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# Removal kinetics of organic compounds and sum parameters under field conditions for Managed Aquifer Recharge

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## **Highlights:**

removal of trace organics and sum parameters during bank filtration

late data aggregation

removal kinetics: redox conditions, temporal removal, threshold concentration, residual concentration, site specifics, large database

**Abstract** Managed aquifer recharge (MAR) provides efficient removal for many organic compounds and sum parameters. However, observed in situ removal efficiencies tend to scatter and can not be predicted easily. In this paper, a method is introduced which allows to identify and eliminate biased samples and to quantify simultaneously the impact of (i) redox conditions (ii) kinetics (iii) residual threshold values below which no removal occurs and (iv) field site specifics. It enables to rule out spurious correlations between these factors and therefore improves the predictive power. The method is applied to an extensive database from three MAR field sites which was compiled in the NASRI project (2002-2005, Berlin, Germany). Removal characteristics for 38 organic parameters are obtained, of which 9 are analysed independently in 2 different laboratories. Out of these parameters, mainly pharmaceutically active compounds (PhAC) but also sum parameters and industrial chemicals, four compounds are shown to be readily removable whereas six are persistent. All partly removable compounds show a redox dependency and most of them reveal either kinetic dependencies or residual threshold values, which are determined. Differing removal efficiencies at different field sites can usually be explained by characteristics (i) to (iii).

**Key words** bank filtration; removal; kinetics; trace organics; multi-tracer, statistical analysis, threshold concentration, residual concentration, pharmaceutical residues

## 1 INTRODUCTION

Managed Aquifer Recharge (MAR) describes intentional infiltration, treatment and storage of water in aquifers. It provides efficient removal for many organic water parameters (compounds and sum parameters) but it is a difficult task to quantify removal under field conditions: Observed concentrations often tend to scatter and may be biased by subsurface mixing of different waters, e.g. ambient groundwater or bank filtrate of different age. The removal efficiency is affected by different environmental parameters, such as redox potential and residence times (e.g. Stuyfzand et al., 2007, Heberer et al., 2008, Baumgarten et al., 2011). In addition, factors such as threshold values (residual concentrations below which no removal occurs) and field site specifics may have an impact but have so far achieved little attention in the literature. In this context, the surface water concentration at the time of infiltration is crucial. Furthermore, observed removal efficiencies depend on the analytical limit of quantification (LOQ). If the interaction of these factors is not considered properly, the data evaluation might be biased by spurious correlations and lead to data misinterpretation. For example, removal efficiencies appear to depend on redox conditions or appear to be field site specific, while in fact, they are simply the consequence of longer flow times – which are site specific and will also affect redox conditions. Likewise, different sites may have different surface water concentrations, residence times and aquifer characteristics. On the other hand, field site specific removal may occur without correlation to one of the analysed factors.

Frequently, removal efficiency is determined with strict a priori assumptions. Several methods comprise the calculation of a mean value per observation well (Denneke 1997, Stuyfzand et al., 2007) or with box plots (Grünheid et al., 2005, Heberer et al., 2008, Massmann et al., 2008a). Stuyfzand (2007) explicitly considers redox conditions and the flow time to calculate removal with a half life approach. However, for all these approaches data are aggregated at an early stage, transient effects are not considered explicitly and removal kinetics are inferred rather than deduced by the data. These effects are accounted for in complex reactive biogeochemical models (e.g. Greskowiak et al., 2006), that have a limited applicability because they are very time and cost consuming and therefore often not realizable.

The presented method overcomes these difficulties, quantifies the removal efficiencies and kinetics and is applicable to large databases. This allows to reduce the impact of outliers and statistical dispersion. The most advanced method of evaluation is described in Stuyfzand (2007). However, for the currently available database (KWB, 2009) a method is developed that does not infer removal characteristics a priori, but determines the type of kinetic directly from the data.

We present a method to quantify removal of organic water parameters during MAR. The method consists of the following elements: (i) The determination of flow time for each sample, based on observed tracer data and surface water concentrations, (ii) the identification and subsequent exclusion of mixed samples, (iii) the determination of organic parameter concentrations at the time of infiltration by flow time and retardation and (iii) the quantification of the removal as the difference between concentration at the time of infiltration and the actual groundwater concentration, taking account for the residence time. The evaluation is carried out individually for different redox conditions by a combination of a statistical analysis (providing precise condition dependent removal efficiency) and a graphical

analysis to determine removal kinetics. The combination of both approaches allows to quantify significant removal processes and to rule out spurious correlations.

The data for this study (KWB, 2009) were collected within the NASRI project between 2002 and 2005 at two bank filtration (BF) sites (Tegel BF, Wannsee BF) and one basin aquifer recharge site (Tegel AR) in Berlin. In total, 38 organic parameters were analysed, of which 9 were measured in parallel by two working groups (Table 1). The working groups are TU ORG (Jekel, 2006), TU Drug (Heberer & Jekel, 2006) and BWB (Dünnbier, Dlubek). Furthermore, it contains additional geochemical parameters, of which chloride, boron,  $^{18}\text{O}$  and temperature are used as tracers.

Results of various aspects of the NASRI project at these field sites have previously been published. For the Tegel BF site results were reported on transient hydraulics and transport (Wiese & Nützmann, 2011; Wiese, 2006), environmental tracers (Massmann et al., 2008c) and organic compounds (Grünheid et al., 2005). Details of the Wannsee BF site were presented focussing on redox conditions (Massmann et al., 2008a), re-aeration due to water-level fluctuations (Massmann & Sültenfuß, 2008, Kofahl et al., 2009), phenazone type PhACs (Massmann et al., 2008a) and antimicrobial residues (Heberer et al., 2008). Transient hydraulics and geochemistry for the infiltration zone at the Tegel AR are given in Greskowiak et al. (2005), while redox conditions, Pharmaceutically Active Compounds (PhACs) as well as bulk organic carbon behaviour along a transect were described by Massmann et al. (2006) and Grünheid et al. (2005). Finally, Greskowiak et al. (2006) modelled the reactive, redox dependant degradation of the analgesic phenazone at the Tegel AR site.

Table 1: List of analysed organic compounds, analytical methods and limits of quantification (LOQ).

Compound	Affiliation	Method of analysis	LOQ (ng/L)
AAA (Acetylaminoantipyrine)	metabolite analgesic	6	50
AMDOPH (1-acetyl-1-methyl-2-dimethyl-oxamoyl-2-phenylhydrazide)	metabolite analgesic	1	5
		6	50
AMPH (1-acetyl-1-methyl-2-phenylhydrazide)	metabolite analgesic	6	50
Bentazone	herbicide	1	5
Bezafibrate	blood lipid regulator	1	50
Carbamazepine (CBZ)	antiepileptic	2	5
		6	50
Clarithromycin	antibiotic	3	0.2
Clindamycin	antibiotic	3	0.1
Clofibric acid	metabolite of blood lipid regulator	1	10
Diclofenac	analgesic / anticonvulsants	1	5
DP (1,2-dihydro-1,5-dimethylpyrazol-3-one)	metabolite analgesic	6	50
EDTA (ethylenediaminetetraacetic acid)	complexing agent	7	2000
FAA (formylaminoantipyrine)	metabolite analgesic	6	50
Indometacine	analgesic / anticonvulsants	1	30
Iopromide	x-ray contrast agent	4	20
Mecoprop	herbicide	1	5
MTBE (methyl-tertiary-butyl-ether)	fuel additive	8	30
N-(phenylsulfonyl)-sarcosine (NPS)	metabolite of a corrosion inhibitor	1	30
NDSA-Isomers (Naphthalenedisulfonic acid)	industrial chemicals	5	30
o,p'-DDA (2-(2-chlorophenyl)-2-(4-chlorophenyl)acetic acid)	metabolite of an insecticide	1	10
PDP (1,2-dihydro-4-isopropyl-1,5-dimethylpyrazol-3-one)	metabolite analgesic	6	50
Phenazone	analgesic	6	50
p,p'-DDA (2,2-bis(4-chlorophenyl)acetic acid)	metabolite of an insecticide	1	10
Primidone	analgesic / anticonvulsants	2	5
Propyphenazone	analgesic / anticonvulsants	1	10
		6	50
Roxithromycin	antibiotic	3	0.2
Sulfadimidine (SDMD)	antibiotic	3	3
Sulfamethoxazole (SMX)	bacteriostatic antibiotic	3	1
		4	20
Trimethoprim	antibiotic	3	2

## 2 METHODS

### 2.1 Analytical methods

The analysed compounds and their affiliation are listed in Table 1. The method of analysis and Limit of Quantification (LOQ) are listed in the third and fourth column. Several compounds are determined in parallel by 2 laboratories.

Methods 1 and 2 were applied by the working group TU DRUGS. Method 1 (derivatizing with pentafluorobenzyl bromide) was primary used for analyzing the acidic residues like clofibric acid, diclofenac etc. For neutral compounds method 2 (silylation with N-(tert.-butyldimethylsilyl)-N-methyl-trifluoroacetamide) was applied. The methods are described by Reddersen and Heberer (2003).

Method 3 was applied by the working group TU Drugs. (Heberer et al., 2008)

Method 4 was applied by the working group TU ORG and is a combination of solid phase extraction (SPE) and MS/MS-quantification. (Putschew et al., 2001, Hartig 2000). Method 5 is carried out by the working group TU ORG. It is describe by Storm et al. (1999).

The analyses of method 6 were applied in the laboratory of the BWB. The method follows Zühlke et al. (2004).

The analyses of method 7 were applied in the laboratory of the BWB. The method follows DIN 38413-P10.

Analyses of method 8 were carried out in the laboratory of the BWB. The method is developed within the BWB follows the internal protocol BWB 03-02.

Chloride was analysed according to the DIN EN ISO 10304-1 (D20) method, Boron with the DIN EN ISO 11885 (E22) method at the BWB laboratory. Stable isotope measurements ( $\delta^{18}\text{O}$ ,  $\delta\text{D}$ ) were carried out at the Alfred Wegener Institute, research Unit Potsdam. Method details are described in Meyer et al. (2000).

### 2.2 Flow time

The flow time for each sample is determined by a 1-D transient multi-tracer approach ( $\delta^{18}\text{O}$ , temperature and chloride). The tracer input signal of the surface water is shifted by a date dependent flow time to fit the breakthrough curve in each observation well. Most flow times are determined with  $\delta^{18}\text{O}$  because it is an ideal tracer and shows pronounced seasonal surface water variations. However, monthly sample intervals set a lower limit of resolution of 1 to 2 months. Shorter flow times are determined with temperature for which a retardation factor of 2 is taken into account. Temperature is more suitable for short flow times since retardation doubles the time shift compared to conservative tracers and logging data often provides continuous time series with a much higher resolution than obtained by sampling. The shortest flow times which can be determined with this method are about two to three days. In cases in which sampling of surface water and groundwater started simultaneously the corresponding first concentrations of environmental tracer in the surface water are not known and flow time cannot be determined. Consequently, the samples are disregarded in further analysis.

The underlying assumptions are that dispersion can be neglected and no preferential flow occurs. This is probably true, since dispersivity typically is one order of magnitude lower than the problem scale (Gelhar et al. 1992). The current analysis refers to observation wells, that

basically show parallel flow and lower dispersion than abstraction wells with convergent flow. For maximum flow times around 100 days dispersion effects are in the order of 10 days, which is generally lower than the time scale of the regarded processes. Furthermore, preferential flow would be detected as mixing (see below).

### **2.3 Mixing**

Groundwater samples at bank filtration sites may be biased due to mixing of different waters, either ambient groundwater (Hiscock and Grischek, 2002) or bank filtrate of different age (Wiese, 2006). Mixing is identified by using the tracers chloride, boron and propyphenazone.

Propyphenazone is an indicator for old bank filtrate at the field site Tegel BF (Reddersen et al., 2002). It is very sensitive because groundwater concentrations are up to about 10 times higher than presently found in surface water. Taking into account the variability in surface and ground water as well as the measurement accuracy the following criteria for mixing were applied:

- Boron: groundwater concentrations differ at least 10 µg/l or 10% from corresponding concentration at the time of infiltration
- Chloride: groundwater concentrations differ at least 4 mg/l or 10% from the corresponding concentration at the time of infiltration
- Propyphenazone: groundwater concentration of the sample is twice the limit of quantification (LOQ) and more than 25% higher than the corresponding concentration at the time of infiltration.

If two of the criteria are fulfilled, the sample is classified as subsurface mixing and is not included in the further evaluation. Most mixed samples are identified at Tegel BF, due to vertical stratification of different ages of bank filtrate (Wiese & Nützmann 2011).

### **2.4 Retardation study**

Many organics are adsorbed to the aquifer material, hence their residence time is longer than the flow time of water and conservative tracers. The degree of sorption depends on the strength of the interaction between the compound and the adsorbing matrix and is described with a retardation factor. Retardation factors were determined with a literature study. Experimental retardation values are available for 13 parameters. Within the NASRI project 7 retardation factors were determined during column experiments (Jekel, 2006, Licht et al., 2005). Referenced values for comparable conditions (sandy aquifer, low sedimentary organic carbon) are used for further 6 parameters (Braids, 2001, Broholm et al., 2001, Buss et al., 2006, Grischek et al., 1997, Heberer and Jekel, 2006, Jørgensen et al. 1998, Mersmann et al., 2003, Scheytt et al., 2006, Stuyfzand et al., 2007, Tuxen et al., 2000). Eight retardation values are applied based on similarity considerations regarding the substances' structural characteristics (Table 2). For 17 parameters no physically based values are available, hence a retardation factor equal to one is applied – thereby considering a worst case scenario. The residence times of the compounds and sum parameters are determined by multiplying the flow time with the retardation factor.

The retardation has the underlying assumption of linear equilibrium sorption. This may not generally be true, but appears appropriate considering the data basis. In case evidence for more complex sorption mechanisms dominate, the analysis may be biased.

## 2.5 Removal calculation

Removal can only be calculated if the respective surface water concentration is known. For each parameter and groundwater sample the time of infiltration is determined by starting at the sampling date and subtracting the residence time. The corresponding substance concentration at time of infiltration is acquired by linear interpolation between surface water concentrations. In cases the time of infiltration is less than 2 weeks prior to the first measured surface water concentration, this concentration is applied as source concentration. A time of 2 weeks is chosen because this is half of the monthly sampling interval. For earlier times of infiltration the concentration becomes undefined, and therefore also the respective groundwater concentration is disregarded in further analysis.

$$R_{abs} = c_{sw} - c_{gw} \quad \text{Equation 1}$$

where  $R_{abs}$  is the absolute removal [ $\mu\text{g/l}$ ],  $c_{sw}$  the surface water concentration at the time of infiltration [ $\mu\text{g/l}$ ] and  $c_{gw}$  [ $\mu\text{g/l}$ ] is the ground water concentration.

Removal is calculated as (i) the absolute and (ii) the relative difference between the concentration at the time of infiltration and the observed groundwater concentration.

## 2.6 Redox classification

The predominant electron acceptors are used to classify the redox state for each sample: 'O<sub>2</sub>', 'NO<sub>3</sub><sup>-</sup>', 'Mn<sup>++</sup>', 'Fe<sup>++</sup>' and 'mixed' with threshold values adapted from McMahon and Chapelle (2008). Samples classified as 'mixed' are not in equilibrium and exhibit electron acceptors of different zones simultaneously. The current classification only refers to the redox zone of the groundwater at sampling time, nevertheless some sampled water may have previously passed through other redox conditions, which is discussed in chapter 3.3.

## 2.7 Statistical evaluation

Previous investigations have stated that in general, the removal of trace organics depends on redox conditions (Stuyfzand, 2007) and frequently also on field site characteristics (Schmidt, 2005). Furthermore, the calculated removal may also depend on how the values below the LOQ are treated. To account for these effects, the mean removal is calculated for different classifications, according to Equation 2.  $R_i$  is the mean removal of class  $i$ ,  $j$  is the counter of the class members (see below).

$$R_i = \frac{\sum_j R_{abs,j}}{\sum_j c_{sw,j}} \times 100 \quad \text{Equation 2}$$



Removal for the following classifications are calculated:

- five classes of redox conditions ‘O<sub>2</sub>’, ‘NO<sub>3</sub><sup>-</sup>’, ‘Mn<sup>++</sup>’, ‘Fe<sup>++</sup>’, mixed
- four classes field site specifications: all data, Tegel BF, Tegel AR and Wannsee BF
- two methods for regarding the limit of quantification (LOQ): for concentrations  $c_{gw} < LOQ$  then either  $c_{gw} = 0$  or  $c_{gw} = LOQ/2$

This approach results in 20 classes with two values for each method regarding values below LOQ. In cases when the treatment of LOQ leads to a difference of less than 10%, the mean of both values is provided, when it is larger than 10% a range of values is provided, if the difference is higher than 50% the trend is described in words. The results for the first four redox classes for data of all field sites are presented in Table 2.

## 2.8 Graphical evaluation

The graphical evaluation is carried out for the same classes as the statistical evaluation. Values below LOQ are plotted as provided, either as LOQ/2 or as 0. Data are visualised by two scatter plots of concentration at time of infiltration  $c_{sw}$  and groundwater concentration  $c_{gw}$ , both with the respective flow time as abscissa (e.g. Figure 1). Different colours allow differentiating the three field sites. The LOQ is indicated as a horizontal line.

The time dependent removal can be quantified with a half-life approach:

$$\begin{aligned} c_{gw} &= c_{thr} + (c_0 - c_{thr}) 0.5^{t/t_{1/2}} & \text{for } c_0 > c_{thr} \\ c_{gw} &= c_0 & \text{for } c_0 \leq c_{thr} \end{aligned} \quad \text{Equation 3}$$

where  $c_{gw}$  [µg/l] is the ground water concentration,  $c_0$  [µg/l] is the concentration at the time of infiltration,  $c_{thr}$  [µg/l] is a residual threshold concentration below which no removal occurs.

$t$  [d] is the flow time and  $t_{1/2}$  [d] is the half-life.

Some organic water parameters show a removal during infiltration, which is faster than the shortest determined flow time. The removal of these can be better quantified with a linear regression of the form

$$c_{gw} = c_0 (a - bt) \quad \text{Equation 4}$$

where  $a$  [-] is the fraction of removal that occurs rapidly during infiltration and  $b$  [1/d] defines the time dependent component. A linear removal in the subsurface is chosen because it empirically reflects the slope of the observed concentrations, but extrapolation might not be possible, for longer times an exponential approach may be more appropriate. The respective units differ for the parameters DOC (Dissolved Organic Carbon), UV254 (UltraViolet adsorption at 254 nm) and SUVA (Specific Ultraviolet Absorption at 254 nm).

The approach of removal calculation is chosen to mitigate the impact of scattering and inaccuracies. It would be possible to calculate a removal percentage for each pair of surface and ground water concentration, but the mean of the percentage value would be biased for low surface water concentrations and not reflect the net removal.

### 3 RESULTS AND DISCUSSION

The number of samples that are available for interpretation is reduced for two reasons: First, several samples are subject to mixing processes and second, for organic water parameters with high residence times the corresponding concentration at the time of infiltration is prior to the first sampling campaign and therefore no removal can be calculated. For these reasons 29% of the original data is not used. A number of 9992 concentration values remains for interpretation of which 42% belong to 'O<sub>2</sub>' conditions, 6% to 'NO<sub>3</sub><sup>-</sup>' conditions, 7% to 'Mn<sup>++</sup>' conditions and 14% to 'Fe<sup>++</sup>' conditions. The latter condition hardly occurs at Tegel AR (1 sample). The mixed redox state comprises 31% of the concentration values and is only used for consistency check.

The results of the combined statistical and graphical evaluation are summarized in Table 2. Results show that four parameters are readily removable (clarithromycin, D-erythromycin, roxithromycin, trimethoprim, (removal efficiency >95%) and 7 parameters are persistent (1,5-NDSA, bezafibrate, indometacine, NPS, p,p'DDA, sulfadimidine, removal efficiency <30%). For all parameters which are in-between and only partly removed, the magnitude of removal depends on the redox conditions. The removal is usually monotonic with regard to redox, i.e. it either increases or decreases continuously. Hence, the number of samples in each redox class is generally large enough to smooth statistical noise sufficiently. Minor discontinuities exist for some parameters (DOC, MTBE) but they are not regarded as significant.

Table 2: Observed removal efficiency of 38 organic parameters, given as percentage of surface water concentrations. Text entries are used if most data points are close to LOQ or few data points are available.

Retardation values without asterisk denote literature derived values, one asterisk denotes an estimation based on structural similarity and physical properties. Two asterisks denote the initial assumption with a value of one. The right column indicates other factors which may affect removal: T: time, Th: threshold value, S: site specific removal, M: Metabolite. For details of the latter refer to Table 3.

	removal by redox zone [%]				retardation factor	non-redox impact	
	O2	NO3	Mn	Fe			
sum parameters	AOBr (BWB)	16	23	37	78	1**	Th,S
	AOBr (TU-Org)	17	32	59	68	1**	Th,S
	AOI (BWB)	4	13	38	58	1**	
	AOI (TU-Org)	8	31	56	63	1**	Th
	AOX (BWB)	17	25	36	58-84	1**	
	DOC (BWB)	29	28	29	26	1**	T,Th
	DOC (TU-Org)	32	35	34	31	1**	T,Th
	SUVA (BWB)	3	-3	-8	-12	1**	
	SUVA (TU-Org)	-1	-9	-9	-9	1**	
	UV_254 (BWB)	30	25	20	16	1**	T,Th
UV_254 (TU-Org)	32	32	27	24	1**	T,Th	
individual substances	1,5 NDSA (TU-Org)	6	-4	3	6	1.05*	
	1,7 NDSA (TU-Org)	47	57	29	20	1.05	Th
	2,7-NDSA (TU-Org)	54	47	28	22	1.05*	Th
	AAA (BWB)	95	98	90	56	1.8*	T,M
	AMDOPH (BWB)	25	4	-4	-6	1.5*	T,Th,M
	AMDOPH (TU-Drug)	26	1	10	1	1.5*	T,Th,M
	AMPH (BWB)	some removal		increase		1.8*	M
	Bentazone (TU-Drug)	between 22 and 88%, redox discontinuous				1.1	T
	Bezafibrate (TU-Drug)	some removal. less for Fe conditions				1.5*	
	Carbamazepine (BWB)	16	8	23	51	1.4	T,Th,S
	Carbamazepine (TU-Drug)	14	8	20	50	1.4	T,Th,S
	Clarithromycin (TU-Drug)	>96	>96	>96	>96	1**	
	Clindamycin (TU-Drug)	95	97	98	27	1**	T,S
	Clofibric acid (TU-Drug)	70	66	90	51	1.3	T
	D-Erythromycin (TU-Drug)	>97	>97	>97	>97	1**	T
	Diclofenac (TU-Drug)	91	85	61	61	1.4	T
	DP (BWB)	some removal		increase		1**	M
	EDTA (BWB)	11	-6	-14	-15	1.2	S
	FAA (BWB)	94	93	less than O2/NO3		1.8*	T,M
	Indometacine (TU-Drug)	some removal				1**	T
	Iopromide (Tu-Org)	94	95	99	70	1.1	S
	Mecoprop (TU-Drug)	53-69	19	81-93	39	1.1	
	MTBE (BWB)	26	22	20	24	1.05	S
	NPS (TU-Drug)	slight removal				1**	
	o,p'-DDA (TU-Drug)	apparently persistent				1**	
	PDP (BWB)	all groundwater values <LOD			occurrence	1**	M
	Phenazone (BWB)	91	73	46	6	1	
	p,p'-DDA (TU-Drug)	slight removal				1**	
	Primidone (TU-Drug)	9	-2	-4	9	1.2	
	Propyphenaz. (BWB)	>58	56-95	42-79	0 to -54	2	S
Propyphenaz. (TU-Drug)	84	67	48	-9	2	S	
Roxithromycin (TU-Drug)	>99	>99	>99	>99	1.3*		
Sulfadimidine (TU-Drug)	sometimes increase		often increase		1**		
Sulfamethox. (TU-Drug)	41	47	74	89	1.05	T,S	
Sulfamethox. (TU-Org)	31	40	77	86	1.05	S	
Trimethoprim (TU-Drug)	>95	>95	>95	>95	1**		

### 3.1 Redox conditions

A significant redox discontinuity exists for clofibric acid and mecoprop that is interpreted as a cross correlation effect to flow time. The similar chemical structure allows a comprehensive interpretation of both compounds' behaviour (see below).

Using the graphical interpretation it is determined whether other factors superpose the redox-dependent removal and the removal efficiency as presented in Table 2 may not be a predictive value. Graphical interpretation yields that for 20 compounds removal is affected by at least (i) residence time, or (ii) a residual threshold concentration, or (iii) site characteristics (Table 3). These specifics are mainly determined for oxic conditions, for other redox conditions often insufficient data are available. Therefore, a missing entry in the respective column indicates that the particular behavior could not be observed within the present dataset, but not necessarily that it can be ruled out.

### 3.2 Determination of kinetics

Removal kinetics and potential cross correlation effects are also determined by means of the graphical evaluation. Three examples (Figure 1 to Figure 3) illustrate how removal kinetics are determined.

Example 1: Carbamazepine (measured by BWB, Table 1) is removed by 16% under oxic conditions (Figure 1, Table 2). Groundwater concentrations decrease with time, which can be described by an envelope with a  $T_{1/2}$  of 35 days and a  $c_{thr}$  of 0.3  $\mu\text{g/l}$  (Equation 2, Table 3). These parameters are also applied to simulate the groundwater concentrations starting from the surface water concentrations. The simulation results (Figure 1c) are very similar to observed groundwater concentrations (Figure 1b).

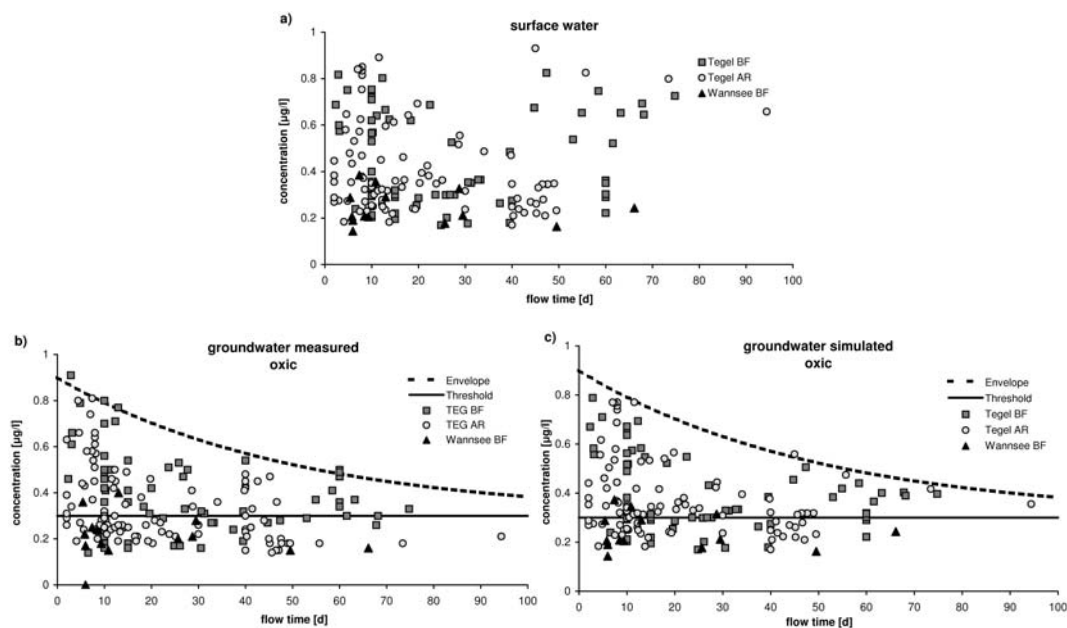


Figure 1: Removal characteristic for Carbamazepine (BWB) for oxic groundwater conditions. The plots show a) surface water concentration, b) observed groundwater concentration and c) simulated groundwater concentration (according to Equation 3). Each marker represents a sample. The envelope corresponds to a half life of 35 days with a threshold concentration of 0.3  $\mu\text{g/l}$ .

The removal of carbamazepine under 'Fe<sup>++</sup>' reducing conditions is about 50%. The high removal is a combination of two effects: The mean flow time is 54 days (compared to 23 days for oxic conditions) and therefore removal is more efficient. Furthermore, the lower redox conditions enhance removal. While the mean flow time is similar for 'Mn<sup>++</sup>' and for 'Fe<sup>++</sup>' reducing conditions, the removal increases from 20% to 50%. For 'Fe<sup>++</sup>' reducing conditions the residual threshold is lower, i.e. groundwater concentrations down to values of 0.1 µg/l are observed (Figure 2). The half life appears to be identical to oxic conditions.

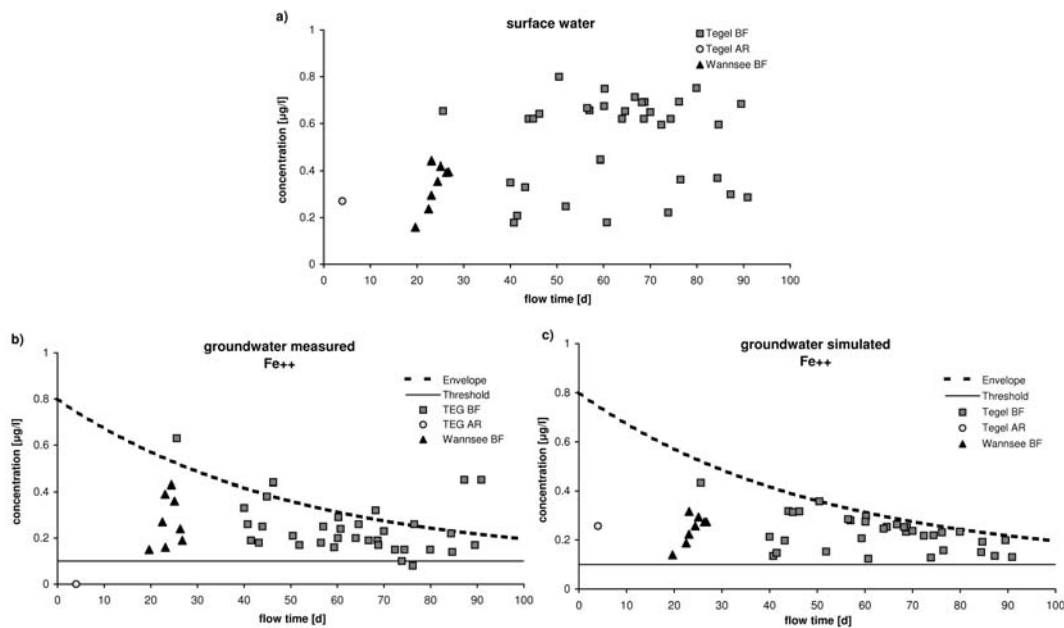


Figure 2: Removal characteristic for Carbamazepine (BWB) for Fe<sup>++</sup> groundwater conditions. The plots show a) surface water concentration, b) observed groundwater concentration and c) simulated groundwater concentration (according to Equation 3). Each marker represents a sample. The envelope corresponds to a half life of 35 days with a threshold concentration of 0.1 µg/l.

Example 2: The removal efficiency of sulfamethoxazole (measured by TU Drug) for oxic conditions is 41% (Figure 3). Concentrations for long flow times are significantly lower than for shorter flow times. The removal characteristics can be described by an envelope that follows an 1<sup>st</sup> order decay with a half life of 30 days. Furthermore, calculating the decay of each observed surface water concentration applying Equation 3 results in a point cloud with similar properties to the observed concentrations (compare Figure 3b and 3c).

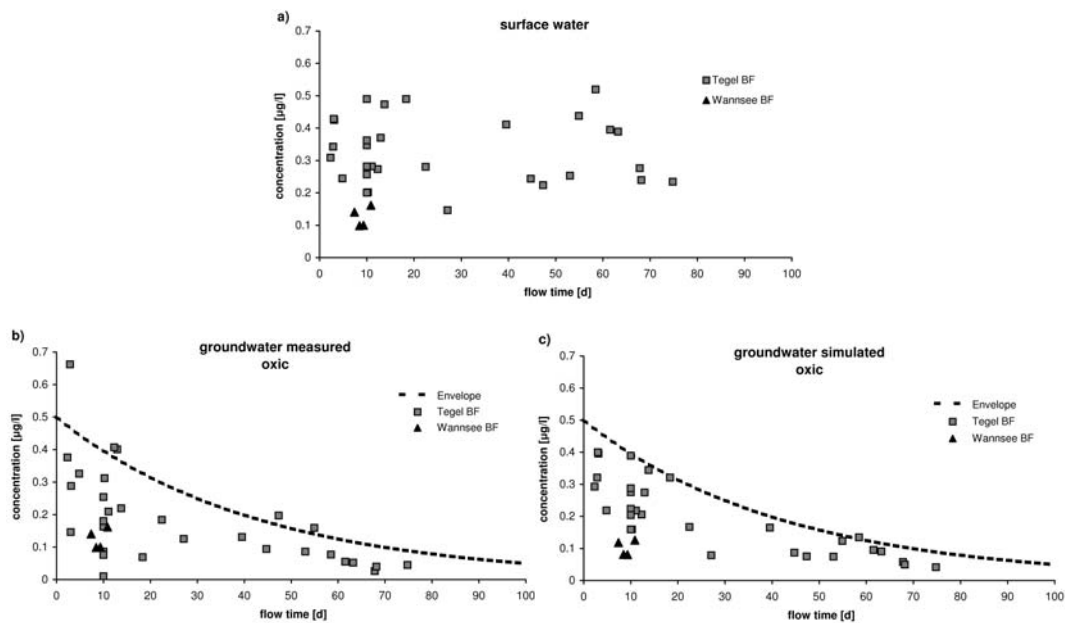


Figure 3: Removal characteristic for sulfamethoxazole (TU Drug) for oxic groundwater conditions. The plots show a) surface water concentration, b) observed groundwater concentration and c) simulated groundwater concentration (according to Equation 3). Each marker corresponds represents a sample. The envelope corresponds to a half life of 30 days.

The removal efficiency of sulfamethoxazole (measured by TU Org) for oxic conditions is 31% and 10% points lower compared to the values measured by TU Drug. The difference can be explained by the kinetics which are determined. The removal efficiency is lower because the samples have a significantly lower flow time with a mean of 9 days compared to 26 days for the samples measured by TU Drug (i.e. different samples were measured).

Results of both groups show minimum concentrations of about 0.05 µg/l, which could be an indication for a residual threshold concentration. Nevertheless this hypothesis cannot be validated for the present data, because the data can be described sufficiently by an exponential decay. The removal of sulfamethoxazole for 'Mn<sup>++</sup>' and 'Fe<sup>++</sup>' reducing conditions is 74% and 89%, respectively and much higher compared to 'O<sub>2</sub>' and 'NO<sub>3</sub><sup>-</sup>' reducing conditions. Partly this can be attributed to flow times that are double as long, but also the removal processes are more effective.

Removal of sulfamethoxazole shows complex kinetics, Baumgarten et al. (2011) found residual threshold concentrations of 0.12 µg/l for source concentrations between 0.24 and 0.36 µg/l. For higher source concentrations the residual threshold concentration decreases, which is interpreted as result of microbial removal. Complementary, we observe considerable removal of 0.2 and 0.5 µg/l at Tegel BF and a no removal (i.e. residual threshold) of source concentrations around 0.12 µg/l at Wannsee BF. On the other hand the column studies show that removal is less efficient for lower redox conditions (Baumgarten et al., 2011), while we find it more efficient at the field sites (Table 2). This might be result of adaptation time, which are already more than two years for oxic conditions and might be even longer for lower redox. For the other compounds and sum parameters the removal characteristics are determined analogously (Table 2 and Table 3). For 10 compounds most groundwater concentrations are below LOQ or only few values are available, thus the removal cannot be calculated reliably. In these cases the trend is given verbally.

**Table 3: Compounds for which removal is impacted by factors other than the redox zone (Table 2). For parameters of the temporal kinetic refer to equation 3 and 4. Residual threshold concentrations are values below which no removal occurs. Site specific behaviour is related to significant differences in removal for at least one of the field sites and redox zone.**

	Temporal kinetic	Residual threshold concentration $C_{thr}$	Site specifics
AOBr (BWB)		'O <sub>2</sub> ' and 'NO <sub>3</sub> <sup>-</sup> ' ca. 5 µg/l, 'Mn <sup>++</sup> ' 3 µg/l, 'Fe <sup>+++</sup> ' 2 µg/l	no oxic removal at Tegel AR, reason unknown
AOBr (TU-Org)			
AOI (TU-Org)		'Fe <sup>+++</sup> ': 2-5 µg/l	
DOC (BWB)	all redox: c0=7.1 mg/l, a=0.76, b=0.001	4 to 5 mg/l for all sites and redox	
DOC (TU-Org)	all redox: c0=7.2 mg/l, a=0.71, b=0.001		
UV_254 (BWB)	'O <sub>2</sub> ':c0=15.9 1/m, a=0.74, b=0.0015	8 to 10 1/m all redox	stronger redox dependence at Wannsee BF
UV_254 (TU-Org)	'O <sub>2</sub> ':c0=15.8 1/m, a=0.73, b=0.002		
1,7 NDSA		'O <sub>2</sub> ' and 'NO <sub>3</sub> <sup>-</sup> ' 0.05 µg/l, 'Mn <sup>++</sup> ' and 'Fe <sup>+++</sup> ': 0.1 to 0.2 µg/l	
2,7-NDSA		0.015 µg/l	
AAA	'O <sub>2</sub> ': T <sub>1/2</sub> =12 d		
AMDOPH (BWB)	'O <sub>2</sub> ': c0=0.21 µg/l, a=0.85, b=0.0035	0,05-0,1µg/l	
AMDOPH (TU-Drug)	'O <sub>2</sub> ': c0=0.35 µg/l, a=0.95, b=0.0055		
Bentazone	'O <sub>2</sub> ': hints for exponential removal		
Carbamazepine (BWB)	'O <sub>2</sub> and Fe <sup>+++</sup> ': T <sub>1/2</sub> : 35 d	'O <sub>2</sub> ': 0,3 µg/l	Higher removal at Tegel BF conditions due to significantly higher flow time
Carbamazepine (TU-Drug)		'Fe <sup>+++</sup> ': 0.1 µg/l	
Clindamycin	'O <sub>2</sub> ': T <sub>1/2</sub> =1.5-2.5 d		'Fe <sup>+++</sup> ' site specific due to previous redox
Clofibrac acid	'O <sub>2</sub> ', probably 'NO <sub>3</sub> <sup>-</sup> ', 'Mn <sup>++</sup> ': T <sub>1/2</sub> =10-23 d		
D-Erythromycin	'O <sub>2</sub> ': T <sub>1/2</sub> =2 d		
Diclofenac	'O <sub>2</sub> ': T <sub>1/2</sub> =3 d	'O <sub>2</sub> ': 0.01 µg/l	'Fe <sup>+++</sup> ' site specific due to previous redox
EDTA			increase at Tegel BF, reason unknown
FAA	'O <sub>2</sub> ': T <sub>1/2</sub> =14 d		
Indometacine	'O <sub>2</sub> ': hints for time dependent removal		
Iopromide	'O <sub>2</sub> ': T <sub>1/2</sub> : 1.5-3d		Removal for 'Fe <sup>+++</sup> ' conditions is site specific due to previous redox
Mecoprop	due to chemical similarty probably similar kinetics to clofibrac acid		
MTBE			no consistent trend
Propyphenaz. (BWB)			Some increase at Tegel BF, probably due to undetected mixing
Propyphenaz. (TU-Drug)			
Sulfamethox.(TU-Drug)	'O <sub>2</sub> ': T <sub>1/2</sub> =30 d		'Fe <sup>+++</sup> ': slightly higher removal at Wannsee BF, probably due to stricter redox
Sulfamethox. (TU-Org)	observed flow time too short		

### **3.3 Interpretation of residual threshold concentration**

While the removal efficiency can be determined quite straightforward, the underlying mechanisms are much more difficult to determine and frequently remain unknown. Remaining initial concentrations from abiotic reactions tend to reach equilibrium and therefore tend to be proportional to the initial concentrations.

A residual threshold concentration can be observed when microbial energetic use requires a minimum initial concentration (Schlegel, 1992). Therefore the existence of a residual threshold concentration is a hint for microbial activity which may imply energetic use of the respective compounds (Baumgarten et al. 2011). In case the compound is a co-substrate in a microbial process, residual concentrations of the co-substrate can remain when the primary substrate is depleted. In this case a residual threshold concentration would be the result of enzymatic activity, that requires a minimum concentration of reagents.

The environment has very low concentrations of biodegradable organic carbon. After the first meter, the DOC consumption is low and around 5-10  $\mu\text{g/d}$ . Considering that DOC consists of a high number of different compounds which are removed, it appears possible that specialized bacteria exist which are able to use low concentrations of trace organics as energy source. The aquifer has been exposed to the trace organics during many years, which may promote microbiological specialisation. For SMX this behaviour has been observed by Baumgarten et al. (2011).

The observed residual threshold concentrations support the hypothesis that microbial activity promotes removal. However, further research is necessary for to support the hypothesis and determine type and pathway. Several compounds with slow time dependent removal are quite polar (AAA, AMDOPH, clofibric acid, FAA, SMX), therefore their retardation may not be caused by classical adsorption but by more complex processes such as surface complexation. In this case sorption would potentially be highly variable since it would be affected by pH, redox and the availability of free hydroxide or oxide surfaces. But without biological removal, complex sorption may induce a time shift only and no net decrease on a long term. Nevertheless, a net decrease is always observed. The long observation duration of 26 month with a maximum flow time of three month (for the relevant samples) strongly suggest, that this is representative and not just an intermediate effect. It may be possible, that surface complexation is followed by biodegradation, due to better adaptation and higher local concentrations of trace organics. It may also be induced by competitive adsorption, which leads to desorption effects. There are more basic studies needed to determine the extent of these combined mechanisms of adsorption and subsequent biodegradation.

### **3.4 Cross correlation effects**

Frequently removal efficiencies are expressed as percentage as mean value for a number of samples. Redox conditions have the most important impact, but additional factors such as flow time, residual threshold values or field site specifics may contribute to removal or even exceed the relevance of redox conditions. In the following examples are discussed, where spurious correlations bias an interpretation which is only based on redox conditions, and removal kinetics have to be considered.



This analysis implies that the main residence time is in the sampled redox zone itself, which is generally true for the field sites. Water infiltrating at deeper parts of the lakes exhibits lower redox conditions than water infiltrating at shallow shore-line areas. This was shown by Wiese & Nützmann (2009) for Tegel BF and by Massmann et al. (2008b) for Wannsee BF. This pattern continues in the groundwater, where redox zones are stratified and the general flow is horizontal (Massmann et al., 2008b).

At Tegel BF a large unsaturated zone exists which partly contains atmospheric oxygen (Wiese & Nützmann, 2009) so that the flow path may include a passage of considerable length under oxic conditions, while the observed redox state is lower in the sample. This is relevant for clindamycine and iopromide. Both parameters are readily removable (>94%) with a half life of less than 3 days for 'O<sub>2</sub>' to 'Mn<sup>++</sup>' redox conditions at all field sites and groundwater concentrations rapidly fall below LOQ. For iron reducing conditions, however, they show apparent removal efficiencies of 97% and 96% at Tegel BF, but only 27% and 70% at Wannsee BF, respectively. At Tegel BF, a short residence time under more oxidizing conditions, distorts the observed removal for 'Fe<sup>++</sup>' reducing samples. Consequently, for both compounds, the removal efficiency for iron reducing conditions in Table 2 is not the mean of all sites but only refers to Wannsee BF. Less pronounced hints exist for other parameters such as 1,7 naphthalenedisulfonic acid (NDSA), diclofenac and sulfamethoxazole (SMX). The opposite effect may occur when oxic water previously has passed an area with lower redox conditions (McMahon and Chapelle, 2008). This is not considered to be relevant, as only 4 oxic samples show nitrate concentration <0.5 mg/l. Removal characteristics (Table 3) can only be discussed exemplarily due to restricted article length.

Carbamazepine shows highest removal efficiency at Tegel BF (14% 'O<sub>2</sub>' increasing to 58% for 'Fe<sup>++</sup>'), while the maximum removal at Tegel AR and Wannsee BF is 20% and sometimes removal even shows negative values. Negative removal occurs only for classes with less than 5 members. Removal at Tegel BF is highest because carbamazepine shows time dependent removal ( $t_{1/2}$ =35 days) and the mean flow times for the redox classes vary between 27 day for 'O<sub>2</sub>' and 105 days for 'Mn<sup>++</sup>' conditions. Flow times for individual redox zones vary between 6 and 29 days At Tegel AR and between 12 and 24 days at Wannsee BF. In addition, carbamazepine shows residual threshold concentrations between 0.1 and 0.3 µg/l. Therefore, in addition to the flow time effect, the removal efficiency also increases with higher surface water concentration, which is around 1 µg/l at Tegel BF and 0.3 µg/l at Wannsee BF. This is one example where removal efficiencies are field site specific, but this can be attributed to removal kinetics which are generally valid.

For clofibric acid (2-(4-Chlorophenoxy)-2-methylpropanoic acid) the highest removal occurs in the 'Mn<sup>++</sup>' zone which may be explained by a cross correlation effect with flow time. For oxic conditions time dependent removal is identified, but there are not enough values to determine kinetics for 'NO<sub>3</sub><sup>-</sup>' and 'Mn<sup>++</sup>' reducing conditions. Nevertheless, such a kinetic appears reasonable. The 'Mn<sup>++</sup>' zone shows a mean flow time of 62 days, while the 'O<sub>2</sub>' and 'NO<sub>3</sub><sup>-</sup>' zone only show 26 and 18 days, respectively and therefore a kinetic removal of clofibric acid under 'Mn<sup>++</sup>' is a reasonable explanation for the high removal. The mean flow time for 'Fe<sup>++</sup>' reducing conditions is 55 days, hence the removal can not be explained by flow time and therefore is least effective.

Mecoprop ((RS)-2-(4-chloro-2-methylphenoxy)propanoic acid) shows similar behaviour as clofibric acid, with highest removal efficiencies for the zones 'O<sub>2</sub>' and 'Mn<sup>++</sup>', and longest flow times for the 'Mn<sup>++</sup>' zone. Hints exist for a time dependent removal kinetic, but it can not be determined since the data quality is not as good as for clofibric acid, (the number of data points is 134 and 182, the ratio of mean surface water concentration to LOQ is 3 and 4, respectively).

Both compounds have a very similar chemical structure. Compared to clofibric acid mecoprop has a methyl group at the aromatic ring, the side chain is identical. For both compounds the reactivity of the aromatic ring is low, so it is expected that the removal of both compounds occurs due to the same side chain reaction. Consequently and analogue to mecoprop, the highest removal for the 'Mn<sup>++</sup>' zone is interpreted mainly as cross correlation effect of highest flow time and temporal kinetic. However, the removal of mecoprop appears to be slightly lower than that of clofibric acid. This may be based in steric interference of the methyl group. Some indications exist that a faster removal under 'Mn<sup>++</sup>' conditions contributes to high removal rates. Samples with a flow time less than 25 days show >95 removal for clofibric acid (6 samples) and >79% removal for mecoprop (4 samples). However, the sample numbers are too low for a conclusive interpretation and from the geochemical point of view it appears improbable that removal is most effective for 'Mn<sup>++</sup>' redox conditions. Further research is necessary at this point.

Propyphenazone concentrations are elevated under iron reducing conditions. This behaviour only appeared at the field site Tegel BF, where some samples with slight mixing must have been overlooked (Table 2, Table 3).

For most parameters site specific removal can be explained by the abovementioned mechanisms. Only for EDTA and MTBE no conclusive interpretation has been found. For the six metabolites it has to be taken into account that their concentration may increase in the groundwater.

The presented method allows to identify removal characteristics and to reduce uncertainty by eliminating ambiguous data. An uncertainty analysis is facilitated by statistical numbers and graphical representation, which are to be interpreted with expert knowledge. The determination of non redox removal characteristics includes a subjective component. The assumption of redox dependent removal is reasonable for all partly removable compounds but this assumption alone frequently does not allow a conclusive interpretation because the majority of compounds and parameters are also affected by factors other than redox. The removal process can be represented more accurately when time dependent kinetics and residual threshold concentrations are considered and the results have a relevantly higher predictive value.

#### **4 CONCLUSIONS**

A method is developed which allows analysing the removal kinetics during bank filtration of organic water parameters. It is applicable to large data bases. The residence time and initial surface water concentration for each ground water concentration is determined and the removal is calculated. This allows different types of evaluation and compared to previous approaches the data may be aggregated at a later stage.

For a general overview removal efficiencies are evaluated for each substance under different redox conditions. The core innovation of the method is that different removal kinetics are distinguished and determined from the data itself so there is no need to assume kinetics a priori. It can be shown that these kinetics affect the removal for the majority of the water parameters. Thereby it is possible to interpret why removal efficiencies vary at different field sites.

- The analysed organic parameters show removal efficiencies between 0% and >99%.
- Redox conditions are a principal factor of impact for the removal since all partly removable parameters show a pronounced dependence on the redox conditions.
- However, in many cases redox conditions alone are not sufficient to predict removal (Table 3). Removal kinetics frequently account for different removal efficiency at different field sites.
  - For 15 parameters the removal increases with flow time.
  - Nine parameters show a residual threshold value below which removal becomes insignificant. To the authors knowledge it is the first study where residual threshold values are determined from field data.
  - Three parameters show site specific behaviour that cannot be explained by removal kinetics.

The existence of residual threshold concentrations for several compounds is a hint for microbial removal activity. Nevertheless, further research is needed to determine type and pathway.

Removal in this study only means that the analysed compounds can no longer be determined. Metabolites are not considered and should be taken into account when conducting an overall risk assessment.

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