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Biological degradation of pharmaceuticals in municipal wastewater treatment: Proposing a classification scheme

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ABSTRACT

A simple classification scheme is suggested to characterize the biological degradation of micropollutants such as pharmaceuticals, musk fragrances and estrogens during wastewater treatment. The scheme should be a basis for the discussion about potential removal efficiencies. Hence, the biological degradation of 25 pharmaceuticals, hormones and fragrances was studied in batch experiments at typical concentration levels using activated sewage sludge originating from nutrient-eliminating municipal wastewater treatment plants.

Since pseudo first-order degradation kinetics was observed for all compounds down to ng L^{-1} levels, the removal rates can be predicted for various reactor configurations. Therefore dilution of wastewater (e.g. by extraneous water) is expected to reduce the degree of biological removal. Wastewater segregation and treatment at the source are therefore to be favoured for elimination of persistent micropollutants over centralized end-of-pipe treatment. For reactor configurations typical for nutrient removal in municipal wastewater, the derived formula for predicting removal allows the identification of three groups of micropollutants according to their degradation constant k_{biol}: compounds with $k_{biol} < 0.1\,L\,g_{SS}^{-1}\,d^{-1}$ are not removed to a significant extent (<20%), compounds with $k_{biol} > 10\,L\,g_{SS}^{-1}\,d^{-1}$ transformed by >90% and in-between moderate removal is expected. Based on the degradation of a heterogeneous group of 35 compounds (including literature data), state of the art biological treatment schemes for municipal wastewater are not efficient in degrading pharmaceuticals: only 4 out of 35 compounds are degraded by more than 90% while 17 compounds are removed by less than 50%.

1. Introduction

A multitude of organic substances is used in households, including pharmaceuticals, personal care products, detergents and disinfectants. About 3000 substances are registered in the EU for pharmaceutical purposes alone. In 1993, 559,000 tons of personal care products were produced and applied in Germany alone (Daughton and Ternes, 1999).

After their use, most of these organic compounds enter the domestic sewage. During sewage treatment these substances are only partially eliminated (Berset et al., 2004; Clara et al., 2005; Joss et al., 2004; Miao et al., 2004; Paxeus, 2004; Petrovic et al., 2003; Strenn et al., 2003; Ternes et al., 2003). They are

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consequently introduced into the surface waters with the effluents and are present in the receiving waters at concentrations in the ng–μg L^{-1} range (Anderson et al., 2004; Giger et al., 2003; McArdell et al., 2003; Metcalfe et al., 2003; Tixier et al., 2003; Wiegel et al., 2004). Residues of these organic pollutants may reach the groundwater (Drewes et al., 2003; Kreuzinger et al., 2004; Masters et al., 2004; Sacher et al., 2001) or even drinking water (Heberer, 2002a; Heberer et al., 2002; Stackelberg et al., 2004; Ternes et al., 2002; Webb et al., 2003). Furthermore, endocrine effects of estrogens have been reported in surface water at concentration as low as a few ng L^{-1} (Desbrow et al., 1998; Länge et al., 2001; Routledge et al., 1998). Due to the quantities and diversity of chemical compounds consumed, there is concern about organic micropollutants reducing the quality of the aquatic environment as well as of drinking water resources (Heberer, 2002a).

An emerging task for municipal wastewater treatment plants would be to act as a barrier for micropollutants, preventing the emission of potentially harmful substances into the aqueous environment. Therefore the fate of micropollutants during wastewater treatment and the mechanisms relevant for their removal need to be understood (Ternes et al., 2004b). In the present paper, the biological degradation of pharmaceuticals, hormones and personal care products is studied at concentrations found in municipal wastewater and a simple classification scheme characterizing compound degradability during state of the art wastewater treatment is proposed. The present study is only covering active ingredients of pharmaceuticals and target polycyclic musk fragrances: further studies are clearly needed for the identification of degradation products as well as for correlating the compound concentrations in relation to the overall toxicity.

2. Material and methods

Batch experiments were performed with sewage sludge from a conventional activated sludge treatment plant (CAS) and from a membrane bioreactor (MBR), both fed with the same municipal wastewater (Joss et al., 2004). The CAS plant is equipped for nitrification, partial denitrification and chemical phosphorus removal (wastewater treatment plant WWTP Kloten/Opfikon, 55,000 population equivalents, solids retention time 11 ± 1 d). The MBR pilot plant is fed with primary effluent of the WWTP Kloten/Opfikon at a feed flowrate proportional to the flow in the sewer (100 population equivalents; nitrification, denitrification and biological phosphorus removal; sludge retention achieved by standard micro and ultra-filtration modules from Kubota, Mitsubishi and Zenon; solids retention time of 30–40 d). Sludge samples where taken from the plants less than 4 h before the start of the experiments, including a 2-h incubation period inside the batch reactor.

Fig. 1 shows the schematic setup of the stirred (1 revolution per second) batch reactors used in this study. The acrylic glass vessels were equipped with oxygen sensors and an aeration control unit allowing the soluble oxygen concentration to be maintained between 3 and 4 mg O_2 L^{-1}. This concentration was logged by a LabView application (National Instruments, Austin, TX) and its decrease during the non-aerated intervals

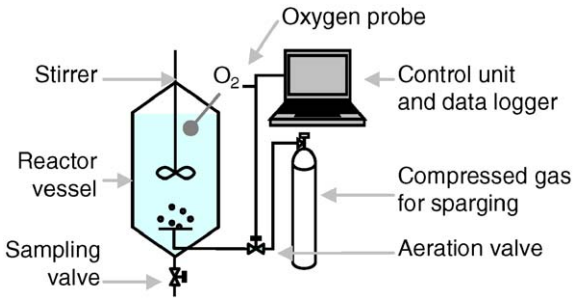

Figure 1 – Schematic setup of the batch reactors used. Seven litres of incubation volume were continuously stirred and intermittently aerated to control the soluble oxygen concentration.

showed the oxygen uptake rate. The experiments were performed at lab temperature (17 ± 1 °C). The pH of CAS was 7.1–7.7 and 7.5–8.1 for the MBR (no pH correction was performed). The sludge concentration in the batch experiments was diluted to 0.51 g_{SS} L^{-1} with the tertiary effluent of the corresponding plant to a total volume of 7.5 L (Table 1). This dilution slows the degradation reaction down in comparison of that of a full-scale reactor, so there was increased experimental resolution for compounds with high degradation rates. For both CAS and MBR sludge, three batch experiments where run simultaneously (Table 1): (i) the control batch without sludge, (ii) an experiment with diluted sludge and (iii) an experiment with diluted sludge and substrate (i.e. addition of primary effluent).

For all test compounds (Table 2), the reactor was spiked at a concentration of 3 μg L^{-1}. In some cases (e.g. paracetamol, Fig. 2) the observed initial concentration was significantly higher due to the concentration originally present in the wastewater filled into the reactor. As confirmed by literature (Anderson et al., 2004; Giger et al., 2003; Metcalfe et al., 2003; Tixier et al., 2003; Wiegel et al., 2004) this range is typical for municipal wastewater.

Samples of 300 mL were taken from the batch vessels with sludge (100 mL for each analytical method) at the following times: 0′, 1′, 2′, 5′, 10′, 20′, 40′, 1 h30′, 3, 6, 12, 24, 48 h. The control experiments without sludge were sampled after 0′, 2′, 20′, 2, 24, 48 h. All samples were collected in amber glass bottles.

The pH was reduced to 3.0 immediately during sampling (pre-addition of 0.53 mL H_2SO_4 1 M into the sampling bottle) and the samples subsequently filtered (GF8 Schleicher & Schuell, Dassel, Germany). The samples were then split up for the three analytical methods, surrogate standards were added and final pH adjustment done, followed by storage for up to 4 h at 4 °C. The acidic drugs and iodinated contrast media were subsequently subjected to solid phase extraction (SPE) after a maximum of 24 h (storage at 4 °C). The samples for the antibiotics were frozen directly after final pH adjustment and stored at −20 °C for less than 5 days prior to SPE.

2.1. *Analysis*

The detailed description of the methods is published elsewhere. Here a summary is given as well as the literature where detailed methods are found.

Table 1 – Composition of the batch experiments performed

	Effluent	Activated sludge (mixed liquor)	Substrate (primary effluent)
Conventional activated sludge plant (CAS)			
COD ($mg L^{-1}$)	29	3150	275
SS ($g L^{-1}$)	<0.005	3.2	n.a.
Control CAS: volume (L)	7.5	0	0
Batch CAS: volume (L)	6.3	1.2	0
Batch CAS+wastewater: volume (L)	5.1	1.2	1.2
Membrane bioreactor (*MBR*)			
Chemical O_2 demand COD ($mg L^{-1}$)	14	3675	340
Suspended solids SS ($g L^{-1}$)	<0.005	3.5	n.a.
Control MBR: volume (L)	7.5	0	0
Batch MBR: volume (L)	6.4	1.1	0
Batch MBR+wastewater: volume (L)	5.3	1.1	1.1

n.a.: value not available.

Table 2 – Sorption coefficient for activated sludge $K_{d,sec}$ and degradation rate constant k_{biol} observed in batch experiments with activated sludge from nutrient-removing municipal wastewater treatment plants

Use	Compound	$K_{d,sec}$ ($L g_{SS}^{-1}$)	k_{biol} for CAS ($L g_{SS}^{-1} d^{-1}$)	k_{biol} for MBR ($L g_{SS}^{-1} d^{-1}$)
Antibiotic	Azithromycin	0.38±0.09[a]	⩽0.13	⩽1.5
	Clarithromycin	0.26±0.095[a]	⩽0.5	⩽2.0
	(Anhydro-) erythromycin	0.165[c]	⩽0.12	⩽1.1
	N^4-acetyl-sulfamethoxazole	n.a.[d]	5.9–7.6	3.2–5.0
	Roxithromycin	n.a.	⩽0.2	⩽0.3
Antiphlogistic	Diclofenac	0.016±0.003[b,e]	⩽0.1	⩽0.1
	Fenoprofen	0.026[e]	10–14	3.3–5.9
	Ibuprofen	0.007±0.002[b]	21–35	9–22
	Indomethacin	0.028[e]	⩽0.3	⩽0.21
	Naproxen	0.013[e]	1.0–1.9	0.4–0.8
	Paracetamol	0.0004[c]	58–80	106–240
Contrast agent	ATH	n.a.	1.3–1.9	1.1–1.3
	DAMI	n.a.	1.9–4.9	1.9–4.5
	Diatrizoate	n.a.	⩽0.1	⩽0.1
	Iohexol	n.a.	1.8–2.4	1.1–2.0
	Iomeprol	n.a.	1.2–1.6	0.5–1.0
	Iopamidol	n.a.	⩽0.36	⩽0.1
	Iopromide	0.011±0.001[b]	1.6–2.5	1.0–2.0
	Iothalamic acid	n.a.	⩽0.24	⩽0.14
	Ioxithalamic acid	n.a.	0.2–0.7	0.3–0.6
Lipid regulator	Bezafibrate	n.a.	2.1–3.0	3.4–4.5
	Clofibric acid	0.005±0.003[b]	0.3–0.8	0.1–0.23
	Fenofibric acid	n.a.	7.2–10.8	0.4–1.7
	Gemfibrozil	0.075[e]	6.4–9.6	0.5–1.8
Nootropic	Piracetam	n.a.	2.5–4.3	2.8–4.9

The range indicates the 95% confidence interval obtained from two batch experiments (12 samples each, taken over two days). The sign "⩽" indicates that the lower limit was beyond experimental resolution. CAS: full-scale conventional activated sludge process; MBR: pilot-scale membrane bioreactor; tendentially lower values partly due to higher sludge age (inert matter; Fig. 8). n.a.: data not available.

[a] Göbel et al. (2005b).

[b] Ternes et al. (2004a).

[c] Jones et al. (2002).

[d] Value assumed smaller than for sulfamethoxazole (260±170; Göbel et al., 2005b).

[e] Urase and Kikuta (2005).

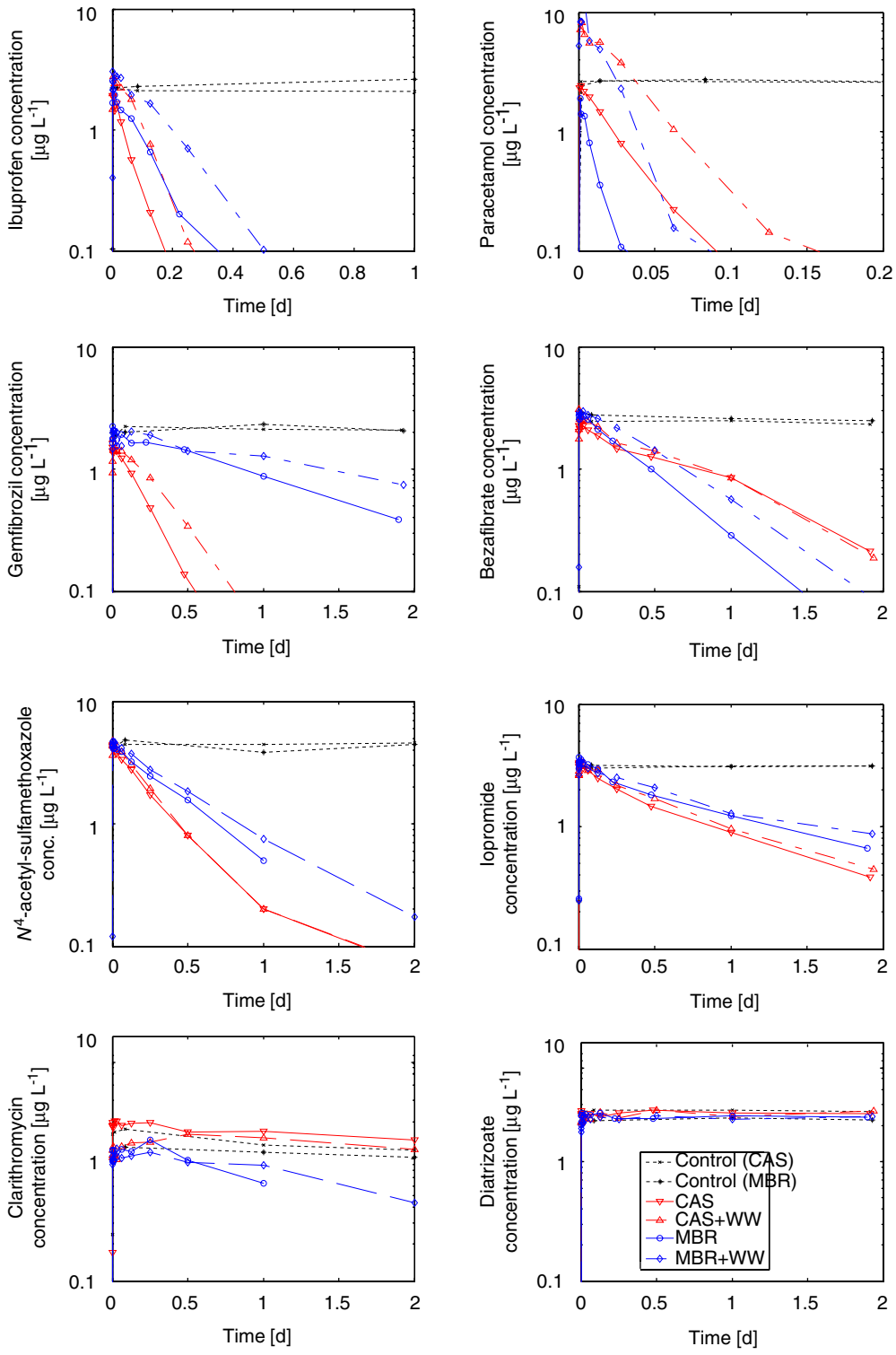

Figure 2 – Biological removal of pharmaceuticals observed in batch experiments. Batch experiments were performed with conventional activated sludge (CAS) or membrane bioreactor sludge (MBR). WW: untreated wastewater (i.e. primary effluent) added as substrate.

2.1.1. *Macrolide and sulfonamide antibiotics*

Aqueous samples (Göbel et al., 2004) were filtered through 0.45 µm cellulose nitrate filters (Schleicher & Schuell, Dassel, Germany) and subsequently enriched by solid-phase extraction on polymeric cartridges (Oasis HLB, Waters). The analysis was performed using reversed-phase liquid chromatography (150 × 2 mm YMC Pro C18, Stagroma, Reinach, Switzerland) coupled to electrospray mass spectrometry in positive ionization mode (TSQ Quantum Discovery, Thermo Finnigan, San Jose, CA). Solid samples (Göbel et al., 2005a) were

extracted using pressurized liquid extraction prior to enrichment and analysis. The following compounds were analysed: azithromycin, erythromycin, clarithromycin, roxithromycin, sulfadiazine, sulfamethazine, sulfamethoxazole, N^4-acetyl-sulfamethoxazole, sulfapyridine, sulfathiazole, trimethoprim. Erythromycin was measured as sum of parent compound and anhydro-erythromycin.

2.1.2. *Contrast media and other compounds (Hirsch et al., 2000; Ternes et al., 2005)*

For the clean up, a solid-phase extraction using two stacked cartridges (RP-C_{18ec}/ENV+) was applied, eluting only the latter. Separation was performed using reversed-phase liquid chromatography (125 × 4.6 mm Chromolith Performance RP-18 endcapped) prior to detection by tandem electrospray mass spectrometry (API 4000, Applera, Foster City, CA USA) in the ESI-(+) mode. The following compounds were analysed: ATH (5-amino-2,4,6-triiodo-2,3-dihydroxipropyl-amid-phthalic acid), DAMI (desmethoxyacetyl-iopromide), diatrizoate, iohexol, iomeprol, iopamidol, iopromide, iothalamic acid, ioxithalamic acid, paracetamol and piracetam.

2.1.3. *Acidic drugs (Löffler and Ternes, 2003; Ternes et al., 2005)*

The samples were adjusted to pH 2. The method consists of solid-phase extraction on Oasis MCX cartridges (60 mg). Separation and identification were performed by LC tandem MS using electrospray ionization in the negative ion mode. The following compounds were analysed: bezafibrate, clofibric acid, diclofenac, fenofibric acid, fenoprofen, gemfibrozil, ibuprofen, indomethacin and naproxen.

Limit of quantification of all compounds was $\leqslant 0.05\,\mu g\,L^{-1}$, except for piracetam and sulfonamide antibiotics ($\leqslant 0.2\,\mu g\,L^{-1}$).

Numerical models, regression and accuracy estimation of the degradation rate constant k_{biol} was calculated with Matlab software (V7.01, The Mathworks Inc., Natick, USA). The limit of resolution for k_{biol} was in the range of $0.1\,L\,g_{SS}^{-1}\,d^{-1}$ (except for antibiotics, where no coherent results were obtained, as discussed in the next section).

3. Results and discussion

3.1. *Deriving pseudo first-order degradation kinetics from batch experiments*

Fig. 2 shows typical examples obtained for micropollutant removal in the batch reactor. The control experiments run without biologically active sludge confirm that the removal is due to interaction with sludge (X_{SS}). An exponential decrease of the concentration over time can be seen for all the compounds in which transformation was observed (i.e. k_{biol} beyond experimental resolution limit of $0.1\,L\,g_{SS}^{-1}\,d^{-1}$). Accordingly the removal is described with kinetic of pseudo first order (Schwarzenbach et al., 2003):

$$\frac{dC}{dt} = k_{biol} X_{SS} S, \tag{1}$$

where C is the total compound concentration ($\mu g\,L^{-1}$), S the soluble compound concentration ($\mu g\,L^{-1}$), t the time (d), k_{biol} the reaction rate constant ($L\,g_{SS}^{-1}\,d^{-1}$), and X_{SS} the suspended solids concentration ($g_{SS}\,L^{-1}$).

The "first order" refers to the direct proportionality of the transformation rate to the soluble substance concentration S. The term "pseudo" refers to its proportionality to the sludge concentration X_{SS}, which can be assumed to be constant for short-term batch observations.

3.1.1. *Effect of sorption and volatilization*

To avoid laborious measurement of the sorbed compound, it may be useful to reformulate Eq. (1) using only the soluble concentration S and assuming sorption equilibrium. The sorption coefficient K_d is defined for equilibrium conditions in a spiked batch (Ternes et al., 2004a; Wang and Grady, 1995):

$$K_d = \frac{X}{X_{SS} S}, \tag{2}$$

where K_d is the sorption coefficient of secondary sludge ($L\,g_{SS}^{-1}$), X the sorbed compound concentration expressed per unit of reactor volume ($\mu g\,L^{-1}$)

$$C = S + X = S(1 + K_d X_{SS}). \tag{3}$$

It is assumed that sorption is fast compared to biological degradation (Wang and Grady, 1995). From sorption experiments in batch reactors operated with $4\,g_{SS}\,L^{-1}$ activated sludge (Ternes et al., 2004a), where after 0.5 h equilibrium was observed, it is estimated that $k_{sor} \geqslant 25\,L\,g_{SS}^{-1}\,d^{-1}$. If $k_{biol} < 0.1 \cdot k_{sor} < 2.5\,L\,g_{SS}^{-1}\,d^{-1}$, which is the case for most of the compounds investigated, sorption equilibrium can be assumed (see also Appendix A). Substituting Eq. (2) and (3) into Eq. (1), the observed decrease in compound concentration in solution can be expressed:

$$\frac{dS}{dt} = \frac{-k_{biol}}{1 + K_d X_{SS}} X_{SS} S. \tag{4}$$

If less than 10% of a compound is sorbed, the term $K_d\,X_{SS} = X/C \leqslant 0.1$ can be neglected. In the case of the batch experiments described in this study ($X_{SS} = 0.51\,g_{SS}\,L^{-1}$), this applies to most pharmaceuticals studied, since for these hydrophilic compounds K_d is $< 0.2\,L\,g_{SS}^{-1}$ (Table 2; only for the macrolide antibiotics azithromycin and clarithromycin K_d is $> 0.2\,L\,g_{SS}^{-1}$ and the term $K_d \cdot X_{SS}$ cannot be neglected; Göbel et al., 2005b; Ternes et al., 2004a).

For *volatilization*, the following has to be considered: if the Henry coefficient $H < 0.1\,m_{reactor}^3\,m_{air}^{-3}$, the rising gas bubble is in equilibrium with the dissolved concentration after 0.5 m rising height for fine bubble aeration. Assuming no elimination by sorption and biological degradation, stripping can therefore be described in the batch system with

$$\frac{dS}{dt} = -H\,q_G\,S, \tag{5}$$

where H is the dimensionless Henry gas water partitioning coefficient ($L_{wastewater}\,L_{air}^{-1}$) and q_G the air applied per volume of reactor and time ($L_{air}\,L_{reactor}^{-1}\,d^{-1}$).

The fraction stripped ($\eta_{stripped}$) or the stripping efficiency in the batch system is

$$\eta_{stripped} = 1 - \frac{S_{\theta_h}}{S_0} = \exp(-q_G \theta_h H) \cong HQ_G \quad \text{for } HQ_G < 0.1, \tag{6}$$

where θ_h is the batch time or hydraulic retention time of a plug flow reactor (d^{-1}) and Q_G the $q_G \times \theta_h$ air required; 5–15 $L_{air}\,L^{-1}_{wastewater}$ for conventional activated sludge systems, up to 25 $L_{air}\,L^{-1}_{wastewater}$ for membrane bioreactor and the laboratory batch reactor.

From the investigated compounds in the EU project POSEIDON only the musk fragrances are slightly volatile with an $H \cong 0.005$ (Poseidon, 2005). The stripping efficiency of this compounds is therefore <10%, but negligible for all of the compounds described in this paper ($H < 10^{-5}$, Schwarzenbach et al., 2003).

Table 2 shows the observed degradation rate constant k_{biol} as obtained by the regression of the measured concentrations according to Eq. (4). For azithromycin, erythromycin, clarithromycin and roxithromycin only the upper limit of the degradation rate constant could be identified (regression fit and estimated accuracy did not allow for better resolution). For all sulfonamide antibiotics (except N^4-acetyl-sulfamethoxazole; Fig. 2), unexplained variations of the concentration over time were observed (the variation was clearly beyond the analytical resolution but did not fit our model). It is speculated that unknown conjugation and deconjugation may occur during contact with activated sludge.

3.2. *Impact of reactor configuration*

For modelling biological degradation, sorption and desorption the following differential equation system has to be considered for each compartment of a reactor cascade (Fig. 3):

$$\frac{dS_i}{dt} = \frac{1+R}{\theta_h}(S_{i-1} - S_i) - k_{sor} X_{SS,i} S_i + k_{des} X_i - k_{biol} X_{SS,i} S_i,$$
$$\frac{dX_i}{dt} = \frac{1+R}{\theta_h}(X_{i-1} - X_i) + k_{sor} X_{SS,i} S_i - k_{des} X_i, \tag{7}$$

where i is the (index) compartment number (1 to n), $i-1$ the preceding compartment, R the flow rate of the sludge recycle relative to the flow rate of the treated wastewater: $R = Q_{sludge\ recycle}/Q_{wastewater}$ (dimensionless), k_{sor} the rate constant for sorption (absorption and adsorption) ($L\,g_{SS}^{-1}\,d^{-1}$), k_{des} the rate constant for desorption (d^{-1}), and θ_h the hydraulic retention time; $\theta_h = V/Q_{wastewater}$ (d).

The first term accounts for the compartment's in- and outflow, sorption is accounted by the term $k_{sor}\ X_{ss,i} \cdot S_i$, desorption by $k_{des}\ X_i$ and biological degradation by $k_{biol}\ X_{ss,i}\ S_i$. If volatilization is not negligible, a corresponding term (Eq. (5)) is to be added to the first equation (dS/dt).

If the excess sludge is withdrawn at the end of the reactor system (or from return sludge) and sludge growth is assumed to occur mainly at the beginning (due to the fast heterotrophic growth and flocculation of inlet particulates), the sludge concentration ($X_{SS,i}$) results similar in all compartments:

$$X_{SS,i} = X_{SS} = SP\frac{\theta_X}{\theta_h}, \tag{8}$$

where θ_x is the solid retention time (d) and SP the pecific sludge production per volume of wastewater treated ($g_{SS}\,m^{-3}$).

After sludge withdrawal, the return sludge $X_{SS,0}$ is

$$X_{SS,0} = X_{SS} - \frac{SP}{1+R} = X_{SS}\left(1 - \frac{\theta_h}{\theta_x(1+R)}\right). \tag{9}$$

For the first compartment, the following influent ($i-1$) values are to be taken:

$$S_0 = S_{i-1,i=1} = \frac{C_{in} + RS_n}{1+R}, \tag{10}$$

$$X_0 = X_{i-1,i=1} = X_n\left(1 - \frac{\theta_h}{\theta_x(1+R)}\right). \tag{11}$$

By definition, adsorption and desorption are related to the sorption coefficient K_d

$$K_d = \frac{k_{sor}}{k_{des}}. \tag{13}$$

Assuming sorption equilibrium (see Appendix A) as well as comparable biologic activity in all compartments (anoxic and aerobic), the relative reduction in soluble compound concentration can be calculated for a cascade of mixed reactors as follows:

$$\frac{S_{out}}{S_{WW}} = \frac{1 + K_{d,prim} X_{SS,WW}}{1 + K_d X_{SS}} \times \frac{1}{(1+R)\left[\left(1 + \frac{k_{biol} X_{SS}}{(1+R)(1+K_d X_{SS})}\frac{\theta_h}{n}\right)^n - 1\right] + \frac{1+K_d\,SP}{1+K_d X_{SS}}}, \tag{14}$$

where S_{WW} is the soluble concentration in the wastewater before mixing with return sludge ($\mu g\,L^{-1}$), $K_{d,prim}$ the sorption coefficient of the primary sludge ($L\,g_{SS}^{-1}$), $X_{SS,WW}$ the primary sludge content of wastewater before mixing with return sludge ($g_{SS}\,m^{-3}$), and n the total number of cascaded reactors (dimensionless).

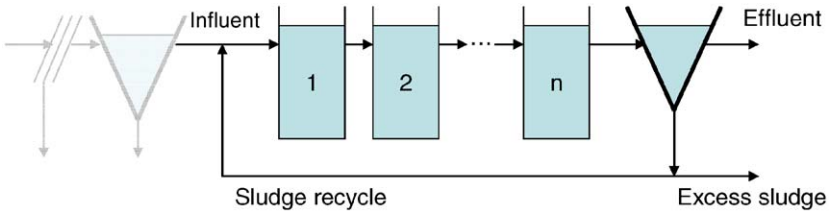

Figure 3 – Schematic drawing of the biological steps of a wastewater treatment facility considered in the following model. Primary treatment is not considered. The number of compartments depends on the reactor configuration.

A similar formula is obtained for plug-flow reactors (ideally $n = \infty$) and for sequencing batch reactor ($\theta_h/(1+R)$ is the cycle time minus sedimentation and decantation time; R the ratio of retained to decanted volume):

$$\frac{S_{out}}{S_{WW}} = \frac{1 + K_{d,prim} X_{SS,WW}}{1 + K_d X_{SS}} \times \frac{1}{(1+R)[e^{(\theta_h k_{biol} X_{SS})/((1+R)(1+K_d X_{SS}))} - 1] + (1 + K_d SP)/(1 + K_d X_{SS})} \quad (15)$$

Fig. 4 shows model predictions of the compound removal calculated by solving Eq. (7) for compounds with $K_d \leqslant 0.1\,L\,g_{SS}^{-1}$.

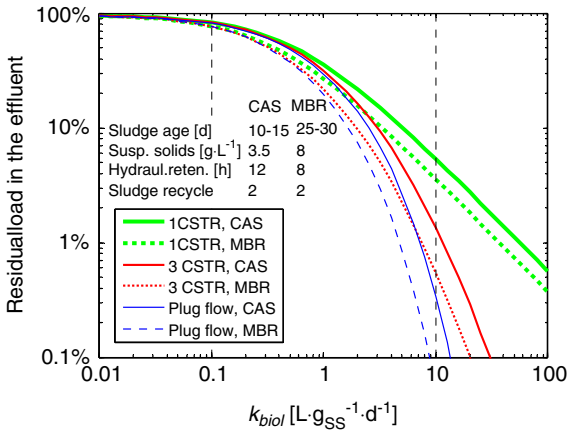

Figure 4 – Expected relative micropollutant removal for a typical nutrient-eliminating municipal wastewater treatment plant. Assumptions: sorption not relevant ($K_d \leqslant 0.1\,L\,g_{SS}^{-1}$); MBR with 8 h hydraulic retention time, CAS with 12 h; sludge recycle twice the influent flow; sludge age and concentration indicated next to the respective curves. CAS: conventional activated sludge treatment plant; CSTR: completely stirred reactor with one or three cascaded compartments; MBR: membrane bioreactor.

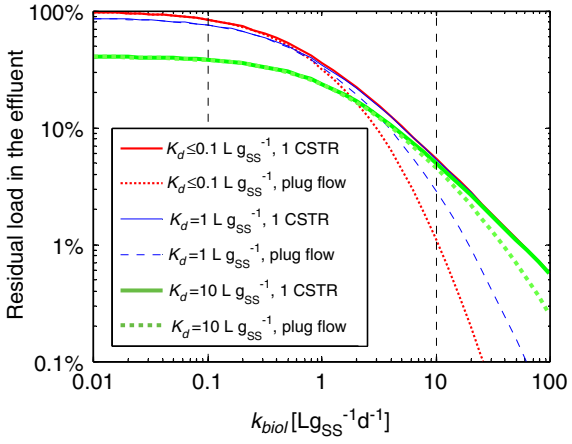

Figure 5 – Impact of the sorption coefficient (K_d) on the compound removal. With increasing sorption, the difference between a plug flow configuration and a single stirred compartment vanishes. Assumptions as made in Fig. 4 for CAS.

The same result is obtained with Eq. (14), respectively 15, since sorption is not relevant due to the low K_d value. The figure shows, that the subdivision of the reactor volume into a cascade of compartments, significantly improves the removal of non-sorbing and biologically degradable compounds compared to a single mixed reactor. Further the following subdivision of compound according to their degradability is proposed:

- $k_{biol} < 0.1$ (L g$_{SS}^{-1}$ d^{-1}): no substantial removal by degradation (<20%; for strongly sorbing compounds with $K_d > 1\,L\,g_{SS}^{-1}$, the removal may be greater due to transfer to sludge; Fig. 5).
- $0.1 < k_{biol} < 10$: partial removal (i.e. between 20% and 90%).
- $k_{biol} > 10$: more than 90% removal by biological degradation; specific degradation efficiency strongly dependent on reactor configuration.

Fig. 4 should not be used to compare the performance of MBRs with CAS systems without considering additional information (e.g. inert content and microbial composition influence k_{biol}; Fig. 7).

Fig. 5 shows, that in case of significant sorption ($K_d > 0.1\,L\,g_{SS}^{-1}$) the impact of dividing the reactor volume into cascades becomes less significant (i.e. the removal of the plug flow configuration gets increasingly similar to a single mixed compartment, even for compounds with high degradation constants k_{biol}). This is due to the fact, that with increasing K_d the soluble concentration is increasingly controlled by sorption/desorption, while the influent load is having limited impact.

3.3. *Biological activity*

Fig. 6 gives an overview of kinetic degradation rate constants for 35 pharmaceuticals, hormones and personal care products in nutrient-eliminating sludge. According to these data and Eq. (7), the load of only four compounds (ibuprofen, paracetamol, 17β-estradiol and estrone) out of 35 are expected to be biological transformed by more than 90% ($k_{biol} > 10\,L\,g_{SS}^{-1}\,d^{-1}$). Sixteen compounds are expected to be partially removed ($0.1 > k_{biol} > 10$), whereas no remarkable biological transformation is predicted for 17 compounds ($k_{biol} < 1$; among others most of the macrolide and sulfonamide antibiotics observed). The results of Fig. 6 are generally in good agreement with data found in the literature (Beausse, 2004; Buser et al., 1999; Heberer, 2002a,b; Ternes, 1998). However, some studies differ significantly from our results (diclofenac and indomethacin in Ternes, 1998, fenoprofen, ibuprofen, indomethacin, gemfibrozil and estrogens in Urase and Kikuta, 2005): at least part of the difference may be explained by (i) substantially higher experimental pharmaceutical concentration, (ii) sludge origin (sludge age, wastewater composition, flow scheme) or (iii) sludge handling prior to batch experiments (e.g. artificial substrate dosing, sludge storage).

Fig. 7 shows that there is significant variability of reaction rate constants k_{biol} observed when comparing different

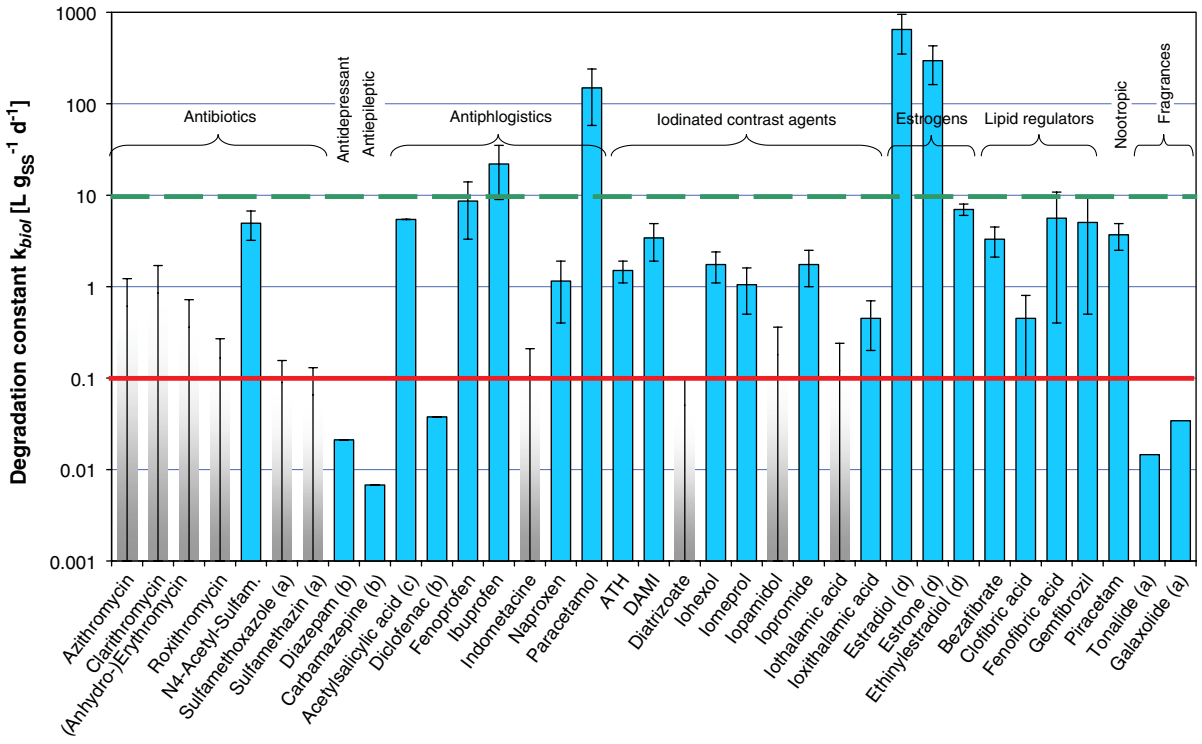

Figure 6 – Kinetic degradation constants of 35 pharmaceuticals, hormones and personal care products observed in sludge from nutrient-removing municipal wastewater treatment plants: the average of CAS and MBR batch experiments is indicated (data of Table 2 unless indicated). The error bars indicate the 95% confidence interval. The lines at k_{biol} 0.1 and 10 L g_{SS}^{-1} d^{-1} indicate the limits for less than 20% and more than 90% removal expected for nutrient-removing municipal wastewater treatment (see Fig. 4). The faded columns indicate values for which the limited experimental resolution allows only identifying an upper limit for k_{biol} (upper error bar). Literature data: (a) (McArdell et al., 2005); (b) (Umweltbundesamt, 2003); (c) (Ternes, 2000); (d) (Joss et al., 2004).

sludge types. The following sludge characteristics are expected to be of significant influence:

- Diversity of the activity of the biomass due to either differences in microbial population or the expressed enzymatic activity (e.g. sludge age; Clara et al., 2005; Ternes et al., 2004b).
- The fraction of active biomass within the total suspended solids (Fig. 8).
- Floc size of the sludge for compounds being well degraded (Fig. 7 and Joss et al., 2004).

For most compounds with a k_{biol} below 50 L g_{SS}^{-1} d^{-1}, the slightly lower transformation rate constants found in MBR as compared to CAS sludge is assumed to be caused by the higher inert matter accumulation in the MBR sludge (Fig. 7; MBR: 30–40 days sludge age; CAS: 10–12 days). This was also confirmed by the maximal respiration rate measured by means of oxygen uptake (data not shown). Nevertheless, for some compounds a significantly higher difference in activity was observed between type of sludges. A 10 times smaller k_{biol} was seen in the MBR for fenofibric acid and gemfibrozil (Fig. 2), while for piracetam and bezafibrate the MBR performed at a significantly higher rate compared to the CAS. Since the two plants were fed with the same wastewater

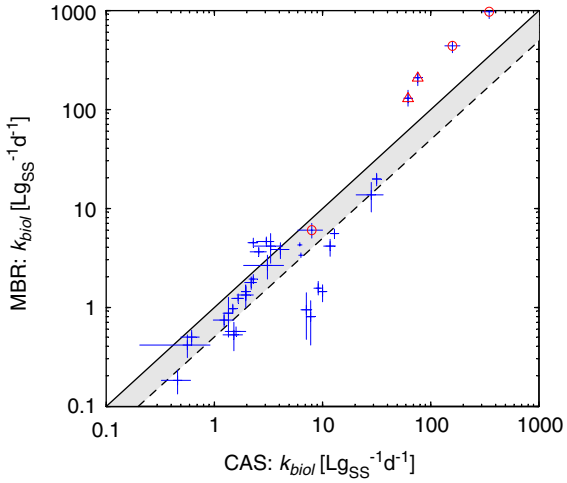

Figure 7 – Comparison of the k_{biol} observed with sludge originating from a membrane bioreactor (MBR, 30–40 d sludge age) and from a conventional activated sludge plant (CAS, 10–12 d) operated in parallel at proportional feed flow and on the same wastewater. The length and width of the crosses indicate a 95% confidence interval. The solid line indicates identity, while the dotted line represents the expected activity reduction due to accumulation of inert matter at a higher sludge age (Fig. 8). Circles indicate oestrogen data taken from (Joss et al., 2004). Triangles indicate paracetamol.

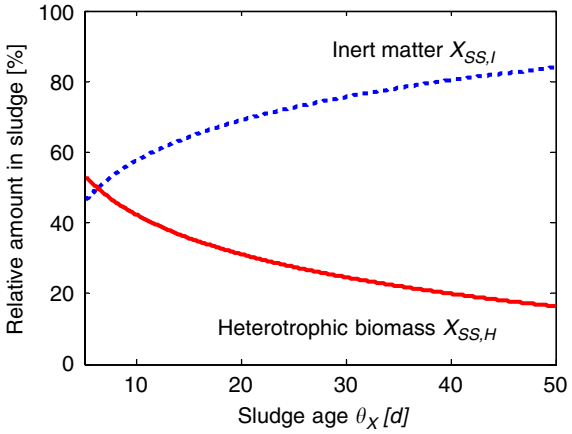

Figure 8 – Relative amount of inert particulate matter ($X_{SS,I}$) and heterotrophic biomass ($X_{SS,H}$) in activated sludge as a function of the sludge age. Calculation according to Koch et al. (2001). For our CAS (sludge age 10–12 d), the relative amount of heterotrophic biomass per dry sludge matter is about twice as high as for our MBR (sludge age 30–40 d).

at a proportional flow, feed characteristics are ruled out as cause of the performance difference.

The data obtained for paracetamol supports the hypothesis, that increasing of biological diversity (the higher sludge age of the MBR may issue in a diverse microbial population or the lower sludge loading may influence the expression of biocatalytic pathways) and/or diffusive mass transfer limitation (due to smaller flocs in MBR) might be the reason for the higher k_{biol} observed for estradiol, estrone and paracetamol (Fig. 7; Joss et al., 2004).

The present study is not conclusive on whether the addition of substrate (i.e. primary effluent) influences the degradation of micropollutants: this assumption was postulated by (Joss et al., 2004) to explain the difference in oestrogen removal found between batch experiments and sampling campaigns on full-scale plants. Some compounds show a lag phase upon substrate addition (Fig. 2, gemfibrozil, paracetamol and ibuprofen), but the lack of data points impedes quantification: higher amounts of substrate or chemostat experiments are required to obtain conclusive data.

4. Conclusion

In spite of a certain variability in activity amongst different sludge types and reactor configurations, compounds can be divided into different classes according to their persistence in state of the art wastewater facilities: (i) no removal ($k_{biol} < 0.1\,L\,kg_{SS}^{-1}\,d^{-1}$), (ii) partial removal ($0.1 < k_{biol} < 10$) and (iii) transformation by more than 90% ($k_{biol} > 10$). For many compounds municipal wastewater treatment represents an obligatory and final treatment step prior to release into the environment. Therefore, quantifying the degradability is an important task to discuss integrated solutions for mitigation (e.g. use restrictions or ban, requirement of source treatment, requirement of advanced end-of-pipe treatment).

An overview of k_{biol} values shows, that biological degradation in municipal wastewater treatment contributes only to a limited extent to the overall load reduction of pharmaceuticals. Further Eqs. (14) and 15 support that (i) dilution of wastewater (e.g. rain or infiltration) reduces micropollutant degradation for a given reactor loading, (ii) treatment at the source is favourable if dilution can be avoided and (iii) dividing of the available reactor volume into reactor cascades can appreciably improve performance.

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Appendix A

A.1. *Kinetic model of the sorption equilibrium*

In a batch reactor without biological activity sorption equilibrium is reached according to the following formula:

$$S_t = S_0 - \left(S_0 - \frac{C_0}{1 + K_d X_{SS}}\right)\left(1 - e^{-k_{des}(1+K_d X_{SS})t}\right), \quad (A.1)$$

$$X_t = X_0 - \left(X_0 - \frac{C_0 K_d}{1 + K_d X_{SS}}\right)\left(1 - e^{-k_{des}(1+K_d X_{SS})t}\right), \quad (A.2)$$

where is the S_t is the soluble compound concentration as a function of time ($\mu g\,L^{-1}$), S_0 the initial soluble compound concentration ($\mu g\,L^{-1}$), C_0 the initial total compound concentration ($\mu g\,L^{-1}$), K_d the sorption coefficient ($L\,g_{SS}^{-1}$), X_{SS} the suspended solids concentration ($g_{SS}\,L^{-1}$), k_{ads} the rate constant for sorption ($m^3\,g_{SS}^{-1}\,d^{-1}$), k_{des} the rate constant for desorption (d^{-1}), t the time (d), X_t the sorbed compound concentration as a function of time ($\mu g\,g_{SS}^{-1}$), and X_0 the initial sorbed compound concentration ($\mu g\,g_{SS}^{-1}$).

A.2. *Impact of sorption kinetic*

Ternes et al. (2004a) found that 0.5 h after spike addition sorption equilibrium is (already) reached in batch experiments run with a sludge concentration of $4\,g_{SS}\,L^{-1}$. Assuming an analytical accuracy of $\pm 10\%$ and according to Eqs. (A.1) and (A.2) it can be stated that equilibrium was reached to $\geqslant 90\%$:

$$1 - e^{-k_{des}(1+K_d X_{SS})t} \geqslant 90\%. \quad (A.3)$$

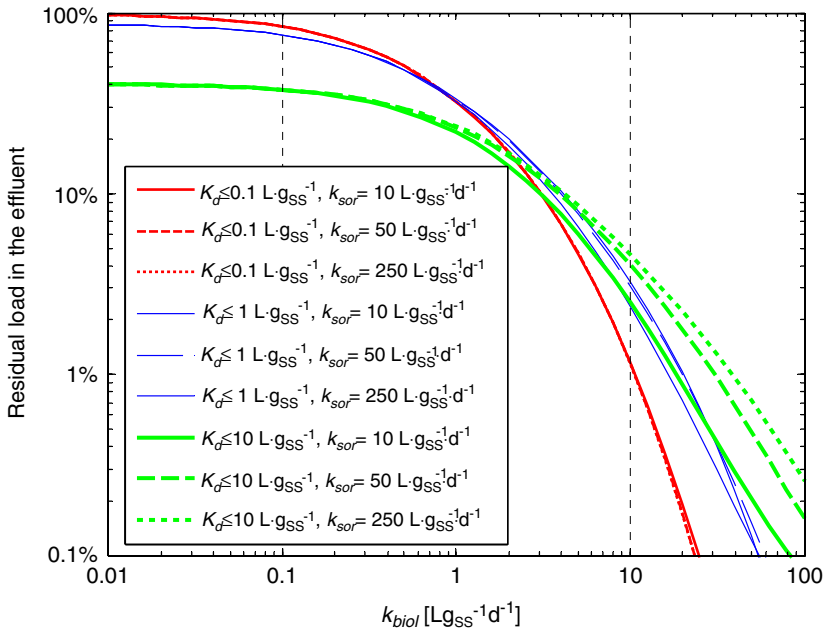

Figure A1 – Modelled compound removal for plug flow configuration as a function of the biologic degradation constant k_{biol} for compounds with different sorption coefficient K_d and assuming different sorption kinetic (k_{sor}).

Since compounds with K_d up to $2\,L\,g_{SS}^{-1}$ (galaxolide and tonalide) have been studied and $X_{SS} = 4\,g_{SS}\,L^{-1}$, $t = 1/48$ d, it therefore can be concluded that $k_{sor} \geqslant 25\,L\,g_{SS}^{-1}\,d^{-1}$.

According to Eq. (7), sorption can be assumed close equilibrium if the sorption substance mass flux is ten times bigger than the degradation:

$$k_{biol} X_{SS,i} S_i \leqslant 10 k_{sor} X_{SS,i} S_i. \quad (A.4)$$

Therefore sorption equilibrium can be assumed for compounds being degraded at a rate of $k_{biol} \leqslant 2.5\,L\,g_{SS}^{-1}\,d^{-1}$.

Figure A1 shows, that in case of plug flow configuration, the model of Eq. (7) is sensitive on the parameter k_{sor} only for compounds with $K_d > 1\,L\,g_{SS}^{-1}$ and $k_{biol} > 1\,L\,g_{SS}^{-1}\,d^{-1}$. No impact of sorption kinetic is seen in case of a single mixed compartment configuration (data not shown). The removal of several cascaded compartments is between the single CSTR and the plug flow configuration.

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