1 **Introducing sequential managed aquifer recharge technology (SMART)**

2 **- From laboratory to full-scale application**

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14 15 16 **Abstract**

17 Previous lab-scale studies demonstrated that stimulating the indigenous soil microbial
18 community of groundwater recharge systems by manipulating the availability of
19 biodegradable organic carbon (BDOC) and establishing sequential redox conditions in
20 the subsurface resulted in enhanced removal of compounds with redox-dependent
21 removal behavior such as trace organic chemicals. The aim of this study is to advance
22 this concept from laboratory to full-scale application by introducing sequential managed
23 aquifer recharge technology (SMART). To validate the concept of SMART, a full-scale
24 managed aquifer recharge (MAR) facility in Colorado was studied for three years that
25 featured the proposed sequential configuration: A short riverbank filtration passage
26 followed by subsequent re-aeration and artificial recharge and recovery. Our findings
27 demonstrate that sequential subsurface treatment zones characterized by carbon-rich (>3
28 mg/L BDOC) to carbon-depleted (≤1 mg/L BDOC) and predominant oxic redox
29 conditions can be established at full-scale MAR facilities adopting the SMART concept.
30 The sequential configuration resulted in substantially improved trace organic chemical
31 removal (i.e. higher biodegradation rate coefficients) for moderately biodegradable

compounds compared to conventional MAR systems with extended travel times in an anoxic aquifer. Furthermore, sorption batch experiments with clay materials dispersed in the subsurface implied that sorptive processes might also play a role in the attenuation and retardation of chlorinated flame retardants during MAR. Hence, understanding key factors controlling trace organic chemical removal performance during SMART allows for systems to be engineered for optimal efficiency, resulting in improved removal of constituents at shorter subsurface travel times and a potentially reduced physical footprint of MAR installations.

Keywords: Aquifer recharge and recovery; biofiltration; clay; redox conditions; riverbank filtration; sequential treatment.

1. Introduction

The increasing demand for drinking water supplies has resulted in an increased interest in using impaired water sources (e.g., surface water receiving wastewater discharge; recycled water) to supplement aquifers via natural treatment processes such as managed aquifer recharge (MAR). Due to the interplay of hydro-geochemical and biological processes during MAR, opportunities exist to improve the water quality of infiltrating water. However, impaired water like recycled water often contains trace organic chemicals (TOrc) including pharmaceuticals, personal care products, household chemicals and emerging disinfection by-products, which are not efficiently removed during conventional biological wastewater treatment (Joss et al. 2006). While MAR is still considered a ‘black-box’ natural treatment technology, fundamental knowledge about the fate and transport of TOrc and pathogens during subsurface treatment in an aquifer is essential for the assessment and design of MAR facilities (Regnery et al. 2013).

Our previous research under controlled conditions at the laboratory-scale has suggested that the composition and availability of the primary substrate, namely the amount of biodegradable dissolved organic carbon (BDOC) in the recharged source water, plays a major role in influencing microbial community structure and function (i.e., xenobiotic

biotransformation capability) in subsurface systems (Rauch-Williams et al. 2010; Li et al. 2012, 2013, 2016; Alidina et al. 2014a, 2014b). In these laboratory-scale soil column systems simulating MAR, lower primary substrate concentrations and a higher humic content in the recharged source water resulted in higher soil microbial diversity at the phyla and species level and promoted biotransformation rates of TOrC during recharge.

Furthermore, several studies identified redox conditions as one of the important driving factors for removal of chemical contaminants in subsurface systems like MAR. Based on extensive field studies, Wiese et al. (2011) stated that redox conditions have the most important impact on removal efficiency of TOrC but added that additional factors such as subsurface travel time, residual threshold concentrations or field site specifics may contribute to removal or might even exceed the importance of predominant redox conditions. The relationship between redox conditions and subsurface travel time, however, and their influence on attenuation is complex and often variable over the range of contaminants and environmental conditions (Regnery et al. 2015a). During simulated MAR at the laboratory-scale, the majority of TOrC show enhanced removal under oxic redox conditions (Burke et al. 2014; Regnery et al. 2015a). Although anoxic to anaerobic subsurface conditions are beneficial for the removal of nitrate (Rivett et al. 2008) or certain substance groups such as certain disinfection-byproducts (Pitot et al. 2011), iron, manganese, and other inorganic trace elements are mobilized under reducing subsurface conditions and usually require post-treatment of the recovered groundwater. Main driving factors for redox zonation in MAR systems are the availability of oxidizing agents such as oxygen and nitrate, of reducing agents (organic matter, reduced mineral phases), nutrients, the biological activity of the soil microbial community, and subsurface travel time (Grützmacher and Reuleaux 2011; Regnery et al. 2013). These drivers are controlled by many natural, site-specific as well as design and operation-related variables. Site-specific variables are among others aquifer geochemistry, indigenous soil microbial community, temperature, or natural groundwater recharge, whereas design and operation-related variables comprise factors such as carbon composition of the recharged source water, distance between infiltration basins and wells, well depth, pumping rate etc. Moreover, a thorough understanding of the role of sorptive processes in MAR may

provide opportunities to enhance the attenuation capabilities of MAR facilities. In case of low soil organic carbon (f_{oc}), other sorptive processes such as interactions with mineral surfaces (e.g., clay) gain importance and can increase the effective travel time of compounds (e.g., ionic compounds) compared to the hydraulic residence time, allowing microbes more time for biotransformation and/or mineralization of substances.

The concept of stimulating the indigenous microbial community by manipulation of the primary substrate and establishing sequential redox conditions in the subsurface for enhanced removal of compounds with redox-dependent removal behavior is an approach aiming for optimal residence times based on the degradation kinetics of contaminants present in impaired source water (Regnery et al. 2013). Our goal is to advance this concept from laboratory- to full-scale application by introducing sequential managed aquifer recharge technology (SMART). We hypothesize that a multi-sequence configuration, featuring carbon-rich and predominantly anoxic subsurface conditions followed by carbon-depleted and predominantly oxic conditions, can result in an optimized treatment performance of impaired water related contaminants. As outlined in our previous literature review (Regnery et al. 2013) and illustrated in Figure 1, a logical and cost-effective treatment train at full-scale features an initial treatment via short riverbank filtration (RBF) passage for the depletion of BDOC and nutrients, exhibiting a transition from oxidizing conditions in the river to reducing conditions in the riverbank. The initial treatment is followed by re-aeration of the recovered RBF water through surface spreading or engineered aeration, returning to a predominantly oxic subsurface passage, but under carbon-depleted conditions for enhanced attenuation of less-degradable compounds. For shallow groundwater, the lifting energy requirement during pumping is in general low and re-aeration can usually be achieved during surface spreading. However, at full-scale application several aspects of surface spreading MAR design must be taken into consideration for maintaining rapid infiltration rates in infiltration basins to prevent algae growth and clogging-related issues.

To validate the concept of SMART at full-scale, we chose a full-scale MAR facility in Colorado that featured the proposed sequential configuration motivated by local water

right issues: A short RBF passage, which is subsequently followed by artificial recharge and recovery (ARR) via surface spreading basins. We extensively monitored water quality changes at the full-scale RBF facility during previous studies (Hoppe-Jones et al. 2010; Betancourt et al. 2014; Regnery et al. 2015b) and moreover characterized subsurface heterogeneities (e.g., dispersed clay) and flow paths at the full-scale ARR facility (Parsekian et al. 2014). Here, we evaluate and compare the removal efficiencies of the sequential treatment steps that exhibit distinct differences during groundwater recharge (e.g., redox conditions in the aquifer, organic carbon load in the source water) and discuss further implications for MAR operation using SMART. Besides bulk organic parameters, 19 TOrC were selected for the performance assessment based on their physiochemical properties, occurrence in South Platte River water, and potential to serve as performance indicators for sequential MAR treatment (Drewes et al. 2008; Regnery et al. 2015a). Due to the occurrence of dispersed clay aggregates throughout the MAR site, we performed additional laboratory batch experiments with two different soils from the ARR facility and montmorillonite clay to investigate the role of sorption to clays in attenuation of TOrC during MAR. While different clay materials provide different sorption capacities, it was beyond the scope of this study to develop sorption isotherms or to further characterize the clay materials.

2. Experimental Approach

2.1. Field site description

After facing severe drought conditions over a period of several years, the city of Aurora, Colorado, launched the Prairie Waters Project in 2009/2010 to supplement its drinking water supply. A MAR system consisting of RBF galleries and an ARR facility as part of an advanced water treatment train was constructed along the South Platte River in Brighton, Colorado (Regnery et al. 2015b). A schematic (Figure S1) and a detailed description of the field site are provided in the Supporting Information (SI).

2.2. Sample collection and analysis

A targeted sampling campaign was performed between September and November 2012 to evaluate full-scale MAR performance, with additional water samples collected from

individual ARR recovery wells and the RBF combined collector during summer and fall in 2013 and 2014 as described in the SI. Measurements of physicochemical properties, organic and inorganic bulk parameters such as dissolved organic carbon (DOC), UV absorbance at 254 nm (UV_{254nm}), specific UV absorbance (SUVA), anions, and cations followed Standard Methods (APHA 2012). A complete description of analytical procedures is provided in the SI. Analysis of TOrC was performed by high performance liquid chromatography coupled with tandem mass spectrometry using an isotope dilution method as reported in Teerlink et al. (2012). Physicochemical properties of selected TOrC and their respective method detection limits are summarized in Table S1 (SI).

2.3. Grouping of wells for performance assessment

The proportion of recharged water at selected recovery and monitoring wells at both sites was determined as detailed in the SI. Native alluvial plain groundwater samples were collected from a monitoring well nearby the ARR site (Figure S1; red circle outside slurry wall). South Platte River water samples and riverbank filtrate samples collected from the RBF combined collector were analyzed to assess overall RBF performance. The RBF combined collector, which combines the recovered groundwater from all operational RBF wells before it is delivered to the ARR facility, is diluted with native landside groundwater in the range of 30 – 35%. Among all ARR wells, the degree of dilution with native landside groundwater varied. For the evaluation of ARR performance, selected recovery and monitoring wells were compiled into the following bins of similar dilution percentages and travel time estimates (Figure S1, SI):

- a) Four recovery wells and three monitoring wells with less than 2 weeks of subsurface travel time and less than 20% dilution (blue circles); thereof one recovery well and two monitoring wells with less than 10 days travel time;
- b) Eight recovery wells and one monitoring well with equal or more than 2 weeks of subsurface travel time and less than 20% dilution (orange circles);
- c) Three recovery wells and one monitoring well revealed long subsurface travel time (months) and more than 50% dilution with native groundwater (green circles).

Three RBF recovery wells that are characterized by less than 10 days travel time and less than 15% dilution with native groundwater (Regnery et al. 2015b) were selected to compare the performance of RBF (i.e., representing carbon-rich, anoxic conditions) and ARR (i.e., carbon-limited, oxic conditions) in terms of water quality improvement under minimized influence by dilution and considering comparable subsurface travel times. In addition, samples were collected from the ARR combined collector in 2012 to determine the quality of the water delivered to the downstream water treatment plant (referred to as RBF/ARR treatment). Based on exact ARR recovery well production rates during the study period (provided by Aurora Water, CO), water collected from the ARR combined collector was mainly composed of groundwater recovered from high producing wells with less than 20% dilution and equal or more than 2 weeks of travel time. The contribution of wells with more than 50% dilution with native groundwater and long subsurface travel times to the combined collector was less than 15%.

2.4. Batch sorption experiments

To assess the influence of dispersed clay at the ARR facility on attenuation of analyzed TO_{RC}, abiotic batch sorption experiments were carried out in the laboratory according to a previously developed protocol (Teerlink 2012). Two different ARR soils with $\leq 0.3\%$ f_{oc} (i.e., sand with 6% clay and sandy clay loam with 23% clay, respectively) from the central spreading basin were tested in addition to bentonite, a 100% montmorillonite clay (Sigma Aldrich, St. Louis, MO). Organic carbon in bentonite is on average below 0.3%. Both field soils had been exposed to recharged RBF filtrate (and TO_{RC} therein) for approximately 6 months. Due to maintenance, the infiltration basin was dry for one month prior to soil sampling. A description of the experimental and analytical procedures is provided in the SI.

3. Results and Discussion

3.1. Redox zonation and fate of bulk parameters during SMART

The first step in the SMART concept relies on the quick consumption of readily available electron donors and acceptors during the initial phase of infiltration. During RBF passage at the Prairie Waters Project site, the large reduction in DOC ($51 \pm 8\%$) and UV_{254nm}

absorbance ($51 \pm 9\%$) coincided with the reduction of nitrate ($63 \pm 18\%$) and dissolution of manganese, indicating a shift of redox conditions from oxic conditions in the stream to suboxic (absence of dissolved oxygen) and predominantly anoxic (denitrifying) conditions during subsequent infiltration through porous media (Table 1). Accordingly, dissolved oxygen concentrations decreased from on average 5.4 ± 1.1 mg/L in the stream (Regnery et al. 2015b) to below 1 mg/L in the combined RBF filtrate. Dissolved iron concentration varied highly across RBF recovery wells (0.003 – 0.2 mg/L) compared to 0.04 ± 0.02 mg/L in South Platte River. SUVA values in South Platte River water and RBF filtrate samples were 2.0 ± 0.2 and 2.2 ± 0.3 L/mg m respectively, indicating no significant change in DOC aromaticity during RBF passage of less than 10 days on average.

Subsequently, the combined RBF filtrate was delivered to the ARR site via underground piping runs and discharged into individual cells of the infiltration basins through concrete culverts covered with large rocks. Spreading water across these rocks resulted in re-aeration of the previously anoxic water. Hence, dissolved manganese is reduced more than an order of magnitude during infiltration, suggesting that the ARR maintains predominantly oxic conditions throughout its infiltration depths. This is corroborated by dissolved oxygen levels of 3.3 ± 0.1 mg/L in the recovered groundwater from ARR wells characterized by equal or more than 2 weeks of subsurface travel time. Dissolved manganese (0.02 ± 0.01 mg/L) and iron (0.01 ± 0.008 mg/L) concentrations in recovered groundwater throughout the ARR site are below the U.S. Environmental Protection Agency secondary maximum contaminant limit (MCL) of 0.05 mg/L and 0.3 mg/L, respectively.

Table 1. Selected bulk water quality parameters in river water, riverbank filtrate, recovered groundwater after SMART treatment compared to native groundwater (background) at the Prairie Waters Project, Colorado.

	South Platte River (n = 5)	RBF treatment ¹ (n = 12)	RBF/ARR treatment ² (n = 5)	Native groundwater (n = 3)
DOC [mg/L]	6.4 ± 0.3	3.1 ± 0.5	2.1 ± 0.1	2.2 ± 0.4
UV _{254nm} [m ⁻¹]	13.1 ± 1.1	6.5 ± 1.2	3.2 ± 0.1	3.4 ± 1.0
SUVA [L/mg m]	2.0 ± 0.2	2.2 ± 0.3	1.5 ± 0.1	1.6 ± 0.4

Ammonia [mg N/L]	1.1 ± 0.6	0.3 ± 0.1	n.a.	n.a.
Nitrate [mg N/L]	6.2 ± 0.8	2.3 ± 1.1	2.7 ± 0.2	5.7 ± 1.8
Phosphate [mg/L]	3.4 ± 0.9	1.3 ± 0.4	<0.5 (DL)	<0.5 (DL)
Manganese [mg/L]	0.07 ± 0.01	0.9 ± 0.3	0.02 ± 0.01	<0.0001 (DL)
Iron [mg/L]	0.04 ± 0.02	0.02 ± 0.01	0.01 ± 0.01	0.01 ± 0.004
pH	7.4 ± 0.04	7.1 ± 0.15	7.1 ± 0.06	6.9 ± 0.10

¹Collected at riverbank filtration (RBF) combined collector; ²collected at aquifer recharge and recovery (ARR) combined collector; DL = detection limit; n.a. = data not available.

Due to the presence of oxic redox conditions, complete denitrification was not expected to occur at the ARR site. Indeed, nitrate concentrations observed in groundwater at the ARR site changed only slightly from 2.3 ± 1.1 mg NO_3^- -N/L in the recharged RBF filtrate to 2.7 ± 0.2 mg NO_3^- -N/L in samples collected from the ARR combined collector. However, nitrate concentrations in the native groundwater were elevated (5.7 ± 1.8 mg NO_3^- -N/L) compared to ARR wells, possibly due to agricultural impacts in the vicinity of the ARR site. A further decrease in DOC ($33 \pm 5\%$), $\text{UV}_{254\text{nm}}$ absorbance ($51 \pm 1\%$), and SUVA ($30 \pm 5\%$) occurred during recharge at the ARR site. DOC (2.1 ± 0.1 mg/L), $\text{UV}_{254\text{nm}}$ absorbance (3.2 ± 0.1 m⁻¹), and SUVA (1.5 ± 0.1 L/mg m) values in recovered groundwater at the ARR combined collector were in the same range as those measured in native groundwater (Table 1). While phosphate was not completely attenuated during RBF passage ($63 \pm 11\%$), no break through of phosphate was observed at any of the ARR recovery and monitoring wells. These results confirm that through re-aeration and sequential infiltration of water, which has been significantly reduced in available electron donors, oxic and oligotrophic conditions can be sustained in the subsurface during a subsequent infiltration.

3.2. Attenuation of trace organic chemicals during sequential RBF and ARR treatment

Select TOrC with varied degrees of biodegradability (Table S1, SI) were analyzed in order to assess the removal efficiency during SMART treatment. Their concentrations in the South Platte River water, RBF filtrate collected from the RBF combined collector, native groundwater, recovered groundwater from the ARR combined collector and binned ARR wells (with similar travel time and dilution percentage) are summarized in Table 2. The only target analytes present in native groundwater above their respective

detection limit were DEET (60 ± 36 ng/L), sulfamethoxazole (56 ± 18 ng/L), atrazine (14 ± 10 ng/L), and sucralose (533 ± 157 ng/L). DEET (insect repellent), sulfamethoxazole (veterinary antibiotic drug), and atrazine (herbicide) in groundwater from the alluvial plain most likely originate from homesteads and anthropogenic activities such as farming in the close vicinity of the MAR facility.

Atenolol, diphenhydramine, triclocarban, and trimethoprim were immediately attenuated during the short anoxic RBF passage and were not detected above their respective detection limit in the RBF filtrate recharged at the ARR site (Figure 2 and Table 2). The predicted and experimental biodegradability of the antihistamine diphenhydramine (Wu et al. 2010) and the antimicrobial triclocarban (Ying et al. 2007) in soil under aerobic and anoxic conditions is slow (i.e., half-lives of several months), pointing towards a more sorption-dominated attenuation process (e.g., organic rich colmation layer in the riverbed, dispersed clay in the riverbank) during the short RBF passage (i.e., on average less than 15 days). This is corroborated by the literature-derived soil water distribution coefficient of diphenhydramine ($K_d = 438$ L/kg), which is the highest for all analyzed TOrC in this study (Table S1, SI). Furthermore, the weak acidic drug diphenhydramine was shown to sorb to clay minerals with cation exchange being the most important mechanism (Li et al. 2011). The cationic beta-blocker atenolol and the antibiotic trimethoprim are characterized by fast biodegradation during MAR irrespective of prevalent redox conditions in the aquifer (Regnery et al. 2015a). Due to their (partial) positive charge at neutral pH, interactions with soil particles based on cation exchange are likely to retard their transport in the aquifer compared to conservative inorganic tracers, which could extend the time available for biodegradation (Schaffer et al. 2012; Burke et al. 2013). In addition, temperature and pH dependent sorption of trimethoprim to montmorillonite clay has been demonstrated (Bekçi et al. 2007).

Table 2. Concentrations in ng/L of 19 analyzed trace organic chemicals in river water, riverbank filtrate, native groundwater, and recovered groundwater after SMART treatment at Prairie Waters Project, Colorado. Average travel times and percent dilution with native groundwater provided for ARR wells.

Concentration [ng/L]	South Platte River (n = 5)	RBF treatment ¹ (n = 12)	RBF/ARR treatment ² (n = 5)	ARR wells <2 weeks, <20% dil. (n = 21)	ARR wells >2 weeks, <20% dil. (n = 24)	ARR wells >4 weeks, >50% dil. (n = 8)	Native ground water (n = 3)
Atenolol	515 ± 249	<10	<10	<10	<10	<10	<10
Atrazine	7 ± 4	11 ± 4	14 ± 1	14 ± 4	13 ± 4	18 ± 10	14 ± 10
Caffeine	490 ± 246	10 ± 6	<10	<10	<10	<10	<10
Carbamazepine	282 ± 40	172 ± 47	137 ± 7	157 ± 18	144 ± 16	77 ± 19	<25
DEET	233 ± 74	115 ± 92	52 ± 43	42 ± 36	49 ± 50	96 ± 92	60 ± 36
Diclofenac	68 ± 31	16 ± 10	<10	<10	<10	<10	<10
Dilantin	145 ± 45	66 ± 39	<25	25 ± 17	<25	30 ± 12	<25
Diphenhydramine	59 ± 36	<25	<25	<25	<25	<25	<25
Gemfibrozil	626 ± 123	46 ± 43	<10	<10	<10	<10	<10
Meprobamate	142	55 ± 36	<25	<25	<25	<25	<25
Naproxen	379 ± 148	17 ± 16	<10	<10	<10	<10	<10
Primidone	102 ± 14	61 ± 19	52 ± 6	59 ± 9	57 ± 7	34 ± 14	<25
Sucralose	12,688 ± 7,139	7,643 ± 3,380	4,025 ± 1,305	6,100 ± 2,000	4,843 ± 2257	2,680 ± 773	533 ± 175
Sulfamethoxazole	881 ± 209	308 ± 193	74 ± 8	52 ± 18	58 ± 29	147 ± 51	56 ± 18
TCEP	317 ± 59	119 ± 61	65 ± 13	84 ± 37	55 ± 34	37 ± 18	<10
TCPP	1,515 ± 397	502 ± 263	169 ± 56	138 ± 91	130 ± 103	148 ± 54	<25
TDCP	660 ± 78	227 ± 139	75 ± 47	89 ± 61	62 ± 45	36 ± 21	<50
Triclocarban	48 ± 41	<10	<10	<10	<10	<10	<10
Trimethoprim	502 ± 269	<10	<10	<10	<10	<10	<10

¹ Collected at riverbank filtration (RBF) combined collector; ² collected at aquifer recharge and recovery (ARR) combined collector.

Caffeine, diclofenac, gemfibrozil, and naproxen, all characterized as well to moderately biodegradable, were not completely removed during the short RBF passage, but were immediately attenuated during infiltration at the ARR site (Figure 2 and Table 2). Between ARR basin influent (i.e., RBF combined filtrate) and the closest ARR monitoring and recovery wells, gemfibrozil and naproxen were consistently removed to below the detection limit during estimated travel times of less than 10 days (Figure 3). Diclofenac, gemfibrozil, and naproxen were not detected above their respective detection limit in any of the ARR groundwater monitoring and recovery wells (Table 2). Diclofenac was present at low levels (68 ± 31 ng/L) in the river and was attenuated by $56 \pm 17\%$ (i.e., 29 ± 11 ng/L) in the three RBF wells with less than 10 days travel time and 15% dilution (Figure 3). Water from the RBF combined collector, which is diluted with native groundwater by approximately 30 – 35%, contained 16 ± 10 ng/L diclofenac (Table 2). Traces of caffeine in the range of 11 – 29 ng/L were detected in a few ARR groundwater samples, insinuating that primarily physical sorptive processes, especially in the presence of clay materials, could attenuate this biodegradable compound in soil-aquifer systems instead of immediate biotransformation (Karnjanapiboonwong et al. 2010; Lin et al. 2010). As binding by physical sorption is reversible, desorption is likely to occur for highly water-soluble compounds such as caffeine if ambient conditions change.

Concentrations of moderately degradable to relatively recalcitrant chemicals, such as the insect repellent DEET, the pharmaceuticals dilantin, meprobamate, sulfamethoxazole, and the chlorinated flame retardants TCEP, TCPP, and TDCP were depleted between 50% and 65% in the combined RBF filtrate (Figure 2). Their overall removal increased on average by more than 25% during subsequent ARR treatment. While the vast reduction of moderately degradable to relatively recalcitrant TOrC in the RBF combined filtrate is related to dilution with native groundwater (approximately 30 – 35%), the attenuation of TOrC during ARR exceeded by far the observed decrease in conservative organic tracers carbamazepine and primidone based on dilution alone (Figure 3). Considering similar subsurface travel times, sulfamethoxazole was with $86 \pm 4\%$ substantially better attenuated under carbon-depleted and oxic conditions during less than

10 days ARR passage, compared to $34 \pm 15\%$ during 10 day RBF characterized by carbon-rich and anoxic conditions. This removal confirms reports that sulfamethoxazole is removed most effectively under oxic conditions (Wiese et al. 2011, Baumgarten et al. 2011, Regnery et al. 2015a).

Although the moderately biodegradable compound dilantin showed considerable variation in removal effectiveness, dilantin exhibited a removal of $62.3 \pm 26.3\%$ at ARR wells with less than 2 weeks of subsurface travel time and was attenuated below detection limit in ARR wells that are further away from the infiltration basins (Table 2). Similar to dilantin, DEET removal was highly variable during RBF and ARR. DEET was attenuated less than 35% between river and the three RBF recovery wells with less than 10 days travel time but attenuated more than 60% during the comparable 10 day ARR passage (Figure 3). DEET removal was on average 60% for all analyzed ARR wells but exhibited a high variability during different samplings; the compound was also present in the background groundwater. Due to substantial mosquito emergence at the ARR site in summer months, additional input of DEET into the infiltration basins from non-point sources (e.g. during maintenance operations) cannot be excluded. These findings also point to the fact that sustaining oxic conditions during subsurface treatment is beneficial for many TOxCs resulting in a faster attenuation.

During times when high infiltration rates were not maintained during recharge cycles, removal might have been enhanced for select TOxC by direct or indirect photolysis in the shallow water body, as the open water surface of the ARR infiltration basins is extensively exposed to sunlight. Photolysis of compounds such as diclofenac and sulfamethoxazole is well documented (Buser et al. 1998; Monteiro and Boxall 2010) whereas sorption to sandy soils is negligible (Table S1, SI and Avisar et al. 2010; Lin and Gan 2011). However, water samples collected directly from the open water body in the vicinity of the influent culverts exhibited similar concentrations of target analytes than those measured in the recharged RBF filtrate collected directly from the combined collector, which minimizes the relevance of photolysis as a potential removal mechanism for the analyzed TOxC.

Attenuation of the flame retardants TCEP ($80 \pm 4\%$), TCPP ($89 \pm 4\%$), and TDCP ($89 \pm 7\%$) during SMART treatment within a short overall subsurface travel time (on average 1 month) was substantial. In general, the chlorinated organophosphate triesters are characterized by poor biodegradability in surface water and aquifers (Muir 1984; Reemtsma et al. 2008). Furthermore, TCEP and TCPP were not affected by photolysis when exposed to natural sunlight for up to two weeks (Regnery and Püttmann 2010). In contrast to organophosphate triesters used as insecticides or warfare agents (which hydrolyze more readily due to differences in physicochemical properties), most flame retardants are stable against hydrolysis at neutral pH (Reemtsma et al. 2008). However, hydrolysis of organophosphate triesters can be substantially accelerated at basic pH (Mabey and Mill 1978), in the presence of dissolved metals (Stone and Torrents 1995; Pehkonen and Zhang 2002), in the presence of clay materials (Soma and Soma 1989), or by specific microbial enzymes such as organophosphorus hydrolase, organophosphorus acid anhydrolase, and aminopeptidase P (Pehkonen and Zhang 2002; Aubert et al. 2004; Singh et al. 2006). For potential application in bioremediation, Takahashi et al. (2008) isolated TCEP and TDCP degrading bacterial strains from cultures with environmental samples using both organophosphates as the sole phosphate source. TCEP and TDCP were substantially degraded by *Sphingomonas*- and *Acidovorax*-related bacteria in enriched cultures through cleavage of the phosphoester bond and dehalogenation, respectively (Takahashi et al. 2008). Whereas phosphate-sufficient conditions are known to repress the expression of genes involved in phosphorus utilization, it was suggested that the presence of divalent cations such as cobalt, copper, and manganese could increase the activity of expressed enzymes in soil (Singh et al. 2006). Coincidentally phosphate was depleted at the ARR facility (Table 1), while manganese (33 mg/kg) and iron (1091 mg/kg) were present in significant concentrations in soil retrieved from the ARR infiltration basins because of metal oxide deposition during surface spreading of reduced RBF filtrate.

During drinking water treatment, activated carbon filtration has been shown to be a very effective process for removal of chlorinated flame retardants (Stackelberg et al. 2007). Westerhoff et al. (2005) reported the removal of TCEP during simulated drinking water

treatment (4 hours contact time) as a function of powdered activated carbon (PAC) dosage: $90 \pm 1\%$ removal of TCEP by PAC dosage of 20 mg/L whereas almost no removal occurred at dosage of 1 mg/L PAC ($14 \pm 6\%$). Interestingly, sorption percentages of TCEP and TCPP onto terrestrial humic acids, which were added to spiked water samples in the range of 0 mg/L to 50 mg/L DOC, were all below 16% in experiments conducted by Pang et al. (2013). Based on their calculated soil water partition coefficients (Table S1) and their moderate water solubility, TCEP and TCPP exhibit a low to average affinity to partition into soil. Kawagoshi et al. (1999) reported that TCEP and TCPP behaved as dissolved forms in groundwater with no distribution in suspended solids. Nevertheless, TCEP, TCPP, and TDCP (which has a higher soil affinity) were found in substantial concentrations in bottom sediment samples from a waste disposal site in Osaka Bay, Japan (Kawagoshi et al. 1999) and in marine and riverine sediments from a heavy industrialized coastal area in Japan (Ishikawa et al. 1985).

Given the low percentage of organic matter in soil at both the RBF (f_{oc} 0.05%) and ARR (f_{oc} 0.3%) facilities, it is assumed that other than hydrophobic interactions might play a role in chlorinated flame retardant attenuation as discussed in section 3.3. Furthermore, the conditions present at the ARR site (i.e., oxic conditions, low DOC, high dissolved manganese, low phosphorus) could be favorable for the expression of enzymes that catalyze the hydrolysis of organophosphate esters. The concentration of BDOC in the recharged source water and the prevailing redox condition in the subsurface both influenced the removal performance of the chlorinated flame retardants in our previous laboratory-scale experiments using well-adapted soil column systems filled with native alluvial material (>95% sand, f_{oc} <0.1%). Enhanced attenuation was demonstrated during simulated SMART conditions for TCEP (half-life of 3.5 days), TCPP (3.9 days), and TDCP (5.6 days) under oxic, low BDOC conditions after seven days residence time, while almost no attenuation occurred during anoxic (14 days residence time) soil column conditions. For TCPP and TDCP half-lives in the range of 16 to 18 days were observed under suboxic, low BDOC conditions within nine days residence time (Regnery et al. 2015a).

3.3. Effect of clay materials on trace organic chemical attenuation

As summarized in Figure S2 (SI), negligible sorption (<10%) to sand from the ARR site was observed for gemfibrozil, naproxen, DEET, diclofenac, dilantin, sulfamethoxazole, TCPP, atrazine, carbamazepine, and primidone. Except for TDCP, sorptive losses to the walls of the glass vials in the absence of soil or bentonite were less than 15% for all analytes in solution. For TDCP, they accounted for losses of up to 45%. As expected based on published literature, the partially positive charged drugs atenolol and trimethoprim, as well as the uncharged antihistamine diphenhydramine, antimicrobial triclocarban, and the stimulant caffeine showed strong sorption to montmorillonite clay and sandy clay loam, but all five compounds also revealed substantial sorptive interactions with sand containing 6% clay. For all tested TOrC in this experiment (except sucralose), the pure montmorillonite clay removed the greatest percentage of the initial TOrC concentration from the aqueous solution, followed by the sandy clay loam, which has a higher clay percentage than the sand. No sorption to any of the tested soils was observed for sucralose. Our results suggest that clay, rather than organic carbon, is the dominant sorbent at the investigated ARR facility. In general, sorption to clay gains importance for organic contaminant removal at high clay/organic carbon ratios in soils (i.e., >40). This ratio is exceeded by far in the sandy clay loam aggregates that are dispersed throughout the ARR infiltration basins and implies that sorptive processes might play a role in the attenuation and retardation of specific TOrC during SMART treatment. During controlled sorption experiments, TCEP, TCPP, and TDCP were removed from spiked (i.e., 2 µg/L) RBF filtrate in the presence of pure montmorillonite clay at a dosage of 1 g per 10 mL and 24 hours contact time by $85 \pm 3\%$, $77 \pm 5\%$, and $100 \pm 0\%$, respectively (Figure S2, SI). In the presence of sandy clay loam, sorptive losses from the aqueous phase were in the range of $37 \pm 17\%$ (TCEP), $53 \pm 30\%$ (TCPP), and $71 \pm 24\%$ (TDCP), respectively.

However, substantial desorption from the field soils (i.e., sand, sandy clay loam) was observed for the flame retardants (i.e., 24 hours contact time with non-spiked RBF filtrate), which resulted in additional concentrations of TCEP (91 – 300 ng/L), TCPP

(827 – 1,917 ng/L), and TDCP (70 – 212 ng/L) in the aqueous solution. Highest flame retardant concentrations resulted from sandy clay loam during desorption experiments. Though we were not able to further identify the responsible sorption processes for chlorinated flame retardants to the utilized clay materials, our results speak for a reversible sorptive process which can result in a release of compounds with environmental half-lives of more than a few days if hydro- or geochemical conditions (i.e., ionic strength, pH, organic carbon load) change during recharge events. With the exception of caffeine, none of the other TOrC underwent desorption suggesting that these compounds either were held more tightly to the soil, never occurred at the infiltration basins, or were degraded following sorption before the experiment started. Traces of caffeine desorbed from sandy clay loam, emphasizing our discussion that primarily physical sorptive processes could attenuate the highly water soluble stimulant caffeine during MAR instead of immediate biotransformation. However, the overall contribution of sorption to clay for selected TOrC to the overall observed attenuation is difficult to assess at the field-scale given the heterogeneous distribution of sandy clay loam aggregates and clay containing sand across the infiltration basins.

3.4. Impact of SMART on treatment performance

Findings of this study demonstrated that sequential subsurface treatment zones characterized by carbon-rich to carbon-depleted and predominant oxic conditions can be established at full-scale MAR facilities adopting the SMART concept. The initial RBF passage at the Prairie Waters Project, while infiltrating oxic river water, quickly became anoxic due to the oxidation of BDOC (3 – 4 mg/L) and remaining ammonia concentrations present in the South Platte River water (Table 1). The subsequent ARR facility fed with re-aerated RBF filtrate, in contrast, exhibited carbon-depleted and oxic redox conditions, which were previously revealed in controlled soil column experiments to facilitate exceptional removal of moderately biodegradable TOrC within shortest subsurface travel times (<10 days) as compared to anoxic subsurface conditions (Regnery et al. 2015a). By adopting the SMART concept and utilizing RBF followed by ARR, the Prairie Waters Project likely created a predominant carbon-depleted and oxic environment in the second infiltration stage. This sequence resulted in significantly

improved TOrC removal (i.e., higher biodegradation rate coefficients) compared to just extending travel times in an anoxic aquifer, as commonly practiced in conventional RBF systems.

Given the higher biotransformation rate constants under oxic, carbon-depleted MAR conditions, travel times during the second infiltration step could potentially be reduced. Figure 4 shows that there is almost no difference in removal efficiency between recovery wells with less than two weeks and more than two weeks travel time for moderately degradable TOrC under oxic and low BDOC conditions at the ARR facility. It is likely that under these conditions most of the TOrC attenuation happens within the first few meters of infiltration. This offers opportunities to further reduce the physical footprint of the recharge facility while still maintaining similar water qualities. Furthermore, the initial anoxic RBF passage facilitated denitrifying microbial processes, resulting in depleted nitrate concentrations before the water is recharged into a predominantly oxic aquifer where no further reduction of nitrate will occur.

In order to transfer the SMART concept to other sites, several aspects need to be considered. The main role of the first infiltration step during SMART is the reduction of electron donors. In biologically active systems like RBF or soil-aquifer treatment, this can be achieved during short travel times and usually comes with the additional benefit of achieving denitrification. However, for denitrification of elevated nitrate concentrations ($>8 \text{ mg NO}_3^- \text{-N/L}$) an additional carbon supply is required, which might be provided by particulate organic carbon deposits in sediments. Establishing oxic conditions in the second infiltration stage of SMART will depend on the oxygen demand of the RBF filtrate, the layout of the aeration system, and the oxygen demand of the soil within the second infiltration facility. The second infiltration step requires an engineered recharge facility that is comprised of alluvial material characterized by high hydraulic conductivity and relatively low f_{oc} content. The *in situ* deposition of oxidized manganese (after re-aeration) during the second infiltration step can be maintained over a long time period without compromising hydraulic properties of the infiltration basin. However, at elevated iron concentrations ($>0.5 \text{ mg/L}$) in the reduced water of the first SMART treatment step,

iron hydroxides will deposit on the surface of the subsequent infiltration step, which will require more frequent cleaning cycles or a tailored engineered iron filtration step prior to infiltration. In addition, the re-aeration step could also be replaced by an intermediate ozonation step since chemical oxidation using a strong oxidant offers opportunities for removal of TOrC persistent to biodegradation (Drewes and Jekel 1998; Hübner et al. 2012).

This study also revealed that dispersed clay aggregates as well as the deposited manganese at the ARR spreading basins provided additional sorption/binding sites for less hydrophobic compounds such as the chlorinated flame retardants. In a recent study, Valhondo et al. (2014) implemented a permeable layer supplemented with small amounts of iron oxide ($<0.1\%$ in volume) and clay ($\leq 1\%$ in volume) at the bottom of an infiltration basin to increase the diversity and number of sorption sites as part of a reactive barrier. Thus, additional opportunities exist to integrate reactive barriers into the SMART concept. Additional studies at full-scale installations are underway to further demonstrate the benefits of SMART compared to traditional MAR operations.

4. Conclusion

The concept of establishing sequential subsurface treatment zones characterized by carbon-rich to carbon-depleted and predominant oxic conditions could be demonstrated at a full-scale MAR facility. The sequence of redox zonation featured the most-favorable conditions for a variety of water quality goals in one treatment train. A SMART treatment system can use highly impaired source water while providing effective DOC removal (likely also reduced regrowth potential), denitrification, pathogen attenuation, manganese removal, and effective removal of a variety of TOrC. All of these water quality benefits are delivered with no chemical addition, minimal maintenance, and a low energy footprint compared to other advanced treatment strategies. Understanding the key factors controlling TOrC removal performance during SMART allows for systems to be engineered for optimal efficiency, resulting in improved removal of constituents at shorter travel times. By operating at shorter retention time, such designs also allow for smaller physical footprints relative to yield.

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Figure 1

Figure 1. Conceptual design of a sequential managed aquifer recharge system based on optimized redox zonation and availability of biodegradable dissolved organic carbon (BDOC) in the recharged source water.

Figure 2

Figure 2. Percent removal of 18 trace organic chemicals during solely riverbank filtration (RBF) passage (i.e., samples collected at RBF combined collector) and RBF passage followed by artificial recharge and recovery (ARR) treatment (i.e., ARR combined collector), respectively. Error bars are indicated by black lines.

Figure 3

Figure 3. Removal efficiencies for selected trace organic chemicals during a short subsurface passage of less than 10 days and less than 20% dilution with native groundwater. Grey bars represent the carbon-rich and anoxic RBF passage, blue bars represent the carbon-depleted and oxic ARR passage. Error bars are indicated by black lines.

Figure 4

Figure 4. Trace organic chemical removal performance at ARR monitoring and recovery wells with less than 2 weeks (blue bars) and more than 2 weeks (orange bars) subsurface travel time, respectively. Error bars are indicated by black lines.