Environmental Science & Technology
Article
pubs.acs.org/est

Quantifying Lake Water Quality Evolution: Coupled Geochemistry, Hydrodynamics, and Aquatic Ecology in an Acidic Pit Lake

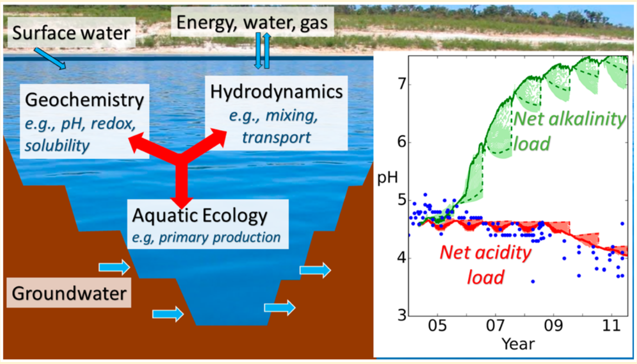
S. Ursula Salmon,*,† Matthew R. Hipsey,† Geoffrey W. Wake,‡ Gregory N. Ivey,‡
and Carolyn E. Oldham‡

†UWA School of Agriculture and Environment, University of Western Australia, (M087) 35 Stirling Hwy, Crawley, Western Australia, Australia 6009

‡School of Civil, Environmental and Mining Engineering, University of Western Australia, (M051) 35 Stirling Hwy, Crawley, Western Australia, Australia 6009

Supporting Information

ABSTRACT: Assessment of water quality evolution in the thousands of existing and future mine pit lakes worldwide requires new numerical tools that integrate geochemical, hydrological, and biological processes. A coupled model was used to test alternative hypothesized controls on water quality in a pit lake over ~8 years. The evolution of pH, Al, and Fe were closely linked; field observations were reproduced with generic solubility equilibrium controls on Fe(III) and Al and a commonly reported acceleration of the abiotic Fe(II) oxidation rate by 2−3 orders of magnitude. Simulations indicated an ongoing acidity loading at the site, and the depletion of Al mineral buffering capacity after ~5 years. Simulations also supported the existence of pH limitation on nitrification, and a limitation on phytoplankton growth other than the commonly postulated P and DIC limitations. Furthermore, the model reproduced the general patterns of salinity, pH, Al, and Fe during an uncontrolled river breach in 2011, however, incorporating sediment biogeochemical feedbacks is required to reproduce the observed postbreach internal alkalinity generation in the lake. The modeling approach is applicable to the study of hydrological, geochemical, and biological interactions for a range of lake and reservoir management challenges.



INTRODUCTION

The utility of a water body for environmental values, domestic and industrial water supply, agriculture, recreation, or other uses, depends upon the water quality. Key state variables include the biogeochemical master variables pH and redox potential, alkalinity, salinity, and the concentration of nutrients, oxygen, metals, and algal biomass. Predicting values for these parameters presents a formidable challenge, as water quality is affected by physical, biological and geochemical processes, with many nonlinear interactions and feedbacks. While it is well established how variables, such as chlorophyll-a and oxygen will respond to changes in hydrology and nutrient loading,[1−3] there are many cases where more complex, coupled controls on water quality need to be taken into account.

The need for prediction tools that couple geochemistry to hydrodynamics and aquatic ecology is particularly clear in the case of the thousands of new lakes referred to as pit lakes or mine lakes. Pit lakes form after the cessation of open cut mining of, for example, metals, uranium, coal, mineral sands, and clay.[4−10] The water quality of pit lakes will determine whether they become sustainable water resources or, alternatively, localized but long-term environmental hazards, with the potential to also affect downgradient systems.[11−13] A subset of pit lakes are acidic and often contain high concentrations of dissolved Fe, SO_4, and Al.[14,15] Addition of alkalinity leads to relatively fast precipitation of Fe(III) and Al as (oxy)hydroxides or hydroxysulfate minerals; these reactions release protons and thus constitute "buffering systems" that must be overcome before the pH will increase.[16] Ongoing acid generation may also occur due to pyrite oxidation in adjacent waste dumps, mined landforms (including pit walls), and underground mine workings, resulting in a sustained external acidity loading onto pit lakes[5,8,15,17,18] and natural water bodies.[19−21]

Enhanced in situ alkalinity generation via stimulation of organic matter-driven reactions in lake sediments has been suggested as a potential remediation technique for acidic pit lakes, either by direct addition of labile carbon or stimulation of primary productivity through nutrient amendment.[22−30] However, in the field these processes may be limited by the availability of labile organic matter.[15,26,31] A synthesis of data from long-term field mesocosm trials in Germany concluded

Received: March 18, 2017
Revised: July 25, 2017
Accepted: July 28, 2017

DOI: 10.1021/acs.est.7b01432
Environ. Sci. Technol. XXXX, XXX, XXX−XXX

that remediation attempts through either organic matter or nutrient input will be hampered by reoxidation of sulfides formed during alkalinity generation after water column overturn.[28] The challenges associated with this proposed remediation technique when tested at the field scale highlight the critical need for validated numerical tools to better quantify and test our conceptual models of management strategies prior to implementation, in both natural and anthropogenically modified environmental systems. Furthermore, it may be critical to make decisions regarding factors that affect water quality, such as pit lake bathymetry and surrounding landforms, during or even prior to commencement of mining.

Although there are thousands of existing and future pit lakes worldwide, there are relatively few studies on numerical prediction of pit lake water quality evolution in scientific journals.[32,33] Earlier studies focused on changing water and mass balances as the pit filled and, in some cases, the geochemical evolution of pit water quality.[32,34−36] The physical limnology of pit lakes has been extensively studied with numerical models,[37−41] and Moreira et al.[42] coupled physical processes to geochemistry in order to model stable geochemically controlled stratification in a pit lake. Other studies have modeled the geochemical processes in detail, with simplification of the hydrodynamics.[43−48]

In this Article, we detail the application of a recently developed numerical model that couples geochemical equilibria and kinetics with physical and biological processes. With a first-principles approach to process representation and no calibration of geochemical equilibrium processes, model scenarios are used to quantitatively test the hypothesized controls on water quality evolution[49] by comparing simulated concentrations to field observations as processes are switched on/off and parameter values varied. The case study site provides a highly suitable test case for the coupled model, given the well constrained surface hydrology and biogeochemistry from a 2004−2005 field campaign, additional monitoring data up to 2012, and limited biological or sediment activity up to 2011.

■ FIELD SITE: 2004−2005 COMPREHENSIVE SAMPLING

The case study site, Lake Kepwari, is a former open cut coal mine WO5B, located ~160 km southeast of the Western Australia capital, Perth (33°27′35.53″S, 116°13′10.03″E, WGS84) in the Collie Coal Basin. There are numerous acidic pit lakes in the basin.[50] Sub-bituminous coal seams are interlayered with sandstone and siltstone;[51] the sulfur and carbonate content of the coal is relatively low. Mining and dewatering in the WO5B pit ceased in 1997. From 1999 onward, to accelerate filling of the pit, water from the adjacent river was diverted into the pit through a valve-regulated offtake during winter months in years when river flow was sufficiently high. The lake reached its capacity volume of ~24×10^6 m^3 (24 GL), as limited by overflow culverts, in 2004, resulting in a pit lake approximately 65 m deep with a surface area of approximately 1 km^2 (see Figure SI-S1). The pit landforms and adjacent overburden piles were landscaped and revegetated; any previously exposed coal seams were covered during landscaping or submerged.

Characterization of the lake included high temporal resolution measurements of lake temperature profiles and meteorological forcing at a station installed at the deepest point in the lake from Oct 2003−March 2006, as well as profiling and water quality grab sampling from multiple locations and depths on several occasions in 2004−2005.[40,49,52] The pH and concentrations of some elements were also measured regularly by the mining company in grab samples from the edge of the lake. During the 2004 river inflow, water quality in the river was sampled, as was a point inflow of surface runoff during a rain event. Limited groundwater quality data were available for the region.[49]

Based on the 2004−2005 field data and water/mass/energy balance calculations, hypotheses regarding the dominant processes controlling water quality in the pit lake were formed.[49] Temperature-driven stratification of the lake water column occurred in the summer months (Figure SI-S2 and SI-S3), enhanced by sheltering from mining landforms.[40] An earlier study of the hydrogeology of the area indicated regional groundwater flow past the lake;[51] dewatering was also required during mining, indicating ready connection to the groundwater system. A detailed energy balance over the lake (see Supporting Information (SI)) indicated that an annual throughflow of ~2 GL of warmer groundwater (measured to be 17 °C) was required to reproduce the hypolimnetic temperature measured during summer months.[52]

The observed increase in the concentrations of the conservative components Cl, Mg, Ca, K, and Na in the epilimnion in summer was hypothesized to be due to evapoconcentration. Well-mixed, homogeneous conditions were observed in the winter after overturn. The pH in the lake in 2004−2005 was less than 5, despite being ~95 % filled with river water (pH ~7). Mineral saturation index calculations indicated that the Al and Fe(III) hydroxide phases gibbsite and ferrihydrite were potentially close to solubility equilibrium with solution, as well as the Al hydroxysulfate phases basaluminite[53,54] and jurbanite. Solution was either over- or under-saturated with respect to other minerals commonly reported to control aqueous concentrations in mine lakes and other waters affected by acid mine drainage, such as gypsum and schwertmannite.[14,55,56]

Mass balances over the lake, using the (limited) reported measurements of groundwater quality, suggested ongoing acidity loading, for example, inflow of Fe(II), followed by oxidation and precipitation of Fe(III):

$$Fe^{2+} + \frac{1}{4}O_2 + H^+ \Rightarrow Fe^{3+} + \frac{1}{2}H_2O \tag{1}$$

$$Fe^{3+} + 3H_2O \Leftrightarrow Fe(OH)_3(s) + 3H^+ \tag{2}$$

Likely sources of Fe loading into pit lakes include adjacent mine waste rock and underground workings, or the oxidation of pyrite in exposed (now submerged) pit wall surfaces in the lake.[8,9,15,41,57−59] Iron concentrations of up to 20 mg L^{-1} were reported by the mining company for groundwater close to the lake. Concentrations may be higher at other locations around the lake, for example there are no bores in the waste rock material adjacent to the lake. Experiments with Lake Kepwari sediments[60,61] indicated that early sediment diagenesis in the lake was organic carbon-limited; furthermore, mass balance calculations over the lake also suggested that if alkalinity generation was occurring in the lake sediments, it was not sufficient to lead to an increase in alkalinity in the lake.[49]

The lake remained oxic during the 2004−2005 field campaign, with dissolved oxygen (DO) in the hypolimnion remaining above 50 % saturation. Concentrations of organic matter, chlorophyll-a (chl.a) and phosphorus (P) were low, indicating that the lake was oligotrophic. In the years with controlled winter river inflow, this was a source of P and nitrogen (N), and mass balances indicated that the lake was a P sink. It was hypothesized that primary productivity was limited by the scavenging of P by sorption onto Fe and Al hydroxides,[10] with addition of neutralizing river alkalinity causing precipitation of these phases. Ammonia was observed to accumulate in the oxic hypolimnion, despite oxic conditions, which was hypothesized to be due to a reduced rate of nitrification at the low pH.[62−64]

Depth profiles of Fe(II)/total Fe and dissolved organic carbon (DOC) concentrations suggested slight accumulation of Fe(II) and depletion of DOC in the epilimnion during stratified periods. It was hypothesized that the presence of Fe(II) in the oxic water column, up to 40 % of the total Fe in the epilimnion,[49] was due to slow oxidation as a result of low pH,[65] and that photoreduction of Fe(III),[66] linked with photooxidation of DOC, may have occurred in the epilimnion, as has been observed in acidic surface waters elsewhere.[67−69] Other suggested sources of Fe(II) were shallow groundwater inflows, and sinks of DOC were enhanced flocculation and sedimentation with Al and Fe(III).[70−73]

2005 TO 2011 RIVER BREACH

River diversion to the lake occurred in 2005, 2007, and 2008, and additional samples were collected up to Aug 2011 by the mining company and Kumar et al.[74] In August 2011, an unusual rain event resulted in an uncontrolled breach of the river into the lake, including overtopping of overflow culverts and decant of an unknown volume back to the river.[75] Connection to the river ceased in late September 2011,[76] and no inflow to the lake occurred in 2012.

MODEL DESCRIPTION

The inflow, outflow, stratification, and mixing dynamics were simulated using the Dynamic Reservoir Simulation Model (DYRESM). DYRESM is a 1D/quasi-2D Lagrangian code that includes parametrizations for inflows, outflows, surface thermodynamics, wind mixing and deep mixing processes. The model has been widely used for simulation of stratified lakes and reservoirs where horizontal motions are not of critical importance[77,78] including pit lakes.[38−41,52]

The Computational Aquatic Ecosystem Dynamics Model (CAEDYM[79]) has been widely used to simulate the dynamics of oxygen, carbon, N, P, and plankton for a variety of aquatic environments.[80−88] Aqueous speciation and solubility equilibrium control by mineral phases were accounted for in the current version of the CAEDYM code by including a flexible number of principal chemical components that are subject to solution of mass-action expressions, implemented according to the approach outlined in Parkhurst and Appelo[89] (see SI). The capability to simulate several additional redox processes as kinetically controlled reactions was also included. Rate expressions for the pH-dependence of Fe(II)[65,90−92] and NH_4[62,64] oxidation were included, as well as a photochemical reaction between DOC and Fe(III).[66,68] Limited availability of P in pit lakes is often attributed to association with phases such as Fe (oxy)hydroxides;[93−97] sorption of P to $Fe(OH)_{3(s)}$ was also implemented, with a Langmuir isotherm,[98−100] including allowance for the pH-dependence of the maximum sorbed P concentration on Fe(III) minerals (see Figure SI-TS3-S1). All model equations and constants, as well as computational aspects, are given in the SI.

MODEL CONFIGURATION

Bathymetric data were obtained from the mining company (Figure SI-S1 and Table SI-S1). Components included in the aqueous speciation configuration were SO_4, Cl, Na, K, Mg, Ca, dissolved inorganic carbon (DIC), Al, Fe(II), Fe(III), Zn, SiO_2, PO_4, NH_4, and NO_3, where the chemical species listed represents the total concentration of the component. Implementation of various Fe and Al solubility equilibria was tested for phases indicated as likely by saturation index calculations, as further described below. Inorganic precipitates were subject to constant settling at a user-defined rate. Additional state variables included in the model were DO and detrital dissolved and particulate organic carbon, N, and P. The model was configured to have three phytoplankton groups (cyanobacteria, chlorophytes, diatoms) with internal N and P stores, in analogy with Romero et al.[80] Although CAEDYM simulates zooplankton, they were not considered in this study as mean abundances were very low, between 0.01 and 0.1 individuals m^{-3}, mainly small rotifers (unpublished data). Instead the general mortality parameter for phytoplankton was increased slightly to account for mild grazing pressure. The particulate organic carbon and phytoplankton were subject to Stoke's settling. Resuspension was not tested; particles falling on sediments were assumed to be buried and no longer available to the water column. A summary of the water quality model is shown in Figure SI-S4. The effect of parameter/process uncertainty was tested by manually changing parameter values or switching processes on/off.

As mentioned above, laboratory experiments on sediments from the lake[60,61] and mass balance calculations[49] indicated that negligible alkalinity generation occurred in the lake sediments in 2004−2005, due to limited availability of autochthonous or allochthonous organic carbon.[31] A comprehensive sediment diagenesis module,[101] which was developed in parallel to the lake model described above,[79] was therefore not included in this current study, and sediment−water fluxes of dissolved species were set to zero.

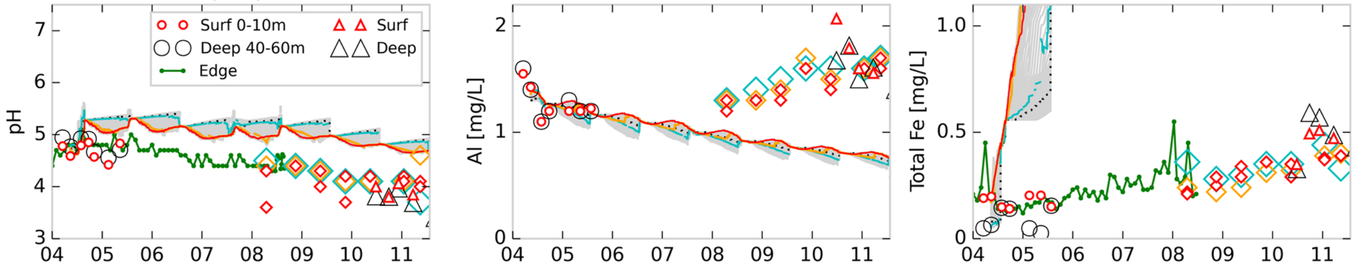
Groundwater throughflow of 2.2 GL/year as per the 2004−2005 energy balance calculations was continued throughout the simulations up to 2012, as were surface inflows, with chemistry assumed to be constant with time. Groundwater concentrations were assumed constant with depth for all species except Fe, where initial simulations showed that influx of high concentrations of Fe at all depths led to accumulation of Fe(II) in the hypolimnion, which was not observed in the field. As the acidity load on the lake, including the depth distribution, was unknown, Fe concentrations were increased in groundwater inflows near the surface and decreased at depth. This is consistent with the likely source of the acidity load (oxidation of pyrite in waste materials) being closer to the surface where atmospheric oxygen is readily available. All data sources, calculations, and assumptions used for model inflows and initial conditions are described in detail in the SI.

RESULTS AND DISCUSSION

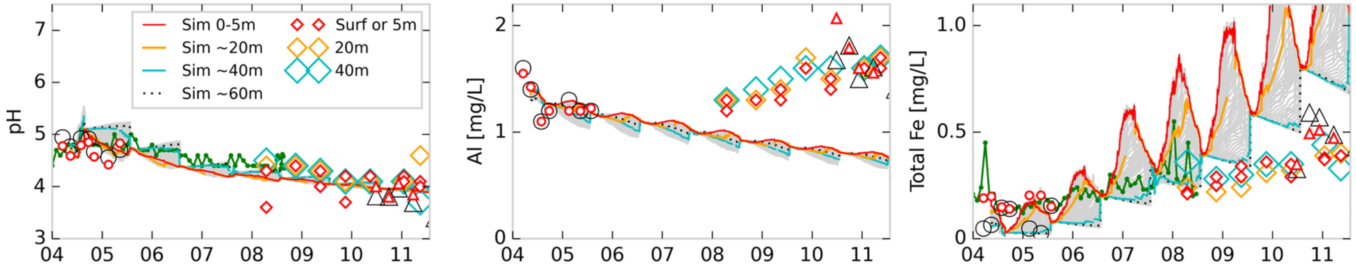
Stratification and Conservative Ions. The model captured the thermal stratification of the lake over the summer months (November−February) and overturn during the winter months (June−August) in 2004−2011 (prebreach, Figures SI-

DOI: 10.1021/acs.est.7b01432

a) No solubility equilibria



b) Ferrihydrite



c) Ferrihydrite and gibbsite

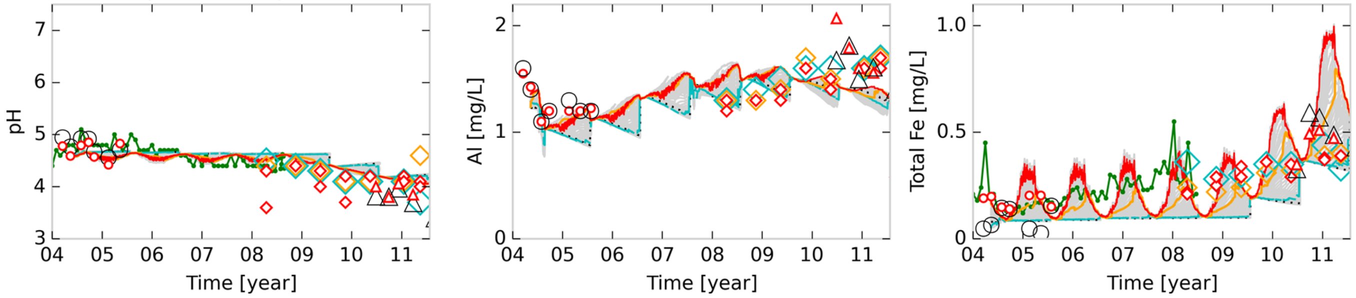


Figure 1. pH (left), Al (middle), and total dissolved Fe (right) in simulations: (a) with no solubility controls, and with solubility equilibrium control by (b) ferrihydrite and (c) ferrihydrite and gibbsite. Legends apply for all panels. In these simulations, Fe(II) in the groundwater inflow is equivalent to 15 mg/L (see SI), and the Fe(II) oxidation rate scaling is 1000×. Simulation results are shown for different depths (see legend), and all depths (gray shading). Field data are from (i) 2004−2005 grab samples from depth profiles,[49] averaged over the upper (Surf 0−10m) or lower (Deep 40−60m) part of the lake, (ii) 2008−2011 grab samples from the mining company, from 0 or 5 m depth (Surf or 5m) or 20 or 40 m depth, and (iii) 2010−2011 grab samples from literature,[74] from the surface of the lake (Surf) or from just above lake sediments (Deep). Green dots indicate grab sampling by the mining company from the edge of the lake.

S2, SI-S3, and SI-S5). For salinity and conservative ions, simulations captured both the observed evapoconcentration of the epilimnion over summer months and the longer-term rising trend. The presence of ~2.2 GL/year of 17 °C groundwater throughflow was supported by simulations without this inflow not capturing the observed warming trend in the hypolimnetic temperatures in the lake in the high-resolution 2004−2005 data, and the short- or long-term water quality (Figure SI-S6). As expected, given the water balance over the lake, the simulated concentrations were simply a function of the assumed inflow concentrations. Indications were that under continued conditions similar to pre-2011, solutes in the lake would have been subject to ongoing evapoconcentration.

Solubility Equilibrium Controls. With no mineral solubility equilibria initially implemented in the model, the 2004 winter inflow of carbonate alkalinity due to river diversion led to a rapid increase in the simulated pH (Figure 1a), and for the remainder of the simulation the pH was greater than field observations. Furthermore, in the absence of solubility equilibrium control on Fe(III) by $Fe(OH)_{3(s)}$ precipitation, the total dissolved Fe concentration was much greater than that observed in the lake. The Al concentration, responding to dilution only, matched the observed decrease in concentrations during the 2004 river inflow, however, the subsequent continued decrease was not consistent with later field observations.

With solubility equilibrium with ferrihydrite alone implemented into the model, precipitation of $Fe(OH)_{3(s)}$ led to lower pH and Fe concentrations, which were then closer to those observed in the field (Figure 1b). However, the later Al concentrations were again underestimated. When both ferrihydrite and gibbsite solubility equilibrium were used in the simulation, or ferrihydrite and basaluminite (not shown), the pH was again buffered at a level close to that observed in the field. Dissolution of gibbsite during periods with no river inflow led to Al concentrations that best matched the field observations (Figure 1c) and overall this simulation configuration had the least error (see Text SI-S5). With the solubility equilibria in place, the evolution of pH and Fe and Al concentrations were tightly coupled, as is further demonstrated below.

Simulations where solubility equilibria with jurbanite was implemented did not reproduce water quality observations, consistent with mineralogical studies of Al precipitates in AMD environments.[53]

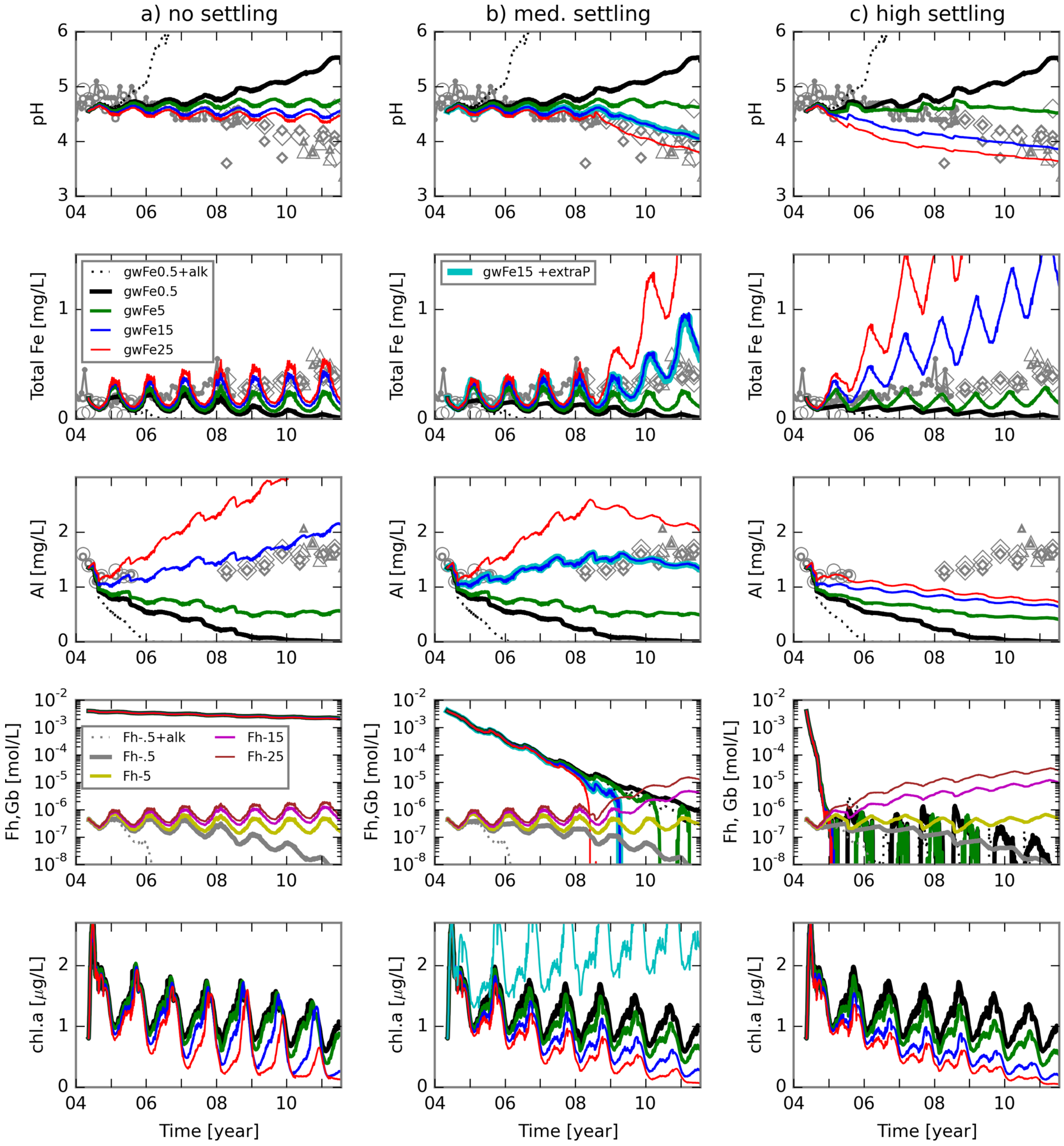


Figure 2. From top: pH, total dissolved Fe, Al, gibbsite (Gb), and ferrihydrite (Fh; NB separate color key), and chl.a, for simulations with (a) no settling, (b) medium settling (1×10^{-6} m/s), and (c) high settling (1×10^{-5} m/s), and different Fe(II) acidity-equivalents loading in groundwater (see SI), ranging from 25 to 0.5 mg/L and 0.5 mg/L with net positive alkalinity (+alk). For medium settling, an additional simulation is included with additional P in inflows (see SI). For pH, Fe, and Al, gray symbols are the same data as shown in Figure 1. See SI for performance assessment statistics.

Saturation index calculations with the 2010–2011 data suggested that the solution was close to solubility equilibrium with respect to goethite, rather than ferrihydrite as was found for the 2004–2005 data. Simulations with goethite solubility equilibrium rather than ferrihydrite resulted in the same evolution of pH and Al as in Figure 1c, but very low Fe concentrations in solution. Ferrihydrite is known to convert over time to the thermodynamically more stable goethite, where the conversion rate is influenced by solution chemistry; for example, conversion occurs more quickly with higher Fe(II) and lower Al concentration.[102−105] Gradual conversion of ferrihydrite to goethite may explain the slight overestimation of Fe concentrations in the epilimnion toward the end of the simulations. Future simulations could incorporate a kinetic

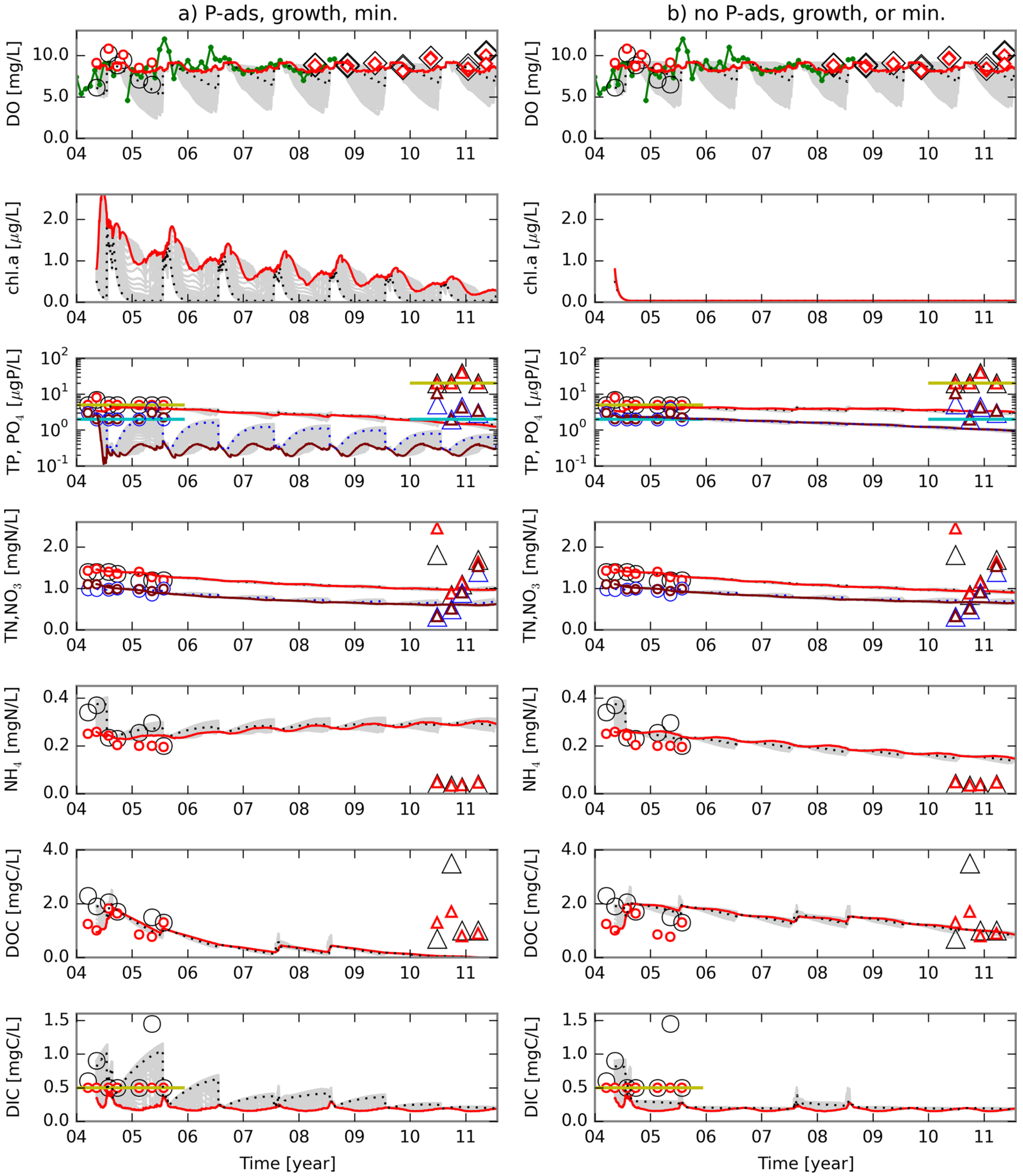


Figure 3. From top: DO, chl.a, TP and PO_4, TN and NO_3, NH_4, DOC, and DIC, in simulations configured with (a) P adsorption to Fh, phytoplankton growth, and organic matter mineralization and (b) no adsorption, growth, or mineralization. Solid lines indicate simulation results averaged over 0−10 m depth, dotted lines are 40−60 m depths; gray shading indicates simulation results from all depths. Red symbols indicate shallow (0−10 m, red) or deep (40−60 m, black) samples, except for PO_4 and NO_3 (brown-shallow, and blue-deep). DO from edge sampling by the mining company is also shown (green line and dots). Horizontal lines indicate detection limits for TP and DIC (yellow) and PO_4 (light blue). See Figure SI-S9 for detail of 2004−2006.

expression for conversion of ferrihydrite to goethite over time. Aluminum phases may also change over time; alternatively, aqueous species, such as Al_{13}, and interaction with aluminosilicate minerals may require consideration.[106−111]

Net External Acidity Load and Mineral Buffering. The 2004−2011 evolution of the coupled pH, Al, and Fe could not be reproduced without an ongoing load of net acidity on the lake. For comparison, simulations where the Fe(II)-based acidity in groundwater was also accompanied by bicarbonate alkalinity, such that the total alkalinity was positive, resulted in rapid and sustained removal of Fe and Al from solution, and increase in pH (Figure 2). Furthermore, reproducing field observations required the initial presence of gibbsite, which buffered pH and Al concentrations, but which was depleted after approximately 5 years (Figures 2 and SI-S7). The initial amount of gibbsite required to reproduce field observations depended upon the settling rate as well as the acidity load; depletion occurred either because of complete dissolution or gradual settling out of the water column and burial.

Fe(II) Oxidation Rate. Oxidation of Fe(II) by oxygen was implemented as a kinetic process, but it was not known whether the Fe(II) oxidation rate (eq 1) in the lake would reflect abiotic rates (given the oligotrophic conditions in the lake), or higher rates due to the commonly observed effect of microbial mediation or autocatalytic oxidation.[55,65,112−114] However, with the abiotic rate of Fe(II) oxidation (Fe(II) oxidation rate scaling = 1), field pH and the associated behavior of Fe and Al concentrations were not simultaneously reproduced under any tested conditions, where the Al concentration was coupled to acidity generation from Fe reactions through gibbsite dissolution (Figure SI-S8). Furthermore, the Fe concentration was dominated by Fe(II), whereas in the field the total Fe was observed to be only ~40 % Fe(II) in May 2005.[49] With a 100 or 1000 times scaling up of the abiotic oxidation rate, the simulated Fe concentrations were closer to those observed in the field; accelerated Fe(II) oxidation rates are consistent with observations in acidic environments elsewhere.[65,112] With the highest scaling factor (1000), virtually all Fe(II) was removed from solution. With Fe(II) oxidation scaling factor of 100, a minor amount of Fe(II) was present in the epilimnion, as was observed in the field (Figure SI-S8). Depending on the depth distribution assumed for Fe in groundwater in these simulations, with a scaling factor of 100, Fe(II) also accumulated below the thermocline, which was not observed in the field, suggesting that inflows in the field occurred at even shallower depths. The model input data would require further refinement through measurement of groundwater acidity concentrations at different depths. However, the long-term evolution of pH and concentrations of Fe and Al after annual overturn was insensitive to the tested range of groundwater Fe concentration depth distributions, or to whether the abiotic Fe(II) oxidation rate was scaled up by 2 vs 3 orders of magnitude, indicating that in this system, the external acidity loading was the dominant control on the long-term lake water quality.

Links between Geochemistry, Nutrients, and Primary Productivity. In 2004−2005, the simulations displayed similar annual patterns to those that were observed in the field data with respect to partial DO drawdown and accumulation of DIC, NH_4, and PO_4 in the hypolimnion, as well as a decreasing trend in DOC from 2004 to 2005 (Figures 3 and SI-S9). The main factor causing these patterns in the simulations was microbial mineralization of organic matter in the water column and vertical mixing limitation due to thermal stratification. As hypothesized, the ammonia accumulation was enhanced due to limited nitrification under the acidic conditions; in simulations where the pH increased over time (e.g., Figure 2), the ammonia concentrations decreased dramatically as pH increased (Figure SI-S10). However, the selected rate parametrization resulted in the nitrification rate being reduced to zero in the lake, which in the longer term led to greater ammonia accumulation in the water column than observed in the field (Figure 3). With further refinement of the nitrification rate parametrization to allow ongoing, low level nitrification at the pH in the lake, the simulations would more closely reproduce the field observations.

Comparison with longer-term data indicated that the model underestimated the 2010−2011 DOC concentration. The observations of chl.a concentrations below 0.03 μg/L in 2010−2011 indicate that the DOC source is unlikely to have been primary production by phytoplankton in the water column, unless a rapid reduction in chl.a occurred prior to the 2010 measurements. To test if the rate of DOC mineralization was limited in the lake, simulations were performed with the extreme case of conservative behavior of DOC (no mineralization). This resulted in improved long-term persistence of DOC, and lower chl.a and NH_4 concentrations, which were then closer to those observed in the field (Figure 3). However, the observed 2004−2005 depth trends were then not reproduced, and there were alternative explanations for the discrepancy between modeled and observed NH_4 (see above) and chl.a (see below). This scenario is also unlikely as microbes are reported to have greater resilience to lower pH conditions than phytoplankton.[115] There is also the possibility that organic carbon was generated in the lake by benthic algae; growth of benthic algae was observed in laboratory microcosms with lake water[74] and has been observed elsewhere in acidic pit lakes;[116,117] however, if occurring in this system, its significance remains unclear.

Simulation results were insensitive to the rate of the photochemical reaction of DOC and Fe(III) included in the model. The underestimation rather than overestimation of longer-term DOC concentrations, and simulation of the presence of Fe(II) by implementing Fe(II) in inflows and pH limitation of oxidation, suggests that this process is not required to explain major trends in water quality evolution. For other systems, further investigation of model parametrization is required, potentially with higher resolution timesteps, which were not practical for the longer-term simulations in this study.

Simulations with sorption of P to ferrihydrite led to reduced PO_4 and chl.a concentrations. Furthermore, chl.a concentrations were then sensitive to variation in the Fe load and particle settling rate (Figure 2), as these parameters affected the removal of P from the water column. However, in simulations with a higher P load (within the uncertainty in the input data, see SI), the sorption capacity became saturated and chl.a increased over time (Figure 2), as did DOC. In some simulations, solution also became oversaturated with respect to the Fe(III) phosphate phase strengite.

However, irrespective of the external P load, with the same phytoplankton growth rates that have reproduced field observations in other systems[80] the model was not able to reproduce the 2010−2011 field observations of very low chl.a coincidental with the presence of measurable PO_4 (<0.03 μg/L chl.a and up to ~11 μgP/L;[74] see Figure 3). The two most commonly hypothesized limitations on primary production in acidic lakes are P and DIC.[94,115,118−121] Both limitations are included in the model; in the simulation with additional bicarbonate alkalinity inflows in groundwater, chl.a growth was the same as the equivalent Fe loading without alkalinity (Figure 2), indicating that DIC was not a limiting factor. Possible explanations for the low pelagic chl.a include that growth is limited by factors not accounted for in the model, such as toxicity of Al or other metals.[122−125]

DOI: 10.1021/acs.est.7b01432

2011 River Breach. Simulations of the Aug 2011 uncontrolled river breach are associated with large uncertainty due to the poorly constrained volume and water quality of the initial river inflow, an unknown amount of which decanted back to the river. Nevertheless, the preliminary simulations captured the general water quality patterns observed after the river breach with respect to the development of a surface layer of less saline water, which persisted until overturn in 2012 (Figure SI-S11). The model also reproduced the rapid initial drop in Al in this layer and Fe (Figure 4) due to precipitation. Furthermore, the observed subsequent increase in Al due to gibbsite redissolution as Fe was removed from solution, was also captured, as was the subsequent gradual decrease in Al due to the ongoing influx of river alkalinity. However, after the connection to the river was closed, the model did not capture the trend of increasing pH up to early 2012, with the associated further decrease in Al concentrations. Organic carbon was not measured in the river during the breach; however, there was an immediate postbreach increase in the lake DOC concentration, which then dropped in early 2012 (Figure SI-S11). This postbreach increase in alkalinity was therefore likely due to organic matter imported during the breach driving internal alkalinity generation in lake sediments, a process which was not included in the current model configuration. These observations indicated that ongoing addition of river water may lead to stabilization of the lake near neutral pH, as has indeed been reported as a result of subsequent further (controlled) river inflows.[126] Future simulations with a sediment diagenesis module[79] activated could be used to investigate the postbreach sediment-water coupling in the lake, and other pit lakes where river inflow and throughflow has occurred.[97,127,128]

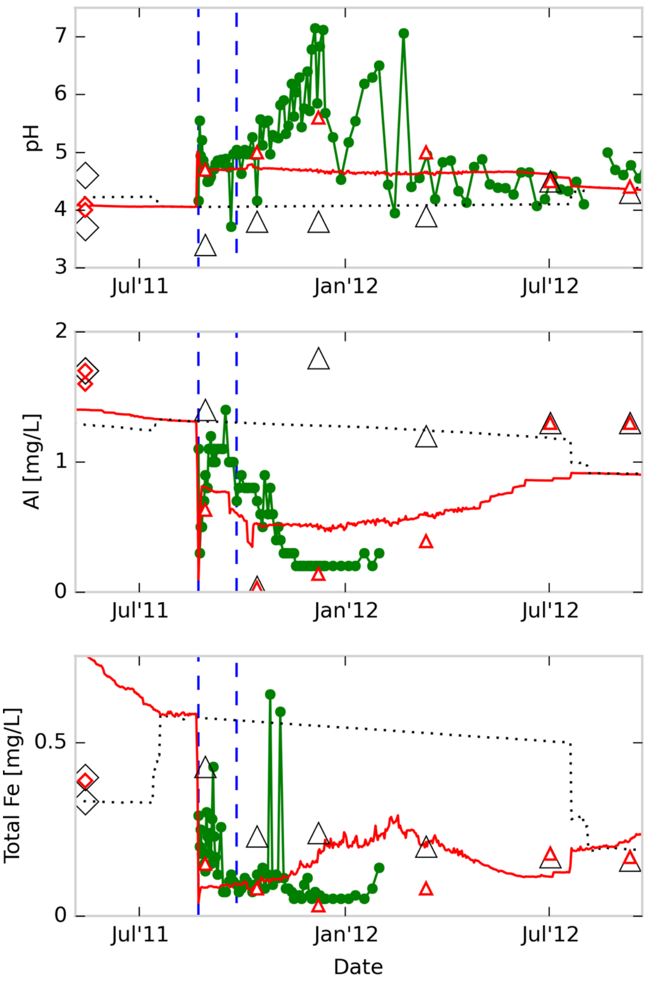


Figure 4. pH, Al, and total Fe during/after the river breach in August 2011. Red lines and symbols are for 0−10 m simulation results and field data, respectively; black dotted lines and triangles indicate deeper (40−60 m) simulation results and samples, respectively. Black diamonds indicate samples from 20 or 40 m depth. Green dots indicate grab sampling from the edge of the lake. Dashed vertical blue lines indicate start and end of the river breach connection to the lake (see text).

Environmental Modeling Implications. The numerical modeling approach presented here constitutes an important tool for formulation and desktop testing of alternative scientific hypotheses. Application to field sites allows identification of knowledge gaps that require further field data collection, such as the likely duration of the acidity load,[58,59] or general improved model implementation. The quantitative approach can also be applied to optimization of the design of field campaigns, with respect to the spatial and temporal resolution of sampling required to capture the effects of short- and long-term water quality controls. Future studies should include rigorous assessment of model sensitivity, equifinality, predictive uncertainty, and performance assessment[129−132] and improved parametrization of groundwater−lake interaction. This work has nonetheless demonstrated that the model can reproduce the geochemical water quality evolution in a pit lake, and with further refinement and testing against well-constrained field observations, will ultimately be able to provide an improved, quantitative basis for management and remediation strategies of pit lakes. The results and integrated modeling approach are also readily applicable to other natural or anthropogenically impacted systems where feedbacks between geochemistry, biology, and physical processes in water column and sediments affect water quality evolution, including for example lakes at higher pH where carbonate minerals control water quality,[14,45] or other systems where Fe and Mn redox chemistry and mineral solubilities affect nutrient cycling and primary production.[133−135]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b01432.

> Theory and numerical approach for geochemical model parametrization, sources and derivations of input and field data, bathymetric data, additional model results, and performance assessment statistics (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: microbialite@gmail.com.

ORCID

S. Ursula Salmon: 0000-0002-3372-4959

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This project was funded by the Western Australian Centre for Excellence in Sustainable Mine Lakes and by Australian Research Council Project LP0454252. S. Katsev, C. McCullough, and three anonymous reviewers are thanked for helpful comments on an earlier version of the manuscript. C. Harkin (Premier Coal Limited) and C. McCullough kindly provided monitoring data for 2006−2012. Premier Coal Limited did not request any changes to the manuscript. We acknowledge the UWA Centre for Water Research for providing the DYRESM-CAEDYM code that was used as a basis for the model development reported in this study.

■ REFERENCES

(1) Smith, V. H. Eutrophication of freshwater and coastal marine ecosystems - A global problem. *Environ. Sci. Pollut. Res.* **2003**, *10* (2), 126−139.

(2) Mallin, M. A.; Johnson, V. L.; Ensign, S. H.; MacPherson, T. A. Factors contributing to hypoxia in rivers, lakes, and streams. *Limnol. Oceanogr.* **2006**, *51* (1), 690−701.

(3) Smith, V. H.; Joye, S. B.; Howarth, R. W. Eutrophication of freshwater and marine ecosystems. *Limnol. Oceanogr.* **2006**, *51* (1), 351−355.

(4) Miller, G. C.; Lyons, W. B.; Davis, A. Understanding the water quality of pit lakes. *Environ. Sci. Technol.* **1996**, *30* (3), 118A−123A.

(5) Castro, J. M.; Moore, J. N. Pit lakes: their characteristics and the potential for their remediation. *Environ. Geol.* **2000**, *39* (11), 1254−1260.

(6) Castendyk, D. N.; Eary, L. E. Nature and Global Distribution of Pit Lakes. In *Mine Pit Lakes: Characteristics, Predictive Modeling, and Sustainability*; Society for Mining, Metallurgy, and Exploration, Inc.: Littleton, CO, 2009; Vol. 3, pp 1−11.

(7) Geller, W.; Schultze, M.; Kleinmann, B.; Wolkersdorfer, C. *Acidic Pit Lakes: The Legacy of Coal and Metal Surface Mines*; Springer: Berlin, 2013; p 525.

(8) Castendyk, D. N.; Eary, L. E.; Balistrieri, L. S. Modeling and management of pit lake water chemistry 1: Theory. *Appl. Geochem.* **2015**, *57* (0), 267−288.

(9) Castendyk, D. N.; Balistrieri, L. S.; Gammons, C.; Tucci, N. Modeling and management of pit lake water chemistry 2: Case studies. *Appl. Geochem.* **2015**, *57* (0), 289−307.

(10) Tucci, N. J.; Gammons, C. H. Influence of Copper Recovery on the Water Quality of the Acidic Berkeley Pit Lake, Montana, U.S.A. *Environ. Sci. Technol.* **2015**, *49* (7), 4081−4088.

(11) Geller, W.; Klapper, H.; Salomons, W. *Acidic Mining Lakes: Acid Mine Drainage, Limnology, and Reclamation*; Springer: New York, 1998; p 435.

(12) Doupe, R. G.; Lymbery, A. J. Environmental risks associated with beneficial end uses of mine lakes in southwestern Australia. *Mine Water Environ.* **2005**, *24*, 134−138.

(13) McCullough, C. D.; van Etten, E. J. B. Ecological Restoration of Novel Lake Districts: New Approaches for New Landscapes. *Mine Water Environ.* **2011**, *30* (4), 312−319.

(14) Eary, L. E. Geochemical and equilibrium trends in mine pit lakes. *Appl. Geochem.* **1999**, *14* (8), 963−987.

(15) Blodau, C. A review of acidity generation and consumption in acidic coal mine lakes and their watersheds. *Sci. Total Environ.* **2006**, *369* (1−3), 307−332.

(16) Totsche, O.; Pöthig, R.; Uhlmann, W.; Büttcher, H.; Steinberg, C. E. W. Buffering mechanisms in acidic mining lakes - a model-based analysis. *Aquat. Geochem.* **2003**, *9*, 343−359.

(17) Werner, F.; Bilek, F.; Luckner, L. Impact of regional groundwater flow on the water quality of an old post-mining lake. *Ecological Engineering* **2001**, *17* (2−3), 133−142.

(18) Pellicori, D. A.; Gammons, C. H.; Poulson, S. R. Geochemistry and stable isotope composition of the Berkeley pit lake and surrounding mine waters, Butte, Montana. *Appl. Geochem.* **2005**, *20* (11), 2116−2137.

(19) Martin, A. J.; Calvert, S. E. Hydrological and geochemical controls governing the distribution of trace metals in a mine-impacted lake. *Environmental Geology* **2003**, *43*, 408−418.

(20) Edraki, M.; Golding, S. D.; Baublys, K. A.; Lawrence, M. G. Hydrochemistry, mineralogy and sulfur isotope geochemistry of acid mine drainage at the Mt. Morgan mine environment, Queensland, Australia. *Appl. Geochem.* **2005**, *20* (4), 789−805.

(21) Moncur, M. C.; Ptacek, C. J.; Blowes, D. W.; Jambor, J. L. Spatial variations in water composition at a northern Canadian lake impacted by mine drainage. *Appl. Geochem.* **2006**, *21* (10), 1799−1817.

(22) Castro, J. M.; Wielinga, B. W.; Gannon, J. E.; Moore, J. N. Stimulation of sulfate-reducing bacteria in lake water from a former open-pit mine through addition of organic wastes. *Water Environ. Res.* **1999**, *71* (2), 218−223.

(23) Frömmichen, R.; Kellner, S.; Friese, K. Sediment conditioning with organic and/or inorganic carbon sources as a first step in alkalinity generation of acid mine pit lake water (pH 2−3). *Environ. Sci. Technol.* **2003**, *37*, 1414−1421.

(24) Frömmichen, R.; Wendt-Potthoff, K.; Friese, K.; Fischer, R. Microcosm studies for neutralization of hypolimnic acid mine pit lake water (pH 2.6). *Environ. Sci. Technol.* **2004**, *38* (6), 1877−1887.

(25) Brugam, R. B.; Gastineau, J.; Ratcliff, E. The neutralization of acidic coal mine lakes by additions of natural organic matter: A mesocosm test. *Hydrobiologia* **1995**, *316* (2), 153−159.

(26) Wendt-Potthoff, K.; Frömmichen, R.; Herzsprung, P.; Koschorreck, M. Microbial Fe(III) reduction in acidic mining lake sediments after addition of an organic substrate and lime. *Water, Air, Soil Pollut.: Focus* **2002**, *2*, 81−96.

(27) Lessmann, D.; Fyson, A.; Nixdorf, B. Experimental eutrophication of a shallow acidic mining lake and effects on the phytoplankton. *Hydrobiologia* **2003**, *506-509* (1−3), 753−758.

(28) Geller, W.; Koschorreck, M.; Wendt-Potthoff, K.; Bozau, E.; Herzsprung, P.; Büttner, O.; Schultze, M. A pilot-scale field experiment for the microbial neutralization of a holomictic acidic pit lake. *J. Geochem. Explor.* **2009**, *100* (2−3), 153−159.

(29) Davison, W.; George, D. G.; Edwards, N. J. A. Controlled Reversal of Lake Acidification by Treatment with Phosphate Fertilizer. *Nature* **1995**, *377* (6549), 504−507.

(30) Fisher, T. S. R.; Lawrence, G. A. Treatment of acid rock drainage in a meromictic mine pit lake. *J. Environ. Eng.* **2006**, *132* (4), 515−526.

(31) Koschorreck, M.; Tittel, J. Natural alkalinity generation in neutral lakes affected by acid mine drainage. *J. Environ. Qual.* **2007**, *36* (4), 1163−1171.

(32) Davis, A.; Bellehumeur, T.; Hunter, P.; Hanna, B.; Fennemore, G. G.; Moomaw, C.; Schoen, S. The nexus between groundwater modeling, pit lake chemogenesis and ecological risk from arsenic in the Getchell Main Pit, Nevada, USA. *Chem. Geol.* **2006**, *228* (1−3), 175−196.

(33) Schafer, W. M.; Eary, L. E., Approaches for Developing Predictive Models of Pit Lake Geochemistry and Water Quality. In *Mine Pit Lakes: Characteristics, Predictive Modeling, and Sustainability*; Society for Mining, Metallurgy, and Exploration, Inc.: Littleton, CO, 2009; Vol. 3, pp 115−126.

(34) Lewis, R. L. Predicting the steady-state water quality of pit lakes. *Mining Engineering* **1999**, *51*, 54−58.

(35) Kringel, R.; Nitsche, C.; Haferkorn, B. Limnology of sulfur-acidic lignite mining lakes III: Approach and limitation in predicting chemical properties. *Verh. Internat. Verein. Limnol.* **2000**, *27*, 416−419.

(36) Tempel, R. N.; Shevenell, L. A.; Lechler, P.; Price, J. Geochemical modeling approach to predicting arsenic concentrations in a mine pit lake. *Appl. Geochem.* **2000**, *15* (4), 475−492.

(37) Böhrer, B.; Heidenreich, H.; Schimmele, M.; Schultze, M. Numerical prognosis for salinity profiles of future lakes in the opencast mine Merseburg-Ost. *International Journal of Salt Lake Research* **1998**, *7*, 235−260.

(38) Hamblin, P. F.; Stevens, C. L.; Lawrence, G. A. Simulation of vertical transport in mining pit lake. *Journal of Hydraulic Engineering* **1999**, *125* (10), 1029−1038.

(39) Balistrieri, L. S.; Tempel, R. N.; Stillings, L. L.; Shevenell, L. A. Modeling spatial and temporal variations in temperature and salinity

during stratification and overturn in Dexter Pit Lake, Tuscarora, Nevada, USA. *Appl. Geochem.* **2006**, *21* (7), 1184−1203.

(40) Huber, A.; Ivey, G. N.; Wake, G.; Oldham, C. E. Near-surface wind-induced mixing in a mine lake. *Journal of Hydraulic Engineering* **2008**, *134* (10), 1464−1472.

(41) Castendyk, D. N.; Webster-Brown, J. G. Sensitivity analyses in pit lake prediction, Martha Mine, New Zealand 1: Relationship between turnover and input water density. *Chem. Geol.* **2007**, *244* (1−2), 42−55.

(42) Moreira, S.; Boehrer, B.; Schultze, M.; Dietz, S.; Samper, J. Modeling Geochemically Caused Permanent Stratification in Lake Waldsee (Germany). *Aquat. Geochem.* **2011**, *17* (3), 265−280.

(43) Morin, K. A.; Hutt, N. M. Prediction of water chemistry in mine lakes: The minewall technique. *Ecological Engineering* **2001**, *17* (2−3), 125−132.

(44) Castendyk, D. N.; Webster-Brown, J. G. Sensitivity analyses in pit lake prediction, Martha mine, New Zealand 2: Geochemistry, water-rock reactions, and surface adsorption. *Chem. Geol.* **2007**, *244* (1−2), 56−73.

(45) Eary, L. E. Predicting the effects of evapoconcentration on water quality in mine pit lakes. *J. Geochem. Explor.* **1998**, *64* (1−3), 223−236.

(46) Davis, A.; Ashenberg, D. The aqueous geochemistry of the Berkeley Pit, Butte, Montana, U.S.A. *Appl. Geochem.* **1989**, *4* (1), 23−36.

(47) Bozau, E.; Bechstedt, T.; Friese, K.; Frömmichen, R.; Herzsprung, P.; Koschorreck, M.; Meier, J.; Volkner, C.; Wendt-Potthoff, K.; Wieprecht, M.; Geller, W. Biotechnological remediation of an acidic pit lake: Modelling the basic processes in a mesocosm experiment. *J. Geochem. Explor.* **2007**, *92* (2−3), 212−221.

(48) Nixdorf, B.; Uhlmann, W.; Lessmann, D. Potential for remediation of acidic mining lakes evaluated by hydrogeochemical modelling: Case study Grunewalder Lauch (Plessa 117, Lusatia/Germany). *Limnologica* **2010**, *40* (2), 167−174.

(49) Salmon, S. U.; Oldham, C. E.; Ivey, G. N. Assessing internal and external controls on lake water quality: Limitations on organic carbon-driven alkalinity generation in acidic pit lakes. *Water Resour. Res.* **2008**, *44* (10), W10414.

(50) Lund, M. A.; McCullough, C. D.; Kumar, N. R., The Collie Pit Lake District, Western Australia: An overview. In *International Mine Water Association (IMWA) Symposium*; McCullough, C. D., Lund, M. A., Wyse, L., Eds.; International Mine Water Association: Bunbury, Australia, 2012; pp 287−294.

(51) Varma, S. *Hydrogeology and Groundwater Resources of the Collie Basin, Western Australia*; HG5, Water and Rivers Commission of Western Australia: Perth, Australia, 2002.

(52) Huber, A. *Internal Mixing in a Mine Lake*; ; M.Sc. Thesis, University of Western Australia, 2006.

(53) Jones, A. M.; Collins, R. N.; Waite, T. D. Mineral species control of aluminum solubility in sulfate-rich acidic waters. *Geochim. Cosmochim. Acta* **2011**, *75* (4), 965−977.

(54) Sanchez-Espana, J.; Yusta, I.; Diez-Ercilla, M. Schwertmannite and hydrobasaluminite: A re-evaluation of their solubility and control on the iron and aluminium concentration in acidic pit lakes. *Appl. Geochem.* **2011**, *26* (9−10), 1752−1774.

(55) Nordstrom, D. K.; Alpers, C. N. Geochemistry of acid mine waters. In *The Environmental Geochemistry of Mineral Deposits*, Plumlee, G. S., Logsdon, M. J., Eds.; Society of Economic Geologists: Chelsea, MI, USA, 1999; Vol. *6A*, pp 133−160.

(56) Yu, J. Y.; Park, M.; Kim, J. Solubilities of synthetic schwertmannite and ferrihydrite. *Geochem. J.* **2002**, *36* (2), 119−132.

(57) Ulrich, K. U.; Bethge, C.; Guderitz, I.; Heinrich, B.; Neumann, V.; Nitsche, C.; Benthaus, F. C. In-Lake Neutralization: Quantification and Prognoses of the Acid Load into a Conditioned Pit Lake (Lake Bockwitz, Central Germany). *Mine Water Environ.* **2012**, *31* (4), 320−338.

(58) Banwart, S. A.; Malmström, M. E. Hydrochemical modelling for preliminary assessment of minewater pollution. *J. Geochem. Explor.* **2001**, *74* (1−3), 73−97.

(59) Lapakko, K. A. Preoperational assessment of solute release from waste rock at proposed mining operations. *Appl. Geochem.* **2015**, *57* (0), 106−124.

(60) Read, D. J. *The Role of Labile Dissolved Organic Carbon in Influencing Fluxes Across the Sediment−Water Interface: From Marine Systems to Mine Lakes*; Ph.D. Thesis, University, University of Western Australia, 2008.

(61) Pham, H. A. *The Dynamics of Microbial Ferric and Sulfate Reduction in Acidic Mine Lake Sediments and Their Impact on Water Quality*; Ph.D. Thesis, University, University of Western Australia, 2009.

(62) Jeschke, C.; Falagán, C.; Knöller, K.; Schultze, M.; Koschorreck, M. No Nitrification in Lakes Below pH 3. *Environ. Sci. Technol.* **2013**, *47* (24), 14018−14023.

(63) Schindler, D. W.; Frost, T. M.; Mills, K. H.; Chang, P. S. S.; Davies, I. J.; Findlay, L.; Malley, D. F.; Shearer, J. A.; Turner, M. A.; Garrison, P. J.; Watras, C. J.; Webster, K.; Gunn, J. M.; Brezonik, P. L.; Swenson, W. A. Comparisons between Experimentally-Acidified and Atmospherically-Acidified Lakes During Stress and Recovery. *Proceedings of the Royal Society of Edinburgh Section B-Biological Sciences* **1990**, *97*, 193−226.

(64) Huesemann, M. H.; Skillman, A. D.; Crecelius, E. A. The inhibition of marine nitrification by ocean disposal of carbon dioxide. *Mar. Pollut. Bull.* **2002**, *44* (2), 142−148.

(65) Singer, P. C.; Stumm, W. Acidic mine drainage. Rate-determining step. *Science* **1970**, *167* (3921), 1121−1123.

(66) King, D. W.; Aldrich, R. A.; Charnecki, S. E. Photochemical Redox Cycling of Iron in NaCl Solutions. *Mar. Chem.* **1993**, *44* (2−4), 105−120.

(67) Collienne, R. H. Photoreduction of iron in the epilimnion of acidic lakes. *Limnol. Oceanogr.* **1983**, *28* (1), 83−100.

(68) Herzsprung, P.; Friese, K.; Packroff, G.; Schimmele, M.; Wendt-Potthoff, K.; Winkler, M. Vertical and annual distribution of ferric and ferrous iron in acidic mining lakes. *Acta Hydrochim. Hydrobiol.* **1998**, *26* (5), 253−262.

(69) Friese, K.; Herzsprung, P.; Witter, B. Photochemical degradation of organic carbon in acidic mining lakes. *Acta Hydrochim. Hydrobiol.* **2002**, *30* (2−3), 141−148.

(70) Effler, S. W.; Owens, E. M. Impact of Lake Acidification on Stratification. *J. Environ. Eng.* **1985**, *111* (6), 822−832.

(71) Kastl, G.; Sathasivan, A.; Fisher, I.; Van Leeuwen, J. Modeling DOC removal by enhanced coagulation. *Journal American Water Works Association* **2004**, *96* (2), 79−89.

(72) Gregor, J. E.; Nokes, C. J.; Fenton, E. Optimising natural organic matter removal from low turbidity waters by controlled pH adjustment of aluminium coagulation. *Water Res.* **1997**, *31* (12), 2949−2958.

(73) Bethwell, C.; Mutz, M. Effect of acid mine drainage on the chemical composition and fall velocity of fine organic particles. *Ecological Engineering* **2005**, *24* (1−2), 75−87.

(74) Kumar, R. N.; McCullough, C. D.; Lund, M. A.; Larranaga, S. A. Assessment of factors limiting algal growth in acidic pit lakes-a case study from Western Australia, Australia. *Environ. Sci. Pollut. Res.* **2016**, *23* (6), 5915−5924.

(75) McCullough, C. D. Consequences and opportunities from river breach and decant of an acidic mine pit lake. *Ecological Engineering* **2015**, *85*, 328−338.

(76) McCullough, C. D.; Ballot, E.; Short, D. Breach and decant of an acid mine lake by a eutrophic river: River water quality and limitations of use. In *First International Conference on Mine Water Solutions in Extreme Environments*; InfoMine Inc.: Lima, Peru, 2013; pp 317−327.

(77) Imberger, J.; Patterson, J. C., A dynamic reservoir simulation model-DYRESM:5. In *Transport Models for Inland and Coastal Waters*; Fischer, H. B., Ed.; Academic Press: New York, 1981; pp 310−361.

(78) Yeates, P. S.; Imberger, J. Pseudo two-dimensional simulations of internal and boundary fluxes in stratified lakes and reservoirs. *International Journal of River Basin Management* **2003**, *1* (4), 297−319.

(79) Hipsey, M. R.; Hamilton, D. P. *Computational Aquatic Ecosystem Dynamic Model: CAEDYM v3 Science Manual*; Centre for Water Research, University of Western Australia, 2008.

(80) Romero, J. R.; Antenucci, J. P.; Imberger, J. One- and three-dimensional biogeochemical simulations of two differing reservoirs. *Ecol. Modell.* **2004**, *174* (1−2), 143−160.

(81) Li, Y.; Gal, G.; Makler-Pick, V.; Waite, A. M.; Bruce, L. C.; Hipsey, M. R. Examination of the role of the microbial loop in regulating lake nutrient stoichiometry and phytoplankton dynamics. *Biogeosciences* **2014**, *11* (11), 2939−2960.

(82) Bocaniov, S. A.; Smith, R. E. H.; Spillman, C. M.; Hipsey, M. R.; Leon, L. F. The nearshore shunt and the decline of the phytoplankton spring bloom in the Laurentian Great Lakes: insights from a three-dimensional lake model. *Hydrobiologia* **2014**, *731* (1), 151−172.

(83) Trolle, D.; Spigel, B.; Hamilton, D. P.; Norton, N.; Sutherland, D.; Plew, D.; Allan, M. G. Application of a Three-Dimensional Water Quality Model as a Decision Support Tool for the Management of Land-Use Changes in the Catchment of an Oligotrophic Lake. *Environ. Manage.* **2014**, *54* (3), 479−493.

(84) Robson, B. J.; Hamilton, D. P. Three-dimensional modelling of a Microcystis bloom event in the Swan River estuary, Western Australia. *Ecol. Modell.* **2004**, *174* (1−2), 203−222.

(85) Silva, C. P.; Marti, C. L.; Imberger, J. Physical and biological controls of algal blooms in the Rio de la Plata. *Environ. Fluid Mech.* **2014**, *14* (5), 1199−1228.

(86) Spillman, C. M.; Imberger, J.; Hamilton, D. P.; Hipsey, M. R.; Romero, J. R. Modelling the effects of Po River discharge, internal nutrient cycling and hydrodynamics on biogeochemistry of the Northern Adriatic Sea. *Journal of Marine Systems* **2007**, *68* (1−2), 167−200.

(87) Machado, D. A.; Imberger, J. Modeling the impact of natural and anthropogenic nutrient sources on phytoplankton dynamics in a shallow coastal domain, Western Australia. *Environ. Fluid Mech.* **2014**, *14* (1), 87−111.

(88) Hipsey, M. R.; Salmon, S. U.; Mosley, L. M. A three-dimensional hydro-geochemical model to assess lake acidification risk. *Environmental Modelling & Software* **2014**, *61*, 433−457.

(89) Parkhurst, D. L.; Appelo, C. A. J. *User's guide to PHREEQC (version 2)—A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations*, 99-4259; U.S. Geological Survey: Denver, CO, 1999; p 312.

(90) Wehrli, B. Redox reactions of metal ions at mineral surfaces. In *Aquatic Chemical Kinetics*; Stumm, W., Ed.; Wiley: New York, 1990; pp 311−336.

(91) Stumm, W.; Morgan, J. J. *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 3rd ed.; John Wiley & Sons, Inc.: New York, USA, 1996; p 1022.

(92) Millero, F. J. The Effect of Ionic Interactions on the Oxidation of Metals in Natural-Waters. *Geochim. Cosmochim. Acta* **1985**, *49* (2), 547−553.

(93) Kapfer, M. Assessment of the colonization and primary production of microphytobenthos in the littoral zone of acidic mining lakes in Lusatia (Germany). *Water, Air, Soil Pollut.* **1998**, *108*, 331−340.

(94) Woelfl, S.; Tittel, J.; Zippel, B.; Kringel, R. Occurrence of an algal mass development in an acidic (pH 2.5), iron and aluminium-rich coal mining pond. *Acta Hydrochim. Hydrobiol.* **2000**, *28* (6), 305−309.

(95) Kleeberg, A. Phosphorus sedimentation in seasonal anoxic Lake Scharmutzel, NE germany. *Hydrobiologia* **2002**, *472* (1−3), 53−65.

(96) Kleeberg, A.; Grüneberg, B. Phosphorus mobility in sediments of acid mining lakes, Lusatia, Germany. *Ecological Engineering* **2005**, *24* (1−2), 89−100.

(97) Herzsprung, P.; Schultze, M.; Hupfer, M.; Boehrer, B.; von Tümpling, W. V.; Duffek, A.; Van der Veen, A.; Friese, K. Flood effects on phosphorus immobilisation in a river water filled pit lake-Case study Lake Goitsche (Germany). *Limnologica* **2010**, *40* (2), 182−190.

(98) Chao, X. B.; Jia, Y. F.; Shields, F. D.; Wang, S. S. Y.; Cooper, C. M. Numerical modeling of water quality and sediment related processes. *Ecol. Modell.* **2007**, *201* (3−4), 385−397.

(99) Zhou, A. M.; Tang, H. X.; Wang, D. S. Phosphorus adsorption on natural sediments: Modeling and effects of pH and sediment composition. *Water Res.* **2005**, *39* (7), 1245−1254.

(100) Zhang, G. S.; Liu, H. J.; Liu, R. P.; Qu, J. H. Removal of phosphate from water by a Fe-Mn binary oxide adsorbent. *J. Colloid Interface Sci.* **2009**, *335* (2), 168−174.

(101) Paraska, D. W.; Hipsey, M. R.; Salmon, S. U. Sediment diagenesis models: Review of approaches, challenges and opportunities. *Environmental Modelling & Software* **2014**, *61*, 297−325.

(102) Boland, D. D.; Collins, R. N.; Miller, C. J.; Glover, C. J.; Waite, T. D. Effect of Solution and Solid-Phase Conditions on the Fe(II)-Accelerated Transformation of Ferrihydrite to Lepidocrocite and Goethite. *Environ. Sci. Technol.* **2014**, *48* (10), 5477−5485.

(103) Hansel, C. M.; Learman, D. R.; Lentini, C. J.; Ekstrom, E. B. Effect of adsorbed and substituted Al on Fe(II)-induced mineralization pathways of ferrihydrite. *Geochim. Cosmochim. Acta* **2011**, *75* (16), 4653−4666.

(104) Hansel, C. M.; Benner, S. G.; Fendorf, S. Competing Fe(II)-induced mineralization pathways of ferrihydrite. *Environ. Sci. Technol.* **2005**, *39* (18), 7147−7153.

(105) Pedersen, H. D.; Postma, D.; Jakobsen, R.; Larsen, O. Fast transformation of iron oxyhydroxides by the catalytic action of aqueous Fe(II). *Geochim. Cosmochim. Acta* **2005**, *69* (16), 3967−3977.

(106) Casey, W. H.; Phillips, B. L.; Furrer, G., Aqueous aluminum polynuclear complexes and nanoclusters: A review. In *Nanoparticles and the Environment*; Banfield, J. F., Navrotsky, A., Eds.; The Mineralogical Society of America: Washington, D.C., 2001; Vol. *44*, pp 167−190.

(107) Furrer, G.; Phillips, B. L.; Ulrich, K. U.; Pöthig, R.; Casey, W. H. The origin of aluminum flocs in polluted streams. *Science* **2002**, *297* (5590), 2245−2247.

(108) Furrer, G.; Trusch, B.; Müller, C. The formation of polynuclear Al_{13} under simulated natural conditions. *Geochim. Cosmochim. Acta* **1992**, *56* (10), 3831−3838.

(109) Sanchez-Espana, J.; Yusta, I.; Gray, J.; Burgos, W. D. Geochemistry of dissolved aluminum at low pH: Extent and significance of Al-Fe(III) coprecipitation below pH 4.0. *Geochim. Cosmochim. Acta* **2016**, *175*, 128−149.

(110) Zhao, H.; Liu, H. J.; Qu, J. H. Effect of pH on the aluminum salts hydrolysis during coagulation process: Formation and decomposition of polymeric aluminum species. *J. Colloid Interface Sci.* **2009**, *330* (1), 105−112.

(111) McDonald, L. M., Jr.; Evangelou, V. P.; Bertsch, P. M. The potential role of sediment mineralogy in regulating aluminum concentrations in lakewater. *Water, Air, Soil Pollut.* **1998**, *104*, 41−55.

(112) Kirby, C. S.; Brady, J. A. E. Field determination of Fe2+ oxidation rates in acid mine drainage using a continuously-stirred tank reactor. *Appl. Geochem.* **1998**, *13* (4), 509−520.

(113) Tamura, H.; Goto, K.; Nagayama, M. Effect of ferric hydroxide on oxygenation of ferrous ions in neutral solutions. *Corros. Sci.* **1976**, *16* (4), 197−207.

(114) Jones, A. M.; Griffin, P. J.; Collins, R. N.; Waite, T. D. Ferrous iron oxidation under acidic conditions - The effect of ferric oxide surfaces. *Geochim. Cosmochim. Acta* **2014**, *145*, 1−12.

(115) Nixdorf, B.; Krumbeck, H.; Jander, J.; Beulker, C. Comparison of bacterial and phytoplankton productivity in extremely acidic mining lakes and eutrophic hard water. *Acta Oecologica* **2003**, *24*, S281−S288.

(116) Nixdorf, B.; Kapfer, M. Stimulation of phototrophic pelagic and benthic metabolism close to sediments in acidic mining lakes. *Water, Air, Soil Pollut.* **1998**, *108*, 317−330.

(117) Koschorreck, M.; Tittel, J. Benthic photosynthesis in an acidic mining lake (pH 2.6). *Limnol. Oceanogr.* **2002**, *47* (4), 1197−1201.

(118) Nixdorf, B.; Fyson, A.; Krumbeck, H. Review: Plant life in extremely acidic waters. *Environ. Exp. Bot.* **2001**, *46*, 203−211.

(119) Nixdorf, B.; Mischke, U.; Lessmann, D. Chrysophytes and chlamydomonads: pioneer colonists in extremely acidic mining lakes (pH < 3) in Lusatia (Germany). *Hydrobiologia* **1998**, *369/370*, 315−327.

(120) Spijkerman, E. Phosphorus limitation of algae living in iron-rich, acidic lakes. *Aquat. Microb. Ecol.* **2008**, *53* (2), 201−210.

(121) Tittel, J.; Bissinger, V.; Gaedke, U.; Kamjunke, N. Inorganic carbon limitation and mixotrophic growth in Chlamydomonas from an acidic mining lake. *Protist* **2005**, *156* (1), 63−75.

(122) Vrba, J.; Bojkova, J.; Chvojka, P.; Fott, J.; Kopacek, J.; Macek, M.; Nedbalova, L.; Papacek, M.; Radkova, V.; Sacherova, V.; Soldan, T.; Sorf, M. Constraints on the biological recovery of the Bohemian Forest lakes from acid stress. *Freshwater Biol.* **2016**, *61* (4), 376−395.

(123) Kalin, M.; Wheeler, W. N.; Olaveson, M. M. Response of phytoplankton to ecological engineering remediation of a Canadian Shield Lake affected by acid mine drainage. *Ecological Engineering* **2006**, *28* (3), 296−310.

(124) Neil, L. L.; McCullough, C. D.; Lund, M. A.; Evans, L. H.; Tsvetnenko, Y. Toxicity of acid mine pit lake water remediated with limestone and phosphorus. *Ecotoxicol. Environ. Saf.* **2009**, *72* (8), 2046−2057.

(125) Smith, K. S.; Balistrieri, L. S.; Todd, A. S. Using biotic ligand models to predict metal toxicity in mineralized systems. *Appl. Geochem.* **2015**, *57* (0), 55−72.

(126) McCullough, C. D.; Harkin, C. Engineered Flow-through Closure of an Acid Pit Lake: A Case Study. In *Mine Closure 2015*; Fourie, A. B., Tibbett, M., Sawatsky, L., van Zyl, D., Eds.; InfoMine Inc.: Vancouver, Canada, 2015.

(127) Delgado-Martin, J.; Juncosa-Rivera, R.; Falcon-Suarez, I.; Canal-Vila, J. Four years of continuous monitoring of the Meirama end-pit lake and its impact in the definition of future uses. *Environ. Sci. Pollut. Res.* **2013**, *20* (11), 7520−7533.

(128) McCullough, C.; Schultze, M. Riverine Flow-Through of Mine Pit Lakes: Improving both Mine Pit Lake and River Water Quality Values? Presented at the 10th International Conference on Acid Rock Drainage (ICARD) and International Mine Water Association (IMWA) Annual Conference, Santiago, Chile, 2015.

(129) Ramin, M.; Stremilov, S.; Labencki, T.; Gudimov, A.; Boyd, D.; Arhonditsis, G. B. Integration of numerical modeling and Bayesian analysis for setting water quality criteria in Hamilton Harbour, Ontario, Canada. *Environmental Modelling & Software* **2011**, *26* (4), 337−353.

(130) Kim, D.-K.; Zhang, W.; Hiriart-Baer, V.; Wellen, C.; Long, T.; Boyd, D.; Arhonditsis, G. B. Towards the development of integrated modelling systems in aquatic biogeochemistry: a Bayesian approach. *J. Great Lakes Res.* **2014**, *40*, 73−87.

(131) Zhang, W. T.; Arhonditsis, G. B. A Bayesian hierarchical framework for calibrating aquatic biogeochemical models. *Ecol. Modell.* **2009**, *220* (18), 2142−2161.

(132) Bennett, N. D.; Croke, B. F. W.; Guariso, G.; Guillaume, J. H. A.; Hamilton, S. H.; Jakeman, A. J.; Marsili-Libelli, S.; Newham, L. T. H.; Norton, J. P.; Perrin, C.; Pierce, S. A.; Robson, B.; Seppelt, R.; Voinov, A. A.; Fath, B. D.; Andreassian, V. Characterising performance of environmental models. *Environmental Modelling & Software* **2013**, *40*, 1−20.

(133) Kopacek, J.; Hejzlar, J.; Kana, J.; Norton, S. A.; Stuchlik, E. Effects of Acidic Deposition on in-Lake Phosphorus Availability: A Lesson from Lakes Recovering from Acidification. *Environ. Sci. Technol.* **2015**, *49* (5), 2895−2903.

(134) Gantzer, P. A.; Bryant, L. D.; Little, J. C. Controlling soluble iron and manganese in a water-supply reservoir using hypolimnetic oxygenation. *Water Res.* **2009**, *43* (5), 1285−1294.

(135) Davison, W. Iron and Manganese in Lakes. *Earth-Sci. Rev.* **1993**, *34* (2), 119−163.

DOI: 10.1021/acs.est.7b01432