A flexible approach for coupled reactive transport modelling in post-mining areas

MIKE MÜLLER[1] & HEIKE BÜTTCHER[2]

1 Hydrocomputing UG (haftungsbeschränkt) & Co. KG, Zur Schule 20, D-04158 Leipzig, Germany
mmueller@hydrocomputing.com
2 Ingenieurbüro für Grundwasser GmbH, Nonnenstr. 9. D-04229 Leipzig, Germany

Abstract The River Pleiße flows through the dump of the open pit lignite mine Witznitz close to Leipzig, Germany, and is impacted by discharging groundwater with high iron concentrations. A two-dimensional (2D) reactive transport model was set up based on an existing 3D model and an extensive study of dump development. A new template-based tool for reactive transport was developed, giving the modeller great flexibility without the need for programming. Primary and secondary iron oxidation, as well as dissolution, precipitation and exchange processes, were modelled. A comparison of modelled and measured values shows a good correspondence, indicating that the model can represent the important processes. Modelling results show the influence of spatial variability and provide quantitative results for long-term water quality developments in the subsurface and fluxes to the river. The newly developed modelling tool can be used for a variety of hydogeochemical problems.

Key words water; rivers; groundwater; River Pleiße, Germany; PCGEOFIM; PHREEQC; coupled modelling

INTRODUCTION

The water quality of the River Pleiße south of Leipzig, Germany, is significantly influenced by lignite mining activities. The water colour becomes yellowish-brown or ochre, especially during low flow periods, indicating inflow of iron from the adjacent mining dumps. Besides the undesirable visual effect, it causes sedimentation of iron ochre with negative impacts on aquatic flora, organisms at the river bottom, as well as fish and the ecosystem as a whole. This threatens the good ecological condition or potential according to the EU Water Framework Directive. The dump of the former open pit mining site Witznitz (operating from 1943 to 1993) is located 15 km south of the city of Leipzig and currently represents the most important source of iron for the River Pleiße. The course of the river was changed due to mining in the mid-1960s so that it cuts through the dump. The current rise of the groundwater table causes direct water inflow from the dumps. It is expected that the number of other dumps in the catchment that discharge into the River Pleiße will increase due to further regional rise of the groundwater table.

SITE DESCRIPTION

The investigation site is located south of the city of Leipzig. Figure 1 shows the site, including the River Pleiße that flows through the area from southeast to north. The section between the inflow of the River Wyhra and the Neukieritzsch site directly crosses the lignite mining dump. The next section until Trachenauer Wehr is located next to the dump. As can be seen from the groundwater contours representing the current situation after a period of rising groundwater tables, the dumps in both sections discharge into the River Pleiße.

Groundwater hydrodynamics are calculated with a 3D model based on the finite volume model PcGeofim (Müller *et al.*, 2003; Sames *et al.*, 2010) (see section "The Models PcGeofim & PHREEQC" under "Modelling Approach"). Modelling results clearly show a further increase in groundwater levels.

The groundwater quality of the dump in the investigation area is characterized by spatial variability. The concentration of dissolved iron has an average value of 1050 mg/L, with a range from 26 to 4510 mg/L. This variability can be attributed to differences in geological material as well as in duration and intensity of contact with oxygen during excavation and variations in hydraulic conductivities. The northern part of the dump has an average iron concentration of

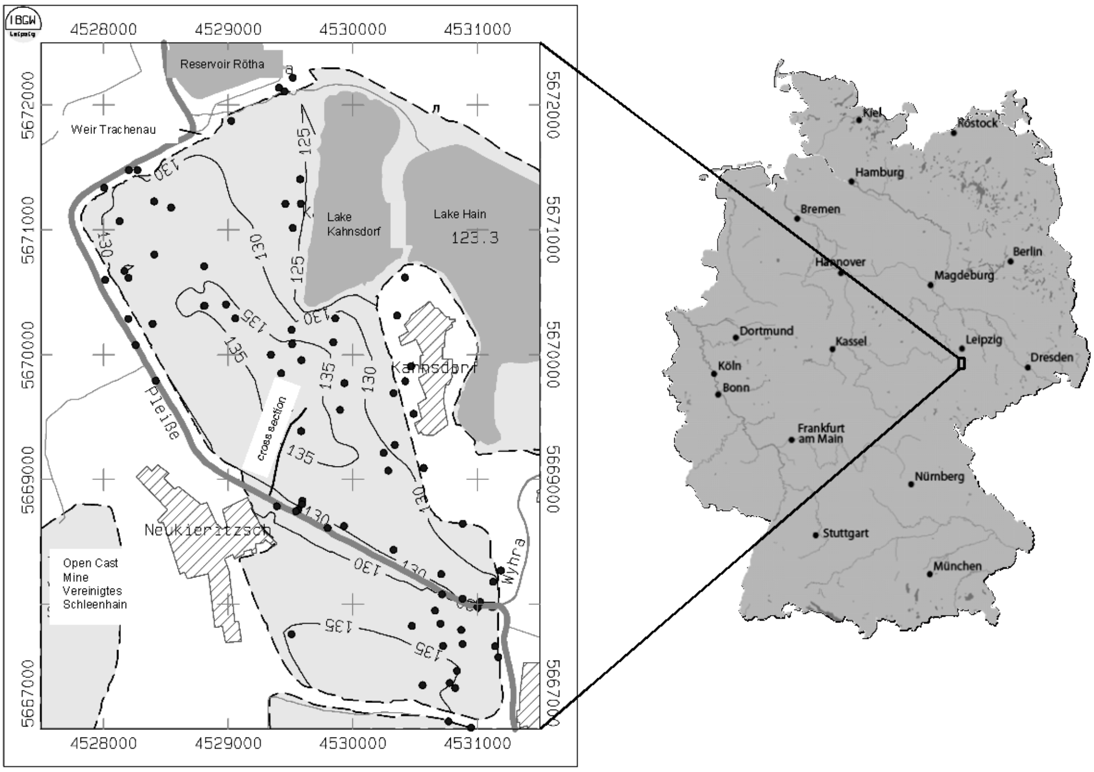

Fig. 1 Investigation site of dump Witznitz with River Pleiße, Lake Kahnsdorfer See, Lake Hainer See and groundwater contours based on data from 2007. Black dots represent observation wells. Areas with dashed outlines are dumps. The location of the model cross-section is labelled "Schnitt".

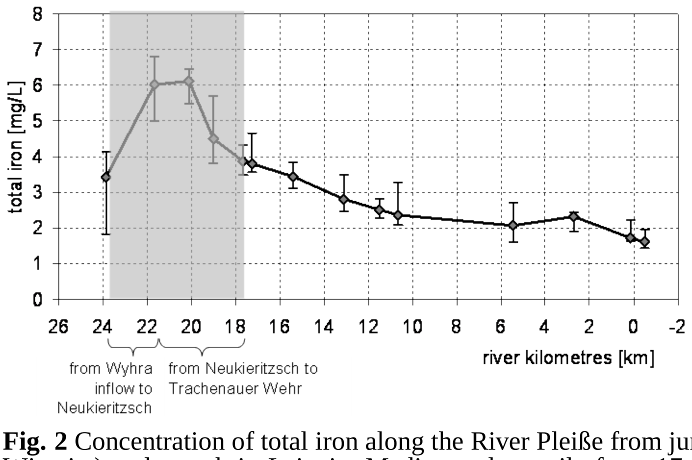

Fig. 2 Concentration of total iron along the River Pleiße from junction with River Wyhra (start of dump Witznitz) and mouth in Leipzig. Median and quartile from 17 measurement campaigns with flows of < 4 m^3/s (Source: Monitoring by SGL GmbH).

500 mg/L compared with an average 1500 mg/L for the southern part. The pH value is 5.3, calcium concentrations average at 480 mg/L and sulphate at 3700 mg/L.

The concentration of dissolved iron in the River Pleiße for low flow periods is shown in Fig. 2. The increased concentrations where the river crosses the dump (grey area in Fig. 2) can be clearly seen. It can be concluded that the high iron concentrations in dump groundwater have a significant impact on the water quality of the river.

The mineral composition of the dump was reconstructed based on an extensive study of the archived descriptions of mining activities. The genesis of the dump body in combination with premining geological conditions was used to reconstruct a representation of the structure of the dump. Based on this, all important constituents such as iron minerals and alkaline minerals, e.g. calcite, were quantified and assigned to the layers and spatial sections of the dump model.

REACTIVE TRANSPORT MODELLING

Modelling approach

The reactive transport modelling uses a newly developed modelling tool that couples the finite volume groundwater flow and transport model PcGeofim and the hydrogeochemical simulator PHREEQC (Parkhurst & Appelo, 1999). Nine cross-sections from the dump towards the river were used for modelling. Only one cross-section, shown in the centre of in Fig. 1, is presented here. The spatial discretization is 50 m in the horizontal and 5 m in the vertical direction using the subsurface parameters from the existing 3D groundwater model (IBGW 2009-2010). The flow is from the aquifer into the river.

The hydrogeochemical processes considered are shown in Fig. 3. A comparable geochemical conceptual model was used by Lenk & Wisotzky (2007) for the dump at mining site Inden (North Rhine-Westphalia, Germany). The iron disulfide oxidation initiates a process chain including buffering processes such as calcite dissolution ($CaCO_3$), silicate weathering (represented as kaolinite $Al_2Si_2O_5(OH)_4$ and K-Mg silicate) and cation exchange. In addition, there are several concomitant processes such as gypsum precipitation ($CaSO_4$), iron hydroxide precipitation ($Fe(OH)_3$) as well as the formation of siderite ($FeCO_3$). Silicate weathering can cause precipitation of aluminium hydroxide ($Al(OH)_3$) and silicium dioxide (SiO_2).

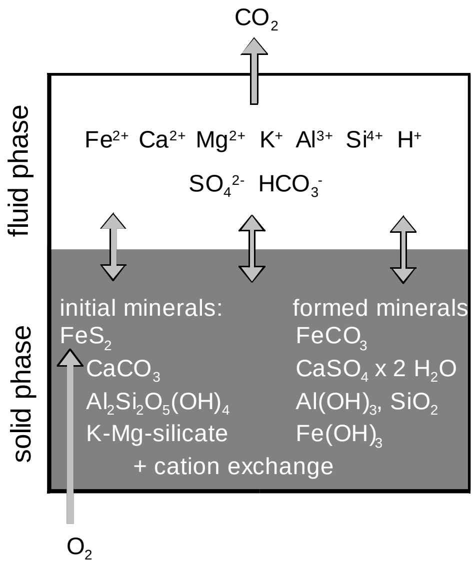

Fig. 3 Conceptualization and processes of the hydrogeochemical model.

The models PcGeofim & PHREEQC

PcGeofim (Müller *et al*., 2003; Sames *et al*., 2010) is a multidimensional finite volume groundwater model that has been developed since the 1970s. It has several special features to represent the conditions in mining areas such as pit lakes, rivers entering and leaving pit lakes, and temporally changing aquifer geometry. PHREEQC (Parkhurst & Apello, 1999) is a widely used hydrogeochemical batch model for equilibrium and kinetic reactions. Both models provide good representations for their domains. A newly developed online model coupling tool combines the features of both models.

Coupling principle

PcGeofim calculates the groundwater flow and the migration of non-reactive species (migrants). For each coupling time step, PHREEQC calculates the changes in dissolved concentrations due to chemical reactions. These changes result in different concentrations in the next time step in PcGeofim. The coupling is sequential, meaning that each model calculates a full time step before the next exchange. Since no density effects are modelled, there is no feedback of concentration changes on the flow regime.

Implementation

The coupling is implemented mainly in the programming language Python that is powerful when it comes to string manipulation, which is a large part of the coupling implementation. The coupling is programmed using the object-oriented paradigm. PcGeofim stores the concentration for all migrants and all active cells in a file, calls an external process in which the Python program takes care of the chemical calculations in the PHREEQC program. After the chemical calculations PcGeofim reads the result back. The Python program utilizes a user-defined translation table to associate species names in PcGeofim to those in PHREEQC. The PHREEQC input files are assembled using templates. These templates are text files, one file for each PHREEQC keyword, that contain PHREEQC input instructions. There are placeholders starting with "$" where the actual numbers for concentrations or other dynamic information belong. Figure 4 shows an example for the keyword EXCHANGE. This approach gives the user full flexibility to change the chemical processes as needed without resorting to programming.

After generating the input files, the Python program starts PHREEQC and, after the geochemical calculations for this time step are finished, reads its output and translates the information back into a format readable by PcGeofim. This procedure is repeated for each exchange time step

```
EXCHANGE    $counter #$lupe_is_jz_mg
CaX2        $cax2    #$pcg_cax2
MgX2        $mgx2    #$pcg_mgx2
KX          $kx      #$pcg_kx
FeX2        $fex2    #$pcg_fex2
AlX3        $alx3    #$pcg_alx3
HX          $hx      #$pcg_hx
```

Fig. 4 Example for an input template for the keyword EXCHANGE. The placeholders starting with "$" will be replaced by actual numbers or other dynamic information.

Site-specific adaptations

The storage in the solid phase is important. Since PHREEQC is started anew for each time step, the Python program stores the information about the solid phase and uses it to generate the input files for PHREEQC. Furthermore, the distribution of primary pyrite oxidation during dump formation is randomly distributed using a Gaussian distribution based on a user-supplied mean value and a standard deviation for each run. This accounts for the spatial variability of primary iron and sulphate concentrations in the groundwater.

Model generalisation

The newly developed tool for coupled modelling can be used for other hydrogeochemical tasks. The main advantage is the flexibility of the approach allowing the user to add or remove PHREEQC keywords without resorting to programming as needed to adapt the tool to the specific problems. The approach can be combined with more recent developments in this area like IPhreeqc (Charlton & Parkhurst, 2011) or PhreeqPy (Müller, 2011; Müller *et al*., 2011) to improve flexibility and performance.

RESULTS

The development of water quality in the cross section was modelled to account for primary iron oxidation caused by oxygen entrapped during mining and secondary iron oxidation by oxygen entering from the land surface. Figure 5 shows the ratio of sulphate and iron obtained from measured values and from the model. The deviation from the stoichiometric ratio of Fe–S in iron disulfide can be clearly seen. The model can reproduce this deviation because it takes the buffer, dissolution and precipitation processes into account, as described in section "Modelling approach".

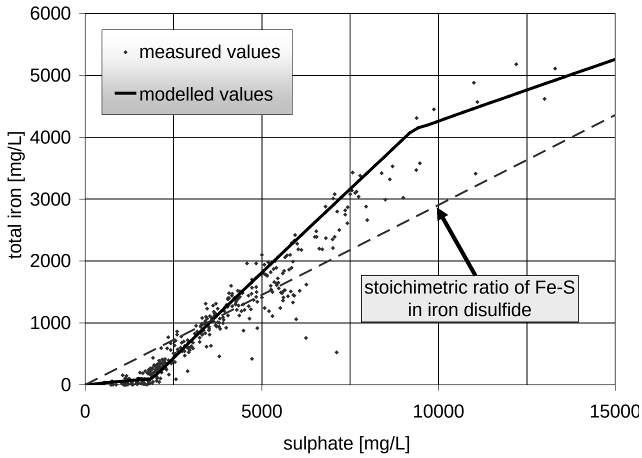

Fig. 5 Modelled ratios between iron and sulphate concentrations in the groundwater of the dump *versus* measured ratios. The deviation from the stoichiometric ratio between Fe and S in iron disulfide can be clearly seen and is due to associated hydrogeochemical processes.

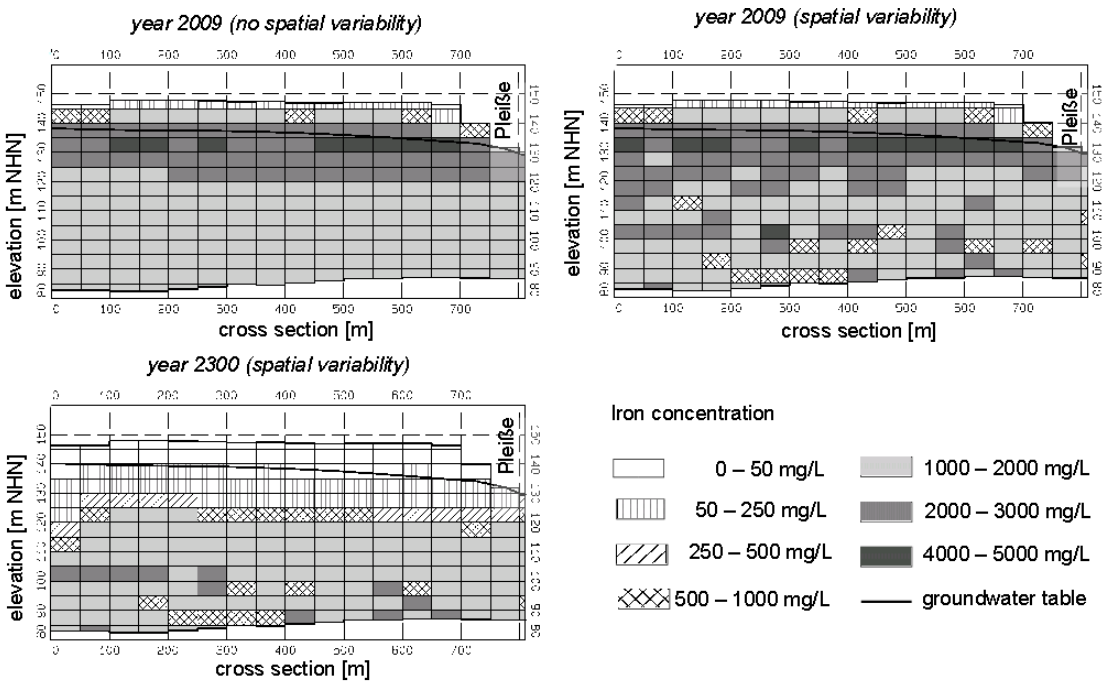

Fig. 6 Modelled iron concentrations and groundwater tables along cross-section "Schnitt" (see Fig. 1) for 2009 (without and with spatial variability) and for the year 2300 (with spatial variability).

Figure 6 shows cross-sections with the distribution of modelled iron concentrations. The upper left graph shows the results for 2009 without spatial variability. The concentrations close to the groundwater table reach 3000–4000 mg/L, while the lower layers have 1000–2000 mg/L. This distribution can be attributed to secondary iron oxidation due to oxygen entering from the atmosphere.

The upper right graph in Fig. 6 shows the results for 2009 with spatial distribution. This distribution was obtained with Monte Carlo simulations using different distributions of oxygen amount for primary iron oxidation. While there are still higher concentrations close to the groundwater table and lower in deep layers, the heterogeneity reduces the difference.

After 300 years of modelling, as shown in Fig. 6 upper right graph, the concentrations in upper and middle layers are lower with values around 250 mg/L due to flushing effects. The lower layers still have higher concentrations because the hydraulic conductivities in these layers are lower, preventing flushing.

The fluxes from the dumps into River Pleiße were quantified. The iron flux until 2100 is about 1000 kg/day, slowly decreasing to 200 kg/day over the next 300 years. The flushing for dissolved iron dominates the first 200 years. Later the solution of mineral phases becomes more important. The sulphate fluxes follow a similar temporal pattern. The sulphate flux until 2100 is about 3600 kg/day and decreases to about 2000 kg/day until 2400. The cause for the slower decreases of sulphate compared to iron concentrations can be attributed to gypsum solution from the subsurface matrix. The spatial variability causes variation in flux of up to 9% compared to the scenario without spatial variability.

CONCLUSIONS

The new tool for reactive transport modelling presented here provides a useful instrument for investigations of the impact of dumps on river water quality accounting for spatial variability in the subsurface. Primary and secondary iron oxidation, as well as several other chemical processes can be modelled, yielding a good representation of the system. The model results help to quantify the probable long-term behaviour of the system, providing the basis for decision. The coupled tool is general enough to be applicable for other hydrogeochemical problems because new PHREEQC keywords can be easily added into the coupling without programming.

REFERENCES

Charlton, S. R. & Parkhurst, D. L. (2011) Modules based on the geochemical model PHREEQC for use in scripting and programming languages. *Computers and Geosciences*, doi:10.1016/j.cageo.2011.02.005.

IBGW GmbH (2009–2010) Auswirkungen des Grundwasserwiederanstiegs und der daraus folgenden Exfiltration eisenbelasteter Grundwässer aus den Kippen des ehemaligen Tagebaus Witznitz in die Fließgewässer Plei-ße und Wyhra (Teile 1–4). *Unveröffentlichter Bericht, Leipzig.*

Lenk, S. & Wisotzky, F. (2007) Chemische Beschaffenheit und modellierte Genese von Grundwässern in Braunkohlenabraumkippe des Tagebaus Inden. *Grundwasser* 12, 301–313.

Müller, M. (2011) PhreeqPy - Python Tools for Working with PHREEQC. http://www.phreeqpy.com.

Müller, M., Parkhurst, D. L. & Charlton, S. R. (2011) Programming PHREEQC Calculations with C++ and Python – a comparative study. In: *MODFLOW and More 2011: Integrated Hydrologic Modeling – Conference Proceedings.* (ed. by R. Maxwell, E. Poeter, M. Hill & C. Zheng), S.632–636.

Müller, M., Sames, D. & Mansel, H. (2003) PCGEOFIM – A finite volume model for more? In: *MODFLOW and More 2003: Understanding through Modeling. Proceedings of the Conference* (ed. by E. Poeter, C. Zheng, M. Hill & J. Doherty), 16–19 September, Golden, Colorado, USA.

Parkhurst, D. L. & Appelo, C. A. J. (1999) User's Guide to PHREEQC - a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. *Water Resources Investigations Report 99-4259, Denver, Colorado.*

Sames, D., Blankenburg, R., Brückner, F. & Müller, M. (2010) PCGEOFIM®-Anwenderdokumentation. Leipzig.