

Redox processes in the Oderbruch aquifer (northern Germany)

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Abstract A groundwater field study was conducted in the German Oderbruch, a region beside the Oder River on the border with Poland, to identify, understand, and quantify redox processes in the aquifer, which is continually recharged by river water. The results were subsequently modelled by combining a detailed redox process model including the kinetic approach outlined by STEADYSED1 (Van Cappellen & Wang, 1995) with non-stationary transport. The model accounts for several redox components in the solid and fluid phases. Non-redox reactions, such as sorption, precipitation, and dissolution are also modelled. In particular precipitation of rhodochrosite is considered. Measurements show that O₂ and NO₃⁻ are obviously consumed in the first few metres after infiltration. Mn and Fe (hydr)oxide reduction are the most relevant redox processes in the part of the aquifer observed. Mn concentrations in the groundwater, which are comparatively high with a distinct maximum at 150 m from the river, were simulated successfully. The maximum measured Mn concentration is 0.12 mmol l⁻¹. Fe increases from 0.005 to 0.03 mmol l⁻¹ along the groundwater streamlines.

Key words geochemistry; groundwater modelling; redox processes; surface water infiltration; transport

INTRODUCTION

In natural aquatic systems, redox processes often are important controls on solute chemistry. The concentration of redox components reflects and influences the geochemical environment and thus the behaviour of chemical components in the system. The migration of dissolved constituents, such as metals and organic compounds, is substantially affected by redox components and redox reactions. An understanding of redox is thus important, and in particular, when point or non-point source redox sensitive pollutants contaminate and affect groundwater.

Redox processes are of particular importance at the interface between surface water and groundwater, either through bed sediments or in aquifers. Redox components are thus a typical research focus in sedimentological studies of surface water bodies, i.e. in the sediments of lakes, rivers, and the ocean.

Although redox processes may be important in controlling groundwater chemistry, less attention has been given to understanding the redox processes in aquifers which are recharged from rivers or lakes. In sediments, redox fronts can be observed on the scale of centimetres, whereas the distance of the redox front in aquifers is much longer because the flow velocity in groundwater can be much greater than through fine-grained sediments. Although groundwater velocities are small, advective transport in aquifers generally is important, while as a rule, it is not important in sediment studies.

Recently, several studies have been published demonstrating the use of computer models to understand the complex interaction of chemistry, biochemistry and transport of redox species. These papers focus on the concentration of the species and less on the energetic phenomena accompanying redox chemistry (Boudreau, 1986; van Cappellen *et al.*, 1996; Soetart *et al.*, 1996; Park & Jaffe, 1996; van den Berg *et al.*, 2000). Biochemistry is modelled as a kinetic reaction. In one of very few studies Hunter *et al.* (1998) utilise a novel approach for groundwater research, which was used successfully in sediment studies. The quasi-kinetic approach is also preferred by Keating & Bahr (1998). The expert system approach presented by Chapelle *et al.* (1995) points in the same direction: "this methodology is based on measurable water chemistry parameters ... it provides a better description of predominant redox processes in groundwater systems than more traditional Eh-based methods".

SITE DESCRIPTION

The Oderbruch, Germany's largest polder region, has been artificially drained over the past 250 years (Fig. 1). A major part of the region now (2001) lies below the river water level and a levee prevents the predominantly agricultural-use area from flooding. The steep hydraulic gradient between the level of the River Oder and the groundwater level of the aquifer results in continual lateral infiltration of river water into the shallow, confined aquifer. Several redox-controlled, chemical changes occur when oxic river water enters into the anoxic environment. The water becomes progressively more reduced, making the region ideal for groundwater redox studies.

Hydrogeological setting

A 1 km² exemplary field-site "Bahnbrücke", located adjacent to the River Oder in the northern Oderbruch, was chosen for detailed investigation. The instrumentation consists of 24 conventional piezometers at varying depths, and three multilevel wells located at distances from 3 to 620 m from the river (Fig. 2). The area was intensively surveyed and monitored for relevant hydraulic and hydrochemical parameters. A three-dimensional (3-D) transient hydraulic model serves as a base for investigating groundwater flow paths for different river levels.

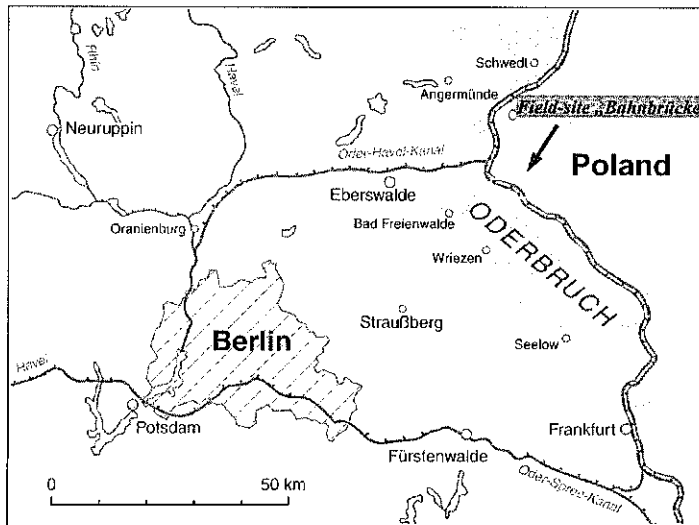


Fig. 1 Location of the Oderbruch aquifer and the experimental field-site “Bahnbrücke”.

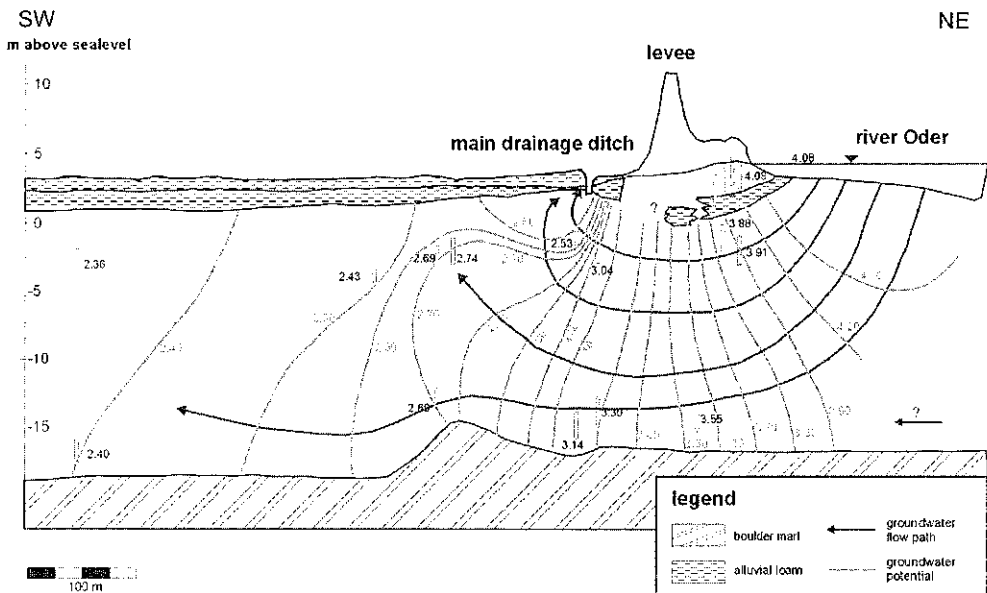


Fig. 2 Vertical schematic cross-section through the aquifer at the field site; filter-levels are shown; water-level data as measured on the 28 September 1999; schematic flow paths included.

The 20–22 m deep aquifer consists of glacio-fluvial sands and gravel. It is bounded by a boulder marl at the base and an alluvial loam at the top. The upper parts of the aquifer are mainly fine to medium sized sands with hydraulic conductivities ranging from 5.5×10^{-5} to $4.0 \times 10^{-4} \text{ m s}^{-1}$, becoming coarser with depth (hydraulic conductivities of $2.9\text{--}8.9 \times 10^{-4} \text{ m s}^{-1}$). Due to the strong current in the river, the bed sediments are generally coarse and highly permeable, and hydraulic contact between

the river and groundwater is unrestrained (hydraulic conductivities of from 9×10^{-4} to $1.5 \times 10^{-3} \text{ m s}^{-1}$). Mean flow velocities vary from $0.5\text{--}1.5 \text{ m day}^{-1}$ near the river to $0.2\text{--}0.3 \text{ m day}^{-1}$ further inland.

Most of the groundwater recharge occurs from a main drainage ditch, which is parallel to the levee 150 m from the river. The resulting infiltration is complex and has a strong vertical component (see Fig. 2). For modelling within the current study, only the deeper groundwater paths (13 and 20 m below sea level) were evaluated because they are the most representative of processes within the Oderbruch aquifer.

METHODS

Surface- and groundwater samples were collected every two months over one year. Measurements of Eh, pH, O_2 , temperature and conductivity were carried out in the field using a flow cell. Samples were filtered through $0.45 \mu\text{m}$ membrane filters immediately after sample retrieval to prevent, or at least retard, Fe and Mn precipitation. Sample aliquots were acidified with nitric acid for cation analysis. Alkalinity was measured soon after the samples were returned to the laboratory. The complete suite of analyses was generally performed one day after sampling. Water samples were analysed for Ca, Mg, K, Na, Cl, NO_3^- , Br, SO_4^{2-} and NO_2^- by ion chromatography (Dionex DX 500), for Mn and Fe by ICP (Jobinyvon), for NH_4^+ , PO_4^{3-} and S (Uvicon 931 Kontron), SiO_2 (Dr 2000 Hach) by photometry, and for DOC by a DOC-Analyser (Shimatzu).

WATER CHEMISTRY

During bank-filtration of oxic river water a sequence of redox reactions occur with increasing travel and reaction time of the infiltrating water (Fig. 3). The redox state of the system can best be described by the Fe^{2+} and particularly the Mn^{2+} content of the water. Of the electron acceptors present in the river water, O_2 and NO_3^- are probably consumed within the first few metres or even decimetres along the groundwater flow path and are not observed in any of the observation wells.

As a result of Mn (hydr)oxide reduction, the Mn^{2+} concentration of the water continuously increases from the river to a distance of 150 m, where it reaches a maximum of $5\text{--}6 \text{ mg l}^{-1} \text{ Mn}^{2+}$. The Mn^{2+} concentration then decreases to less than 1 mg l^{-1} at 620 m from the river.

While the reduction of Mn (hydr)oxides is certainly the source for Mn^{2+} in solution, groundwater Mn^{2+} concentration is controlled by the saturation of Mn carbonate (MnCO_3 , rhodochrosite). Rhodochrosite is the most common reduced Mn(II) mineral in nature (Berner, 1980). It commonly precipitates in aquatic systems according to reaction (1), and consequently removes Mn^{2+} from the groundwater:



It appears that the precipitation of rhodochrosite is encouraged when the dissolution of Mn and Fe (hydr)oxides produces a more alkaline and thus CO_3^{2-} richer solution. The similar decrease in Mn^{2+} concentration, alkalinity, and pH at 150 m from the river, which is 300–350 m travel distance on a lower flow path (Fig. 2), suggests that rhodo-

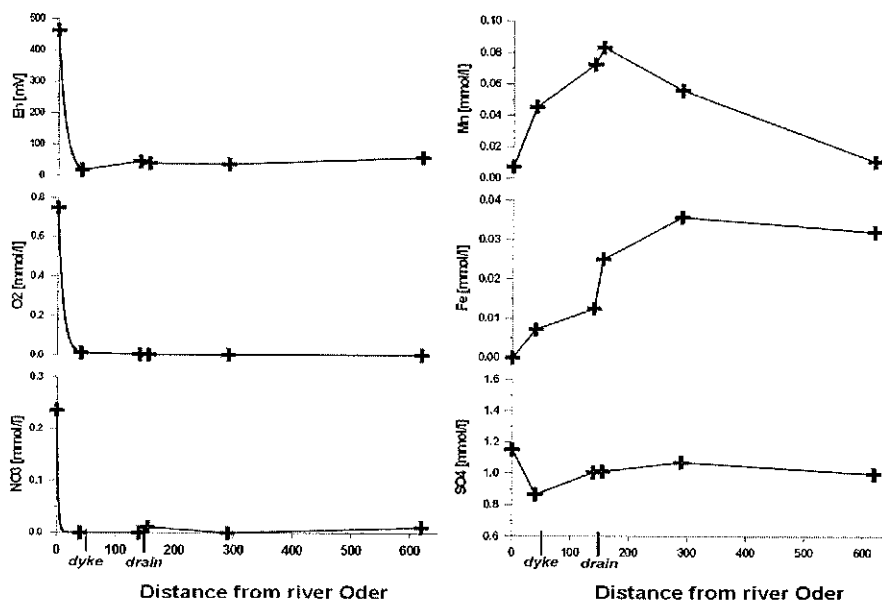


Fig. 3 Eh and concentrations of O₂, NO₃⁻, Mn²⁺, Fe²⁺ and SO₄²⁻ in the deeper groundwater levels with increasing distance of the river.

chrosite is precipitating. Similar observations were reported by Matsunaga *et al.* (1993).

Whereas groundwater Mn²⁺ concentration increases to 150 m from the river and then decreases to 620 m, the Fe²⁺ concentration increases along the transect reaching a maximum of 2–5 mg l Fe²⁺ at 620 m. The redox conditions do not reach the post-oxic, ferrous precipitates, and SO₄²⁻ is not reduced, i.e. S²⁻ was not detected. The SO₄²⁻ content of the groundwater is about 100 mg l⁻¹, which is similar to the river water concentration.

The groundwater composition was relatively constant over the one-year collection period. The modelling approach, therefore, is focused on finding (quasi) steady-state solutions of the differential equations.

CONCEPTUAL MODEL

The concept of the system is that redox processes are biogeochemically controlled and that bacteria and other micro-organisms are degrading organic matter. The redox concept is similar to that incorporated in the STEADYSED1 model (van Capellen & Wang, 1995), which focuses on the concentration of the redox components in fluid and solid phases.

The conceptual model assumes a steady state for organic matter in the aquifer:

$$C_{org} = C_{0,org} \exp(-\lambda_x x) \quad (2)$$

with organic depletion constant λ_x . The spatial exponential depletion along the flow direction is to address locally different availability and reactivity of organic carbon. The maximum concentration and reactivity of organic carbon is expected adjacent to

the river. The distance x is measured along the streamlines in the Bahnbrücke section. The position $x = 0$ is located at the interface between the river and the aquifer and $C_{0,org}$ denotes the DOC concentration at the boundary.

Redox reactants in the solid phase can be described by the differential equation:

$$\frac{\partial}{\partial t} C_s = -f(C_s) \lambda C_{org} \quad (3)$$

where the function f denotes the fraction of the redox process on total degradation of organic matter and λ the degradation constant. For f , a formulation according to the Michaelis-Menten kinetics with concentration $C_{1/2}$ corresponding to the half-saturation concentration of the reaction is used:

$$f(C) = \frac{C}{C + C_{1/2}} \quad (4)$$

For the redox reactants in the groundwater, advection and dispersion have to be taken into account. Thus:

$$\frac{\partial}{\partial t} C_f = \frac{\partial}{\partial x} \left(D \frac{\partial}{\partial x} C_f \right) - v \frac{\partial}{\partial x} C_f - Ff(C_f) \lambda C_{org} \quad (5)$$

holds with groundwater flow velocity v and with diffusivity D . F denotes the solid-fluid-phase conversion factor. For a reaction product in groundwater:

$$\frac{\partial}{\partial t} C_f = \frac{\partial}{\partial x} \left(D \frac{\partial}{\partial x} C_f \right) - v \frac{\partial}{\partial x} C_f - Ff(C_s) \lambda C_{org} \quad (6)$$

Fluid phase components involved in redox reactions in the solid and fluid phases are described by the same differential equation except that the sign of the last term is different. The redox term represents a sink for electron acceptors in water, and represents a source for electron acceptors in the solid phase.

To incorporate the mineral precipitation and dissolution processes, the differential equation is expanded by an additional term:

$$\frac{\partial}{\partial t} C_f = \frac{\partial}{\partial x} \left(D \frac{\partial}{\partial x} C_f \right) - v \frac{\partial}{\partial x} C_f - Ff(C_f) \lambda C_{org} - \alpha (KC_f - C_i) \quad (7)$$

where α represents a transfer coefficient and K the equilibrium constant of the process.

MODEL IMPLEMENTATION AND RESULTS

According to equations (5) to (7), the transport of redox components is simulated by a one-dimensional equidistant finite-difference unsteady reaction-transport model using the software MODELMAKER™ (software from Cherwell Ltd, Oxford, UK). The common suite of redox reactions— aerobic respiration, denitrification, Mn and Fe reduction, and methanogenesis—are addressed in the model. Because the Oderbruch measurements only show oxygen and nitrate in groundwater close to the river, the redox reactions of highest priority are those affecting Mn.

Concerning Mn, the model incorporates biodegradation reactions with manganese (IV) oxide as the oxidizing agent, which releases aqueous Mn ionic species and carbonaceous species, through precipitation/dissolution reactions (e.g. rhodochrosite). Initially, only one degradation reaction of all redox reactions that were described by van Capellen & Wang (1995), the reaction with MnO_2 as an oxidizing agent, is considered. Furthermore, it is assumed initially that the availability of hydrogen carbonate as a reactant in equation (1) is not a limiting factor for the reaction. There is a prescribed boundary concentration for aqueous Mn at the inflow position ($x = 0$); see Table 1 for a listing of input parameters. Mn and organic carbon concentrations in the solid correspond with the average field observations.

Table 1 Simulation parameters (last column indicates input (i) or optimized (o) values).

Parameter	Unit	Value	i/o
Bulk solid density of aquifer	kg dm^{-3}	2.600	i
Pore velocity	m day^{-1}	1.00	i
Element length	m	10.0	i
Average content of Mn oxide	mole kg^{-1} solid	0.005	i
Limiting concentration of Mn oxide	mole kg^{-1} solid	0.005	o
Maximal content of biodegradable organic carbon	mole kg^{-1} solid	0.00001	i
Degradation rate of organic carbon	day^{-1}	0.0008	o
Spatial depletion constant of organic carbon	m^{-1}	0.003	o
Start concentration of aqueous Mn in the pore water	mole l^{-1}	1×10^{-6}	i
Recharge concentration of aqueous Mn at $x = 0$	mole l^{-1}	1×10^{-6}	i

In addition to transport parameters (e.g. pore velocity) and element size, the Mn content in the solid (as MnO_2), the maximum organic carbon in the solid, the initial Mn concentration of the fluid, and the inflow Mn concentration, are model input parameters and are related to average field observations. The solubility of MnCO_3 (only dependent on pH and aqueous carbonate species concentrations) is a thermodynamic-model input parameter. Reaction parameters, such as the degradation constant, depletion constant of organic carbon, limiting concentration of MnO with respect to the organic carbon degradation precipitation rate of rhodochrosite, are optimized. The model input and optimized parameters are summarized in Table 1. The initial parameter values are identical to the default values used by van Capellen & Wang (1995). The fitted parameter values are within the expected range.

In the current formulation of the model, advection is treated at a constant pore velocity. The model runs until a (quasi-)steady state is reached (after 3000 days).

DISCUSSION

As a first result, the hydrogeochemical behaviour of Mn along the Bahnbrücke section is reproduced well by the model (Fig. 4). The profile of Mn contents along the transect was verified by the model calculation with a mean deviation of 5.41×10^{-6} [mol l^{-1}], which is approximately 6% of the maximum.

The main factors controlling the Mn distribution are:

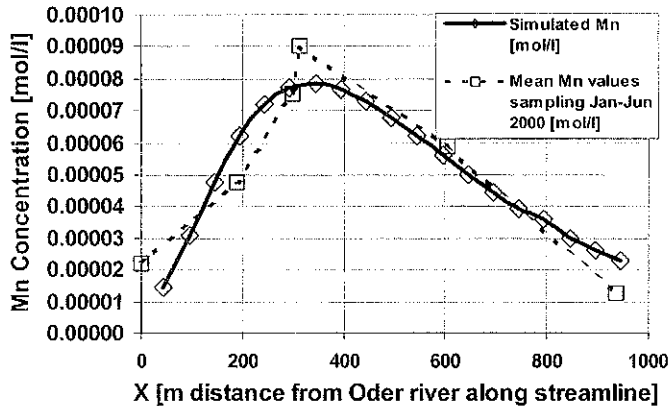


Fig. 4 Simulated and observed Mn concentration distribution along a flow path at the Bahnbrücke section.

- the abundance and spatial distribution of biodegradable organic carbon in the aquifer,
- the abundance and spatial distribution of Mn (III/IV) oxides as reactants of degradation of organic carbon,
- the limiting concentration of Mn (III/IV) oxides (van Capellen & Wang, 1995); at lower contents of Mn (IV) oxide, the degradation rate is assumed independent of concentration,
- the degradation rate of the redox reaction of Mn oxides with organic carbon giving rise to free Mn ion species ($\text{Mn}^{2+}_{\text{aq}}$) and carbonate species ($\text{CO}_{2\text{aq}}$, HCO_3^- , CO_3^{2-}),
- the relation between the concentration of free Mn ion species and carbonate species with respect to an oversaturation/undersaturation of rhodochrosite in the pore water,
- the precipitation/dissolution rate of rhodochrosite,
- the pore velocity (and dispersivity) in the aquifer.

The breakthrough behaviour of aqueous Mn is caused by the interference of biodegradation processes (dissolution of MnO_2) and precipitation processes (formation of interstitial rhodochrosite). From the fluid–aquifer interface, along the first 300 m of the streamline away from the river, dissolution of MnO_2 dominates. MnO_2 is undersaturated along the entire flow path. Due to the depletion of bio-degradable organic carbon, free aqueous Mn species are probably less available so that precipitation of rhodochrosite prevails at greater distances.

CONCLUSION AND OUTLOOK

Preliminary results of a field and modelling study shows that redox fronts occur in aquifers which are recharged by surface water. The combination of measurements and modelling will provide a better understanding of factors controlling the concentrations of all redox species and show the interaction among redox fronts, carbon chemistry, and pH.

In the next modelling stage, the carbonate species concentrations, the pH, calcite precipitation/dissolution, and concentrations of the Fe–Mn redox pairs will be included to describe the precipitation/dissolution of rhodochrosite. The initial evaluation of the

hydrochemical groundwater analyses along the “Bahnbrücke” transect indicates that Mn oxides are undersaturated and rhodochrosite is oversaturated along the entire transect. Also, the future modelling will consider the changing velocity along a representative streamline, calculated by a 3-D groundwater flow model, and dispersion.

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