Coupled Modeling of Iron Loads from Lignite Mining Dump Groundwater to the Pleiße River

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ABSTRACT

The lignite mining dump of Witznitz in Central Germany is characterized by iron concentrations in groundwater up to 4 g/L. Rising groundwater levels after the mine was closed in 1993 have resulted in the discharge of consistently high iron loads to the adjacent Pleiße river.

The quantity of groundwater discharge to the stream is described by a 3D groundwater flow model using the program PcGeofim. In order to predict the groundwater hydrogeochemistry, a batch model using the PHREEQC geochemical modeling package was firstly set up to reproduce the genesis of dump groundwater by considering the processes of iron disulfide weathering, solution of calcite and silicates as well as the formation of new minerals such as gypsum and siderite. The model was calibrated using a set of 350 groundwater analyses from 50 wells in the dump and investigations on the solid phase of the dump material. As a result, the mean iron disulfide degree of weathering was determined to be 18% of the total dump iron disulfide.

Based on this, both models were coupled using a Python script by implementing the hydrogeochemical batch model including mineral phases into each cell of the groundwater flow model. Thereby, the spatial variability of the degree of iron disulfide weathering was taken into account by Monte Carlo simulations. As a result, groundwater solute concentrations were predicted to decline in conjunction with the groundwater recharge and solution of the secondary mineral pool takes place, whereas the velocity of the process is determined by the rate of groundwater recharge as well as groundwater flow. Implementing the Pleiße river as a boundary condition in the model makes it possible to predict the quality and quantity of groundwater discharge into the river.

Keywords: reactive solute transport modeling; iron loads; dump aquifer; PcGeofim

INTRODUCTION

The surface water quality of the Pleiße river in the lignite mining area south of Leipzig, Germany, shows total iron concentrations of up to 6 mg/L during periods of low water. Besides the visual impact, the high iron concentration results in iron clogging of the river bottom as well as negative effects on the aquatic ecosystem. By this, the achievement of a good ecological potential in accordance to the European Water Framework Directive is hindered.

Iron originates from the lignite mining dumps alongside the river, whose groundwater exfiltrates into the river. Due to iron disulfide oxidation of tertiary sediments, the dumps are often rich in bivalent dissolved iron. During the transition from the anoxic groundwater to the aerated environment of the river, oxidation to trivalent iron takes place as well as further formation of iron(3)-hydroxides or -hydroxysulfates, respectively. The process is accompanied by the formation of acidity.

One major source of iron in the Pleiße river is the dump of the former surface mine Witznitz, which was operated between 1946 and 1993. Dump material mainly consists of quaternary flood sediments and tills as well as tertiary marine overburden and the adjacent sediments of the removed coal seams. After the devastation of the original river bed, the Pleiße river was relocated directly across the dump during the 1960s. Following the termination of operations, uplift of the groundwater table, which was formerly lowered by mining activities, began. This is connected with a direct discharge of dump groundwater into the river.

Recent mean total iron concentrations measured in dump groundwater are 1050 mg/L, whereas the mean pH is slightly acidic at 5.3. The ionic balance is decisively influenced by the concentrations of both calcium (480 mg/L) and sulfate (3700 mg/L). The spatial variability of iron concentrations is great, ranging from 26 to 4510 mg/L. This is due to a varying geochemical composition of the source material of the dump as well as a differing intensity of oxygen contact and iron disulfide weathering taking place during fore field drainage and dump formation as well as on active mining slopes and exposed dump surfaces.

In order to predict future dump-originated solute inputs to the Pleiße river, a reactive solute transport model was developed for the Witznitz dump, which allows a spatially differentiated calculation of groundwater discharge to the river both in quantity and quality.

METHODOLOGY

Reactive solute transport modeling was realized by coupling the groundwater flow and solute transport model PcGeofim (Blankenburg et al., 2013) with the hydrogeochemical simulator model PHREEQC (Parkhurst & Appelo, 1999). By coupling the two models, it is possible to take into account reactions within the liquid phase, interactions between liquid and solid phase, such as iron disulfide weathering, as well as gas exchange processes in combination with transport modeling.

Model coupling was taken out by a programming script using the language Python. For each time step in the model, groundwater flow and solute transport was calculated, taking into account 11 different migrating solutes. Using the solute concentrations resulting from this calculation, hydrogeochemical batch calculations were carried out between liquid, solid and gas phases for each cell. Thereby, the pH, which is a non-conservative parameter, is recalculated in every batch calculation based on the charge balance. The resulting solute concentrations are then used for the groundwater flow and solute transport calculation of the next time step. Solid phase contents and cation exchange allocation are saved using internal storage.

Groundwater flow model

The 3D groundwater flow model of the Witznitz dump is part of a large-scale model which comprises the whole lignite mining area south of Leipzig. The surrounding consists of mining dumps as well as active mining areas with a still massive lowering of the groundwater table. PcGeofim calculations are based on the method of finite volumes.

The model grid of the Witznitz dump is 62.5 x 62.5 m. In vertical direction the dump is divided into six aquifer layers and coupled onto the adjacent natural aquifers. The hydraulic conductivity of the dump aquifer was calculated from the silt and clay content using an empirical relationship according to Kaubisch (1986). Kf-values of the upper dump are in the order of 10^{-6} m/s, whereas the lower dump is characterized by values in the order of 10^{-8} m/s. Groundwater flow therefore takes place primarily in the upper part of the dump aquifer. Surface waters such as the Pleiße river as well as mining lakes are implemented as boundary conditions. Groundwater recharge is derived from the catchment model ArcEGMO (Becker et al., 2002) and amounts to an average of 80 mm/yr considering the whole dump body.

The groundwater flow model was calibrated using measured hydraulic heads from 65 piezometers within the dump body. The standard deviation between measured and calculated hydraulic heads was 1.3 m.

Hydrogeochemical batch model of dump genesis

The batch model represents the genesis path of dump hydrogeochemistry originating from the initial unweathered substrates during dump formation to the recent monitored conditions. Similar modeling approaches were used *e.g.* by Wisotzky & Obermann (2001) for the Rhineland lignite mining area.

The primary minerals of the model are iron disulfide FeS_2, calcite $CaCO_3$, clay minerals (for the sake of simplicity represented by kaolinite $Al_2Si_2O_5(OH)_4$) as well as primary silicates such as feldspars or micas (fig. 1). The mineral contents were derived from the measured contents in the original geological layers that now form the dump body, taking into account the portions of the single layers in the dump structure.

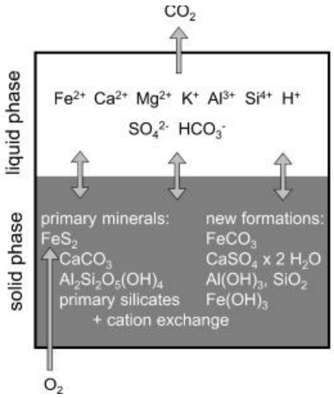

Figure 1 Hydrogeochemical process model

This results in an overall initial iron disulfide content of 2.1 mass-% and calcite content of 0.5 mass-% for the purpose of the model. Kaolinite is simplistically assumed to be abundant, whereas the weathering of primary silicates is coupled to the turnover of iron disulfide and fitted during calibration.

A stepwise addition of oxygen leads to an oxidation of iron disulfide and a release of iron, sulfate und acidity. Buffering is primarily provided by calcite and after depletion at lower pH values by clay mineral solution. Dissolution of primary silicates is a kinetically slow process which takes place in parallel with the processes mentioned before. As a result, the ionic strength of the liquid phase increases. On one hand, CO_2 originating from calcite weathering degasses in part; on the other hand, new mineral phases start to form. Siderite ($FeCO_3$) is a transient mineral formation of the released iron, which, however, gets resolved at lower pH values. A further new mineral formation is represented by gypsum ($CaSO_4x2H_2O$). Solution of silicates and clay minerals leads to the formation of aluminum hydroxide as well as silicon dioxide. Beyond that, precipitation of a mineral phase of trivalent iron is implemented in the model, as weathering of iron disulfides takes place mainly during unsaturated oxic conditions. At pH values > 3, iron hydroxides, oxyhydrates, or hydroxisulfates are formed. Exhibiting higher degrees of crystallization, part of these are irreversibly fixed within the dump substrate and are therefore stable against reductive dissolution during the uplift of the groundwater table. In the model this irreversible reaction was considered by an additional iron sink, which is coupled to the degree of iron disulfide weathering. Finally, the model takes into account the cation exchange of calcium, manganese, potassium, iron, and aluminum with an overall exchange capacity of 2.1 $cmol_c$/kg, which reflects the measured mean conditions in soil samples obtained from the dump body.

The model was calibrated using 350 chemical analyses from 50 monitoring wells and piezometers within the dump body as well as 87 soil samples, which were mainly analyzed for sulfur and carbon species as well as main cations and the cation exchange capacity. Based on the measurements, the process model was adjusted by varying solubility products of mineral phases, the portion of irreversibly bound trivalent iron minerals as well as the maximum partial pressure of CO_2. The computational realization was done by means of the simulator PHREEQC using the database wateq4f.dat.

Solute transport model of dump discharge

Model coupling of the groundwater flow and solute transport model with the hydrogeochemical batch model was realized alongside nine representative 2D vertical-plane cuts crossing the dump in groundwater flow direction to the Pleiße river. In principal, 3D modeling would also be possible. The advantage of the 2D cuts, however, is a clarity, which facilitates an understanding of the ongoing processes.

Discretization of the cuts was 50 m in the horizontal and 5 m in the vertical direction. Parameterization of hydraulic conductivity as well as hydraulic boundary conditions and groundwater recharge was taken from the 3D groundwater flow model of the Witznitz dump.

The hydrogeochemical batch model was implemented into every model cell using a Python script for model coupling. It considers primary iron disulfide oxidation taking place by fore field drainage and trapped oxygen during dump construction as well as on active mining slopes previous to the fill-up of the dump with groundwater. Spatial variability of the degree of iron disulfide oxidation as a percentage of the initial iron disulfide content was taken into consideration by Monte Carlo simulations using a random generator based on a normal statistical distribution to calculate the turnover for every model cell.

Secondary iron disulfide oxidation takes place via the dump surface after the termination of the dump formation. It is accounted for by an additional oxygen input and corresponding iron disulfide turnover, which decreases successively with the age of the dump as growing vegetation reduces the oxygen input by soil respiration and iron disulfide minerals get less accessible to weathering due to passivation. In cases of oxic conditions close to the dump surface as a result of iron disulfide depletion, the formation of schwertmannite is allowed to take place according to the formula $Fe_{16}O_{16}(OH)_{9.2}(SO_4)_{3.4}x36H_2O$ (Bigham et al., 1996) in addition to the processes defined in the hydrogeochemical batch model.

The model was calibrated by using the same analytical data as for the calibration of the hydrogeochemical batch model, but also considering spatial patterns in total iron concentrations, particularly, variation with depth. Fitting parameters were given by the degree of primary iron disulfide oxidation including its standard deviation for Monte Carlo simulations to reproduce the measured variation of iron concentrations as well as by the quantity of secondary iron disulfide oxidation via the dump surface. The calculation was carried out beginning from the termination of dump formation, which is between 1951 and 1970 for the single cuts, for a time interval of 450 years.

RESULTS AND DISCUSSION

Grundwater flow regime

Groundwater dynamics within the Witznitz dump are essentially determined by surrounding surface waters (fig. 2). Due to comparably low hydraulic conductivities a groundwater cap is formed within the northern part of the dump at a level of +140 m above sea level (a.s.l.).

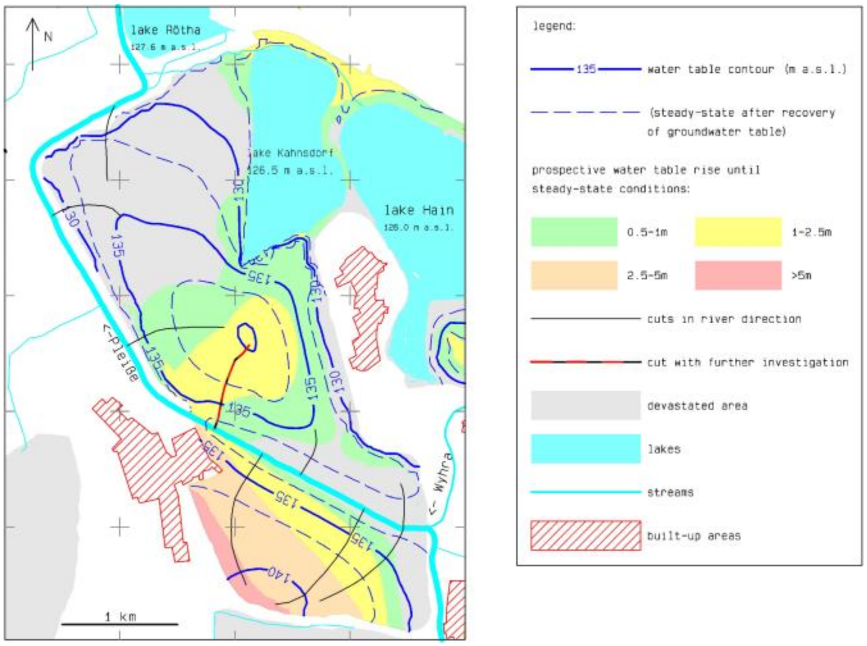

Figure 2 Steady-state water table contours, prospective rise and cuts in river direction for the transport model

Groundwater flow from the dump takes place to the Pleiße river, as well as to the mining lakes Kahnsdorf and Hain. The dump body south of the river is characterized by a groundwater flow to the river from southeastern direction at steady-state conditions after the completion of the groundwater table uplift.

In the northern part of the dump the groundwater table uplift is nearly complete. Future rises are below 2.5 m (fig. 2). By contrast, in the southern part of the dump there is a future rise of up to 6 m expected, which is caused by a further groundwater uplift in the dump surroundings. By means of the large-scale model, this could be considered in the groundwater flow calculation of the Witznitz dump.

The modeled groundwater inflow from the Witznitz dump to the Pleiße river amounts to 0.78 m^3/min for steady-state conditions.

Hydrogeochemistry of dump genesis

The model of dump genesis was realized by a stepwise increase of the degree of iron disulfide weathering releasing iron, sulfate, and acidity to the groundwater. Subsequently, several accompanying reactions take place, which are shown in the upper left plot of fig. 3 in relation to the sulfate concentration, which serves as an indicator of the degree of iron disulfide weathering.

The first buffering process is given by the solution of calcite and lasts up to sulfate concentrations of approximately 1800 mg/L.

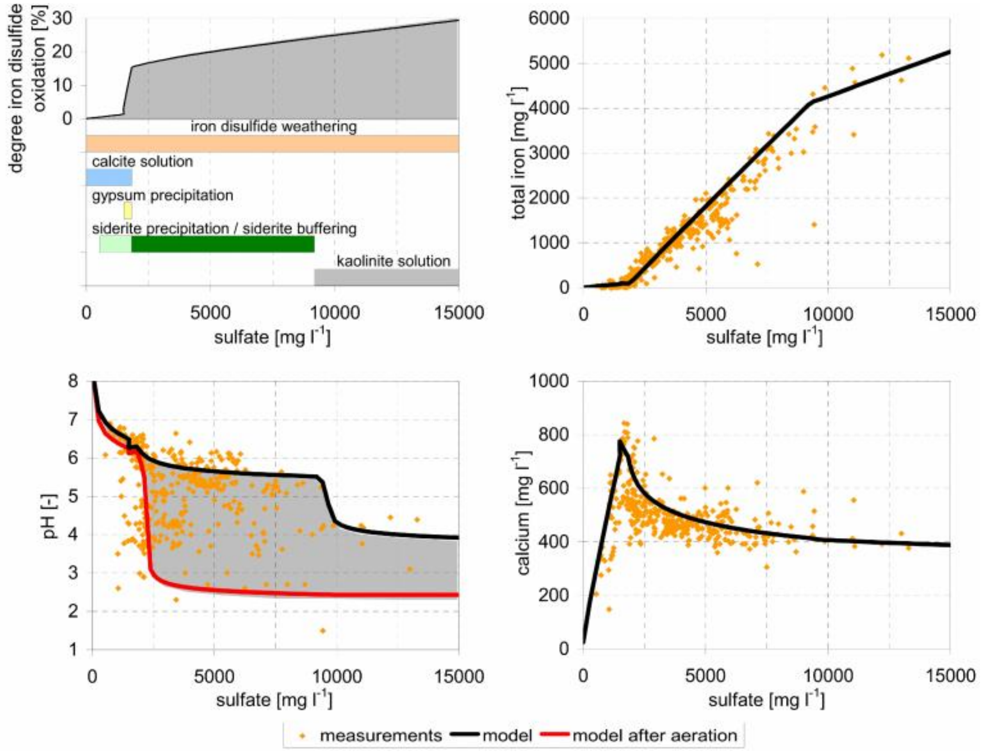

Figure 3 Mineral transformations during iron disulfide weathering and development of iron and calcium concentrations as well as pH as a function of the master variable sulfate; measurements and batch model

As a result of the rising calcium and sulfate concentrations in the solution, precipitation of gypsum starts at sulfate concentrations of about 1500 mg/L. It stops in parallel with the calcite solution as calcium is needed for the formation of gypsum. Siderite precipitation starts at sulfate concentrations of approximately 500 mg/L and similarly terminates with the end of calcite solution as carbonate for siderite formation is no longer available. At sulfate concentrations higher than 1800 mg/L resolution of siderite takes place connected with the release of hydrogen carbonate, which serves as a buffering mechanism up to sulfate concentrations of about 9200 mg/L. Afterwards solution of clay minerals represented by kaolinite begins.

Concentrations of total iron increase with rising sulfate concentrations (fig. 3, upper right plot). At sulfate concentrations of up to 1800 mg/L iron concentrations are low, which is due to siderite fixing. At higher sulfate concentrations, there is a clear rise in iron concentrations, as iron is firstly released by iron disulfide weathering and secondly by the resolution of siderite minerals. The slope of the curve decreases at sulfate concentrations above 9500 mg/L because of a depletion of siderite. The model results fit well with the measured data.

The pH decreases with an increasing degree of iron disulfide weathering (fig. 3, lower left plot, black line). During calcite buffering, the pH is above 6.3, within the siderite buffering interval it amounts to 5-6, whereas buffering by clay minerals (represented by kaolinite) results in a pH of about 4. Principally, iron appears in bivalent form in the dump groundwater. Trivalent iron occurs in traces only, as firstly the groundwater is anoxic due to prevalent iron disulfides and secondly trivalent iron is precipitated at pH values greater than 3. Nonetheless, partial aeration took place during groundwater sampling. Because of the low hydraulic conductivity of the dump material, part of the samples had to be taken from the standing water in the pipe after dry pumping on three consecutive days. This led to an iron oxidation and precipitation of hydroxides or hydroxysulfates respectively, which is connected with a release of acidity and a decrease of the pH. Measurements are mostly in between the black (no aeration) and the red line (full aeration) in the plot, indicating a partial aeration during the sample procedure.

Calcium firstly shows an increase (fig. 3, lower right plot), which is due to calcite dissolution. Concentrations decrease again with the beginning of gypsum precipitation to a level of 400 to 600 mg/L. Measurements fit well with the model.

The considered solubility product pK_{sp} of the mineral phase calcite is -8.48, which is in line with the value of the wateq4f.dat database. With respect to gypsum, pK_{sp} was selected as -4.53, which represents a very slight supersaturation of +0.05 for precipitation to occur compared to the considered database. Based on the measurements, pK_{sp} of siderite was determined to be -9.25, which implies a supersaturation of +1.2. This is in line with the findings of Lenk & Wisotzky (2007). This is possibly due to surface effects during the process of precipitation or the formation of mixed iron(2)-calcium-carbonates. Matching measured liquid and solid contents resulted in the assumption that one third of the iron released during iron disulfide weathering gets irreversibly bound by the formation of trivalent iron oxyhydrates. The maximum allowed partial pressure of CO_2 is 30%.

Resulting from the batch model, the great variability of measured groundwater quality data can be described by the variation of the degree of iron disulfide oxidation, which is a consequence of the varying exposure of the dump material connected with a differing contact to oxygen. The overall mean degree of iron disulfide weathering determined from the mean sulfate concentration of the dump groundwater, which is 3660 mg/L, amounts to 18%.

Future development of dump groundwater quality and solute discharge

The coupled groundwater flow and reactive solute transport model was realized for nine vertical-plane cuts in groundwater flow direction to the Pleiße river (fig. 2). In the following, one cut representing the groundwater flow from northern direction to the Pleiße river in the region of the river crossing the dump is investigated in detail (red-black dashed cut in fig. 2).

By implementing the hydrogeochemical batch model into every model cell, the model simulates the discharge of the solutes originating from iron disulfide oxidation with the groundwater flow. Considering a homogenous distribution of the iron disulfide oxidation rate, iron concentrations in the cut for the year 2010 are between 2000 and 4000 mg/L in the upper part and between 1000 and 2000 mg/L in the lower part of the dump (fig. 5). Concentrations are reproduced in the model by considering the iron disulfide turnover during the dump formation and shortly thereafter. Low hydraulic conductivities and slow groundwater flow lead to the preservation of high iron concentrations in the dump body for long time intervals. The vertical concentration gradient is due to the oxygen input via the dump surface leading to a secondary iron disulfide oxidation next to the primary one within the whole dump body. For the year 2100, the model predicts a clear reduction of iron concentrations in the upper aquifer because of diluting effects by groundwater recharge and the solute discharge to the river. This effect continues into the future. Correspondingly, modeled concentrations for the year 2300 are below 250 mg/L in the upper aquifer. In contrast, solute discharge from the lower aquifer is small, as the hydraulic conductivity is comparably low in this part of the dump.

Results considering a random distribution of the iron disulfide oxidation rate using Monte Carlo simulations show the same trend, though iron concentrations in the cut are additionally influenced by scattering.

Solute fluxes from the dump into the direction of the Pleiße river were calculated as weighted means per length of the respective river section combining the results of all nine cuts. From this, iron loads of approximately 1000 kg/d are calculated for a time interval of the next 100 years (fig. 4). Afterwards fluxes decline to 190 kg/d in 2400. Derived sulfate loads are in the order of 3500 kg/d during the next 100 years and decline to 2000 kg/d until 2400. Compared to iron the decrease of fluxes with time is less significant, as there is a great pool of gypsum bound in the dump, whose resolution takes place during a very long time interval. Monte Carlo simulations show similar solute fluxes compared to the homogenous distribution of iron disulfide oxidation, which indicates that spatial variability is averaged in the dump discharge.

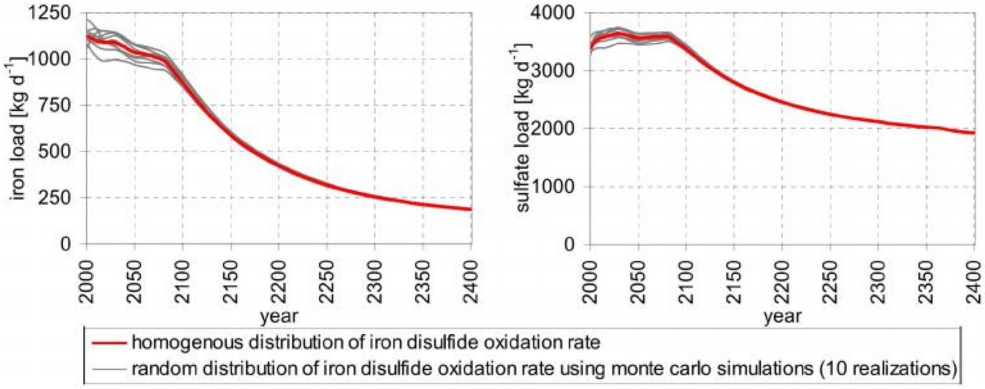

Figure 4 Modeled fluxes of iron and sulfate from the dump in direction of the Pleiße river

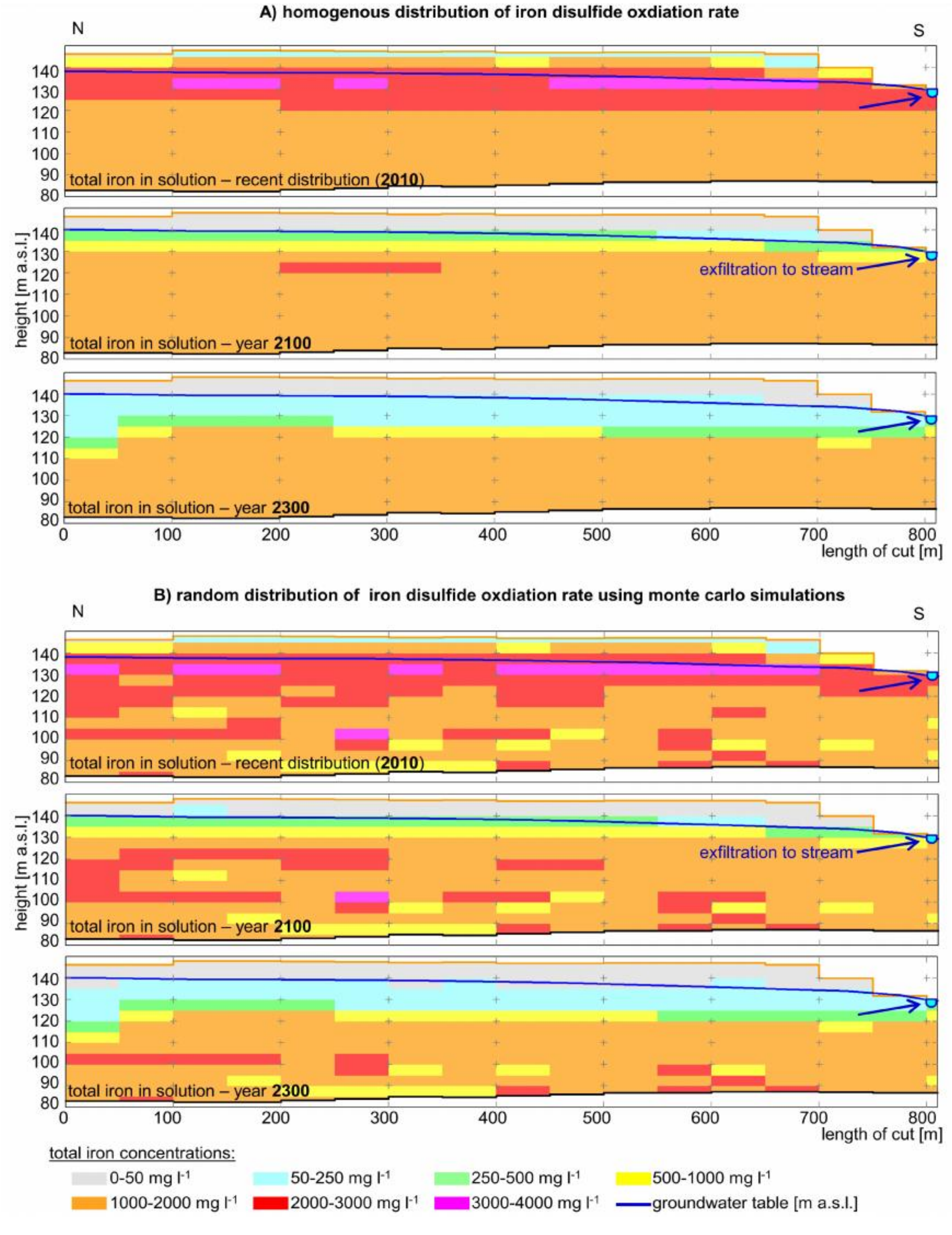

Figure 5 Modeled concentrations of total iron in den liquid phase along the red-black dashed cut (cf. Fig 2), time slices 2010, 2100 and 2300

CONCLUSION

The presented study is based on a large data pool of groundwater analyses and investigations on the solid phase of the dump material. This allows a detailed examination of the ongoing processes and the derivation of a process-oriented model. It was therefore possible to determine the relevance of single mineral phases during the genesis of the dump groundwater and to derive the solubility products of the participating mineral phases. This enables extrapolation to other areas with a less comprehensive pool of data.

The wide scattering of measured iron and sulfate concentrations is most likely due to the varying degree of iron disulfide oxidation. During solute transport modeling this was taken into consideration by a Monte Carlo simulation.

The newly developed model coupling allows a precise prediction of the future development of dump hydrogeochemistry and the expected solute fluxes into the Pleiße river, indicating that the process of solute discharge from lignite mining dumps exhibiting low hydraulic conductivities takes place on very long time intervals.

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REFERENCES

Becker, A., Klöcking, B., Lahmer, W. & Pfützner, B. (2002) *The Hydrological Modeling System ArcEGMO*, in: Singh, V.P. & Frevert, D.K. (eds.), Mathematical Models of Large Watershed Hydrology, Water Resources Publications, Littleton / Colorado, pp 321–384.

Bigham, J.M., Schwertmann, U., Traina, S.J., Winland, R.L. & Wolf, M. (1996) *Schwertmannite and the chemical modeling of iron in acid sulfate waters*, Geochimica et Cosmochimica Acta, vol. 60, no. 12, pp. 2111–2121.

Blankenburg, R., Mansel, H., Sames, D. & Brückner, F. (2013) *Consideration of Open Cast Mining Progress and more using the Finite Volume Model PCGEOFIM*, in: Maxwell, R., Hill, M., Zheng, C. & Tonkin, M. (eds.), MODFLOW and More 2013 – Conference Proceedings, pp. 283–286.

Kaubisch, M. (1986) *Zur indirekten Ermittlung hydrogeologischer Kennwerte von Kippenkomplexen, dargestellt am Beispiel des Braunkohlenbergbaus*, doctoral thesis, Technical University of Freiberg, 129 pp.

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

Parkhurst, D.L. & Appelo, C.A.J. (1999) *User's guide to PHREEQC (Version 2) – a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations*, Water Resources Investigations Report 99-4259, Denver, Colorado, 312 pp.

Wisotzky, F. & Obermann, P. (2001) *Acid mine groundwater in lignite oberburden dumps and its prevention – the Rhineland lignite mining area (Germany)*, Ecological Engineering, vol. 17, pp. 115–123