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Research Article

Model Based Raw Water Quality Management – Manganese Mobilization Induced by Bank Filtration

In many countries bank filtration is used as the first step of drinking water treatment. River water percolates the riverbed and aquifer sediments which serve as a natural filter removing substances like nitrate, particular and dissolved organic matter and trace elements. Raw water quality, therefore, depends on both river water quality as well as hydrogeochemical processes within the sediment. Exemplified by the case study of Auf dem Grind, Well II (Düsseldorf, Germany), the geohydraulic and hydrogeochemical processes of a catchment area that is strongly influenced by bank filtration were investigated. Raw water extracted from Well II showed significantly elevated manganese concentrations compared to river water and to raw water from other wells in the catchment area. A reactive transport model was developed for retracing the measured raw water quality. Retrospective modeling revealed the principles of long and midterm changes in raw water quality, especially fluctuations in manganese concentrations. Based on the model-scenario, the effects of varying river water qualities and/or agricultural fertilization practices can be predicted. The quantitative understanding of coupled hydrogeochemical and hydraulic processes enables the development of sustainable strategies optimizing raw water quality, e.g. with regard to a cost effective water treatment.

Keywords: DOC (dissolved organic carbon); Hydrogeochemical modeling; Riverbank filtration

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1 Introduction

In the last few decades, pollution and climate change have increasingly affected drinking water supply. Spatial and temporal allocation of potable water has shortened due to a decrease in raw water quality. More than ever, drinking water supply requires sustainable management of water resources, not only regarding quantity, but also quality.

Compared to groundwater, surface water is undoubtedly more variable in quality und temperature. In particular, river water is at risk of permanent or sudden pollution from industrial, agricultural and domestic sources. In densely populated and industrialized urban areas natural groundwater resources often do not meet the demand. As a consequence, groundwater originating from riverbank filtration (RBF) has become an important source for drinking water supply in many countries [1 – 3]. For example, along the densely populated Rhine valley area, more than 20 million people rely on bank filtration. Cities like Düsseldorf or Basel totally and partially receive drinking water from riverbank filtration plants, respectively.

RBF can be used as a first step of water treatment. The substrate of the riverbed and aquifer sediments serve as a natural filter that significantly lowers the concentrations of many surface water pollutants as well as bacteria and viruses during percolation [3 – 9]. On the other hand, hydrogeochemical processes can also cause a mobilization of reduced substances like manganese during RBF.

However, manganese concentration in raw water is an important factor in the regulation of drinking water treatment steps. Applied water treatment is designed to remove mainly organic but also inorganic compounds by inducing ozone in the first step. Ozone is a strong oxidizing agent. Besides organic substances, dissolved manganese is also oxidized to permanganate. In a second step permanganate is reduced to manganese at the surface of activated carbon filter systems. In this context, the amount of induced ozone and filtration performance of raw water are influenced by the manganese concentration.

The development of sustainable strategies for optimizing raw water quality, e.g., with regard to a cost effective water treatment, requires knowledge of potential sources of substances and their concentrations. However, current understanding of RBF is mainly based on empirical data [3]. In this context, a better understanding of aquifer conditions and hydraulic controls, as well as redox processes that determine the hydrogeochemical environments and mobilization patterns, is demanded. The efficiency of RBF systems depends on factors like river water quality (pH, dissolved organic carbon (DOC) and redox conditions), hydrogeological conditions, residence time and temperature [6]. A quantitative and qualitative manage-

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Abbreviations: DOC, Dissolved organic carbon; **RBF**, Riverbank filtration; **TIC**, Total inorganic carbon

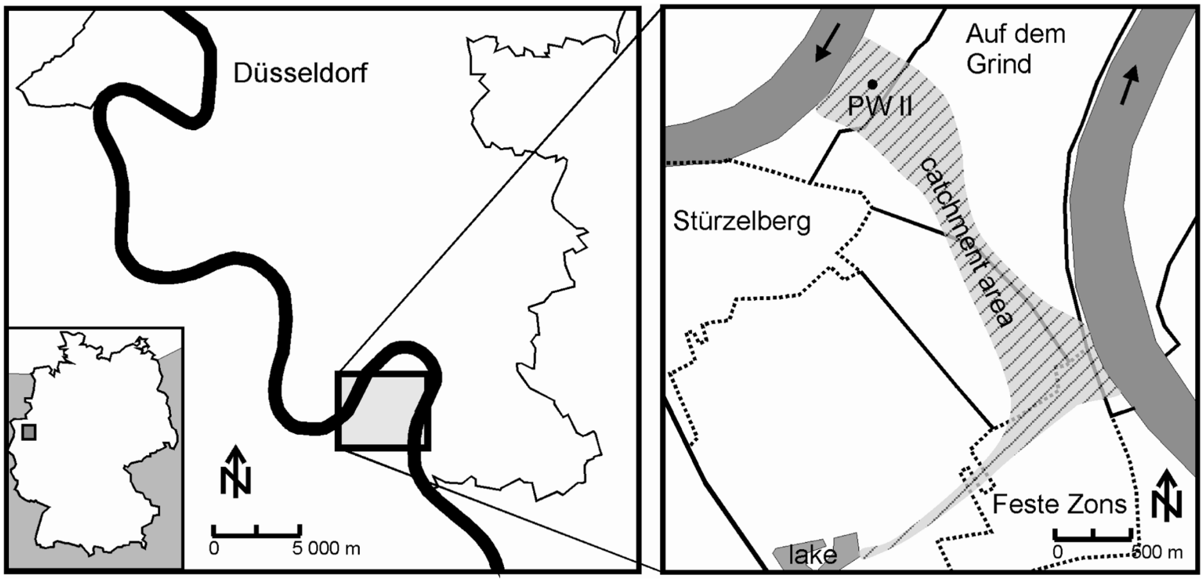

Figure 1. Location of the study area, Auf dem Grind – Pumpwerk (Well) II, Düsseldorf waterworks.

ment of RBF systems also requires knowledge of the interaction between complex geohydraulic and hydrogeochemical processes. In general, however, recent practices in economic resources control do not involve aspects of the hydrogeochemical and geohydraulic groundwater system [10, 11].

Within the framework of the InnoNet program funded by the Federal Ministry of Economics and Technology, a network of research institutes (TU Clausthal, IWW), an engineering company (delta h GmbH) and five water suppliers worked in close cooperation to develop a planning and management tool focused on water quality problems. This user oriented management tool is based on a reactive transport model that calculates the hydrogeochemical and geohydraulic processes under consideration of temporal and spatial dynamics in agricultural land use, bank filtration and industrial pollution. The tool features a simple input model structure, short calculation times (a few minutes per model run) and a high grade of plausibility of model results.

In this paper the development of the reactive transport model is exemplified by the case study of Auf dem Grind in Düsseldorf, Germany, a catchment area strongly influenced by bank filtration. The extracted raw water of Well II shows significantly elevated manganese concentrations compared to river water. A reactive transport model was developed in order to identify and quantify relevant processes for the local mobilization of manganese. Retrospective modeling revealed the principles of long and midterm changes in raw water quality, especially fluctuations in manganese concentrations. Based on prognosis modeling using the software-code PHREEQC [12], the reactive transport model provides a platform to test the efficiency of agricultural and industrial measures on raw water quality development.

2 Area of Investigation

2.1 Hydrogeological and Hydrochemical Setting

Exemplified by the case study of Auf dem Grind, Well II, Düsseldorf, Germany, the geohydraulic and hydrogeochemical processes of a catchment area that is strongly influenced by RBF were investigated [13]. The catchment area Auf dem Grind is situated on a peninsula surrounded by the river Rhine, a few kilometers upstream of the city of Düsseldorf, in West Germany (see Fig. 1). The average runoff of the river Rhine at Düsseldorf is 2200 m^3/s [1]. Seven horizontal filter wells extract approximately 30 million m^3 of water annually for drinking water supply.

The aquifer consists of 20–25 m of Quaternary (Pleistocene) fluvial sands and gravels. The average permeability and porosity of the aquifer is between $3 \cdot 10^{-3}$ and $9 \cdot 10^{-3}$ m/s and 0.2–0.24, respectively. The Quaternary sediments are underlain by fine Tertiary (Oligocene) sands, with a lower permeability of about $1 \cdot 10^{-5}$ m/s.

The concentrations of various solute species in the extracted groundwater were routinely monitored in all producing wells. More than 240 analyzed samples reflected the development of raw water quality in Well II from the beginning of the production period in 1958 until 2006 (see Fig. 2). Unfortunately, the recorded data has a gap from 1978 to 1990. Nevertheless, the raw water extracted from Well II showed significantly elevated manganese concentrations compared to river water and raw water from other wells in the catchment area. Average manganese concentrations increased from 0.3 mg/L at the beginning, to 1.0–1.5 mg/L in a period from the early to the late 1970s. Between 1980 and 1990 the treated raw water showed a purple color after ozonation which indicated high concentrations of permanganate. Within this time period the ozone demand exceeded recent induced concentrations. High permanganate concentrations, as well as an increased ozone demand, implied high manganese concentrations within the extracted raw water during the data gap period. After 1990, concentrations declined to the previous concentration level of approx. 0.3 mg/L, while iron concentrations remained constant below a value of 0.07 mg/L. Coupled to the increase of manganese concentrations, nitrate concentrations decreased from about 20 mg/L to only a few mg/L almost simultaneously. Except for chloride and sulfate concentrations, the other parameters remained largely constant over the observation period. Concentrations of hydrocarbonate fluctuated due to seasonal variations from 200 to 250 mg/L and calcium con-

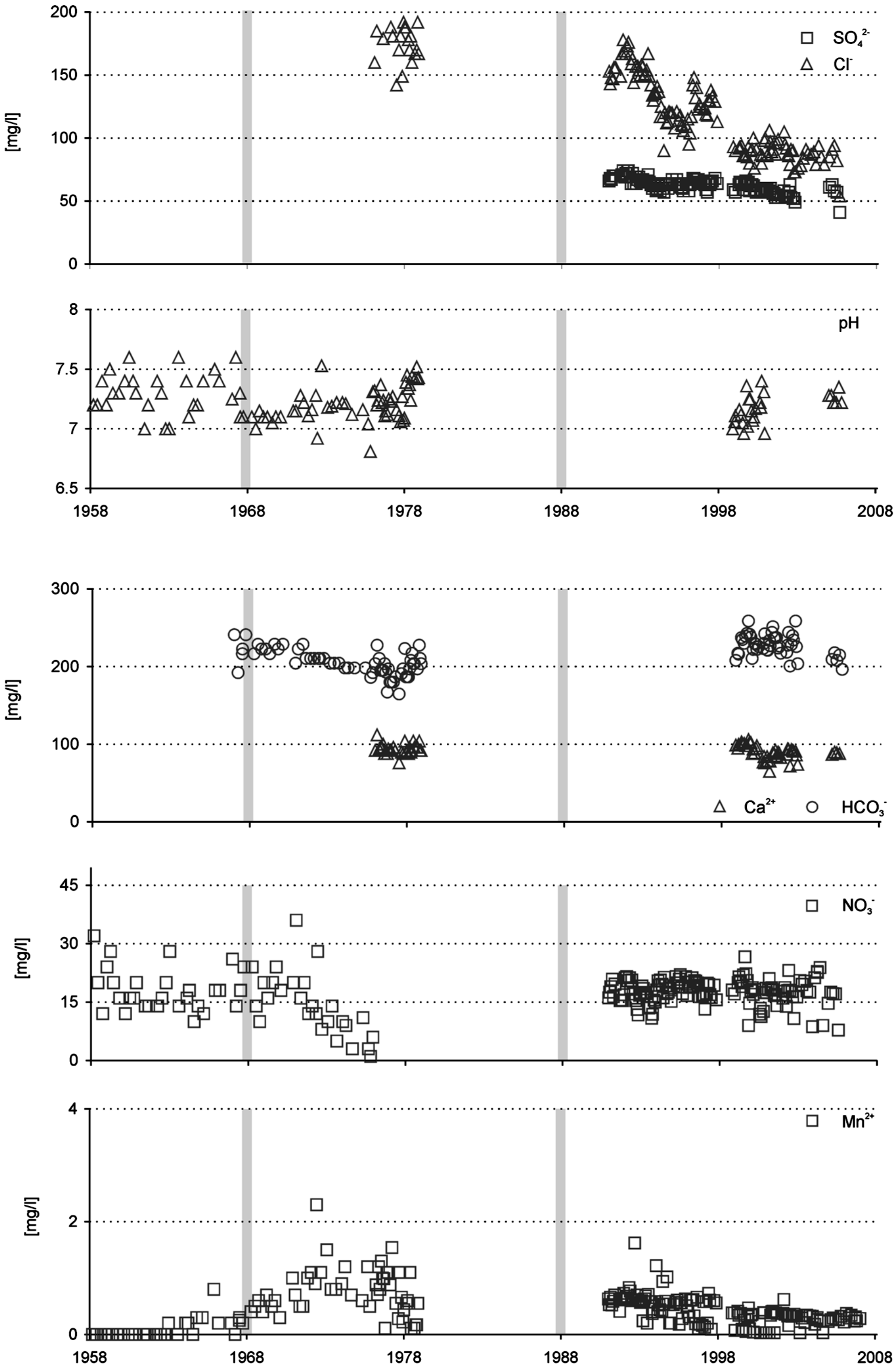

Figure 2. Development of raw water quality from 1958–2006.

centrations ranged between 75 and 105 mg/L. Likewise, the pH was also a subject to seasonal variations and ranged between 7.0 and 7.5. In the data at hand, sulfate concentrations decreased from approx. 75 to 55 mg/L, and chloride concentrations from approx. 200 to 80 mg/L.

2.2 Supplementary Investigations

Close to the screens of Well II, two core drillings were carried out down to the base of the Quaternary aquifer for use as monitoring wells. The reddish brown color of the Quaternary sediments indicated small amounts of iron oxides and hydroxides. There was a

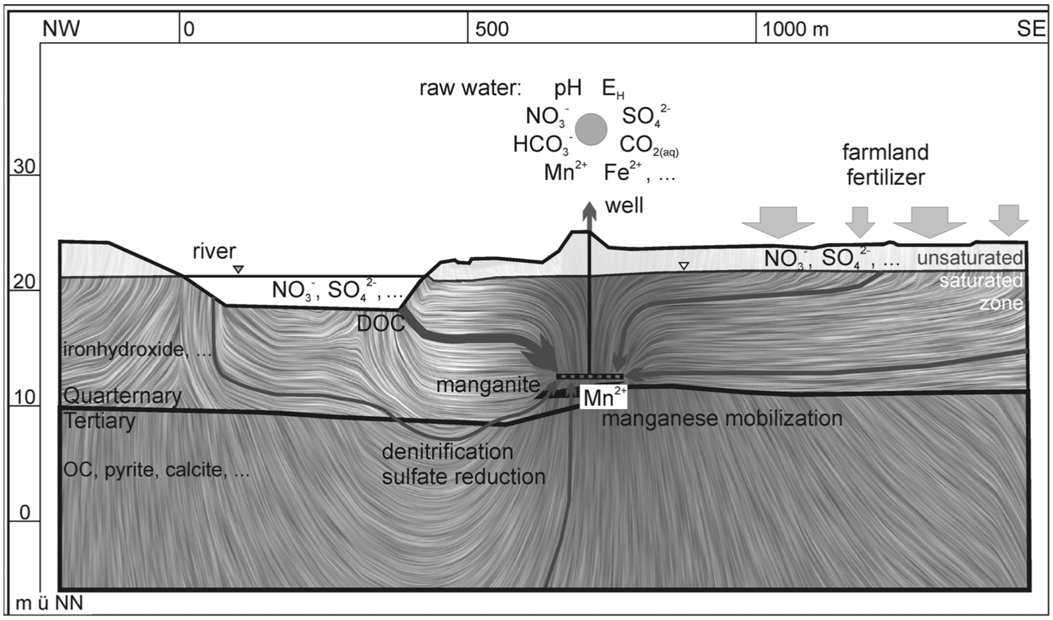

Figure 3. Schematic NW-SE cross-section and relevant hydrogeochemical processes with an influence on raw water quality. By means of a Schlieren-technique (SPRING®), the modeled groundwater flow is shown. Below the river Rhine a zone of groundwater stagnation exists.

layer with black coated gravels close to the aquifer base. These coatings were analyzed using a scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDX). The spectroscopy analyses revealed that the coatings consist of manganese oxides and/or oxidhydrates. Bulk samples were analyzed with standard methods for organic and inorganic carbon as well as sulfur and pyritic sulfur. In contrast to the oxidized sediments of the aquifer, underlying Tertiary sediments contained minor amounts of pyrite (FeS_2) and organic carbon. Small amounts of calcite appeared in both geological units.

2.3 Groundwater Flow Modeling

In a first step, using the software package SPRING® [14] a 3D groundwater flow model was established to identify the provenience of extracted groundwater flows and to quantify the flow rates. The calculated catchment area of Well II is shown in Fig. 1. The modeled groundwater flow within the aquifer in a northwest-southeast cross-section is demonstrated in Fig. 3. Mixing fractions of relevant groundwater flows are shown in Tab. 1. The raw water mainly consisted of RBF that predominantly flows from the nearby Rhine water infiltration zone in a southeastward direction towards the well [13]. A smaller fraction originated from the distant Rhine water infiltration zone at the southeastern bank of the peninsula. Minor parts of the extracted groundwater were recharged under agriculturally used land southeast of the well and originated from infiltrating surface water from a former quarry pond in the hinterland of the peninsula, respectively. Most important, extracted raw water also comprised 2.6% of groundwater that derives from the underlying fine grained Tertiary sediments. This groundwater flow can be split into two partial flows: (i) ascending saline groundwater and (ii) RBF after inter-percolation of Tertiary sediments.

Based upon a non reactive transport calculation with SPRING®, the mean residence times of prevailing ground water flows were calculated with a defined dispersivity of 15 m (see Tab. 1). Mean residence times were derived from calculated breakthrough curves of a non reactive tracer in the well that was induced at the filtration zones and the groundwater surface.

3 Reactive Transport Modeling

3.1 Model Conceptualization and Time Variant Input Data

The reactive transport model is based on a conceptual model that integrates information about site specific geology, groundwater hydraulics and hydrochemistry.

Extracted raw water was composed of several groundwater partial flows, each with a different provenience and a different chemical alteration caused by hydrogeochemical processes along the flow paths (see Tab. 1). Hydraulic flow path characteristics and the mixing fractions of ground water from different flow paths were derived from the groundwater flow model.

3.1.1 Riverbank Filtration (RBF)

Most of the extracted water originated from RBF at the nearby infiltration zone. Its chemical composition was mainly influenced by short and long term variations in the river Rhine's water quality and microbial mediated processes in the filtration zone.

River quality represented an important time variant model input parameter. The quality of Rhine water deteriorated after 1950, caused by rapidly growing industry and an increasing density of urban settlements in the Rhine valley. Until the beginning of 1970s, oxygen concentration decreased below a concentration of 5 mg/L, while the concentration of DOC and trace elements like manganese or iron increased [1].

The measured and estimated development of Rhine water quality since 1952 used in modeling is shown in Fig. 4 for the parameters of

Table 1. Flow rates and mixing fractions of relevant groundwater flows toward Well II, catchment area Auf dem Grind, Düsseldorf waterworks.

Provenience	Volume (Mio. m^3/a)	Mixing Fraction in Raw Water (%)	Average Flow Time (years)
Riverbank filtrate from NW (nearby Rhine water infiltration zone)	5.546	*82.9*	0.07
Riverbank filtrate from SE (distant Rhine water infiltration zone)	0.397	*5.9*	7.5
Infiltrating surface water from SE (distant lake water infiltration zone)	0.198	*3.0*	12.5
Natural groundwater recharge	0.372	*5.6*	3.0[a)]
Riverbank filtrate after inter-percolation of tertiary sediments	0.105	*1.56*	15.0[a)]
Ascending deep saline groundwater	0.070	*1.04*	>>1000

[a)] Approximation based upon flow modeling.

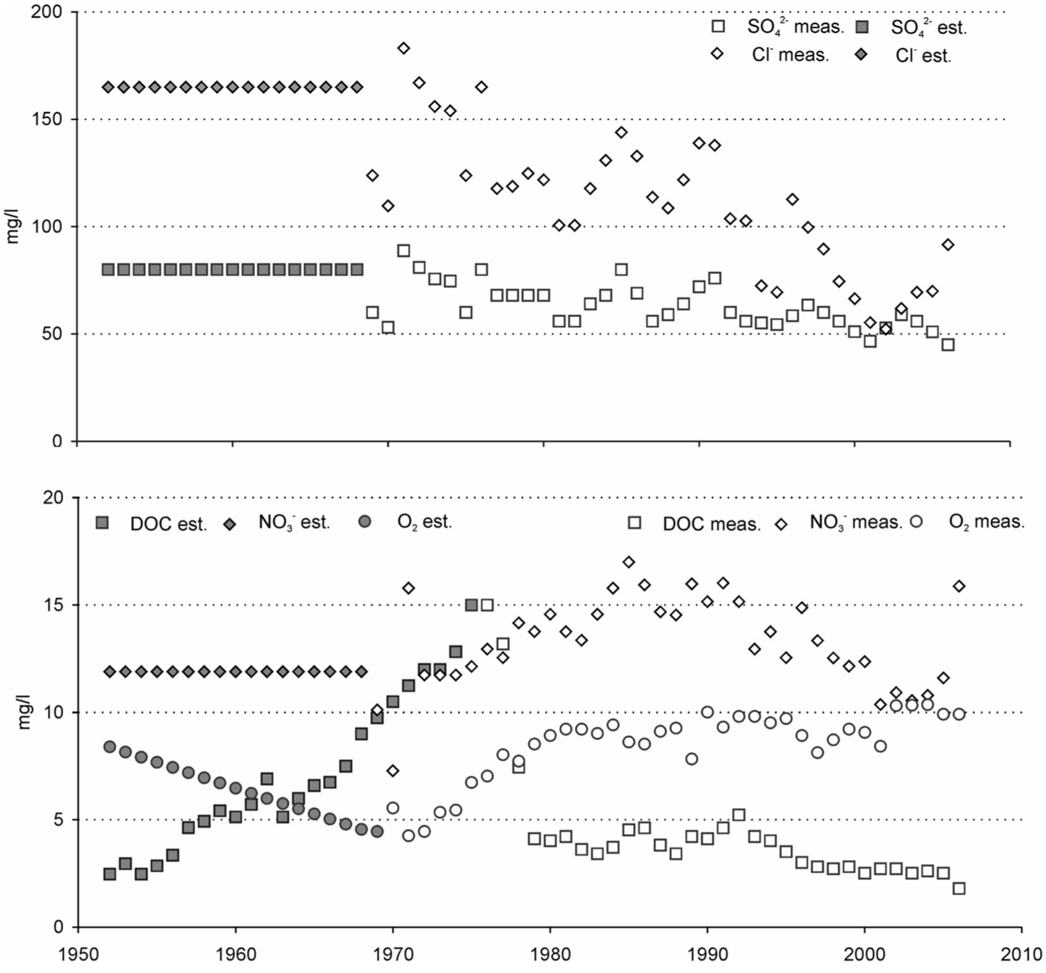

Figure 4. Time variant model input – development of river Rhine water quality. Between 1969 and 2008 integrated data from measurement stations Bad Honnef and Flehe (meas.) are shown. Before 1969 the input data are estimated (est.) for sulfate chloride nitrate and oxygen. DOC is estimated between 1952 and 1975.

sulfate, chloride, nitrate, dissolved oxygen and dissolved organic carbon (DOC). To represent significant trends and to harmonize different datasets from the adjacent measurement stations Flehe (approx. 7.0 km downstream) and Bad Honnef (approx. 80 km upstream), annual mean values were used. Although incomplete, data from Flehe are preferentially used to generate model input time series. Missing data were completed by trend based extrapolation from Bad Honnef data. For DOC and $O_{2(aq)}$, only data from the Bad Honnef measurement station was used.

In the past 30 years mean annual sulfate concentrations have decreased slightly from 80 to 50 mg/L. Long term chloride concentrations decreased from about 160 to 70 mg/L, with considerable fluctuations. At the end of the 1970s Rhine water quality improved significantly as a consequence of bringing sewage plants into service and an intensified monitoring of direct dischargers. DOC concentrations decreased from about 15 to 3 mg/L within 3 years. The mean annual concentration of dissolved oxygen slowly increased from 6.5 to 10 mg/L. Nitrate concentrations ranged nearly unaf-

Table 2. Average input water qualities.

Parameter	Unit	Mean River Rhine Water 2006	Rain Water 1998	Deep Saline Groundwater
Temperature	°C	15	10.00	10.00
pH	–	8.00	5.00	6.70
DOC	mg/L	2.80	0.00	0.00
Oxygen	mg/L	9.00	1.00[a]	0.00
Sulfate	mg/L	45.00	2.00	10.00
Chloride	mg/L	91,00	0.50	1500.00
TIC	mg/L	183.00	0.77[a]	635.00
Nitrate	mg/L	6.60	2.00	0.00
Ammonium	mg/L	1.45	0.75	0.50
Sodium	mg/L	53.70	0.40	540.00
Potassium	mg/L	5.58	0.50	0.00
Magnesium	mg/L	7.61	0.10	40.00
Iron	mg/L	0.00	0.00	10.00
Manganese	mg/L	0.00	0.00	0.10

[a] To calculate the concentrations of dissolved oxygen and total inorganic carbon, rain water is equilibrated with atmospheric partial pressures of oxygen and carbon dioxide.

fected from 10 to 15 mg/L, typically. A small decrease in nitrate concentrations was noticed since the mid 1990s.

Average seasonal changes in river water quality were simulated by modifying the parameters temperature, nitrate, DOC and dissolved oxygen. To calculate the development of raw water quality a backdated input in river water quality also has to be considered, with respect to mean residence times of ground water in the model stream tubes. Thus, river water quality from 1952 to 1969 has to be estimated. In the 1970s DOC concentration reached a maximum while oxygen concentrations hit a low mark [1]. Between 1952 and 1975 DOC concentrations raised steadily while oxygen declined linearly. For other parameters constant values were specified.

The composition of infiltrating river water changed during the infiltration process. Degradable DOC content in the river water decomposed within the first few decimeters after infiltration [2, 15–17]. This process influences the content of total inorganic carbon, pH and other components relevant for drinking water production. Seasonally varying river water composition clearly affected degradation processes within the infiltration zone. In winter conditions, $O_{2(aq)}$ decreased from 11 to 6 mg/L during infiltration, whereas in summer oxygen was completely reduced due to increased microbial activity [18]. Depending on the residence time, degradation of solid bound, non mobile organic carbon (OC) causes an additional decrease in oxygen and nitrate concentrations. Iron and manganese oxides and hydroxides are available in the filtration zone and the aquifer, but are virtually insoluble under present oxidizing conditions. Manganese oxides and hydroxides can be reductively dissolved merely under oxygen depleted conditions.

Preliminary considerations of raw water quality imply that in the period of high DOC and low $O_{2(aq)}$ concentrations in the 1970s, $O_{2(aq)}$ had been consumed completely by a high load of DOC during infiltration. In the absence of oxygen, manganese had been mobilized reductively from oxides and hydroxides in the sediments of the river bed. Although the river water quality has clearly improved in the last decades, manganese concentration remained at the level of 0.3 mg/L. Nowadays river water and riverbank filtrate remain under oxidizing conditions [1]. Except for local and short term conditions during summer months, manganese mobilization from river sediments is implausible. Thus, a different mechanism of manganese mobilization has to be considered.

3.1.2 Groundwater from Tertiary Sediments

Groundwater flow modeling showed that a minor fraction of the extracted groundwater originated from the underlying fine grained Tertiary sediments. This groundwater flow can be split into two partial flows: (i) ascending saline groundwater and (ii) river bank filtrate after inter-percolation of Tertiary sediments. Mixing fractions of both water types at total flow from underlying Tertiary sediments were determined by means of chloride concentrations in raw water. The chemical composition of deep saline groundwater was derived from groundwater analyses from deep monitoring wells in the north of the peninsula and is tabulated in Tab. 2. The ascending deep saline groundwater represents an additional source of manganese.

Due to the content of pyrite and biodegradable organic carbon in the Tertiary sediments, a typical redox sequence developed during inter-percolation of groundwater from the Quaternary aquifer. In the percolating RBF first, oxygen and nitrate were mainly reduced by pyrite. Ferrous iron and sulfate concentrations increased. Subsequently sulfate was reduced by organic carbon. Precipitation of iron sulfides may cause a decrease of the ferrous iron concentration. Reentering the Quaternary sediments, reduced species (e.g., Fe^{2+}, HS^-) get in reactive contact with manganese oxides and hydroxides that are contained as coatings on sediment grains. A reductive dissolution of manganese takes place. The dissolution of manganese oxides by ferrous iron proceeds rapidly at a time scale of hours under most natural conditions [19].

3.1.3 Surface Water

Surface water from a quarry pond in the hinterland of the peninsula infiltrated into the Quaternary aquifer and mixed in the well. The quarry pond itself was loaded with groundwater recharged under farmland in the south of the peninsula. Thus, the infiltrating surface water was strongly influenced by agricultural induced input of substances like nitrate and sulfate. Within the quarry pond, nitrate was reduced by biological and microbiological decomposition. The infiltrating groundwater was adjusted to groundwater quality, measured within a downstream monitoring well.

3.1.4 Recharged Groundwater

A small fraction of extracted raw water was natural groundwater recharged within the peninsula and its hinterland. The hinterland is an agricultural area predominantly utilized for mixed farming. The input of nitrate, sulfate, calcium etc. into the groundwater was subject to temporal dynamics. Analogue to the regional development in fertilization intensity which was derived from regional nitrogen surplus balances (www.lanuv.nrw.de/umweltindikatoren-nrw) [20], it was assumed that the input of nitrate and accompanying fertilizer compounds had increased until the mid 1980s. At maximum, a nitrate concentration of 60 mg/L and a sulfate concentration of 130 mg/L were assumed. Thereafter, fertilization intensity decreased to a level of 60% of the maximum value.

In the reactive transport model, rainwater with a constant composition (see Tab. 2) reacted with the induced fertilizer and soil air within the unsaturated zone. Thereby, a given amount of a magnesium-calcite reacted with the seepage water to adjust the pH to 7.0. The recharged groundwater percolated the Quaternary aquifer within an average of three years. Along the flow path groundwater

Table 3. Number of cells, flow rates, mean residence time and geochemical composition of relevant stream tubes toward Well II, catchment area Auf dem Grind, Düsseldorf waterworks.

	Parameter	Units				
Riverbank Filtrate from NW	Cells		1			
	Volumetric flow rate	m^3/a	$5.55 \cdot 10^6$			
	esidence time	d/cell	20			
	Calcite	mol/L	0.40			
	Ironhydroxide	mol/L	0.04			
	Manganite	mol/L	0.04			
	Organic Carbon	mol/L	1.00			
Riverbank Filtrate from SE	Cells	–	1	2–8	9	
	Volumetric flow rate	m^3/a		$0.397 \cdot 10^6$		
	Residence time	d/cell	20	365	365	
	Calcite	mol/L	0.40	0.08	0.08	
	Ironhydroxide	mol/L	0.04	0.04	0.04	
	Manganite	mol/L	0.04	0.04	0.28	
	Organic Carbon	mol/L	1.00	0.00	0.00	
Infiltrating Surface Water from SE	Cells	–	1	2–12		
	Volumetric flow rate	m^3/a		$0.198 \cdot 10^6$		
	Residence time	d/cell	365	365		
	Calcite	mol/L	0.08	0.08		
	Ironhydroxide	mol/L	0.00	0.04		
	Manganite	mol/L	0.00	0.04		
Natural Groundwater recharge	Cells		1-2	3		
	Volumetric flow rate	m^3/a		$0.372 \cdot 10^6$		
	Residence time	d/cell	365	365		
	Calcite	mol/L	0.08	0.08		
	Ironhydroxide	mol/L	0.04	0.04		
	Manganite	mol/L	0.04	0.28		
Riverbank Filtrate After Inter-percolation of Tertiary Sediments	Cells	–	1	2	3–15	16
	Volumetric flow rate	m^3/a		$0.105 \cdot 10^6$		
	Residence time	d/cell	20	365	365	365
	Calcite	mol/L	0.40	0.08	0.08	0.08
	Pyrite	mol/L	0.00	0.00	0.08	0.00
	Ironhydroxide	mol/L	0.04	0.04	0.00	0.04
	Manganite	mol/L	0.04	0.04	0.00	0.28
	Organic Carbon	mol/L	1.00	0.00	1.00	0.00
Ascending Deep Saline Groundwater	Cells	–	1			
	Volumetric flow rate	m^3/a	$0.070 \cdot 10^6$			
	Residence time	d/cell	365			
	Calcite	mol/L	0.08			
	Pyrite	mol/L	0.28			
	Organic Carbon	mol/L	1.00			

equilibrated with the available amounts of calcite and iron hydroxides.

To test model plausibility, the chemical composition of groundwater was compared with measured data of groundwater samples extracted from downstream monitoring wells.

3.2 Model design

Based upon this conceptualization, a reactive transport model was developed to identify and quantify relevant processes for the local mobilization of manganese and to retrace the measured raw water quality. The model calculated the development of surface and groundwater along different flow paths that reflect varying input functions and geochemical conditions in the aquifer. Based on the local equilibrium assumption of aqueous solutions including minerals and gas phases using the standard database wateq4f [21], equilibrium calculations were coupled with multiplicative Monod-type kinetics in order to model the sequential oxidative degradation of dissolved organic matter (DOC) and solid bound, non mobile organic carbon (OC) along different flow paths.

Geohydraulic aspects of the 3D groundwater flow system were extracted and transferred into the reactive transport model. The simplification of the geohydraulic system allowed a comprehensive modeling of hydrogeochemical aspects [22]. Hydraulic flow path characteristics and the mixing fractions of groundwater from different flow paths were derived from the groundwater flow model. The reactive transport model consisted of several model stream tubes. Each stream tube was defined by a series of cells (1D column).

Based on the number of recharge or infiltration zones, the catchment area was abstracted by five model stream tubes. Each stream tube represented a discrete recharge or infiltration zone and a

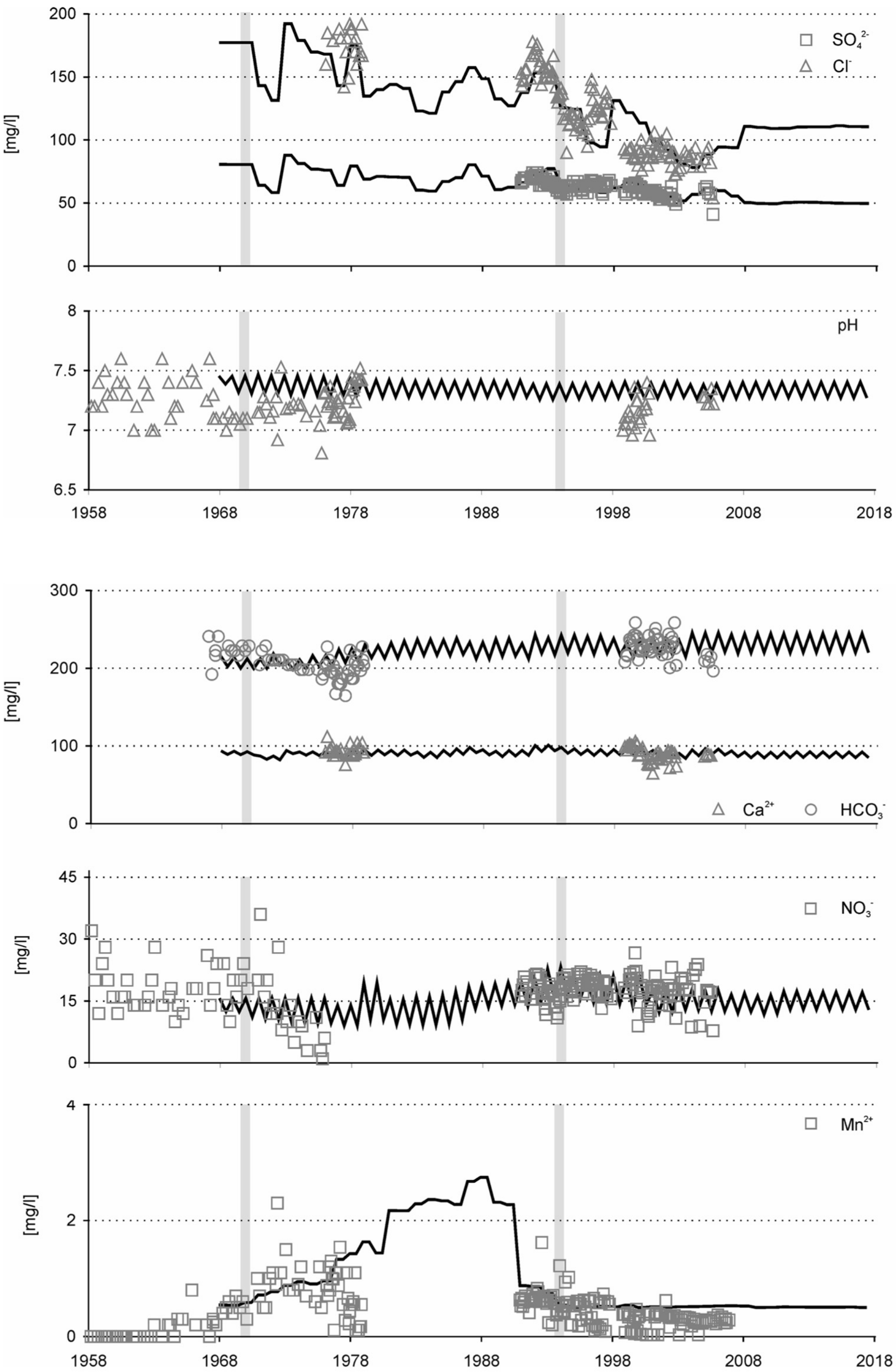

Figure 5. Development of raw water quality from 1958–2006 (symbols show measured data, lines show model results).

defined volumetric flow rate. Length of the flow path, number of cells, flow times, volumetric flow rates and reactive solid phases within the aquifer are listed in Tab. 3. For each model stream tube, a time step was specified for advective transport of water and solute species from cell to cell. The definition of a time step implied a temporal resolution for reactive transport calculations that enabled an implementation of kinetic calculations.

Site specific rate constants of both DOC and OC decomposition were derived from measured total inorganic carbon concentration increase between river water and groundwater of a downstream monitoring well, under consideration of the decrease in nitrate and oxygen concentrations. In this context, a temperature dependency on decomposition was noticed and implied into the model. For modeling, a scenario with an average summer temperature of 20°C and winter temperature of 10°C was defined. In summer, the decomposition of DOC and OC is 30 and 14 times higher than in winter, respectively. The decomposition of DOC and OC was realized by a kinetically controlled irreversible oxidation of CH_2O.

The resulting groundwaters of each model stream tube were synchronously mixed. The mixed water represented the modeled raw water for an explicit time that can be directly compared with time corresponding measured data.

Flow path and residence times determined the chemical alteration of the groundwater due to the sequence of hydrogeochemical zones and contact times between reactive solid phases and solute species in the flowing groundwater. Phase assemblages and amounts of reactive phases of different hydrogeochemical zones are listed in Tab. 3.

4 Results

Model results are shown in Fig. 5. In this diagram, modeled and measured data can be directly compared. Looking at the long term trends, the model retraces the concentration levels, as well as temporal trends, for all parameters. This applies to both non reactive solute species like chloride and sulfate, as well as solute species like calcium, hydrocarbonate and hydrogen ions (pH). Variations in chloride and sulfate concentration in raw water were caused by changes in river water quality. Whereas, hydrogeochemical processes in the infiltration zone and the aquifer superimposed calcium, hydrocarbonate concentrations and pH. Seasonal variations in raw water quality reflect short term fluctuations in raw water quality with respect to pH but also nitrate, calcium and hydrocarbonate concentrations. Measured data and model results typically achieved an annual maximum in winter, while concentrations decline in summer months. In this context, model data represented annual fluctuations in raw water composition by calculating the average raw water for summer and winter season. In this calculation extreme values were not considered.

The modeled manganese concentrations gave a fair match to measured data. Model results showed a clear increase in manganese concentrations up to a maximum of approximately 3 mg/L within the data gap period from 1978 to 1990.

Modeled long term trends of manganese concentration, as well as other parameters like pH, calcium, hydrocarbonate and sulfate concentration, agreed with measured data of raw water quality. By retracing a large number of parameters, the plausibility of model results was tested. Thereby, the reactive transport model was confirmed in its underlying hydrogeochemical and geohydraulic processes.

5 Discussion

The retrospective modeling results revealed the principles of long and midterm changes in raw water quality among other fluctuations in manganese concentration. In this context, model results of the catchment area of Auf dem Grind showed that manganese concentration in raw water was the result of two processes. Due to the pollution of Rhine water in the 1970s with degradable dissolved organic substances, the aquifer became extensively anoxic. Under oxygen depleted conditions manganese oxides and hydroxides were reductively dissolved during percolation of riverbed sediments. The increase in pH caused by the dissolution of oxides and hydroxides was buffered by the equilibrium of calcite and carbonic acid. Until 1976 the nitrate concentration decreased due to an increased denitrification by DOC. Analogue to the DOC concentration of river water (see Fig. 4), the modeled manganese concentration was expected to decrease after 1976. At this point the second effect of river Rhine water pollution makes an impact. With 15 and 8 years retardation manganese charged groundwater from the Tertiary sediments and RBF from southeastern direction, respectively, mixes within the well. Anoxic and DOC loaded groundwater originating from RBF infiltrated the Tertiary sediments. Already low nitrate concentrations were completely reduced by pyrite and/or reactive organic carbon within the Tertiary sediments. Reentering the Quaternary sediments after approximately 15 years of percolation reduced species (e.g., Fe^{2+}, HS^-) reacted with manganese oxides and hydroxides contained in the form of coatings on sediment grains within the layer near the aquifer basement. A reductive dissolution of manganese takes place. After approximately 8 years infiltrating RBF from the southeast direction reached the well. Along the flow path DOC reacted with manganese compounds coupled to a mobilization of manganese near the aquifer basement. As a consequence, river water pollution had a second impact on raw water quality which was time delayed due to the slow percolation of sediments.

Between 1988 and 1994 the modeled manganese concentration dropped as a consequence of the sudden decrease of DOC within the river Rhine water in 1976 to 1979 (see Fig. 4).

At the end of the 1970s, Rhine water quality improved significantly. Nowadays river water and RBF are predominantly oxidized where manganese oxides and hydroxides remain insoluble. Thus, recent manganese concentrations originate from manganese mobilization due to infiltrating Tertiary groundwater. In the past and recent days the intensity of manganese mobilization depended on the concentration of reducing agents in groundwater from Tertiary sediments and the mixing fraction of this groundwater in the extracted water. However, the mixing fraction is a function of production rate and river water level. In this context, hydraulic controls of groundwater flow play a decisive role in raw water quality, but are not definitely clarified in detail.

A reactive transport model that calculates the development of raw water quality for all relevant parameters has proven to be an appropriate tool to reveal principles of long and midterm changes in raw water quality. Moreover, based on model-scenario effects of varying river water quality, agricultural fertilization practices and/or mixing fractions can be predicted. The quantitative understanding of coupled hydrogeochemical and hydraulic processes enables the development of sustainable strategies for optimizing raw water quality, e.g., with regard to a cost effective water treatment.

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