Reactive transport modelling of iron-II and sulphate in the former Lusatian lignite mining areas

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Abstract

Decades of dewatering during open pit lignite mining in Lusatia affected geochemistry in the overburden dumps and surrounding aquifers. Due to the groundwater drawdown they became oxidised and act as sulphate- and iron-source. In order to understand the progression and duration of the sulphate- and iron release into the groundwater and the transport into rivers and lakes, reactive transport modelling was applied. Based on preceding projects, the present work utilized reactive transport simulations with an enhanced geochemical concept, that was applied to the latest results of groundwater flow modelling and an improved description of geochemical inventory. First modelling results from the 'Nordraum' site of the current study are shown for the simulated period of 2000 – 2100. They underline the longevity of sulphate storage in the former overburden dumps and also point out the influence of the unworked aquifer parts. Dissolved sulphate and iron-II will have elevated groundwater concentrations over more than one hundred years after the expiration of lignite mining and thus at least until 2100. The mass fluxes of sulphate and iron-II into lakes, rivers and streams in the 'Nordraum' model site decline slowly only towards the end of the simulated period.

Key words: Mine water, Reactive transport modelling, Iron, Sulphate

Introduction

Decades of dewatering during open pit lignite mining in Lusatia affected geochemistry in a large region. Due to the groundwater drawdown not only the sediments in the resulting overburden dumps became oxidized, but also vast parts of surrounding unworked aquifers. Since this massive oxidation cannot not be reversed within a couple of years both of them still act as a source of acidity, iron and sulphur. Aquifers in the Lusatian area are to date typically characterized by concentrations of sulphate from 1300 mg/L to 3800 mg/L, iron from 120 mg/L to 1000 mg/L and moderate pH values from 4.9 to 6.4 (30% and 90% percentile concentration from Bilek 2012). This contamination becomes finally apparent in the downstream rivers and lakes.

In order to describe the (bio-)geochemical processes within these former mining sites, reactive transport modelling is applied within an ongoing series of projects since 2003. Main focus is laid to the progression and duration of the sulphate- and iron release from the geological units into the groundwater and the flux into rivers and lakes. The target is to prove whether the environmental objectives of the European Union's Water Framework Directive can be achieved. The recent project builds on results of the preceding ones and precisifies them. They roughly comprise:

- a methodology to convert results of the complex, PCGEOFIM based hydraulic model into input for the reactive transport simulation code PHT3D (Graupner et al. 2014),

- extensive chemical analysis of groundwater and soil materials,

- the calculation of spatially distributed pyrite oxidation in the modelling area,

- a thereupon based geochemical conception for processes describing the fate of iron and sulphate in dumps and aquifers after pyrite oxidation.

This paper presents the revised modelling methodology and first results from reactive transport calculations based on an enhanced geochemical concept and an improved description of geochemical inventory, that were applied to the latest groundwater flow results.

Methods

Modelling sites

Fig. 1 shows the five considered modelling areas situated in the former Lusatian open pit lignite mining district, each of them comprising multiple dumps and pit lakes. The area encompassed by each model reaches from 540 km² (model area 'Greifenhain/Gräbendorf') to 1214 km² (model area 'Nordraum') . The mining history and a more detailed site description are given in Krümmelbein et al. (2012) and Graupner et al. (2012) respectively.
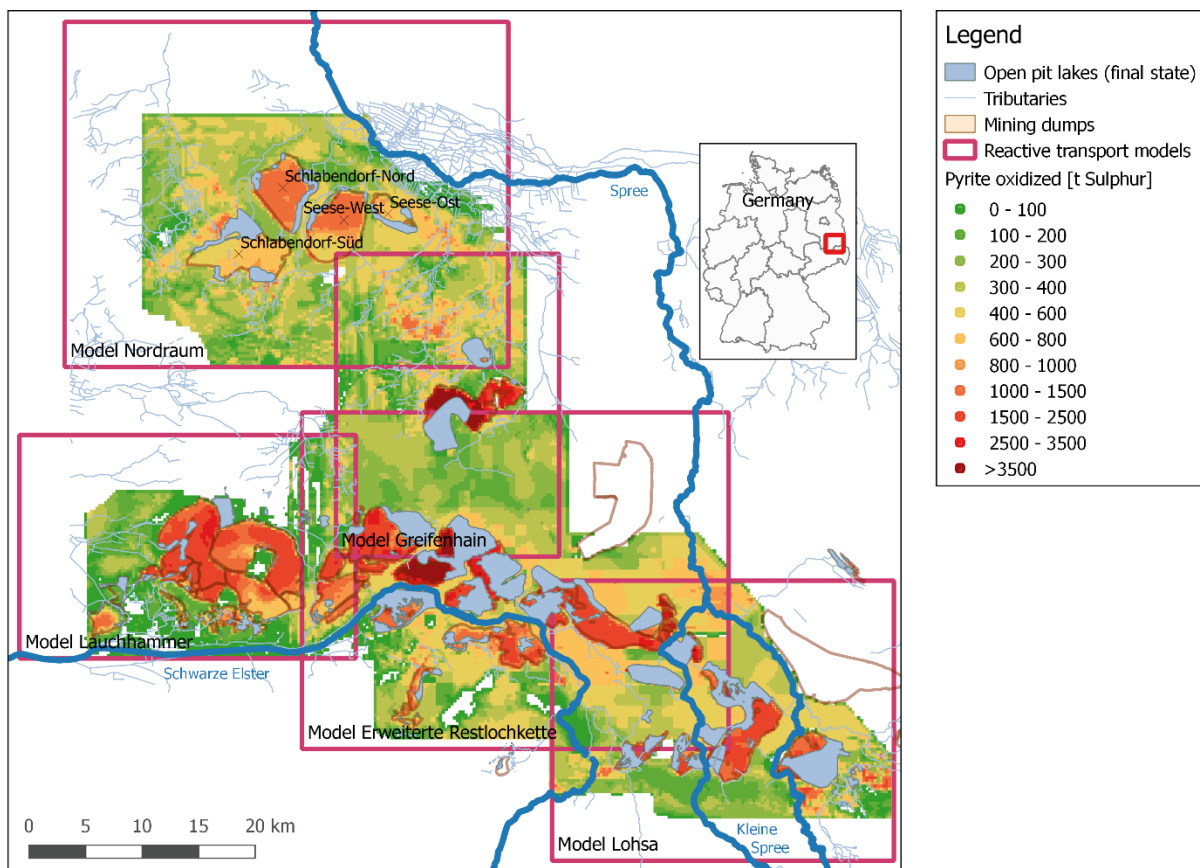

Figure 1 *Overview of study sites location and spatial distribution of sulphur masses from pyrite oxidation in a 200 m x 200 m grid within the scope of evaluation at the year 2000. Former mining sites in the 'Nordraum' model area are labelled.*

Input data and simulation software

Reactive transport modelling was performed using the reactive transport code PHT3D V2.10 (Prommer et al. 2003), which allows the simulation of complex hydrogeochemical processes and refers to the chemical reaction code PHREEQC (Parkhurst & Appelo 1995) and the transport code MT3DMS (Zheng 2005). PHT3D is designed to use flow results from MODFLOW (Harbaugh 2005) simulations. Groundwater flow in the present study sites, however, is described by sophisticated PCGEOFIM flow models already which are continuously maintained since years. In order to use their results they need to be transformed from PCGEOFIMs finite elements approach to PHT3Ds finite

differences which was done by the HistoGIS code (Graupner et al. 2014). PHT3D uses the resulting cell based flow rates as **hydraulic input** and calculates reactive transport on them. Applying this procedure avoids the setup of another complex hydraulic model.

As can be seen from fig. 2, particular attention was laid to the determination of **initial geochemical conditions** since they determine the sensitive source term in the predictive modelling. The procedure starts with a historical exploration to gain pre-mining pyrite concentrations assigned to geological layers. Following, PYROX (Wunderly 1994, Wunderly et al. 1996) is applied to calculate the spatially distributed turnover of pyrite by historical groundwater drawdown progression and therewith varying oxygen feeds. The resulting easily mobilised amount of sulphate for the year 2000 is used together with a spatially distributed buffering potential to calculate the hydrochemical starting concentrations (distribution of dissolved species and phases) for the final reactive transport simulation with PHT3D.
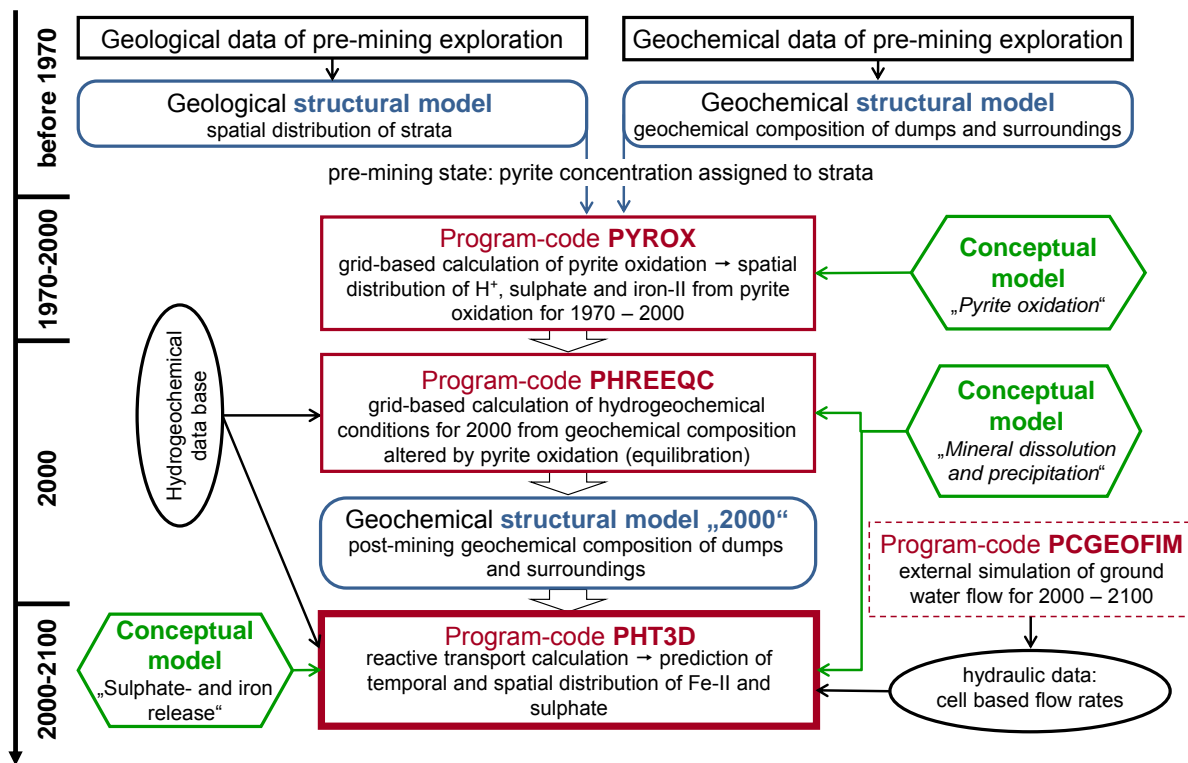

Figure 2 *General work flow for the delineation of geochemical initial conditions in the reactive transport modelling to predict the fate of iron-II and sulphate.*

Geochemical boundary conditions describing the chemical composition of lakes, rivers and streams complete the set of input data for the reactive transport modelling. They were delineated from up to date, long term monitoring data in the area. Future trends were assumed basing on remediation objectives and present trends, but they are less sensitive towards the reactive transport model as most of the surface waters are characterized by effluent flow. Concentration of iron-II and sulphate in groundwater recharge was set to 11 mg/L and 200 mg/ respectively.

Discretization and transport parameter

Each of the five reactive transport models was implemented with a horizontal discretization of 250 m x 250 m, a vertical discretization according to the flow model, excluding vertical refinements. The temporal discretization corresponded that of the flow simulation, with a minimum stress period duration of one year. Porosity was transferred from the flow model, whereas other hydrogeological parameters were assumed to be constant: longitudinal dispersivity (50 m), horizontal transversal

dispersivity (5 m), vertical dispersivity (0.5 m), effective molecular diffusion coefficient ($1 \cdot 10^{-9}$ $m^2 \cdot s^{-1}$). Temperature was set to 10 °C.

Geochemical concept

Implemented chemical entities from the standard PHREEQC thermodynamic data base are summarized in tab. 1. Partial chemical equilibrium was assumed with microbial sulphate reduction and feldspar-weathering being kinetically determined. Sulphate reduction rate was described by a Michelis-Menten-kinetic with regard to sulphate, a half saturation constant of $2 \cdot 10^{-4}$ mol/L and a site characteristic reaction rate constant of $6.34 \cdot 10^{-13}$ $mol \cdot L^{-1} \cdot s^{-1}$. Feldspar weathering rate based on results of Bilek (2004) with $1.4 \cdot 10^{-11}$ mol $L^{-1} \cdot s^{-1}$ for pH < 3 with $5.4 \cdot 10^{-12}$ mol $L^{-1} \cdot s^{-1}$ for pH > 4.5 and a linear progression between these values.

Table 1 *Chemical components, minerals and cation exchange species implemented in the reactive transport models.*

Chemical entity	Immobile	Kinetic
Al, C-IV, Ca, Fe-II, Mg, SO_4^{2-}, Si, K	-	-
pH, pe	-	-
$S_{reduced} = Fe^{2+} + SO_4^{2-}$	-	x
Gypsum: $CaSO_4{:}2H_2O_s = Ca^{2+} + SO_4^{2-} + 2H_2O$; k= $10^{-4,58}$	x	-
Calcite: $CaCO_{3,s} = CO_3^{2-} + Ca^{2+}$; k=$10^{-8,48}$	x	-
Kaolinite: $Al_2Si_2O_5(OH)_{4,s} + 6H^+ = H_2O + 2H_4SiO_4 + 2Al^{+3}$; k=$10^{7,435}$	x	-
$SiO_{2(a)}$: $SiO_{2,s} + 2H_2O = H_4SiO_4$; k=$10^{-2,71}$	x	-
$CO_{2,g}$: $CO_{2,\,g} = CO_{2,aq}$; k = $10^{-1.468}$	x	-
Feldspar: $KAlSi_3O_{8,s} + 8H_2O = K^+ + Al(OH)_4^- + 3H_4SiO_4$; k=$10^{-20,573}$	x	x
Cation exchange species: Ca^{2+}, Mg^{2+}, Fe^{2+}	x	-

(Bio-)geochemical processes implemented in the reactive transport models were delineated by explaining present ground-water quality data with chemical equilibrium modelling (Bilek 2014). The major processes cover:

- subsequent delivery of Fe-II, sulphate and H^+ from the immobile storage (gypsum, secondary silicates, cation exchanger),

- dissolution/precipitation of calcite and gypsum according to their solubility product,

- kinetic weathering of K-feldspar as slow buffer reaction after calcite depletion,

- cation exchange of Fe^{2+}, Ca^{2+}, Mg^{2+},

- microbial sulphate reduction with a simplified formulation as a sink for Fe^{2+} and SO_4^{2-} = $FeSO_4$.

Fig. 3 illustrates the connection between the chemical entities by the whole of the implemented (bio-)geochemical processes. They reproduce the dominating processes for sulphate and iron storage, transformation and transport as proven by the reproduction of groundwater quality data. The authors are aware, that especially iron is affected by further complex mineral dissolution and precipitation reactions. But at the present state neither availability of field data nor a thereupon proven concept would allow a more complex implementation.
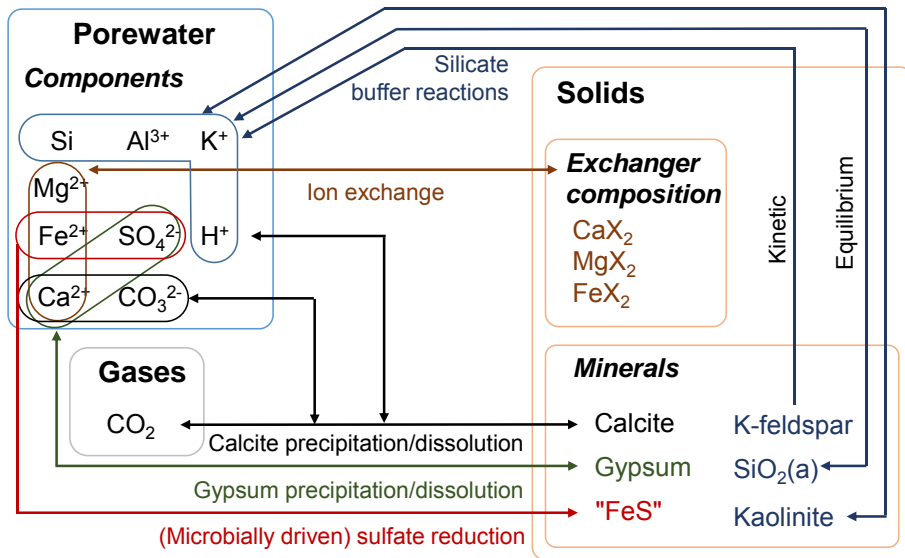
Figure 3 *Geochemical concept of the reactive transport models: reactions after buffering and storage from pyrite oxidation products.*

Results

As an example results from the model area 'Nordraum' are presented in this paper. Fig. 3 shows the spatial distribution of sulphate concentrations in the upper of two model layers at 2010 and 2100. It becomes evident, that not only mining dumps, but also some parts of surrounding unaffected aquifers will be contaminated with high sulphate concentrations at the end of the simulated period. The depletion of sulphate in the model is mainly driven by groundwater recharge (sulphate concentration 200 mg/L) and it's duration depends on the amount of gypsum representing the sulphate source term. Thus the mining dumps Schlabendorf-Nord and Seese-West but also the south-east region in the unworked aquifer with high pyrite oxidation (fig. 1) are subject to sulphate concentrations above 1.7 g/L beyond 2100.
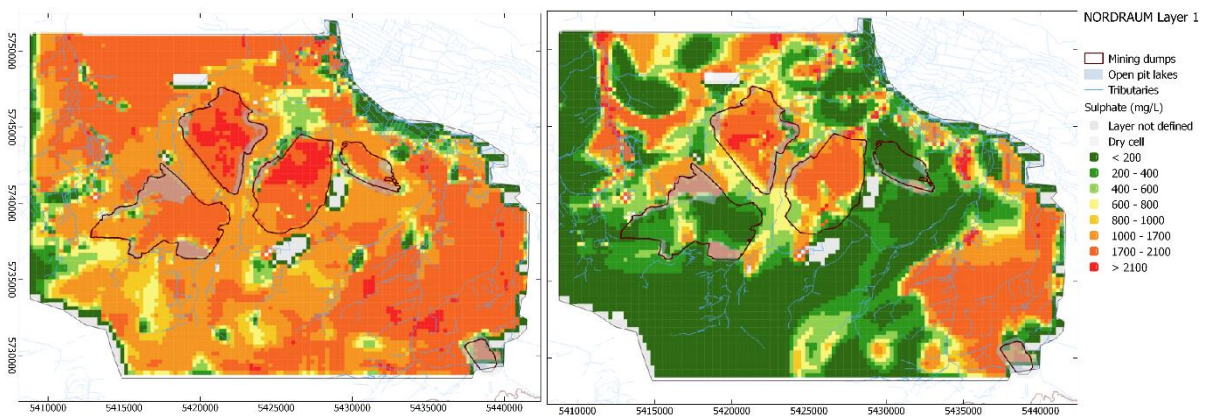

Figure 3 *Spatial distribution of sulphate in the 'Nordraum' area. Left: 2010, right: 2100.*

Fig. 4 illustrates a similar behaviour for the concentration development of dissolved iron-II in the 'Nordraum' area. Comparing sulphate with iron-II, no significant difference is visible for areas subject to elevated concentrations in 2100. For the mining dumps Seese-West and Schlabendorf-Nord and the unworked southeast aquifer region the simulation predicts concentrations above 100 mg/L iron in the groundwater.
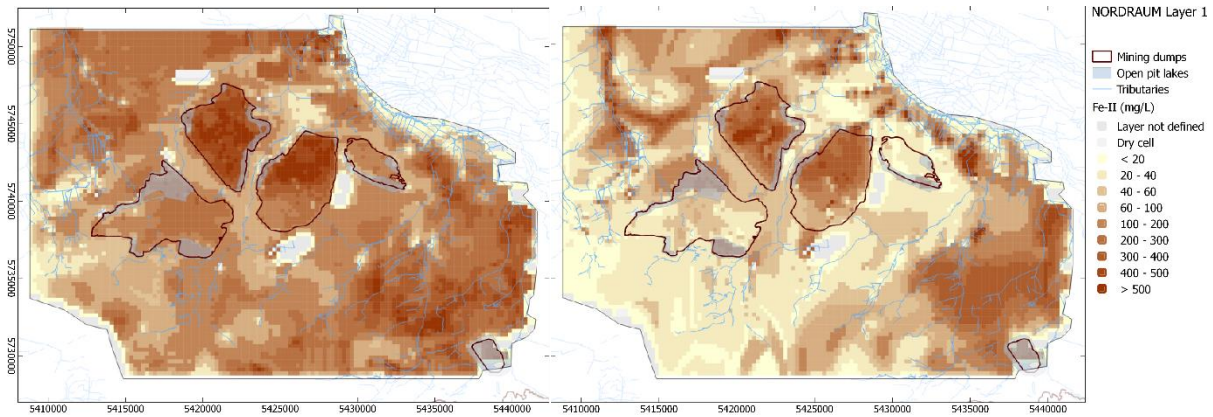
Figure 4 Modelled spatial distribution of Fe-II in the 'Nordraum' area. Left: 2010, right: 2100.

In order to illustrate the longevity of the attenuation processes, fig. 5 shows the development of total sulphate and iron-II masses in the 'Nordraum' model area. Gypsum and iron at the exchanger represent the immobile source terms and are slowly depleted only. The dissolved components sulphate and iron-II are – by definition – in equilibrium with these immobile sources and fall below specific equilibrium concentrations when the source term is depleted. Further, sulphate reduction with a typical maximum rate of $6.34 \cdot 10^{-13}$ mol·L^{-1}·s^{-1} influences the attenuation process marginally only.
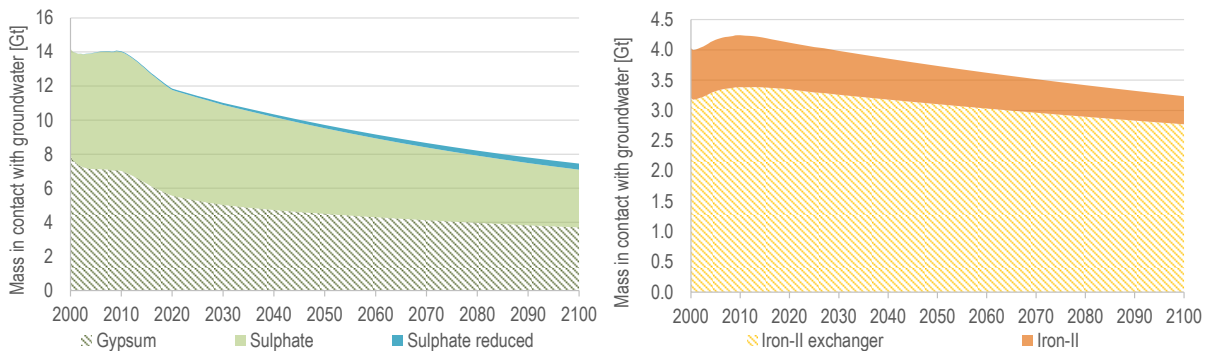

Figure 5 Modelled development of total masses in contact with groundwater in the 'Nordraum' model area. (The volume saturated with groundwater instead of total cell volumes were used for calculation of total mass, thus representing the mobilizable/mobile masses.)

Most of the tributaries and lakes are effluent in the 'Nordraum' model area. Following, their water quality is directly influenced by the conditions in the upstream aquifers. Fig. 6 summarizes annual mass fluxes from groundwater into surface water boundary conditions for selected years. The steep decline of fluxes to lakes is caused by the reduced water inflow as the lakes reach their final water table. Rivers and streams, however, get better connected with the groundwater by groundwater table recovery and thus show an increasing flux until to date. This tendency only slowly turns into a decline due to depletion of the sources. Care must be taken transferring these results to the effect on water quality in rivers and lakes. The model describes fluxes out of groundwater but not the processes within the adjacent boundary zone (interstitial) where further transformation reactions occur before the water enters a lake or stream.
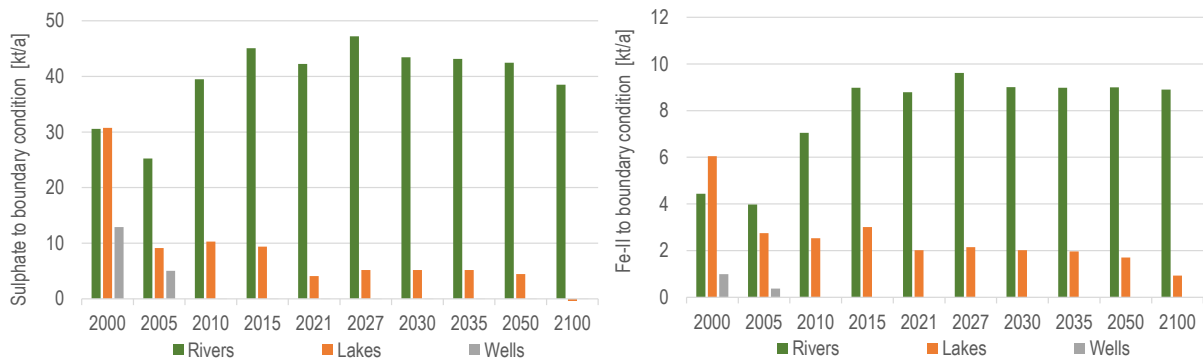
Figure 6 *Modelled total diffuse groundwater borne mass flux into surface water in the 'Nordraum' model area.*

Conclusions

Multi-mine reactive transport models were implemented to determine the effects on both groundwater composition and fluxes into surface waters in the former Lusatian open pit lignite mining district. Their geochemical concept was designed to reflect regional quality effects on a large scale, rather than giving information at specific points. The simulations finally predict, that due to decades of groundwater drawdown pyrite oxidation in the mining dumps themselves, but also in the unworked bedrock constitute a source for elevated concentrations of sulphate and ferrous iron.

Mining affected groundwater quality will be an issue beyond 2100. As an example the overall situation for rivers and streams in the 'Nordraum' area indicates a minor improvement for the water quality until 2100. The results are generally in good agreement with previous work (Graupner 2014, ARGE 2012), added that also unworked aquifers partly constitute a long term source for iron and sulphate. Future work needs to take into account the interaction between the five model areas concerning the mass fluxes across the model area boundaries.

Acknowledgements

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