

REPORT

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LABORATORY COLUMN EXPERIMENTS ON OPTIONS FOR REDOX CONTROL IN INFILTRATION PONDS FOR ARTIFICIAL RECHARGE

Project acronym: OXIRED-2 WP3

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Colophon

Title

LABORATORY COLUMN EXPERIMENTS ON OPTIONS FOR REDOX CONTROL IN INFILTRATION PONDS FOR ARTIFICIAL GROUNDWATER RECHARGE

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Abstract

The redox environment is of utmost importance for the removal of organic compounds during artificial recharge. Within the research project OXIRE2 five laboratory sand column experiments with natural sediments from the Lake Tegel infiltration pond and with micro-sieved surface water from Lake Tegel (Berlin) were performed to study the possibility to control the redox environment. Special emphasis was given to the sediments, the set-up of the column experiments, and the contact time within the column. The sediment was used either untreated or heated to 200°C or 550°C to study the effect of activation of organic carbon at 200°C and the effect of at least partial removal of natural organic carbon at 550°C. Additionally, an artificially produced iron coated sand was used for a two-layer experiment to increase the residence time of compounds susceptible to sorption within a given redox zone.

Results reveal an immediate decrease of oxygen content at the outflow of the column in every experiment. Likewise, the redox potential also dropped significantly and immediately after the experiments started. However, the redox potential was significantly lower (approximately – 200 mV) in the experiments with the untreated or slightly heated sediments, and higher (about + 300 mV) for the experiment with the sediment heated up to 550°C. The redox zones known in natural environments developed also within the experiments even down to sulfate reduction at experiment No. 2.

Ozonation of the influent water did not change the redox environment at the outflow of the column indicating a high reduction capacity of the natural sediment in the column within the duration of the experiments of up to 19 days. A constant input of ozone and an extended duration of the experiments might lead to a depletion of organic carbon in the sand column which could increase the redox potential. However, a complete depletion of organic carbon is very unlikely for managed aquifer recharge systems.

The two-layer experiment with natural sand and artificially produced iron coated sands revealed that the iron coated sands had no influence on the redox system and only slight effect on the transport of ions. However, combining layers with different functionality might show great opportunities for designing and controlling redox systems especially with specific residence times in different redox zones for certain compounds in mind.

Zusammenfassung

Das Redoxmilieu ist von größter Bedeutung für den Abbau von organischen Substanzen bei der künstlichen Grundwasseranreicherung. Im Rahmen des Projektes OXIRED-2 wurde die Möglichkeit der Steuerung des Redoxmilieus anhand von Laborsäulenversuchen mit natürlichem Sediment vom Standort am Tegeler See und Wasser vom Tegeler See (Berlin) untersucht. Besondere Aufmerksamkeit wurde den eingesetzten Sedimenten gewidmet, dem entsprechenden Aufbau des Versuchs und der Reaktionszeit in der Säule. Die Sedimente wurden entweder unbehandelt eingesetzt oder bei einer Temperatur von 200°C bzw. 550°C behandelt, um den Effekt der Aktivierung des organischen Kohlenstoffs bei 200°C bzw. den Effekt einer Verminderung des Kohlenstoffgehalts (550°C) zu ermitteln. Zusätzlich wurden künstlich hergestellte Eisensande im Zuge eines Experiments mit zwei Sedimentlagen eingesetzt, um die Verweilzeit derjenigen Substanzen zu erhöhen, die an einem solchen Sediment verstärkt sorbiert werden.

Die Ergebnisse zeigen eine sofortige Verminderung des Sauerstoffgehalts am Ausgang der Säule bei jedem der durchgeführten Experimente. In gleicher Weise verminderte sich auch das Redoxpotential deutlich und umgehend nach Beginn des jeweiligen Experiments. Allerdings war das Redoxpotential mit etwa -200 mV bei den Experimenten mit dem unbehandelten oder bei 200°C behandelten Sediment deutlich niedriger als bei den Versuchen mit dem bei 550°C erhitzten Sediment (ca. +300 mV). Die auch unter natürlichen Verhältnisse ausgebildeten Redoxzonen konnten auch in den Experimenten beobachtet werden, bis hin zur Sulfat-reduzierenden Zone bei Experiment 2.

Die Ozonierung des Vorratswassers änderte nichts an den Redoxbedingungen am Ausgang der Säule, was auf die hohe Reduktionskapazität der natürlichen Sedimente in der Säule für die gewählte Versuchszeit von 19 Tagen hinweist. Eine konstante Eingabe von Ozon und eine längere Versuchsdauer könnten allerdings zu einem Aufbrauch des organischen Kohlenstoffs in der Säule führen und dies zu einem insgesamt höheren Redoxpotential. Allerdings dürfte ein derartiger vollständiger Aufbrauch des organischen Kohlenstoffs für künstliche Grundwasseranreicherungsanlagen auszuschließen sein.

Die 2-Schicht Experimente mit natürlichem Sand und künstlich hergestellten Eisensanden zeigten, dass die Eisensande keinen Einfluss auf das Redoxsystem hatten und nur einen marginalen Einfluss auf den Stofftransport in der Säule. Allerdings birgt die Verbindung von Schichten mit unterschiedlicher Funktionalität große Möglichkeiten zur Gestaltung und Steuerung des Redoxsystems insbesondere im Hinblick auf die Verweilzeiten von bestimmten Substanzen in unterschiedlichen Redoxzonen.

Résumé

La qualité du milieu redox est essentielle pour l'élimination des composés organiques dans les systèmes de recharge artificielle de nappes. Dans le cadre du projet OXIRED-2, les possibilités pour contrôler le milieu redox ont été examinées au moyen d'essais en colonne en laboratoire, effectués avec du sédiment naturel ainsi qu'avec de l'eau, tous les deux échantillonnés du lac Tegel (Berlin). Une attention particulière a été consacrée aux sédiments utilisés, à la configuration d'essai et au temps de réaction dans la colonne. Les sédiments ont été employés de manière non-traitée ou traités à une température de 200°C ou 550°C, pour déterminer l'effet de l'activation du carbone organique à 200°C et respectivement l'effet d'une diminution de la teneur de carbone à 550°C. En outre, au cours d'une expérience effectuée avec deux couches de sédiments, des sables ferrugineux artificiels ont été utilisés pour augmenter le temps de séjour des composés qui sont adsorbés de manière plus ou moins intense par un tel sédiment.

Les résultats montrent une diminution immédiate de la teneur en oxygène à la sortie de la colonne au cours de chacune des expériences effectuées. De la même façon, le potentiel redox a fortement diminué dès le début de l'expérience. Toutefois, le potentiel redox de -200 mV environ au cours des expériences effectuées avec le sédiment non-traité ou traité à 200°C, était beaucoup plus bas que lors des essais effectués avec le sédiment chauffé à 550°C (+300 mV environ). Lors des expériences, il était possible d'observer les zones redox également formées dans des conditions naturelles, jusqu'à la zone sulfato-réductrice lors de l'expérience 2.

L'ozonisation de l'eau n'a pas abouti à une modification des conditions redox à la sortie de la colonne, ce qui fait remarquer la capacité de réduction élevée des sédiments naturels dans la colonne pour la période d'essai de 19 jours. Un dosage d'ozone constant en combinaison avec une plus longue durée d'essai pourrait toutefois mener à un épuisement du carbone organique dans la colonne et, par conséquent, à un potentiel redox plus élevé. Il est cependant peu probable qu'un épuisement total du carbone organique ait lieu dans des systèmes de recharge artificielle.

Les expériences à deux couches effectuées au moyen de sable naturel et de sable ferrugineux artificiels ont prouvé que les conditions redox n'étaient pas affectées par les sables ferrugineux et que ces derniers n'ont eu qu'une influence marginale sur le transport des composés dans la colonne. Toutefois, la combinaison des couches présentant des fonctions différentes ouvre la voie vers de nombreuses possibilités concernant la conception et la régulation des systèmes redox, particulièrement en vue des temps de séjour de certains composés dans les différentes zones redox.

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Chapter 1 Introduction

1.1 Background

Managed Aquifer Recharge (MAR) is a technical measure to increase available groundwater resources using surface water while utilizing the natural attenuation capacity of the subsurface passage to improve the water quality. MAR systems consist of several parts, including the infiltration pond, a subsurface passage, and an abstraction facility (Figure 1).

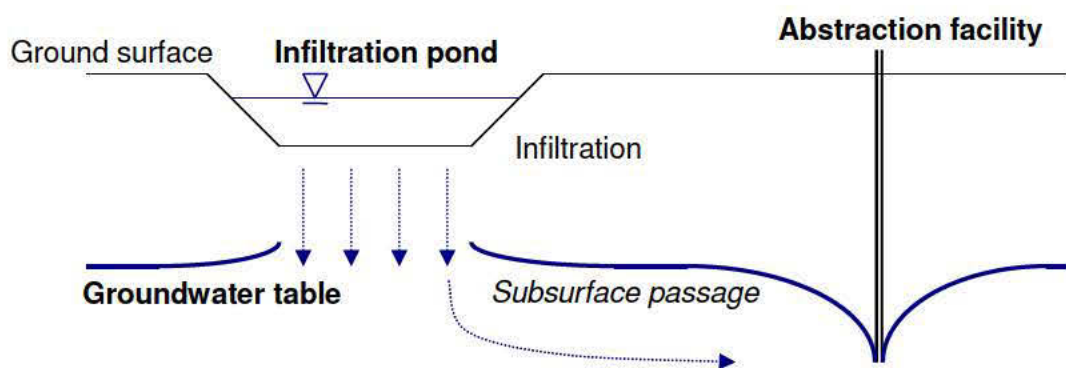


Fig. 1: Schematic cross section of a typical Artificial Recharge (AR) system (modified from Grützmacher & Reuleaux 2010)

During infiltration and subsurface passage a multitude of hydro- and geochemical processes take place (e.g. filtration, sorption, biological and chemical degradation of dissolved compounds) leading to a significant change in water chemistry. Amongst other environmental conditions like pH, ambient and water temperature, electrical conductivity, the redox potential plays a major role for degradation and transformation processes. Microorganisms and redox reactions often exhibit interdependencies with microorganisms that are adapted to the redox zones on the one hand and influence the redox environment on the other hand.

1.2 Redox Zonation

Redox reactions are characterized by an electron transfer between a reductant and an oxidant. The reductant acts as an electron donor while the oxidant is the electron acceptor.

For a redox reaction $wB_{\text{red}} + xC_{\text{ox}} \Rightarrow yD_{\text{ox}} + zG_{\text{red}}$ the application of the law of mass action, Gibbs free energy G and $\Delta G = nFE$ yields the Nernst-Equation:

$$E = E^\circ + \frac{RT}{nF} \cdot \ln \left(\frac{[D_{ox}]^y \cdot [G_{red}]^z}{[B_{red}]^w \cdot [C_{ox}]^x} \right) \quad [\text{Apello \& Postma 1996}] \quad (1)$$

with: R = gas constant = 8.314×10^{-3} kJ/mol K

T = absolute temperature [K]

[x] = concentration or chemical activity of compound x [mol/l]

n = number of transmitted electrons

F = Faraday's constant = 96.42 kJ/V.g

E° = standard potential for standard conditions [V]

E = potential [V]

The (redox) potential E is an indicator for the redox reactions taking place. The redox reactions result in a sequence of redox reactions from highly oxidized conditions to highly reducing conditions. Reduction reactions have to be coupled to oxidation processes and vice versa. It is generally observed in natural environments that redox processes proceed sequentially from the highest energy yield downward. Oxygenated water that is infiltrated in an aquifer rich in organic matter will first be freed from its oxygen content, then from its nitrate content, and subsequently sulfate is reduced. The effect of such sequences of redox reactions on water chemistry is illustrated in Fig. 2. In some cases, the disappearance of a reactant is monitored, while in other cases it is the appearance of a reaction product which is measured. It has been proposed to classify redox environments in terms of the presence or absence of indicative redox species rather than the redox potential itself.

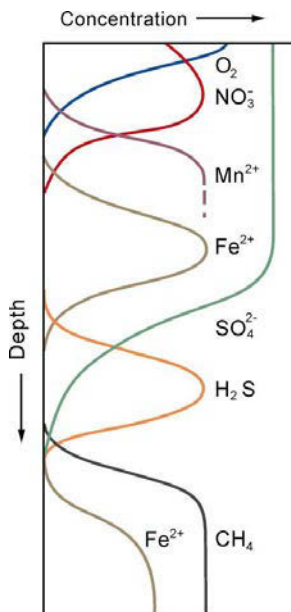


Fig. 2: The sequence of reduction processes as reflected by groundwater composition.

As groundwater travels along a flow path over a considerable distance and time, it becomes increasingly more reduced. This redox zoning may also be apparent at MAR sites and even within the bottom layer of the infiltration basin. However, during artificial recharge hardly all redox zones subsequent are encountered. Therefore, an approach that focuses on the oxidizing zone based on the classification by McMahon & Chapelle (2008) was introduced in IC-NASRI [Wiese et al 2009].

Tab. 1: Classification of Redox Zones (based on [McMahon & Chapelle 2008]) applied for the interpretation of NASRI data [Wiese et al. 2009]

Redox zone	Redox species			
	Oxygen O ₂ [mg/L]	Nitrate NO ₃ ⁻ [mg/L]	Manganese Mn ⁺⁺ [mg/L]	Iron Fe ⁺⁺ [mg/L]
O ₂ -zone (oxic)	≥ 0.5	any	< 0.05	< 0.1
NO ₃ -zone (suboxic)	< 0.5	any	< 0.05	< 0.1
Mn-Zone (anoxic)	< 0.5	< 0.5	≥ 0.05	< 0.1
Fe-Zone (anoxic)	< 0.5	< 0.5	any	≥ 0.1
Mixed zone	does not meet the criteria above			

1.3 Redox Zones at Infiltration Systems

It has long been noted that attenuation of organic and inorganic compounds is often related to the redox conditions. For MAR sites Grützmaier et al. (2010) compiled the removal of several compounds and substance groups relevant for drinking water treatment and their redox dependent removal during subsurface passage. For many substances, removal does not primarily depend on the redox condition. However some compounds exhibit a significant dependency on the redox conditions.

Substances and substance groups that show enhanced removal under **oxic conditions** are:

- cyanotoxins (microcystins – for others no information is available),
- ammonium
- DOC
- some pesticides (ureas, penoxy-herbicides),
- pharmaceuticals, x-ray contrast media and their transformation products (e.g. clindamycine, phenazone, propyphenazone, diclofenac, ibuprofen, iopromide, AAA, AMDOPH, AMPH, DP, FAA),
- some other trace organics (1,7-NDSA, 2,7-NDSA)

Under **anoxic to anaerobic conditions** the following substances and substance groups show enhanced removal:

- nitrate
- most disinfection-byproducts (THMs)
- some pesticides (triazines)
- some pharmaceuticals and x-ray-contrast media (sulfamethoxazole, carbamazepine, AOI)
- highly soluble chlorinated hydrocarbons (e.g. PCE)

Thus, a sequence of redox conditions may show a favorable effect on the elimination of a suite of compounds. Depending on the source water quality at MAR sites it may be favorable to develop intentionally a set of redox zones, from oxidizing conditions in the infiltration basin to more reducing conditions along the infiltration path.

As the infiltrating water will usually be saturated with oxygen due to direct contact with the atmosphere in the infiltration pond, oxic conditions will usually prevail upon direct infiltration. If none of the substances or substance groups that show enhanced removal under anoxic to anaerobic conditions (e.g. nitrate, THMs) occur in source water at drinking water relevant concentrations a complete oxic passage should be targeted in order to avoid iron- and manganese mobilization and thus, further post-treatment.

Tab. 2 gives an overview of substances and substance groups with redox-dependent removal characteristics and their respective optimum residence times compiled from existing publications.

Tab. 2: Time-dependent removal under oxic conditions (Grützmacher & Reuleaux 2010).

Substance / substance group	Residence time under oxic conditions		
	for up to 25 % removal	for up to 50 % removal	for 99 % removal
cyanobacterial toxins (microcystins)	no information	no information	> 9 d*
Ammonium	no time-dependency reported		
DOC	> 2 d**	> 30 d** (for high DOC not possible)	not possible
some pesticides (ureas, phenoxy-herbicides)	no time-dependency reported		
<i>PhACs and x-ray contrast media</i>			
clindamycine	> 2 d***	> 3.4 d***	> 25 d***
Diclofenac	> 10 d***	> 23 d***	> 200 d***
Iopromide	no information	> 7 d ⁺	no information
Phenazone	no information	> 2 d ⁺	no information
propyphenazone, AAA, AMDOPH, AMPH, DP, FAA	no time-dependency reported		
other trace organics (1,7-NDSA, 2,7-NDSA)	no time-dependency reported		
inorganic trace elements	Fe and Mn will be mobilized as soon as anoxic conditions prevail		

* Grützmacher et al. (2009)

** Lenk et al. (2006)

*** NASRI data from Berlin (Wiese et al. 2009)

+ Stuyfzand et al. (2007)

For substances and substance groups with enhanced removal under oxic conditions (Tab. 2), an optimum travel time in the oxic zone would be 30 d. After that diclofenac is the only substance for which additional travel time would create a benefit. If 30 d cannot be established, a minimum of 5 days should be achieved, in order to obtain a relevant decrease in DOC, algal toxins and pharmaceuticals. After 15 days maximum removal of microcystins, iopromide and phenazone is achieved and a further decrease in clindamycine, diclofenac and DOC concentration.

1.4 Aim of the Study

Observations from MAR systems and results from various studies on attenuation of pollutants in groundwater have shown that there is a significant decrease in concentration during flow in subsurface systems and that this reduction is often related to the redox zones. The aim of this study was to evaluate the possibility to influence and control the redox system such that elimination of pollutants is optimized. The study was set up as a laboratory experiment using saturated sand columns. The experiments were performed using natural sediments from the artificial recharge pond at Lake Tegel and natural surface water from Lake Tegel in order to upscale the results from the column experiments to infiltration pond scale. The experiments are the basis for modeling and interpretation of the possibilities to control the redox system within a managed artificial recharge system that will be documented in other reports (D 3.3 and D3.4).

Chapter 2

Materials and Methods

2.1 Setup column experiments

The aim of the experiments was to investigate the influence of different column setups on the physico-chemical parameters, on the tracer breakthrough, and most importantly on the redox environment. The following effects were studied in the experiments:

a) effect of ozonation,

b) effect of different sediments:

natural sediments

thermally treated sediments (200°C, 550°C)

two-layer experiments with artificially produced iron coated sands

A total number of five column experiments were performed between May and October 2010. In the course of each column experiment lithium bromide was applied as a tracer in order to acquire information about the relevant transport parameters (e.g. flow velocity, dispersion, retardation). The tracer solution of lithium bromide had a concentration of 10 mg L⁻¹. Lithium bromide was chosen as a tracer because the background concentration of both, lithium and bromide were below detection limit in all sediment and water samples used for the experiments. Bromide is known to have a so-called conservative transport characteristic without chemical reactions or sorption. Lithium also shows a high mobility, but has a known sorption behavior which can be used to characterize ion exchange and sorption within the column. Both ions can be analyzed in a rapid and cost-effective manner.

During each experiment the physico-chemical parameters pH, oxidation-reduction potential (ORP), electric conductivity (EC), and oxygen content were logged with devices and probes from WTW (*Wissenschaftlich Technische Werkstaetten*). For the column experiments 3, 4, and 5 the oxygen content of the inflow was logged as well during the whole experiment. The measuring interval was 10 minutes to log the physico-chemical parameters during the experiments. The general layout of the column experiments is presented in Fig. 3.

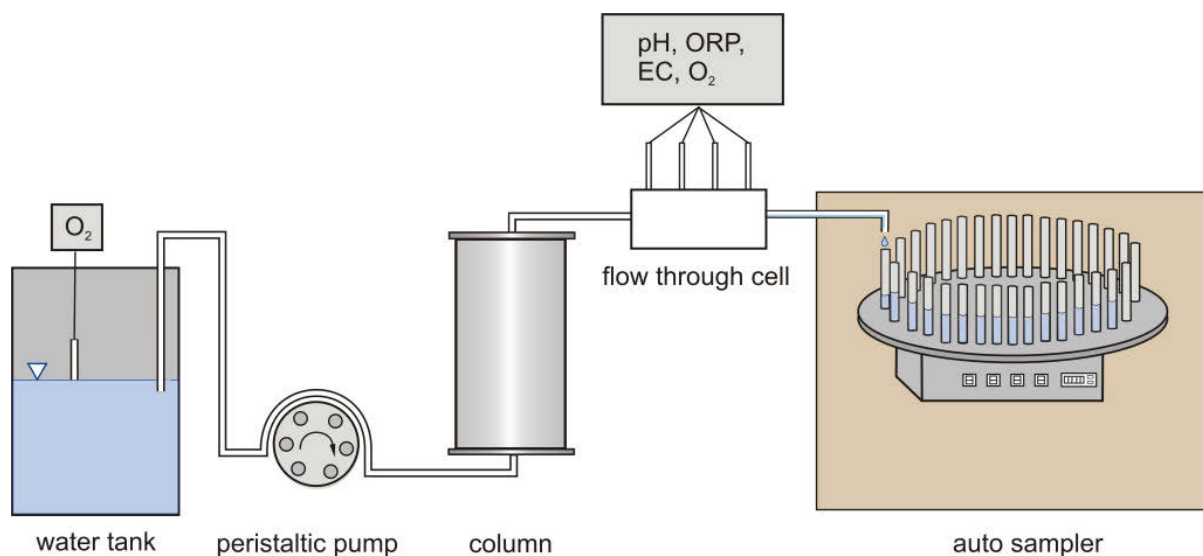


Fig. 3: Design of the column tests

Homogenized sediment was manually packed into the stainless steel column. The column has an inner diameter of 13.5 cm and a height of 35 cm. The sediment was added in approximately 3 cm increments and tapped lightly with a plunger. Care was taken to avoid obvious layering of the material or segregation of sediment by particle size. A gauze net was placed at the bottom and at the top of the column to prevent leaching of fine sediment particles. The bulk density ranges between 1.73 and 1.87 $g\ cm^{-3}$. The water flow is oriented from bottom to top in order to avoid oxygen inclusions in the column. With a porosity of 0.35, one pore exchange took between 20.9 h and 29.4 h depending on the water flow rate, which varied slightly in the experiments.

The column effluent was collected in fractions of approximately 75 mL with a fraction collector and frozen in the refrigerator. From all the samples collected, an appropriate subset of samples was chosen for laboratory analyses. After the experiment, the sand column was segmented and stored in case of further analyses.

The column was run with natural surface water from Lake Tegel, that was micro-sieved before sampling. The experiments were always started with an initial phase of 2 days with the above mentioned natural micro-sieved water. This phase was followed by a phase with the same water but this time it was ozonated water. The ozonated water was used throughout the main phase of the column experiment, but ozonation was only performed once before the water was used. Then, the tracer was added to the ozonated water. The tracer passage was followed again by a short period of ozonated water without tracer flowing through the column. Finally, the column experiments ended with a phase, where natural water without ozonation was applied. Beside the tracer and the ozonation, all other

parameters (e.g. flow rate) were kept the same during one experiment. The experiments took place at room / ambient temperature of approximately 21°C.

The following table summarizes the boundary conditions and settings of the column experiments.

Tab. 3: Boundary conditions and settings of the column experiments

No. of experiment	Layout of column, sediment	C_{org} content of sediment f_{OC} [kg_{OC} / kg_{total soil}]	Duration of column experiment [days]	Pumping rate [L h⁻¹]	One pore exchange [h]
1 (preliminary experiment)	Sediment not pretreated	0.0017	14	0.084	20.9
2	Sediment not pretreated	0.0017	14	0.078	22.4
3	Sediment pretreated at 200°C for 24 h	0.0019	11	0.078	22.4
4	Sediment pretreated at 200°C for 24 h 10 cm iron coated sand at column exit (within anaerobic zone)	0.0019	19	0.060	29.2
5	Sediment pretreated at 550°C for 8 h 10 cm iron coated sand at column entry (within aerobic zone)	0.0006	13	0.067	26.5

2.2 Test sediment

One type of natural sediment was used in all experiments, though each experiment was conducted with fresh sediment. The sediment was obtained from a MAR infiltration pond near Lake Tegel in Berlin / Germany (Fig. 4). This sediment was sampled from a depth of 0 to 0.5 m below surface at the bottom of the pond after the infiltration ponds were emptied for maintenance. The sediment used for the experiments presented here has already been used for other studies and will also be applied within further experiments within the OXIREO project.

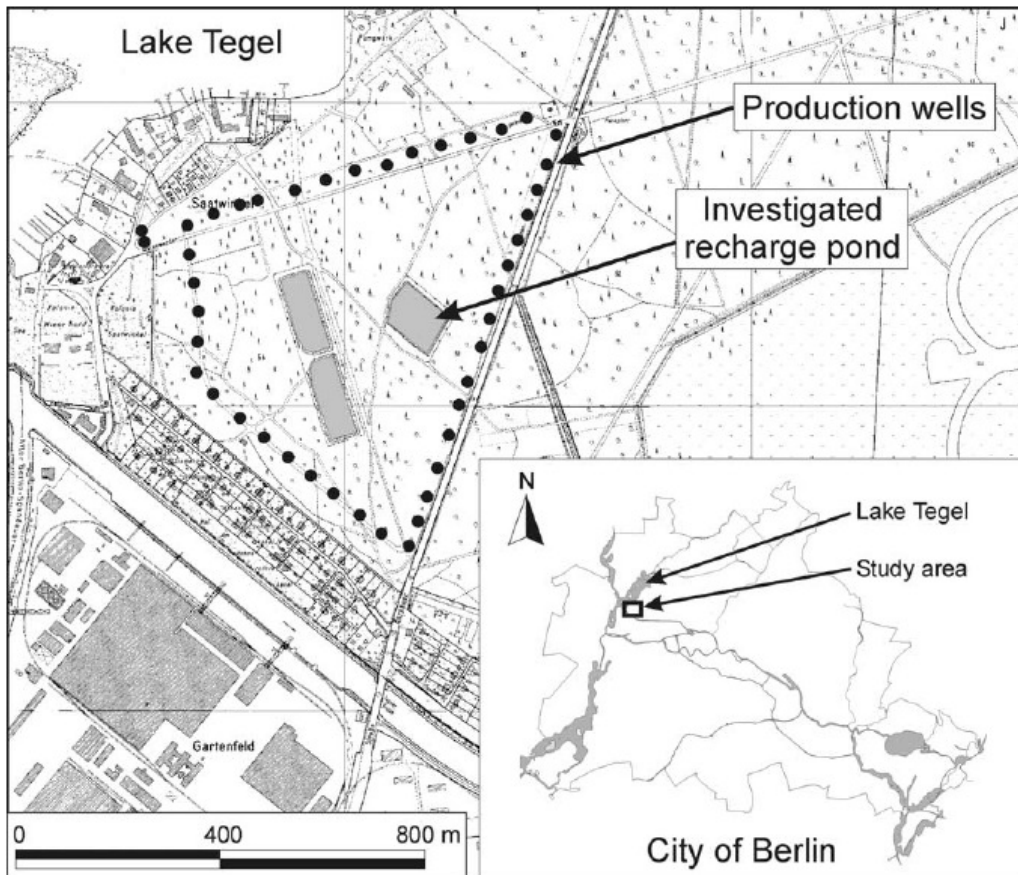


Fig. 4: Location of the infiltration pond Lake Tegel (Greskowiak et al. 2005)

The sediment consists of a medium grained sand and has a medium grain size of 0.38 mm. The hydraulic conductivity was determined using sieve analysis and was calculated to be $5.6 \cdot 10^{-4} \text{ m s}^{-1}$ (Hazen). The sediments' hydraulic conductivity can therefore be rated as pervious.

A second type of sediment was used as an artificial sediment (iron-coated sand) to simulate a two-layer system. The iron-coated sand was produced in the laboratory using artificial quartz sand with a grain size of 0.5 – 1.0 mm. First, a stock solution was prepared by dissolving $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in de-ionized water. Afterwards the sand was saturated in an acid solution with a pH of approximately 1. After rinsing and drying, the sand was brought into contact with the stock solution. The mixture of sand and iron oxide solution was placed in an drying at 50 °C for 96 h. After washing the sand again with de-ionized water, it was dried again at 50 °C for 96 h. Further details on the coating process are provided by Lai et al. (2000).

Iron coated sand was used to increase sorption for compounds inclined to sorb at a position in the column that is either at the beginning or at the end of the column. At the beginning of the column the redox environment is assumed to be still aerobic with oxidizing conditions whereas redox conditions near the outflow of the column are at least less oxidizing or even

anaerobic. However, the redox potential was only measured in the influent and the effluent, but not within the column.

Special emphasis was given to the treatment of the sediments. At first, two experiments were conducted with sediments that had not been treated with heat. The following two experiments were conducted with a thermal treatment of the sediment of 200°C for 24 hours. The final experiment was conducted with sediment that was treated for 8 hours at a temperature of 550°C. Treatment of the sediments was performed to study the influence of organic carbon within the sediment and its role for the redox environment.

2.3 Water

The influent water for the column experiments was sampled prior to each experiment at the microsieve facility Lake Tegel.

During the column experiments ozonated and not-ozonated Lake Tegel water was applied. The ozonation was performed at the Chair for Water Quality Control Center of the Technical University Berlin (Prof. Dr. Jekel). For the ozonation gaseous ozone was produced from pure oxygen and directly introduced into the water in a 4-L-semi-batch stirred tank reactor. The in-gas and off-gas ozone concentration, dissolved ozone and gas flow rate were measured continuously and an ozone mass balance was set up automatically. Ozonation was conducted without temperature adjustment at 20 – 25°C. The chemical properties of ozonated and not-ozonated water are compiled in Table 4.

Tab. 4: Chemical properties of ozonated and not-ozonated Lake Tegel water, Experiment # 5, one grab sample

<i>Type of water</i>	<i>Electric conductivity [$\mu\text{S}/\text{cm}$]</i>	<i>Oxidation-reduction potential [mV]</i>	<i>Oxygen content [mg L^{-1}]</i>	<i>pH</i>	<i>DOC [mg L^{-1}]</i>	<i>Calcium [mg L^{-1}]</i>	<i>Potassium [mg L^{-1}]</i>	<i>Sodium [mg L^{-1}]</i>	<i>Nitrate [mg L^{-1}]</i>	<i>Sulfate [mg L^{-1}]</i>	<i>Chloride [mg L^{-1}]</i>
Lake Tegel (not-ozonated)	721	333	7.3	7.9	8.9	103.2	6.7	40.9	6.6	103.6	54.9
Lake Tegel (ozonated)	732	424	21.0	8.0	8.8	101.7	6.6	40.4	6.6	101.3	53.3

The electrical conductivity and the pH value in both samples were in the same range. The main difference was the oxygen content which had a concentration of 21 mg L^{-1} after ozonation. Also, the ORP was different, with a lower value (around 330 mV) in the not-ozonated water and a higher value (approximately 420 mV) in the ozonated water. The chemical composition was similar in both samples.

2.4 Chemical Analysis

Throughout the column tests water samples (approximately 75 mL each) from the effluent of the column were collected at hourly intervals. The influent Lake Tegel water was sampled once per day. The following parameters were analyzed in all water samples:

- Cations (potassium, calcium, sodium, magnesium, lithium, iron, manganese, ammonia),
- Anions (chloride, bromide, fluoride, nitrate, sulfate),
- Dissolved organic carbon (DOC) and total organic carbon (TOC),
- Carbonate hardness (CH) (selected samples)
- Total hardness (TH) (selected samples).

The main ions were analyzed using inductively coupled plasma emission spectroscopy (*ICP-AES Trace Scan Thermo Jarrell*) and atomic absorption spectroscopy (*AAS-Analytik Jena NovAA 400G*) for the cations and ion chromatography (*Dionex DX 120*) for the anions. Limit of quantification was 0.05 mg/L for the anions and cations, except for lithium (LOQ of 0.1 mg/L).

The chemical composition of the infiltration pond sediment was analyzed with XRF (x-ray fluorescence) using a Panalytical PW 2400. The TOC of the sediment and water was analyzed with a TOC Analyzer (*Elementar LiquiTOC*). Limit of quantification for organic carbon was 0.1 mg/L.

2.6 Theoretical considerations and sand column transport characteristics

The one-dimensional convective-dispersive solute transport through a homogeneous medium, with linear and reversible equilibrium sorption without degradation of the solute, under steady-state flow can be described by the Convective-Dispersive Equation (CDE):

$$R_f \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v_{p,avg} \frac{\partial C}{\partial x} \quad (1)$$

where R_f is the retardation factor [-], C the normalized concentration (C/C_0) in the fluid phase at distance x [m] and time t [s], D is the hydrodynamic dispersion coefficient [$m^2 s^{-1}$] and $v_{p,avg}$ the average pore water velocity [$m s^{-1}$]. Molecular diffusion was neglected because of the high pore water velocity. Hydromechanic dispersion can be described as

$$D_L = \alpha_L \cdot v_{p,avg}^b \quad (2)$$

where D_L is the longitudinal hydromechanic dispersion coefficient [$m^2 s^{-1}$] and α_L the longitudinal dispersivity [m]; b has values between 0.9 and 1.2. Studies indicated that for

most purposes b could generally be taken as unity for sandy sediments (Freeze and Cherry, 1979). Studies on packed sand columns have found dispersivity to be higher under unsaturated conditions (Jin et al., 2000). Other studies found a decrease in dispersivity with desaturation in packed sand columns (James and Rubin, 1986; Wierenga and van Genuchten, 1989). Many factors contribute to changes in the hydrodynamic properties of sediment under unsaturated conditions, including the existence of regions of immobile water (two-region immobile water model), a wider variety in pore water velocities when media is unsaturated or an increase in air-filled pore space that increases the tortuosity of the solute flow path with desaturation (De Smedt and Wierenga, 1984).

An adequate analytical solution of Eq. (1) is presented by van Genuchten and Parker (1984). This analytical solution was used to obtain the retardation factors R_f .

$$R_f = \frac{v_{p,avg}}{v_{sp,avg}} = 1 + \frac{b}{\rho_b} \cdot K_d \quad (3)$$

where ρ_b is the bulk density [kg L^{-1} or: g cm^{-3} if water density = 1.000 g cm^{-3}], θ the volumetric water content [-], and K_d the sorption distribution coefficient [L kg^{-1}]. Retardation factors observed in column studies often differ from values determined by batch equilibration experiments (Porro et al., 2000). Increasing retardation factors could be due to decreasing water content, as expected from Eq. (3), or due to limitations in availability of sorption sites in batch vs. column experiments, or due to rate-limited geochemical reactions and physical nonequilibrium present under flowing (column) vs. static (batch) conditions (Hutchison et al., 2003).

The sorptive exchange of substances between the water phase and the solid phase may be described by sorption coefficients, that are defined as the ratio of the concentration of the substance in the solid phase c_{sorb} (mg kg^{-1}) and in water c_w (mg L^{-1}) at equilibrium. The simplest case of an isotherm occurs with a linear regression and a distribution coefficient K_d (L kg^{-1}).

$$c_{sorb} = K_d \cdot c_w \quad (4)$$

The distribution coefficient can also be derived from column tests using Eq. (3).

Chapter 3 Results

Column experiment 1 was a preliminary test, in order to optimize the set-up and functionality of the column configuration and to acquire first information on transport behavior. The description and discussion of the results focus on the physico-chemical parameter and the chemical analysis. The evaluation of the hydraulic parameters from the tracer breakthrough curves can be found in the UIT report (D3.3).

3.1 Breakthrough curves of the tracers

During each experiment lithium bromide was applied as a tracer with a concentration of 10 mg L^{-1} . A volume of 2 L ozonated water with tracer flowed through each column. The tracer breakthrough curves for the column experiments 2 to 5 are shown in Fig. 5 - 8.

In all cases, the bromide peak appears first. However, the lithium peak follows in all experiments with a delay between 2 (experiment 2) and 15 hours (experiment 4).

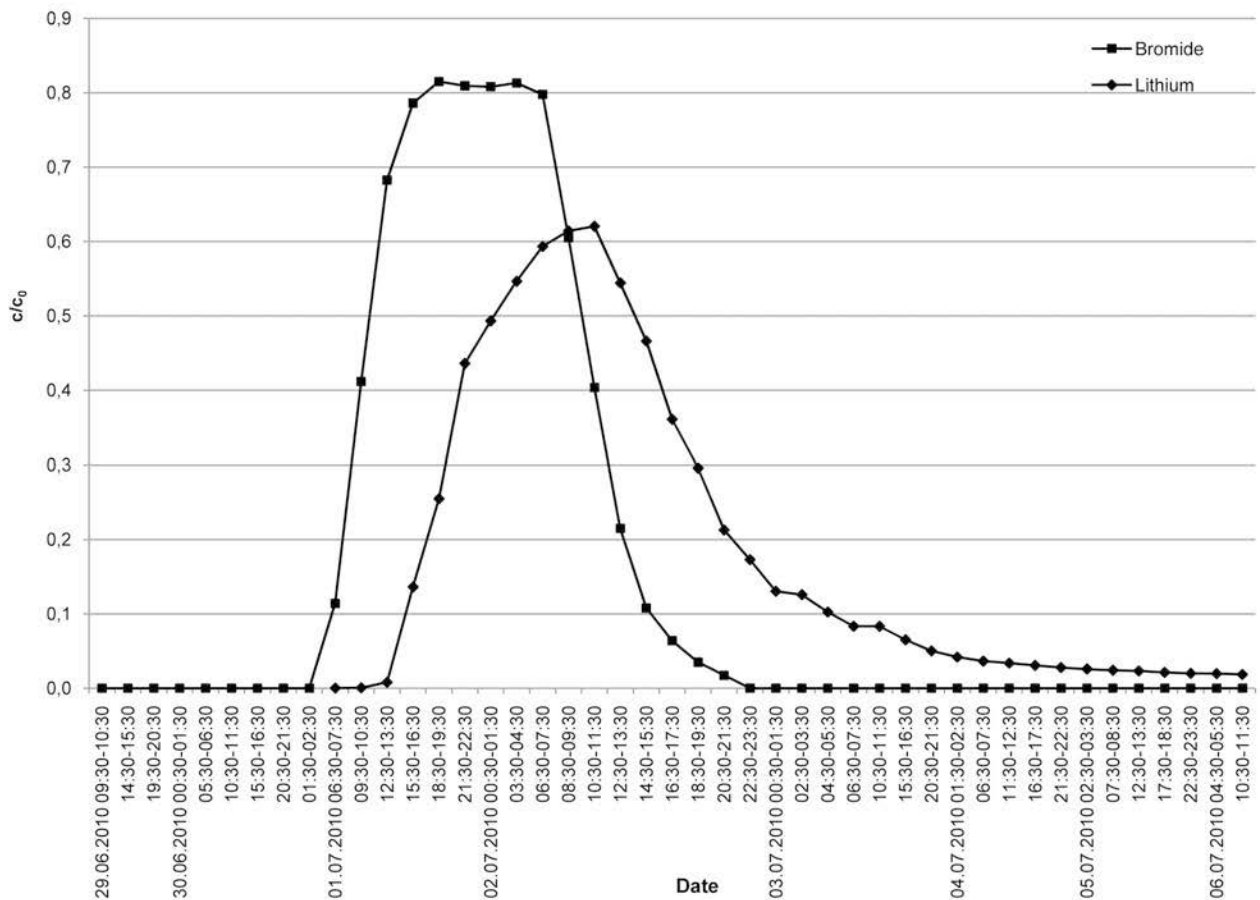


Fig. 5: Tracer breakthrough curves column test 2

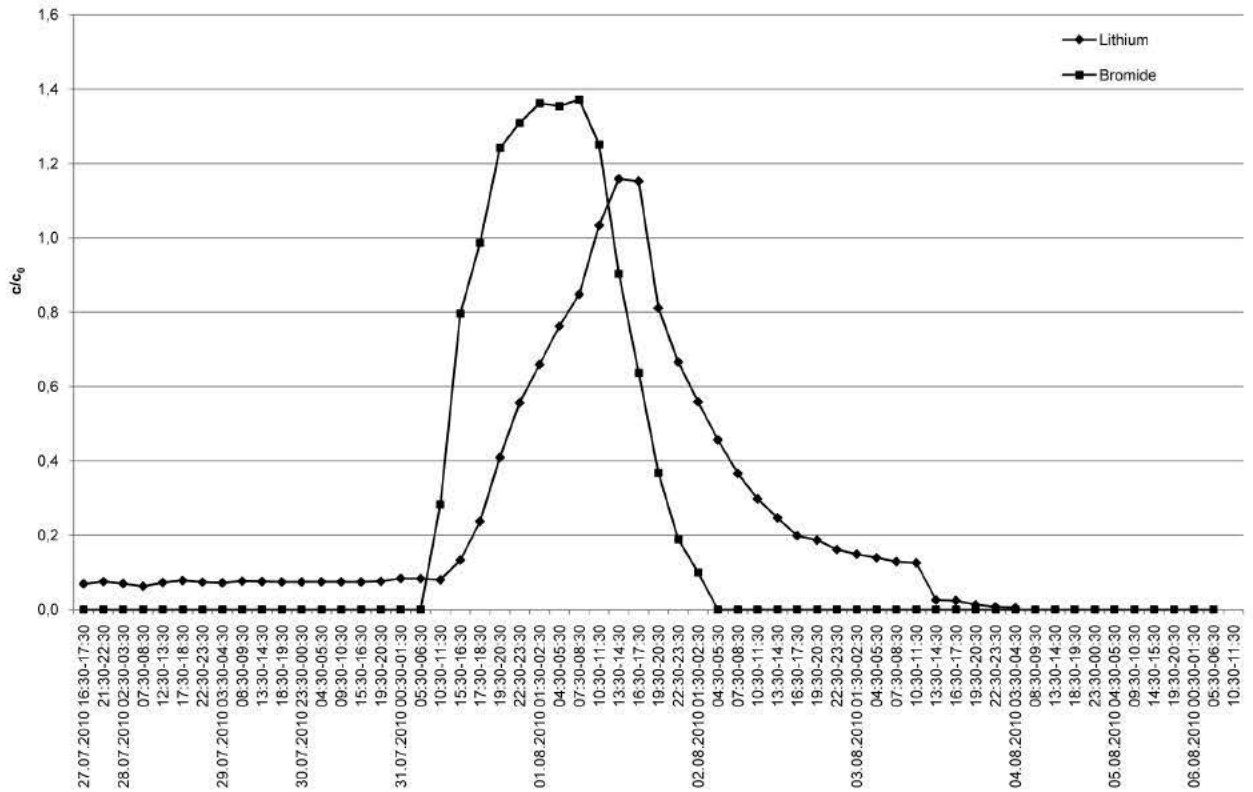


Fig. 6: Tracer breakthrough curves column test 3

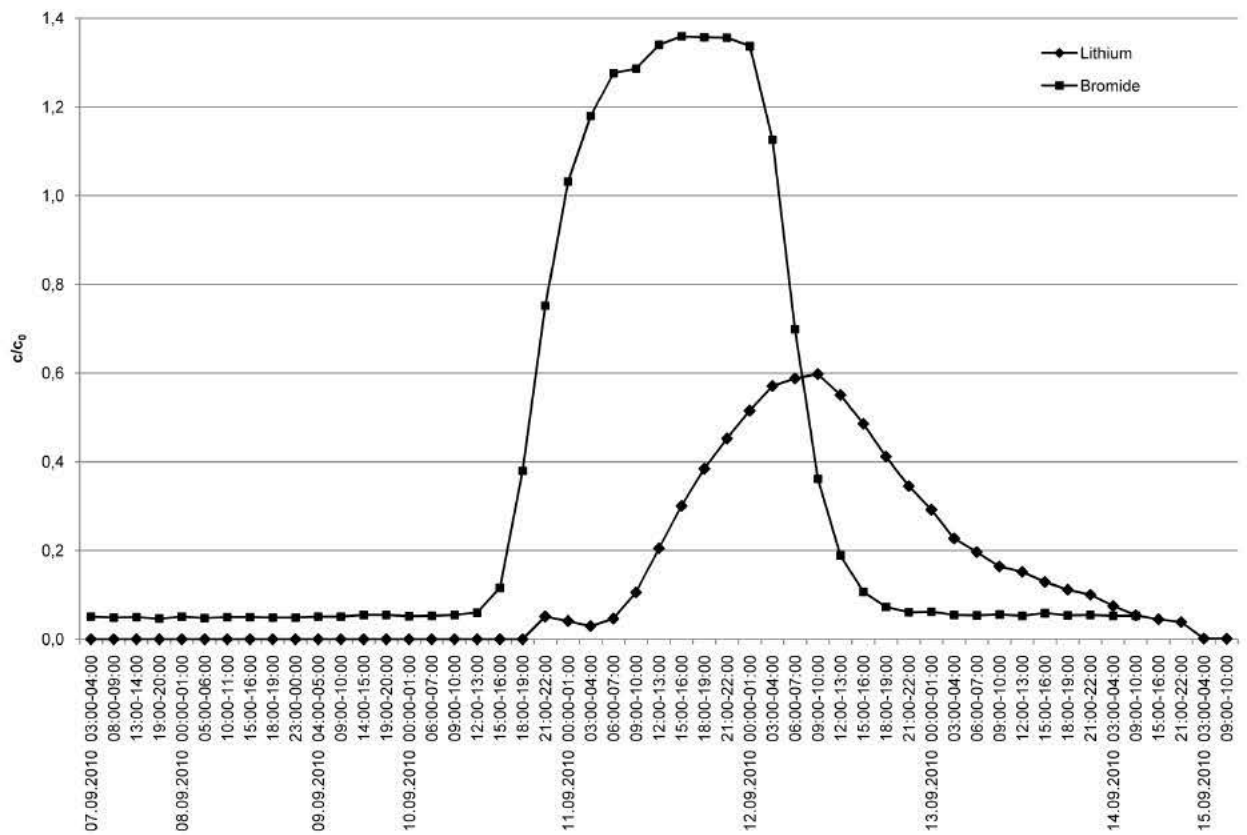


Fig. 7: Tracer breakthrough curves column test 4

3.2 Physico-chemical parameters

The physico-chemical parameters pH, ORP, electric conductivity, and oxygen content were logged during each experiment (Fig. 9 – 12).

The initial electric conductivity in all experiments was around $700 \mu\text{S cm}^{-1}$. However, different trends were observed during the experiments. In experiment 2 the electric conductivity ranges between 700 and $800 \mu\text{S cm}^{-1}$. The breakthrough of the tracer is also reflected by a temporal increase of the electric conductivity. This reflection of the breakthrough of the tracer was only observed that clearly in column experiment 2, in the other experiment the effect of the tracer was small or not observable. In column experiment 3 the electric conductivity continuously decreases over the test period from $> 1,000 \mu\text{S cm}^{-1}$ at the beginning to app. $700 \mu\text{S cm}^{-1}$. In the experiments 4 and 5 the electric conductivity remains more or less stable.

Of all parameters, the pH shows the smallest variation. The pH values ranged between 6.5 and around 7 in all experiments showing neutral conditions throughout all of the experiments. This was especially important as the pH may also influence the redox environment.

The oxygen concentrations were measured in the inflow and in the outflow (except for column experiment 2, where only the outflow was measured). General inflow concentrations were around 7 mg/L oxygen, whereas concentrations increased to almost 20 mg/L oxygen after ozonation. The outflow oxygen concentrations in column experiments 2-4 decrease rapidly at the beginning of the test and remain stable at very low concentrations around the detection limit of 0.1 mg L^{-1} . The change of the inflow from non-ozonated Lake Tegel water to ozonated Lake Tegel water showed up with clearly higher but constantly decreasing oxygen concentration at the inflow but this is not reflected in the outflow. Only in experiment 5 slightly higher oxygen concentrations were detected after the change from non-ozonated to ozonated water. The inflow oxygen concentrations increase every time fresh inflow water was connected to the system as depicted in Fig. 9-12 by the dashed lines.

In the column experiments 2-4 a fast decrease of the oxidation-reduction potential was observed reflecting the low oxygen concentrations and showing reducing conditions in the column. The ORP started in these experiments at values around +600 mV and dropped immediately after the start of pumping. Steady-state conditions were reached within the first three days with an ORP at around -200 mV. After the oxidants are depleted in the column, reducing conditions are predominant in these three experiments. Even the change of inflow from not-ozonated to ozonated water did not lead to an increase of oxygen in the outflow. In column experiment 5 (sediment has been pre-heated at 550°C and has therefore a lower organic carbon content) the ORP also decreases at the beginning. However, the ORP then

remains stable at a value of approximately 300 mV. This indicates the strong influence of the organic carbon content in the sediment on the redox conditions within the column.

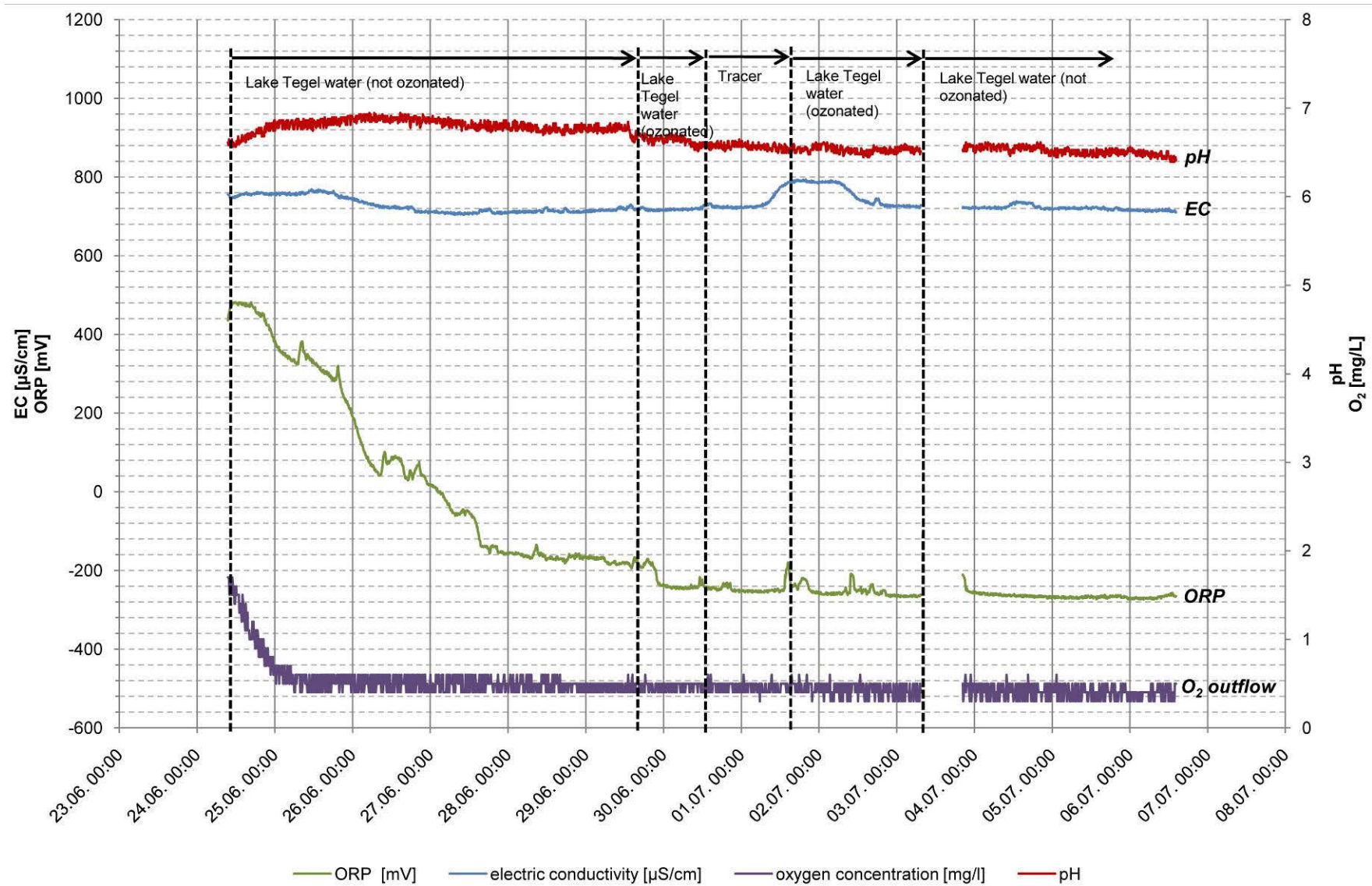


Fig. 9: Physico-chemical parameters column test 2

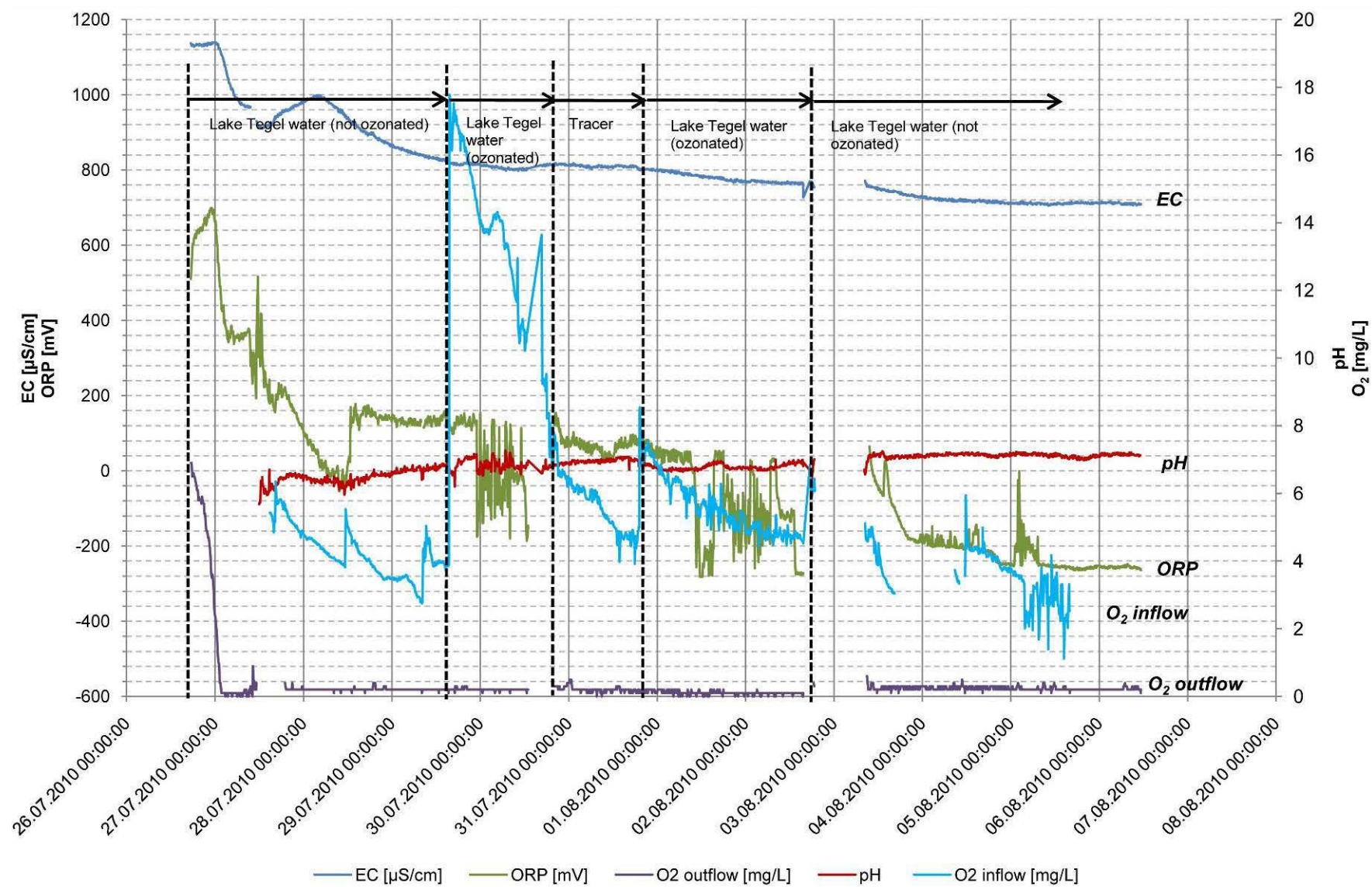


Fig. 10: Physico-chemical parameters column test 3

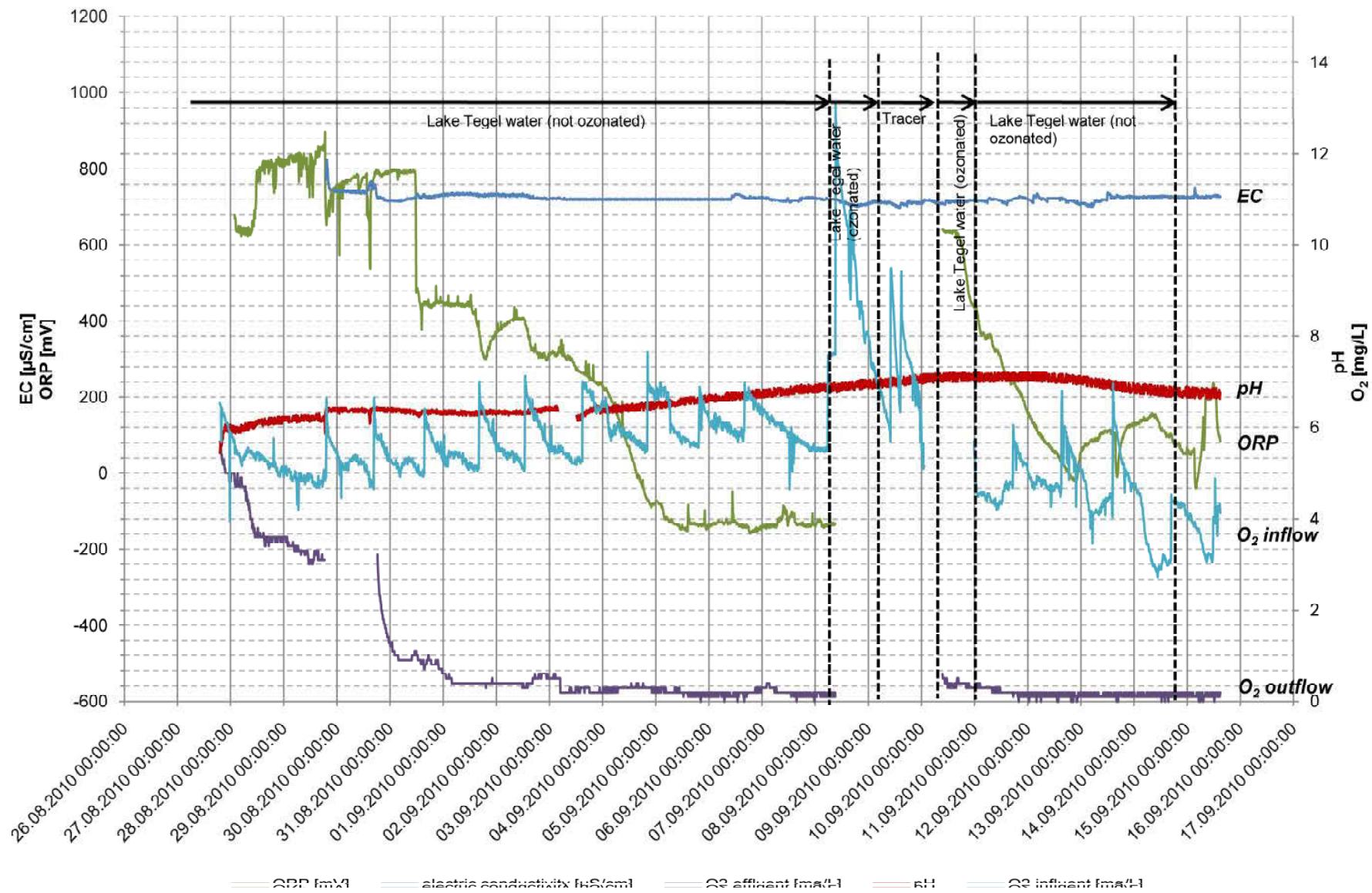


Fig. 11: Physico-chemical parameters column test 4

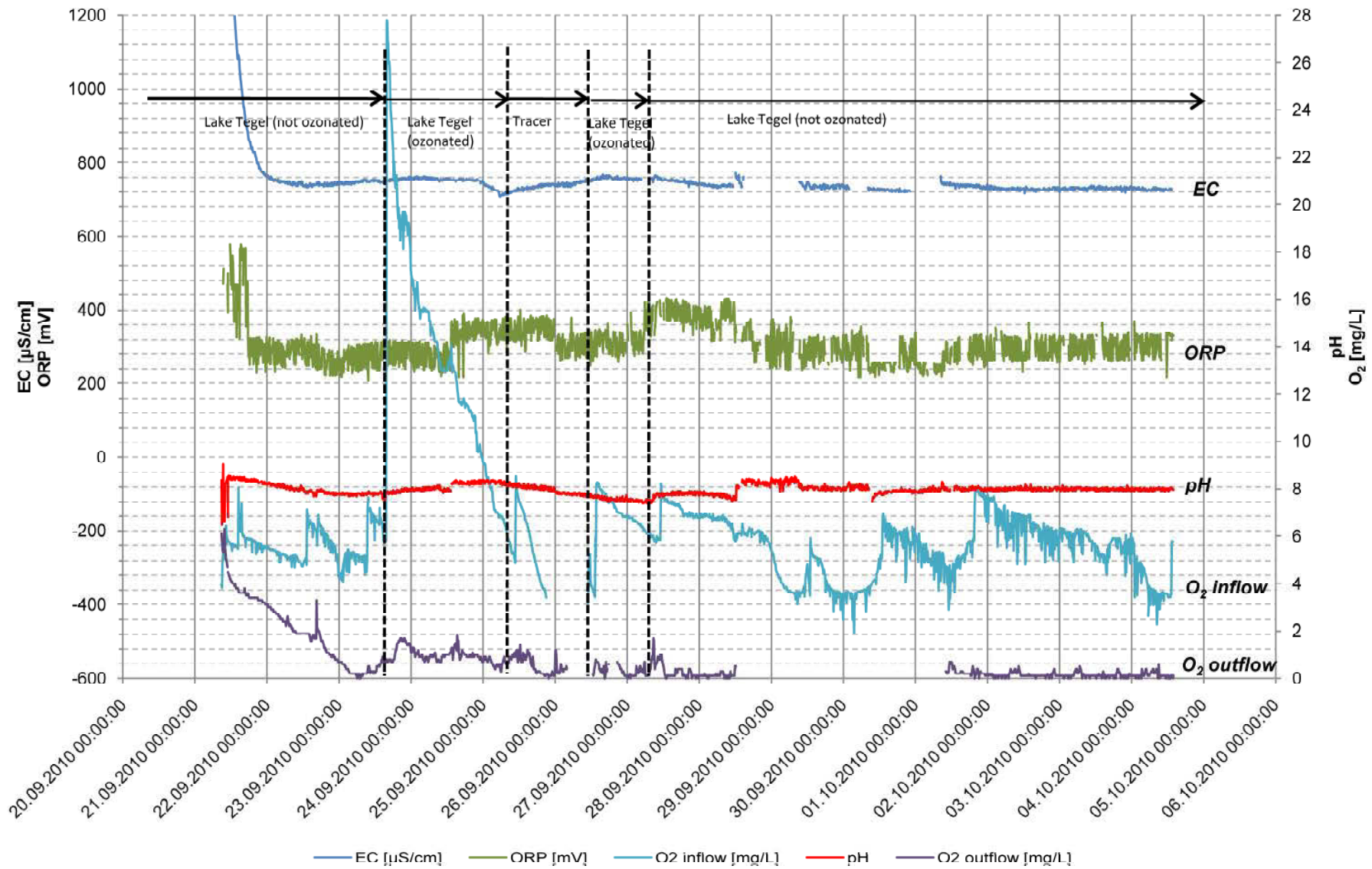


Fig. 12: Physico-chemical parameters column test 5

3.3 General ions and parameters

The results of the chemical analysis of the outflow samples are compiled in the annex.

Water samples from Lake Tegel both, ozonated and without ozonation were analyzed as well as the effluent at the outflow of the column. During the column tests 3, 4, and 5 the influent was sampled daily. In Tab. 5 the results of the influent analysis and a statistical evaluation of the results are compiled.

Tab. 5: Analytical results of influent water from Experiments # 2, 3, 4, 5; average of 35 samples (ozonated and not-ozonated)

bdl. – below limit of quantification, * tracer, for LOQ see paragraph 2.4

	<i>Chloride</i>	<i>Bromide</i>	<i>Nitrate</i>	<i>Sulfate</i>	<i>Potassium</i>	<i>Sodium</i>	<i>Calcium</i>	<i>Magnesium</i>	<i>Lithium*</i>	<i>Iron (total)</i>	<i>Manganese</i>	<i>DIC</i>	<i>DOC</i>	<i>DC</i>
	<i>mg/L</i>	<i>mg/L</i>	<i>mg/L</i>	<i>mg/L</i>	<i>mg/L</i>	<i>mg/L</i>	<i>mg/L</i>	<i>mg/L</i>	<i>mg/L</i>	<i>mg/L</i>	<i>mg/L</i>	<i>mg/L</i>	<i>mg/L</i>	<i>mg/L</i>
Median	56.3	0.56	7.0	105.6	7.2	41.7	102.0	13.6	0.02	bdl.	0.07	35.7	7.0	42.3
Mean	62.4	2.2	7.2	112.1	8.1	42.2	96.2	12.9	0.07	bdl.	0.07	35.1	9.0	44.1
Maximum	76.7	8.9	8.9	144.0	14.5	48.2	114.8	14.5	0.79	bdl.	0.12			
Minimum	52.9	0.49	5.1	29.0	6.4	38.3	67.1	9.3	0.01	bdl.	0.05			

The inflow chloride concentrations range between 76.7 and 52.9 mg L⁻¹. The sulfate concentrations in the inflow are mostly > 100 mg L⁻¹. The nitrate concentrations are between 8.9 and 5.1 mg L⁻¹. The sodium and potassium concentrations range between 38.3 and 48.2 mg L⁻¹ and 6.4 and 14.5 mg L⁻¹, respectively. During column test 3 lower calcium concentrations were analyzed between 70 and 80 mg L⁻¹. During the column tests 4 and 5 the calcium concentrations are higher > 100 mg L⁻¹. Also, the magnesium concentrations decrease from column test 3 to column test 5 and range between 9.3 and 14.5 mg L⁻¹. Iron was not analyzed above the limit of quantification (0.05 mg/L) in any inflow sample and the manganese concentrations ranged between 0.05 and 0.12 mg L⁻¹. The ozonated Lake Tegel water as well as the non-ozonated water was analyzed in order to obtain information on the influence of ozonation on the inorganic composition. The direct comparison of the analytical results indicates that the ozonation has no influence on the analyzed inorganic parameters.

The oxygen content and the nitrate concentrations in the outflow show a fast depletion during the experiments (Fig. 13). At the beginning of the experiments (2 and 5) high nitrate concentrations (max. 14.5 mg L⁻¹) were analyzed in the outflow samples. Within 24 to 48 hours the nitrate concentrations decrease below the detection limit or to approximately 1 mg L⁻¹, respectively. Low nitrate concentrations were analyzed throughout the whole time in experiments 3 and 4.

In the column experiment 2 decreasing sulfate concentrations indicate starting sulfate reduction. In the other experiments no evidence on sulfate reduction was found. Generally, the sulfate concentrations were > 100 mg L⁻¹.

The effluent chloride concentrations ranged between 70 and 50 mg L⁻¹ and did not change while passing the columns. The fluoride concentrations in column experiment 5 decrease at the beginning of the experiment. However, in all other experiments the fluoride concentrations remain stable (0.8 – 0.2 mg L⁻¹) and do not change between inflow and outflow. The effluent sodium concentrations are quite similar in all experiments and range between 35.0 mg L⁻¹ and 61.8 mg L⁻¹. The effluent potassium and calcium concentrations are in the same range as the influent concentrations. Iron was analyzed below the detection limit or in low concentrations <1 mg L⁻¹. Manganese was not detected in column experiment 5. However, in all other experiments the manganese concentrations ranged between 5.7 mg L⁻¹ (starting phase of experiment 3) and 0.1 mg L⁻¹.

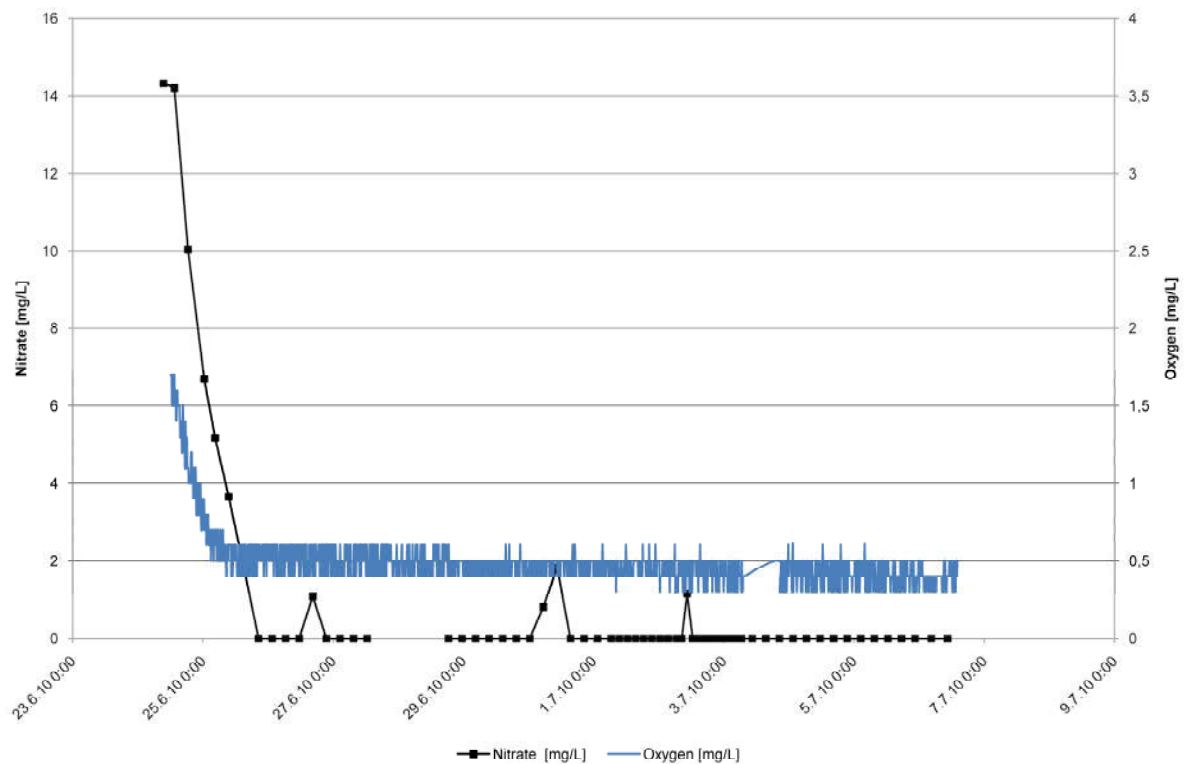


Fig. 13: Oxygen and nitrate concentrations in column test 2

In column experiment 3 a removal of DOC was observed during the experiment. The DOC concentrations decreased from 50.3 mg L⁻¹ at the beginning of the experiment to 10.8 mg L⁻¹ at the end of the experiment. High DOC concentrations at the beginning of the experiments are attributed to the elution of DOC in the first phase of the experiment. However, this effect was not observed in the other experiments. Most likely this effect was due to an activation of organic carbon due to thermal treatment at 200°C. In experiment 4 the sediment was also treated at 200°C but the column was used as a 2-layer-column where the iron-coated sand was free of organic carbon.

Chapter 4

Summary and conclusions

The experiments presented here should reveal the possibility to influence and control the redox environment at infiltration ponds in order to influence the elimination of several relevant compounds like DOC and PHACs. In this study sand column experiments with natural sediment and water from artificial recharge ponds with some variations on the sediments and on the sediment layers were used to determine the possibility to control the redox environment.

In total, five laboratory sand column experiments were performed. The experiments differ in the pretreatment of the sediment and the sediment layers. The following pretreatments were applied to the sediments:

- Experiment #1:
 - Preliminary test
- Experiment #2:
 - Sediment from infiltration pond (not pretreated)
- Experiment #3:
 - Sediment infiltration pond (pretreated 24h at 200°C)
- Experiment #4:
 - Sediment infiltration pond (pretreated 24h at 200°C);
 - 10cm iron coated sand column exit (within anaerobic zone)
- Experiment #5:
 - Sediment infiltration pond (pretreated 8h at 550°C);
 - 10cm iron coated sand column entry (within aerobic zone)

The short-term column experiments were conducted at water-saturated conditions to study the infiltration conditions at MAR sites. The experiment temperature (20°C to 25°C) reflected typical summer conditions for the Berlin area. The sediment was sampled at an infiltration pond at Lake Tegel. For all experiments Lake Tegel water was applied, which was additionally ozonated for certain periods. Due to this setup with natural sediment from the AR pond Lake Tegel and water from Lake Tegel the results from the experiment elucidated the observations from the field, especially the observed low redox potential in the infiltration water in the initial phase of infiltration at AR pond Lake Tegel.

Column experiments 2-4 show a fast decrease of oxygen content and redox potential. Reducing conditions (lower than ± 0 mV) were predominant in these column experiments

after 3 days and reached generally values around -200 mV. After oxygen reduction and denitrification, even beginning sulfate reduction could be observed in column test 2.

The effect of ozonation was clearly observed in the influent with oxygen concentrations increasing to almost 20 mg/L. This also changed the concentrations of the trace compounds in the influent as shown by a parallel study. However, the effect on the column conditions and on the effluent were by far not that obvious. Due to the natural conditions regarding microbiology and due to the organic carbon in the water and in the sediment and due to available nutrients microbially catalyzed redox reactions proceeded even the influent was ozonated. It could be speculated that for ongoing ozonation of the influent and after all organic carbon in the sediment and in the water is used redox conditions might eventually change to oxidizing conditions. However, this did not occur during the experimental duration of 14 days. The effect of ozonation was constrained to the influent water.

The thermal treatment of the sediment at 200°C did not lead to different natural redox conditions compared to the redox conditions developing for untreated sediment. However, the decrease in redox potential and respective ions shows the high reactivity of this thermally treated sediment. Most likely the thermal treatment has even increased the reactivity comparable to the reactivity of activated carbon. Microbiology has not been studied specifically but based on the data it could be inferred that microorganisms were not completely removed from the sediment or that there was a fast buildup with microorganisms from the influent water. No precautions were taken for sterile handling of the equipment nor of the sediment and water used for the experiment.

In column experiment 5 (sediment pretreated at 550°C) the redox potential remained stable at values between +200 and +300 mV (oxidizing conditions), values that are significantly higher compared to the other experiments. From this experiment it can be concluded that a thermal treatment of the natural organic carbon at 550°C not only leads to a reduction of organic carbon (f_{OC} 0.06 %) but also to less reactivity of the remaining organic carbon. Furthermore, it can be assumed that microorganisms will be removed almost completely and that recovery time for microbiological activity is significantly longer compared to the thermal treatment at 200°C.

As expected, the implementation of iron coated sand in the column had no effect on the redox conditions within the column, but the transport characteristics of sorptive compounds may have changed with an increased residence time within the area of the iron coated sand. This was shown in a parallel study and is discussed in report D3.3. Generally, the effect of iron coated sands on sorption and on mobility of trace compounds and major ions was negligible.

The experiments have shown relatively simple ways to influence the redox potential at for the R site Tegel by thermal treatment of sediments. Ozonation did not have an observable influence on the redox potential but it influenced strongly the influent water. In natural environments it may lead to a significant decrease of concentrations of compounds that are transformed under oxidizing conditions and it may also lead to a reduced amount of dissolved organic carbon in the infiltration water. Further research may take into account ambient and influent temperature as well as flow velocity of the infiltration water.

Chapter 5 Bibliography

C.A.J. Apello, D. Postma, 1996. Geochemistry, groundwater, and pollution; A.A.Balkema Publishers.

F. De Smedt, F., P.J. Wierenga, 1984. Solute transport through columns of glass beads. Water Resour. Res. 20, 225 – 232.

R.A. Freeze, J.A. Cherry, 1979. Groundwater. Prentice-Hall, Englewood Cliffs, NJ.

J. Greskowiak, H. Prommer, G. Massmann, C.D. Johnsten, G. Nützmann, A. Pekdeger, 2005: The impact of variably saturated conditions on hydrogeochemical changes during artificial recharge of groundwater , Applied Geochemistry vol 20, p. 1409 – 1462, Elsevier.

G. Grützmacher, M. Reuleaux, 2011: Literature study on redox control for infiltration ponds and other subsurface systems. Report KompetenzZentrum Wasser Berlin.

G. Grützmacher, B. Wiese, I. Hülshoff, D. Orlikowski, E. Hoa, Y. Moreau-Le Golvan, 2009: Bank filtration and aquifer recharge for drinking water production: Application, efficiency and perspectives – an integration of NASRI-outcomes and international experiences ; Kompetenzzentrum Wasser Berlin.

B. Hölting, W. G. Coldewey, 2008: Hydrogeologie: Einführung in die Allgemeine und Angewandte Hydrogeologie, 7. Auflage, Spektrum Verlag.

J.M. Hutchison, J.C. Seaman, S.A. Aburime, D.E. Radcliffe, 2003. Chromate transport and retention in variably saturated soil columns. Vadose Zone J. 2, 702-714.

R.V. James, J. Rubin, 1986. Transport of chloride ion in a water-unsaturated soil exhibiting anion exclusion. Soil Sci. Soc. Am. J. 50, 177-181.

M. Jekel, Organics group TUB, 2006: Organic substances in Bank Filtration and Groundwater Recharge – Process Studies.

Jin, Y., Chu, Y., Li, Y., 2000. Virus removal and transport in saturated and unsaturated sand columns. J. Contam. Hydrol. 43, 111-128.

C.H. Lai, S. L. Lo, H. L. Chiang, 2000: Adsorption/desorption properties of copper ions on the surface of iron- coated sand using BET and EDAX analyses, Chemosphere Vol. 41, p. 1249-1255, Elsevier.

S. Lenk, F. Remmler, C. Skark, U. Schulte-Ebbert, 2006: Technische Konzepte und abgestimmte Betriebsweisen zur optimalen Anpassung der Uferfiltration an lokale Randbedingungen - Abschlußbericht zum Teilprojekt B1 im BMBF-Forschungsvorhaben Exportorientierte Forschung und Entwicklung auf dem Gebiet der Wasserver- und -entsorgung Teil 1: Trinkwasser. Institut für Wasserforschung GmbH Dortmund.

G. Mattheß, 1994: Lehrbuch der Hydrogeologie Band 2 - Die Beschaffenheit des Grundwassers, Verlag Gebrüder Borntraeger.

G. Massmann , J. Greskowiak , U. Dünnebier , S. Zuehlke , A. Knappe , A. Pekdeger, 2006: The Impact of variable temperatures on the redox conditions and the behaviour of pharmaceutical residues during artificial recharge ; Journal of Hydrology Vol 328, p.141-156.

- G. Massmann, J. Greskowiak, U. Dünnbier, S. Zuehlke, A. Pekdeger, 2005: The impact of alternating redox conditions on groundwater chemistry during artificial recharge in Berlin; 5th international symposium Aquifer recharge 2005.
- G. Massmann, T. Heberer, G. Grützmacher, U. Dünnbier, A. Knappe, H. Meyer, A. Mechlinski, A. Pekdeger, 2007: Trinkwassergewinnung in urbanen Räumen – Erkenntnisse zur Uferfiltration in Berlin. Grundwasser – Springer Verlag.
- G. Massmann, A. Nogeitzig, T. Taute, A. Pekdeger, 2007: Seasonal and spatial distribution of redox zones during lake bank infiltration in Berlin, Germany. *Environment & Geology*.
- G. Massmann, U. Dünnbier, T. Heberer, T. Taute, 2008: Behaviour and redox sensitivity of pharmaceutical residues during bank filtration – Investigation of residues of phenazone-type analgesics. *Chemosphere* vol. 71, p. 1476 - 1485.
- U. Miehe, C. Hinz, E. Hoa, G. Grützmacher, 2009: DOC & Trace removal via ozonation & underground passage – expected benefit and limitations (OXRED1), KWB-Report.
- A. Pekdeger, 2006: Hydrogeochemical processes during bank filtration and ground water recharge using a multi-tracer approach; NASRI.
- I. Porro, M.E. Newman, F.M. Dunnivant, 2000. Comparison of batch and column methods for determining strontium distribution coefficients for unsaturated transport in basalt. *Environ. Sci. Technol.* 34, 1679-1686.
- P. J. Stuyfzand, W. Segers, N. van Rooijen, 2007: Behavior of pharmaceuticals and other emerging pollutants in various artificial recharge systems in the Netherlands, pp. 231-245. In P. Fox (Ed.): ISMAR6 - 6th International Symposium in managed aquifer recharge - Management of aquifer recharge for sustainability ACACIA, Phoenix, Arizona, Phoenix, Arizona, USA.
- M.Th. van Genuchten, J.C. Parker, 1984. Boundary conditions for displacement experiments through short laboratory soil columns. *Soil Sci. Soc. Am. J.* 48, 703-708.
- P.J. Wierenga, M.Th.van Genuchten, 1989. Solute transport through small and large unsaturated soil columns. *Ground Water* 27, 35-42.
- B. Wiese, D. Orlikowski, I. Hülshoff, G. Grützmacher, 2009: Removal of 38 organic water constituents by bank filtration in Berlin – a comprehensive analysis of NASRI data (IC-NASRI); Kompetenzzentrum Wasser Berlin gGmbH, Berlin.