Effects of boundary conditions on the cleaning efficiency of riverbank filtration and artificial groundwater recharge systems regarding bulk parameters and trace pollutants

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ABSTRACT
Drinking water is often produced from surface water by riverbank filtration (RBF) or artificial groundwater recharge (AGR). In this study, an AGR system was exemplarily investigated and results were compared with those of RBF systems, in which the effects of redox milieu, temperature and surface water discharge on the cleaning efficiency were evaluated. Besides bulk parameters such as DOC (dissolved organic carbon), organic trace pollutants including iodinated X-ray contrast media, personal care products, complexing agents, and pharmaceuticals were investigated. At all studied sites, levels of TOC (total organic carbon), DOC, AOX (adsorbable organic halides), SAC (spectral absorption coefficient at 254 nm), and turbidity were reduced significantly. DOC removal was stimulated at higher groundwater temperatures during AGR. Several substances were generally easily removable during both AGR and RBF, regardless of the site, season, discharge or redox regime. For some more refractory substances, however, removal efficiency turned out to be significantly influenced by redox conditions.

Key words | artificial groundwater recharge, bank filtration, dissolved organic carbon (DOC), iopamidol, temperature, trace pollutants

INTRODUCTION
Drinking water is often produced from raw water obtained from surface water by riverbank filtration (RBF) or artificial groundwater recharge (AGR), as illustrated in Figure 1. The underground passage is acting as a physical filter (depending on the grain size and distribution of the substrate), removing, e.g. bacteria and algae present in the surface water. Moreover, the substrate provides surfaces for physico-chemical sorption processes and acts as a habitat for microorganisms. Sorption and biological degradation contribute to the clean-up of the infiltrated water and many organic trace pollutants are partly or completely removed. Admixture of natural groundwater can either reduce pollutant or nutrient concentrations present in the infiltrate (when groundwater is less contaminated) or increase them, e.g. when nitrate is released from nearby farmland.

Depending on many factors such as the availability of oxygen and nutrients (organic carbon, nitrogen species, phosphate), retention time, temperature, mineral composition of the substrate and chemistry of the water infiltrating, site specific redox settings develop. Though at many sites certain redox conditions prevail during most times of the year, seasonal changes are common. For example, aerobic and anaerobic conditions may alternate during conditions of low water and flooding, causing dissolution or precipitation of, e.g. manganese and iron species and oxides. Especially for AGR sites, discontinuous flooding can cause abrupt changes in the chemistry and redox milieu of a site compared with RBF sites. Moreover, even at sites characterized as generally aerobic, anaerobic redox markers such as methane can be detected, indicating the co-existence of different redox conditions within one aquifer (Alewell et al. 2008).

Surface water bodies might be polluted by accidental spills during storage and transport of chemicals or hazardous substances via ship, railroad or pipelines. Even more spectacular hazards become evident to the public when
chemical plants or refineries fail and chemicals or hazardous substances are released into the environment or directly into surface or groundwater. Severe examples comprise the recent red sludge accident at Kolontár in Hungary (2010), the capsizing of a tank ship transporting sulfuric acid (near Lorelei, Germany, 2011) or the release of pesticides during the extinction of a fire at a chemical plant in Zürcherhalle, Switzerland (1986). Besides the accidental spills, continuous pollution of streams occurs by wastewater treatment plant effluents, untreated wastewater (e.g. Götz et al. 2010), or application of agrochemicals and pesticides. A source of short-term, but high concentration pollutant release is the runoff of untreated urban stormwater, where mainly particle-bound compounds such as higher molecular polyaromatic hydrocarbons occur (Zgeib et al. 2011). Due to the various sources of pollution, the spectrum of trace pollutants reported to be detected in surface waters is very large.

Surface water is used as a raw water source in AGR and RBF for drinking water production and pollution of streams and lakes may impair the quality of drinking water. For the safe operation of their drinking water treatment facilities, operators are interested in the cleaning efficiency and the robustness of their AGR or RBF systems. Therefore, in this study, changes in water quality parameters were investigated in dependency of relevant boundary conditions. Of special interest was, besides bulk parameters such as dissolved organic carbon (DOC), the behavior of organic trace pollutants such as iodinated X-ray contrast media (Figure 2), naphthalenesulfonates, complexing agents, pharmaceuticals and personal care products. Several compounds of these substance classes have been reported to be persistent and to survive the AGR and RBF process. Some examples detected in bank filtrate, artificially enriched groundwater and sometimes also in natural groundwater comprise amidotrizoic acid, iopamidol, 1,5-naphthalenedisulfonate (1,5-NDS), ethylene diamine tetraacetic acid (EDTA), sotalol, sulfamethoxazole, and carbamazepine, for which concentrations up to several 100 ng/L each are reported (e.g. Grischek et al. 1997; Sacher et al. 2001; Grünheid et al. 2005; Storck et al. 2010).

Vulnerability of groundwater sources for microbial and chemical pollution, e.g. due to preferential flow or leaching of sewers can be indicated by other wastewater-related compounds such as caffeine, cholesterol or the artificial musk galaxolide and the X-ray contrast media iohexol, iopromide, iomeprol, which are known to be less persistent during RBF (Storck et al. 2010). Most of the compounds mentioned above are considered emerging contaminants (Richardson 2009; Richardson & Ternes 2011) and occur regularly in the Rhine. The aim was to identify factors having an impact on the removal of bulk parameters or trace pollutants and to identify substances being refractory under certain conditions. Exemplarily, an AGR site in Basel (Switzerland) was investigated and findings from this AGR site were compared with results from nine RBF sites in the US and in Germany (Storck et al. 2010).

SITE DESCRIPTION

The investigated AGR site is located north east of Basel, Switzerland, along the river Wiese. Surface water from the river Rhine is first treated by rapid sand filtration and then infiltrated in forested infiltration sites, covered by episceletic fluviosols of 30–100 cm. Infiltration capacity ranges from 200 to 2,000 mm/d (Schütz et al. 2008). Even after decades of use, scraping off the uppermost soil layer to maintain infiltration capacity is not necessary due to the intense activity of earthworms and other soil fauna (e.g. Schütz et al. 2008) and the intermittent mode of infiltration (10 days of flooding, 20 days without). After a mean retention time of 7–30 days, water is abstracted from the aquifer, which consists mainly of gravel and sand, and undergoes further treatment prior to distribution to the consumers. Annual water abstraction accounts for 14–15 million m³. General redox settings are aerobic (oxygen saturation 50–95%), though there is evidence of small-scale zones with more reducing...
conditions including release of N₂O and methanogenesis (Alewell et al. 2008). However, iron and manganese concentrations in abstracted water did not exceed 0.02 mg/L. The pH in the wells ranged from 7.0 to 8.3. During events of high turbidity of the Rhine surface water, abstraction for infiltration is stopped. For a detailed site description see Rüetschi (2004). US and German RBF sites used for comparison were located on the rivers Rhine, Elbe, Ruhr, Missouri, Platte, and Great Miami. These RBF sites exhibited different redox milieu conditions, ranging from aerobic to strictly anaerobic, and retention times ranging from 1 to 150 days. For a detailed description of the RBF sites and the corresponding results see Storck et al. (2010).

MATERIALS AND METHODS

Surface water and water from monitoring or abstraction wells was sampled at regular intervals depending on the approximate retention time of the sites. Samples were analyzed for bulk parameters total organic carbon (TOC), DOC, adsorbable organic halides (AOX), spectral absorption coefficient at 254 nm (SAC), the organic trace pollutants iodinated X-ray contrast media (amidotrizoic acid, iopamidol, iohexol, iopromide, iomeprol), personal care products (caffeine, galaxolide), complexing agents (EDTA) and pharmaceuticals (sotalol, sulfamethoxazole, carbamazepine), and further for 1,5-NDS (RBF-sites only) and the steroid cholesterol. Samples for galaxolide analysis were spiked with an internal standard, cleaned up by solid phase extraction and analyzed on a gas chromatograph–mass spectrometer system (limit of quantification (LOQ) 27 ng/L, relative standard deviation of replicate measurements 5%). A detailed description of all other analytical methods applied at the AGR and RBF field sites is given in Storck et al. (2010).

Removal efficiency for each compound was calculated by subtracting the mean concentration in the monitoring well from mean surface water concentration and dividing the result by the mean surface water concentration. The result of the latter operation is multiplied by 100 to
obtain the mean percentage of removal. Concentrations < LOQ, which occurred occasionally in the wells, were set to the value of LOQ for calculation. Consequently, the true removal efficiency is a bit larger than the calculated value and percentage of removal is therefore labeled with ‘>’.

For better comparability, DOC time series were normalized by linear z-transformation. Normalization by z-transformation is used to scale data with different means and standard deviations. Therefore, the mean of a DOC concentration time series of one well was subtracted from every single datum point of this time series and the result was divided by the standard deviation of the series, resulting in the single values of z-transformed DOC concentration. The mean of this transformed series is 0 and the standard deviation 1.

RESULTS AND DISCUSSION

At virtually all sites investigated, TOC, DOC, AOX, SAC, and turbidity were reduced significantly. As an example, DOC-removal from an AGR site in Switzerland is presented (Figure 3). Though DOC concentration in the Rhine surface water used for infiltration was often exceeding 1.5 mg/L, concentration peaks of DOC in the Rhine were compensated at the AGR site and DOC concentrations in the corresponding wells ranged mostly between 0.4 and 0.6 mg/L, resulting in an average DOC removal of 72% (Figure 3(a)). The high percentage of DOC removal at the AGR site is slightly exceeding the range of 6–64% reported for similar systems and laboratory column-experiments (Kuehn & Mueller 2000; Grünheid et al. 2005; Gruenheid et al. 2008; Rauch-Williams et al. 2010; Storck et al. 2010; Baumgarten et al. 2011; Wiese et al. 2011).

A slight tendency towards elevated DOC levels in abstracted water in winter/early spring was observed. Exemplarily, DOC data of three wells were normalized by z-transformation for better comparability to identify contemporaneous peaks in different wells. Time series of z-transformed DOC concentration seemed to correspond within these wells (Figure 3(b)). Maxima of z-transformed DOC in the wells corresponded with minima of groundwater temperature (Figure 3(c)) rather than with minima of infiltrated Rhine water temperature (Figure 3(d)). Vice versa, minima of z-transformed DOC in the wells (Figure 3(b)) corresponded with maxima of groundwater temperature (Figure 3(c)) rather than with maxima of infiltrated Rhine water temperature (Figure 3(d)). Differences of temperature in abstracted water of 5 °C caused increase or decrease in mean DOC removal by ≤ 0.2 mg/L (approximately 10% of the input concentration). However, this effect could not be clearly established for every single well.

The observed temperature dependency of DOC removal is in accordance with findings by Gruenheid et al. (2008). The latter authors reported on temperature dependent differences in laboratory column experiments (retention time 6.3 days) and determined a removal of 26% at 25 °C and 17% at 5 °C. At the RBF sites, where natural fluctuation of the initial DOC concentrations and removal due to many influencing parameters such as floods, runoff events, etc. is much higher than in a lab experiment, no significant relation of DOC removal to seasonal effects could be established. In contrast to RBF, for the AGR site, the boundary conditions are much more constant due to the initial clean-up of surface water by fast sand filters prior to infiltration, which facilitates the identification of a temperature effect.
The contribution of dilution via admixture by natural groundwater to the observed overall DOC removal turned out to be negligible during running infiltration (Storck & Alewell 2009). Long-term volumes of infiltrated and abstracted water are balanced out and the ratio of infiltrated to abstracted water (Figure 3(e)) seemed to have little impact on DOC removal. Mean concentrations of persistent organic trace pollutants such as EDTA, carbamazepine, and sulfamethoxazole were similar in the Rhine and in the wells (Figure 4), underlining the small quota of dilution.

Moreover, the main removal of DOC was always observed closest to the infiltration zone, which is consistent with the literature data (e.g. Sontheimer 1991; Rüetschi 2004; Rauch-Williams & Drewes 2006; Oren et al. 2007), but increased retention times were related to an increased DOC removal within one aquifer.

Similar to DOC at the AGR site, a positive impact of temperature on the removal of trace pollutants during RBF is reported for a few less biodegradable compounds such as 1,5-NDS, 1,3,5- and 1,3,6-naphthalenetrisulfonates, 2-amino-4,8-naphthalenedisulfonate, iopamidol, and DTPA (diethylene triamine pentaacetic acid) (Storck et al. 2010). For iopamidol, this effect was strongest and accounted for improved in particular the removal of substances less biodegradable (Storck et al. 2010). A very prominent example is iopamidol, being rather persistent at aerobic conditions and short retention times, while removal during RBF seems to be enhanced at more anaerobic conditions (Storck et al. 2010). Interestingly, at the generally aerobic AGR site, iopamidol was removed by >76% (Figure 4). At the latter site, methanogenesis occurs on the micro-scale (Alewell et al. 2008) indicating also strictly anaerobic redox milieu conditions. Thus, iopamidol may be mainly removed due to the reducing milieu at the micro-scale, confirming the results from RBF sites. In contrast, EDTA, sulfamethoxazole, carbamazepine, and amidotrizoic acid were rather persistent at the AGR site (Figure 4) and at most RBF sites (Storck et al. 2010). Due to fluctuations of amidotrizoic acid concentrations in the Rhine, mean amidotrizoic acid concentration in the wells of the AGR site slightly exceeded mean concentration in the Rhine. Still, Grischek et al. (1997) and Storck et al. (2010) reported on a beneficial effect of prolonged residence times during RBF on the removal of EDTA at anaerobic or denitrifying sites.

Several substances turned out to be generally easily removable during both AGR and RBF, regardless of the site investigated, season, discharge or redox regime. Some examples are iopromide, iohexol, iomeprol, caffeine, and galaxolide (Figure 4).

High discharge of rivers often causes lower concentrations of pollutants in surface water. At an RBF site located on the lower Rhine (residence time 7–20 days), persistent compounds such as sulfamethoxazole, 1,5-NDS and carbamazepine showed a little tendency towards better removability at low discharge, while there was no removal at all during high discharge (Figure 5). The less persistent compound sotalol was almost completely removed under either discharge regime. Low surface water concentrations

![Figure 4](https://iwaponline.com/wst/article-pdf/66/1/138/442918/138.pdf)

**Figure 4** | Concentration level of organic trace pollutants in the Rhine near Basel and in abstraction wells of an AGR site (2–4 years). At x-axis, mean percentage of removal during AGR is shown. ‘>’ indicates the inclusion of values <limit of quantification in the calculation.
of hardly degradable compounds seem thus to accompany little removal of these compounds during RBF. Hence, a higher removal efficiency was achieved at low discharge (i.e. the absolute cleaning capacity of the system was higher), while during high discharge, removal efficiency was lower. Still, the resulting concentrations in the abstraction wells were lower or the same during high discharge compared with low discharge due to the dilution in the stream during flood periods.

CONCLUSION

For most substances, removal was affected neither by temperature nor by discharge, thus AGR and RBF are very robust treatment processes. For AGR, similar to reports for RBF, redox conditions turned out to be a key factor and determined the removal of certain trace pollutants. However, the role of nutrient availability on redox milieu and on the biological degradation and removal of trace pollutants has to be further investigated. Elevated temperatures seem to stimulate the removal of DOC during AGR and the removal of less biodegradable trace pollutants during RBF, but the effects are small and could not be established at every site. Substances being persistent at AGR and RBF sites comprised mainly EDTA, sulfamethoxazole, carbamazepine, and amidotrizoic acid.

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