures retrieved from other acid mine drainage
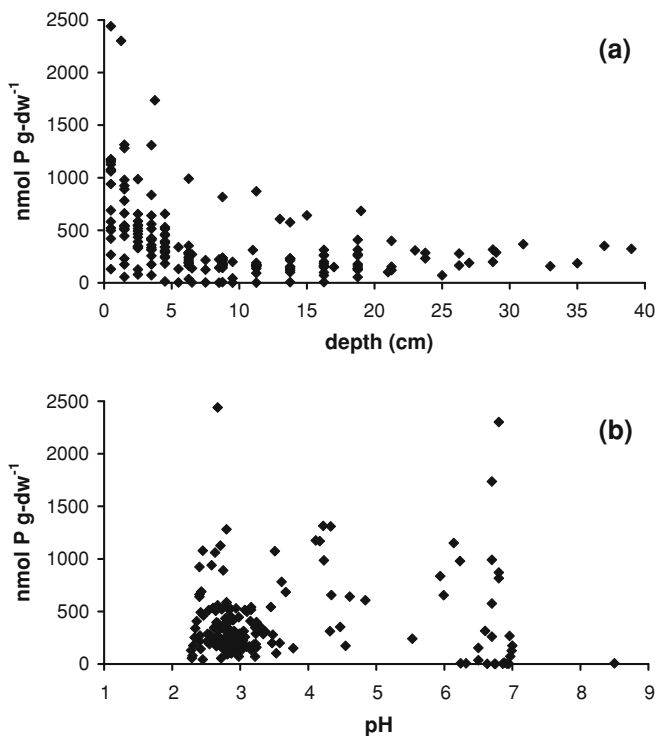
Fig. 3.73 Relationship between **a** sediment depth and microbial biomas and **b** sediment pH and microbial biomass

environments. The next relative genera were *Dokdonella*, *Frateuria*, *Dyella*, *Rhodanobacter*, *Fulvimonas*, and *Luteibacter*, but sequence similarities were ≤91%. The second largest group of clones also belonged to the Gammaproteobacteria. Again, they resembled phylotypes retrieved from AMD environments, but sequence similarities to the next cultivated species were ≤89%. Other important genera (several percent of the clones) that are also well-known from other acidic habitats were Acidobacteria, Alphaproteobacteria of the *Acidiphilium* group, *Acidimicrobium*, *Sulfobacillus*, *Leptospirillum*, *Chloroflexi*, and *Entotheonella*. The diversity of archaeal clones was low. All of them belonged to the Thermoplasmatales and were related to phylotypes from the Río Tinto and other acid mine drainage sites (sequence similarities 89–99%).

Blöthe et al. (2008) investigated the prokaryotic diversity in the sediments of Lake 77 in Lusatia, Germany. The sediments of this lake possess geochemically different zones, an upper acidic zone I (pH 3), a transition zone II, and a weakly acidic zone III (pH 5.5). Zone I and zone III were studied separately by 16S rRNA based community analysis. Denaturing gradient gel electrophoresis (DGGE) screening revealed 40 and 42 different phylotypes in zones I and III, respectively.

A large fraction of the clones (45 and 43% in zones I and III, respectively) belonged to the phylum *Acidobacteria*, which is remarkably different from Lake 111 (discussed above). Other sequences detected in both zones were affiliated to *Nitrospira*, Cytophagales, Alpha-, Gamma-, and Deltaproteobacteria. Among the Alphaproteobacteria, many belonged to the genus *Acidiphilium*, members of which have also been cultured from pit lake sediments (Küsel et al. 1999). No archaeal sequences were obtained. While sequences related to Firmicutes, *Actinomyces*, and Betaproteobacteria were only found in zone I, sequences related to *Verrucomicrobia* subdivision 5, *Thermus/Deinococcus*, *Bacillus/Clostridium*, and an uncultured group were only obtained from zone III. These findings are comparable to those of Becerra et al. (2009), who studied an old abandoned mine site in Massachusetts where an AMD-generating zone (GZ; pH 1.7–2.4) and an AMD-attenuating zone (AZ; pH 4.5–6.0) could be distinguished. The authors detected 44 and 45 operational taxonomic units (OTUs) at the GZ and AZ, respectively. *Acidobacteria* were important components of the community in both zones, and Alphaproteobacteria were also present in GZ and AZ. Members of the Nitrospira (*Leptospirillum*) were only detected in the GZ, where they comprised the majority of clones. Similar to the findings of Blöthe et al. (2008), clostridia were only important in the higher pH AZ. However, Becerra et al. (2009) also undertook a rarefaction analysis, which revealed that sampling was inadequate for covering bacterial diversity in both zones and that GZ and AZ could contain 3.1–4.4 and 1.3–1.7 times the number of OTUs found in the clone library.

It can be concluded that results have to be complemented by additional studies, including rarefaction analysis, to really understand diversity in pit lake sediments. Future research should aim at obtaining a better taxonomic resolution of some groups and include comparative rRNA-based analyses of sophisticated culture or microcosm approaches.

Microbially Mediated Sediment Processes

In general, the same sequence of terminal electron-accepting microbial processes from oxic respiration to methanogenesis may be expected in pit lakes sediments as in natural sediments, although it is evident that the absolute or relative intensities of processes differ considerably due to the extreme chemistry.

A special case is the littoral sediment, which is often sandy with a patchy distribution of microphytobenthos (Sect. 3.3.2.3) or colonized by bulbous rush, *Juncus bulbosus* (Chabbi 1999). In the practically unvegetated littoral sediment of Lake 111, relatively deep oxygen penetration (up to 24 mm) has been observed. The accompanying diffusive oxygen fluxes of 3.1 ± 1.6–8.4 ± 0.4 mmol m^{-2} d^{-1} (Koschorreck et al. 2003a, 2004) were an order of magnitude lower than in natural lakes (Wendt-Potthoff and Koschorreck 2002), which indicates a relatively low respiratory activity. The general presence of Fe(II) in acidic pit lake sediments suggests that microbial Fe(II) oxidation should make an important contribution to O$_2$ consumption near the oxic sediment–water interface. However, no in situ

evidence for this process was found by Koschorreck et al. (2003a), and the observed disappearance of dissolved Fe(II) was rather due to jarosite precipitation within the sediment. In contrast, a laboratory incubation of the same sediment revealed a potential biological Fe(II) oxidation rate of 0.65 mmol cm^{-3} h^{-1} (Wendt-Potthoff and Koschorreck 2004). The range of CO_2 production rates in this sediment was 6–42 mmol m^{-2} d^{-1}, with maximum values in the summer months (Koschorreck et al. 2004), which is higher than in the profundal sediment and comparable to natural lakes. This suggests that heterotrophic aerobic activity was responsible for O_2 consumption in the littoral sediment of Lake 111. The same study reported potential iron reduction rates in the range of 6–45 mmol m^{-2} d^{-1}, depending on the season. The depth of maximum activity varied, and potential Fe(III) reduction was regularly detected near the sediment surface. Active zones generally showed elevated most probable number (MPN) counts of acidophilic Fe(III) reducing bacteria. This suggests Fe(III) reduction by oxygen-tolerant organisms such as *Acidiphilium* or *Acidobacterium*, which have been shown to carry out Fe(III) reduction under micro-oxic conditions (Coupland and Johnson 2008; Johnson and Bridge 2002).

Many littoral sites in acidic pit lakes are colonized by *Juncus bulbosus*, e.g. Lake 108 in Lusatia (Chabbi 1999). The plant roots release oxygen into the sediment, which stimulates microbial Fe(II) oxidation and the formation of ferric crusts (plaques) around the roots. Contrary to other plants, the crusts are not directly attached to the root, but a space is left which is colonized by microorganisms (Chabbi 1999). High numbers of Fe(III) reducing bacteria and other organisms have been found to be associated with the roots (Küsel et al. 2003), which apparently live from root exudates. The CO_2 they generate during respiration is beneficial for the plants in an environment with limited inorganic carbon (Koschorreck et al. 2004).

Iron plaques also form on leaf litter sedimenting in the acidic pit lakes. Although this process triggers trapping of fine particulate material and biofilm formation, it leads to incomplete decomposition, making the leaves only a temporary carbon source (Schlief and Mutz 2005). However, compared to streams affected by acid mine drainage, iron plaque formation was weaker on sedimented leaves in a pit lake, which was accompanied by higher fungal biomass and respiration rates (Schlief and Mutz 2005).

Nitrate reduction and manganese reduction are not important in acidic pit lake sediments, since their nitrate and Mn concentrations are low (Schultze et al. 2010). Low nitrate concentrations are common because nitrification is inhibited at low pH.

Iron reduction is the dominant terminal electron accepting process for the oxidation of organic matter, hydrogen, or reduced sulfur in acidic pit lake sediments (Johnson 1995; Küsel and Dorsch 2000; Langner 2001). Signs of microbial Fe(III) reduction are reported from most investigated sediments, even the extremely metal-rich Berkeley pit (Twidwell et al. 2006), but few studies report quantitative in situ rates. Generally, maxima of potential Fe(III) reduction are accompanied by elevated viable counts of Fe(III) reducing microorganisms (e.g. Koschorreck et al. 2007a; Meier et al. 2004; Wendt-Potthoff et al. 2002). Despite this correspondence, viable counts are too low to explain the observed activities, which is easily seen if cell-based rates are calculated (e.g. Meier et al. 2005). More effort is needed to detect and isolate

the organisms responsible for Fe(III) reduction in such systems. If available, Fe(III) reduction rates are comparable to or even higher than those found in iron-rich freshwater environments (Table 3.27), although physiologically and phylogentically different organisms are responsible for the observed activities. However, comparison is not trivial, since there is no good standard for quantifying in situ Fe(III) reduction, such as ^{35}S-sulfate used for in situ sulfate reduction measurements. Rates based on Fe(II) fluxes are not necessarily the same as those from anoxic batch incubations with total Fe(II) determined over time.

Despite the generally large sulfate pools and cultivation-based detection of sulfate-reducing bacteria in acidic pit lake sediments, sulfate reduction is only rarely detected. Similar to Fe(III) reduction, there are often reliable signs of this process, but no quantification of the activity. For example, laboratory incubations revealed sulfate reducing activity in the littoral zone of Lake Kepwari, Australia (Read et al. 2009). This is in contrast to the well-studied Lake 111, where sulfate reduction was measured in a deep small basin (Meier et al. 2004), but not in the littoral zone (Koschorreck et al. 2004). However, another acid, nutrient-rich pit lake, Cueva de la Mora in the Iberian Pyrite Belt, had much higher sulfate reduction rates in the mixolimnetic compared to the monimolimnetic zone (Wendt-Potthoff et al. 2012). Examples of spontaneous (without substrate addition or other treatments) sulfate reduction rates in pit lakes are given in Table 3.28. Low pH alone does not preclude sulfate reduction, and H_2S or organic acid concentrations observed in pit lake environments are too low to be inhibitory (Koschorreck 2008). Competition with iron reduction and electron donor limitation are more likely explanations (Blodau and Peiffer 2003; Koschorreck 2008), and this aspect is further discussed in the following subsection.

In contrast to natural freshwater ecosystems, methanogenesis is generally negligible in acidic pit lakes. This is not a consequence of the low pH, as methane formation is an important process in acid peatlands, swamps, and mires (Bergman et al. 1998; Cadillo-Quiroz et al. 2006). Methane formation is inhibited by the high sulfate concentrations in the sediments (in the g L^{-1} range, see Sect. 3.2 on pit lake chemistry). In a lake acidified by volcanism, methanogenesis was found to take place in deeper sediment layers, where the pH value was above 4 and sulfate reduction became sulfate limited (Koschorreck et al. 2008). Low concentrations of methane (10–60 μmol L^{-1}) were detected in the sediments of Lake 166 in Lusatia (Blodau et al. 1998). The Spanish pit lake Cueva de la Mora, which is considerably enriched in carbon and nutrients, also had methane concentrations between 15 and 70 μmol L^{-1} in the monimolimnetic sediments, but incubation assays failed to detect methanogenic activity (Wendt-Potthoff et al. 2012).

Iron and Sulfate Reduction and Potential for Remediation

If sulfate and iron reduction coexist in a given sediment, these reactions might reverse the acidification caused by pyrite oxidation, and to a certain extent, pyrite will be formed again. Generally, the addition of suitable substrates to pit lake

Table 3.27 Fe(III) reduction (FeR) in pit lake (P.L.) sediments and natural freshwater sites; n.a.: not available

Lake	Type, location	Sediment pH	Method	FeR (nmol cm^{-3} d^{-1})	FeR (mmol m^{-2} d^{-1})	Reference
Lake 77, zone I[a]	P.L., Germany	≈3	Batch incubation	204		Küsel and Dorsch (2000)
Lake 77, zone I[a]	P.L., Germany	≈3	Batch incubation	250		Peine et al. (2000)
Lake 77, zone II[b]	P.L., Germany	3	Batch incubation	710		Blöthe et al. (2008)
Lake 77, zone II[b]	P.L., Germany	5.5	Batch incubation	895		Blöthe et al. (2008)
Lake 116 littoral	P.L., Germany	3– >6	Pore water profile/flux	150	6.9	Blodau et al. (1998)
Lake 116 pelagial	P.L., Germany	3– >6	Pore water profile/flux	50	3.8	Blodau et al. (1998)
Lake Niemegk	P.L., Germany	2.6–5	Pore water profile/flux	5,000		Langner (2001)
Cueva de la Mora mixolimnion	P.L., Spain	2.8–3.2	Batch incubation	585–627	6.06	Wendt-Potthoff et al. (2012)
Lake 117	P.L., Germany	6	Pore water profile	150–260	2.6	Koschorreck et al. (2007b)
Lake 111	P.L., Germany	2.7	Batch incubation	670		Wendt-Potthoff (unpublished)
Great Ghost Lake	Oligo-mesotrophic, Taiwan	n.a.	In situ accumulation of Fe(II)		5.07	Wann et al. (1997)
Baldeggersee littoral	Eutrophic lake, Switzerland	n.a.	flux		0.06	Schaller et al. (1997)
Baldeggersee pelagial	Eutrophic lake, Switzerland	n.a.	Flux		0.15	Schaller et al. (1997)
Kalix River estuary	Estuary, Sweden	n.a.	Pore water profile		0.77	Widerlund and Ingri (1996)

[a] probably an underestimate, since only dissolved Fe(II) was measured; [b] incubated at 15°C, although the maximum sediment temperature was 12°C

Table 3.28 Sulfate reduction (SR) in the sediments of acid lakes measured by ^{35}S tracer technique. The lakes are pit lakes except Lake Caviahue, which is a glacial lake acidified by volcanism

Lake	pH of water	pH of sediment	SR (nmol cm^{-3} d^{-1})	SR (mol m^{-2} d^{-1})	References
Reservoir 29	2.7	3.8	16–152		Gyure et al. (1990)
Lake 111 (10 m)	2.6	>4	1.6–7.2		Meier et al. (2004)
Lake 116	3	>6	17–130	1.2–5.2	Blodau et al. (1998)
Lake 76	2.8	>6	70		Blodau et al. (2000)
Lake 77	3	>5	6		Peine et al. (2000)
Lake 117	3.1	6	57–265		Koschorreck et al. (2007b)
Cueva de la Mora (mixolimnion)	2.5	2.8–3.2	4.5–314	13	Wendt-Potthoff et al. (2012)
Cueva de la Mora (monimolimnion)	3.6–4.3	4.3–4.9	0.2–2.3	0.1	Wendt-Potthoff et al. (2012)
Lake Caviahue	2.6	3	33		Koschorreck et al. (2003)

sediments increases both iron and sulfate reduction (e.g. Becerra et al. 2009; Koschorreck et al. 2007a; Küsel and Dorsch 2000; Langner 2001; Meier et al. 2005; Wendt-Potthoff et al. 2002). However, many pit lake sediments do not show sulfate reduction at all, and the estimated times for neutralization in others are very long (several hundreds or more than a thousand years: Blodau and Peiffer 2003; Peine and Peiffer 1998; Wendt-Potthoff et al. 2012). The long times for neutralization are due to a considerable reoxidation of sulfides in lake systems (Koschorreck and Tittel 2007), which is hard to control during any in situ remediation approach (Geller et al. 2009; Chap. 4). Blodau and Peiffer (2003) demonstrated that the neutralization process is constrained by organic matter quality and thermodynamic effects, which together control the relative rates of sulfate and iron reduction. Substantial amounts of iron sulfides were only formed at a simultaneous partial thermodynamic and solubility equilibrium of the involved biogeochemical processes. If this is not reached, the sediments remain in an Fe(III) reducing and sulfide oxidizing state, despite addition of organic matter and nutrients. In addition to organic matter quality and low pH, which thermodynamically favors Fe(III) reduction, the supply of reactive Fe(III) is a key factor. This is demonstrated by many cases in addition to those discussed by Blodau and Peiffer (2003). For example, the deep part of Lake 111, which in contrast to the rest of the lake shows low rates of sulfate reduction (Meier et al. 2004; Table 3.28) has been excluded from lake overturn for several years and has developed a small reduced bottom water body. This might have greatly reduced the supply of Fe(III) to the sediments. Lake Caviahue, a glacial lake acidified by volcanism with active sulfate reduction, not only had substantial production of biomass, which was precipitated by volcanic ash following an eruption, but also has a relatively low iron content compared to acidic pit lakes (Koschorreck et al. 2003b; Table 3.28). As a consequence,

it might not be sufficient to add a cheap carbon source or lime to an acidic pit lake to neutralize it, but biological production and inflows of iron, carbon, acidity, and sulfate have to be studied carefully to plan a sustainable treatment, if necessary.

In conclusion, despite restricted colonization by benthic invertebrates and practical absence of some microbial processes typical for freshwater lakes, the sediments of acidic pit lakes show considerable microbial diversity compared to extremely acid mine sites, and biomasses and total microbial activities comparable to natural lakes. Further research is necessary to unravel the true microbial diversity of pit lake sediments and its relation to environmental factors. It will be both of scientific and practical interest to better quantify rates of Fe(III) reduction (also in natural freshwater bodies) and to identify and isolate the organisms responsible for Fe(III) reduction at acid and intermediate pH values. This should include the more systematic study of different habitats in acidic pit lakes, such as littoral and profundal zones, vegetated and unvegetated sediments, and chemoclines in meromictic lakes. If neutralization of an acidic pit lake is attempted, such studies will complement approaches to get reliable estimates on carbon and nutrient supply, inflows of iron, acidity, and sulfate, which are all necessary to plan realistic and sustainable treatment options.

3.4 Modeling of Pit Lakes

Donald S. Dunbar

3.4.1 Introduction

The long-term planning and allocation of financial resources required for effective monitoring and remediation of pit lakes can benefit immensely from defensible predictions of physical and geochemical pit lake properties in advance of lake formation. In this section, we consider numerical computer models that are designed to simulate the evolution and spatial distribution of physical and/or geochemical properties of pit lakes. The discussion is limited to models designed for long-term simulations spanning decades or even centuries. Other types of pit lake models, such as those designed for predicting biological productivity will not be addressed.

Model predictions can provide regulators, mine operators, and other stakeholders with information critical to anticipating and addressing water quality concerns that are likely to arise after cessation of mining and dewatering, such as: filling rates and the timing of overtopping; water column stability, stratification, overturning, and the onset of meromixis, and; the evolution and spatial distribution of pH, sulfate, dissolved metals, and other chemical species.

Flooded open pits, unlike most natural lakes, are typically deep and steep-sided with large values for the relative depth, z_r, given by

$$Z_r(\%) = 100\frac{Z_m}{d},$$ (3.27)

where Z_m is the maximum depth and d is the mean lake diameter (Gammons and Duaime 2006). Defining $d = 2\sqrt{A/\pi}$ for lake surface area A yields

$$Z_r(\%) = 50Z_m\sqrt{\frac{\pi}{A}}$$ (3.28)

The small fetch (i.e. length of lake surface exposed to wind-energy) and large depth result in relatively ineffective downward transfer of wind energy, thereby limiting vertical mixing. Natural lakes that exhibit strong stratification and are poorly mixed typically have z_r values greater than 4; by contrast, well-mixed natural lakes have z_r values generally less than 2.

Pit lakes, and their related environmental issues, share common characteristics that provide a unique challenge to computer modelers. The large relative depth has important implications for the downward penetration of thermal and wind energy, and their concomitant effects on vertical mixing and stability. Unlike natural lakes, which typically have a layer of organic matter at the bottom, the bottom of a pit lake–initially at least–consists of bare (and commonly, oxidized) rock. In addition, the time scales for environmental issues related to pit lakes often span decades or even centuries.

3.4.2 Physical Properties of Pit Lakes

3.4.2.1 Water Density

Density in freshwater lakes is largely determined by temperature. The density of pure liquid water attains a maximum of 0.99998 g/cm^3 at 3.94 °C. Therefore, dense lake bottom waters tend to remain near 4 °C while the temperature near the surface varies in response to inflows and atmospheric conditions.

The addition of dissolved salts to freshwater results in an increase in density. Seawater, for example, has a density approximately 2.8% greater than freshwater. Pit lakes contain water that has a wide range of dissolved salts and other geochemical species due to inflows of groundwater, precipitation, and surface inflow that has contacted exposed pit wall surfaces. Thus, both water temperature and salinity influence the density of water in pit lakes. The density of pit lake water is calculated by applying an empirical equation of state relating water temperature and the concentration of dissolved ions (salinity) to water density. Salinity can be accurately determined by measuring the conductivity of the water. The equation of state for water is nonlinear with temperature for a fixed conductivity, and nearly linear with conductivity for a fixed temperature (Fig. 3.74).
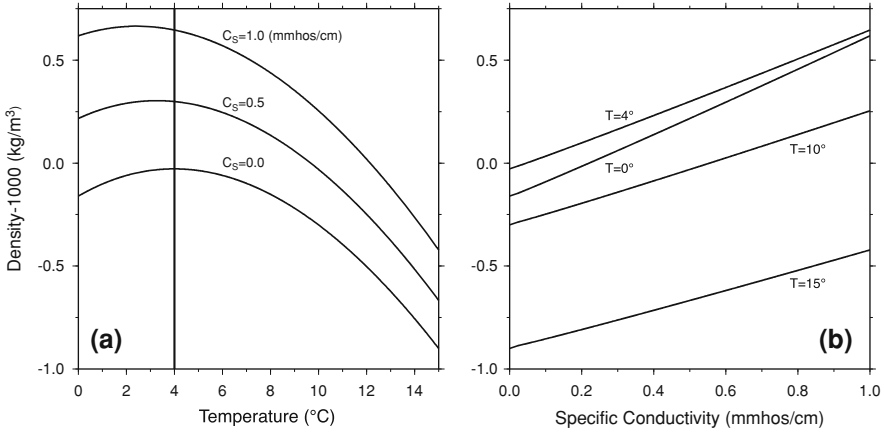
Fig. 3.74 Water density for different values of **a** temperature T, and **b** specific conductivity

3.4.2.2 Vertical Stability

Deep, freshwater lakes typically have at least two layers: a bottom hypolimnion, whose waters are at least seasonally isolated from the atmosphere (and sometimes perennially stagnant), and an upper epilimnion, which is well mixed by the wind. The two layers are separated by a relatively thin thermocline defined by a strong thermal gradient.

The physical stability of a stratified system can be described by the tendency for the upper and lower water layers to mix. The energy required to vertically mix two water masses increases with the density difference between the two layers. Specifically, given two layers of density ρ_1 and ρ_2, of equal volume and thickness, h, the energy required to mix the two volumes completely, ignoring viscous dissipation of energy, is:

$$\frac{gh\Delta\rho}{2} \tag{3.29}$$

Figure 3.75 shows the energy required to raise the center of mass of the original two layers to their geometric center.

Increasing density with depth decreases the tendency of two water masses to mix. Large density contrasts across the density gradient, or pycnocline, suppress mixing and therefore increase the vertical stability of the water column.

Dimictic Lakes

Many natural and pit lakes experience regular, seasonal ice cover, with the timing and duration dependent primarily on latitude and altitude, but also on inter-annual variability of air temperature, wind velocity, and solar radiation. A period of ice
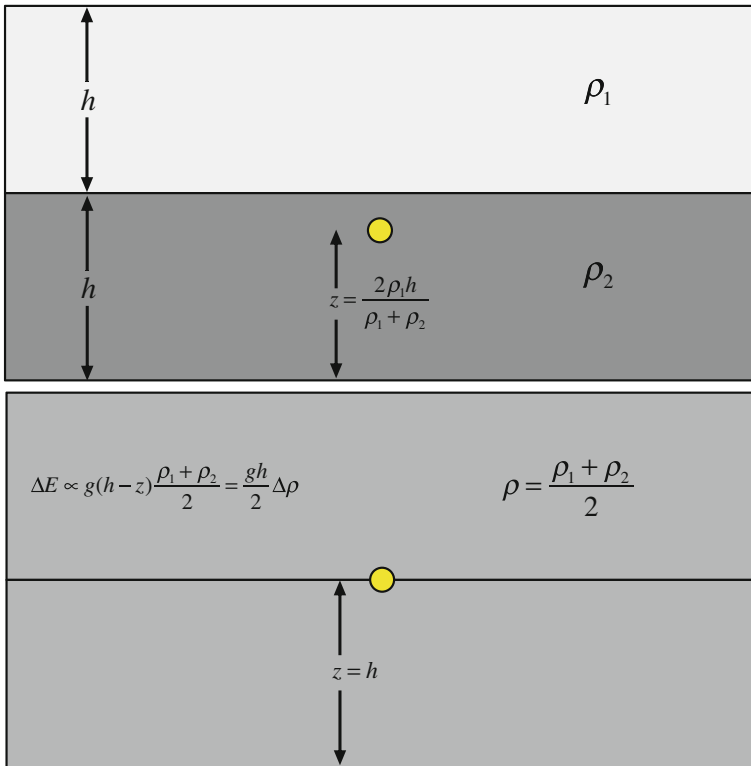
Fig. 3.75 Energy required to completely mix two equal water volumes with different densities. The *yellow dot* marks the location of the centre of mass

cover, and the changes in lake temperature that precede and follow it, profoundly affect the physical properties of lakes. From thermally stratified conditions in late summer, lake surface waters cool and increase in density as fall approaches until a temperature of approximately 4 °C is reached, at which point maximum density is attained and the lake convectively mixes. The degree of mixing depends on the lake depth and vertical density gradient. Some lakes mix fully every year, while others mix fully only occasionally. If meromixis has occurred due to high bottom layer solute concentrations and a stable monimolimnion has formed, then complete mixing is inhibited and is limited to the upper layers of the lake.

If the temperature decreases sufficiently, then ice will begin to form, thickening over the winter months. The lake will again become thermally stratified, with less dense 0 °C water in a surface layer overlying warmer, denser water below. The ice thermally insulates surface waters from the cooler air above and eliminates wind mixing. Snow accumulates on the ice, storing water until it thaws with the arrival of warmer temperatures. With the formation of ice, the level of the lake will often drop as surface inflows decrease or stop altogether. Some solutes may become supersaturated immediately under the ice due to salt expulsion as the ice forms.

During the subsequent spring and summer thaw, the snow and ice melt and their volumes are added to the lake over a relatively short interval together with runoff from the surrounding watershed. This sudden influx of water (freshet) may represent a significant portion of the annual surface water budget.

As surface waters warm and the ice and snow melt, the water density increases as the temperature climbs toward 4 °C. Again, convective mixing occurs, and in the case of most natural lakes, complete overturning. The twice-annual cycle of fall-winter and spring-summer overturning is the defining characteristic of dimictic lakes. Because of their importance in lake dynamics, ice formation and thawing are important processes to include in models of pit lakes where this occurs (Hamblin et al. 1999; Patterson and Hamblin 1988; Rogers et al. 1995).

3.4.3 Geochemical Processes Influencing Pit Lake Chemistry

The density structure of stratified lakes has an important influence on the chemical and biological processes occurring in both the water column and sediments. In particular, the restricted mixing across the pycnocline can result in the depletion of O_2 and the accumulation of other chemical species associated with the breakdown of organic matter in the lake interior. In natural aquatic systems, dissolved oxygen is consumed principally by bacterially-mediated oxidation of organic matter (OM; Fenchel and Blackburn 1979; Stumm and Morgan 1981). OM produced in the surface waters (i.e. plankton, zooplankton) is delivered to the interior of the lake and lake bottom via the settling of organic detritus.

Due to the downward transport of OM, the oxidation reactions associated with its degradation occur throughout the water column. Organic matter is oxidized or remineralized by both aerobic and anaerobic bacteria. These remineralization reactions are redox processes in which electrons are transferred from the reductant (OM) to an electron acceptor (oxidant). In shallow lakes, much of the oxidation of OM occurs at the sediment–water interface, while in deeper lakes, significant OM oxidation can occur in bottom water (Hamilton-Taylor and Davison 1995; Northcote and Johnson 1964). Collectively, these oxidation processes result in depletion of oxygen in the bottom waters. Without deep water mixing and associated replenishment of oxygen, or where the OM flux to bottom waters is high (as in productive or eutrophic lakes), oxygen-consuming reactions can completely deplete oxygen in bottom waters leading to anoxia.

In aerobic environments, oxygen is preferentially used as the final electron acceptor in the oxidation of OM. Once oxygen is depleted, other electron acceptors are employed. Based on decreasing free energy yield, thermodynamics dictates that electron acceptors are used in the order: $O_2 > NO_3^- \approx Mn^{IV}$-oxides $> Fe^{III}$-oxides $> SO_4^{2-}$ (Froelich et al. 1979; Sigg et al. 1991; Stumm and Morgan 1981). Once oxygen has been exhausted as an oxidant, nitrate will be employed as the electron acceptor for OM oxidation, followed by Mn-oxides.

The development of anoxic bottom waters can greatly influence the behavior of trace elements. Of particular importance is the reduction of sulfate, which liberates hydrogen sulfide (H_2S). In most mine pit lake scenarios, sulfate is readily available at concentrations capable of generating significant quantities of hydrogen sulfide. Many trace elements (e.g. Fe, Co, Ni, Zn, Cd, and Pb) react rapidly with free sulfide to precipitate insoluble sulfide minerals (Balistrieri, Murray et al. 1994; Stumm and Morgan 1981). Consequently, the precipitation of metal sulfides, and their subsequent settling to the lake floor, can provide an effective mechanism for removing trace elements from the water column (Achterberg et al. 1997; Green et al. 1989).

The same redox processes outlined above for the water column occur within sediments and submerged mine tailings. Accordingly, lacustrine sediments containing organic matter are often devoid of dissolved oxygen within a few millimeters of the sediment–water interface, even if bottom waters are fully saturated with dissolved oxygen (Martin et al. 2003; Pedersen et al. 1993). This sometimes has important implications for the chemistry of waters seeping out of a perched pit lake where seepage to groundwater is important.

3.4.4 Pit Lake Model Characteristics

3.4.4.1 Basic Properties

Pit lake hydrodynamic models may be classified based on the number of spatial dimensions they include. Generally, the complexity and demands imposed on computer resources (i.e. memory, disk space, and CPU cycles) and the quantity of field data required for model initialization and inputs increases significantly with the number of dimensions.

These considerations, and the very long time periods over which a model may be required to simulate pit lake properties, impose severe constraints on the number of spatial dimensions that may be reasonably included in a model design. Models used to simulate pit lakes over long time periods usually include just one spatial dimension, with temporal variation of water properties occurring only in the vertical, and with water properties in the horizontal dimensions assumed to be isotropic.

The validity of applying a one-dimensional model to a particular pit lake is often done without justifying the assumptions implicit in the model design. The key assumption is that lake properties in the vertical change much more slowly than in the horizontal.

Horizontal gradients occur within pit lakes for a variety of reasons. For example, a strong wind blowing on the lake surface will temporarily create a small surface slope by piling water toward one side of the lake. This tilts the isopycnals, resulting in horizontal thermal and salinity gradients. When the wind stops, both a surface and internal seiche may develop which persist until friction dissipates the energy as heat. In addition, inflows of fresh and treated water can be a source of lateral inhomogeneity. When the sources of the horizontal gradients cease, the

time over which the gradients relax and vanish is generally much shorter than the typical time scale over which comparable changes in vertical properties occur.

If necessary, the validity of the one-dimensional assumption may be tested by calculating the Lake Number (Atenucci and Imerito 2002), which takes into account the stability of the water column, and the destabilizing effect of the wind.

$$L_N = \frac{(z_g - z_0)Mg(1 - z_T/z)}{A^{1/2}(1 - z_g/z) \int\limits_{A(z_H)} \rho_0 u_*^2 dA} \tag{3.30}$$

where $\rho(z)$ is the vertical profile of water density; z_g, z_0, z_T and z_H are the center of volume, center of gravity, height of the center of the metalimnion, and height of the water column, respectively (measured upward from the pit bottom); M is the total mass of water; g is the acceleration due to gravity; A is the plan view area of the lake surface; and u is the surface friction velocity. For values of $L_N \gg 1$ the one-dimensional assumption is considered to be valid.

The equations governing the conservation of momentum, mass, and heat are expressed in three spatial dimensions. To reduce this number from three to one vertical dimension, the equations are laterally integrated; thus, models based on this modified set of equations are referred to as laterally integrated models.

3.4.4.2 Turbulence and Mixing

A fundamental difficulty in modeling the physical processes in many hydrodynamic systems, including pit lakes, is the broad range of spatial and temporal scales that are observed in nature. In natural hydrodynamic systems, there is always a cascade of kinetic energy from large spatial scales through to small scales due to nonlinear interactions. At the smallest scales, viscosity becomes important and the energy is finally dissipated as heat. This energy cascade is the signature of turbulent systems and is an important cause of mixing. In practice, it is impossible to model turbulent systems exactly because of the lower bound on spatial resolution in the computational grid used to represent the physical system being modeled.

All processes that occur on scales smaller than the minimum model resolution must be included using a turbulent energy closure scheme (Moin et al. 1991). Ignoring sub-grid scale dissipation of energy creates aliasing–a transfer of small-scale energy to larger spatial scales that produces numerical instabilities and model failure. A common approach to solving this problem is to parameterize the small-scale turbulent processes using an analogue to molecular diffusion. Specifically, mixing at the small-scale end of the turbulent cascade is assumed to be isotropic, and is approximated by a term that includes a turbulent diffusion coefficient. In the vertical component of the momentum equation, this term appears as:

$$\frac{\partial}{\partial z}\left(K(z)\frac{\partial u}{\partial z}\right), \tag{3.31}$$

where $K(z)$ is the vertical turbulent diffusion coefficient and u is the horizontal current velocity. This analogue treats sub-grid scale turbulence in the same way as molecular diffusion, except that the diffusion coefficient is a variable that depends on other properties of the system (Kipfer et al. 2000; Osborn 1980; Weinstock 1978).

Wind is a principle source of kinetic energy for turbulent mixing in pit lakes. Surface wind stress creates vertical current shear, which in turn generates turbulence. The Wedderburn number, an indicator of wind-driven mixing rates in pit lakes, is defined by

$$W = \frac{g' h_m^2}{u_*^2 L} \tag{3.32}$$

where $g' = \Delta\rho/\rho$ is the reduced gravity corresponding to the density jump $\Delta\rho$ across the bottom of the surface mixed layer; h_m is the surface mixed layer thickness; L is the length of the lake; and u_*^2 is the kinematic shear stress due to the wind. For $W \ll 1$ observations and scaling arguments suggest that the mixed layer deepens rapidly due to shear production of turbulent energy (Monismith 1985).

Other mechanisms exist for transporting and releasing energy for mixing within a pit lake. The vertical density structure of a pit lake leads to spectral decomposition of the horizontal velocity field into a set of internal vertical modes that are excited by surface winds, resulting in horizontal currents throughout the water column. Modes are characterized by their number of zero crossing points. Vertical current shear resulting from this modal excitation can generate turbulence and mixing (Hamblin et al. 1999).

Another source of mixing can occur at the interface of a monimolimnion and an overlying, cooler hypolimnion. The differential molecular diffusion rates of heat and salt (heat diffuses at approximately 100 times the rate of dissolved salts) can cause destabilizing heating at the bottom of the hypolimnion, resulting in convective mixing.

3.4.4.3 Pit Shell Morphometry

The pit shell morphometry is a fundamental component of pit lake models. In one-dimensional, laterally integrated models, it is expressed as a curve or function relating elevation, z, above the pit bottom to the corresponding plan view area, $A(z)$, of the pit shell. Shell volume between two elevations can then be calculated from the expression:

$$V(z_1, z_2) = \int_{z_1}^{z_2} A(z) dz \tag{3.33}$$

These data are typically extracted from maps or digital engineering drawings of pit shells.

Hydrologic Balance in Pit Lakes

The hydrologic balance for a pit lake determines the filling rate, final lake elevation, and volume, and is often complex, with many distinct components, including:

- surface and sub-surface inflows of natural runoff, tailings, and treated water
- groundwater inflows/outflows
- precipitation/evaporation/sublimation (ice/snow)
- removal via pumping

Surface and subsurface inflows can consist of water diverted from nearby streams as well as water from treatment plants, tailings, and onsite water collection facilities. Inflows may be seasonal due to variable rates of precipitation, evaporation, and ice/snow melt. At high latitudes, it is common to have a freshet, or peak in the annual inflow corresponding to increased temperatures and subsequent rapid ice and snow melt.

Groundwater flows may be directed into or out of a pit lake, and are often a major component of the water balance. The depth and intensity of these flows over time depend on hydrological gradients in the water table enclosing the pit shell and may be difficult to quantify accurately without extensive field data.

Other types of inflows and outflows occur in pit lakes. For example, the Main Zone pit lake at the Equity Silver Mine site near Houston, BC (Canada) receives a surface discharge of relatively dense slurry (neutralization sludge) that penetrates downward through the lake as a density flow (Crusius et al. 2003). The flow generates shear turbulence that entrains ambient lake water and transports it downward. The entrainment increases the volume and decreases the density of the descending flow, causing it to decelerate. Over the summer months, this mechanism results in large-scale redistribution of water properties and is an important mechanism for surface metal removal (Dunbar 2008). In addition, clean water is pumped into an adjacent stream from a depth of 20 m in the lake.

At the Island Copper Mine saltwater pit lake near Port Hardy, BC (Canada), treated water is injected through a pipe directly into the hypolimnion at a depth of approximately 220 m (Fisher 2003).

3.4.4.4 Energy Balance in Pit Lakes

The primary components in the energy balance for pit lakes are the contributions of wind and surface heat fluxes to the surface momentum flux. Subsurface flows, including groundwater and density inflows from high conductivity discharges, may also affect the heat budget. Less frequently, geothermal sources make a significant contribution (Henderson-Sellers 1986). The net heat flux is given by (Balistrieri et al. 2006):

$$H_{NET} = [H_{SW}(1 - A_{SW})] + [H_{LW}(1 - A_{LW})] - H_{LWB} - H_E \pm H_C \qquad (3.34)$$

where the components include incident short (H_{SW}) and long (H_{LW}) wave radiation; long wave outgoing (blackbody) radiation (H_{LWB}); sensible heat (H_C), and latent heat of evaporation (H_E). The fraction of incident radiation absorbed by a pit lake is determined by the reflectivity or albedo (A) of the lake, which varies depending on latitude, lake color, surface roughness due to waves, and the frequency of the incident radiation.

Radiation fluxes are divided between: direct solar short wave radiation (280–2,800 nm); incoming long wave radiation (greater than 2,800 nm) emitted from clouds and water vapor; and outgoing long wave radiation emitted by the pit lake surface. Short wave radiation is usually measured directly, while long wave radiation is more often calculated from cloud cover, air temperature, and humidity. Short wave radiation with a wavelength of less than 700 nm is classified as penetrative, while longer shortwave radiation is non-penetrative. The former exhibits exponential decay with depth while the latter adds energy only at the lake surface.

Approximately 45% of the incident short wave radiation is penetrative (Gates 1966). The penetrative depth is determined by the transmissivity of the pit lake water and follows the Beer-Lambert Law given by:

$$P(z) = P_0 10^{-\mu z}$$

where P_0 is the incident shortwave power, and μ is a coefficient that is dependent on the lake properties.

3.4.5 Model Inputs and Outputs

Pit lake models require input data of various types to perform calculations and generate output. *Initial values* are required for some variables at the beginning of the simulation (e.g. pit morphometry; initial lake depth, temperature, salinity, and geochemical composition), while time-series of *boundary values* are required for input variables that change during a model simulation (e.g. meteorological variables, surface and sub-surface inflows).

The following is a list of input data required for a time-dependent, laterally-averaged (one-dimensional) pit lake model, although specific data requirements will depend on the particular application and model design:

- Initial Values

  – Pit morphometry

    pit area versus elevation
    elevation of pit bottom, spillway, and crest

  – Lake Properties

    surface elevation
    temperature

     salinity
     pH
     concentrations of all chemical species of interest

- Boundary Values

  – Inflows/Outflows

     Surface inflows
     groundwater (elevation dependent inflow/outflow)
     waste treatment plant discharge (inflow)
     pumping (outflow)

  – Inflow Properties

     temperature
     salinity
     pH
     concentrations of all chemical species of interest

  – Meteorological

     air temperature
     relative humidity
     wind speed
     precipitation
     evaporation
     incident short wave radiation
     incident long wave radiation
     cloud cover

Ideally, all time-series data required for a pit lake model simulation are available as measurements from stations at or near the lake. Since this is often not the case, proxy data must be substituted for unknown values. Suitable proxy meteorological data may be available from permanent data collection stations. Environment Canada, for example, maintains an on-line database of historical meteorological data that are easily accessible. These data are often not comprehensive, however, and may need to be supplemented from other sources.

Numerical weather forecast and climate models are often a good source of proxy data. For example, regional values of short and long wave radiation and other variables are available through the Internet from the National Centers for Environmental Predictions (NCEP; Glahn and Ruth 2003).

3.4.6 Model Verification and Sensitivity

In principal, all pit lake models should be verified against measurements to validate their use in a particular application. However, it is often not possible to

undertake thorough model verification, either because a complete data set is unavailable, or because of the nature of the model application (e.g. a 200 year simulation of a pit lake for a mine that is in the design phase). Such circumstances may require a certain amount of faith in a model based on an established record of previous successful verifications.

Of equal importance is the need to conduct sensitivity analyses for model inputs (Castendyk and Webster-Brown 2007a, b; Romero and Melack 1996). This entails a systematic variation of key model input variables through values that bracket anticipated ranges. This is particularly important in nonlinear hydrodynamic systems that can exhibit unpredictable, chaotic behavior due to strong nonlinearities (Pattantyús-Ábrahám et al. 2008). In pit lakes where there are numerous inflows, a well designed sensitivity analysis will determine the dependence of lake stratification and stability on inflow properties (Castendyk and Webster-Brown 2007a, b). The thoroughness of a sensitivity analysis for a pit lake model is often constrained by the time required to complete a single model simulation, which may extend to several days or more depending on the model and simulation complexity.

3.4.7 Examples of Pit Lake Models

3.4.7.1 DYRESM

The one-dimensional Dynamic Reservoir Simulation Model, or DYRESM, is one of the most frequently used and cited numerical models for simulating pit lake hydrodynamics. It was developed by the Center for Water Research at the University of Western Australia where it continues to be maintained and made available through the Internet.

DYRESM has been successfully applied to studies of natural and artificial lakes, reservoirs, and pit lakes (Balistrieri et al. 2006; Hamblin et al. 1999; Hamilton and Schladow 1997; Patterson et al. 1984). While the current version of DYRESM available from UWA does not include ice formation, modified versions that include this process have been successfully tested (Patterson and Hamblin 1988). At present DYRESM is limited to modeling pit lake hydrodynamics; however, it can also be run together with the Computational Aquatic Ecosystem Dynamics Model (CAEDYM; Hipsey, et al. 2006). However, CAEDYM does not, at present, simulate the geochemical processes associated with pit lakes.

3.4.7.2 PitMod

PitMod is a proprietary, one-dimensional model developed by Lorax Environmental Services in Vancouver, BC (Canada). It is specifically designed to model pit lake hydrodynamics and geochemistry (Crusius et al. 2002). PitMod

incorporates many of the physical processes included in DYRESM as well as including an ice formation algorithm (Rogers et al. 1995). Most significantly, however, PitMod simulates an extensive set of geochemical reactions by coupling to the PHREEQC geochemical speciation model (Parkhurst et al. 1999). This allows PitMod to perform simulations of a century or more in length that include the evolution of both the geochemical and physical properties of a pit lake.

Like DYRESM, the structure of PitMod is based on a set of vertical layers. The values of geochemical variables required by PHREEQC, such as pH and chemical species concentrations, are maintained and adjusted in PitMod based on modeled pit lake physical processes. At each time step, PHREEQC is implemented within all layers to calculate the equilibrium concentrations of geochemical variables.

PitMod is designed to predict the physical and chemical properties of pit lakes, given suitable estimates for environmental input variables. Model results provide details of the chemistry in vertical layers over time.

3.4.7.3 PitMod: Physical Component

The physical component of PitMod simulates the evolution of the pit lake stratification by predicting salinity, temperature, density (calculated from salinity and temperature) and dissolved oxygen concentration. The physical component of the model is a one-dimensional stack of variable thickness layers. Each layer is assumed to be homogeneous in all water properties. The principal physical processes simulated by PitMod include:

- *Solar heating* of the lake surface: thermal energy from the sun is added to surface waters, thereby altering the temperature and density. Heat is transferred to deeper layers through penetrative absorption, diffusion, mixing, and convection. Similarly, the model allows for geothermal heat where it is considered important.
- *Vertical mixing* as a function of the lake density stratification—kinetic energy from the wind causes adjacent water layers to mix to varying degrees, depending on the vertical density structure of the lake.
- *Convective mixing* due to static instabilities in the water column density, i.e. when water in a layer is denser than the water in the underlying layer.
- *Oxygen consumption* in the water column and sediments is a critical parameter in the geochemical state of the pit lake. Oxygen is introduced to the surface waters through interaction with the atmosphere and is distributed through the water column by mixing and diffusion across adjacent layers. Oxidation of organic matter in the water column and sediments consumes oxygen; if the consumption rate of oxygen in a given layer exceeds its rate of replacement, the layer becomes anoxic.

Along with these processes, PitMod can accommodate the introduction of external source water, or the removal of resident water at any depth in the lake.

3.4.7.4 PitMod: Geochemical Component

The geochemical component of PitMod employs PHREEQC, a geochemical model originally produced by the USGS (Parkhurst et al. 1999). PHREEQC is capable of a wide variety of aqueous geochemical calculations, including:

- speciation and saturation index calculations;
- mineral and gas equilibrium;
- surface complexation (adsorption) reactions;
- ion exchange reactions; and,
- redox reactions.

PHREEQC was selected because it is widely and extensively used, has been rigorously validated, and the computer code is freely available on the Internet. In addition, it includes several thermodynamic databases including WATEQ4F and Minteq. Furthermore, PHREEQC's treatment of aqueous solution chemistry is valid from freshwater through to the high ionic strength media often observed in pit lake systems (Parkhurst personal communication 1998).

PHREEQC requires a comprehensive set of chemical input data to characterize the pit lake water. For a typical simulation of mine-impacted waters, this would include pH, temperature, the controlling redox couple, and the concentrations of oxygen, secondary oxidants (e.g. nitrate and sulfate), major cations, major anions, and trace metals.

PitMod integrates the effect of all inputs on the physical and geochemical properties of the pit lake by solving the set of governing hydrodynamic equations followed by calls to PHREEQC routines that calculate equilibrium concentrations of all chemical species within each model layer. PHREEQC predictions are based on thermodynamic principles and a database that includes hundreds of chemical species. Figure 3.76 shows the sequence of steps in a typical application of PitMod.

The output of PHREEQC includes the equilibrium concentration and speciation of all aqueous components, as well as the equilibrium concentrations of all minerals. Water quality is predicted for each model layer as a function of time, yielding vertical profiles of each parameter. PHREEQC predicts whether a metal will remain dissolved, precipitate from solution, react with an existing mineral by ion exchange, or adsorb to a particle. An important case occurs in anoxic waters, where PHREEQC can predict, for a given metal and dissolved sulfide content, whether or not the metal sulfide will precipitate.
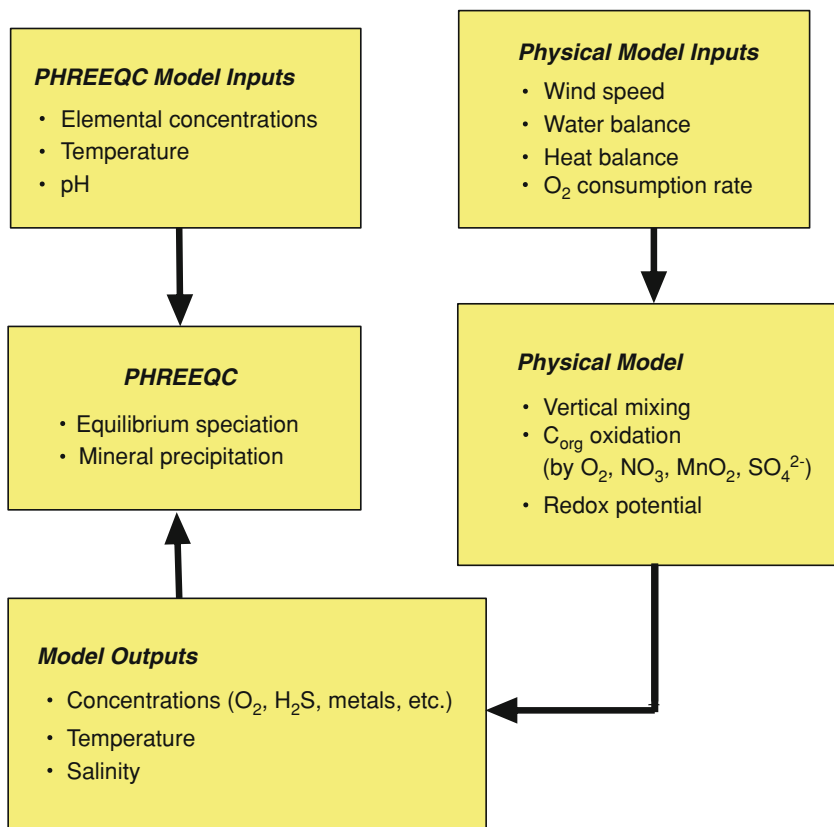
Fig. 3.76 Components of PitMod, a coupled physical-geochemical pit lake model

3.4.8 Case Studies

### 3.4.8.1 The Equity Silver Mine

The Equity mine site is located in south-central British Columbia, Canada (54°11.59′N, 126°15.90′W). The two Equity pits produced silver, copper, and gold from 1981 to 1994. Subsequently, both pits flooded with groundwater and surface runoff. In addition, the larger Main Zone pit receives seasonal surface discharge of relatively dense treatment slurry (ARD neutralization sludge) as well as runoff from the slightly higher Waterline pit lake (Table 3.29).

Water quality in the Main Zone pit lake is characterized by elevated trace metal concentrations in the epilimnion (particularly zinc) during late spring and summer, and significantly lower values in the hypolimnion. The water level in the Main Zone pit is managed by pumping water from a depth of 20 m to a nearby stream.

Table 3.29 Properties of the Main Zone (MZ) and Waterline (WL) pit lakes

Pit Lake	Surface Elev, m	Depth, m	Area, m^2	Volume, 10^6 m^3
MZ	1,255	130	175,812	9.80
WL	1,270	45	37,979	0.70
MZ:WL		2.9:1	4.6:1	14:1
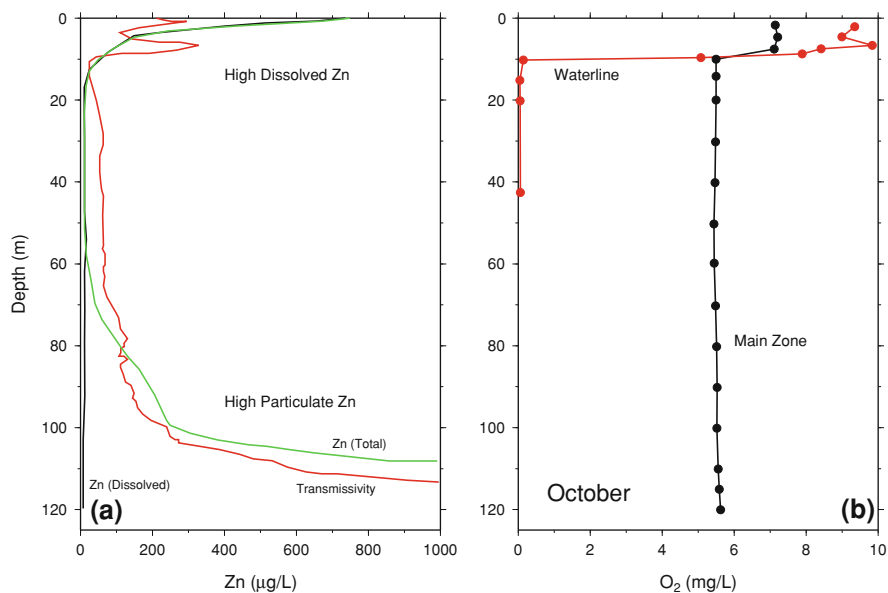
Fig. 3.77 Vertical profiles from the Equity Mine of **a** dissolved Zn, total Zn, and transmissivity in the Main Zone pit lake **b** dissolved oxygen in the Waterline and Main Zone pit lakes during October 2001

The neutralization sludge slurry discharged to the surface of the Main Zone pit lake contains high concentrations of zinc particulates and low concentrations of dissolved zinc. The slurry flow penetrates downward as a density current along the pit wall to the bottom layer of the lake. This is evident in the high particulate zinc concentrations found below 100 m in conjunction with high turbidity (Fig. 3.77a). In addition, the slurry is well oxygenated and delivers dissolved oxygen to the hypolimnion (Fig. 3.77b). In contrast, the Waterline pit lake oxygen remains permanently stratified, despite Waterline being much shallower (Fig. 3.77b).

Typically, both pit lakes are covered by up to 1 m of ice from November through May. During late spring and early summer, drainage into the lakes is greatly enhanced by melting snow and ice. In addition, the flow of surface water from Waterline into Main Zone increases. The latter flow, combined with runoff down the pit walls, increases the flux of trace metals into the Main Zone surface waters. The value for [Zn] measured at 1 m depth during June 2001 was 800 µg/L.
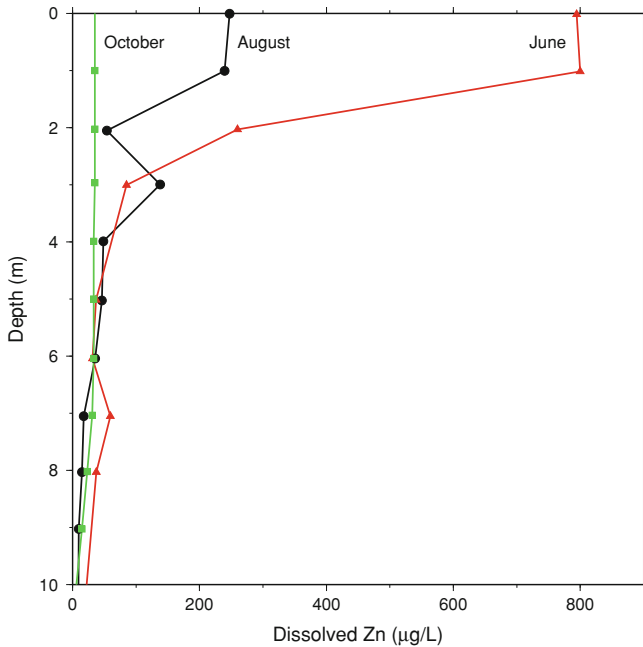
Fig. 3.78 Vertical profiles from the Equity Mine of dissolved Zn in the Main Zone pit lake during June, August, and October 2001
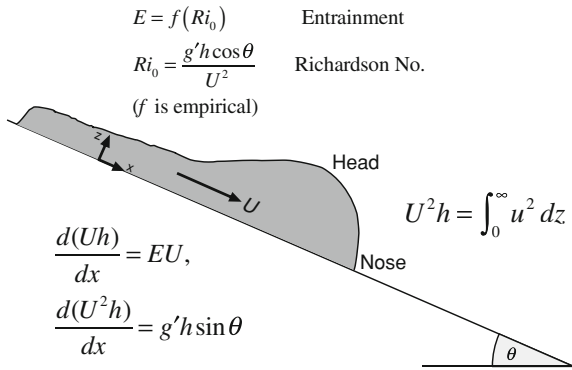
This value subsequently decreased to 250 μg/L in August, and to 40 μg/L by October 2001 (Fig. 3.78).

Experiments carried out within limnocorrals located in the Main Zone pit lake show that algae can facilitate removal of dissolved zinc through both surface adsorption and biological uptake (Martin et al. 2003). High rates of removal were observed after fertilization of limnocorral surface waters stimulated algal growth. The Main Zone pit lake is oligotrophic, however, and naturally occurring algal concentrations are insufficient to account for the observed rates of zinc removal observed between June and October 2001.

PitMod was used to help explain temporal changes in zinc concentration during 2001 within the Main Zone pit lake. The model showed that surface discharge of neutralization sludge slurry, and subsequent density flow down the pit wall, is responsible for the observed zinc concentrations.

Density flows occur in pit lakes when a relatively dense liquid or slurry enters less dense receiving waters and travels downward along the pit walls in response to gravity. The behavior of the density flow depends on its volume flux and excess density. As the flow accelerates toward the lake bottom, the velocity gradient between the quiescent lake water and the outside surface of the density flow generates shear turbulence. This results in mixing between the two water masses and a transfer of momentum from the density flow to the lake water.

**Fig. 3.79** Schematic and equations governing the properties of pit lake density flows

$$E = f\left(Ri_0\right) \qquad \text{Entrainment}$$

$$Ri_0 = \frac{g'h\cos\theta}{U^2} \qquad \text{Richardson No.}$$

$(f$ is empirical$)$

Head

$$U^2h = \int_0^\infty u^2\,dz$$

Nose

$$\frac{d(Uh)}{dx} = EU,$$

$$\frac{d(U^2h)}{dx} = g'h\sin\theta$$

θ

Table 3.30 Mean water balance for the Main Zone pit lake during the period simulated by the model from June 29, 2001 to August 28, 2002

Slurry contact pond surface	30.0 L/s	63.4%
Waterline inflow	9.6 L/s	20.4%
Surface inflow	4.7 L/s	9.9%
Net precip/evap	3.0 L/s	6.3%
Total	47.3 L/s	100%

The vertical component of this momentum causes some of the lake water to be entrained, and to move downward with the slurry. At the same time, mixing of slurry with some of the lake water increases the volume of the density flow and decreases its relative density, causing it to decelerate. Depending on the volume flux and density of the slurry, and the density and depth of the lake, the density flow will either reach the lake bottom or separate from the pit wall near a level of neutral buoyancy above the lake bottom. A schematic of a density flow together with the governing equations are shown in Fig. 3.79.

From late June, 2001 through late August, 2002 a comprehensive set of physical and water quality measurements were made in the Main Zone and Waterline pit lakes as part of a three year Canadian National Science and Engineering Research Council (NSERC) and industry funded study. Additional data were used to construct a detailed water balance for the lake during the same period, including: lake surface level; precipitation and evaporation; and pumping and slurry discharge rates (Table 3.30). These provided data inputs for a 425 day PitMod simulation of the evolution of water properties in the Main Zone pit lake. For this simulation, all geochemical processes were ignored and the PHREEQC module was not required. All changes in modeled concentrations were therefore the result of physical processes only.

Time-series of zinc and copper concentrations were extracted from the model output, corresponding to depths of 1, 5, and 100 m in the Main Zone pit lake and then compared with field measurements at the same depths. The data reveal two occurrences of elevated zinc and copper concentrations at a depth of 1 m in June
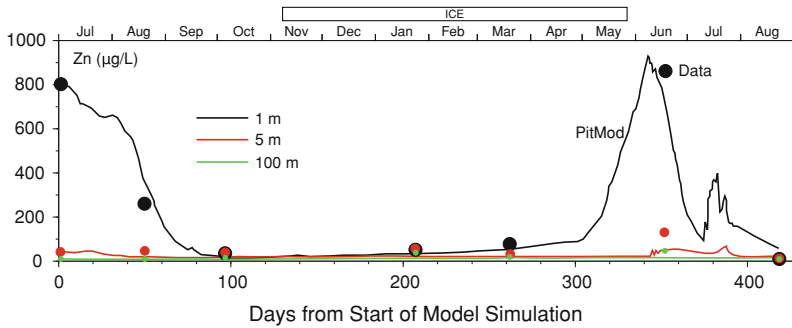
Fig. 3.80 Comparison of modeled and measured dissolved Zn concentrations from the Equity Mine at depths of 1, 5, and 100 m in the Main Zone pit lake

of both 2001 and 2002. In both cases, subsequent measurements revealed a large decrease over the following two to three months.

The model time-series for zinc agree well with the measured zinc concentrations (Fig. 3.80). In the absence of any geochemical or biological mechanism in the model, the results support the hypothesis that the entrainment and subsequent downward transport of surface waters by the relatively dense slurry is responsible for the rapid removal of dissolved trace metals from the surface waters of the Main Zone pit lake. These results indicate that surface water entrainment may be an important mechanism for the removal of trace metals in other pit lakes that receive similar inflows of relatively dense slurries.

3.4.8.2 A High Latitude Pit Lake

This example focuses on both the physical and geochemical evolution of a pit lake located at high latitude. Three scenarios were modeled using PitMod. The scenarios differ only in the depths that two inflows are discharged to the pit lake–one from a contact pond (CP), and the other an overflow from an existing pit lake. The three scenarios are: CP and overflow both enter at the surface; CP discharged at depth; overflow enters at the surface, and CP and overflow both discharged at depth

The relevant physical and hydrodynamic processes simulated by PitMod under these conditions include:

- solar heating of the lake surface by short- and long-wave radiation;
- cooling by emission of long-wave radiation
- sensible heat and latent heat of evaporation
- wind mixing;
- convective mixing due to vertical density instabilities; and
- oxygen (oxidant) consumption in the water column and sediments.

The relevant geochemical processes modeled by the PHREEQC component of PitMod include:

- speciation and saturation index calculations;
- mineral and gas equilibrium;
- surface complexation (adsorption) reactions;
- ion exchange reactions; and
- redox reactions.

PitMod requires the following input for these three simulations:

- pit shell morphometry;
- daily or hourly meteorological data, including: wind speed and direction; precipitation; evaporation; relative humidity; short- and long-wave radiation; cloud cover (%).
- water balance with daily values of inflows and outflows;
- areas of exposed pit-wall geology and predicted chemistry from different rock units; and
- flow volumes and water chemistry of inflows and outflows, including both surface runoff, waste rock seepage chemistry, consolidation water from reclaimed tailings and groundwater (Table 3.31).

PitMod accommodates various types of data depending on their availability. Where data are missing or unavailable, surrogates are specified based on experience at similar pit lakes or from other data sources. Specifically, regional data for short and long wave radiation were obtained from the National Centers for Environmental Prediction (NCEP) global model database managed by NOAA (National Oceanic and Atmospheric Administration).

In the PitMod simulations, the pit lake receives inflows from tailings consolidation, water surface runoff from the surrounding watershed, seepages from a waste rock facility, highwall runoff, direct precipitation to the surface of the lake, and groundwater. These inflows are introduced into the pit lake at elevations and times appropriate for each scenario, and are allowed to mix and evolve according to the model equations governing lake physics and geochemistry.

To estimate the contributions from pit wall runoff, the surface area of each exposed rock unit was digitized and input to PitMod as a surface area vs. depth profile. The chemistry from each unit (Table 3.32) was then added to the pit lake during the filling process until the corresponding pit wall area was submerged by the lake, at which point it was no longer considered reactive. Therefore, the loading of dissolved material to the lake from each rock unit decreases as the lake fills (Table 3.31, Table 3.32).

To account for exposure and repeated flushing and rinsing of salts and metals from the pit wall rocks, concentrations for certain parameters were permitted to decay over time. The concentrations provided in Table 3.32 are the initial levels prescribed.

Table 3.31 Summary of water quality of major inflows for selected species; all units in mg/L, except for Cd and Hg, which are in µg/L, and pH

	Waste rock seep 1	Waste rock seep 2	Tailings surface water	Consolidation water	Ground water	Runoff
pH	7.7	7.46	7.7	5.5	7.5	6.4
As	25.7	25.6	1.33	15.7	0.205	0.010
Sb	2.40	2.40	0.104	1.16	0.0037	0.001
Cd	0.5	0.5	0.55	0.93	0.25	0.1
Cu	0.0249	0.113	0.412	0.674	0.001	0.050
Fe	0.0021	0.0025	0.051	107	2.23	0.030
Pb	0.0142	7.37	0.00147	0.0825	0.0045	0.003
Mn	8.76	84	56.0	45.6	0.463	0.500
Hg	0.077	0.08	0.92	1.44	0.006	0.3
Se	0.140	2.65	0.134	0.220	0.005	0.0025
Tl	0.001	0.001	0.00153	0.00258	0.0001	0.001
Zn	0.11	386	0.048	0.079	0.012	0.050
Sulfate	1,995	38,850	13,700	15,900	20	60

Table 3.32 Water quality of inflows from various pit wall geologic units; all units in mg/L, except for Cd and Hg, which are µg/L, and pH

	Unit 1	Unit 2	Unit 3	Unit 4	Unit 5	Unit 6	Unit 7	Unit 8	Unit 9
pH	7.8	8.0	7.8	7.8	7.7	7.8	4.47	4.5	6.4
As	0.269	0.563	0.900	0.900	6.13	16.8	0.341	0.327	0.01
Sb	0.697	0.362	0.250	0.250	0.130	2.4	0.0012	0.0012	0.001
Cd	0.5	0.5	0.5	0.5	0.5	0.5	0.3	0.44	0.5
Cu	0.004	0.007	0.017	0.017	0.016	0.017	0.024	0.031	0.02
Fe	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.44	0.03
Pb	0.017	0.017	0.017	0.017	0.015	0.023	0.00077	0.00098	0.005
Mn	0.39	0.314	1.22	1.22	0.181	4.8	0.121	0.155	0.5
Hg	0.76	0.76	0.76	0.76	0.76	0.76	0.76	0.0006	0.3
Se	0.172	0.164	0.170	0.170	0.118	0.171	0.0023	0.003	0.0025
Tl	0.001	0.001	0.001	0.001	0.001	0.001	0.0001	0.0001	0.001
Zn	0.097	0.083	0.085	0.085	0.062	0.163	0.135	0.172	0.05
Sulfate	81	138	772	772	1345	1010	32	41	60

3.4.8.3 Scenario 1: CP and Overflow Discharged at Surface

PitMod predicts that the pit lake will fill in approximately 42 years. Throughout this period, a salinity gradient develops due to the presence of highly saline tailings pond water and progressive submergence of exposed pit walls relative to exposed lake surface area (the lake has a very small catchment, only marginally larger than the area of the open pit itself). In other words, as precipitation falls on the pit catchment, it will contact either the pit wall (picking up salinity) or the lake surface (adding no salinity to the lake).
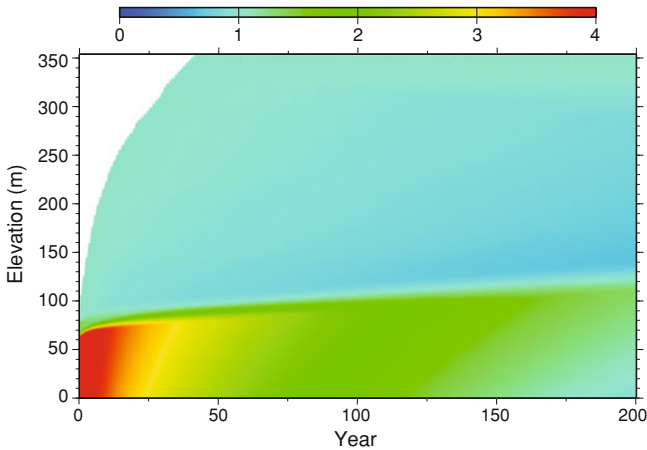
Fig. 3.81 Scenario 1: predicted salinity from a 200 year PitMod simulation (g/L)

The initial pit lake surface area is very small, so virtually 100% of the precipitation will contact exposed rock units on the pit walls, thereby contributing a maximum amount of salts to the emerging pit lake. As the lake grows and the surface area increases, a progressively larger fraction of the precipitation will fall directly on the lake surface. The result is higher salinity water at depth within the pit lake and comparatively fresher water near the surface (Fig. 3.81). The enhanced vertical salinity gradient will increase the stability of the water column.

When the pit lake is partially full, it will begin to behave in a relatively consistent fashion from year to year. Starting in the early spring under ice-cover, the water column will develop a vertical structure in which surface water immediately below the ice has a temperature slightly greater than 0 °C. The temperature then increases with depth to a value near 4 °C—the temperature of maximum water density. The upper layers of the modeled water column display a complex structure resulting from the residual signatures of past mixing events. This structure is ubiquitous in high latitude pit lakes and has also been seen at Equity Silver pit lakes (Lorax 2005).

Typically, ice on high latitude lakes begins to melt and pull away from the pit lakeshore in May or June, and as the air temperature warms during April and May, fresh melt-water is steadily added to the surface waters at the water–ice interface, decreasing surface water salinity (Bergmann and Welch 1985). As the ice melts the surface layer salinity decreases, the temperature increases, and the water column passes through isothermal conditions (Fig. 3.82). The increased salinity difference across the halocline results in greater physical stability of the upper water column with a corresponding resistance to wind mixing and turnover. As a result, even though the lake surface water warms through the temperature of maximum density, the salinity decrease combined with the salinity gradient formed through the lake filling process prevents the surface water from becoming
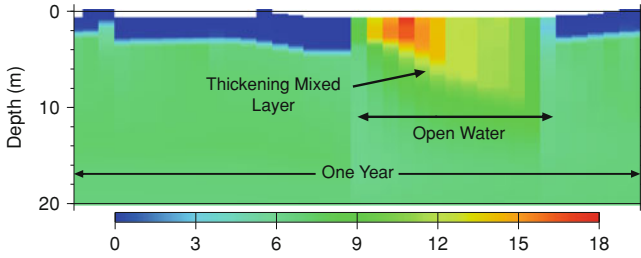
Fig. 3.82 Scenario 1: predicted temperature in the upper 20 m during year 55 of a 200 year PitMod simulation

denser than the water below. Therefore, the lake water column does not experience a spring turnover.

Mixing will only occur to a depth of 5–20 m (depending on wind strength and the magnitude of the salinity gradient). Physical stratification will persist and strengthen through the summer as surface water temperature continues to increase. With the onset of fall, the temperature differential between surface and intermediate water will decrease and wind mixing will begin to erode the density structure of the upper water column, deepening the pycnocline and increasing the salinity of the surface layer as more saline water is mixed into the surface layer from below (Fig. 3.82).

As a result, the water column will be less stable in fall than in spring–a phenomenon observed at the Equity Silver Waterline pit lake in central British Columbia, and at other high latitude lakes. Although the fall turnover should extend to greater depths than in spring, it will likely only affect the upper water column as more saline, and therefore denser, intermediate and deep water hinder deeper mixing.

Fall turnover in similarly stratified pit lakes penetrates to depths of 10–50 m depending on the placement and strength of the halocline. The depth of fall turnover varies from year to year, depending on the quantity of freshwater entering the lake surface during spring, the magnitude of the existing salinity gradient, and the wind speed and duration. PitMod predicts that the wind-mixed layer will occasionally extend to a depth of 20 m.

In the late fall and early winter thermal stratification will strengthen, with cooler water overlying denser 4 °C deep water. Ice will form in late fall and the water column will then become insulated from surface wind energy, remaining quiescent until spring, when the cycle will start again.

Given this impediment to whole-lake mixing, the pit lake deep waters will evolve towards reducing conditions over time. As is typical of lakes with small catchments and low nutrient inputs (deep lakes in particular), it is likely that the pit lake will be poorly productive (oligotrophic) and as a result, the in situ oxygen demand will be very low. Nevertheless, the imposed barriers to mixing combined with deep, isolated waters indicate that the dissolved oxygen will be fully consumed in regions of the lake before it has completed its filling, provided that CP and overflow inputs are not injected at depth, as in Scenarios 2 and 3. Once
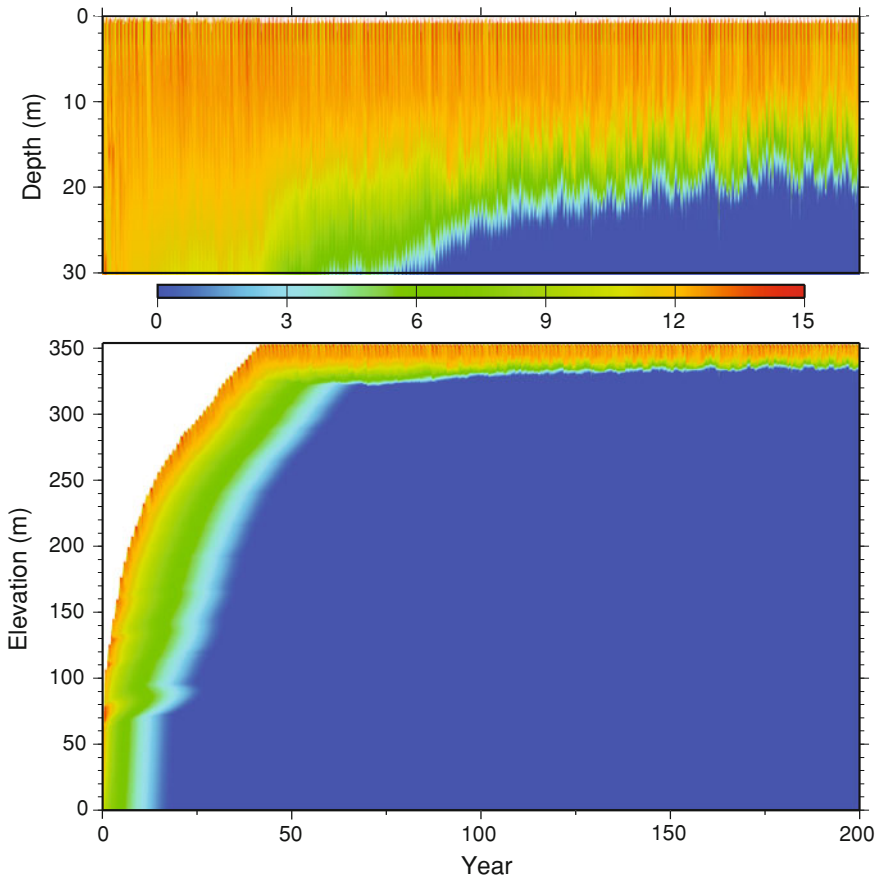
Fig. 3.83 Scenario 1: predicted dissolved oxygen concentration from a 200 year PitMod simulation (mg/L)

dissolved oxygen has been removed, secondary oxidants will be employed and the deep lake will experience sulfate reduction, sulfide formation, and the precipitation of a variety of solid-phase sulfide minerals.

Figure 3.83 shows the predicted dissolved oxygen concentration during Scenario 1 (discharge of CP and overflow at surface). As the pit fills with water in the early stages, the water column will remain reasonably well oxygenated until approximately year 10, when the lake is roughly 200 m deep. At this time, dissolved oxygen in the bottom layers will become depleted due to the absence of complete turnover. Salinity gradients within the interior of the lake will be sufficiently large to limit wind mixing and seasonal turnover to the upper 20 m, resulting in stagnation in the bottom portion of the pit lake (Fig. 3.83).
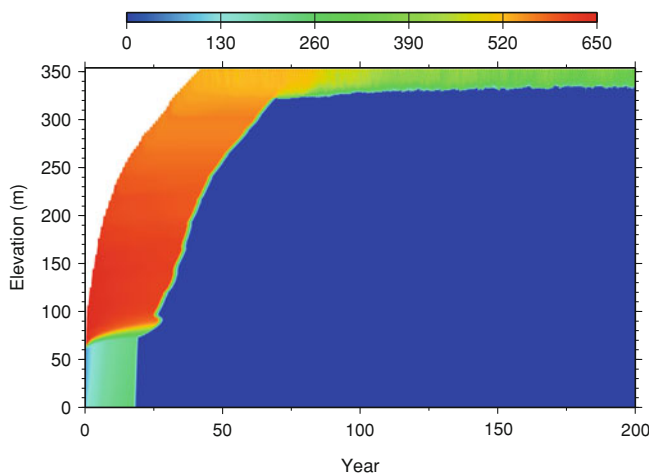
Fig. 3.84 Scenario 1: predicted dissolved nitrate concentration from a 200 year PitMod simulation (μg/L)

The depletion of oxygen in the interior of the pit lake will result in the utilization of secondary oxidants; specifically, nitrate (Fig. 3.84), Fe-oxides (Fig. 3.85), Mn-oxides, and sulfate. The evolution of nitrate–the first of the secondary oxidants to be consumed–resembles that of dissolved oxygen in that the nitrate concentration will begin to decrease with time once oxygen has been depleted (Fig. 3.84). Within 15 years of the start of pit filling, the interior of the water column will start to lose nitrate through denitrification.

Iron shows evidence of its use as a secondary oxidant in deep water beginning at approximately year 18, when the concentration of dissolved Fe will increase to 50 μg/L. This addition of dissolved Fe to bottom water is due to the reductive dissolution of Fe-oxides, which liberates dissolved ferrous Fe (Fe^{2+}) to solution. However, the increase in the inventory of dissolved Fe^{2+} is transitory due to the precipitation of Fe as Fe-monosulfides (FeS), which commences following sulfate reduction. The commencement of sulfate reduction can be seen in Fig. 3.86, which shows the presence of detectable sulfide at 20 Year.

Once most of the trace metals have been precipitated as insoluble sulfide minerals, dissolved sulfide concentrations will increase, particularly within the interior of the pit lake where there is no source of dissolved oxygen (Fig. 3.86).

With the onset of sulfate reduction in the interior of the pit lake, trace element concentrations will decrease due to their insolubility in the presence of free sulfide (Fig. 3.86). This behavior is illustrated in Fig. 3.87, where dissolved As within the lake interior decreases due to the formation of As sulfide once sulfate reduction starts and most of the dissolved Fe is consumed. Dissolved As will disappear in the interior of the lake, but not in surface waters where oxic conditions will persist.

The As concentration within the pit lake surface mixed layer will decrease with time to a quasi-steady-state value fluctuating between 70 and 130 μg/L (Figs. 3.87 and 3.88). This slow decrease with time corresponds to the progressive decrease in
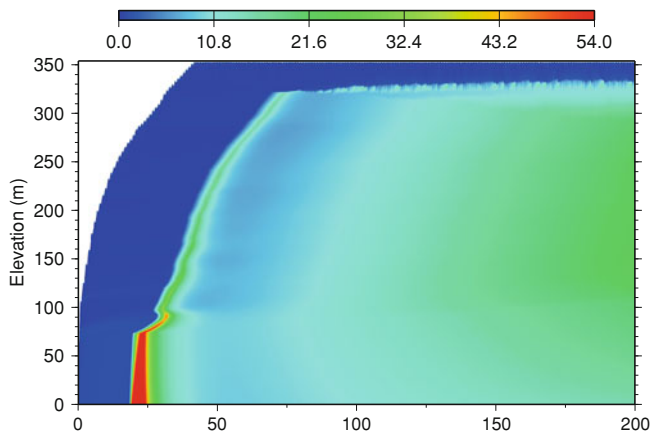
Fig. 3.85 Scenario 1: predicted dissolved Fe concentration from a 200 year PitMod simulation (μg/L)
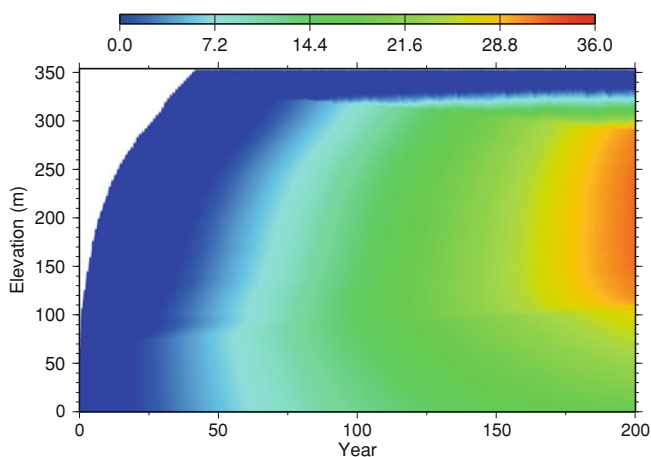
Fig. 3.86 Scenario 1: predicted dissolved HS concentration from a 200 year PitMod simulation (mg/L)

As loading from the highwall as it is submerged by the rising lake surface, and with ongoing removal of As through sorption to Fe- and Mn-oxyhydroxides, which will settle in the water column to the pit lake bottom. In comparison, the surface water sulfate concentration for Scenario 1 will vary little with time (≈ 700 mg/L), as it will behave conservatively in the upper, oxic water column where sulfate reduction will not occur (Fig. 3.89).
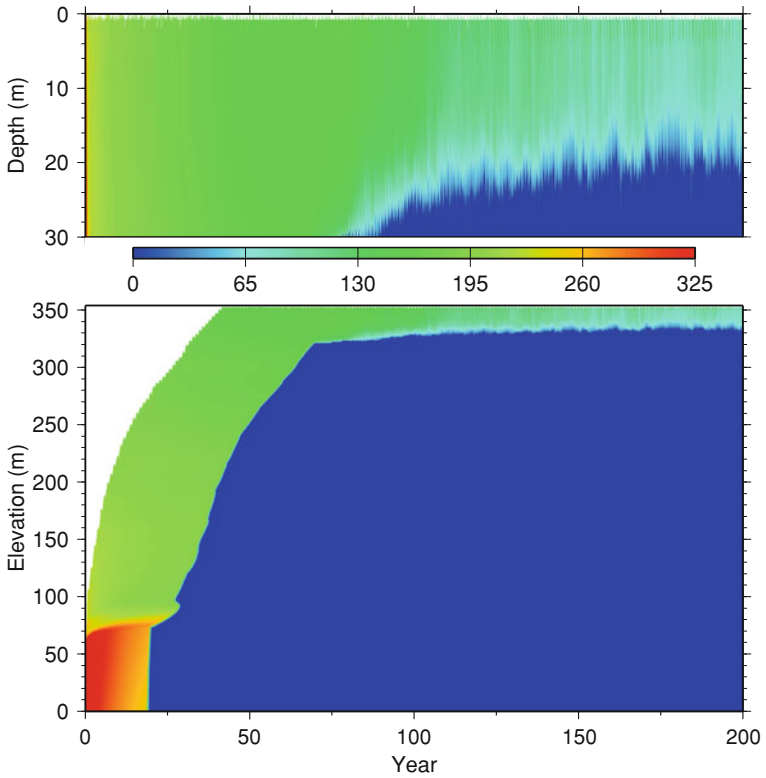
Fig. 3.87 Scenario 1: predicted dissolved As concentration from a 200 year PitMod simulation (μg/L)
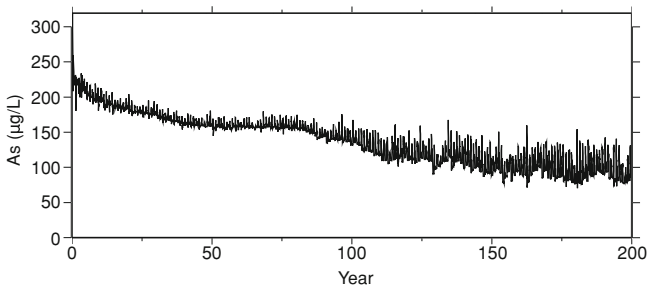
Fig. 3.88 Scenario 1: predicted dissolved As concentration in the surface layer from a 200 year PitMod simulation
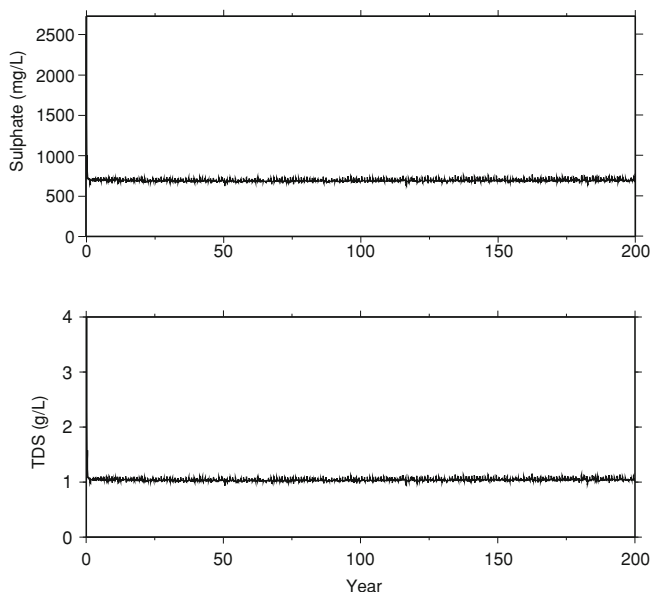
Fig. 3.89 Scenario 1: predicted dissolved sulphate and total dissolved solids concentrations in the surface layer from a 200 year PitMod simulation

3.4.8.4 Scenario 2: Discharge of CP Water at Depth

Scenario 2 differs from Scenario 1 in that CP water is diverted to 10.5 m above the lake bottom instead of being discharged to the lake surface. On a seasonal or annual basis, the behavior of the upper water column of the pit lake in Scenario 2 should be similar to Scenario 1. However, the surface inflow from the CP will be considerably less saline than the tailings water, thereby weakening the stratification in the lake as it fills. Initially, this will result in the lake having a relatively uniform, well-mixed vertical structure. Then, as the lake fills and approaches near steady-state salinity stratification, a more stable structure will develop wherein deep lake mixing will occur through the introduction of CP water at a seasonally dependent temperature.

The effect of water loss from surface overflow on the properties of the pit lake will depend on how much the overflow water differs in density from resident pit lake surface waters. The overflow water is predicted to be only slightly more saline than the pit lake surface water and is therefore expected to sink within the mixed surface layer of the lake to depths of a few tens of meters.

PitMod salinity values for Scenario 2 are presented in Fig. 3.90. As previously suggested, a strongly stratified salinity structure will evolve very early in the filling process as a relatively fresh surface layer forms above a more saline bottom layer. This will be partly due to the introduction of saline contact pond water to the bottom of the pit lake, together with mixing of highly saline tailings pond water
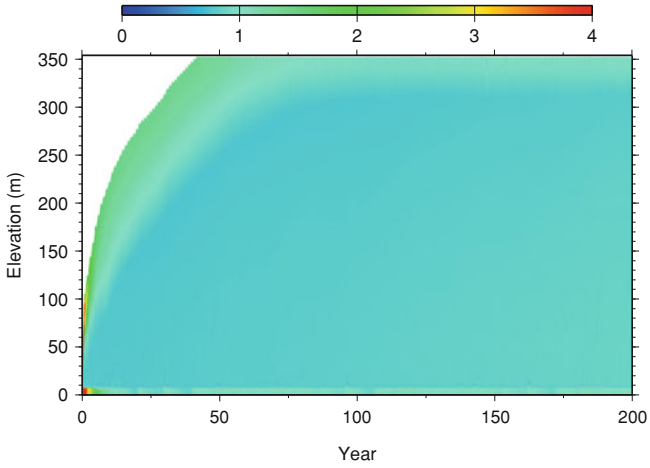
Fig. 3.90 Scenario 2: predicted salinity from a 200 year PitMod simulation (parts per thousand)
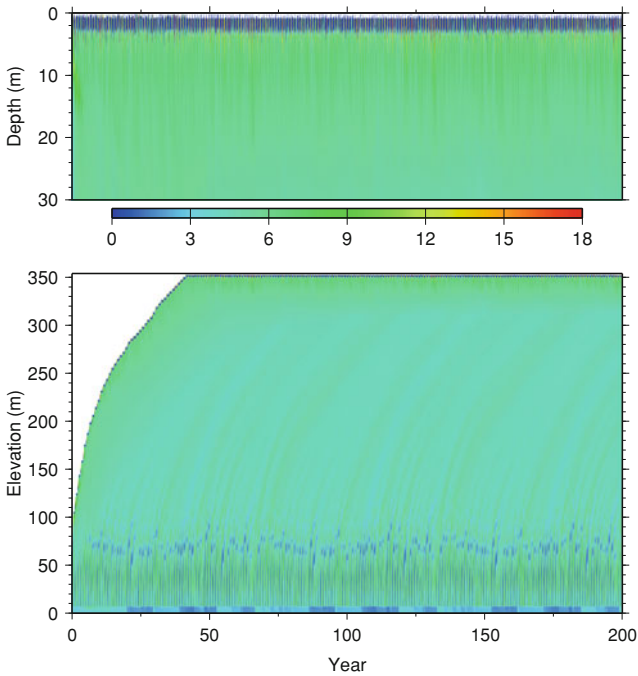
Fig. 3.91 Scenario 2: predicted temperature from a 200 year PitMod simulation (°C)
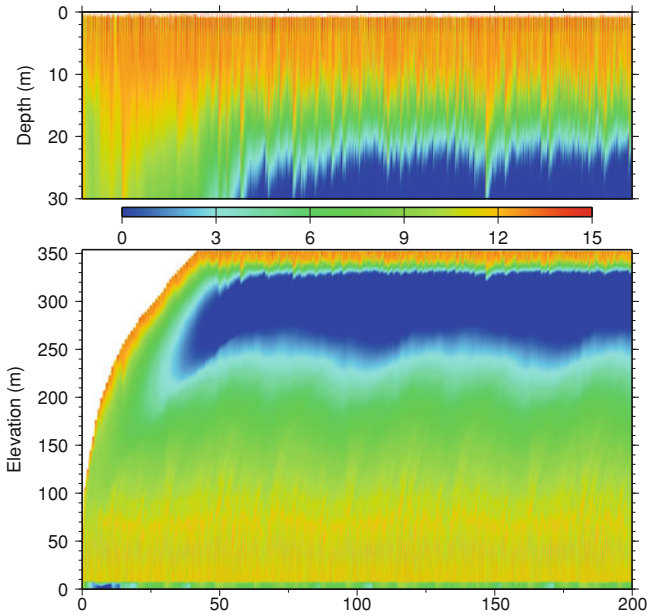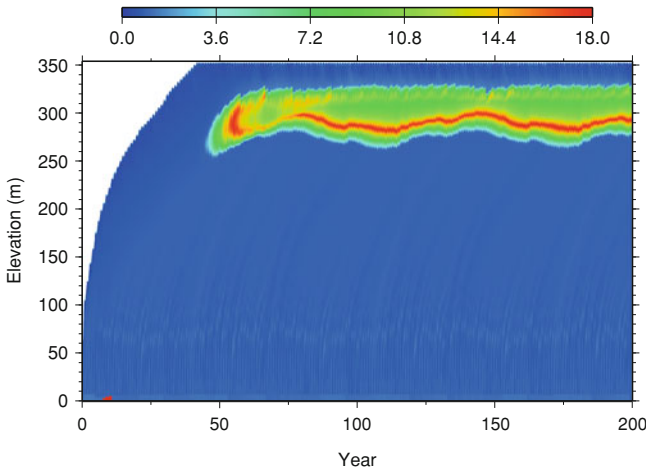
Fig. 3.92 Scenario 2: predicted dissolved oxygen concentration from a 200 year PitMod simulation (mg/L)

into the pit lake surface waters. The predicted influence of this source on the deep waters is visible in the thermal structure of the lake (Fig. 3.91). Seasonal variations are visible as temporal striations within the bottom water caused by seasonal incursions of warm and cold water. Warm water, introduced during the summer, is less dense than the ambient water and therefore tends to mix upward in the water column, while cold fall and spring water is denser and remains near the lake floor.

The seasonal wind-mixed epilimnion will be restricted to the upper few meters; however, fall turnover will penetrate more deeply than in Scenario 1, resulting in a 20–30 m thick inter-annual mixed layer. This will have important implications for the seasonal introduction of dissolved oxygen into the pit lake surface layer and to the addition at the surface of water with disparate chemical qualities originating from below the mixed layer.

An interesting and potentially important consideration involves the decreasing penetration depth of the inter-annual turnover once the pit lake is full and over-flowing occurs (Fig. 3.92). When surface water overflows, and is lost from the lake, it causes a thinning of the mixed layer; that is, fresh surface water is removed from the lake, allowing relatively saline water to move upward toward the lake surface. This is important if discharge water from the pit lake is to be removed from depth, rather than directly from the surface since the chemical gradients within the pit lake tend to be greater in the upper water column.

Fig. 3.93 Scenario 2: predicted dissolved Fe concentration from a 200 year PitMod simulation (µg/L)

Perhaps the most important implication of the Scenario 2 configuration is the impact of the introduction of oxygenated CP water on the geochemical properties of the deep water. In particular, the stable stratification of the water column early in the lake filling process will have an important effect on the oxygen (and secondary oxidant) distribution within the water column (Fig. 3.92). As for Scenario 1, lake productivity was set to oligotrophic conditions in Scenario 2 (i.e. very low productivity; hence, very low oxygen demand); nevertheless, the interior of the pit lake, approximately 220–330 m above the lake floor, evolves to suboxic conditions within 30 years of filling (Fig. 3.92).

The surface mixed layer will remain well oxygenated through direct contact with the atmosphere while bottom water is oxygenated by the introduction of CP water, resulting in an upward migration of water through the lake interior such that lake water 'age' is inversely related to depth (i.e. deep water is youngest, shallow water is oldest). Accordingly, the oxygen concentration of the lake interior will decrease away from the lake floor with time as oxygen is consumed (Fig. 3.92).

As expected, the model predicts a very low dissolved Fe concentration in the surface layer due to the precipitation of particulate oxyhydroxides under oxygenated conditions (Fig. 3.93). This mechanism is also responsible for removing As from the wind-mixed surface layer over time. Similarly, dissolved Fe will remain at low concentrations in the deepest lake waters due to the presence of dissolved oxygen. Within the intermediate water column, dissolved Fe will be remobilized through reductive dissolution, resulting in localized elevated concentrations, and will be removed via sulfide precipitation as the lake water ages within a relatively narrow range of depths.

The corresponding concentration of free sulfide will progressively increase with the age of the lake water until the water contacts the oxygenated wind-mixed surface layer. Sulfide concentration will increase in the water column once oxygen
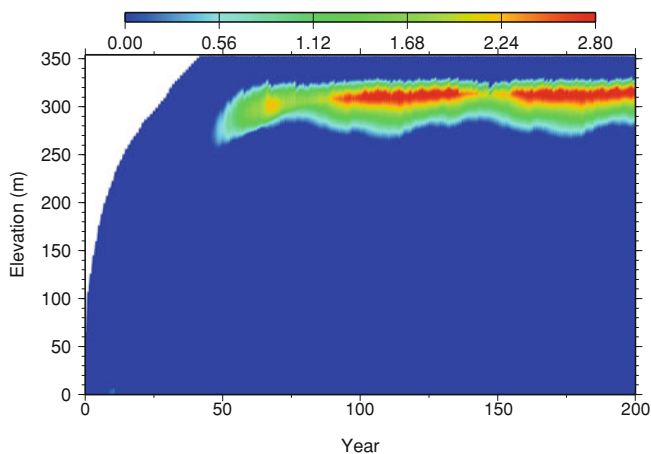
Fig. 3.94 Scenario 2: predicted free sulphide concentration from a 200 year PitMod simulation (mg/L)

has been depleted and the majority of trace metals are consumed within the lake interior (metal sulfide precipitation is the primary sink for free sulfide). Accordingly, sulfide concentration will progressively increase with time and distance from the source of oxygen at lake bottom, reaching a maximum immediately below the wind-mixed surface layer.

Interestingly, dissolved sulfide will increase to relatively high values within the lake interior despite the oligotrophic conditions, due to the relatively long residence time of water within the pit lake basin. Even though the driving force for the creation of free sulfide is weak (i.e. low primary productivity), the concentration will increase as the water of the lake interior has a long residence time before it is exposed to oxygen at the lake surface (Fig. 3.94).

The impact of the pit lake structure on As is illustrated in Fig. 3.95. Arsenic will be introduced into the pit lake primarily in the tailings pond water, and secondarily through highwall runoff and overflow into the lake. In comparison, the CP will add comparatively low concentrations of As to the pit lake. Because of the discharge configuration, the tailings pond water will enter the young lake, followed by the CP water, which will be added to the denser tailings pond water, inducing convective mixing. The addition of highwall and overflow waters to the lake surface will result in the highest modeled surface layer As concentrations (Fig. 3.95).

The contribution of As from the highwall will diminish as the lake level rises. Combined with limited removal through co-precipitation with Fe-oxyhydroxides, this will progressively decrease the concentration of dissolved As in the surface layer (Fig. 3.95).

Loss of As (and other trace elements) in the lake interior will result from sulfide precipitation; however, the proximity and resulting entrainment of low As concentration water immediately below the wind-mixed layer due to sulfide precipitation will promote further decreases in As concentration within the lake surface
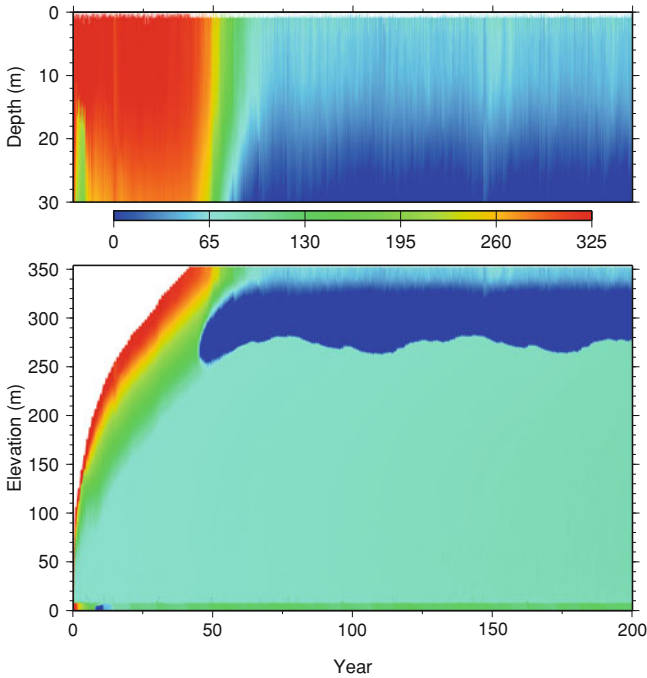
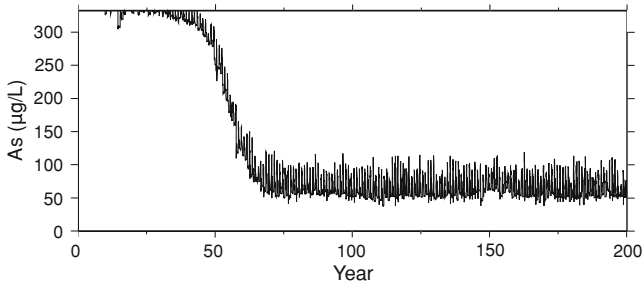**Fig. 3.95** Scenario 2: predicted dissolved As concentration from a 200 year PitMod simulation (μg/L)

(Fig. 3.96). The As concentration in the surface water will decrease with time, from concentrations exceeding 300 μg/L to values of 50–100 μg/L (Fig. 3.96).

In a similar way, the sulfate concentration will decrease over the same period as the less saline CP water is entrained from depth commensurate with the loss of freshwater from the surface layer. The primary water quality issue for this scenario stems from the contributions of total dissolved solids (TDS) and sulfate to the receiving environment, rather than from trace metals (Fig. 3.97).

3.4.8.5 Scenario 3: All Inflows Directed to Depth

Scenario 3 differs from the first two Scenarios in that both overflow and CP inflow to the pit lake are 10.5 m above the pit lake bottom. In this regard, Scenario 3 is similar to Scenario 2 with the addition of overflow water added at this depth.

The effect of discharging overflow water to depth is apparent in the difference in salinity concentrations between Scenarios 2 and 3 (Figs. 3.90 and 3.98). While much of the water column for Scenarios 2 and 3 is of nearly uniform salinity from the start of lake filling, the absence of overflow discharge to the surface layer in Scenario 3 results in an initially fresher surface mixed layer. Salinity eventually will increase as deeper water is gradually transported upward into the surface

Fig. 3.96 Scenario 2: predicted dissolved As concentration in the surface layer from a 200 year PitMod simulation
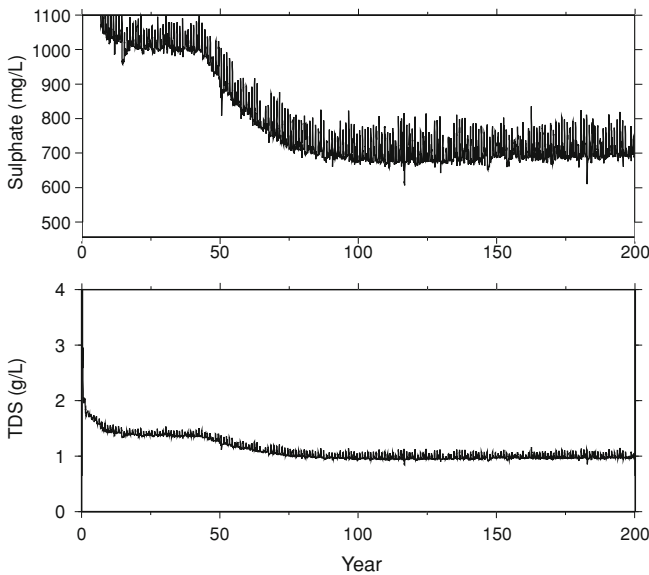

Fig. 3.97 Scenario 2: predicted dissolved sulphate and total dissolved solids concentrations in the surface layer from a 200 year PitMod simulation

layer. As in Scenario 2, the tailings water at the bottom of the lake will be mixed into the water column through the introduction of overflow and CP water at depth (Fig. 3.98).

The modeled temperature further illustrates the impact of redirecting surface waters to the pit lake bottom during the open water season (Fig. 3.99). All of the temperature variation will occur in the surface mixed layer through direct contact with the atmosphere and ice, and in the deepest regions of the lake where overflow and CP waters will be introduced.
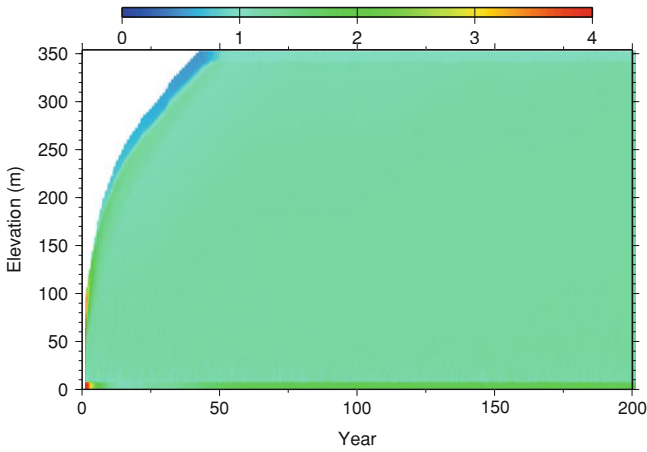
Fig. 3.98 Scenario 3: predicted salinity from a 200 year PitMod simulation (parts per thousand)
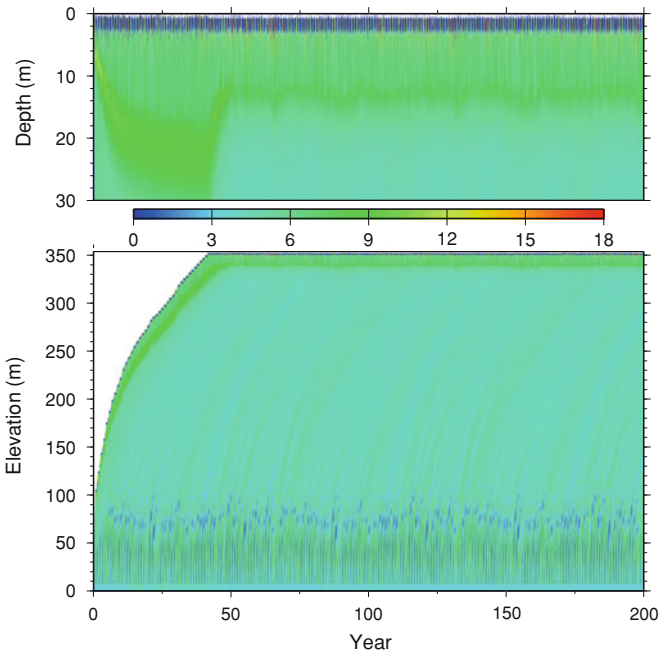
Fig. 3.99 Scenario 3: predicted temperature from a 200 year PitMod simulation (°C)

Dissolved oxygen will be saturated in the surface mixed layer and at depth but will vanish in the intermediate water after the lake has aged 10–20 years (Fig. 3.100). The reason for this distribution of dissolved oxygen is the same as in Scenario 2; that is, as oxygenated water is introduced at depth and migrates slowly
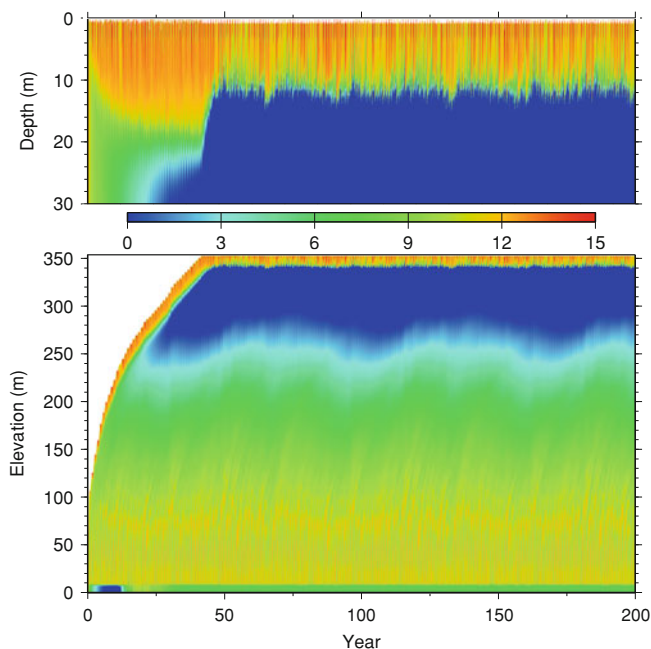
Fig. 3.100 Scenario 3: predicted dissolved oxygen concentration from a 200 year PitMod simulation (mg/L)

upward towards the lake surface, it ages and loses dissolved oxygen even though the oxygen demand in the water column is assumed to be low.

Dissolved Fe in Scenario 3 will behave similarly to Scenario 2, in that the Fe concentration will be very low in the surface and bottom layers due to the presence of dissolved oxygen and the associated stability of Fe oxyhydroxides. However, as the redox potential decreases with time in the water introduced at depth, Fe(III) reduction will eventually occur, resulting in the local maximum in dissolved Fe concentration indicated by the red zone in Fig. 3.101. This Fe maximum will be constrained above by sulfide precipitation combined with dissolved oxygen in the wind-mixed layer, and below by the presence of dissolved oxygen.

Arsenic concentration in Scenario 3 will also resemble Scenario 2 except that the As in the surface layer will decrease to a greater extent (Fig. 3.102). This likely will occur for two reasons: first, the addition of inflow at depth through the discharge of overflow water to the pit floor will enhance the upward migration and entrainment of clean intermediate water into the surface layer, causing As removal from intermediate water through sulfide precipitation. Second, and more importantly, the absence of overflow water, which contains significant concentrations of As, in the surface layer will result in cleaner surface layer water. The modeled surface As concentration will decrease rapidly after the lake over-tops, and within 10 years it should drop to a steady-state concentration of approximately 30 μg/L (Fig. 3.103).
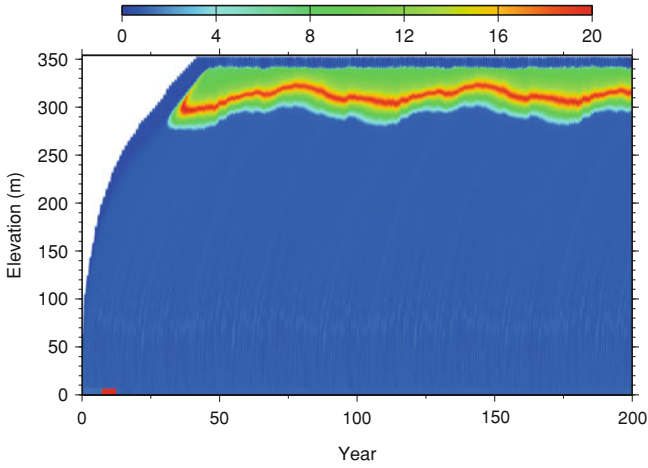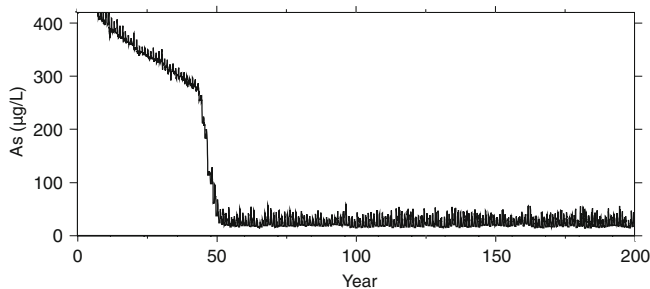
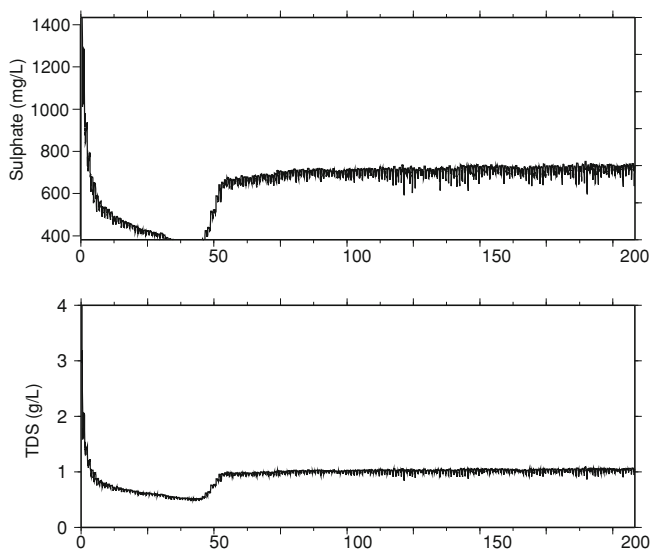**Fig. 3.101** Scenario 3: predicted dissolved Fe concentration from a 200 year PitMod simulation (μg/L)
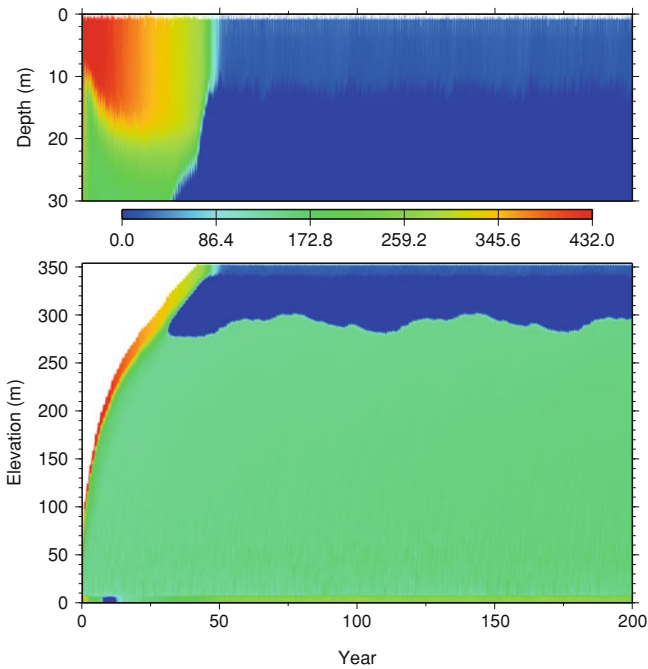
Fig. 3.102 Scenario 3: predicted dissolved As concentration from a 200 year PitMod simulation (μg/L)

Fig. 3.103 Scenario 3: predicted dissolved As concentration in the surface layer from a 200 year PitMod simulation

Fig. 3.104 Scenario 3: predicted dissolved sulphate and total dissolved solids concentrations in the surface layer from a 200 year PitMod simulation

In Scenario 3, sulfate concentration will progressively increase from a low at year 42 to a steady-state concentration of approximately 700 mg/L. TDS will remain relatively constant at 1,000 mg/L (Fig. 3.104).

3.4.9 Conclusions

Pit lakes exhibit a variety of physical and geochemical properties covering a broad spectrum of spatial and temporal scales. Obtaining accurate assessments of future environmental and economic impacts from pit lakes requires reliable predictions of

pit lake water quality. Computer models are an indispensable tool for predicting the spatial distribution and evolution of pit lake properties. However, the gaps in our understanding of many of the important physical and geochemical processes observed in pit lakes ensure that models will always be limited in their ability to mimic nature.

DYRESM and PitMod are examples of models that determine pit lake properties by solving systems of mathematical equations, including mass and energy balances. In addition, PitMod includes surface ice formation and the capabilities provided by the PHREEQC equilibrium chemistry model to predict geochemical properties.

For any pit lake model, the accuracy of its predictions depends strongly on the quality of corresponding input data. More often than not, there are large gaps and deficiencies in data sets used to run model simulations, necessitating the use of proxy data, interpolation, or estimation.

With increases in the speed and capacity of computers showing no sign of abating, and with our increasing understanding of the physical and geochemical processes that determine pit lake properties, it appears certain that the performance of models will continue to improve and their predictions will become increasingly reliable.