Accepted Manuscript

Biotransformation of trace organic chemicals during groundwater recharge: How useful are first-order rate constants?

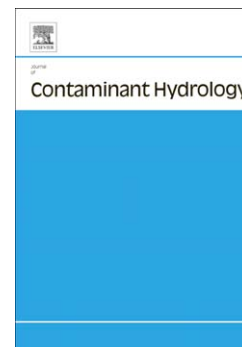J. Regnery[1], A. D. Wing[1], M. Alidina[2], J.E. Drewes[1,3,*]

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Abstract

This study developed relationships between the attenuation of emerging trace organic chemicals (TOrC) during managed aquifer recharge (MAR) as a function of retention time, system characteristics, and operating conditions using controlled laboratory-scale soil column experiments simulating MAR. The results revealed that MAR performance in terms of TOrC attenuation is primarily determined by key environmental parameters (i.e. redox, primary substrate). Soil columns with suboxic and anoxic conditions performed poorly (i.e. less than 30% attenuation of moderately degradable TOrC) in comparison to oxic conditions (on average between 70-100% attenuation for the same compounds) within a residence time of three days. Given this dependency on redox conditions, it was investigated if key parameter-dependent rate constants are more suitable for contaminant transport modeling to properly capture the dynamic TOrC attenuation under field-scale conditions. Laboratory-derived first-order removal kinetics were determined for 19 TOrC under three different redox conditions and rate constants were applied to MAR field data. Our findings suggest that simplified first-order rate constants will most likely not provide any meaningful results if the target compounds exhibit redox dependent biotransformation behavior or if the intention is to exactly capture the decline in concentration over time and distance at field-scale MAR. However, if the intention is to

calculate the percent removal after an extended time period and subsurface travel distance, simplified first-order rate constants seem to be sufficient to provide a first estimate on TOrC attenuation during MAR.

Keywords: Trace organic chemicals; managed aquifer recharge; first-order rate constants; redox conditions; primary substrate; attenuation modeling

1. Introduction

The increasing demand for drinking water supplies in recent years has resulted in steadily growing interest in using impaired water sources (i.e., recycled water, stormwater) for augmentation of potable aquifers via managed aquifer recharge (MAR). MAR systems, such as riverbank filtration and soil aquifer treatment, are natural water treatment processes with the goal to enhance groundwater quantity and quality by taking advantage of hydro-geochemical and biological processes. Since impaired water sources often contain a broad range of inorganic and organic contaminants, knowledge about their fate and transport during subsurface treatment in an aquifer leading to drinking water augmentation is essential for proper design and operation of MAR facilities. Attenuation of organic contaminants such as trace organic chemicals (TOrC) is mainly caused by microbial transformation, while sorption to soil components retards their transport. Modeling fate and transport of TOrC typically requires detailed numerical groundwater flow and multi-component reactive transport models (Greskowiak et al. 2006; Prommer and Stuyfzand 2005; Sharma et al. 2012). However, studies that aim to quantify the attenuation of numerous TOrC characterized by different physicochemical properties often omit a detailed analysis of factors influencing contaminant transport behavior (Henzler et al. 2014). First-order rate constants and linear soil water distribution coefficients provide only a partial description of biodegradation and sorption processes since they neglect the temporal and spatial variability of key environmental parameters. Since the degree of TOrC biotransformation during MAR is determined by the composition of the source water (i.e., availability and make-up of organic carbon serving as primary substrate for microbial metabolism), predominant redox conditions, temperature, and residence time in the subsurface (Massmann et al. 2006; Rauch-

Williams et al. 2009; Laws et al. 2011; Li et al. 2013), changes of these key environmental parameters may enhance, decelerate, and sometimes initiate biotransformation of TOrC.

Previous research revealed that the primary substrate, more specifically the bioavailability of biodegradable dissolved organic carbon (BDOC), directly affects the microbial community structure and function in soil-water systems and as a consequence also TOrC attenuation (Li et al. 2013, 2014; Alidina et al. 2014a). Although high BDOC availability usually results in a greater biomass production of biological active systems, the resulting microbial community usually is less diverse. Oligotrophic conditions, however, can result in an increase in diversity of the microbial community, which can feature the ability to better transform also moderately biodegradable TOrC (Li et al. 2013, 2014; Alidina et al. 2014a,b). Refractory dissolved organic carbon (DOC) is composed of a greater diversity of organic molecules creating a selective pressure for those microorganisms that can express different metabolic functions to utilize these carbon sources as primary substrate (Li et al. 2014). This overall increase in metabolic function (increase in enzymatic diversity) can provide a greater opportunity for co-metabolic transformation of TOrC. Since composition and availability of BDOC usually changes with residence time and travel distance, TOrC attenuation is highly sensitive to changes in primary substrate composition.

The redox environment of MAR systems has been identified as a primary driver for mobility, dissolution, transformation, and toxicity of most TOrC present in infiltrating water (Hoppe-Jones et al. 2010; Wiese et al. 2011; Grützmacher and Reuleaux 2012; Regnery et al. 2013). Microorganisms are adapted to specific redox zones and microbial activity drives redox conditions in the subsurface besides hydro-geochemical reactions. Effluent-impacted waters usually contain high concentrations of BDOC, which serves as an electron donor for soil microorganisms. In a typical recharge situation, a sequence of reduction processes from highly oxidized conditions to reducing conditions will develop over time as a function of travel distance. Dissolved O_2, which usually is enriched in water applied to recharge basins, will be consumed in the initial zone of infiltration, followed by nitrate reduction and subsequent reduction of Mn(IV) and Fe(III) oxides, as well as sulfate providing electron donors are still present (McMahon and Chapelle 2008).

Where no particulate organic matter is deposited and the BDOC of the infiltrating water is characterized by limited bioavailability, less reduced redox conditions in the aquifer will establish.

Though several field studies from MAR sites investigated redox-dependent attenuation of certain TOrC (Drewes et al. 2003; Schmidt et al. 2004; Heberer et al. 2008; Massmann et al. 2006; Wiese et al. 2011), only limited knowledge is available from controlled laboratory-scale studies that systematically investigated and compared the influence of different redox conditions on biotransformation of TOrC in the subsurface (Suarez et al. 2010; Baumgarten et al. 2011; Burke et al. 2014). Burke et al. (2014) compiled the redox dependent degradation behavior of 27 wastewater-derived TOrC in groundwater based on several studies using tank aeration experiments with no soil present. Based on extensive field data from three MAR sites, Wiese et al. (2011) evaluated removal efficiencies for 29 TOrC under different redox conditions at a macro-scale. For TOrC exhibiting redox dependent degradation behavior, biotransformation rates can vary significantly (Greskowiak et al. 2006). Seasonal temperature changes also have an effect on the redox chemistry of groundwater and can lead to significant differences in TOrC removal efficiency (Massmann et al. 2006). Therefore, affecting redox conditions of MAR systems can change the removal performance of redox-sensitive TOrC (Grützmacher and Reuleaux 2011; Regnery et al. 2013; Müller et al. 2013).

Rate constants are considered useful to provide first estimates of the fate of TOrC at field-scale, which is essential for the design and operation of MAR sites. Nevertheless, the question can be asked, how accurate rather simplified first-order rate constants are for model-based prediction of contaminant fate and transport considering the variability of environmental conditions. Thus, the objectives of this study were i) to develop relationships between the attenuation of representative TOrC as a function of retention time, system characteristics, and operating conditions using controlled laboratory-scale soil column experiments simulating MAR and ii) to evaluate if key parameter-dependent rate constants are needed in contaminant transport modeling to properly capture dynamic TOrC attenuation processes at field-scale.

2. Material and methods

2.1. Soil column experiments

Different 1D-soil column systems (PC, C1, C2) equipped with intermediate sampling ports were established and operated for more than five years to simulate prevailing biochemical conditions in MAR systems as described in Table 1. All soil column systems were operated at room temperature (20˚C) in top to bottom (one dimensional) flow at a hydraulic loading rate of 0.094 m d^{-1}. A detailed description of the soil column system's flow characterization and abiotic control experiments to assess whether physical retardation would be a contributing factor in the removal of select TOrC in the column experiments is provided elsewhere (Rauch-Williams et al. 2010; Hoppe-Jones et al. 2012; Alidina et al. 2014b; Drewes et al. 2015). The soil column feed water was either a dechlorinated tap water (City of Golden, Colorado) or a secondary treated wastewater effluent obtained from a local wastewater treatment plant employing nitrification and partial denitrification. To adjust the DOC level in the treated wastewater effluent, feed water was blended with nanofiltered (NF) permeate. NF permeate was produced from tap water filtered through a 80 L min^{-1} NF membrane skid equipped with 21 Dow/Filmtec 4040 NF 270 elements (Midland, MI) at a permeate flux of 20 LMH and a recovery of 85%. Except for column system C2, the column feed water was regularly purged with N_2 gas to keep dissolved O_2 concentrations below 0.5 mg L^{-1} in the feed container. Column feeds were housed in plastic carboys and were delivered to the columns by peristaltic pumps (Masterflex, Cole-Parmer, Vernon Hills, IL). All soil columns were continuously spiked with a mix of 19 TOrCs at environmentally relevant concentrations (ng L^{-1} level) in addition to the ambient level already present in the different feed waters using a high-precision multi-channel pump (Ismatec IPC 8, IDEX, Wertheim, Germany). The TOrC spiking solution was contained in an amber glass bottle maintained at 5˚C and was renewed every other day. The selected TOrCs exhibit different degrees of biodegradability in aerobic biological systems (Table 2) and were previously evaluated to be suitable indicator compounds for the assessment of MAR performance (Drewes et al. 2008; Drewes et al. 2011).

2.2. Redox classification

In order to classify redox conditions, different definitions of what constitutes oxic,

suboxic, anoxic, and anaerobic conditions have been proposed in the literature (i.e., Leahy and Olsen 1997; McMahon and Chappelle 2008; Borch et al. 2010). For the purpose of this study, redox conditions were divided into the three categories oxic, suboxic, and anoxic following the framework for identifying redox processes in aquifer systems developed by McMahon and Chapelle (2008). NH_3/NH_4^+, NO_3^-, Mn^{2+}, Fe^{2+}, and SO_4^{2-} were chosen as redox indicators and their concentrations were measured in the influent and effluent of each soil column system on a weekly basis. Oxic conditions were assumed if neither NO_3^- reduction (expressed as positive ΔNO_3^- value) nor Mn^{2+} above 0.05 mg L^{-1} was detected, which corresponds to dissolved O_2 concentrations equal to approximately 1 mg L^{-1} (Wilson and Bouwer, 1997). Suboxic (ΔNO_3^- <0.5 mg N L^{-1}, Mn^{2+} <0.05 mg L^{-1}) and anoxic (ΔNO_3^- $\geq$0.5 mg N L^{-1}, Mn^{2+} >0.05 mg L^{-1}) conditions were achieved by purging the feed container with N_2 gas (<1 mg L^{-1} dissolved O_2 concentration). Highly reducing conditions (ΔSO_4^{2-} $\geq$0.5 mg L^{-1}, Fe^{2+} $\geq$0.1 mg L^{-1}) were not observed in the soil column systems. The chosen classification of redox conditions acknowledges functional differences in the potency of different electron acceptors.

2.3. Sample collection and analysis

For each experimental soil column condition, a minimum of five TOrC sampling campaigns was carried out during an 18-month period. Column system C2 was sampled over the period of three months in October to December 2011 (oxic, high BDOC) and over two months in September to October 2012 (oxic, low BDOC), whereas both column systems PC (suboxic, low BDOC) and C1 (anoxic, high BDOC) were sampled over a period of four months, from September to December 2011. Water samples for TOrC analysis (100 mL) were immediately preserved with sodium azide to prevent further biotransformation and samples were stored at 5°C pending analysis (<72 hours). Control of redox conditions was accomplished as described in section 2.2.

Anions (i.e., NO_3^-, SO_4^{2-}) were determined using a Dionex IS 90 Ion Chromatography system (Sunnyvale, CA) according to Standard Method 4110B. Cations (i.e. Fe^{2+}, Mn^{2+}) were determined using a Perkin Elmer Elan 6100 inductively coupled plasma mass spectrometry system (Waltham, MA) according to Standard Method 3125B (APHA 2012). NH_3/NH_4^+ was analyzed using the Hach TNTplus^{TM} 830 ammonia kit (method

10205; Loveland, CO). Dissolved O_2 was determined by an YSI Inc. model 55 meter (Yellow Springs, OH). DOC was quantified using a Sievers 5310 TOC analyzer (Ionics Instruments, Boulder, CO) according to Standard Method 5310B. Samples were filtered over 0.45 μm (Pall, Ann Arbor, MI) and were subsequently acidified with H_3PO_4 prior to DOC analysis. BDOC was determined as differential measurements of DOC measured in the soil column influent and effluent after travel time of more than 7 days. Ultraviolet absorbance at 254 nm (UVA) was analyzed using a Beckman UV/VIS spectrophotometer (Fullerton, CA) with a 1-cm quartz cell (Standard Method 5910B). The ratio between UVA and DOC is defined as specific UV absorbance (SUVA). Size exclusion chromatography (SEC) with paired UVA and DOC detection was carried out to measure the molecular weight distribution of heterogeneous natural organic matter in aqueous samples using a LC-600 liquid chromatograph (Shimadzu, Kyoto, Japan) coupled with a SPD-10 A VP UV-VIS detector (Shimadzu, Kyoto, Japan) (Rauch and Drewes 2005; Drewes et al. 2006; Drewes et al. 2011).

TOrC analysis by solid phase extraction (SPE) and high performance liquid chromatography coupled with tandem mass spectrometry (LC/MS-MS) was performed using isotope dilution (Teerlink et al. 2012). Isotope standards were obtained for all target analytes except TCPP and TDCP as detailed in Teerlink et al. (2012). Water samples were extracted by Waters Oasis HLB cartridges (500 mg adsorbate, Milford, MA) using an automated SPE unit (AutoTrace 280, Thermo Scientific, Waltham, MA). LC/MS-MS analysis was performed using an Agilent 1200 HPLC (Santa Clara, CA) and a CTC Analytics HTS PAL autosampler (Lake Elmo, MN) equipped with a 1 mL sample loop for chromatography, coupled with an Applied Biosystems 3200 Q-Trap MS/MS (Foster City, CA) system. Compounds were separated using a 150 mm × 4.6 mm Luna C18 column (Phenomenex, Torrance, CA) with 5 μm particle size. A summary of target compound specific mass spectrometry tuning parameters as well as average surrogate recoveries is provided in Teerlink et al. (2012). The reported TOrC concentrations account for sample loss and ion suppression during analysis as a relative response ratio of standard and surrogate is expressed. Targeted TOrC and their respective quantification limits (LOQ) are summarized in Table 2.

2.4. First-order removal

For all DOC and TOrC data, an exponential first-order decay model (Eq. 1) was used to calculate the degradation rate constant λ:

$$C_{(t)} = C_0\, e^{-\lambda t} \qquad \text{(Eq. 1)}$$

where $C_{(t)}$ is the concentration at time t (ng L^{-1}) and C_0 is the concentration at time 0 (ng L^{-1}).

Each soil column sampling port represents a defined residence time determined through conservative tracer studies (data not shown). The logarithmically transformed average concentration of up to 6 sampling events per experiment for each individual sampling port was plotted against soil column residence time and a linear regression was fitted. Concentrations below the compound respective LOQ were set equal to half the LOQ. A linear relationship is given for the logarithmic form of Eq. 2:

$$\ln C_{(t)} = \ln C_0{}^{-\lambda t} \qquad \text{(Eq. 2)}$$

Half lives ($t_{1/2}$) are defined as the time at which concentration reaches half the initial concentration and were calculated by Eq. 3:

$$t_{1/2} = \frac{\ln 2}{\lambda} \qquad \text{(Eq. 3)}$$

Since other attenuation processes leading to TOrC dissipation besides biodegradation cannot entirely be ruled out, the term DT_{50} will be used in the following instead of $t_{1/2}$ as it reflects the time for the dissipation of 50% of the initial concentration (Beulke and Brown 2001). Although the logarithmic transformation (Eq. 2) assigns a larger weight to smaller concentrations and might result in more conservative DT_{50} values (Beulke and Brown 2001), this approach was chosen to allow for the determination of outliers in the dataset. Removal rate constants were indicated as <0.001 if compounds showed no decrease in concentration over the duration of the experiment (also reflected by a poor coefficient of determination R^2) or if λ turned negative (Burke et al. 2014). The first-order equation was considered acceptable for R^2 values above 0.63. With the exemption of caffeine, the utilized sandy soils with their low soil organic carbon content only pose low sorption potential for the selected TOrC as indicated by the compound-specific soil sorption coefficients (K_d) for sand in Table 2 and results of previous studies (i.e. Rauch-Williams et al. 2010; Alidina et al. 2014b). Therefore, first-order removal rates are

assumed to mainly represent attenuation by biotransformation and were not further corrected for possible attenuation due to sorption.

2.5. Validation with field data

In addition, soil column system derived TOrC degradation rate constants for the moderate biodegradable pharmaceutical drugs diclofenac and gemfibrozil were compared and validated with field data obtained during two synoptic sampling campaigns in December 2012 and April 2013 at the well-characterized San Gabriel Spreading Grounds Test Basin, Montebello Forebay, Los Angeles County, California (Drewes et al. 2015). The expected removal for the selected TOrC at defined residence times (C_t) was calculated based on each laboratory derived degradation rate constant (λ) using the measured Test Basin influent concentrations as initial concentration C_0 according to Eq. 1. The calculated results were compared with the observed removal in the field at the respective residence times ($n \geq 5$) to evaluate how well the computed data correlated with the observed field data.

3. Results and discussion

3.1. Fate of primary substrate during infiltration

Relevant organic water quality parameters in the feed water applied to the soil columns and the changes in NO_3^- and Mn^{2+} after travel through the soil columns are summarized in Table 3. The DOC concentration in the secondary treated wastewater effluent applied to column systems C1 and C2 was on average 8 mg L^{-1}, with UVA values above 14 m^{-1} and SUVA values between 1.7 and 1.8 L mg^{-1} m^{-1}, respectively. On average, NH_3/NH_4^+ concentrations in the nitrified/partial denitrified treated wastewater effluent were still between 6.6 and 7.5 mg N L^{-1} and revealed significant oxygen demand for further nitrification. BDOC levels varied and were in the range of 2.8 to 4.2 mg L^{-1} influencing the subsurface system's redox condition. As electron acceptors are depleted during microbial metabolism of DOC, the redox state of MAR system generally transitions from an oxic setting towards suboxic and anoxic redox states. Hence, the non-N_2-purged secondary treated wastewater effluent did not maintain its previously oxic condition during passage through soil column C2 (Table 3). The NF permeate that was used for

blending contained only 0.26 mg L^{-1} DOC with a SUVA value equal to 0.79 L mg^{-1} m^{-1}. The 70:30 (v/v) NF permeate to secondary treated effluent blend reduced the influent DOC to 3.3 mg L^{-1} and NH_3/NH_4^+ to 0.5 mg N L^{-1}. This reduction was sufficient to maintain oxic conditions throughout soil column C2, as NO_3^- was not reduced and no changes between influent and effluent Mn^{2+} concentrations were observed. The N_2-purged tap water used in column PC exhibited a DOC concentration of 1.2 mg L^{-1} on average and a SUVA value equal to 3.1 L mg^{-1} m^{-1}. This was the highest SUVA value of all applied water blends, suggesting the organic carbon was more aromatic in nature. The tap water feed, purged of dissolved oxygen and low in NO_3^- and NH_3/NH_4^+, exhibited reduction of the small amount of NO_3^- present and resulted in a slight decrease of 0.13 mg N L^{-1}, but Mn^{2+} concentrations stayed well below 0.05 mg L^{-1}.

Organic matter fractionation using SEC-DOC/UVA analyses of the soil column feeds (Figure 1) implied that dilution of secondary treated wastewater effluent with NF permeate reduces the concentration of biopolymers and humic-like substances, but maintained the amount of acids, low molecular weight humic substances and neutrals. Both chromatograms indicate that these low molecular weight fractions are retained to a larger degree than higher molecular weight substances, which are removed by membrane filtration due to size exclusion (Figure 1). Tap water exhibited a similar pattern as the 70:30 (v/v) NF permeate: secondary treated effluent blend but at lower concentrations and with fewer biopolymers and further-reduced humic-like substances.

3.2. First-order TOrC degradation rate constants

Since the non-N_2-purged secondary treated wastewater effluent did not maintain its oxic condition throughout the 1.2-m long soil column C2, this experiment was neglected for the calculation of first-order removal kinetics. Instead, we focused on those three experiments exhibiting consistent redox conditions (as defined in section 2.2.) throughout the soil column system (Table 1). In the following, these experiments are referred to as: Oxic (low BDOC), suboxic (low BDOC), and anoxic (high BDOC) with individual residence times of 7, 9, and 14 days respectively. The derived first-order rate constants and respective DT_{50} values for the selected 19 TOrC are summarized in Table 4. Available literature values of compound-specific first-order rate constants and DT_{50}

values including prevalent redox conditions are presented in Table 5. A graphical example on how first-order kinetics were fit to the experimental data is given in Figure 2 for atenolol (good biodegradability in MAR systems), gemfibrozil, diclofenac (both moderate biodegradability) and primidone (poor biodegradability) under oxic, suboxic, and anoxic conditions ($n \geq 5$). As shown in Figure 2, attenuation of gemfibrozil and diclofenac was highly influenced by the redox condition of the soil/water system. The transient redox condition suboxic resulted in high variability (large error bars) for TOrC that showed fast attenuation under oxic conditions, but poor attenuation under anoxic conditions. Such a high variability under suboxic conditions was not observed for TOrC with either good (i.e. atenolol, caffeine) or poor biodegradability (i.e. primidone, carbamazepine) in subsurface systems, thus experimental or analytical errors could be ruled out. Based on the location of intermediate sampling ports in the columns, a common residence time of 3 days was chosen for comparison of removal performance between the three soil column systems.

3.3. Role of key environmental conditions on TOrC attenuation

The concentration of BDOC and the prevailing redox condition both influenced the removal performance of well and moderately biodegradable TOrC as indicated by the first-order rate constants. However, this effect was more distinct for TOrC with moderate biodegradability (Figure 2 and Table 4). As seen in previous studies (Table 5), no attenuation was observed for the recalcitrant anticonvulsants primidone and carbamazepine, the herbicide atrazine, and the artificial sweetener sucralose during simulated MAR in the laboratory-scale soil column systems. Attenuation of these chemicals was less than 10% throughout all experimental soil column conditions and resulted in DT_{50} values of >2 years. For sucralose it has to be taken into account that the sweetener concentrations in the soil incubation experiments by Buerge et al. (2011) were comparatively high (initial sucralose concentration of 1 mg/kg), which might have influenced the biotransformation process.

Easily biodegradable TOrC such as atenolol, caffeine, and trimethoprim were attenuated more than 80% under both oxic and suboxic conditions during simulated MAR (three days residence time) as illustrated in Figure 3. A similar high removal was observed for

trimethoprim and acetaminophen under anoxic conditions, whereas atenolol and caffeine were attenuated by approximately 50%.

For moderately biodegradable compounds complete removal was demonstrated for diclofenac, gemfibrozil, and naproxen in soil column C2 under oxic conditions within a residence time of three days (Figure 3). In comparison, diclofenac and gemfibrozil, similar to sulfamethoxazole and DEET, exhibited almost no attenuation under anoxic conditions after 3 days residence time. However, sulfamethoxazole and DEET were attenuated more than 70% on average under oxic conditions. Naproxen was attenuated by about 20% under both suboxic and anoxic conditions within three days residence time. Overall, the soil columns with suboxic and anoxic experimental conditions performed poorly (i.e. less than 30% removal of moderately degradable compounds) in comparison to the oxic conditions within a residence time of three days (Figure 3). The optimal redox condition for diclofenac removal is disputed in the literature (Table 5). Several studies reported diclofenac was best removed under anoxic conditions (i.e. Rauch-Williams et al. 2010; Zwiener and Frimmel 2003), while others report the compound was removed best under oxic conditions (Wiese et al. 2011). Improved attenuation of sulfamethoxazole under oxic conditions confirms results reported by Baumgarten et al. (2011) and Grünheid et al. (2005), although these studies observed much slower removal at ng L^{-1} spiking level, requiring at least 14 days for 60% removal (half-lives of only one day were reported at higher spike concentrations).

Enhanced attenuation was also demonstrated for the anticonvulsant dilantin ($DT_{50} = 13.6$ days), the artificial sweetener acesulfame (4.2 days) as well as the chlorinated flame retardants TCEP (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 (Table 4). Similar results were obtained in previous studies (Table 5).

Li et al. (2012, 2013) reported that a reduced amount of BDOC and the corresponding shift towards more refractory primary substrates such as humic material resulted in a more diverse microbial community in biologically active soil systems. However, Li et al. (2013) also revealed that microbial diversity converges with depth, suggesting that after sufficient residence time, BDOC is depleted and both high and low BDOC receiving

soil/water systems exhibit a similar degree of microbial diversity in deeper zones. Thus, while microbial diversity may converge with depth, the redox state of the system will differ depending on the amount and makeup of carbon present in the initial feed. Therefore, if microbial diversity and resulting functionality is the more important controlling factor in TOrC removal, both high and low BDOC receiving soil column systems would have been expected to perform similarly after a certain residence time and result in comparable TOrC rate constants. Since this was not the case, these results underscore the importance of co-existing oxic and low BDOC conditions for enhanced TOrC removal.

Even though carbon-limited conditions (low BDOC) have been demonstrated to result in improved TOrC attenuation, there is likely a threshold where insufficient carbon is present to sustain enough biomass for effective co-metabolic decay. For example, the highly toxic disinfection by-product n-nitrosodimethylamine (NDMA) is biodegradable by MAR systems under most conditions, but has proven to persist in direct-injection settings of deep aquifers recharged with water treated by reverse-osmosis (Mitch et al. 2003). The extremely-limited carbon present in reverse-osmosis permeate and in deep aquifers may simply be inadequate for supporting the requisite biomass for degrading the compound, a hypothesis confirmed in column experiments by Nalinakumari et al. (2010). However, a threshold BDOC concentration may not be required for biotransformation if the organic carbon is sourced from sediment organic carbon. Recently, Patterson et al. (2012) reported the degradation of NDMA in water treated by reverse-osmosis that was recharged into an anaerobic aquifer.

3.4. Estimating TOrC attenuation during MAR

Figure 4 illustrates the field data from the San Gabriel Spreading Grounds Test Basin experiments. The grey diamonds represent measured average concentrations including error bars for each sampled well (n ≥ 5) as well as the Test Basin influent concentration (n = 17). The large error bars for the field samples are related to highly variable TOrC concentrations in the test basin influent during both synoptic sampling campaigns as discussed in Drewes et al. (2015). The dotted lines in Figure 4 indicate the calculated biotransformation of (a) diclofenac and (b) gemfibrozil by simple first-order kinetic (i.e.,

one rate constant for the entire transect neglecting transient redox conditions in the subsurface). Diclofenac and gemfibrozil concentrations were calculated for each of the sampled wells based on the respective residence times and the average Test Basin influent concentration using the laboratory derived rate constants for either oxic (----), suboxic ($———$), or anoxic (- $—$ -) redox conditions, respectively. No other contaminant transport processes (i.e., advection, dispersion, sorption) were considered in this simplified approach. The correlation coefficient (R) between calculated and observed removal were in the range of 0.91 (using the oxic rate constant), 0.92 (suboxic), and 0.81 (anoxic) for diclofenac and 0.96 (oxic), 0.69 (suboxic), and 0.51 (anoxic) for gemfibrozil, respectively. Although R values between 0.7 and 1 indicate a strong positive linear relationship, it appears that including only one rate constant in the first-order kinetic (instead of different rate constants representative of the respective predominant redox states during subsurface passage) can result in a significant over- or underestimation in TOrC decline at defined subsurface residence times/travel distances and might not be appropriate for reliable prediction of TOrC attenuation in the field (Figure 4).

To account for the sequence of redox conditions determined in the underlying aquifer of the San Gabriel Spreading Grounds Test Basin (oxic conditions during infiltration followed by suboxic and anoxic conditions in the underlying aquifer), the first-order kinetic was subdivided into three zones based on available hydrochemical data (i.e., dissolved O_2, NO_3^-, Mn^{2+}, Fe^{2+}, SO_4^{2-} concentrations) for all sampled groundwater wells. Oxic (orange shading) conditions were determined for the first 0.45 days of residence time and predominantly anoxic (purple shading) conditions for >8 days residence time. The redox state in-between was transient and classified as suboxic (green shading). For each compartment (oxic, suboxic, anoxic) the specific laboratory-derived rate constant was used to fit the curve (····) to the field data (Figure 4). R-values for the fitted curve were 0.95 (diclofenac) and 0.97 (gemfibrozil).

4. Conclusion

Results from field and from soil column experiments revealed that MAR performance in terms of TOrC attenuation is determined by specific key environmental parameters. BDOC and redox conditions are tightly linked through electron donor/acceptor

interactions. If the effects of both BDOC concentration and redox state on TOrC attenuation are known, a relationship can be derived between TOrC attenuation, BDOC, redox conditions, and required subsurface residence times. Understanding these key factors allows for MAR systems to be engineered for optimal efficiency, resulting in improved attenuation of TOrC at shorter subsurface residence times.

First-order rate constants for contaminant fate and transport models are in particular sensitive for redox sensitive target compounds. Thus, using simplified first-order rate constants will most likely not capture the decline in concentration over time and distance at field-scale MAR for these TOrC. However, if the focus is not on the initial phase of infiltration and transient redox condition, but to calculate the percent removal after an extended time period and subsurface travel distance, simplified first-order rate constants seem to be sufficient to provide a first estimate on TOrC attenuation during MAR.

Nevertheless, it is also critical to note that biotransformation can only be expected if a minimum BDOC threshold concentration is maintained to support an effective microbial population.

Acknowledgement

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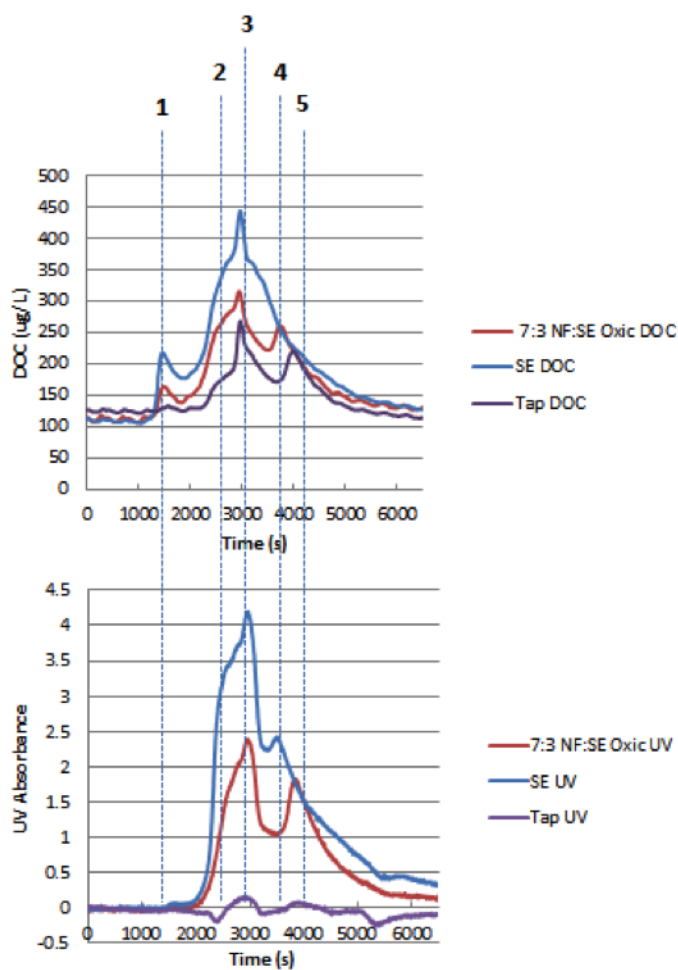
Figure 1. SEC-DOC/UVA chromatograms for soil column influent samples: 70:30 (v/v) NF permeate to secondary treated effluent blend (red), secondary treated effluent (blue), and tap water (purple). Peaks represent (1) biopolymers, (2) humic-like substances, (3) polymer building blocks, (4) acids and low molecular weight humic substances, and (5) low molecular weight neutrals.
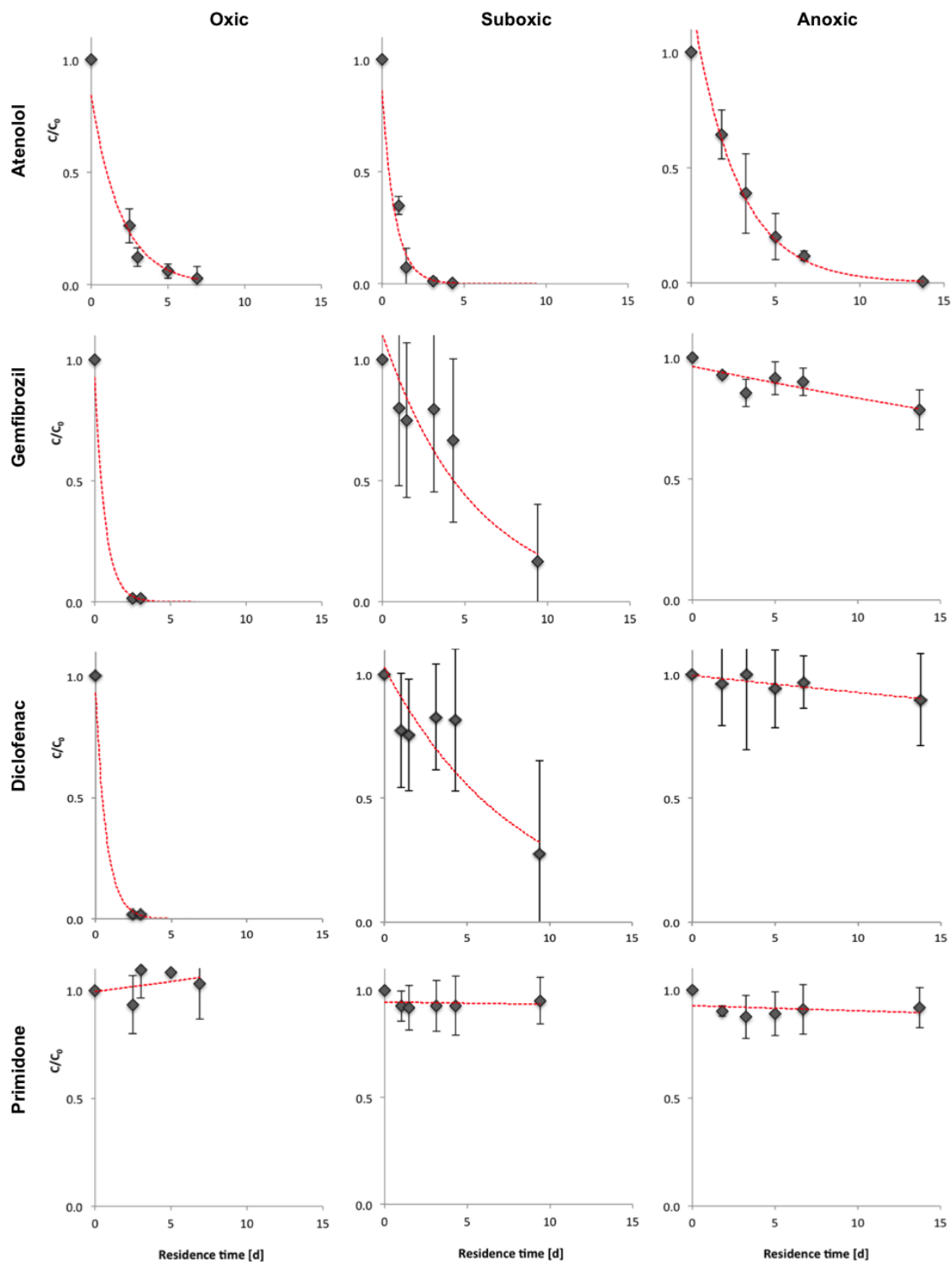
Figure 2. Fit of first-order kinetic to datasets (n ≥ 5) of atenolol, gemfibrozil, diclofenac, and primidone for three different redox conditions (oxic, suboxic, anoxic).
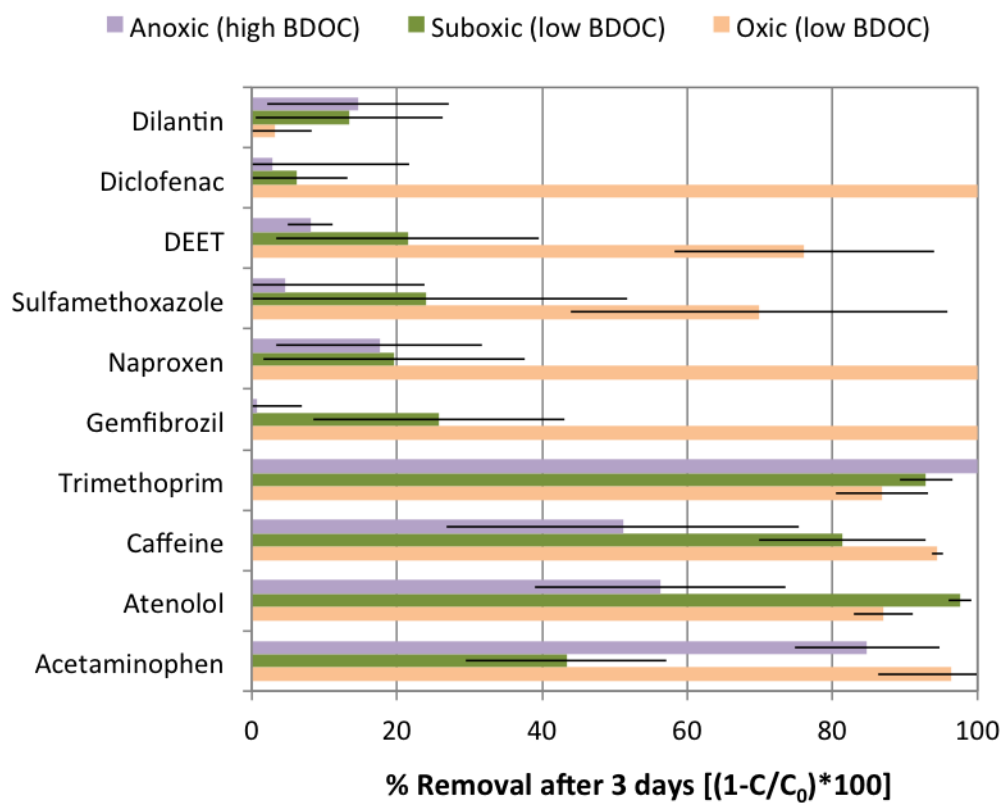
Figure 3. Percent removal of selected TOrC in soil columns under different redox conditions after three days residence time. Black lines indicate error bars.
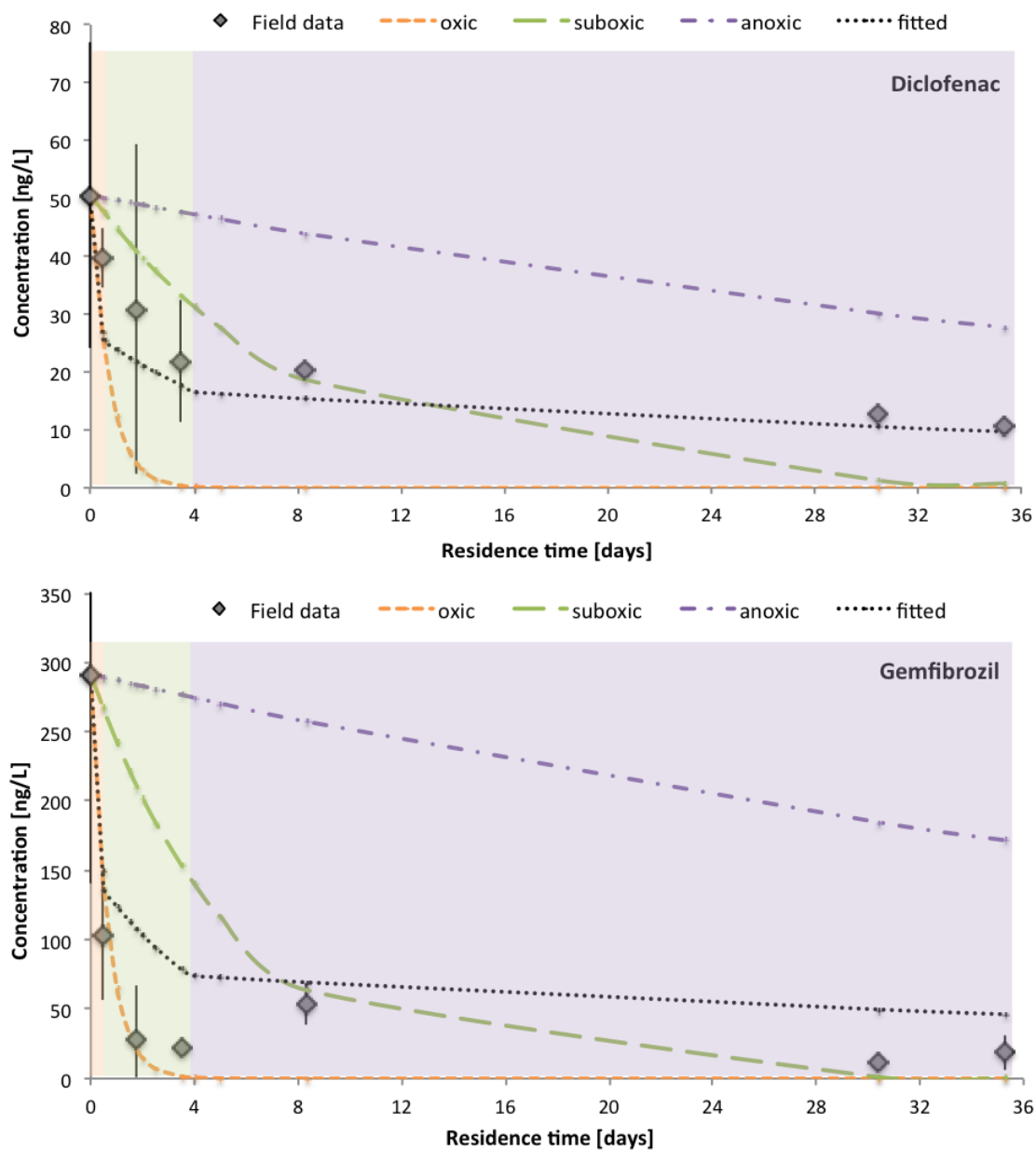
Figure 4. Calculated removal of diclofenac (upper) and gemfibrozil (lower) by simple first-order kinetic using laboratory-derived rate coefficients for either oxic (----, orange), suboxic ($---$, green), or anoxic (- $-$ -, purple) redox conditions, respectively. The fitted removal ($\cdots$) acknowledges the sequence of redox zones determined at the site (shading). Grey diamonds represent average concentrations including error bars for each sampled well (n ≥ 5) and test basin influent concentrations (n = 17).

Table 1. Soil column configuration and operational parameters.

Column system	Design	Media	Conditions	Feed water	Sampling port locations	Residence time
PC	Two 1-m acrylic columns in series, 14 cm inner diameter (i.d.)	Native alluvial material: 93% sand, 2% silt, 5% clay (sieved <2 mm, f_{OC} 0.1%)	Biodegradation under saturated suboxic flow conditions	Tap water, N_2 purged, low BDOC → **Suboxic (low BDOC)**	0 m, 0.06 m, 0.23 m, 0.47 m, 0.8 m, 1.71 m	9 days
C1	Two 1.2-m acrylic columns in series, 14 cm i.d.	Native alluvial material: 93% sand, 2% silt, 5% clay (sieved <2 mm, f_{OC} 0.1%)	Biodegradation under saturated anoxic flow conditions	Secondary treated effluent, N_2 purged, high BDOC → **Anoxic (high BDOC)**	0 m, 0.26 m, 0.56 m, 0.87 m, 1.16 m, 2.41 m	14 days
C2	One 1.2-m acrylic column, 14 cm i.d.	Native alluvial material: 93% sand, 2% silt, 5% clay (sieved <2 mm, f_{OC} 0.1%)	Biodegradation under (un)saturated oxic flow conditions	a) Secondary treated effluent, high BDOC → **Oxic (high BDOC)** b) 30:70 Blend secondary treated effluent/nano-filtration permeate, low BDOC → **Oxic (low BDOC)**	0 m, 0.38 m, 0.47 m, 0.8 m, 1.14 m	7 days

Table 2. Physicochemical properties of selected trace organic chemicals and their respective limit of quantification (LOQ).

Compound	Application	Formula	MW (g/mol)	Log D (pH 7.4)	LOQ (ng/L)	K_d^ (L/Kg)	Biodegradability probability*
Acetaminophen	Analgesic	$C_8H_9NO_2$	151.2	0.40	10	5.00	1.00; 0.99
Acesulfame	Sweetener	$C_4H_5NO_4S$	163.2	-2.77	100	0	0.67; 0.67
DEET	Insect repellent	$C_{12}H_{17}NO$	191.3	2.24	25	0.01	0.92; 0.97
Caffeine	Stimulant	$C_8H_{10}N_4O_2$	194.2	-0.79	10	250	0.66; 0.56
Atrazine	Pesticide	$C_8H_{14}ClN_5$	215.7	2.66	5	0.01	0.01; 0.00
Primidone	Anticonvulsant	$C_{12}H_{14}N_2O_2$	218.3	-0.81	25	0.16	1.00; 0.99
Naproxen	Analgesic	$C_{14}H_{14}O_3$	230.3	0.45	10	0	0.90; 0.96
Carbamazepine	Anticonvulsant	$C_{15}H_{12}N_2O$	236.3	2.28	25	0.03	0.63; 0.41
Gemfibrozil	Lipid regulator	$C_{15}H_{22}O_3$	250.3	1.58	10	0.40	0.76; 0.86
Dilantin	Anticonvulsant	$C_{15}H_{12}N_2O_2$	252.3	2.27	25	-	0.70; 0.79
Sulfamethoxazole	Antibiotic	$C_{10}H_{11}N_3O_3S$	253.3	-0.56	5	2.00	0.45; 0.13
Atenolol	Beta-blocker	$C_{14}H_{22}N_2O_3$	266.3	-1.85	10	1.20	1.33; 1.00
TCEP	Flame retardant	$C_6H_{12}Cl_3O_4P$	285.5	1.44	10	0.03	0.59; 1.00
Trimethoprim	Antibiotic	$C_{14}H_{18}N_4O_3$	290.3	0.28	10	1.87	0.59; 0.92
Diclofenac	Analgesic	$C_{14}H_{11}Cl_2NO_2$	296.2	1.37	10	0.75	0.13; 0.00
TCPP	Flame retardant	$C_9H_{18}Cl_3O_4P$	327.6	2.59	25	8.70	0.57; 1.00
Sucralose	Sweetener	$C_{12}H_{19}Cl_3O_8$	397.6	-0.17	500	0	-0.21; 0.00
TDCP	Flame retardant	$C_9H_{15}Cl_6O_4P$	430.9	3.65	50	-	0.19; 1.00
Iopromide	X-ray media	$C_{18}H_{24}I_3 N_3O_8$	791.1	-3.24	50	0	-0.98; 0.00

^ K_d values for sand, adapted from Drewes et al. (2015).

* Calculated using the linear (1) and non-linear (2) biodegradation probability model BIOWIN (v4.10, EPI SuiteTM, United States Environmental Protection Agency). A probability ≥0.5 indicates fast biodegradation; a probability <0.5 indicates slow biodegradation.

Source: Data calculated using Advanced Chemistry Development (ACD/Labs) Software V8.14.

Table 3. Bulk organic parameters of soil column feed water and change in redox indicators NO_3^- and Mn^{2+} after soil passage.

Column system	Feed water	N_2 -purged	NH_3/NH_4^+ [mg N L^{-1}]	DOC [mg L^{-1}]	BDOC [mg L^{-1}]	UVA [m^{-1}]	SUVA [L mg^{-1} m^{-1}]	ΔNO_3^- [mg N L^{-1}]	Mn^{2+} [mg L^{-1}]*
PC	Tap water	Yes	BDL	1.2±0.3	0.2±0.1	3.7±1.6	3.1±1.5	-0.13±0.1	0.02±0.01
C1	Secondary treated effluent	Yes	7.5±4.9	7.9±1.3	4.2±1.2	14.3±2.4	1.7±0.3	-6.0±2.6	0.7±0.1
C2	a) Secondary treated effluent	No	6.6±4.8	8.0±1.3	2.8±0.9	14.1±1.6	1.8±0.3	-1.0±0.7	0.8±0.4
	b) 30:70 v/v secondary treated effluent:NF permeate	No	0.5±0.1	2.5±0.4	0.2±0.2	4.9±1.4	2.0±0.4	1.0±0.6	0.01±0.0

BDL = below detection limit

*Measured concentration in soil column effluent

Table 4. First-order removal rate constants and DT_{50} values (time required for 50% dissipation of initial concentration) for selected TOrC based on laboratory-scale soil column experiments under different redox and biodegradable dissolved organic carbon (BDOC) conditions.

Redox conditions	Oxic (low BDOC)			Suboxic (low BDOC)			Anoxic (high BDOC)		
	λ [d^{-1}]	R^2	DT_{50} [d]	λ [d^{-1}]	R^2	DT_{50} [d]	λ [d^{-1}]	R^2	DT_{50} [d]
Acesulfame	0.17	0.867	4.2	<0.001	1.000	>700	<0.001	1.000	>700
Acetaminophen	0.36	0.780	1.9	0.4	0.963	1.7	0.49	0.937	1.4
Atenolol	0.51	0.969	1.4	1.3	0.968	0.5	0.38	0.994	1.8
Atrazine	0.0095	0.755	73.0	0.014	0.659	48.8	0.007	0.874	103.4
Caffeine	0.37	0.943	1.9	0.26	0.826	2.7	0.33	0.956	2.1
Carbamazepine	<0.001	1.000	>700	0.02	0.764	35.2	0.007	0.657	106.6
DEET	0.3	0.761	2.3	0.12	0.900	5.9	0.013	0.651	54.6
Diclofenac	1.4	0.973	0.5	0.12	0.868	5.8	0.017	0.915	42.0
Dilantin	0.051	0.736	13.6	0.012	0.729	56.3	0.019	0.828	37.3
Gemfibrozil	1.49	0.973	0.5	0.18	0.900	3.8	0.015	0.764	47.5
Iopromide	0.82	0.973	0.8	0.18	0.825	3.7	0.16	0.916	4.3
Naproxen	1.44	0.973	0.5	0.17	0.899	4.2	0.082	0.876	8.5
Primidone	<0.001	1.000	>700	<0.001	1.000	>700	<0.001	1.000	>700
Sucralose	0.01	0.805	68.6	<0.001	1.000	>700	<0.001	1.000	>700
Sulfamethoxazole	0.5	0.925	1.4	0.049	0.704	14.1	0.009	0.710	81.5
TCEP	0.2	0.897	3.5	n.a.	n.a.	n.a.	<0.001	1.000	>700
TCPP	0.18	0.780	3.9	0.044	0.758	15.9	0.011	0.731	64.8
TDCP	0.12	0.632	5.6	0.039	0.996	17.8	0.006	1.000	121.6
Trimethoprim	0.5	0.884	1.4	0.36	0.753	1.9	0.93	0.954	0.7

Table 5. Overview of published first-order removal rate constants and DT_{50} values for selected TOrC adapted from Henzler et al. (2014). The literature results mostly represent results of laboratory-scale batch and soil column experiments.

Compounds	Literature values	
	λ [d^{-1}]	DT_{50} [d]
Acesulfame		6.1 (oxic)[a]
Acetaminophen	17.1[b]	0.04 (oxic)[b]; 2.1[c]
Atenolol	0.018[d]	39 (oxic)[d]
Atrazine	No degradation (oxic)[b]	
Caffeine	9.5[b]	0.08 (oxic)[b]; 1.5[c]
Carbamazepine	No degradation; 0.0144; 0.0055; 0.0199; 0.0105	35 (oxic); 125-233 (oxic); 328 (oxic); 82
Diclofenac	0.0559; 0.0149; 0.046; 0.013; 0.022	3-20 (oxic); 4.8-29.6; 81 (anoxic); 12 (oxic); 40 (anoxic); 63 (anoxic); 36
Gemfibrozil	0.168[e]; 12.7[b]	4 (anoxic)[e]; 0.04 (oxic)[b]; 17.8, 20.6[f]
Iopromide	1.8-2.0[g]	1.5-3 (oxic)[h]
Naproxen	0.15[e]	5 (anoxic)[e]; 3.1-6.9 (oxic)[i]
Primidone	No degradation	
Sucralose		9 (oxic)[a]
Sulfamethoxazole	0.052; 0.099; 0.25; 0.85; 0.15; 2.14; 0.032	65 (anoxic); 1-9 (oxic); 16 (anoxic); 49 (anaerob); 15 (anoxic); 9-59; 19; 75 (anoxic); 22
TCEP	No degradation (anoxic)[e]	
TCPP	No degradation (anoxic)[e]	
Trimethoprim	0.006, 0.013[d]	116 (anoxic), 53 (oxic)[d]

[a] Buerge et al. (2011); [b] Bertelkamp et al. (2014); [c] Yu-Chen Lin et al. (2010);
[d] Burke et al. (2013); [e] Rauch-Williams et al. (2010); [f] Fang et al. (2012);
[g] Grünheid et al. (2008); [h] Wiese et al. (2010); [i] Monteiro and Boxall (2009).

Highlights

- Redox conditions and BDOC concentrations are primarily affecting TOrC removal.
- Rate constants of moderately-degradable TOrCs are strongly redox dependent.
- Modeling initial infiltration must consider redox dependency of rate constants.