# Assessing the Impact of Different Redox Conditions and Residence Times on the Fate of Organic Micropollutants during Riverbank Filtration

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# Assessing the Impact of Different Redox Conditions and Residence Times on the Fate of Organic Micropollutants during Riverbank Filtration

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## Abstract

Riverbank filtration and artificial groundwater recharge are well established techniques in Germany that are often used as an important component of the established multiple barrier system. Passage of water underground provides several benefits for drinking water treatment. Experience demonstrates that during infiltration and underground transport, processes such as filtration, sorption, and biodegradation produce significant improvements in raw water quality. However, due to industrial and municipal discharges and the influence of agriculture, rivers and lakes are polluted by a number of organic chemicals. In order to assess the impact of those organic micropollutants on the quality of drinking water it is necessary to clarify their fate during infiltration and underground passage.

The fate of organic micropollutants in a river water-groundwater infiltration system is mainly determined by adsorption mechanisms and biological transformations. The purification process of the underground passage starts in the infiltration zone that can be characterized as a gelatinous, biological highly active biolayer which consists of algae, bacteria, fungi and protozoa as well as of organic and inorganic particles. During infiltration, the river water with its dissolved components meets multifaceted biogenous and abiogenous surface structures that aid in intensifying most of the self-cleaning mechanisms that are in principle also present in the free surface water. During biodegradation of substances in water, dissolved and chemically fixed oxygen is consumed, thereby causing shifts in the underlying redox system that affect form and extent of microbial degradation processes. In these redox reactions, available organic substances represent electron donors, while reducible substances in water ($O_2$, $NO_3^-$, $NO_2^-$, $SO_4^{2-}$) and solid phases (Fe(III)-, Mn(IV)-oxides and -hydroxides) act as electron acceptors. In an anaerobic aquifer, concentrations of oxygen, nitrate and sulfate are subsequently depleted whereas levels of ammonia and sulfides increase. At the end of this sequence, that is possibly formed already in the first centimeters of the infiltration zone, stands the reduction of carbon dioxide with the corresponding formation of methane. Depending on local conditions, individual redox zones may vary considerably with regard to their spatial expansion. Since many microorganisms can perform their microbial activity only at certain redox potentials and since the extent of biodegradation is dependent on sufficient residence times and sometimes proceeds retarded, the degradation of organic micropollutants is linked to both the presence of favorable redox conditions and sufficient residence times in these zones. As a consequence, elimination rates of intrinsically degradable substances may vary considerably depending on local geological and hydrochemical conditions as well as on organic loads of surface waters and infiltration zones.

For investigation of the impact of different boundary conditions on the purification capacity of bank filtration, extensive measurement campaigns were carried out at four well-characterized aquifers along the rivers Rhine, Ruhr and Elbe. The different characteristics of these infiltration pathways allowed for detailed investigations concerning the elimination capacity of riverbank filtration at various redox conditions (aerobic, aerobic-denitrifying, denitrifying, strictly anaerobic) and residence times of the infiltrated water in the underground (5-300 days). Analyzed target compounds comprised several contaminants relevant for the aquatic environment, such as complexing agents, aromatic sulfonates, pharmaceuticals (including iodinated X-ray contrast media), and MTBE.

On the basis of a comprehensive evaluation of these investigations, it is obvious that the removal efficiency of bank filtration for different polar organic micropollutants is extremely dependent on the underlying redox processes in the aquifer, since some organic micropollutants (e.g. iodinated X-ray contrast media, carbamazepine, sulfamethoxazol) turned out to be better removable during denitrifying and strictly anaerobic bank filtration, while others (e.g. EDTA, DTPA, diclofenac) were better degradable in aerobic aquifers. Furthermore, it is quite difficult to predict the fate of single substances during bank filtration, since similar compounds often demonstrate huge differences in their elimination rates. The elimination takes place predominantly in the first few meters of the infiltration pathway, even though longer residence times can significantly improve removal rates of individual micropollutants (e.g. naphthalene-1,3,6-trisulfonate).

## Introduction

In Germany, groundwater is used for drinking water production wherever possible. When compared with surface water, groundwater is well protected against most types of pollution, is of relatively regular quality and temperature, and its abstraction can be easily adjusted to short-term fluctuations in consumption. However, exploitation of natural groundwater sources is restricted with regard to quantity. In Germany, this limitation is not given to such an extent for surface waters. However, surface water, particularly river water, is exposed to dangers of permanent and sudden pollution by wastewaters or to disturbances due to storage, transport or application of water-endangering substances, thereby always reflecting its function as receiving water. In order to preserve the protective character of groundwater at least partly when utilizing surface water for drinking water preparation, surface water is subjected to an underground passage via bank filtration or artificial groundwater recharge. Experience demonstrates that during infiltration underground transport processes such as filtration, sorption, and biodegradation produce significant improvements in raw water quality. Underground passage as water treatment procedure combines particle removal, pathogen removal, organic and inorganic chemical removal, peak smoothing in spills, temperature equalization, reduction in DBP formation, and production of a more biologically stable water [1-3].

The effectiveness of bank filtration and artificial groundwater recharge has long been recognized in Germany. As a consequence of various bacterial diseases caused by drinking water from waterworks with direct intake from rivers in the late 19th century (e.g. outbreak of epidemic cholera in Hamburg in 1892/93), direct extraction of surface water for public water supply fell into discredit and was replaced or supplemented by artificial or natural subsoil passage of river water due to its efficiency in removing microorganisms from the infiltrating surface water. Nowadays, approximately 16 % of the drinking water in Germany is produced from bank filtrate or infiltrate. Because of pollution, direct treatment of river water has dropped to 1 %. Water suppliers in Berlin produce approximately 75 % of the drinking water by bank filtration and artificial groundwater recharge. In Germany, more than 300 water works use bank filtration and roughly 50 plants are based on artificial groundwater recharge [1].

Surface water is often affected by industrial, agricultural, and domestic pollution. Various organic micropollutants have been detected in surface waters. Polar organic molecules, such as complexing agents, pesticides, industrial products like aromatic sulfonates, pharmaceutical compounds, and personal care products, are of recent concern. Bank filtration can significantly lower the concentrations of many surface-water pollutants. However, precise predicting and quantifying such reductions is often difficult, since the efficiency of the underground passage depends on several factors. These include the river water quality, geological conditions, porosity of the soil, residence time of the water in the soil, temperature, pH-conditions, and redox status. Thus, the behavior of chemicals and microorganisms during infiltration and underground passage of water depends on many different interacting factors.

The infiltration of surface water into the aquifer is a filtration process in which complex physical, chemical and biological factors have a combined effect on the purification of the infiltrated water. The purification process starts in the infiltration zone that can be characterized as a gelatinous, biologically highly active biolayer which consists of algae, fungi, protozoa as well as of organic and inorganic particles. Purification processes taking place during infiltration are similar to the self-cleaning properties found in surface waters but proceed in the infiltration zone much more intensively. The fate of organic micropollutants is mainly determined by adsorption mechanisms and biological transformations. Microorganisms responsible for the microbial degradation of organic micropollutants obtain their energy by degradation and oxidation of organic carbon. The process of this energy production is primarily based on redox reactions. Energy is released by electron transfer from an electron donor (organic carbon) to an electron acceptor ($O_2$, $NO_3^-$, $NO_2^-$, $Mn(IV)$, $Fe(III)$, $SO_4^{2-}$, $CO_3^{2-}$) and is then stored within the organism biochemically and utilized for its cell growth or reproduction. From the pool of potential electron acceptors microbial communities always prefer those for which the redox reactions provide maximum energy release. The energy gain is highest at aerobic respiration and lowest at methanogenesis. As a consequence, electron acceptors are successively consumed, causing a succession of individual redox zones in the underground. This means for the order of potential electron acceptors, that oxygen is consumed as long as it is available. After its depletion, oxygen is followed up by $NO_3^-$, $Mn(IV)$, $Fe(III)$, $SO_4^{2-}$ and finally by $CO_3^{2-}$ being transformed to methane. Depending on the thickness of the surface sediments, the quality of the infiltrating water, and the hydrochemical, biological and hydraulic boundary conditions of the aquifer, the succession of the redox zones can occur on a flow distance of a few centimeters up to several 10 m. Certain microorganisms can perform their microbial activity only at certain redox conditions implying that the microbial community is variable in the

different redox zones. Furthermore, the extent of biodegradation of an organic micropollutant is dependent on sufficient residence times and sometimes proceeds retarded. Thus, the degradation of organic micropollutants is linked to both the presence of favorable redox conditions and sufficient residence times in these zones. As a consequence, elimination rates of compounds intrinsically degradable in distinct redox zones may vary considerably depending on local geological and hydrochemical conditions as well as on organic loads of surface waters and infiltration zones.

Characteristics of the bank filtrate are often affected by changes of the surface water quality that is characterized by the number of particles, concentration of dissolved organic matter from natural and artificial sources, oxygen, ammonia, nutrients, microorganisms, and other pollutants. The Rhine river is an excellent example how changes in surface water quality influence the characteristics of the corresponding bank filtrate. Figure 1 summarizes the concentrations of ammonia, manganese, and oxygen in the bank filtrate of the Rhine over a period of several years. In the early 1970s, Rhine water was highly polluted. Ammonia was present and nearly no oxygen. Due to the reduction of biodegradable organic material during infiltration the little oxygen present in the surface water and even nitrate were consumed, the aquifer was characterized by an anaerobic redox status, in which iron and manganese were reduced and released from the soil. In the mid 1980s, Rhine water quality improved because of better municipal and industrial wastewater treatment and its oxygen concentrations increased. As a consequence, conditions in the aquifer became aerobic, iron and manganese stayed in the insoluble oxidized form and finally disappeared from the bank filtrate [1].
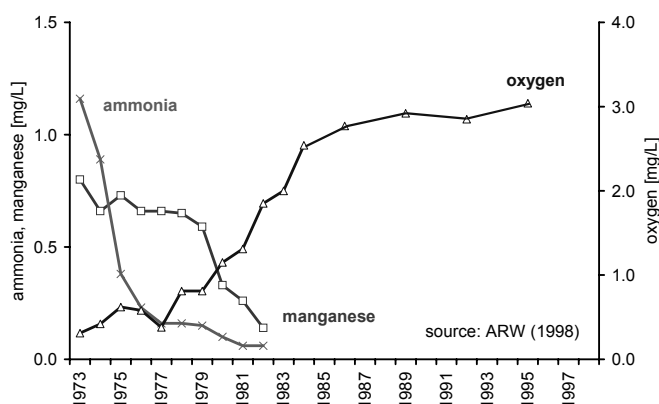


**Fig. 1.** Development of bank filtrate quality at the Rhine river.

Since redox conditions of an aquifer may change over time and from one aquifer to another, it is important to clarify the potential impact of such redox shifts on the removal capacity of riverbank filtration sites with regard to organic micropollutants commonly present in surface waters. Therefore, the present study was performed to investigate the fate of selected organic micropollutants during riverbank filtration at sites that are characterized by different boundary conditions, in particular varying redox conditions (aerobic, aerobic-denitrifying, denitrifying, strictly anaerobic) and travel times of the infiltrated water in the underground (5-300 days).

## Selection of Target Compounds

The selection of individual organic micropollutants to be investigated was carried out under consideration of their ubiquitous application and spreading, their detectability in German surface waters and their physico-chemical properties that should be as diverse as possible. Taking these criteria into account, the following substance classes and single compounds were selected. All target compounds are solely of anthropogenic origin.

*Aminopolycarboxylates*

In several industrial and domestic processes unwanted metal ions cause trouble. In such cases chelating agents like aminopolycarboxylates can be applied that form stable and water-soluble complexes with multivalent metal ions and restrict them from playing their normal chemical role. The global consumption of aminopolycarboxylates in various fields of industry and private households amounts to roughly 200,000 t/a, with an increasing tendency. Important fields of application comprise water softening and treatment, pulp and paper production, agro chemicals, detergents in industry and private households, food processing, galvano industry, textiles, cosmetics, pharmaceuticals, and medical detoxification. Quantitatively prominent representatives of this substance class are ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), and at a progressive rate diethylenetriaminepentaacetic acid (DTPA). Due to their wide fields of industrial and domestic application and their high polarity, aminopolycarboxylates enter our creeks, rivers, and lakes, mainly via industrial and domestic waste waters and can be detected in many European rivers at considerable concentrations in the µg/L range [4].

*Aromatic Sulfonates*

Among other things, aromatic sulfonates have been used for more then 100 years as important building blocks in the production of dyestuffs. Further important application fields comprise optical brighteners, synthetic leather tanning agents, textile auxiliaries, paper chemicals, concrete additives, and intermediates in the manufacture of pharmaceuticals. Due to their complete dissociation in water, aromatic sulfonates are highly soluble in water and enter the aquatic environment via industrial and domestic waste waters. Besides this, their release from concrete liquefiers used on construction sites as well as from building rubble recycling material (naphthalene-formaldehyde condensates) is of certain importance. In running waters in particular substituted naphthalene sulfonates occur. Important representatives are 2-aminonaphthalene-1,5-disulfonate, naphthalene-1,3,6-trisulfonate, napthalene-1,5-disulfonate, napthalene-1-sulfonate, and napthalene-2-sulfonate. Typical surface water concentrations of these single compounds are in the µg/L range, however, at some sites even peak concentrations in the mg/L-range were found [5].

*Pharmaceutical Compounds*

Drugs are prescribed and used for treatment and therapy of a multitude of human diseases. Alone in Germany, the annual consumption volumes of the most frequently used medicaments range often between 10 and 200 tons. Following oral intake, many of the applied pharmaceutically active substances are absorbed only incompletely from the gastro-intestinal tract. The non-absorbed fraction is normally excreted directly, whereas the absorbed fraction leaves the body often in a modified form, e.g. as glucuronide conjugate following metabolic conversion. The excretory products reach the sewage treatment plants, where they are not eliminated in the course of conventional treatment and finally are discharged into the rivers. Conjugates formed within the human body are often cleaved during wastewater treatment, releasing the pharmaceutically active compound originally applied. Effluents of sewage treatment plants often contain pharmaceuticals at concentrations between 0.01 µg/L and more than 1µg/L. In receiving surface waters, concentrations between a few ng/L and several µg/L are detected, depending on the respective waste water portion. Additive levels of all detectable pharmaceutical compounds amount often to more than 1 µg/L. Typical and often found representatives of this substance class are diclofenac (antiphlogistic), carbamazepine (antiepileptic), bezafibrate (lipid-regulator), and sulfamethoxazol (antibiotic) [6,7].

*Iodinated X-Ray Contrast Media*

This substance class comprises various triiodobenzene derivatives. Following application, these compounds can make organs visible that are in other respects not depictable. The contrast medium in the tissue to be investigated absorbs X-rays more strongly than vicinal body tissues providing a sufficiently strong contrast for radiographic analysis. In typical X-ray examinations, these substances are administered in doses of up to 100 g per patient and application. The global application volume of iodinated X-ray contrast media in the field of medical diagnosis amounts to about 3,500 tons per year. Iodinated X-ray contrast media are highly water soluble and stable with the purpose of being metabolically resistant and rapidly excreted from the body (~ 95 % within 24 hours). As a consequence, following administration, they are excreted into waste waters via urine and reach the sewage treatment plants, where they are typically not eliminated. In several sewage treatment plant effluents concentrations of 10 µg/L and more were found. The typical pollution of

German surface waters ranges from 1 ng/L to 1 µg/L. Typical iodinated X-ray contrast media are iomeprol, amidotrizoic acid and iopamidol [8].

*MTBE*

Methyl tertiary-butyl ether (MTBE) that is added to fuel as anti-knocking agent is among the most produced mass chemicals in the US. The addition of MTBE to fuel (up to 15 % by weight) prevents an uncontrolled combustion of the fuel/air-mixture by providing the oxygen necessary for a complete combustion. MTBE is volatile and well water soluble and enters the aquatic environment presumably on diffuse pathways, in particular via air pollution. Direct emissions by leakages and losses of fuel in the course of production, storage and application are certainly also of major importance. Typical MTBE concentrations in German surface waters were found to be in the range of 0.2-0.3 µg/L [9].

## Investigations in the Field

So far, data from systematic studies investigating the impact of residence times and redox conditions on the fate of the mentioned organic micropollutants during riverbank filtration is not available. For investigation of these boundary conditions extensive measurement campaigns were carried out at four well-characterized aquifers along the rivers Rhine, Ruhr and Elbe. Figure 2 shows the particular cross section of each riverbank filtration site studied.
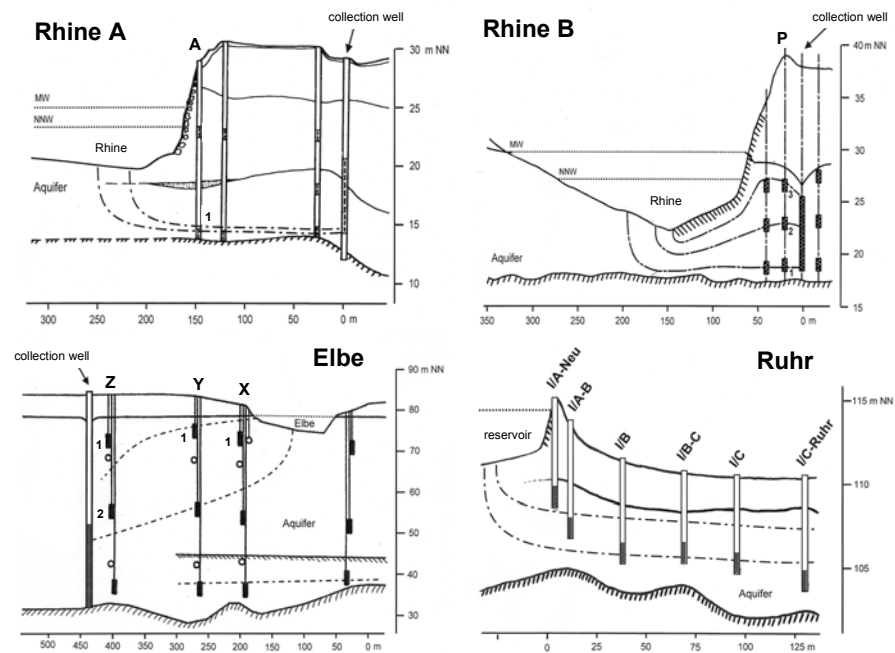


**Fig. 2.** Cross-section profiles of the investigated aquifers.

*Testing Field – Rhine A*

Along the Rhine, several water works extract and treat Rhine bank filtrate for drinking water production. The water works presented here is located in the lower Rhine area. At this site, extraction wells are situated at a distance of about 170 m from the bank in parallel to the river. The wells extract a mixture of Rhine bank-filtered water and natural land-sided groundwater from the sandy-gravely, about 15 m thick terrace deposits of the Rhine. The aquifer is characterized by a pronounced anisotropy of hydraulic conductivities. Thereby, the lower layer shows an at least six-fold higher permeability than the upper layer. Due to an almost impermeable layer at the river bank, the water infiltrates in particular at the river bottom in the

middle of the river. The majority of the water collected by the wells originates from the lower aquifer layer and the produced raw water contains about 60 % Rhine bank filtrate. Redox conditions are predominantly aerobic. Between well gallery and bank line several sampling wells have been constructed that are in contrast to the collection wells not influenced by natural land-sided groundwater. Investigations presented here were conducted at the sampling well A1 with deep filter position. The infiltrated river water needs between 7 and 20 days to pass this well (residence time in the aquifer). Fortunately, this site was investigated intensively already in previous projects, providing an impressive data set covering a period of several months.

*Testing Field – Rhine B*

Also this site is located at the right bank of the lower Rhine forming a gallery of several vertical wells parallel to the bank line situated approximately 60 m from the bank. Again, the infiltration into the clay and fine-sand layers of the 10-12 m thick aquifer proceeds mainly at the river bottom. Between Rhine and collection wells several sampling wells are available, that are typically not influenced by natural land-sided groundwater. The investigated sampling point P provides three independent sampling wells with three different filter depths. Travel times of the infiltrated water to pass the sampling well are approximately 60 days for well P1 (lower layer), 30 days for well P2 (middle layer) and 12 days for well P3 (upper layer). The water extracted by the collection wells is a mixture water of various age and contains approximately a portion of 25-30 % natural land-sided groundwater. Samples were taken in summer 2003 at 14 dates from the Rhine and at 5 dates from the three sampling wells (P1, P2, P3). During the time of sampling in summer 2003, redox conditions were at the edge of aerobic to denitrifying.

*Testing Field – Ruhr*

This study site is a pure testing field situated at the middle course of the Ruhr river. In this area the Ruhr river is dammed in a branch. Due to a retaining weir upstream and the controlled outflow of the reservoir a very constant reservoir water level can be maintained forming a potential gradient of more than 5 m between the surface water and the adjacent about 5 m thick, sandy-gravely and well permeable aquifer. The investigated bank filtrate moves without any natural groundwater influx from the infiltration point at the reservoir bottom along the hydraulic gradient to the water downstream of the reservoir retaining weir. This aquifer was shown to be strictly anaerobic since investigations have demonstrated a completed sulfate reduction already in the infiltration zone. Along the aquifer several sampling wells are available. Travel times are comparatively short and constitute between 5 and 15 days depending on the location of the sampling point. Samples from this testing field were taken in the period from autumn 2002 to summer 2003 at six dates. At each date samples from the surface (reservoir) water and from several sampling wells were investigated.

*Testing Field – Elbe*

This study site is located at the middle course of the Elbe river at its left bank. The water extracting plant used by the local water works comprises of well galleries with several vertical wells situated at a distance of about 300 m from the bank in parallel to the Elbe river. The thickness of the aquifer is about 40-55 m and is characterized by a certain anisotropy of hydraulic conductivities causing intensive mixture effects between river and collection wells. The aquifer can be described as a three-layer system. The middle layer is formed by medium sand with a hydraulic conductivity of about $6 \cdot 10^{-4}$ m/s. The upper and lower layers are formed by coarse sand to gravel, with a hydraulic conductivity of $2 \cdot 10^{-3}$ m/s. Due to silt bands in the lower section of the aquifer an undercurrent of the river with groundwater from the catchment area right-sided to the Elbe occurs. The water extracted by the collection wells contains a portion of approximately 60 % riverbank filtrate. Between well gallery and Elbe bank several sampling wells exist that are not influenced by any land-sided natural groundwater influx. These bank filtrate sampling points were constructed as groups of three sampling wells of different depth. Retention times of the infiltrated water in this aquifer are comparatively long. Within the middle sand layer section, the water needs more than 150 days to reach sampling well Z2. Travel times within the better permeable upper layer (sampling wells X1, Y1, Z1) are between 45 and 80 days. Investigations concerning the redox status have demonstrated denitrifying conditions already in the infiltration zone. Samples from this testing field have been taken so far only once (in April 2003). Samples were taken from the surface water, from three sampling wells of the upper aquifer layer, and from one sampling well of the middle layer.

**Tab. 1.** Characteristics of the investigated riverbank filtration sites

|  | Rhine A | Rhine B | Elbe | Ruhr |
|---|---|---|---|---|
| aquifer thickness | 12-15 m | 10-12 m | 40-55 m | 5 m |
| material | gravel/sand | gravel/sand | gravel/sand | gravel/sand |
| residence time | 7-20 days | 12-60 days | 45-300 days | 5-15 days |
| $K_f$-value | $12 \cdot 10^{-3}$ m/s (deep, A1) to $2 \cdot 10^{-3}$ m/s (high) | $3,0 \cdot 10^{-3}$ m/s to $6,0 \cdot 10^{-3}$ m/s | $0,6 \cdot 10^{-3}$ m/s (depth 2) $2,0 \cdot 10^{-3}$ m/s (depth 1) | $10^{-1}$ m/s to $10^{-3}$ m/s |
| redox conditions | aerobic | aerobic to denitrifying | denitrifying | strictly anaerobic |

As becomes apparent from table 1, investigations at these well characterized bank filtration sites allow, based on a comprehensive data evaluation, conclusions to be drawn concerning the capacity of riverbank filtration for elimination of organic micropollutants at different travel times and redox conditions.


## Results of Investigation


*Aminopolycarboxylates*

Figure 3 shows the results of the studies at the specified riverbank filtration sites with their site-specific characteristics and boundary conditions for EDTA. As can be seen from the diagrams, EDTA can be regularly detected in the bank filtrates of the different sites, even though concentrations are in most cases slightly lower than in the corresponding surface water. The impact of travel times and pathway lengths on EDTA elimination seems to be rather low. With regard to the impact of redox conditions it can be postulated, that the reduction in EDTA concentrations under aerobic conditions is slightly more pronounced than under denitrifying and anaerobic redox conditions.
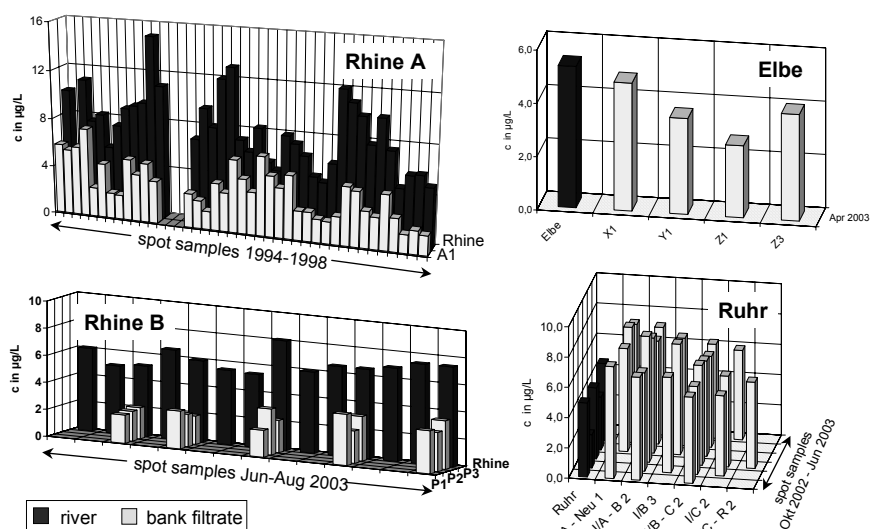


**Fig. 3.** EDTA concentrations in surface waters and bank filtrates.


In the bank filtrate samples from the testing field at the Ruhr surprisingly even higher EDTA concentrations were detected than in the corresponding reservoir surface water. This finding can be ascribed most probably

to the complexing agent DTPA that occurs in the Ruhr river at relatively high concentrations. According to Stumpf et al. [10], DTPA can be partially degraded by microorganisms generating the aminopoly-carboxylates NTA and EDTA as metabolites.

In order to investigate this aspect more precisely, figure 4 shows the progression of the molar aminopolycarboxylate concentrations (NTA, EDTA and DTPA) along the aquifer at the Ruhr. Thereby, mean values were calculated for each sampling point from all measurements performed. The coincidence of DTPA degradation and increase of EDTA concentrations becomes quite obvious. Overall, DTPA is reduced at an intermediate degradation rate while EDTA is only slowly degraded along the aquifer. The reason for observing elevated EDTA concentrations only in the bank filtrate at the Ruhr is most probably due to the fact that DTPA concentrations in Rhine and Elbe are comparatively lower than in the Ruhr, so that such an effect proportionally cannot become noticeable in these rivers. In riverbank filtrates of Rhine and Elbe DTPA could only be sporadically detected. Even in surface waters, DTPA concentrations are often close to the analytical quantitation limit making an evaluation of the results generally difficult. However, DTPA seems to be slightly better degradable than EDTA. The complexing agent NTA can be easily degraded by microorganisms and its elimination turned out to be independent from redox conditions and travel times. According to the results of the present study, the entire elimination of NTA proceeds already in the first few centimeters to meters of the particular underground passage.
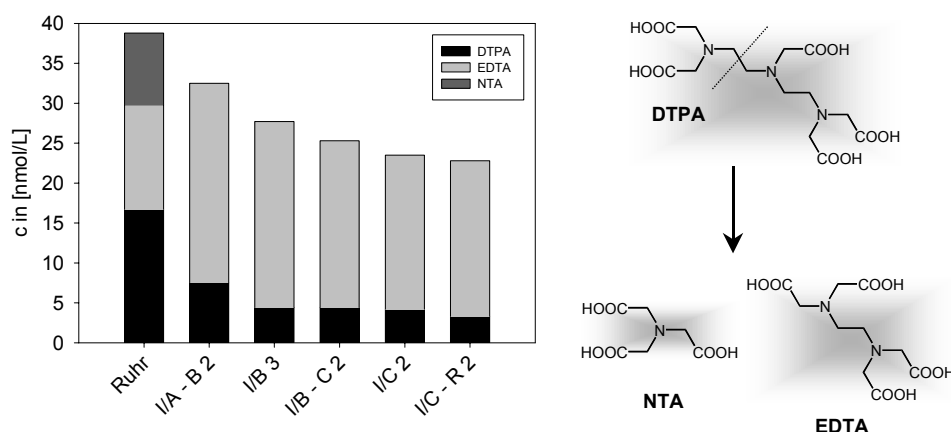


**Fig. 4.** Molar aminopolycarboxylate concentrations along the aquifer at the Ruhr and postulated degradation of DTPA [10].

*Aromatic Sulfonates*

According to the findings of the studies presented here, individual naphthalene sulfonates show major differences with regard to their elimination during riverbank filtration, depending on their molecular structure and substitution rate. However, for the individual naphthalene sulfonates discussed here, the particular extent of elimination turned out to be rather independent from the prevailing redox potential. While the two singly substituted compounds naphthalene-1-sulfonate and naphthalene-2-sulfonate are well eliminated during riverbank filtration, representatives with a higher substitution rate like 2-aminonaphthalene-1,5-disulfonate and naphthalene-1,3,6-trisulfonate show a rather persistent behavior. Independently from the travel time in the underground and from the underlying redox conditions, no decrease in concentration was observable for 2-aminonaphthalene-1,5-disulfonate. This finding emphasizes the fact that the analyzed riverbank filtrate samples were in the present studies indeed free of any major dilution by natural land-sided groundwater. In contrast to 2-aminonaphthalene-1,5-disulfonate, the elimination extent of naphthalene-1,3,6-trisulfonate was significantly dependent on the residence time of the water in the underground. This was observable not only within the testing fields Rhine B and Ruhr, but also by comparison of the aquifers among one another (figure 5). In particular the aquifers Elbe and Rhine B with their comparatively longer retention times showed a more pronounced decrease in naphthalene-1,3,6-trisulfonate concentrations.
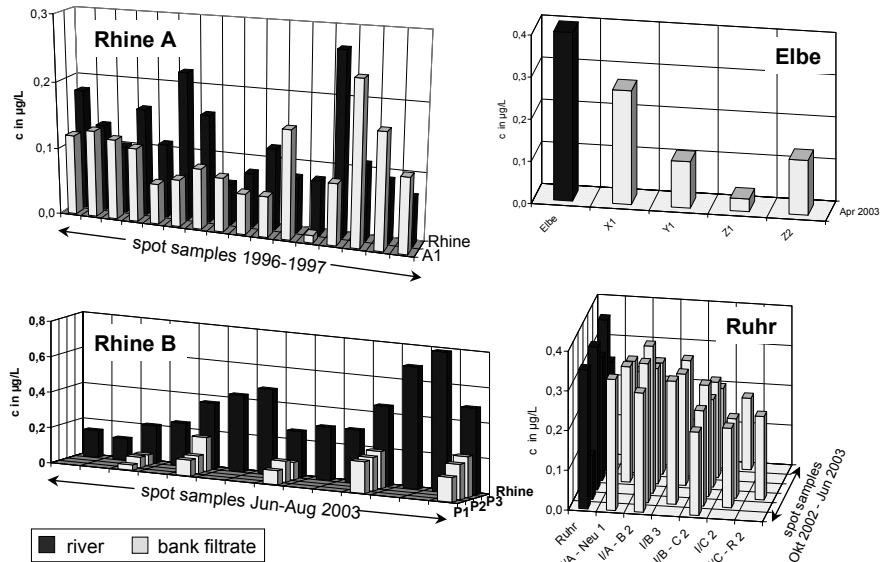
**Fig. 5.** Concentrations of naphthalene-1,3,6-trisulfonate in surface waters and bank filtrates.

*Pharmaceutical Compounds*

The fate of the investigated pharmaceutical compounds during bank filtration has to be evaluated differentially. Even though the lipid-regulator bezafibrate was permanently present in the rivers Rhine, Ruhr and Elbe, it was not detected in any sample of the corresponding underground passage. Thus, bezafibrate is independently from the travel time in the underground and the underlying redox conditions generally well removable during riverbank filtration. The extent of elimination of the antiphlogistic diclofenac, the antiepileptic carbamazepine, and the antibiotic sulfamethoxazol was, however, clearly dependent on the underlying redox milieu. While carbamazepine and sulfamethoxazole were only slightly removable under aerobic and denitrifying conditions, both substances could be only sporadically detected (and then at very low concentrations) in the strictly anaerobic bank filtrate at the Ruhr implying their preferential removal at strictly anaerobic conditions.
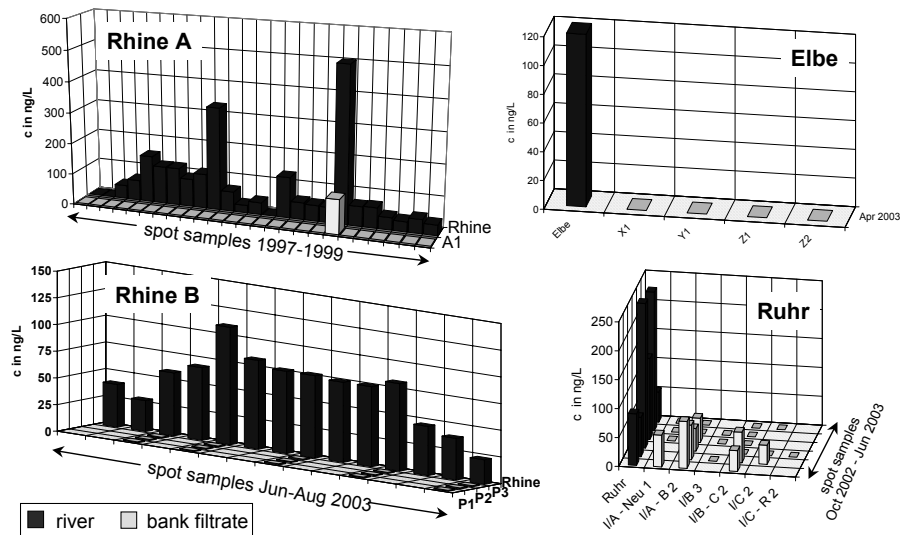


**Fig. 6.** Concentrations of diclofenac in surface waters and bank filtrates.

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On the other hand, diclofenac turned out to be well removable at aerobic and denitrifying redox conditions, while the results from the Ruhr aquifer imply a significantly lower degradation rate during strictly anaerobic riverbank filtration (figure 6).

*Iodinated X-ray Contrast Media*

Also the fate of iodinated X-ray contrast media is clearly dependent on the respective boundary conditions of an aquifer. Iomeprol turned out to be well eliminated during bank filtration, independently from residence times and redox conditions. Amidotrizoic acid, however, is not removable at aerobic conditions, but showed a significant concentration decrease at aquifers providing denitrifying or strictly anaerobic conditions. Similar results were found for iopamidol. However, in comparison to amidotrizoic acid, the removal of iopamidol responds much more sensitively to redox changes in the aquifer. While no removal could be observed for iopamidol at the aerobic aquifer at the Rhine (testing field Rhine A), its concentration level was already significantly lower in the bank filtrate from the aerobic-denitrifying aquifer (Rhine B). At this aquifer, the lowest iopamidol concentrations were detected in particular at those dates when the redox potential was drifted more clearly into the denitrifying region. A good elimination of iopamidol was also observed at the denitrifying Elbe aquifer and at the strictly anaerobic bank filtration site at the Ruhr. Thus, iopamidol might represent a quite sensitive redox marker for this kind of studies.
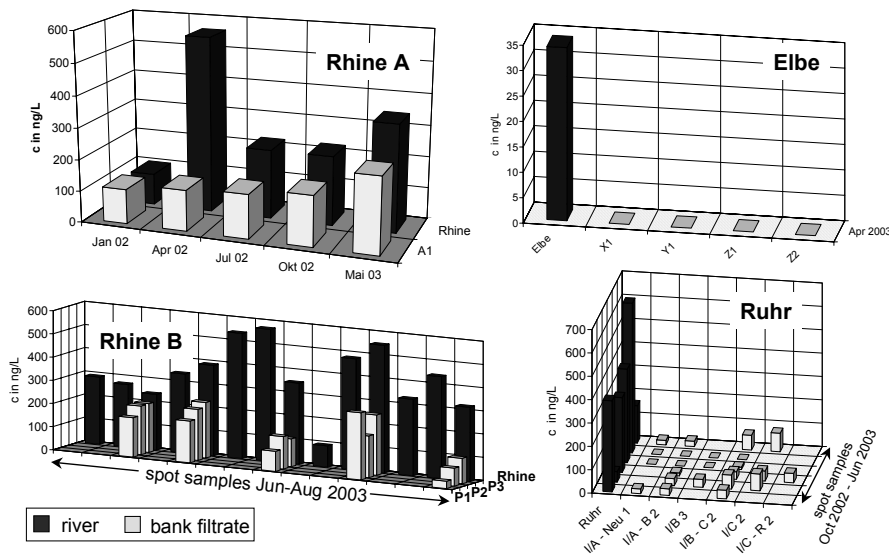


**Fig. 7.** Concentrations of iopamidol in surface waters and bank filtrates.

*MTBE*

During aerobic bank filtration at the Rhine (historical data from testing field Rhine B) MTBE was found to be only insufficiently removed and could be always detected in the raw water of the local water works. Concerning the fate of MTBE during bank filtration at denitrifying and strictly anaerobic milieu conditions no statement can be given so far, since MTBE concentrations in surface waters of the relevant testing fields were often too low and existing data sets are too fragmentary at present.

## Conclusions

The systematic investigations at aquifers with geological and hydrochemical boundary conditions presented here revealed that the extent of elimination of several organic micropollutants is decisively dependent on the underlying redox conditions. Furthermore, the fate of organic micropollutants during riverbank filtration and underground passage can hardly be predicted, since chemically relatively similar compounds

sometimes show quite different elimination rates. The major part of the elimination proceeds always in the first few meters of the infiltration pathway. Nonetheless, longer residence times can significantly improve removal rates of some individual compounds (e.g. naphthalene-1,3,6-trisulphonate). However, it became also apparent that the underlying redox conditions have a more pronounced effect on the removal capacity than residence times of the water in the underground.

# References

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