18th World IMACS / MODSIM Congress, Cairns, Australia 13-17 July 2009
http://mssanz.org.au/modsim09

Integrated model approach on ochre pollution of a stream in Northern Germany

Paetsch, M.

DHI - Water & Environment & Health, Sydney, NSW, Australia
Email: mpa@dhigroup.com,

Abstract: In an intensively agricultural part of northern Germany high nitrogen loads cause impacts on groundwater quality and due to the interaction between groundwater and surface water also affects the surface water quality. To explore and represent the impact, an integrated study about quantity, quality and interactions of surface water and groundwater was executed.

The overall objective was the ongoing ochre pollution in numerous streams in that region, due to their negative effects on ecosystems in hydro-power environments and hydraulic structures. The red ochre makes the water turbid in streams, covers the bed, and smothers the plants. The living conditions for fish and macro invertebrates are getting poor or will be destroyed in the end.

Ochre pollution has its origin in the iron compounds of geological sources, groundwater, soil and the interaction with enhanced, man-made impacts like nitrogen from agricultural land use.

The research included:

- field studies to explore and display the pathways of nitrate and iron,
- chemical analysis of river-, soil- and groundwater,
- chemical analyses of sediment in rivers and aquifers,
- process-oriented modelling of iron formation and transport in groundwater, ochre transport in groundwater and the river, and
- modelling the hydraulic interactions in space and time between the compartments of the soil-groundwater-river system.

To illustrate and calculate the hydraulic interactions, an integrated river-groundwater model was developed. Using the software MIKE11 (DHI, 2009a) and MIKESHE (DHI, 2009b) the relations and interactions between surface water and groundwater were represented. To calculate the life span of denitrification in groundwater environments and the occurrence of iron a PHREEQC (Parkhurst and Appelo, 1999) model was built for three locations with different land-use characteristics. For the calculation of iron transport in the river, the software ECOLAB (DHI, 2009c) was used.

The integrated model gives hints to the lifespan of iron and ochre pollution and leads to a number of possible actions to minimize and to stop ochre pollution. Furthermore the model will be one module of a decision support system for water management purposes in this area.

Keywords: *ochre pollution, integrated modelling, nitrate, iron*

1. INTRODUCTION

The water works Grossenkneten, northern Germany, abstracts about 1.5 million m^3/ a out of 3 wellfields in a catchment area of about 50 km^2 (Figure 1). At the same time this area is used intensively for agriculture and has high value for cultural and touristic purposes. Especially the intense agricultural usage led and leads to impacts on groundwater, indicated by nitrate concentrations (NO_3) in shallow groundwater (< 25 m below surface) up to 300 mg/L (drinking water standard: 50 mg/L). Although several rules for agricultural usage, legal requirements and advice of farmers have been undertaken, the impacts are still high enough to result in high nitrate concentrations in groundwater so that it has to be admitted, that the "nitrate-problem" is not solved yet (DVWK, 2002). One main environmental problem that can likely follow nitrate pollution of groundwater systems is ochre pollution in surface waters. Due to the strong interactions between groundwater and surface water, nitrate in groundwater not only affects groundwater quality and therewith the drinking water supply, but is also the basis of potential deleterious effects on ecosystems in the region like rivers, lakes, streams and wetlands. It changes the biodiversity and distribution of aquatic communities, lead to loss of recreation value and in the long run living conditions will be destroyed for elements of the ecosystem. In the river Lethe the main problem that led to a totally breakdown of living conditions for fish and macro invertebrates is the red ochre. Figure 2 gives an impression of the ochre pollution in the Lethe.

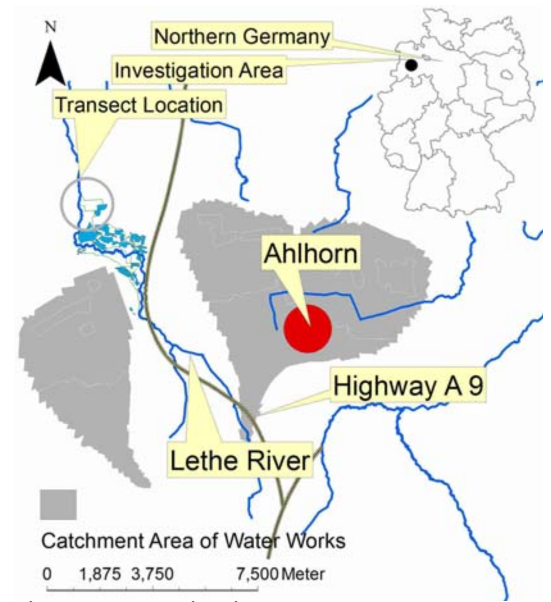


Figure 1. Investigation area

Street sign, coated with iron after lying in the river for some days

Drainage channel into the Lethe

Spot of precipitation of iron sludge at the riverbank – these kinds of iron-spots were found along the river, beginning at the Lethe dam, indicating the local appearance of iron-flow into the Lethe.

Figure 2. Ochre pollution in the river

A clear definition of ochre is vague, because the mineralogical content can vary from a pure iron oxide to a diluted mixture of iron oxide and other minerals (Popelka et al., 2007). The most important mineral of ochre pollution in groundwater and rivers is pyrite (FeS_2), an iron and sulphur compound that can lie unchanged in the soil for thousands of years if oxygen is excluded (Prange, 2007). It is ubiquitous, appearing together with brown coal (lignite) or as fossils and within the Gr-horizon of gley-soils (Koelle et al. 1983). If oxygen reaches pyrite, however, the sulphur and iron separate.

This happens:

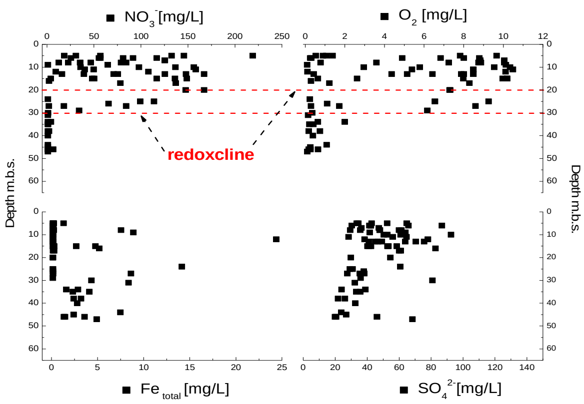
- ***when soil is drained.***
  Then oxygen influx from the atmosphere into the soil's pores creates conditions conducive for pyrite oxidation. Pyrite oxidation leads to release of ferrous ions Fe^{2+}, which are dissolved ions.
- ***when pyrite oxidation can take place in aquifers containing nitrate.***
  The process, that is a well known nitrate sink in nature, the autotrophic-chemotrophic denitrification, will reduce the nitrate (Korom, 1992). The Fe^{2+} ions set free can remain either solved and be transported with the groundwater flow, or they can be further-oxidized to ferric oxide hydrate by nitrate or precipitated as siderite by carbonate.

The dissolved ferrous iron (Fe^{2+}-ions), transported to the river are brought, malicious and colourless, thus invisibly solved in the water column. The iron remains in solution, until transformed to ($Fe(OH)_3$) in the presence of oxygen. Thus, the pathways and ultimate state depend upon many interacting factors that may vary in space and time.

2. MATERIAL & METHODS

2.1. Redox status in regional groundwater

The evaluation of the groundwater quality in existing observation wells (72 regarded wells - average values of the years 1989-2005) in the catchment area of wellfield of water works Grossenkneten (see Figure 1) indicates a sharp vertical chemical zoning of especially nitrate and oxygen (see Figure 3). In particular the influence of the agricultural usage can be identified by increased nitrate concentrations in shallow groundwater. The redox-cline, as a defined boundary between reduced and oxidised environment, is regionally situated between 20 respectively 30 m below ground surface (m.b.s). Regarding a vertical flow velocity of 1 m/a (derived from groundwater age investigations) and a duration of nitrogen load in that specific area of about 50 years, it is likely that in underlying zones already a denitrification process took place.



Red dotted line: Redox-cline depth in metres below the ground surface (mbs). Nitrate concentrations are below the detection limit, Oxygen concentrations are below 2 mg/L.

Figure 3. Redoxcline in regional Groundwater

2.2. Quality analysis in water & sediment

For the evaluation of subset sediment quality and water quality in local transects (Figure 4) the analysis and constructions in Table 1 were carried out.

Table 1. Quality analysis – water & sediment
Parameter sediment: TOC, Fe_{total}, $sulphur_{total}$, disulfide-sulphur
Parameter water: pH, LF, Temp., O_2, NO_3^-, NH_4^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Fe_{total}, Fe^{2+}, $P\text{-}PO_4$, NO_2^-, Cl^-

Action	*Purpose*
River-water: 17 locations, **Soil-water:** 12 locations sampled by suction lysimeters	subset water quality in longitudinal river section subset water quality in lateral inflow to river
Groundwater: 11 multi-level groundwater wells (3 transections: T1, T2, T3), 5-7 different sample depths	detailed representation of depth-dependent local water quality
Sediment in aquifer 9 locations (T1, T2, T3), sampling of material **Sediment in river** 13 locations (not illustrated) sampling of material	representation of: • reactive material • iron content in river sediment

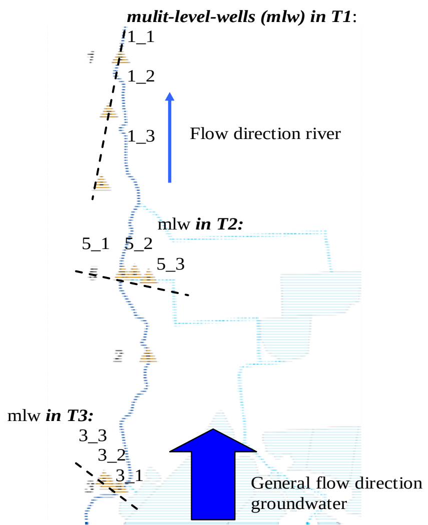


Figure 4. Local transect T1-3 (location see Fig.1)

2.3. Results of subset chemical analysis of sediment and water

Selected results of analysis of river sediment and water are shown in Figure 5. The different colours of the bars left in Figure 5, indicates the status of river water quality with respect to ferrous iron concentration (Fe^{2+}). North of Lethe Dam, high concentrations of ferrous iron (harmful respectively lethal for adult fish) in the river water and high mass-concentrations of total iron in the river sediment indicate a high lateral inflow to the river Lethe. The same trend was found for soil water (not presented in this paper). South of Feldmuehlen Dam the water quality with respect to ferrous iron is in good status respectively barely applicable for adult fish. Nevertheless the high nitrate concentrations indicate that water quality is poor with respect to the requirements of the quality standards of Water Framework Directive (WFD, 2000).

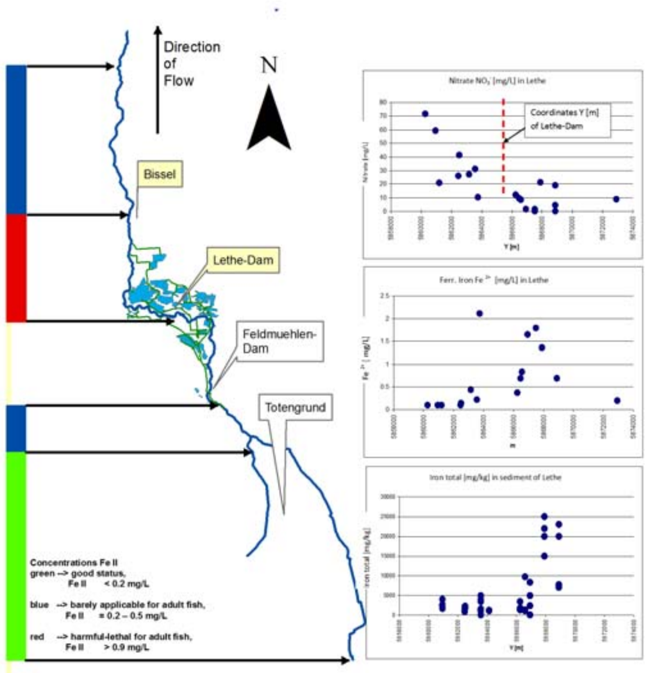


Figure 5. Selected results of water & sediment analysis - Lethe

Results of subset chemical analysis of aquifer sediment and groundwater are shown in Figure 6 as vertical (over the depth) and horizontal (along the transect) pattern of the selected parameters, nitrate, pyrite and iron for the 3 transects.

In Transect 1 the groundwater flowing to the Lethe shows nitrate concentrations up to 200 mg/L and Fe^{2+} concentrations of approximately 5 mg/L. The aquifer sediment along the riverbank contains about 100-200 mg/kg pyrite. The deep groundwater contains about 2 mg/L Fe^{2+}.

The aquifer of Transect 2 contains about 100-2000 mg/kg pyrite 50 m along the riverbank. For further calculations a conservative mass concentration of 1000 mg/kg is used. The relatively high electrical conductivity of the deeper groundwater (> 400 µS/cm) indicates young groundwater age or other sources. It is therefore expected that groundwater with a nitrate concentration of 200 mg/L NO_3 will percolate these sediments in the relatively near future. Since the average travel time is approximately 20 years, a change of nitrate inflow in approximately 10 years time is expected.

The sediments of transect 3 contained about 100-3200 mg/kg pyrite, an average value of 2000 mg/kg is chosen for further calculations. The relatively high electrical conductivity of the groundwater points to a recent age and formation under agricultural land use. It is therefore expected that groundwater with nitrate concentrations of about 100-200 mg/L will percolate the sediments in the near future.

Considering all results of sediment and water analysis, ochre pollution in the river Lethe is mainly caused by regionally increased Fe^{2+} concentration in the groundwater, due to regional denitrification process from pyrite. The aquifer contains mass concentrations from below detection to approximately 3000 mg/kg pyrite in average. The pyrite oxidation is accelerated by high nitrate concentrations, like detected regionally. Typical nitrate concentrations were found between 150 and 250 mg/L from agricultural land and about 0-10 mg/L for forest and grassland. For further calculations, an average nitrate concentration of 130 mg/L is assumed. The local pyrite deposit is situated in a 50 m broad riverbank. High nitrate and Fe^{2+}- concentrations are supplied regionally with the groundwater flow towards the river Lethe. The average horizontal groundwater velocity is calculated from 50 to 200 meters per year. For initial geochemical calculations the lowest detected flow velocity of 50 meters per year was used.

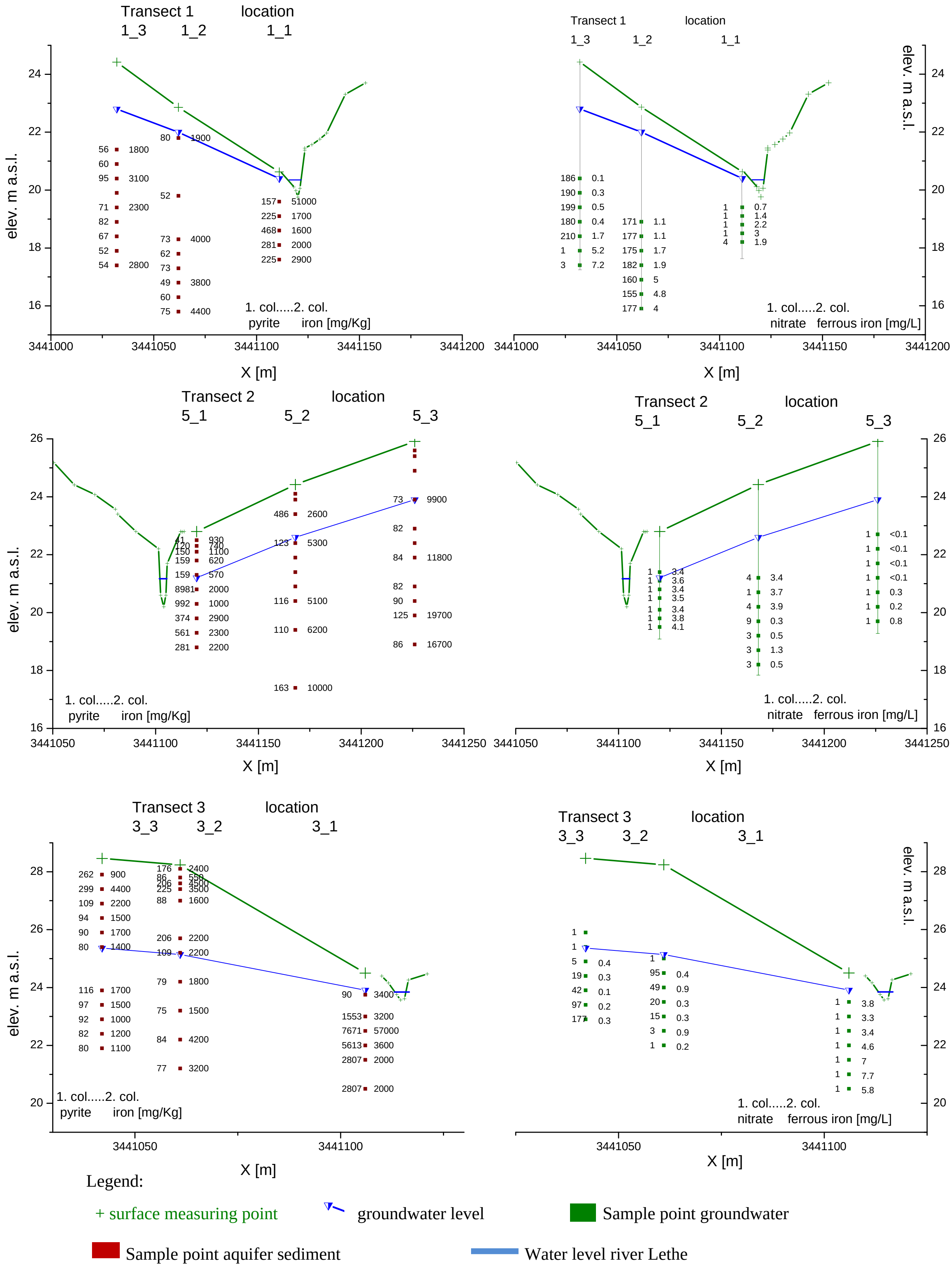


Figure 6. Results of chemical analysis of aquifer sediment and groundwater in transect T1- T3

3. CALCULATION RESULTS

The purpose of the modelling was to represent:

- the interactions between groundwater and surface water,
- the transport of nitrate and ferrous iron in groundwater,
- the transport of ferrous iron in the river,
- the life span of ochre pollution in the river.

Table 2. Software & purpose

Software	*Purpose*
MIKE SHE MIKE 11	Representation of the flow patterns in groundwater, in particular the interaction between groundwater and river.
PHREEQC	The hydrogeochemical modelling allows predictions of the fate and behaviour of nitrate and iron in the local transects.
MIKE 11 - ECOLAB	The modelling of iron transport in the river gives hints about the spatial distribution of the inflow along the riverbanks.

Therefore the different software programs mentioned in Table 2 were used to calculate the configured numerical models. Due to the lack of data – no measurements during a hydrological year – the transport of iron in the Lethe river could not be calibrated. Nevertheless the model could give hints about the process of iron transformation in the Lethe at a given hydrochemical situation as well as informations about the spatial distribution of the influx of iron to the Lethe.

The main question, the life span of ochre pollution in the river Lethe, was estimated with the geochemical software PHREEQC, calculated in different scenarios. The geochemical calculations were made in a one-dimensional approach along a flow path from groundwater to river Lethe. As visually clearly recognizable in the catchment area (see also Figure 2 – iron sludge at the riverbank), the inflow of Fe^{2+}-rich water is a local event and highly heterogeneous. Regarding this heterogeneity along the Lethe, it has to be assumed, that generally the ochre process shows three different stages in this area: *finished*, *active* and *not yet begun*. The process is finished upstream of the Totengrund, whilst downstream zones with an *active* process alternates with process *not yet begun*. At the same time the regional flow pattern differs from the local situation (higher local flow velocity than general regional flow velocity). Hence the results for the duration of the ochre process have a forecast uncertainty. The uncertainty is mainly caused by the variation of the sediment composition, which leads to different hydraulic permeability and different pyrite mass concentrations. Since for this study there was no geophysical analysis, and only sediment analyses (grain size analysis) were executed, the variation can only roughly be assumed. We assumed a factor 10.

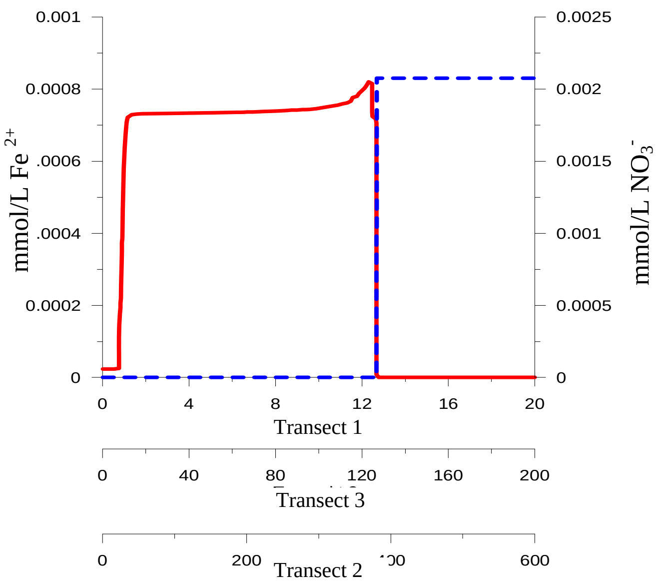


Figure shows the concentrations of the Fe^{2+} (red) and nitrate (blue) in recent groundwater after percolate pyrite containing sediments. The different time scales (years) refer to the typical pyrite concentrations, determined in field investigations.

Figure 7. Ferrous iron and nitrate concentrations

The geochemical calculations were carried out with two fundamentally different water types, described as END and ORIGINAL STATE, representing an oxidized and a reduced water (taken from observation wells in the catchment area – represented in Figure 3). The groundwater velocity in all calculations is assumed to be 50 m per year.

Transect 1 describes a groundwater chemistry, which is affected by intensive agricultural land use. The pyrite deposit is nearly consumed and is estimated to be 200 mg/kg (about 100 mg S_2^-) in a strip of 50 m width. Considering pyrite oxidation and ion exchange, Fe^{2+} is released. The geochemical calculation shows that under these circumstances the release of Fe^{2+} would be terminated after approximately 12 years (see Figure 7). However such high concentrations were found only in some hot spots and it is doubtful that they are present over large areas. The results of the geochemical modelling for Transects 2 and 3 are likewise shown in Figure 7.

Table 3 shows the results of further geochemical calculations with PHREEQC, considering different boundary conditions.

Table 3. Results of geochemical calculations with PHREEQC

Horizontal groundwater velocity	***Nitrate concentration***	***Pyrite-concentration***	***Width of strip containing pyrite***	***Duration of ochre pollution***	***Uncertainty Standard deviation***
m/a	***mg/L***	***mg/kg***	***m***	***a***	***a***
100	128	200	50	13	2
100	260	200	50	6.5	1
100	128	2000	50	130	30
100	128	6000	50	390	100
200	260	6000	50	90	30
100	25	200	50	65	10

4. DICUSSION AND CONCLUSIONS

Due to the spatial heterogeneity, temporal variability, and the insufficient data situation, a forecast about the life span of the ochre pollution problem in the river Lethe is vague. As follows from the semi-quantitative calculations, the ochre pollution will remain a problem as long as the regional impact of nitrate doesn't change and as long as the pyrite deposit isn't consumed. The life span of approximately 12 to 400 years shows the possible period. Since the concentration of nitrate often is twice as much as 128 mg/L and the flow velocities are regionally at 100 m/year, it is very likely that the ochre processes will run 4 times faster than represented in Figure 7. Thus it would be finished during the next 100 years. During this period it has to be assumed that locations where the water quality is still good today will be impaired with strong ochre pollution. Application of an efficient management of fertilizer, which would lead to a minimization of the nitrate surplus, will not obtain an immediate success. The ochre pollution will last as long as the nitrate is consumed. This duration depends on the velocity of flow in the groundwater and becomes estimated with an immediate reduction of the entry on zero, at least 20 years.

REFERENCES

DHI, Water & Environment (Ed.),(2009a), *MIKE_11_ref.pdf. Hørsholm, Dänemark*

DHI, Water & Environment (Ed.),(2009b), *MIKE SHE. Hørsholm, Dänemark*

DHI, Water & Environment (Ed.), (2009c), *ECOLAB. Hørsholm, Dänemark: All DHI docs can be downloaded with the softare from: http://www.dhigroup.com/Software/Download/MIKEByDHI2009.aspx*

DVWK (2002), Kurzfassung aus: Flaig, H., Lehn, H., Pfenning, U., Akkan, Z., Elsner, D., Waclawski, N. (2002): Umsetzungsdefizite bei der Reduzierung der Nitratbelastung des Grundwassers". Materialienband Akademie für Technikfolgenabschätzung Baden-Württemberg, 317 S., 3 Anh.; Stuttgart

Koelle, W., Werner, P., Strebel, O., Böttcher, J. (1983), Denitrifikation in einem reduzierenden Grundwasserleiter. Vom Wasser 61. 125-147.

Korom, S. F. (1992), Natural Denitrification in the Saturated Zone: *A Review Water Resources Research, Vol. 28, No.6, pp. 1657 – 1668*

Parkhurst, D.L. and 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: U.S. Geological Survey Water-Resources Investigations Report 99-4259, 312 p.

Popelka-Filcoff, R. S., J. D. Robertson, M. D. Glascock, Ch. Descantes, (2007), Trace element characterization of ochre from geological sources, *Journal of Radioanalytical and Nuclear Chemistry, 272, 17–27.*

Prange, H., (2007), Ochre Pollution as an Ecological Problem in the Aquatic Environment - Solution Attempts from Denmark, ISBN 10: 3833466324, ISBN 13: 9783833466328, SubTitle: Verockerung als gewässerökologisches Problem - Lösungsansätze aus Dänemark - Published by: Books On Demand.

WFD, (2000), DIRECTIVE 2000/60/EC. European Comission. (http://ec.europa.eu/environment/water/water-framework/index_en.html) 14/05/2009